Basics of Fluorescence Spectroscopy
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Lecture – 06

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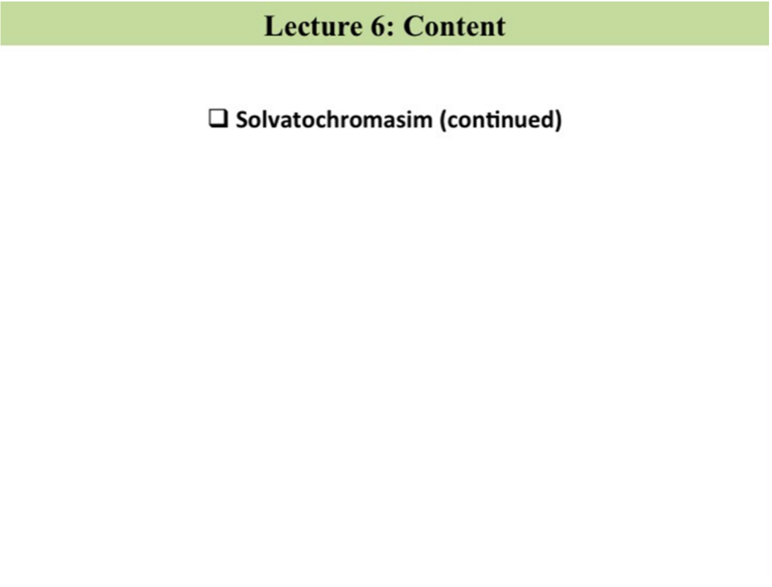

Lecture 6: Content

❑ Solvatochromasim (continued)

Welcome to the Lecture 6 of the course Basics of Fluorescence Spectroscopy. So, till last class, we were discussing about the absorption spectroscopy and in the last class, we are discussing about the effect of solvent on the absorption spectra. It means that how the color of a substance may change by changing the solvent. So, by changing the solvent means changing the solvent property and where we are discussing about the changing the polarity of the solvent.

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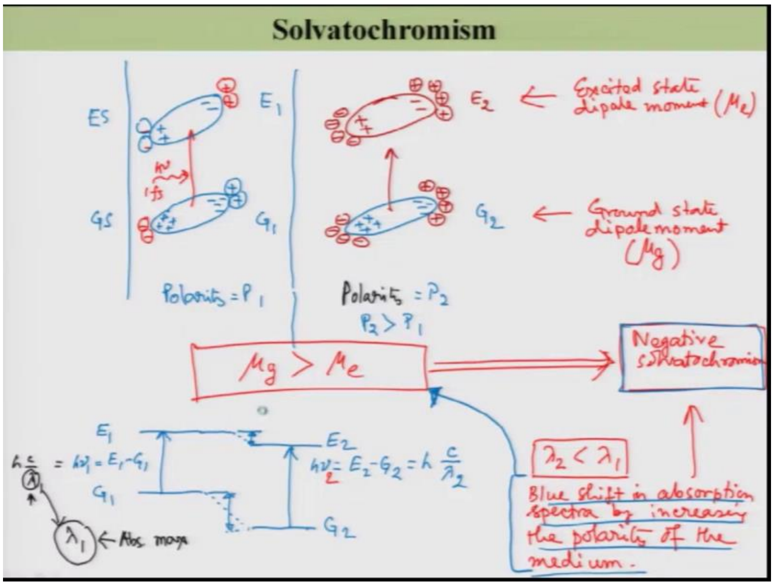

Solvatochromism

Blue shift in absorption spectra by increasing the polarity of the medium.

And in this case we have discussed as shown here; the phenomena of negative solvatochromism, in this case what we have seen that there will be a blue shift in absorption spectra by increasing the polarity of the medium. For the molecule whose right, what is the property of the molecule? The property of the molecule is for that molecule where the ground state dipole moment mu g is greater than excited state dipole moment mu e.

So, let us see that what happen if the situation is just reverse.

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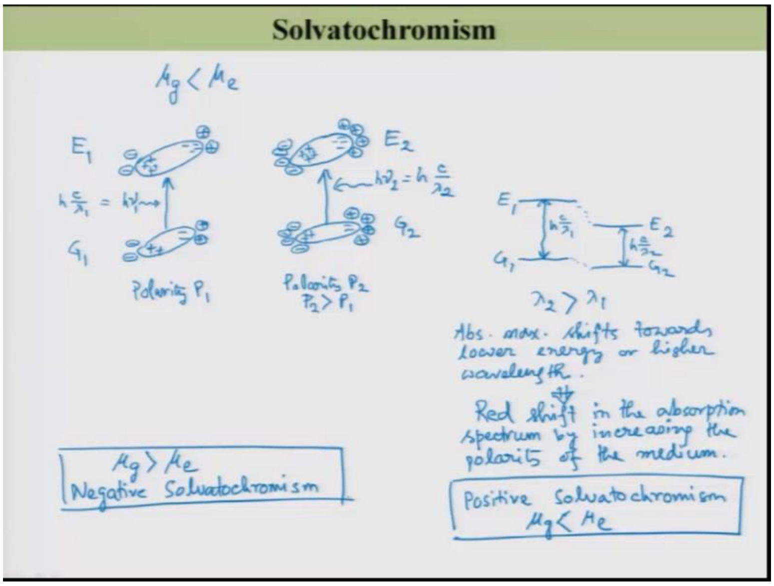

Solvatochromism

Abs. max. shifts towards lower energy or higher wavelength.

Red shift in the absorption spectrum by increasing the polarity of the medium.

What I want to say is that in the case of excited state dipole moment is more than the ground state dipole moment then what will be the situation. So, here my condition is that mu g is less than mu e; so as usual let me take my molecule represented by this ellipsoid over here. So, this is the ground state and this is the excited state. And in this case as I said that ground state dipole moment is less than excited state dipole moment let me define this as 2 positive charges over here and 2 negative charges over here and 4 positive charges over here and 4 negative charges over here.

So, now let me put this molecule in a solvent of polarity P 1 and which obviously going to stabilize both the ground state excited state. And let us say the stabilization is like this so from the solvent point of view, alright. So, this is the solvent dipoles and over here will be something like this. So, the absorption is instantaneous again so that takes only 1 femtosecond or less than the femtosecond. So, when you excite this molecule from ground state to the excited state by light h nu 1; let us say for example which is equal to h c by lambda 1.

So, the electronic transition is instantaneous solvent will remain as it is because it takes time to move around. And let us define the energy here as G 1 ground state energy with polarity 1 and this energy is E 1. Now, I change the solvent from polarity P 1 to polarity P 2; let us see what will happen? Here is my polarity P 2 so that P 2 is greater than P 1. So, P 2 is greater than P 1; in this case the same molecule to positive charge right same dipole moment over here and here as the polarity P 2 is greater than P 1 it will be more solvent. So, let me represent it by 4 solvent dipoles over here.

So, then again I will be going to excite this molecule from ground state to the excited state, and here is my excited state dipole moment is more than the ground state dipole moment, but as the excitation is instantaneous I am not going to have a different solvent structure around this molecule. So, solvent structure will remain as it is in the ground state.

So, let us say this energy over here is G 2 and energy over here is E 2 and this excitation energy is h nu 2 which is equal to h c by lambda 2. So now, I can plot the relative intensities of G 1 E 1; and G 2 E 2 let say this is the level of G 1 and this is the level of E 1 G 1 E 1. So, this is for the polarity P 1 and when the polarity has increased P 2 is greater than P 1 then what we can see is that the energy will be minimized. So, the energy will be minimized so this is my G 2. However, this excited state dipole moment is more, so energy minimization of the E 2 compared to E 1 will be much more compared to the ground state.

So, here this energy minimization will be more than ground state. So, here it will be E 2. So, you see here this energy difference is h c by lambda 1. And in this case this is h c by lambda 2 and these energy is more than this energy. That means, lambda 2 is less than lambda 1; sorry lambda 2 is more than lambda 1 lambda 2 is greater than lambda 1. That means, in this case as you can see that by increasing the polarity the absorption spectra is shifted towards the lower energy; shifted towards the lower energy means longer wavelength. So, I can write here absorption maxima shifts towards lower energy or higher wavelength. This means the red shift in the absorption spectra red shift in the absorption spectrum by increasing the polarity of the medium.

So, this is referred to as the positive solvatochromism. And therefore, the positive solvatochromism, what I saw that mu g is less than mu e. And if as you remembered for the negative solvatochromism what we saw mu g is greater than mu e for negative solvatochromism. So, this is about the effect of solvent on the absorption spectra and based on these one can generate polarity scale what has been done by Reichardt, so this very well known polarity scale which is known as E T N polarity scale, so what I want to say is that is the following: as the absorption spectra changes depends on depending on the polarity of the medium. So, if I have a molecule where the change or the shift in the absorption spectra is reasonably high then by referring the absorption spectra of that particular molecule I can comment on the polarity of the medium. We know the polarity of water is very high polarity of cycle action is very low and so on so forth.

Now, if you have a solvent with unknown polarity you can simply dissolve that particular dye and measure the absorption spectra and if it resembles with the absorption spectra of water then you can say the polarity is near about water. If it resembles to the absorption spectra of the dioxin and then you can say the polarity of that unknown solvent is like dioxin and so on and so forth. So, with this one can actually formulate a polarity scale and which has been done by the Reichardt.

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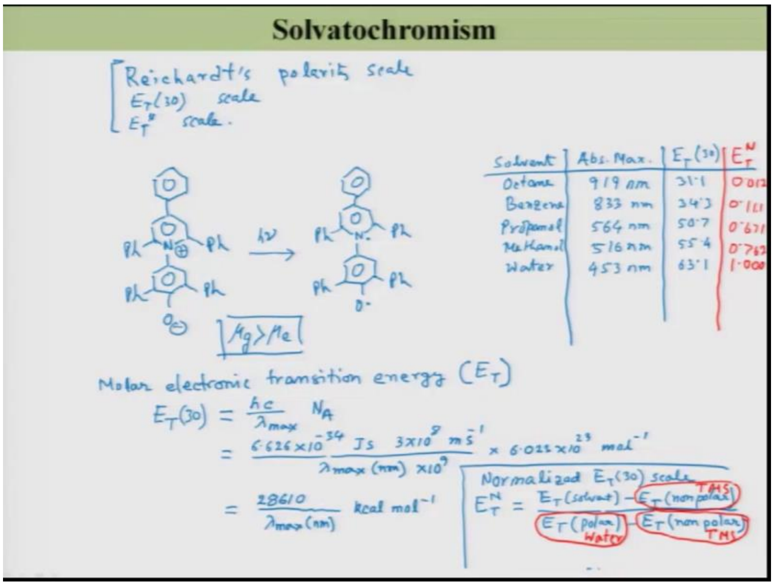

Solvatochromism

Reichardt's polarity scale
$E_T(30)$ scale
E_T^N scale.

$\boxed{\mu_g > \mu_e}$

Solvent	Abs. Max.	$E_T(30)$	E_T^N
Octane	919 nm	31·1	0·012
Benzene	833 nm	34·3	0·111
Propanol	564 nm	50·7	0·671
Methanol	516 nm	55·4	0·762
Water	453 nm	63·1	1·000

Molar electronic transition energy (E_T)

$$E_T(30) = \frac{hc}{\lambda_{max}} N_A$$

$$= \frac{6{\cdot}626\times10^{-34}\ \mathrm{Js}\ \ 3\times10^{8}\ \mathrm{m\,s^{-1}}}{\lambda_{max}(\mathrm{nm})\times10^{-9}} \times 6{\cdot}023\times10^{23}\ \mathrm{mol^{-1}}$$

$$= \frac{28610}{\lambda_{max}(\mathrm{nm})}\ \mathrm{kcal\ mol^{-1}}$$

Normalized $E_T(30)$ scale

$$E_T^N = \frac{E_T(\text{solvent}) - \underset{\text{TMS}}{E_T(\text{non polar})}}{\underset{\text{Water}}{E_T(\text{polar})} - \underset{\text{TMS}}{E_T(\text{non polar})}}$$

So, this is known as Reichardt’s polarity scale or E T 30 scale E T N scale all these are polarity scale; I will explain these things. So, what Reichardt did he took a dye right the structure is something like this. So, you see this molecule is polar it has a large dipole moment in the ground state, but when excited this molecule become radical; that means, the dipole moment decreased. So, in this particular case it is the case of mu g is greater than mu e. So, if I dissolve this molecule in different solvents what I expect, I expect that as the polarity will increase there will be a blue shift in the emission maxima.

So, let us see what are these values? So for this particular dye if I write the solvent over here, then absorption maximum like this. So, for octane is a non polar right; octane this value what he observed is 919 nanometers. So, any change this octane to benzene the value he observed is 833 nanometers, when you change it to propanol he observed it has 564 nanometer, and in case of methanol this is 516 nanometer, and in case of water it is 435 nanometer. So, I can simply plot this different solvent versus absorption maxima and then for the unknown solvent I can find these absorption maxima and can comment about the polarity of the unknown solvent, whether it is like octane or just benzene or propanol like it we can comment on that.

However, we can do one step ahead and find out the molar electronic transition energy. So, molar electronic transition energy right denoted as E T of this particular dye you can calculate. So, molar electronic condition energy is defined as that how much energy is required for this electronic transition for 1 mole of the substance. So, that is nothing but h c by lambda max into Avogadro number; h c divided by lambda max for a particular solvent into Avogadro number; is not it. So, this I can write all the value 6.626 10 to the power minus 34 joule second, c is 3 10 to the power 8 meter per second lambda max is lambda max in nanometer or in meter, so just a write lambda max right lambda max and then this Avogadro number 6.023 10 to the power 23 part mol 1 into 6.023 10 to the power 23 per mol.

So, if we solve this, see the second inverse second cancel out. So, this will is going to be joule and this meter here is also lambda max is in the meter. So, if I want to put this in the nanometer better I write lambda max into 10 to the power 9 if it is represented in nanometer. So, then I will put in 10 to the power 9 in the meter. So, then meter will cancel. Now, if we put all these values over here this will be going to be; now if I convert the joule to calorie. So, then this will going to be 28610 divided by lambda max in nanometer, kilo calorie per mol.

So, I can simply divide like this lambda max to this 28610 kilo calorie per mol and then I can write over here the corresponding values. So, here I will write E T is generally denoted as E T 34 this dye generally E T as I written, but it generally represented as E T 30; that number 30 is nothing but the this dye number because when Reichardt did this study he used to (Refer Time: 18:44) this type of (Refer Time: 18:46) number of dyes. And this particular dye found out to be the most useful one by Reichardt and in his original paper the number of this dye is happens to be number 30 dye. So, it is written as E T 30; E T 30 value of this particular dye. Whenever I dye E T 30; that means, is this particular dye molecule.

So, if I now convert I will get the different values of E T 30 from this equation. So, for these one this will going to be 31.1 and this one is 34.3, this is 50.7, this is 55.4 and this is 63.1. It means that this particular solvent octane has corresponding value of 31.1; these for this particular dye this molar transition energy E T 30 value.

However, as you can see here these values starts from 31 for a very non polar solvent and for the most polar solvent this value is 63.1. So, this is actually not that good scaling, the scale should start from 0 and 1 or 100 and 0 and like that then this scale looks much better. So, then what he did he just normalized. So, instead of E T 30 what he used he used a normalize E T 30. So, let me write over here normalized E T 30 scale which is denoted by E T N. So, this is defined as E T of solvent of your choice minus E T of most non polar one divided by E T of most polar one minus E T of most non polar one.

So, he took the most polar solvent as water. So, here 42 keys this as water and non polar T M S. So, these values are constant values, so these value, this value, these are the constant. so when the solvent is water this value is nothing but 1; when the solvent is water this value is nothing but 1. And when this solvent is T M S; these value is going to be 0, that is it.

Now I convert this E T 30 scale to a normalized a scale or polarity which is known as E T M scale. Now if I just simply write the corresponding value of E T N over here so the octane becomes 0.012, water becomes 1.000 and then methanol is 0.762, propanol is 0.671 and benzene is 0.111. So, what you can see is that we got a thousand polarity scale E T N scale. And this E T N scale is widely used solvent polarity scale because it contains all the interaction, because the shift in the absorption spectra is a resultant of all possible interaction between the solvent and the molecule that is solvatochromism dye in this case that I got 30 dye.

So, if somebody says that the polarity of this particular solvent is something like 0.01 then it is evident that this solvent is non polar solvent, if it is like 0.8, 0.9 then is a polar solvent. So now, let us move to this topic the fate of excited molecule.

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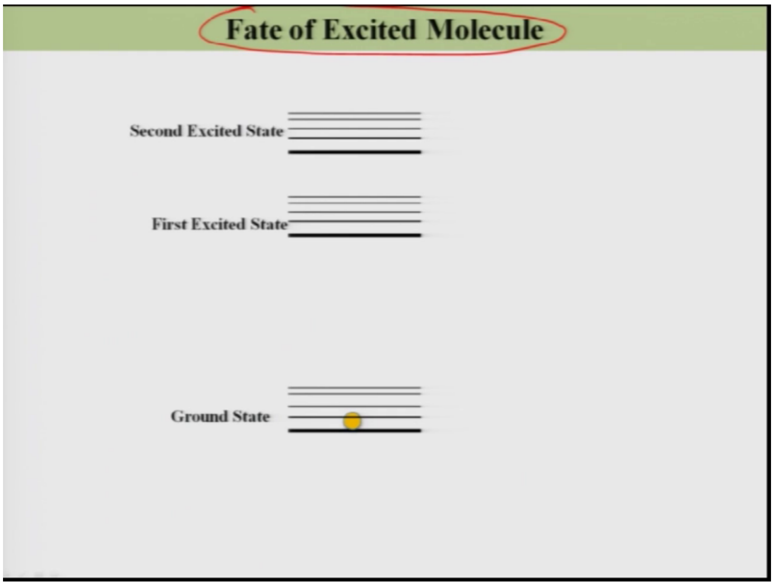

Fate of Excited Molecule

Till now what we have seen is that we are exciting this molecule from one state to the other state by absorption of radiation that we have seen. And that gives me the absorption spectra. So, depending on that from ground state to the first excited state or second excited state that rush inspector change and if we scan the wavelength and plot the absorbance what we are going to get is the absorption spectra.

So, by the absorption of this electromagnetic radiation or light the molecule goes from the ground state to the excited state. Now, the question is after you promote the molecule from ground electronic state to the excited state that is abide by the Franck condones principle right that we have already discussed. So, what is the fate of this molecule? The molecule will remain in the excited state forever or it will undergo some kind of deactivation process and ultimately it will come back to the ground state.

So that is the topic, right now what we are going to discuss and I see the time is up so we are going to discuss on in the next class.

Thank you very much.