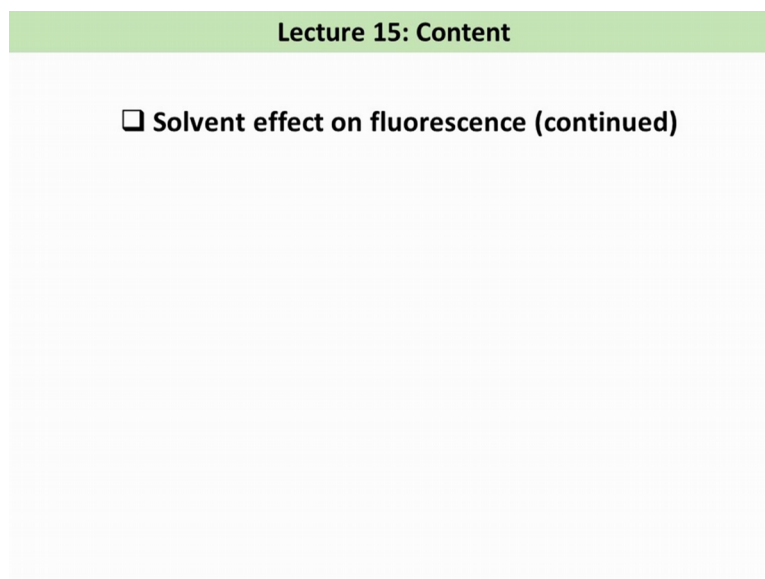


**Basics of Fluorescence Spectroscopy**  
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**Department of Chemistry**  
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**Lecture – 15**

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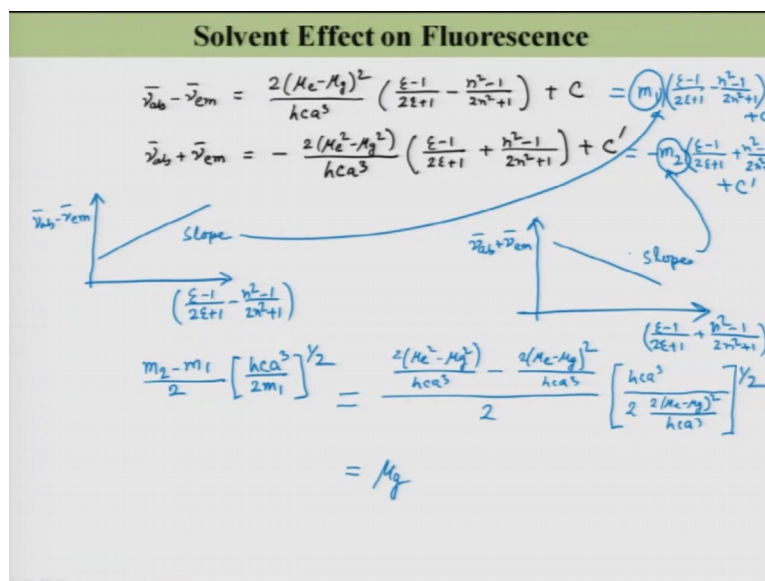
Welcome to the lecture number 15 of this course Basics of Fluorescence Spectroscopy. In lecture 14, what we were discussing is the solvent effect of fluorescence and in that regard what we have seen is that Lippert-Mataga equation. And in the Lippert-Mataga equation what ultimately we have seen is that if we take the fluorescence spectra of your molecule at as a function of different solvent, and then function of different solvent is given by the two quantity is directly constant and the refractive index where the orientational polarizability is expressed as  $\epsilon - 1$  by  $2\epsilon + 1$ , minus  $n^2 - 1$  by  $2m^2 n^2 + 1$ .

So, in that case we will get a straight line and from that slope we will be able to calculate the excited state dipole moment, if constant dipole moment is known all ground state dipole moment if excited state dipole moment is known provided that  $a$ , that is the radius of the cavity is known to us a priori.

So, then I argued that. So, if we want to measure the excited state of moment then from some other technique that we need to know that what is the value of the ground state

dipole moment; obviously, those techniques are available, but what I wanted to show you today that if we and eventually we have started the last day that if we just rewrite that equations right which we have already derived in a different form, then the situation which will come will be so interesting that we will be able to measure the ground and excited state of dipole moment together.

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So, in that regard what we ultimately got is these 2 equation, the first 1 is that nu absorption nu bar right minus nu bar emission is equal to twice, mu e minus mu g whole square by h c a cube right, here this c is because it is in the wave number into epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by twice, n square plus 1 plus that c right that c is for our inherent stock shipped in the molecule right and also we have seen that if we take this nu bar absorption plus nu bar emission right then what we will going to get is minus twice mu e square minus mu g square divided by h c a cube into epsilon minus 1 by twice epsilon plus 1, plus n square minus 1 by twice n squared plus 1 and we will get some other constants right C prime.

So, here what you can see this, this first 1 is nothing but Lippert-Mataga equation right the first 1 is nothing but Lippert-Mataga equation and the second 1 I just did that mu bar absorption plus nu bar emission. So, in this case what will going to get is a negative slope right negative slope. So, let us write this as equal to; let us say this is equal to m 1 right that is my slope, epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by

twice  $n^2 + 1 + c$ , and this will go to be equal to  $m_2$  only this function will be different here is minus, but here will be plus  $\epsilon - 1$  by right plus  $C'$ .

So, now if I plot these 2 the first one is  $\bar{\nu}$  absorption minus  $\bar{\nu}$  emission, then I will get a line like that way. So, slope will go to be this one and if I plot  $\bar{\nu}$  absorption plus  $\bar{\nu}$  emission, then you will get the line like this way and here slope will be equal to  $m_2$ .

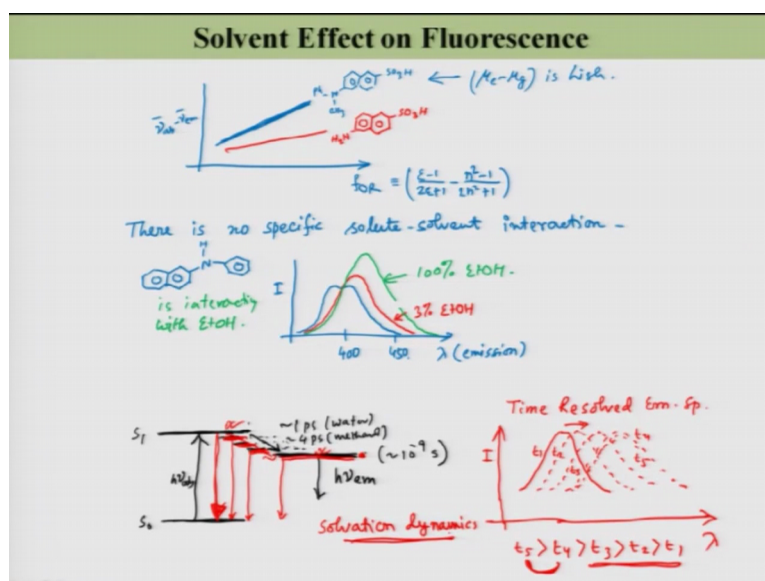
Now, I can tell you that one formula right let me write one formula over here and if I put this value and we will see what will come right if I now calculate  $m_2 - m_1$  divided by  $2$  into  $hc a^3$  by twice  $m_1$  to the power half, if I write that then I know the value of  $m_2$  the value of  $m_1$ ,  $m_1$  is twice  $\mu_e - \mu_g$  whole square by  $hc a^3$  like that and  $m_2$  is twice  $\mu_e^2 - \mu_g^2$  by  $hc a^3$  like that.

So, I can simply plug in all the value of the expression of  $m_1$  and  $m_2$  in this equation and simplify it so that you can just write it over here. So,  $m_2$  is twice  $\mu_e^2 - \mu_g^2$  by  $hc a^3$ , minus  $m_1$  is twice  $\mu_e - \mu_g$  whole square by  $hc a^3$  that whole thing is divided by  $2$  and then I have this quantity right  $hc a^3$  divided by twice  $m_1$  know. So, then  $m_1$  is twice  $\mu_e - \mu_g$  square by  $hc a^3$  right I have this.

If I simplify this is what you will going to see is this is nothing but  $\mu_g$  that you can do it later. So, upon simplification of this expression what you will get this is equal to  $\mu_g$ ; that means, if I know these 2 slope right this slope this  $m_1$  and  $m_2$  separately right then what I will going to get I will get this  $\mu_g$ . Once  $\mu_g$  is known right  $\mu_e$  will be known automatically. So, there is no problem. So, we can measure the ground and excite state of moment by using the solvent dependent change in the fluorescence spectra.

So, as you can see that in this plot right in this plot. So, here is my  $\bar{\nu}$  absorption minus  $\bar{\nu}$  emission versus that  $f o r$ .

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Typically we will write  $f o r$  and you know that this is a function of dielectric constant is refractive index which is nothing but  $\epsilon - 1$  by  $2\epsilon + 1$  like this formed right. So, for different molecule right this feature will be different right. So, for some molecule if this feature is like this, for the other molecule this feature may be something different is something like this.

So, looking at these 2 molecule let us say the molecule here what I am drawn the dependence is this molecule, and this molecule is this one right. In this case I got the slope is more compared to the other right it simply means that the change in the excited state dipole moment from the or the change in the dipole moment; that means,  $\mu_e - \mu_g$  is more for the molecule this one. So,  $\mu_e - \mu_g$  is high that is changing the dipole moment is more where the dependence is more right or the dependence is more.

So, while discussing these I have taken one inherent assumption on this, what is that assumption? The assumption is this solvent right will create a reaction field because of the induced dipole moment by the solute dipole right. So, induced dipole by the solute dipole this it will created a reaction field  $r$  right and then we use that  $r$  for the derivation of this Lippert-Mataga equation and extension of the Lippert-Mataga equation. But we have not explicitly said, but it is true that we have not taken into account any specific solvent interaction; if there is in specific solvent interaction; that means, the solvent is

actually interacting by hydrogen bonding or any other means with the solute molecule then all this description of this solvent dependent emission spectra or solvent dependent fluorescence are not going to be correct.

So, this whatever I have discussed this Lippert-Mataga equation is under the condition that the solvent will not going to have a specific interaction right solvent will not going to have a specific interaction with the solute molecule. So, this is true when there is no specific solute solvent interaction right if there is a specific solute solvent interaction let me let me show you 1 molecule, this is specific solute solvent for this molecule this is a very famous example right, this is for this molecule if you change the solvent right the solvent is let us say ethanol water mixture.

So, you can tune the refractive index nicely. So, in this case the change the change in the emission spectra of this molecule will be anomalous for very low concentration of ethanol? If I may draw briefly over here this is that  $\lambda_{em}$  right emission and this is my intensity of fluorescence right I can represent as  $I$  or a whatever you want. So, when it is like pure water what you will get this emission is something like this right this, maxima is around here is around 400 nanometer, here is around 450 nanometer with a very small amount of ethanol this picture will shift right drastically.

So, a small amount of ethanol in this spectra will shift to like this only three percent of ethanol. Now if I change the ethanol concentration to 100 percent, there will not much change in the emission maxima right. So, when I change this to 100 percent this will be something like this; that means, somehow this molecule is interacting this interacting with ethanol and in this case you cannot apply this Lippert-Mataga equation for this molecule. So, specific interaction has to be should not be present right between the solute and the solvent then this Lippert-Mataga equation is valid and we can easily measure the ground state dipole moment and excited state dipole moment right using this solvent dependency of the emission or fluorescence spectra.

There is another catch over here, another condition over here that condition let me write it or let me explain it using these diagrams over here. So, this is my ground state of this molecule right let me write it as  $S_0$  and I have excited this molecule  $h\nu$  absorption and I have created this excited state these excited state. So, here is my  $h\nu$  absorption that we already have calculated over here, this excited state will stabilize because of the

solvent reorientation right that we already have seen and then that is why this if who are is applicable after when I am talking about this emission part.

So, let us say this is my stabilization till here is my stabilization my stabilization, and then emission is taking place from here  $\lambda$  emission or  $h\nu$  emission  $h\nu$  emission right now from here to here. So, coming from this state to this state right there will be numerous numbers of steps depending on the specific solvent reorientation around the solute dipole. If these process is much much faster than the lifetime of this state; lifetime of the state is about nanosecond that I have said this is about  $10^9$  second and if these process starting from this state is 1 unsolvated right and this S 1 solvated. So, from these to this state if the timescale is much much faster than this emission right will be provided only by this stabilized energy state.

If these process if from here to here if this process right if this process is slower right then from each and every state we will contribute to the fluorescence. So, whatever I said this is true when I have this process is much faster than this process. So, in bulk water right in water or in this process, this process is about picosecond 1 picosecond in methanol with water, in methanol this is about 4 picosecond.

So obviously, this is about thousand times faster right and so, in for everyday I have no issue I can get these things done, but if you use a viscous solvent right like ionic liquids and several other viscous solvents are available, if you use a viscous solvent then these emission right will also get a contribution from these different intermediate states. Let us take let us ask the question in a different way, if you really want to get the information of this state; that means, what we are going to see is emission at 0 time from here nothing has been solvated, no energy minimization, because of the reorientation of the solvent after some time there will be little bit reorientation of the solvent.

So now, the emission will be not this much of energy, but emission will be like this much of energy after some time emission will be this much of energy and at the end emission will be this much of energy; it means that with time the emission spectra will shift; shift towards the longer wavelength or red side. So, it means that if you can somehow take the or if you can somehow measure the emission spectra as in a time resolved mode; that means, immediately after excitation if this is my initial spectra after some time that could be 1 because again that would be 100 femtosecond, that would be 1 nanosecond

depending on your system if you can measure then what you will going to see is that the gradual shift in the emission spectra right gradual shift of the emission spectra as time goes.

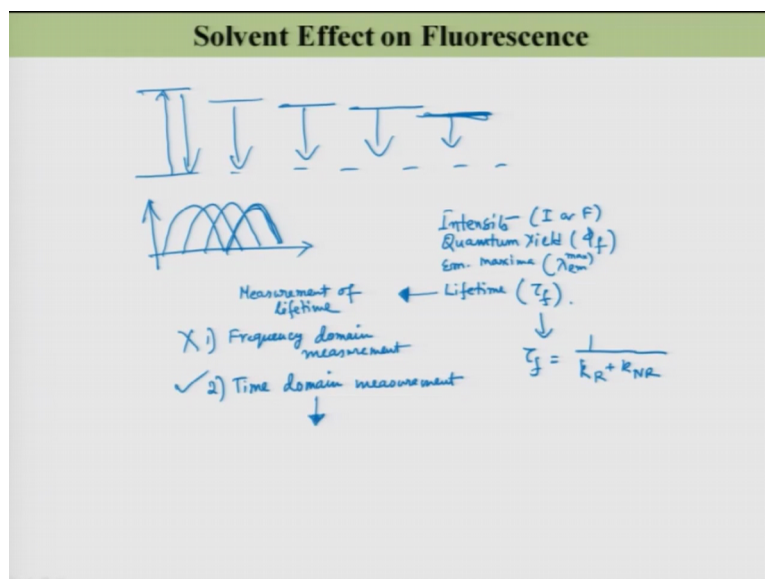
So, basically what you will going to see is the following time resolved emission spectra right. So, initially at early time your emission spectra is something like this, as time goes emission spectra will shift to the longer wavelength here is my wavelength axis over here and here is your intensity right; as time goes your emission spectra will shift, shift, shift and when things are at this position things are at this position then there will be no longer shift, then even you change the time there will be no longer shift. That means, what I said this is  $t_1$  let us say, this is  $t_2$  let us say, this is  $t_3$ , this is  $t_4$ , this is  $t_5$  here  $t_5$  is greater time than  $t_4$  greater than  $t_3$ ,  $t_2$ ,  $t_1$  right here this emission spectra are different, but for these 2 this (Refer Time: 22:06) emission spectra are very same; that means, it has reached these are my fully solvated state. That means, after that time there is no longer any salvation taking place that means, it is reached the most stabilized state and that state what we have seen in our Lippert-Mataga equation.

So, now question is that if I want to get such kind of time resolved emission spectra right then that normal steady state emission spectra is not good enough, because that will going to give me the integrated value of all this emission spectra right that will going to give me the integrated value of all these emission spectra. So, my question is how we will going to get that how will going to get this time resolved emission spectra. If I will be able to measure the time resolution spectra I will be able to see the formation of this state through the intermediate states.

And that is a very interesting topic and the time scale of going from this state to this state is known as the solvation time, and the dynamics is known as the solvation dynamics right. So, eventually by this we will get the solvation dynamics of the solvent of your choice right as I said that in water it is about picoseconds, and as you change the solvent to methanol it increase rate 4 picosecond, 5 picosecond and so on and so forth.

Now let me briefly discuss this thing that how will going to measure this time result emission spectra. So, I think the time is almost up. So, before starting that how will going to measure the times result emission spectra.

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Let me repeat what I said using a diagram; that means, that when I excite my system from here to here, these are my intermediate states right that is what and this is my final state fully solvated state. So, every time I will going to measure I will going to measure the emission like this, this, this, this, this. So, here I will get emission spectra like this way and in this case this will be shifted to the red side, red side, red side and after some time this will remain same as time is up. So, I will finish here and in the next class what I will going to do is I will show you that how will going to calculate this time result emission spectra from the measure the emission intensity as well as the lifetime measurement.

Earlier what I said you that the four different parameter of fluorescence right you remember I said that emission the intensity, I said the quantum yield right I or F. So, this is denoted by  $\phi_f$ , I also said the emission maxima generally denoted as  $\lambda_{em}$  and I also said the lifetime fluorescence lifetime. It is denoted by  $\tau_f$  and I also showed you that this  $\tau_f$  is nothing but  $1 / (k_R + k_{NR})$  radiative and non radiative path process pathway. So, but I have not told you that how will you going to measure this lifetime and this is important to get this time resolution spectra. So, we have to measure the lifetime. So, the measurement of lifetime is important in our case.

There are 2 way we can measure the lifetime the first one is in the frequency domain measurement and the second one is the time domain measurement. I will not going to



discuss the frequency domain measurement in this course, but I will discuss the time domain measurement in this course. In time domain measurement the idea is very simple that you excite your sample with a short light pulse.

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#### Lecture 15: Summary

- ❑ When ground state dipole moment of a molecule is known then it is possible to calculate the excited state dipole moment from the slope of the plot  $(\bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{em}})$  vs  $\left(\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1}\right)$ .
- ❑ To obtain both ground state and excited state dipole moment we need to plot  $(\bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{em}})$  vs  $\left(\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1}\right)$  as well as  $(\bar{\nu}_{\text{abs}} + \bar{\nu}_{\text{em}})$  vs  $\left(\frac{\epsilon-1}{2\epsilon+1} + \frac{n^2-1}{2n^2+1}\right)$  and we can calculate both  $\mu_e$  and  $\mu_g$  from the slopes of the two plots.
- ❑  $(\bar{\nu}_{\text{abs}} + \bar{\nu}_{\text{em}})$  vs  $\left(\frac{\epsilon-1}{2\epsilon+1} + \frac{n^2-1}{2n^2+1}\right)$  shows a negative slope for  $\mu_e > \mu_g$  and a positive slope for  $\mu_g > \mu_e$ .
- ❑  $(\bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{em}})$  vs  $\left(\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1}\right)$  shows a positive slope for any value of  $\mu_g$  and  $\mu_e$ .
- ❑ Lippert-Mataga equation is valid only when there is no specific solute-solvent interaction

And now let us monitor the how the fluorescence intensity will change as a function of time right and with this let me finish here and we will continue on the next lecture.

Thank you very much.