# Basics of Fluorescence Spectroscopy

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## Lecture – 14

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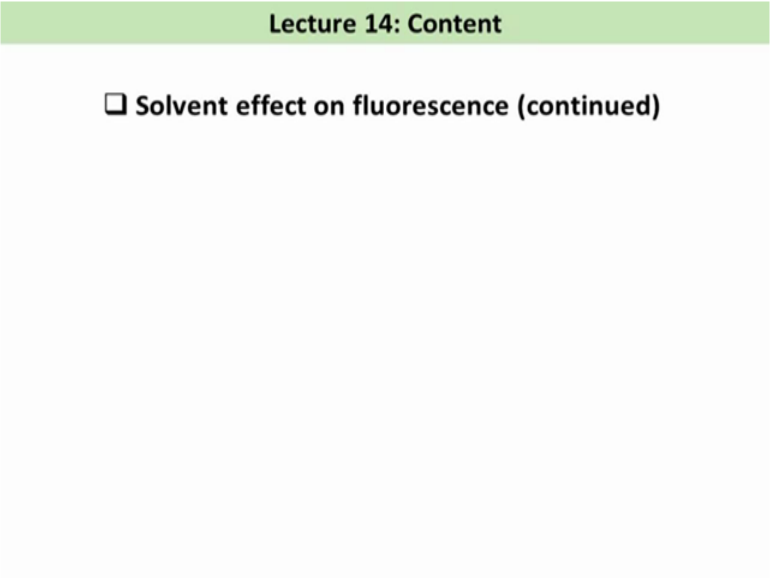

**Lecture 14: Content**

❑ **Solvent effect on fluorescence (continued)**

Welcome back. So, in the last lecture, we were discussing about the solvent effect on fluorescence. And what we have seen is that if you have the solute obviously, having prominent dipole either in the ground state is mu g or in the excited state it is mu e. If you put the solute in the solvent then that solute will going to polarize the solvent both in electronically and in the orientational polarization. And because of this polarization, this solvent will create reaction field around the solute; and because of this reaction field the solute will go in to stabilize. And with this we have estimate or we have calculated the stabilization energy, when you take the solute from vacuum onto a particular solvent both in terms of absorption and in emission.

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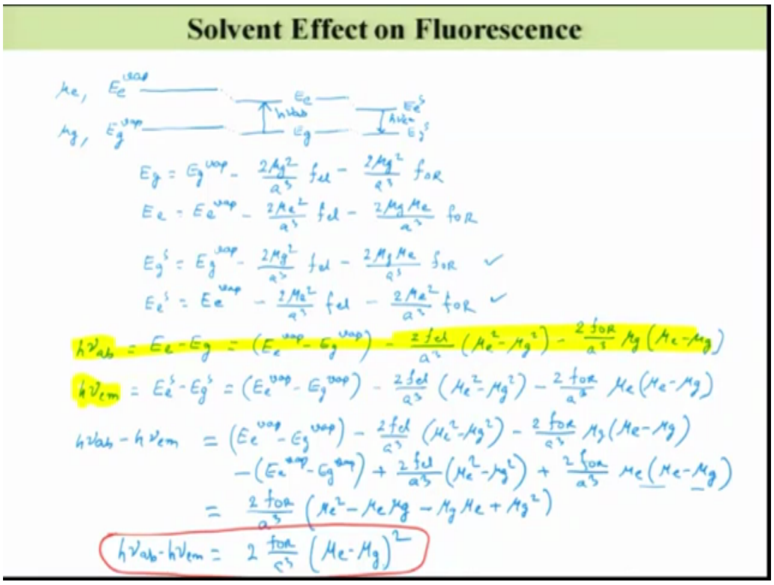

Solvent Effect on Fluorescence

$$E_g = E_g^{vap} - \frac{2\mu_g^2}{a^3} f_{el} - \frac{2\mu_g^2}{a^3} f_{OR}$$

$$E_e = E_e^{vap} - \frac{2\mu_e^2}{a^3} f_{el} - \frac{2\mu_g \mu_e}{a^3} f_{OR}$$

$$E_g^s = E_g^{vap} - \frac{2\mu_g^2}{a^3} f_{el} - \frac{2\mu_g \mu_e}{a^3} f_{OR} \checkmark$$

$$E_e^s = E_e^{vap} - \frac{2\mu_e^2}{a^3} f_{el} - \frac{2\mu_e^2}{a^3} f_{OR} \checkmark$$

$$h\nu_{ab} = E_e - E_g = (E_e^{vap} - E_g^{vap}) - \frac{2 f_{el}}{a^3}(\mu_e^2 - \mu_g^2) - \frac{2 f_{OR}}{a^3}\mu_g(\mu_e - \mu_g)$$

$$h\nu_{em} = E_e^s - E_g^s = (E_e^{vap} - E_g^{vap}) - \frac{2 f_{el}}{a^3}(\mu_e^2 - \mu_g^2) - \frac{2 f_{OR}}{a^3}\mu_e(\mu_e - \mu_g)$$

$$\begin{aligned} h\nu_{ab} - h\nu_{em} &= (E_e^{vap} - E_g^{vap}) - \frac{2 f_{el}}{a^3}(\mu_e^2 - \mu_g^2) - \frac{2 f_{OR}}{a^3}\mu_g(\mu_e - \mu_g) \\ &\quad - (E_e^{vap} - E_g^{vap}) + \frac{2 f_{el}}{a^3}(\mu_e^2 - \mu_g^2) + \frac{2 f_{OR}}{a^3}\mu_e(\underline{\mu_e} - \underline{\mu_g}) \\ &= \frac{2 f_{OR}}{a^3}(\mu_e^2 - \mu_e\mu_g - \mu_g\mu_e + \mu_g^2) \end{aligned}$$

$$\boxed{h\nu_{ab} - h\nu_{em} = 2\frac{f_{OR}}{a^3}(\mu_e - \mu_g)^2}$$

Let us see once again. So, what we found is that if this is the energy level of the particular solute having dipole moment mu g or mu e in the ground state and in the excited state. So, let me write over here. This is the energy E g that is ground state in the vapor that is what we have seen already; this is E e vapor dipole moment here is mu e, here dipole moment is mu g. So, this is in the vapor. So, if you when you put this in a solvent then as we know that the; this energy will go in to stabilize, and I define these energies as E g and E e. And we have seen that the expression of E g and E e in terms of the dipole moment, the polarizability both f e l and f O R.

So, let me write it once again over here. So, this is E g, what we have calculated as E g vapor minus twice mu g square by a cube. As you remember this mu g is the ground state dipole moment and a is the radius of the cavity, f e l minus twice mu g square by a cube f O R. And we got E e equal to E e vapor minus twice mu e square divided by a cube f e l minus twice mu g mu e right mu g mu e divided by a cube f O R then what we said that; obviously, this orientation polarizability is slow, so it will take some time to stabilize the excited state because the creation of the excited state is electronic rearrangement which is instantaneous like a less than a femtosecond. So, the solvent molecule will take some time to reorient themselves to stabilize it, so that stabilize state right stabilize state.

So, this state will going to be further stabilize because of this solvent reorientation, and I termed it as E e s and I termed it as E g s that means, solvated. And we found that E g s is equal to E g vapor minus twice mu g square by a cube f e l minus twice mu g mu e is not it, by a cube f O R. And E e s is E e vapor minus twice mu e square by a cube f e l minus twice mu e square by a cube f O R. So, you got these four equations right. So, what we can do if we take E e minus E g that will going to be my absorption spectra of that particular solute in that particular solvent and then E e s minus E g s is my emission spectra. So, I can write this h nu absorption and here h nu emission.

So, h nu absorption if I calculate, so this h nu absorption will be h nu absorption is equal to E e minus E g, E e minus E g and that we already have seen right. So, this is E e vapor minus E g vapor minus twice f e l divided by a cube mu e square minus mu g square minus twice f O R by a cube mu g into mu e minus mu g. And similarly, I can calculate the h nu emission. So, h nu emission is equal to E e s minus E g s, this is going to be equal to E e vapor minus E g vapor. Then this will going to be equal to minus twice f e l by a cube from here from this equation and this equation, I am writing it by a cube to mu e square minus mu g square minus twice f O R by a cube mu e into mu e minus mu g.

So, now I can do one thing, I can just take h nu absorption minus h nu emission and see what will happen. So, if I just plot, if I just calculate h nu absorption minus h nu emission, so then this quantity minus this quantity, so this will be equal to E e vapor minus E g vapor. So, write again all the term to f e l by a cube mu e square minus mu g square minus 2 f O R by a cube mu g into mu e minus mu g minus again this term E e vapor minus E g vapor plus 2 f e l divided by a cube mu e square minus mu g square plus twice f O R by a cube mu e mu e minus mu g. So, these terms will cancel out. So, this will ended up with twice f O R by a cube.

So, see here mu e square minus mu e mu g. So, here mu e square minus mu e mu g and here is my mu g square mu e mu g. So, this is nothing, but mu e square minus mu e mu g minus then here is my minus, minus minus plus mu g mu e plus mu g square. So, this is equal to twice f O R by a cube mu e minus mu g whole square that is it. So, what I got I got is h nu absorption minus h nu emission is equal to this. So, please take a note on that. So, what is the form of f O R, I said this is a function of both dielectric constant and refractive index.

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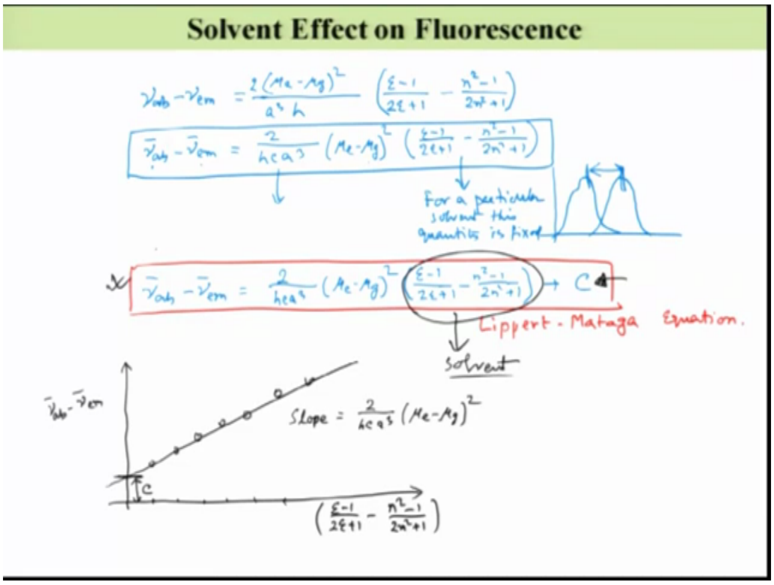

Solvent Effect on Fluorescence

$$\nu_{ab} - \nu_{em} = \frac{2(\mu_e - \mu_g)^2}{a^3 h} \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)$$

$$\boxed{\bar{\nu}_{ab} - \bar{\nu}_{em} = \frac{2}{hca^3} (\mu_e - \mu_g)^2 \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)}$$

For a particular solvent this quantity is fixed

$$\boxed{\bar{\nu}_{ab} - \bar{\nu}_{em} = \frac{2}{hca^3} (\mu_e - \mu_g)^2 \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) + C}$$

Lippert - Mataga Equation.

solvent

So, now what I have I have nu absorption minus nu emission. This will going to be equal to mu e minus mu g whole square by 2 a cube and that h will come over here into f. And f O R I can write I know this f O R is equal to f O R equal to epsilon minus 1 by twice epsilon plus one minus n square minus 1 by twice n square plus 1. So, what I got is this equation and if you want you can change it to the wave number. So, if I change nu to nu bar right and what I have to do I have to divide this b y again another c. So, then I can also write nu bar absorption minus nu bar emission is equal to twice by h c a cube 2 by h c a cube mu e minus mu g square into epsilon minus 1 by twice epsilon plus 1 n square minus 1 by twice n square plus 1. So, this is nothing but the difference in absorption and emission spectra, either in terms of frequency or in terms of wave number.

So, if my absorption is like this and in that particular solvent my emission is like this. So, then this is the difference that is the difference that is my stock shift. But as I have discussed earlier, I said that what is the implication of the Carson's rule, Carson's rule says that the emission will takes place from the lowest vibrational level of the first electronic excited state that and it is also obviously, So, according to the Planck quantum principle, so absorption emission both. That means, is always found that emission maxima is shifted to lower wave length and that the sums even there is no such kind of solvent effect. So, those are the inherent. So, those are the stock shift.

So, that inherent stock shift is because of the vibrational relaxation. So, if you excite a molecule in the higher vibrational level eventually it will come back to the lowest vibrational level of the first singlet excited state and then emission will takes place which is accordance to the Planck quantum principal as I showed you earlier that means, there will be inherent stock shift right inherent. So, these stocks shift, so this one is because of what is because of salvation, it is because of salvation. For this particular solvent for a particular solvent epsilon and n are fixed. So, this is for a particular solvent, this quantity is fixed is not it.

So, for the particular solvent, I got some value of this. And then this part what about this part this part is a constant, it has the particular radius of cavity a h is constant, c is constant, so a is the constant. So, this difference between absorption and emission maxima is guided by this dipole moment of the species, and this is simply because of this solvation differential solvation of the ground and excited state. So, in the absorption and the emission, because absorption is instantaneous, so when we calculate they we calculate we use with the Gaussian dipole moment, but in emission it takes some time the because of reorientation takes some time. So, we have treated it that solvent reorientation because the lifetime of the excited state is not like a very, very small. So, it has a finite lifetime about nanosecond. So, then we calculated this equation.

So, this particular equation is telling me that the shift from the absorption emission is because of the solvent, but I already have inherent stock shift of any such kind of fluorescent molecule, whether it has a more exited state dipole moment or more ground state dipole moment whatever it is I will have a inherent stock shift. So, for a molecule, I have a inherent stock ship again repeating it the same. So, then this equation should be plus something.

So, let me rewrite it over here. So, then this equation should be nu absorption of a nu bar minus nu bar emission is equal to 2 by h c a cube mu e minus mu g whole square epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by twice n square plus 1 plus some constant c. And these particulars constant c is because of the inherent stock shift of this molecule it is because of the vibrational relaxation. So, we got our equation of interest and this equation is known as Lippert-Mataga equation. If you go to Japan, they call this equation as Mataga-Lippert equation because they think that Mataga is the pioneer of this equation, but in Europe is called the Lippert-Mataga equation anyway.

So, in this case, this equation tells me very interesting thing is that if I measure absorption and emission spectra of your particular solute at a different, different solvent. Different solvent means these actually represent my solvent you know this is my solvent these actually represent my solvent. This c is constant is independent of the solvent this c is solvent independent quantity.

So, now if I measure the absorption and emission of the solute at a various solvents then I will get a different value of lambda nu bar emission and nu bar absorption. So, then I take this difference between nu bar absorption minus nu bar emission and I can simply plot the same. So, if I plot the this nu bar absorption minus nu bar emission versus the solvent, solvent is designated as this function epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by twice n square plus 1. If I plot this nu absorption emission for different solvent, so this is solvent one, this is solvent two, this is solvent three, this is solvent 4, 5, 6 like that.

So, what I will get I will get a straight line this is a straight-line equation y equals m x plus c. So, I will get a straight-line with intercept of c and the slope will be equal to two by a c a cube into mu e minus mu g whole square. So, I will get like a different, different points like over here different, different, points and that will corresponds to a straight line where this intercept is equal to c this inherent stock shift, and the slope will be equal to 2 by h c a cube to mu e minus mu g whole square. So, it means obviously, here h c a cube, these are the fixed quantity. And it means that if you do such kind of experiment then the slope is nothing but mu e minus mu g whole square with this constant value. It means that if you know that ground state dipole moment, you will be able to calculate the excite state dipole moment and vice versa; that means, if you know the excited stated dipole moment you will be able to calculate the ground state dipole moment.

Now the question is how is going to measure the ground state dipole moment there are several techniques by which you can measure, but let me tweak this equation in a different way, and I will show you an another interesting outcome of the same. So, what I have done, I have done nu bar absorption minus nu bar emission and we got that equation right and we got this equation nu bar absorption minus nu bar emission we got this equation instead of doing that I can also do nu bar absorption plus nu bar emission and let see what we will get right. So, like I decided to do that right earlier or Lippert and Mataga decided to do that nu bar absorption minus nu bar emission.

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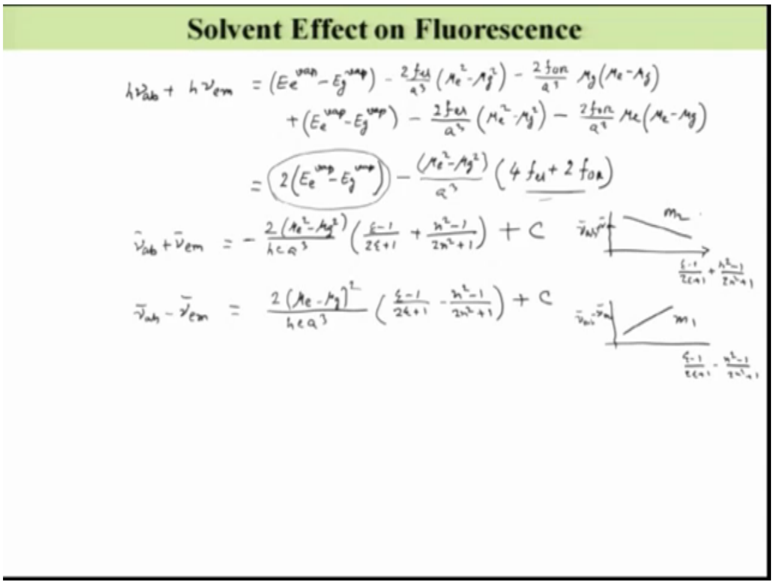

Solvent Effect on Fluorescence

$$h\nu_{ab} + h\nu_{em} = (E_e^{vap} - E_g^{vap}) - \frac{2f_{el}}{a^3}(\mu_e^2 - \mu_g^2) - \frac{2f_{or}}{a^3}\mu_g(\mu_e - \mu_g) + (E_e^{vap} - E_g^{vap}) - \frac{2f_{el}}{a^3}(\mu_e^2 - \mu_g^2) - \frac{2f_{or}}{a^3}\mu_e(\mu_e - \mu_g)$$

$$= \boxed{2(E_e^{vap} - E_g^{vap})} - \frac{(\mu_e^2 - \mu_g^2)}{a^3}(4\underline{f_{el} + 2f_{or}})$$

$$\bar{\nu}_{ab} + \bar{\nu}_{em} = -\frac{2(\mu_e^2 - \mu_g^2)}{hca^3}\left(\frac{\epsilon - 1}{2\epsilon + 1} + \frac{n^2 - 1}{2n^2 + 1}\right) + C$$

$$\bar{\nu}_{ab} - \bar{\nu}_{em} = \frac{2(\mu_e - \mu_g)^2}{hca^3}\left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) + C$$

Let us do the other thing. So, h nu absorption plus h nu emission, I can also do it like that a because I know all these forms. I know what is h nu absorption, I know what is h nu emission, so I can do plus. So, if you do that it will be E e vapor minus E g vapor minus twice f e l by a cube mu e square minus mu g square minus twice f o r by a cube mu g into minus mu e minus mu g plus E e vapor minus E g vapor minus twice f e l by a cube mu e square minus mu g square minus twice f OR by a cube mu e into mu e minus mu g. So, let me rewrite it like this way, this is equal to twice E e vapor minus E g vapor minus so here mu e square minus mu g square by a cube, I will take outside. So, this is equal to mu e square minus mu g square by a cube, this will going to be equal to 4 f e l plus 2 f OR. So, if you do you will get that do not worry, so you see here that is multiplied by mu e. So, these 2 f OR term over here this is I have multiplied it over here. So, 4 f e l will come over here. So, it will be like this only; do not worry.

Now, if I divide it right by h c that means, I will get nu bar absorption plus nu bar emission. So, if I want to get nu bar absorption plus nu bar emission then this will going to be twice mu e square minus mu g square by a cube. So, negative sign will be there because I am writing this as first minus into this quantity a twice f e l plus f O R, twice f e l plus f O R. What is f e l, f e l I said that is n square minus 1 plus twice n square plus 1 and that whole thing complete polarization is epsilon minus 1 by twice epsilon plus 1. So, I rewrite over here. So, this will going to be equal to epsilon minus 1 by twice epsilon plus 1 plus, it is not minus now because of this term this will going to be equal to n square minus 1 by twice n square plus 1. So, obviously, these quantities there, this quantity this quantity is a just constant. So, this is just that constant.

So, it means that the dependence of this nu bar absorption and nu bar emission plus that sum is like this way. So, I can also write this nu bar absorption minus nu bar emission once again over here. So, nu bar absorption minus nu bar emission once again over here let me write, so that is equal to twice mu e minus mu g whole square by oh sorry I missed one thing, this is h c, I missed. So, mu e minus mu g whole square by h c a cube and here that function is minus right, epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by twice n square plus 1. And then that vapor part because of this vapor part I have this c.

So, now I can think of that this is if I plot nu bar absorption minus nu bar emission versus this quantity epsilon minus 1 by twice epsilon plus 1 plus n square minus 1 by twice n square plus 1, I will get a straight line with a negative slope. And in this case if I plot this nu bar absorption plus nu, sorry here is my plus and here is my minus, minus nu bar emission versus epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by twice n square plus 1. Then I will get a straight line with a positive slope. Let us take that this slope is m 1 this slope is m 2 and so we will get this straight line and let me finish the discussion here.

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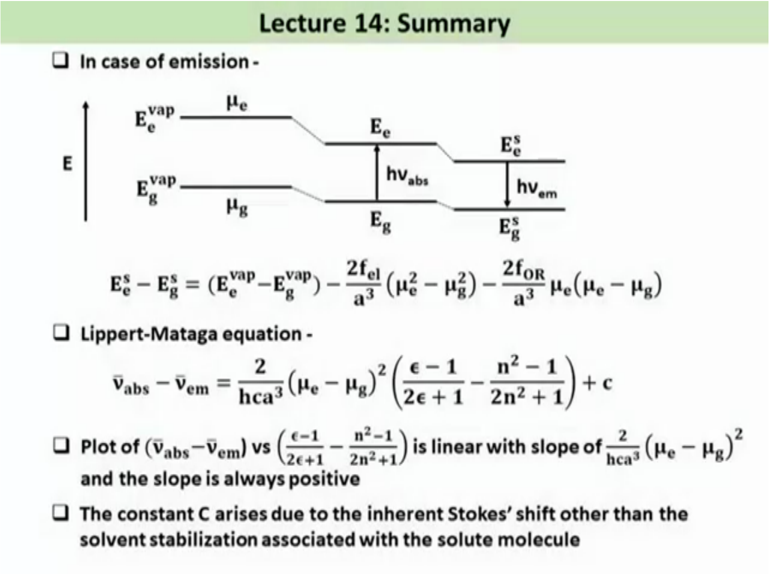

**Lecture 14: Summary**

- ☐ In case of emission -

$$E_e^s - E_g^s = (E_e^{vap} - E_g^{vap}) - \frac{2f_{el}}{a^3}(\mu_e^2 - \mu_g^2) - \frac{2f_{OR}}{a^3}\mu_e(\mu_e - \mu_g)$$

- ☐ Lippert-Mataga equation -

$$\bar{\nu}_{abs} - \bar{\nu}_{em} = \frac{2}{hca^3}(\mu_e - \mu_g)^2\left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) + c$$

- ☐ Plot of $(\bar{\nu}_{abs} - \bar{\nu}_{em})$ vs $\left(\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1}\right)$ is linear with slope of $\frac{2}{hca^3}(\mu_e - \mu_g)^2$ and the slope is always positive
- ☐ The constant C arises due to the inherent Stokes' shift other than the solvent stabilization associated with the solute molecule

And we will go in to see that what is the outcome of this analysis in the next lecture.

Thank you.