Basics of Fluorescence Spectroscopy
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Lecture – 13

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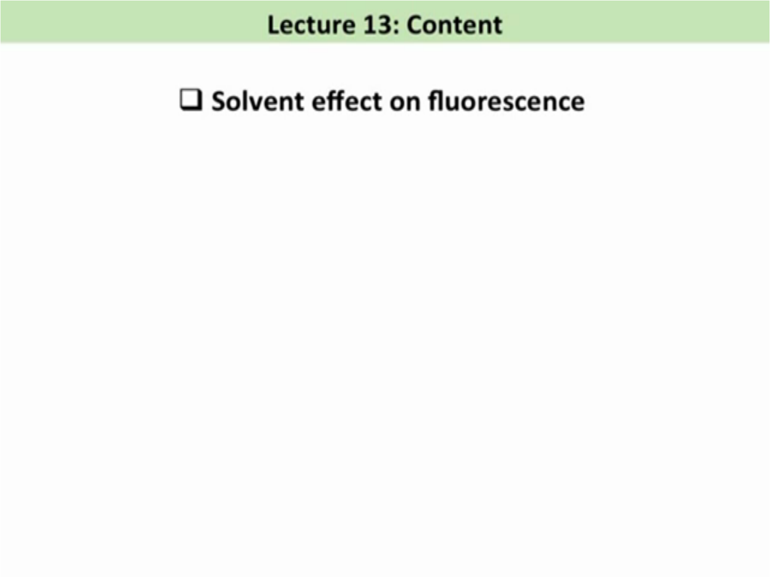

Lecture 13: Content

❑ Solvent effect on fluorescence

Welcome to the lecture number 13. So, in the last lecture, we just have started discussing about the solvent effect on fluorescence that means solvent effect on emission spectra. And we have taken the solute molecule that is responsible for the fluorescence as like this.

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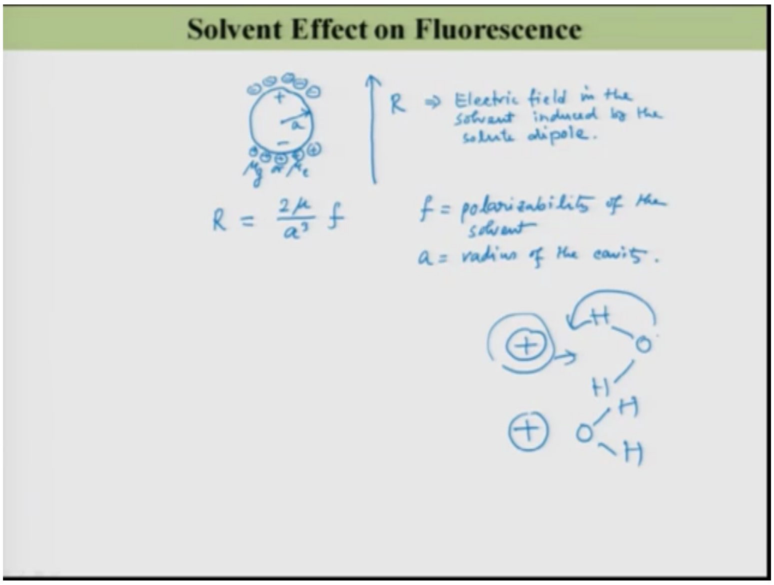

Solvent Effect on Fluorescence

R ⇒ Electric field in the solvent induced by the solute dipole.

$R = \frac{2\mu}{a^3} f$

f = polarizability of the solvent

a = radius of the cavity.

So, this is my solid molecule, having a dipole moment. So, I am just writing it over denoting it over the plus and minus sign. So, the dipole moment could be mu e or mu g depending on it is whether it is in the excited state or in the ground state. So, these solvent molecules will going to be stabilized this solute, and because there is there will be a reaction field we created by the solute molecule to the solvent, so that reaction field R is the electric field in the solvent induced by the solute dipole. So, this is defined as the electric field in the solvent induced by the solute dipole.

And I as I mentioned that the day that this R will be a function of the dipole moment mu, the radius over here which is also a, and the property of the solvent some molecule will be polarized more efficiently, some other not, so that will be the property of solvent. So, R is written as twice there is expression of R twice mu by a cube into f, where f is equal to polarizability of the solvent, and a is the radius of the cavity that is comparatively to the size of the molecule, radius of the cavity.

So, now this polarizability of the solvent are 2 types; one is a electronic polarizability, another is the orientational polarizability. What is electronic polarizability, suppose you have a dipole into the solvent, so the electrons of the solvent molecules are polarized, so that is the electrical polarizability? And the other one is the orientational polarizability; that means, if you have a charge pieces like water, let us say take example of water. So, water that o is partially negatively charged, a is partially positively charged. So, if you have a positive charge over here which is solute and water molecule is present like this way because of the influence of this guy this water will reorient, so that the final arrangement will be something like this. So, that is the reorientation of this water. So, this is called the orientational polarizability.

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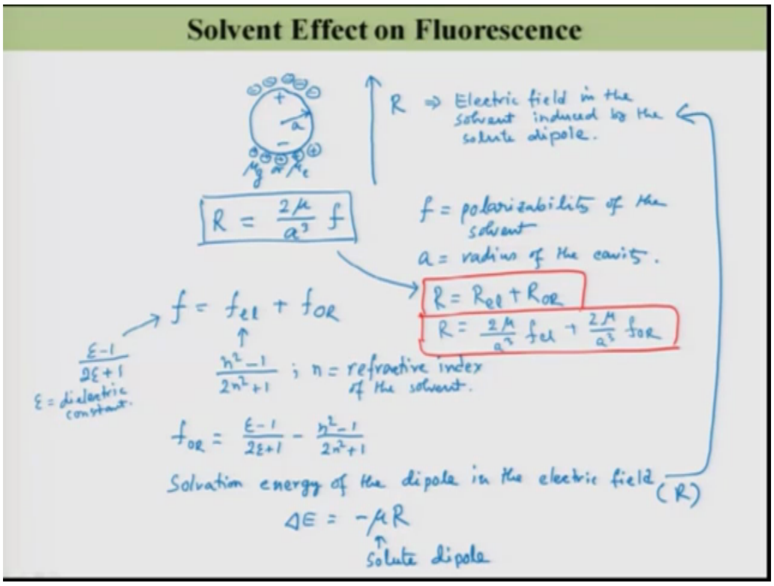

Solvent Effect on Fluorescence

$R \Rightarrow$ Electric field in the solvent induced by the solute dipole.

$\boxed{R = \frac{2\mu}{a^3} f}$

f = polarizability of the solvent

a = radius of the cavity.

$\boxed{R = R_{el} + R_{OR}}$

$\boxed{R = \frac{2\mu}{a^3} f_{el} + \frac{2\mu}{a^3} f_{OR}}$

$f = f_{el} + f_{OR}$

$\frac{\varepsilon - 1}{2\varepsilon + 1}$

ε = dielectric constant.

$\frac{n^2 - 1}{2n^2 + 1}$; n = refractive index of the solvent.

$f_{OR} = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$

Solvation energy of the dipole in the electric field (R)

$\Delta E = -\mu R$

Solute dipole

So, I can write this f as a 2 term, so that that will be additive. So, first is f e l plus f O R. So, this f e l can be written as n square minus 1 by twice n square plus 1. So, this is the reorientation of electron in the solvent as it is instantaneous. So, where n is the refractive index of the solvent. And this f right that is the total polarizability this is a function of the dielectric constant. So, this can be written as epsilon minus 1 by twice epsilon plus 1. So, eventually this f O R is nothing but epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by twice n square plus 1. So, I can simply write f O R is equal to epsilon minus 1 by twice epsilon plus 1 minus n square minus 1 by twice n square plus 1, where this epsilon is the dielectric constant of the medium of the solvent, this epsilon is dielectric constant.

So, let us take this granted because I am not going to show you in detail that how these things are coming. However, one thing is clear to me that if the solvent does not have a permanent dipole then f O R is going to be equal to 0. If the solvent does not have a permanent dipole then f O R going to be equal to 0. And the solvation energy of the dipole, so let me write here solvation energy of the dipole in the electric field which electric field that electric field R, this electric field. So, this electric field R can be written as delta equal to minus mu R. This is the solute dipole this mu is my solute dipole, because it has created the electric field in the solvent that are the reaction field. So, their reaction field going to stabilize that solute, so the delta u will be minus mu into I.

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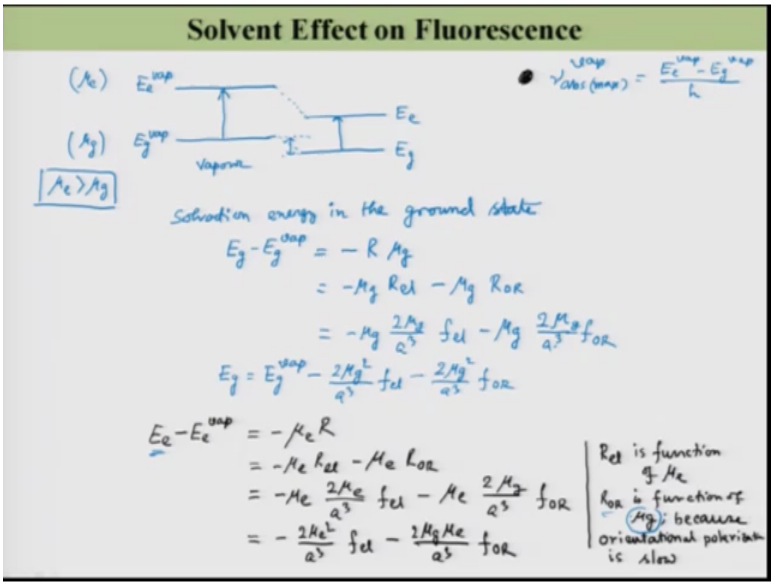

Solvent Effect on Fluorescence

• $\nu_{abs(max)}^{vap} = \frac{E_e^{vap} - E_g^{vap}}{h}$

$\boxed{\mu_e > \mu_g}$

Solvation energy in the ground state

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

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

R_{el} is function of μ_e
R_{OR} is function of μ_g; because orientational polarization is slow

So, now let us see that if I have a solute whose energy is E g vapor in the ground state. Let me draw over here. So, these are the ground and excited state of the solute right and this is in the vapor state g a p vapor state and now there is no solvent. So, if the energy over here is E g vapor, and this energy is E e vapor, and I also said that this is the dipole moment of the ground state and this dipole moment of the excited state. And let us take this another condition over here the condition is mu e is greater than mu g. So, I already have imposed this condition over here that the excited dipole moment is more than the ground state dipole moment. Then in the vapor state if I simply measure the absorption, I will get this much of energy transition. So, the new absorption in vapor will be equal to mu abs, there is a maxima. Let us write max in vapor is equal to E e vap minus E g vapor divided h, E e vap minus E g vap divided by Planck constant.

Now, if I put this solute in solvent then as I showed pictorially while discussing the solvent effect on absorption that this will be stabilized, this will also be stabilized, but the stabilization will be the different extent, this will stabilize less, this will stabilize more and will get lower energy. So, let us see mathematically here first. So, here let us say this energy is E g is not it, and these energies E e So, solvation energy in the ground state let me write that solvation energy in the ground state is this much. So, it is nothing but E g minus E g vapor, this is be equal to minus R into dipole moment of the ground state minus R dipole moment of the ground state, because the solute is in the ground state, so R into mu g. Now, R has to component as I showed, here R is to mu, here R is to mu by a cube into f f is f e l minus f O R. So, from here I can write R equal to R e l plus R O R which is equal to 2 mu by a cube f e l plus 2 mu by a cube f O R. So, I will going to use this equation from now and also use it.

So, this is going to be equal to minus mu g R e l minus mu g R O R. So, I will just simply write the expression of R e l and R O R, which is nothing but 2 mu by a cube and the polarizability electronic polarizability and the orientational polarizability for R O R. So, let me write that minus mu g 2 mu by a cube is the radius of the cavity of your solute a into f e l minus mu g 2 mu by a cube f O R. So, this mu this mu that 2 mu by a cube, this mu is which mu this molecule is in the ground state. So, there should be mu g, so 2 mu g and this also 2 mu g.

So, I will just write it as like this way. So, E g equal to E g vapor minus 2 mu g square by a cube f e l minus 2 mu g square by a cube f O R. So, I got this value of E g. Similarly, I will going to calculate the value of E e. So, I can I can write easily similarly in similar fashion E e minus E e vapor is equal to minus mu into R, but in this case that mu is the mu e the excited state dipole moment of this molecule, so mu e into R. So, this is equal to minus mu e R e l minus mu e R O R. So, this is going to equal to minus mu e twice mu by a cube f e l minus mu e twice mu by a cube f O R.

Now, the question is that which mu I should put over here. This is electronic change electronic change is very fast, so that mu should be mu e; however, this is the orientational change is orientational relaxation. So, although I have excited this molecule from ground to excited state, but the solvent molecule which will see right the excited state just after the excitation those molecules will take some time to reorient themselves, so that means, these reaction field right what we are going to have is very similar to the solvent arrangement in the ground state. So, this mu will be mu g.

So, in this case, R e l is a function of let me write clearly over here, R e l is a function of mu e function of mu e, but R O R is a function of mu g, R O R is function of mu g because orientation polarization is slow. So, then the rest of the part is simple. So, what I will going to have this equal to minus twice mu square by a cube f e l twice mu g mu e by a cube f O R.

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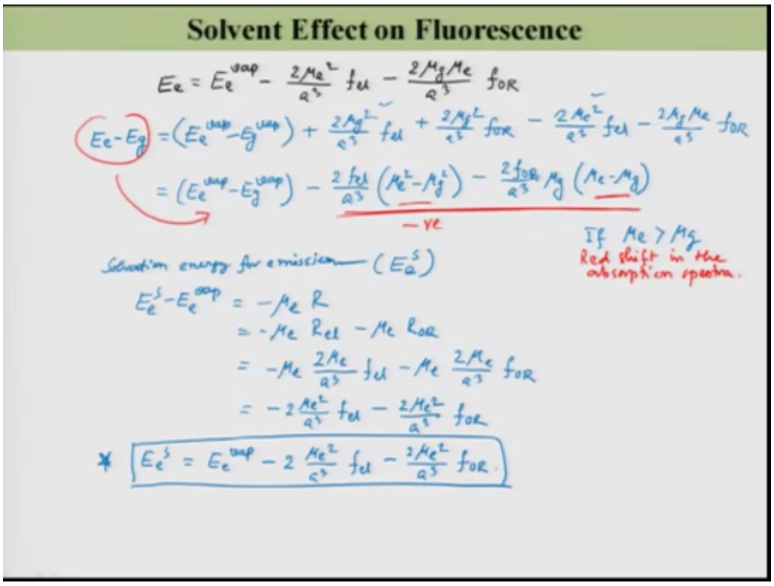

Solvent Effect on Fluorescence

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

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

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

If $\mu_e > \mu_g$
Red shift in the absorption spectra.

Solvation energy for emission — (E_e^S)

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

$$* \quad \boxed{E_e^S = E_e^{vap} - 2\frac{\mu_e^2}{a^3} f_{el} - \frac{2\mu_e^2}{a^3} f_{OR}.}$$

So, I can write this as E e equal to E e vapor minus twice mu e square by a cube f e l minus twice mu g mu e by a cube f O R. So, now if I want to calculate that what is the absorption energy? Similarly I have calculated over here you see. This lambda look here mu absorption maximum vapor is like way. So, I have calculated. So, I can also calculate that mu absorption in the solvent, so that then I have to calculate E e minus E g, is not it E e minus E g. So, let us do it over here. E e minus E g is equal to E e vapor and from the other equation minus E g vapor plus twice mu g square by a cube f e l plus twice mu g square by a cube f O R minus twice mu e square by a cube f e l minus twice mu g mu e by a cube f O R.

So, this is equal to E e vapor minus E g vapor minus I will take this 2 f e l by a cube 2 f e l by a cube from here and from here then this is equal to mu e square minus mu g square. So, then mu e square minus mu g square and then I will also take minus 2 f O R by a cube mu g out then this will going to be equal to mu e minus mu g. So, look at this term. So, I have already said taken that mu e is greater than mu g, if you remember. If mu e is greater than mu g then this quantity is a positive quantity let me change the color orange. So, this is my positive quantity, this is my positive quantity, then the whole thing is negative that means, these energy is less than this energy, because the total thing is negative quantity. This energy is less than this energy means there will be a red shift in the absorption spectra that means, when mu is greater than mu g there is a red shift that what we have seen with those model system like while discussing the solvent effect on absorption spectra. We have seen, but here what we can see is exactly the same thing, but here more mathematical treatment I have shown you over here. So, when mu is greater than mu g then I will see a red shift in the absorption spectra.

Now, what I will going to do I will going to give some time for the relaxation. So, as I said that once you have created this excited state E e, the orientational polarization is slow that means, the solvent we will take some time to solve it, the excited state of your solute molecule. Electronic polarization is fast, but the orientational polarization is slow. So, once you create the excited state, it will take some time the solvent will come and relax, some come and relax. So, that extra stabilization of the state is because of the solvent reorientation, which is under the reorientation or orientational polarizability of the solvent.

So, now, if I give a enough time then instead of using here instead of using mu g for the R O R for that E e state, I will use mu e because I have given enough time for that. So, let us see what will happen for that. So, then in this case this is the solvation energy for emission, so solvation energy for emission. So, in this case E e s, so let us say that this state, the energy of that state is E e s solved it, I just termed it like that. So, E e s minus E e vapor I can calculate that directly. Here the derivation will be exactly same e only the difference is that for R O R, I will going to use mu e, not mu g is not it.

So, let me do it quickly over here. So, this is equal to minus mu e R, this is equal to minus mu e into R e l minus mu e into R O R is equal to minus mu e twice mu e by a cube f e l minus mu e twice mu. In this case, I will write e not g right, because I have given time, so twice mu e by a cube f O R. So, this is equal to minus twice mu e square by a cube f e l minus twice mu e square by a cube f O R. So, I can write E e s equal to E e vapor minus twice mu e square by a cube f e l minus twice mu square by a cube f O R. So, I got that E e s. Similarly, I will also I have to get the E g s, so that we can also do easily. So, I can write E g s minus E g vapor, E g s minus E g vapor, let us do that over here. So, this is another important equation here.

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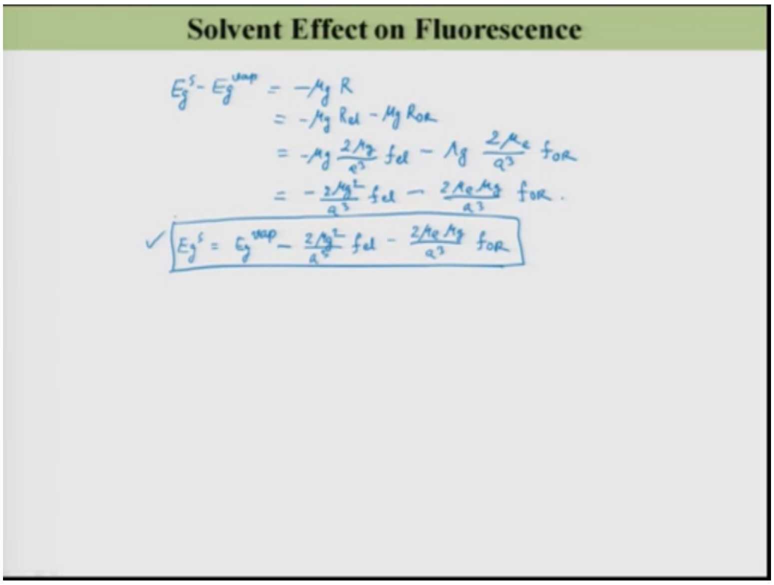

Solvent Effect on Fluorescence

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

So, for that E g s minus E g vapor this is equal to which state ground state, so minus mu g into reduction field R, so minus mu g into R minus mu g R e l minus mu g R OR. So, this is equal to minus mu g twice mu g by a cube f e l, this means that the electron has moved from LUMO to HOMO, draw a excited state to the ground state. So, first electronic polarization is first. So, I use the mu g. However, in this case, you see this mu g R O R that twice mu by a cube that mu, this is the orientational polarizability, but the solvent will stay as that there in the excited state, because it takes time orientational relaxation is slow. So, in this case, I will again use that mu e not mu g. So, this is twice mu e by a cube into f O R and I am almost done over here. So, this is equal to minus twice mu g square by a cube f e l minus twice mu e mu g by a cube f O R. So, I can get this E g s equal to E g vapor minus twice mu g square by cube f e l minus twice mu e mu g by a cube f O R. So, I also got this equation, I got this E g s that is in the emission after emission; what is the energy of the ground state? I got this one E e s before emission, but after stabilization, what is the energy of the excited state and that is it.

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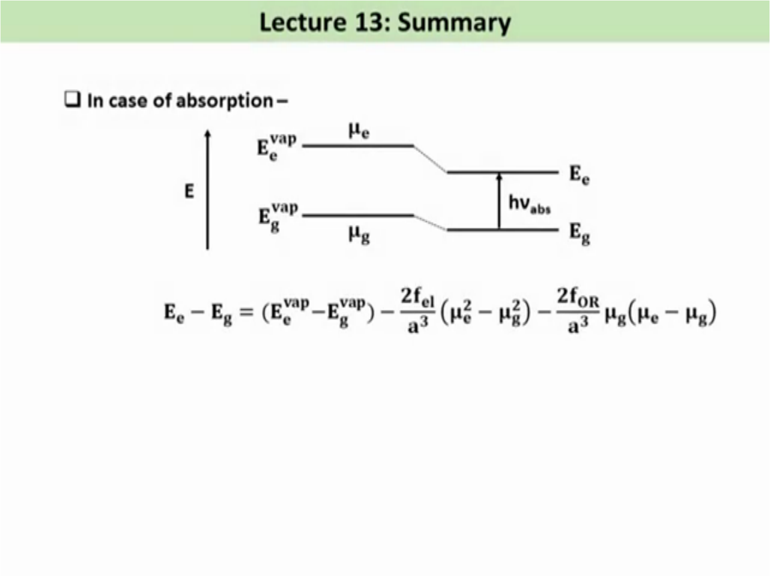

Lecture 13: Summary

❑ In case of absorption –

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

.

So, with this equation, we will continue on the next lecture about what will be the energy of this emission.

Thank you very much.