Basics of Fluorescence Spectroscopy
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Lecture – 07

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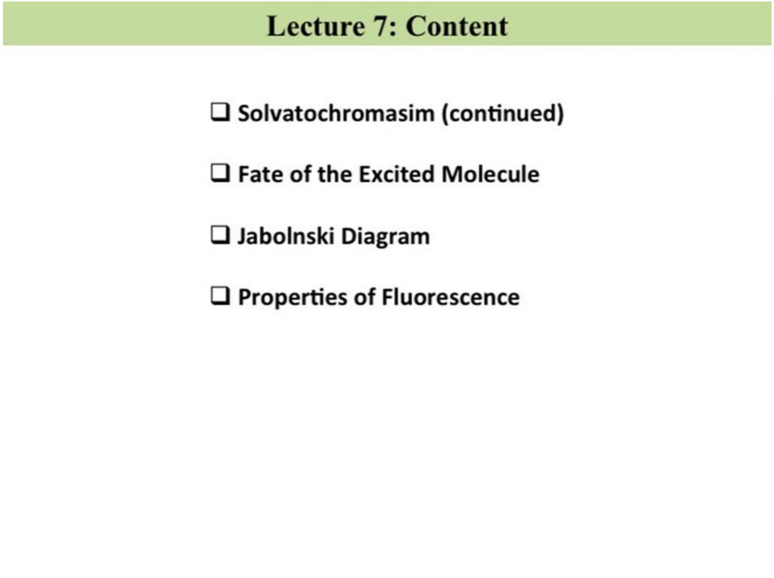

Lecture 7: Content

- ☐ Solvatochromasim (continued)
- ☐ Fate of the Excited Molecule
- ☐ Jabolnski Diagram
- ☐ Properties of Fluorescence

Welcome to the 7th Lecture of this course entitled Basics of Fluorescence Spectroscopy. Till last class we discussed about the various aspect of absorption spectroscopy and today our topic is that what is the fate of a excited state molecule.

So, what we have seen in last 6 lectures that by absorption of radiation one can excite the molecule from ground electronic level to the excited state of the excited electronic level that could be the first excited state or second excited state and so on and so forth. However, my question is now that after you promote the molecule from ground state to the excited state what will be the fate of this molecule in the excited state: whether the molecule will remain in the excited state forever, or the molecule will come back from the excited state to the ground state deactivate by some deactivation process. So, let us see this diagram over here.

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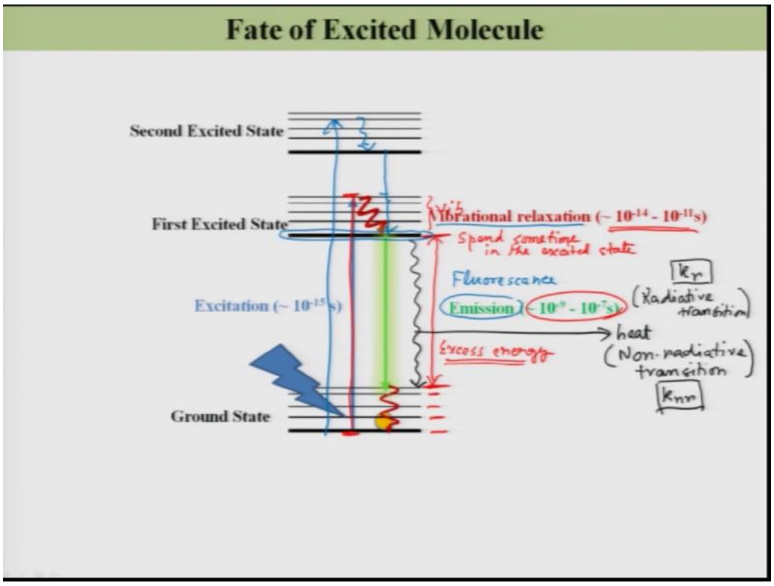

Fate of Excited Molecule

As you know that after shining light the molecule can promote from the ground state to the excited state and this could be at any different vibrational levels; like these are the different vibrational level of this excited state and that obviously will be guided by the Franck on principle, what is the nuclear position of the ground electronic level and the excited state electronic level. That we have already discussed. So now, after you promote the molecule from the ground electronic level to the excited electronic level or what will happen; the molecule will eventually come back to the ground state through several deactivation processes and that will going to discuss today.

So, after you excite the molecule. So to some excited vibrational level is usually the molecule comes back to the lowest vibrational level of the excited electronic state, and that process is known as vibrational relaxation. And that takes place within this 10 to the power minus 14 into 10 to the minus 11 second the in this time scale. So, once the molecule will come to the lowest vibrational level of the excited electronic state then depending on the molecule this molecule can come back to the ground state either in the radiative way or via non-radiative process.

Those details will going to discuss later on, but let us consider that this excess energy that, what is excess energy from here to here either here or here or here it depends on the Franck-Condon principle also because for emission, Franck-Condon principle is also applicable like in absorption. So, the molecule will come back from the excited state to the ground state by emitting the excess energy. Here in this case the excess energy is this much, this is my excess energy, so this is my excess energy. And this excess energy is emitted as light.

So, while exciting you are using this light. The light energy is proportional to this from here to here that is for your excitation, for emission you are getting the light having energy this much and these processes usually takes place in this time region 10 to the power minus nanosecond time region, right, this nanosecond time region.

So, eventually this molecule will come back from the excited state the ground state and the molecule will spend some time in this state; the molecule will spend some time in the excited state. For some molecule these dissipation of excess energy may be as heat may be as a not as light. So I can also have this dissipation as heat.

So, in this case the molecule will not going to emit a different color of light. Here this color of the excitation, color of this emission are different, but in this case of non-genetic transition this there will be no emission of light because it is just a excess energy is emitted as a heat. So, this process is called the radiative transition and this process is called the non-radiative transition, generally represented as k r and k n r.

So, let me show you; and after it come back to the vibrational level of this ground state it will eventually come back to the lowest vibration level of the ground state because that is the Boltzmann allowed level because the energy difference between the 2 vibrational levels are much higher compared to the energy available at the room temperature.

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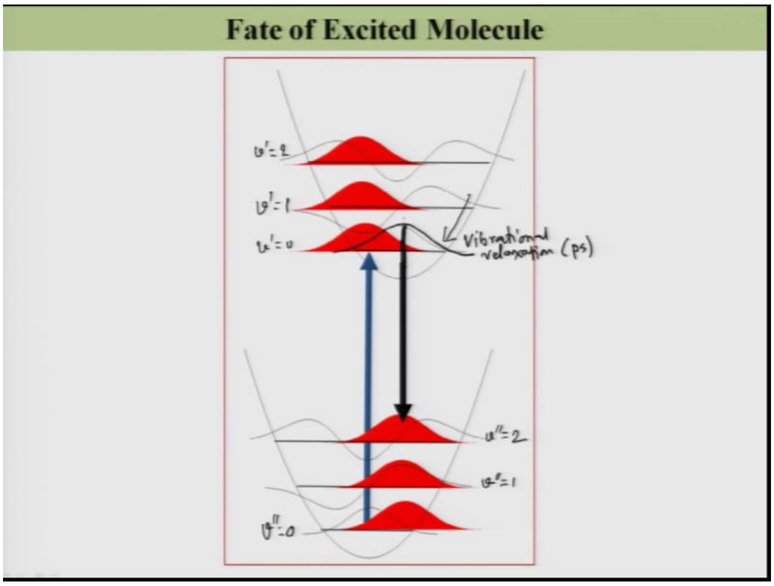

Fate of Excited Molecule

Now what I wanted to show here is that whether this Franck-Condon principle is also applicable in case of deactivation of the excited state molecule. As you remember I showed this diagram where the excitation of this harmonic potential very simplified molecular picture; harmonic potential is most overlap is like v equal to 0 to v 1, this is 0 2, so 0 1 condition is the most intense transition. While the molecule will come back, because I said that although you put the molecule in v equal to 1 or v equal to 2 guided by the Franck-Condon principle eventually the molecule will come back to the v equal to 0 level. So, that is the vibrational relaxation. That takes about the picosecond time scale. So, it will come back to this level.

So, now this is my molecule; this is my function of this molecule. So, these will come from excited state to the ground state by radiative transition. So, here you see the overlap in this case is most in case of g double prime equal to 1; here g double prime equal to 1 and say g double prime equal to 2. So, it also guided by the Franck-Condon principle.

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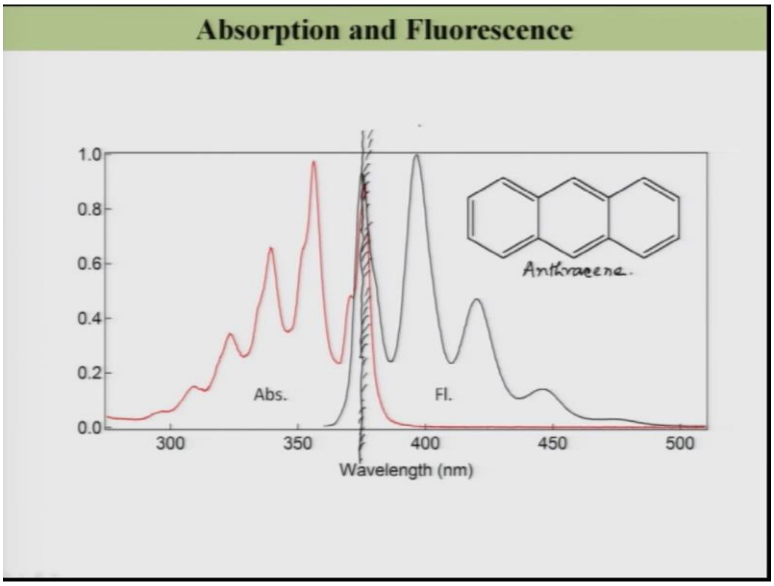

Absorption and Fluorescence

So, that is what I here show the absorption and fluorescence spectra of this molecule anthraeene. Here you see this, this is the 0 0 band, it is less intense the 0 1 band. For the emission again 0 0 band is less intense than the 0 1 band. Now if I put a mirror over here, if I just put a mirror over here this right hand side looks like a mirror image of this left hand side. So, this is known as mirror image. That I will going to discuss later. Before that let me again come to here and let us define few terms here; that as I said that this is vibrational relaxation part, this is emission, and this is known as the fluorescence.

The fluorescence takes little longer time about nanosecond to come from the excited state to the ground state. And in the ground electronic state also there could be vibrational relaxation. And if you now excite your system not from ground state to the first excited state, but from ground state to the second excited state right then again the system usually come to the 0 vibrational level of the first excited state.

So if you excite your system from here to here ultimately this system will come to this particular level, and then the emission process will takes place. All this deactivation process is best represented by one diagram called Jablonski diagram, which is given by the Jablonski.

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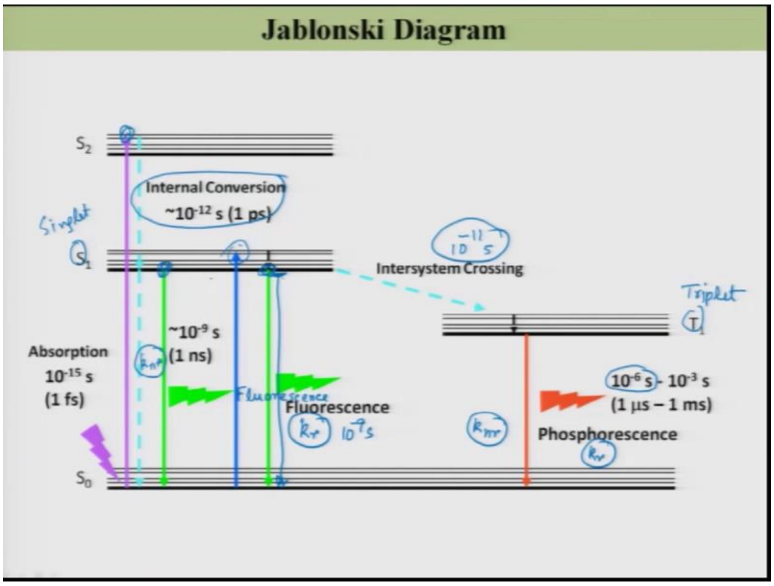

Jablonski Diagram

In this case this S 0 is denoted as the ground electronic level and by the absorption of radiation you can either excite the molecule from S 0 to S 1 the first excited state or S 0 to S 2 which takes a very short amount of time. And then let us let us consider here that you are exciting molecule from ground electronic level to the second excited electronic level. And in that second excited electronic level the molecule will come back eventually to the first excited level and that particular process is known as internal conversion; which takes about a picosecond time. And the system may come back to the ground state by emitting radiation. So, this is the radiative type of transition and that is our fluorescence.

Now the system may also, as I said the; I can also excite the system from S 0 to S 1 in this case that after vibrational relaxation that same fluorescence will going to observe. So, as you can see here another important which I will obviously going to discuss in detail later that another interesting observation that whatever light you are using to excite your system from either from S 0 to S 2 or S 0 to S 1 or the different levels in the S 1 the emission wavelength that means the emission energy from here to here; that emission energy remain same. This is well known kasha’s rule which we are going to discuss later.

Now obviously, the system may come from this S 1 to S 0 without emission of n light that is my non-radiative path. So, here is my k n r here is my k r. Now depending on the spin multiplicity this excited level can be designated as either singlet or triplet; that is why it is written s right this my singlet and here is my triplet; that means, the spin multiplicity is t right here is my triplet.

So in this case the system can also undergo a spring crossover from singlet to triplet set. So, from S 1 to T 1 and that process is known as intersystem crossing. The inter system crossing takes place in around 10 to the power minus 11 or in the time scale intersystem crossing it depends on the molecule. Obviously, whatever I am writing this time constants are typical, but obviously you can see the fluorescence may be in the order of picosecond or internal conversion may be much much faster like in the 10 to the power minus 13 or 10 to the power minus 14 second intersystem crossing could be much slower, but this is a overall time scale in general time scale.

So, once the molecule will come change the state from singlet to triplet then this triplet 2 triplet one like T 1 to S 0 transition will also may takes place, but here what we can see is that this is the spin forbidden transition. So usually this transition takes more time and this is called the phosphorescenc. Here the time constant is about, so here the time is about 10 2 the power minus 16 second or 1 microsecond. So, the fluorescence is I said typically 10 to the power minus 9 second and in this case it is 10 to the power minus 6 second.

So, these time constants that how long right on an average the molecule will take to come back from the zeroth vibrational level of the first singlet excited state to the ground state. That is the characteristic of the molecule and in case of fluorescence this time scale is about 10 to the power minus 9 second. In case of phosphorescence where it is from T 1 to S 0 this time scale is about 10 to the power minus 6 second. And this is just because this for the phosphorescence this transition is not spin allowed completely and in case of fluorescence it is between the same spin multiplicity; so from S 1 to S 0 so the time is less. So this is also one important parameter of the fluorescence which I will going to discuss later.

So, as said that there could be a non-radiative process also. So, in this case this is my k r and this is my k n r. So, k n r is non-radiative; that means the excess energy is emitted not as light not as the radiation, but as heat. So, this is called the non-radiative transitions.

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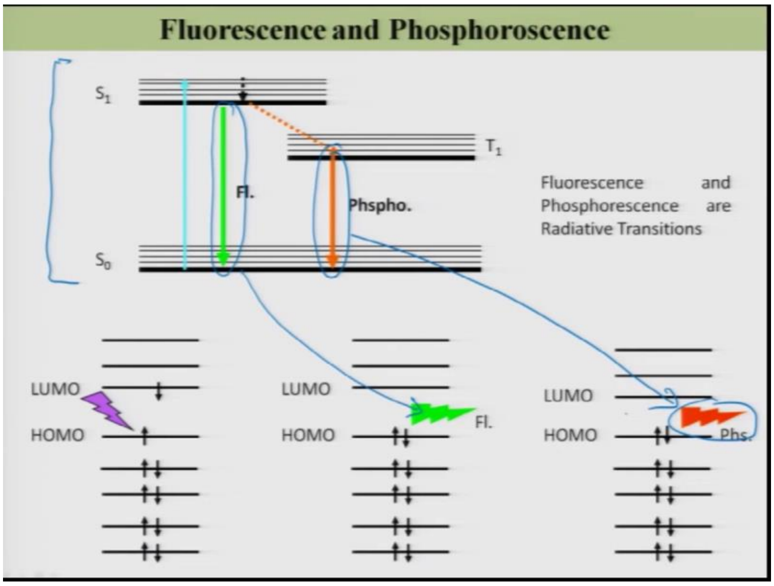
Fluorescence and Phosphoroscence

Fluorescence and Phosphorescence are Radiative Transitions

Now, let us just see a little more about this fluorescence of how things happen. So, this is the modified or simplified Jablonski diagram over here, I have removed most of this S 2 state and so on. So, in this case as I said that when you are exciting your molecule from the ground state to the excited state; that means, you are promoting one electron from HOMO to LUMO or HOMO to LUMO plus 1 where depending on whether this particular transition is allowed or not.

So, when is shine light on electron moves from HOMO to LUMO with retaining is spin orientation. So, in this case the spin multiplicity does not change. So, here what we have that in the excited state the situation is like this and simply this excited state molecule can come back to the ground state; that means, the excited electron from HOMO to LUMO again come back from LUMO to HOMO and then you will get the characteristic fluorescence light out of the system.

However, this is my fluorescence over here. So, this is my fluorescence is what I am showing over here. However, in the excited state that spin may flip and after flipping of the spin. Now the spin multiplicity changes from singlet to triplet and then this transition may takes place so that during the transition spin again flip and that is the forbidden transition and I will get these phosphorescence over here which takes more time than the fluorescence. So, here is my phosphorescence and this is over here.

Now, let us see some properties of the fluorescence as I already mentioned briefly, but now let us write it one by one. So, the first one I said that fluorescence generally occurs from the lowest energy vibrational state of the first singlet excited state and that is my kasha's rule.

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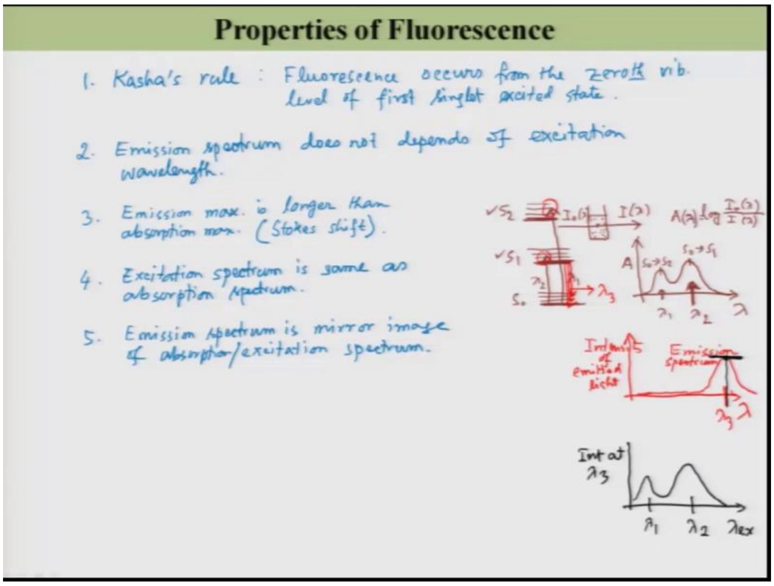

Properties of Fluorescence

1. Kasha's rule : Fluorescence occurs from the zeroth vib. level of first singlet excited state.
2. Emission spectrum does not depends of excitation wavelength.
3. Emission max. is longer than absorption max. (Stokes shift).
4. Excitation spectrum is same as absorption spectrum.
5. Emission spectrum is mirror image of absorption/excitation spectrum.

So, let me write over here: 1 is my kasha's rule, it says that the fluorescence takes place from the zeroth vibrational level of first electronic excited state. Fluorescence occurs from the zeroth vibrational level of first singlet excited state, is not it. I already showed you. It means something; it means that over here whether you are exciting here emission comes from here, whether you are exciting here, emission comes from here, you excite here emission comes from here, same energy level. It means that emission spectrum does not depends on the excitation wavelength

So now let me write my second point over here second point over here that emission spectrum does not depends on excitation wavelength. So, better I explain you this emission what is emission spectrum then. So, what is emission spectra? You know the emission spectra; this is the plot of absorbance versus wavelength. So, let me give you this spectrum once again. So, this is my absorption spectra let us say this is my molecule present in my sample cell and you are measuring the absorption; here is your I 0, here is your I for the particular lambda as I have already said. So, then A is equal to log I 0 by I for this particular lambda. So, this is a function of lambda then. So, a plot of A versus lambda will give you the absorption spectra of the sample.

So, let us say this is how it looks like. So, when you excite over here, you are exciting from the ground electronic state to the first singlet excited state. So, this is my S 0 S 1 transition and in this case this is my S 0 S 2 transition. So, if I now draw the molecular energy level over here, so here is my ground state some vibrational level this is my first excited state some vibrational level, this is my second excited state some vibrational level. So, this is S 0, this is S 1, this is S 2.

So you excite from here to here. So, you get this one right let us say get lambda 2 you exit from here to here you get this a lambda 1; so lambda 2 lambda 1. S there were several vibration levels associated with each electronic level. So, these peaks are not sharp as I said right in the atomic case we will get a sharp line, but in this case we will not get a sharp line. So, this looks like a vibrational band right and this corresponding maxima, these are the maxima this actually corresponds to the each transition over here.

Now you can excite this molecule either here or here either in the S 2 or in the S 1 and then eventually the fluorescence will come. So, when the fluorescence will takes place from here that is a lowest vibration level from here either at this location or at this vibrational level or at this vibrational level because all are all somehow allowed; the Franck-Condon factor may be different, but there will be some factor. So, it is possible that the fluorescence will also come from 0 vibrational level of the first singlet excited state to some different vibrational level of the ground electronic state.

So the wavelength of this emitted light is not 1, it could be many. So, this is now if you somehow measure the intensity of emitted light versus wavelength then for different wavelength the intensity will be the different and if you plot it what you will going to see the intensity is very low very low. That means, no light is coming at this region probably here you will get some maximum over here. So, this one is my let say lambda 3. That means, whether you excite here or excite here these emission characteristic emission maxima is my lambda 3.

So, this is a plot of intensity of emitted light versus wavelength is known as the emission spectrum of this molecule. So, this is referred to my emission spectrum emission spectrum of this molecule. So, this emission spectrum does not depends on excitation wavelength, whether you are exciting over here or over here this emission spectrum will remain same. This is obviously there is some exception, but this is a general rule.

So the third one is again we will come automatically over here as you can see that these absorption guided by the Franck-Condon principle; emission is also guided by the Franck-Condon principle, but emission takes place from the 0 vibrational level so that means, emission wavelength emission maxima is right shifted or in the lower energy compared to the absorption maximum and that is called the stokes shift. So, I can write here that emission takes place at the longer wavelength than the absorption. So, emission maxima is longer than absorption maxima and this is called stokes shift.

Fourth: another property, so here is let me write it and then explain it. Excitation spectrum is same as absorption spectrum. What does it mean? It mean that means these absorption spectrum and these excitation spectrum let me first explain what is excitation spectrum. Excitation spectra is that you measure, you monitor the emission at a particular wavelength and then scan the excitation wavelength. So, what I want to say is this exchange the color. Suppose you are sitting over here at this particular lambda 3 and you are checking; what is the intensity that is it.

However, you are changing the excitation wavelength, earlier to get this emission spectra you have excited the system right either at lambda 1 or lambda 2, but now what you are doing you are changing this lambda continuously. So in this case what you are doing, you are doing that intensity at lambda 3 that is what you are monitoring versus lambda excitation. Then the dependence or spectra whatever you will get will be very similar to this absorption spectrum. You will get a peak at lambda 1, you will get another peak at lambda 2 and so on. So, this is the fourth property that excitation spectra is same as; why it is like that and how we can prove it that we will going to see later.

And the fifth one, the final one is five is emission spectrum is mirror image of absorption or excitation, because they are same. That is what we have already seen, we have already discussed.

And with this let me finish this lecture, and in the next day we will continue from here.

Thank you very much.