# Basics of Fluorescence Spectroscopy
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## Lecture - 36

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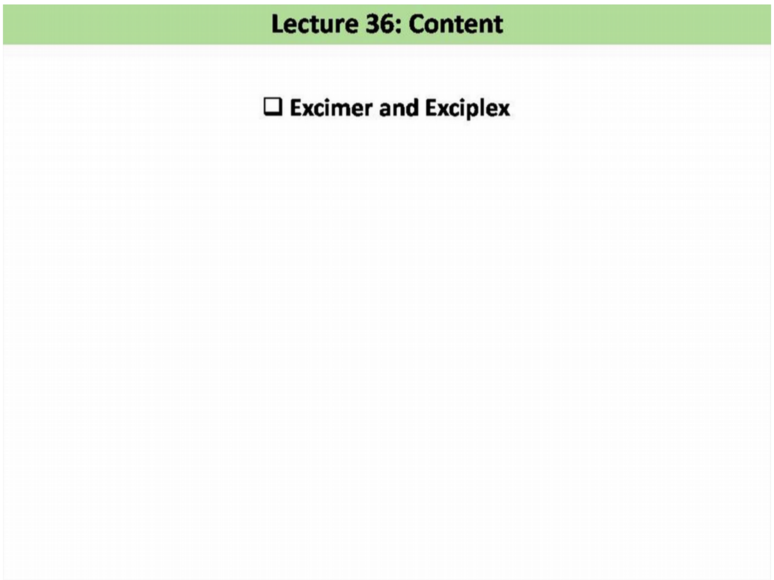

**Lecture 36: Content**

- ☐ **Excimer and Exciplex**

Welcome to lecture number 36. Today we will going to discuss Excimer and Exciplex. So, in some case what has been seen is the fluorescence intensity right is actually keep on changing with the increase in the concentration. You can say that that fluorescence intensity is decreasing by increasing the concentration of the fluorophore is may be because of the inner filter effect or front surface absorption that I have already discussed, but in this case what has been seen is that while the fluorescence of one region is decreasing the fluorescence in other region is increasing itself.

It means that the one part of the emission spectra if you just follow it looks like fluorescence is quenching, but in some other part the fluorescence is actually increasing as a function of the concentration.

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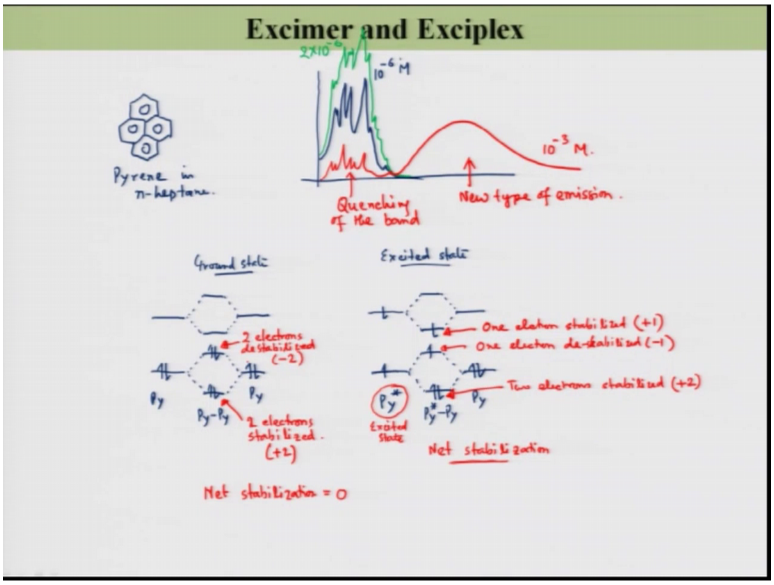

Excimer and Exciplex

Let me show you a specific example then it will be clear to you. If you take this molecule, this is the most famous example this is Pyrene in n-heptane. If you look at the emission spectrum of Pyrene in n-heptane when the concentration is not very high what you will going to see is something like this right this, this is the concentration is about 10 to the power minus 6 molar.

Now, as you increase the concentration of this Pyrene right you will see initially; obviously, the fluorescence intensity will increase right let us say for example, if from 10 to the power minus 6, I make it as 2 into 10 to the power minus 6 right. So, then; obviously, we will going to see the intensity will increase like this. So, here is 2 into 10 to the power minus 6, but if you increase more. For example, about a millimolar then what you will see such kind of emission this is for the 10 to the power minus 3 molar; that means, what you can see here is a quenching of the band and is the new type of emission actually comes into picture; here this new type of emission what you can see over here is explained on behalf of this excimer formation.

To explain this let me take the ground state and the excite state of this Pyrene molecule. So, let us see this is my homo and lumo of this Pyrene monomer one Pyrene molecule, and in the ground state both the electrons are in the lumo right and you have another Pyrene let us say this is my Pyrene, this is my Pyrene and in another Pyrene is also in the ground state both the electrons are occupied in the lumo.

Now, consider that these two Pyrene molecule actually interacting with each other right. So, then their orbital will mix up and I will get a completely different molecular orbital. So, for example, if I now consider that these two these are the itself molecular orbital right homo or lomo and they interact and they form another set of orbital and these two interact and create another set of orbital, these this one is for Pyrene pyrene, but here in this case both the pyrenes are in the ground state. So, these will be occupied two electron this will be occupied by the two electron. So, this is the case of ground state.

However in the exciter state if you look at let us say these are the Pyrene, this is one Pyrene sorry, but this Pyrene molecule is not in the ground state, this is in the exciter state. So, I have one electron over here and I have another electron over here right and here this Pyrene molecule is in the ground state.

So, if I now consider Pyrene one in the exciter state and another in the ground state, then what I will going to see the mixed orbit in this case one two electron will come here and one electron will go there, and in this case one electron will come here.

Now, if you just look at here in this case let me change this one, look at this one two electrons destabilized if I write this destabilization as unity for per electron. So, these two electrons destabilized. If I just write unity one for the destabilization or stabilization then this is minus two because of the two electrons and here two electrons stabilized two electrons stabilized. So, I can write plus 2 in this case and here net stabilization is equal to 0 plus 2 and minus 2 equal to 0.

However in this case you see here one electron stabilized. So, I will write here plus one here one electron destabilized right. So, I will write minus 1 and these 1 2 electrons stabilized. So, I will write here plus 2. So, the net stabilization is there. So, I have a net stabilization right. So, I will going to have net stabilization net stabilization is plus 2 and then I have two electron. So, per electron net stabilization is plus 1.

So, I am going to have this net stabilization only when this Pyrene one of them is in the exciter state. Now if you consider the repulsion term right here I have not consider repulsion term, then if I now draw the potential energy surface for as a function of the Pyrene; pyrene distance then I can simply draw this.

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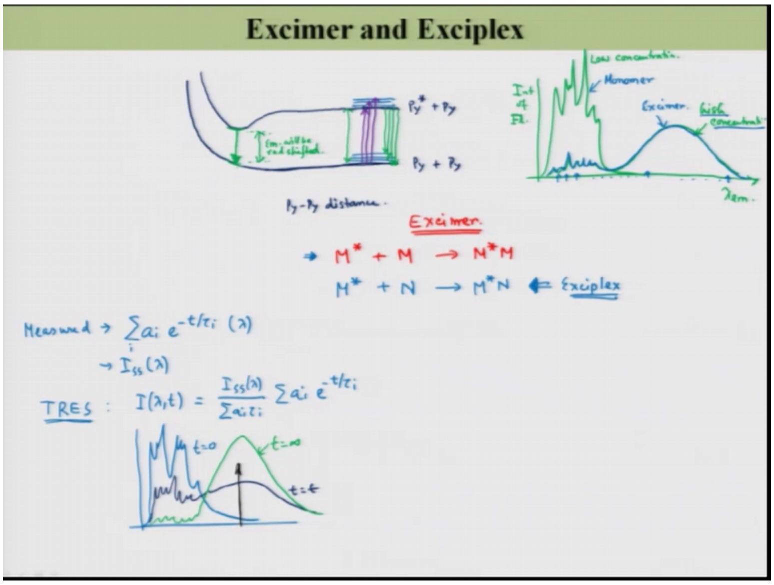
**Excimer and Exciplex**

Excimer.

→ $M^* + M \rightarrow N^*M$

$M^* + N \rightarrow M^*N$ ⇐ Exciplex

Measured → $\sum_i a_i e^{-t/\tau_i} (\lambda)$

→ $I_{ss}(\lambda)$

TRES : $I(\lambda,t) = \frac{I_{ss}(\lambda)}{\sum a_i \tau_i} \sum a_i e^{-t/\tau_i}$

Let us say this is my ground state I am starting from a distance over here, where I consider that one Pyrene and another Pyrene they are far apart and these distance is actually decreasing. So, in the x axis what is the the Pyrene pyrene distance, as the two Pyrene will come close right then this energy must increase because of this repulsion right this electron of this Pyrene this electron of that Pyrene they will refill each other. But when I am I have this Pyrene in the exciter state. So, this is in the ground state right potentializing surface of the two pyrene.

Now, when I have this exciter state; obviously, one of the Pyrene is in the exciter state. So, total energy must be more right here is my one Pyrene is in the ground state, another Pyrene is in the exciter state. So, here I will write P y plus P y and here is my P y star and p y.

So, because of this net stabilization, I showed here this net stabilization right when these 2 Pyrene will approach at some point of time there must be some deep and then; obviously, this because of this repulsion term this will increase right. So, my drawing is not very good I should have drawn this like this way like this. So, this is the correct version.

Now, you look here this pyrene; obviously, will have this corresponding vibrational level when I am drawing at these end of this diagram it means the two pyrenes are not interacted with each other they are far apart right.

So, during any transition like when you are exciting so, this excitation will be either from here to here according to the Franck-Condon principle; like here to here, here to here. So, vibrational fine structures are very nicely visible in case of Pyrene, when Pyrene will relax back from the exciter state to the ground state then emission will start from here and then it can come from here to here from here to here to here right. So, then the vibrational fine structures are visible that in case of pyrene.

However when these Pyrene, pyrene distance decreased right you come up with these stage right the immediate ground state immediate ground state right is not stable at all. Once it will form immediately they will break right and in this case when these Pyrene start and Pyrene will come from this excite state or ground state you would not be able to see such kind of vibrational fine structure.

Moreover you see the energy gap here these gap is less than this gap; that means, these emission will be red shifted and exactly what you can see here in case of Pyrene the at a low concentration the emission is like these, and in the high concentration this is low concentration and in the high concentration these part decreased and new part increased. So, this is high concentration.

Now, if this phenomena right is happening between two Pyrene molecule, such phenomena is called the excimer because this is kind of a dimer formation although I have not discussed the dimerization in the ground state because of this nature of this course, but I would like to tell at this point that in ground state some molecules are prone for the dimer formation and because of the dimer formation. I mean you can see that change in the absorption spec of a molecule for a h type dimer the absorption spec is typically get blue shifted and for the h type dimer (Refer Time: 15:01) type dimer one molecule is forming a dimer with another molecule like this way, right then you will get absorption spectra blue shifted and in j type dimer one molecule is getting dimerized with other molecule like this way head to tail fashion and you will get the absorption spectra red shifted.

In these case what you can see that these dimer formation in the ground state is not visible right, because if you look at this concentration dependent absorption spectra of the because this is my fluorescence intensity, intensity of fluorescence and here is your lambda emission right, but if you look at this absorption spectra this molecule you would not see any change in the absorption spectra. That means, these dimer formation is not happening at the ground state of this molecule and that is what you have seen right in this normal case, that they are repelling right it is not stable, but in the exciter state this dimer formation is visible right. So, that is why it is called the exciter state dimer or excimer. So, such kind of phenomena is known as Excimer right. So, basically what I have defined this M some molecule M in the exciter state is interacting with another M which is in the ground state to form M star M right and this is known as my excimer.

Sometimes it is also possible that one of these molecule which is in the exciter state M star, is actually interacting with a different types of molecule right. Not M, but again these interaction is favorable which will leads to the formation of M star N right. So, this is not a dimer see because here M and here is my N. So, they are not same and these type of case is known as this is type of complex formation right complex formation within M and N, but these are these complex is formed only in the exciter state. So, this is known as exciplex. So, you have excimer exciplex the mechanism is more or less very similar right.

Now, there are few things one can discuss on this excimer or exciplex formation, but let me discuss with the time dissolve study of excimer and exciplex right; obviously, these excimer formations let me talk about this excimer. Obviously, this excimer formation cannot be instantaneous; that means, your you have to excite your molecule right M is now excited to M star, then M star will interact with M and then there will be a formation of excimer obviously, it is not instantaneous it will take some time right.

The time taken for the excimer formation can be easily visualized if you do the time resolve measurement. If you remember as I told you that let us say this is your emission spectra as I showed over here when at the high concentration. So, this is my high concentration, the emission spectra is something like this as I showed.

Now, if you monitor the fluorescence transient at different-different wavelengths, let us say at this wavelength this and many many such kind of wavelengths till here right you have measured with the different wavelengths. So, and the functional form of this different wavelengths let us say a i e to the power minus t by tau i sum over I, depending on your system it could be i equal to 1 and 1 and 2 or it could be a 1 2 3 that that means, it is a may be single exponential biexponential triple exponential and so on and so forth right.

Now, with the help of this steady state intensity you have this at your hand measured, and you also have steady state intensity as a function of lambda this is at a for a particular lambda right this is also at your hand. So, from there you can easily determine the time resolved emission spectra right and that you remember I told you intensity is a function of lambda and time right. So, this is equal to I steady state divided by some over a i tau i, into some over a i e to the power minus t y tau I right. So, this is obviously, a particular lambda I am talking about and this is my time profile.

So, with these at a different-different time you can actually capture how the emission spectra looks like in a given concentration, but that emission spectra is at different-different time. Soon after the soon after the excitation; obviously, the emission spectra will be more monomer like right this is my monomer here is my monomer and this is my excimer.

So, if you do a time resolved studies and then reconstruct the time resolved emission spectra, then what you will see at all the time the emission spectra will be something like this and as time goes these emission. So, this is time t equal to 0 and after sometime you will see little bit has formed time t equal to t, and at time t equal to infinity probably what you will going to see is such kind of thing right. So, from here you will be able to calculate the evolution of these bands with time and you can talk about the formation kinetics right.

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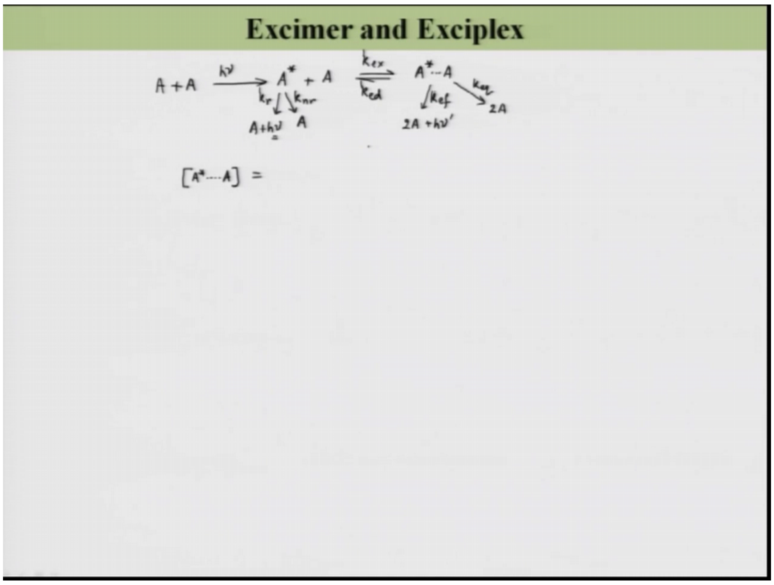

Excimer and Exciplex

$$\begin{tikzcd} A+A \arrow[r, "h\nu"] & A^* + A \arrow[d, "k_r"'] \arrow[dr, "k_{nr}"] \arrow[rr, shift left, "k_{ex}"] & & A^*\cdots A \arrow[ll, shift left, "k_{ed}"] \arrow[d, "k_{ef}"] \arrow[dr, "k_{eq}"] & \\ & A+h\nu & A & 2A+h\nu' & 2A \end{tikzcd}$$

$[A^*\cdots A] =$

Like previously as I have shown this exciter state proton transfer right, I can even model it without any problem. Let us say this is my molecule which is undergoing the excimer formation the two way are present over here and I am exciting with h nu, that is the suitable wavelength for the excitation and I am exciting this to A star one of them right another is like this A and then there is a formation of; obviously, this can break. So, I will write this red constant as a k excimer formation, k excimer dissociation e d which will form A star A, and it has its own radiative red constant. So, I have its k r, it has its own K n r right. So, with this k r it will form a plus h nu and with this k n r it will form only a right. So, then you are back to the previous case here A and A right and the excimer also can come back to the ground state.

Let us say this is for the excimer fluorescence. So, I will write this as K f and it will produce 2 A plus h nu prime because this wavelength is different than this wavelength and it can also undergo some non-relative pathway, and let us mean name it as k q right which will form 2A, but no light.

Now, you see such kind of kinetic model is very complicated kinetic model and, but it is possible to solve with some assumption here and there and basically if we take this photo stationery state assumption then you will be able to solve such kind of model. And under photo stationery state assumption what you can do you can try to find out that the formation of these A star A right is kinetics, and the other dependency on the formation of A star A right, but I am not going to write all those expression here because it is not necessary at this point of time, but as I told you that this excimer and exciplex are the exciter state phenomena and in such in such cases right what it going to see is a formation of a new emission band, which is much broad and red shifted compare to the monomer emission band.

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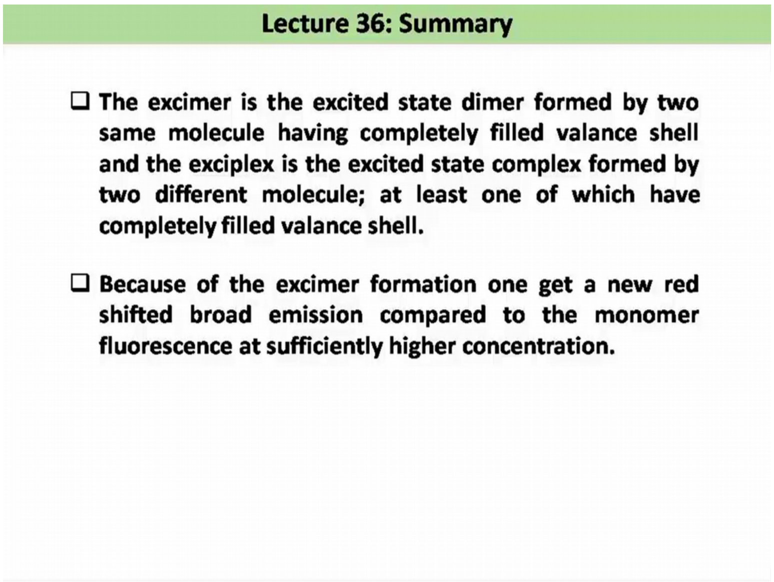

**Lecture 36: Summary**

☐ **The excimer is the excited state dimer formed by two same molecule having completely filled valance shell and the exciplex is the excited state complex formed by two different molecule; at least one of which have completely filled valance shell.**

☐ **Because of the excimer formation one get a new red shifted broad emission compared to the monomer fluorescence at sufficiently higher concentration.**

So, we will finish our discussion on excimer exciplex here and we will continue our discussion in the next lecture.

Thank you very much.