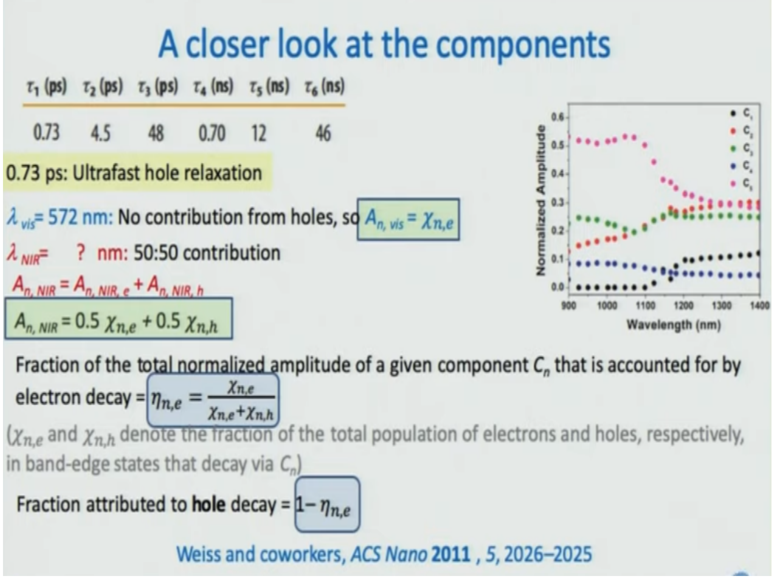
Ultrafast Processes in Chemistry
Prof. Anindya Dutta
Department of Chemistry
Indian Institute of Technology - Bombay

Module No # 13
Lecture No # 61
Radiative and Nonradiative Relaxation Pathways in CdSe Nanocrystals – Part 2

(Refer Slide Time 00:24)



A closer look at the components

τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	τ_5 (ns)	τ_6 (ns)
0.73	4.5	48	0.70	12	46

0.73 ps: Ultrafast hole relaxation

λ_{vis}= 572 nm: No contribution from holes, so $\boxed{A_{n,\,vis} = \chi_{n,e}}$

λ_{NIR}= ? nm: 50:50 contribution

$A_{n,\,NIR} = A_{n,\,NIR,\,e} + A_{n,\,NIR,\,h}$

$\boxed{A_{n,\,NIR} = 0.5\,\chi_{n,e} + 0.5\,\chi_{n,h}}$

Fraction of the total normalized amplitude of a given component C_n that is accounted for by electron decay = $\boxed{\eta_{n,e} = \frac{\chi_{n,e}}{\chi_{n,e}+\chi_{n,h}}}$

($\chi_{n,e}$ and $\chi_{n,h}$ denote the fraction of the total population of electrons and holes, respectively, in band-edge states that decay via C_n)

Fraction attributed to **hole** decay = $\boxed{1-\eta_{n,e}}$

Weiss and coworkers, *ACS Nano* **2011** , *5*, 2026–2025

Right so here we are we are trying to understand how the amplitudes were dealt with in this study by Wiess and cowokers. As discussed they said Lambda Vis to be 572 nanometer where the assumption was that there is no contribution from the electron. So An Vis the amplitude the normalize amplitude is equal to Chi n e. The entire thing is because of hole of electron and then we looking for another wavelength which is designated A NIR there no reason to call it NIR actually it could be a visible wavelength also as all you know.

But this is called NIR because it is obtained from the well we are working with these amplitudes remember. And this amplitude came from the NIR region ok. So this A NIR is probe and even Vis is probe. So what is the wavelength where there is 50 50 contribution. So as you will see we will derive something and from there we will arrive at what Lambda NIR is as well ok. So start with this An at NIR = An at NIR contribution of that from hole plus contribution from electron that is very simply put.

And then what we are looking for is this. An NIR = 0.5 Chi n e + 0.5 Chi n h 50 50 contribution ok. Now see we have 2 equations A n vis = Chi n e and An NIR = 0.5 Chi n e + 0.5 Chi n h. Now remember what is the definition of Chi. Chi is the contribution of electron or hole right to the nth mode of t k right. So irrespective of the wavelength Chi will remain same for a given value of n. This is important to understand in fact when I read the paper for first time I did not understand this. So it required some time for me to sync in.

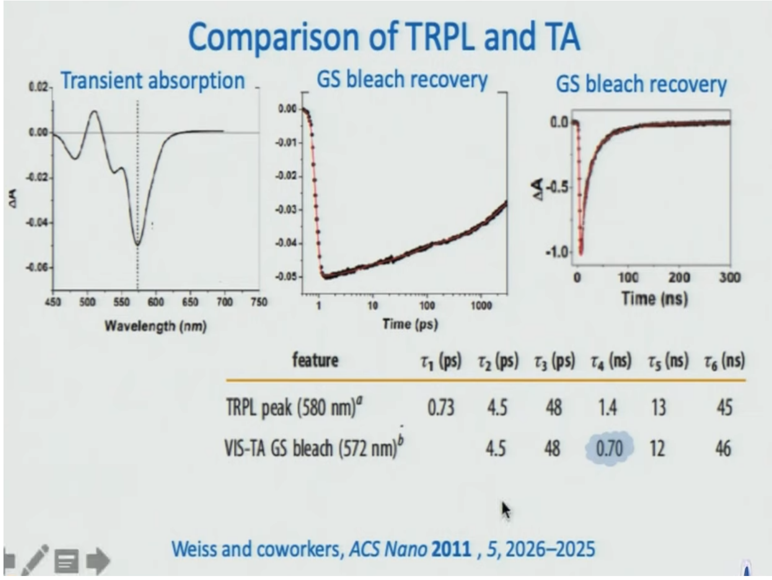
Are we clear about that? It does not matter which wavelength we take as long as we are working with same n the chi respective chi should be same. Chi n should be constant chi n e should be constant, chi n h should also be another constant clear. Now see now if you simplify this with we already have an workable formula for chi n e is not it because this amplitude An Vis is an experimental quantity.

Can we get an expression for chi n h in terms of the amplitudes what will it be? It is quite simple take this value of chi n e and plug it in here. So you will get An NIR = 0.5 An Vis + 0.5 chi n h. So what will be expression for chi n h? Yes but I am proving the same n that is what we are saying. What we are saying is that a particular n value stands for a particular decay mechanism. Now that shows up in all wavelengths all probe wavelength.

At least many probe wavelengths. We are looking at the contribution of the same mechanism of decay in Lambda Vis as well as Lambda NIR. See how did we get all this time constant by a global fit across the wavelength right. So the basic premise of the work is that there are certain fixed decay mechanism. And effects of this can be seen across the probe spectrum. So as long as you work with particular value of n chi n e is the same irrespective of the probe value.

Chi n h is the same irrespective of the probe value. That is the basic premise of the work and that is the part that may not be very easy to understand when we start. Are we convinced? It is otherwise you cannot say that 4.5 picosecond is a particular decay mechanism 4.5 you get from all the wavelengths right. As we saw earlier it shows up in TRPL it shows up in transient absorption visible it shows in NIR as well now that is exactly the point.

(Refer Slide Time 05:08)



Comparison of TRPL and TA

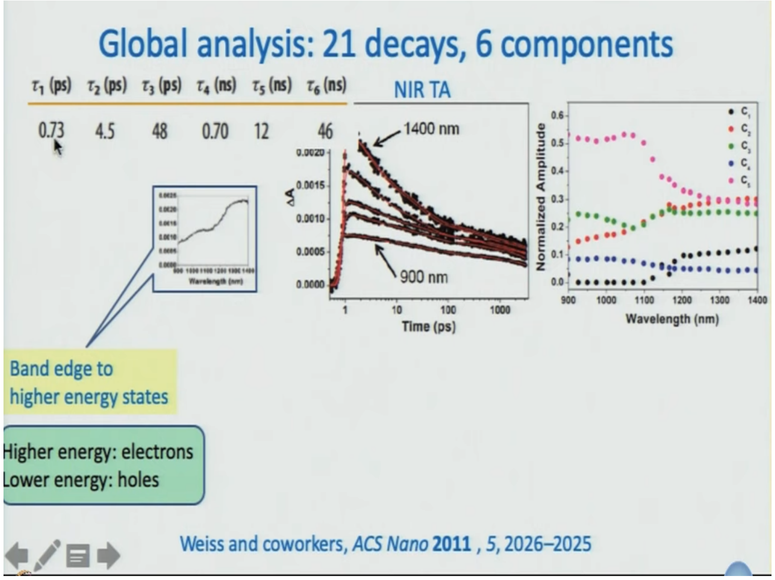
feature	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	τ_5 (ns)	τ_6 (ns)
TRPL peak (580 nm)[a]	0.73	4.5	48	1.4	13	45
VIS-TA GS bleach (572 nm)[b]		4.5	48	0.70	12	46

Weiss and coworkers, *ACS Nano* **2011** , 5, 2026–2025

This is a comparison between time resolved photoluminescence and transient absorption fitted independently and that is the beginning of the story. Fitted independently they get a very good match. First of all where did 6 time constant comes from 3 came from one experiment 3 came from another experiment in PL itself. Now when they do transient absorption again picosecond and nanosecond they get actually the same time constant.

This mismatch is not much and what is very prominently absent in time absorption is 0.73. So then that is why they got encourage and they looked in NIR. And when they did global analysis of the NIR data then they got the same time constant. Of course, they would get the same time constant because the fix a lifetime. But reason why they are they justified fitting the lifetimes is that in any case everything is coming the same.

(Refer Slide Time 05:53)



Global analysis: 21 decays, 6 components

τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	τ_5 (ns)	τ_6 (ns)
0.73	4.5	48	0.70	12	46

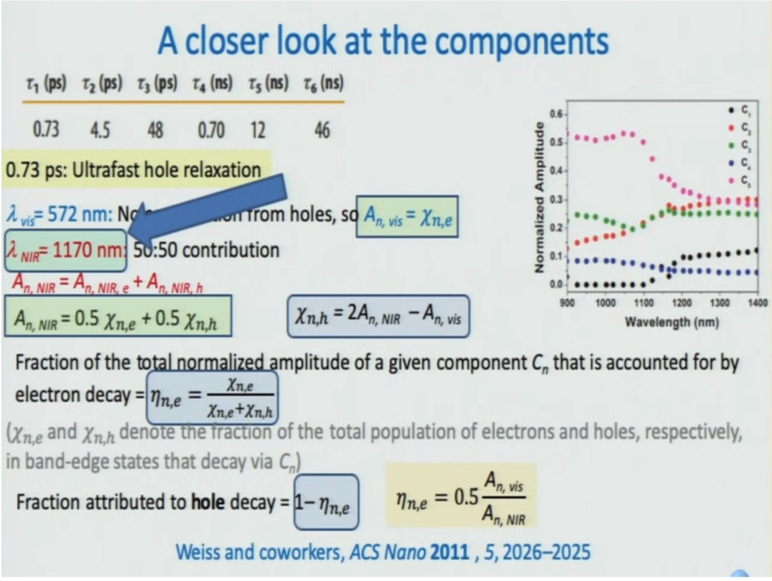
Band edge to higher energy states

Higher energy: electrons
Lower energy: holes

Weiss and coworkers, *ACS Nano* **2011** , 5, 2026–2025

The only problem is that in this time constant if you take 5 instead of 6 this 0.73 and 0.45 you will get this some over I tau I kind of thing and the time constant become less than 4.5 as you go from higher to lower energy probe ok. So the basic premise is that the time constant are the same irrespective of the experiment irrespective of the probe wavelength otherwise this analysis cannot be done this where we were.

(Refer Slide Time 06:40)



A closer look at the components

τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	τ_5 (ns)	τ_6 (ns)
0.73	4.5	48	0.70	12	46

0.73 ps: Ultrafast hole relaxation

λ_{vis}= 572 nm: No [illegible] from holes, so $A_{n,\,vis} = \chi_{n,e}$

λ_{NIR}= 1170 nm: 50:50 contribution

$A_{n,\,NIR} = A_{n,\,NIR,\,e} + A_{n,\,NIR,\,h}$

$A_{n,\,NIR} = 0.5\,\chi_{n,e} + 0.5\,\chi_{n,h}$

$\chi_{n,h} = 2A_{n,\,NIR} - A_{n,\,vis}$

Fraction of the total normalized amplitude of a given component C_n that is accounted for by electron decay = $\eta_{n,e} = \frac{\chi_{n,e}}{\chi_{n,e}+\chi_{n,h}}$

($\chi_{n,e}$ and $\chi_{n,h}$ denote the fraction of the total population of electrons and holes, respectively, in band-edge states that decay via C_n)

Fraction attributed to **hole** decay = $1-\eta_{n,e}$

$\eta_{n,e} = 0.5\frac{A_{n,\,vis}}{A_{n,\,NIR}}$

Weiss and coworkers, *ACS Nano* **2011** , 5, 2026–2025

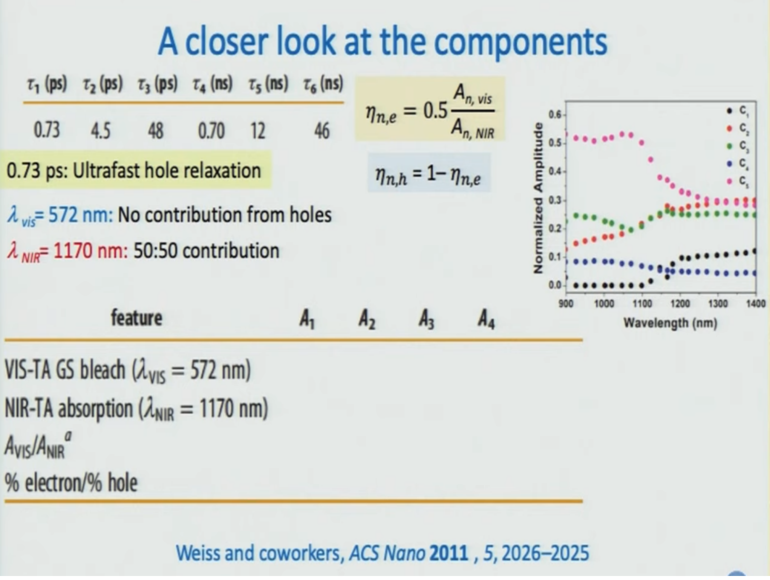
We said we are going to put An NIR = 0.5 An Vis + 0.5 chi n h so what is the expression for chi n h? chi n h = no but then that has to be divide 0.5 also. An NIR - 0.5 chi n e / 0.5 so you get this. Chi n h turns out be 2A NIR - An Vis alright. Now using this what one wants to work out is this Eta n e. So Eta n e turns out to be so you understand what we are doing right. We got the expression for chi n e, we have got the expression for chi n h in terms of measurable quantities that is amplitude normalized amplitudes.

So just plug in the values the numerator for this expression value you get An Vis instead of chi n e. In the denominator you get An Vis + 2 what is this 2 An NIR -An vis. So the denominator An Vis -An Vis cancel each other we are left with 2 An Vis An NIR sorry. So finally you get the expression Eta n e = 0.5 An Vis / An NIR ok right. Now what you want is this Lambda NIR. How will we find that Lambda NIR? In fact I have given you the answer already it is 1170 nanometer.

How will that be obtained? We will just look at the amplitudes. Basically plot the ratios of An Vis and An NIR what we are looking for is Eta An e to be equal to half. When will Eta n e equal to half when this ratio of amplitude = 1. So that they did is they plotted this ratio of An Vis and An NIR and they found that it become 1. So you understand what it will be right. An NIR well An Vis is basically the same through out and this An NIR.

You see there is a inflection here basically the inflection point is 50 50 point. In fact we do not even have to do the ratio from this plot itself the inflection you see the inflection right. So that is where it is. And we can work with that safely because it is only from hole relaxation right. So they determine that Lambda NIR = 1170.

(Refer Slide Time 09:37)



A closer look at the components

τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	τ_5 (ns)	τ_6 (ns)
0.73	4.5	48	0.70	12	46

$$\eta_{n,e} = 0.5\frac{A_{n,\,vis}}{A_{n,\,NIR}}$$

$$\eta_{n,h} = 1 - \eta_{n,e}$$

0.73 ps: Ultrafast hole relaxation

λ_{vis}= 572 nm: No contribution from holes

λ_{NIR}= 1170 nm: 50:50 contribution

feature	A_1	A_2	A_3	A_4
VIS-TA GS bleach (λ_{VIS} = 572 nm)				
NIR-TA absorption (λ_{NIR} = 1170 nm)				
$A_{VIS}/A_{NIR}{}^{a}$				
% electron/% hole				

Weiss and coworkers, *ACS Nano* **2011** , 5, 2026–2025

What is the next step? We have all this we have this 6 time constants we have the expression for Eta n e we have the expression for Eta n h and already we have said that 0.73 picosecond is ultrafast hole relaxation. We know the Lambda Vis and Lambda NIR's. Now what remains to be done is workout the ratios of the amplitude ok of Vis and NIR. And then get this percent electron to percent whole ratio well you can get percent electron or percent hole here for whatever reason they have written it as percent electron to percent hole which is a little strange because you get numbers like 0 that is ok.

As you will see they get the number that in infinity. So I do not know why they want to take the ratio they could have just written it separately then it is their paper not mine what can I do? So understand what is going on here right. See Lambda Vis and Lambda NIR as a specific wavelength. Using them what we work out is a wavelength independent contribution of electron and of hole to each and every relaxation process.

So we say that decision process number 1 0.73 for the electron contribution that I can say without doing anything. Percentage electron contribution is 0 percentage hole contribution is 1. Well that is what we have started with that 0.73 picosecond is a hole relaxation. And then as you go from 1 2 3 4 5 6 you will see that percentage contribution of electron will increase percentage contribution of hole will decrease until at the end you will have no contribution from the hole at all. Are we clear?

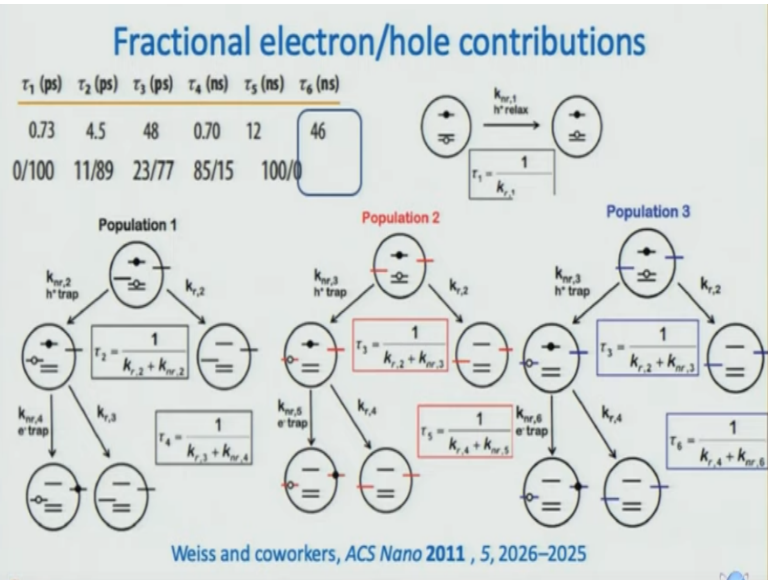
What is the need of working out this 50 50 point. The need of working out this 50 50 point is to arrive at this formula and this is the formula that takes us to Chi n e which is wavelength independent. And from there well that is basically what we work out. So this is the result and here you might notice that instead of A5 A6 only one is taken this is just the sum of the 2. Only one is taken because first of all the contribution is very small and they mean more or less the same kind of thing. Look at the last line and neglect the strange notation.

Let us read the numerator first then the denominators. Percentage electron contribution for the first pathway is 0, for the second pathway is 11%, for the third pathway 23, fourth 85 and fifth and sixth 100. And hole contribution is 100 for pathway number 1, 89 for pathway number 2, 77 for pathway number 3, 15 you see the dramatic change here from 77 it goes to 15 when you go from 48 picosecond to about 700 picoseconds.

700 picoseconds is well of the order of nanosecond so at the moment of well at the point of transition from ultrafast dynamics to fast dynamics. You see there is a significant change over of relative contribution of electron and then this one is electron all the way ok. So to explain this, what they considered you will see why they consider this. They consider 3 kinds of population of nano crystals.

A 3 kinds of population means a one population is one kind of distribution of electron and hole trap. Second with another kind third with another kind ok we will see where all that comes from and why?

(Refer Slide Time 13:46)



Fractional electron/hole contributions

τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	τ_5 (ns)	τ_6 (ns)
0.73	4.5	48	0.70	12	46
0/100	11/89	23/77	85/15	100/0	

Weiss and coworkers, *ACS Nano* **2011** , 5, 2026–2025

Ok another thing if I forget please remind me at the end to say what more could have been done or what more should have been done in this paper and I want you to find out whether it has been done in the 9 years that have passed between the publication of this paper and today alright. So this is what you have the time constants and the contribution. What is numerator and what is denominator?

Very easy to remember because if you remember the first component is only due to hole so denominator is hole numerator is electron ok. So let us go one by one let us look at the first component. First component we do not even want to think this is hole relaxation. So what would be the meaning of hole relaxation is this.

What it is essentially mean is that there is a population I mean the last population where the hole is actually not on the highest level. It is somewhere down below that means the electron has been taken out from a lower energy level while exciting and that hole floats up that is the relaxation ok. So to start with we should write that Tau 1 as 1 / Kr 1 + 1 / Knr 1. But I hope you will agree with me if erase one of this terms in the denominator. Can I erase Kr or Knr?

What can I erase? Kr right here only hole is involved. So hole is going from one level to another level there is no question of emission of light ok it is just relaxation. So I can just erase this. So actually it is 1 / Kr 1 now the convention that is used throughout is Kr or Knr is written and then you write a number in sequence of appearance of that nothing else. So this 1, 2, 3, 4 that we write here is not necessarily correlated with his 1, 2, 3, 4.

And there is another point where we can get confused ok. One needs to be careful about that. In the first one there is no problem because both are one but later on you will see things will get jumped up a little bit. So first one is accounted from hole relaxation. What about the second one? Here what is the contribution of electron? What is the contribution of hole percentage? 11% electron 89% hole ok.

So you can safely say the 11% electron means whatever is in excess electron or hole that is being trapped you can think like that. We have 11 electrons you have 89 holes this is what is involved in relaxation pathway. So what will happen the model that being used is that the 11 electrons will radiatively recombine with 11 holes and the remaining 89 – 11, 78 will get trapped are you clear?

11 % electron, 89 % hole means if you have 100 excitons your handling here well not 100 exciton 100 carriers 11 electrons are there 89 holes are there that are relaxing through this path. So this electron 11 electrons will radiatively re combine with 11 holes and the remaining 78 right 78 holes are going to get trapped because that is the only way to get relaxed by themselves ok. This is definitely a question because who has said that out of 11 electrons 4 do not get trapped right.

So this is one problem we are trying to do so much of detailed analysis ok. But it is still it is a commendable approach that one can learn from ok. So this is one problem if fact I want you to tell me I told you the answer. So the problem is this here after doing so much of calculation finally you are working within the ambit of some approximation. The approximation is that if you have a smaller number of electron or smaller number of holes all of them relax by radiative recombination that actually maynot be true.

Justification for using that is that you have 78 holes that are getting trapped as against 3 electron getting trapped you neglect the 3 electron ok. So this is definitely an approximation that is being used. So do not get the impression that it is an absolute perfect approach. Lots of approximation are, actually involved ok. So I can draw it like this. Let us see what I mean here. First of all this hole relaxation is already taken place in the first 730 femtosecond.

From here 2 pathways are there one is radiative relax you understand what this means right. These 2 lines at the bottom these are energy level in the valence band this one is the lowest energy level of the conduction band. This here is the hole trap this here is the electron trap and you have working with shallow traps there is another approximation. Why do I say you are working with shallow trap because there is no red shifted emission right.

If there were deep traps would not you expect PAL that is red shifted your significant change right. But if there are shallow traps, electron or hole then whatever whenever those trapped electron holes recombine the energy involve will not be very different from the band edge recombination energy. There is why these are all shallow traps that is that comes from the steady state spectrum.

So this is one pathway the radiative pathway now recombination takes place that is why you do not see electron or hole. Electron is designated as filled circle, the hole is designated as an empty circle ok. So this one is given the name Kr 2 and this is where the deviation from this notation up here begins well not really because this is 2 that is also 2 we will see where the deviation comes.

Do you understand Kr2? Kr2 is the rate constant associated with the electron hole recombination in this kind of a situation. So this is band edge electron hole recombination ok and that is associated with what kind of time constant. Something like 4.5 picosecond time constant right. The other thing that is there is Knr 2 where the hole gets trapped alright. So that is one thing and this labeled fast hole trapping.

And the need for using the adjective fast will be apparent in a few minute. Have you understood this diagram? This is the diagram that is easy to understand later on things get a little messed up little bit of hand waving is there ok. Now let us go to the next one 48 picosecond time constant electron contribution 23 whole contribution 77. So if I go by the previous treatment what does this mean? It means 23 electrons radiatively recombine with 23 holes and 77-23, 54 holes relaxed by themselves right.

So what kind of diagram will I get? Similar what I do earlier what will change instead of writing Kr1 Kr2 I have to write Kr3 yes. So this same thing what we write is that Tau 3 = 1 / Kr2 + Knr3 now this is where the deviation begins actually. So see the here it is Kr2 here also it is Kr2 why? Because in both the cases the radiative process is electron hole recombination at band edge there is no reason why we should use a different rate constant there.

However, the non radiative rate constant is definitely different right trapping is definitely different because time constants are different by in order of magnitude. In the first case we are working with 4.5 picosecond time constant. Now we are working with the 48 picosecond time constant 10 times more. And we are saying that the radiative rate constant is the same in both the cases. So, obviously non radiative rate constant is going to be a different.

Will it be larger or will it be smaller? For population 2 will so we have the names we can use the names Knr3 is it larger than or smaller than Knr2 smaller than Knr2 smaller rate constant is associated with longer time constant ok. So, smaller rate constant means what slower basic chemical kinetics. If the rate constant is small the process is slow. So here this is called this hole trapping is called slow hole trapping. Why would we have a fast hole trapping and slow hole trapping?

What could the reasons be? This I think you can tell me. First of all it could be different traps different kind of traps. Where the hole is getting trapped or it could be different density of traps. You have in population 1 perhaps there is a large number of hole traps. In population 2 there may be a smaller number of hole traps right. That is where it is called population 1 and population 2.

Knr2 is smaller, Knr2 is not slower or faster. Time constant is slower or faster you can say well everything is smaller and larger. What I am saying is Tau 3 is larger than Tau 2 and if you look at the expression in the denominator Tau 2 has Kr2 Tau 3 also has Kr2. So now my question was Knr3 and Knr2 which one is larger. Since Tau 3 is larger Knr2 has to be smaller. It is in the denominator that is why I am saying smaller rate constant it is not faster.

Smaller rate constant is associated to with the slower reaction rate = k multiplied by the concentration. So if K is small it will be small so slower process will be slower yes it can be. I mean there is no restriction on what the values of Knr2 and 3 are right. That is not the model that is being used the model is that whenever you have band edge recombination. Band edge recombination is the independent of the number to be honest.

Band edge recombination is 1 electron and 1 hole forget everything else that kind of situation. So band edge recombination has to have a same life time. When trapping take place it is not so easy for the electron and holes to recombined radioactively. That is why it is slows down. That is why when say copper is introduced, a manganese is introduced lifetimes goes from picosecond to hundreds of nanosecond because they are like physically separated right. They are all different entities but not in this case it is in the same particle.

In the same particle when you have an electron and hole it does not matter what it what the situation is in another particle. Do not forget lesser number of holes means what? What we are saying is that we have done 1 photon excitation. So in a single particle there is only 1 electron hole pair. All we are saying is that the distribution is different for a particular relaxation pathway. Total number in any cases is same over the ensemble.

But how many holes are combining with how many electrons in particular path is that being discussed. And the case of a trap is different because in 1 nanoparticle there are many trap states. So you can talk about in a single nanoparticle you can talk about greater density or lesser density of traps. So even for 1 exciton number of traps is going to alter the rate but band edge emission recombination of an electron and a hole in valence band and your conduction band that is constant. Constant, means that has it, own distribution that is why you will get a lifetime.

That is independent of anything. That is why the radiative rate constant have been taken to be the same are you clear now? This is not trapped because if it was a trap emission then what you are saying is definitely correct alright. So this is population 2 and in fact population 3 is very much like population 2 and I show it to you will see. Let us go to this nanosecond time constant now. So we are going to picosecond to nanosecond.

Now there will be a more fundamental change. What happens here 85 electrons 15 holes what does that mean? Electron trap right so what they did and it is not very clear why they did not want to do it in another population. Why they did not use a fourth population? What they did here is that well there is the reason why they did it I will tell you. What they did is this they just now just go with me and see what they said then we will come back to that.

They said that this Tau 4 originate not here but here. Tau 4 originates in nanoparticular where the hole is already trapped. And the reason why they say it is that now here the radiative constant is different picosecond and nanosecond right. Now we come to a situation that you are referring to just before this. Here for a, nanosecond decay the radiative constant cannot be associated with a band edge electron hole pair.

It must involve a situation where one of the carriers is trapped. So here you see a different radiative rate constant is use Kr3 ok. So Kr3 is much smaller you see lifetime is time constant associated is much larger. So 1 / Kr3 + 1 / Knr4 so what will happen? One thing that can happen is that first of all this 2 can recombine and this recombination is different from recombination in the earlier stage because it involves a trapped hole.

That is why the time constant is much bigger, rate constant is much smaller. The other thing that can happen is this electron can get trapped. So you will end up with nanoparticles where electron is trap hole is also trapped thus bound to happen. So now you are created a situation that both are trapped. So if there is any ultralong lifetime in Pl that will come from here ok. Let us if this, traps are completely isolated they would not even recombine. They have to sort of comeback to core and then only recombination can take place ok.

Similarly the next one was associated with population 2 exactly same kind of situation and then population 3. So what they saying is that there are different kinds so it is basic processer are only of 3 kinds ok. But there are different kinds of population with different density of traps that is what shows up in the different time constant in nanosecond timescale. Picosecond is justified by the fundamental trapping and band edge electron hole recombination processes ok.

So this is what they did. Now can you tell me what you honestly think about this analysis. Do you think it make sense? Do you think it all rubbish? Or do you think it is somewhere in between? So what I think is that this model is it requires further verification. It is good model to start with but may not be complete. How can one try to complete this study? But I would think is this is a situation where one can take this out to simulation.

When I say simulation i do not mean protein folding and all it is nothing to do with that. What I am saying is that in this kind of numerical you can do it with things like Math guide. And now I am sure there are better software for this. What one can do is you basically you not be able to fit the data just like fitting is already done. What you need to do is? You need to guess value of Tau 1, Tau 2, Tau 3, Tau 4, Tau 5, Tau 6 right.

And then vary them until you get a good fit. Look at them and see whether they can make good sense. Not all good fit will give you time constant that make any sense or rate constants. So this is something that should be done in cases like this actually the story is incomplete. Did the story get completed in the last 8 years I will leave that to you? To read up and see and if you are doing it, it is to see which paper have cited this paper go through them and see whether this has been complete. Also this people actually published later on.

So I like you to read that as well. Read this paper it is a good example of how one can handle very complicated ultrafast time resolved absorption and emission data that way it is interactive. And it is not necessary that the understanding generated from the data analysis is restricted to nanoparticle. It can actually be extrapolated to other systems molecular systems with comparable or more or less complexity ok. So that is what we wanted to say here. So far we have talked about exciton dynamics in semiconductor and nanoparticle that is the only the beginning of the story.

In the next 2 or 3 module we are going to talk about dynamics of multi excitons and may be just catch upon a very recent paper that has been published on other kinds of carriers that are there polaron trion and so on and so forth. Perhaps we will not go in to too much of detail of that but at least we will mention what they are and what has been seen. But multi exciton dynamics is something I definitely want to talk about and that is essentially single paper by Klimov. Ok