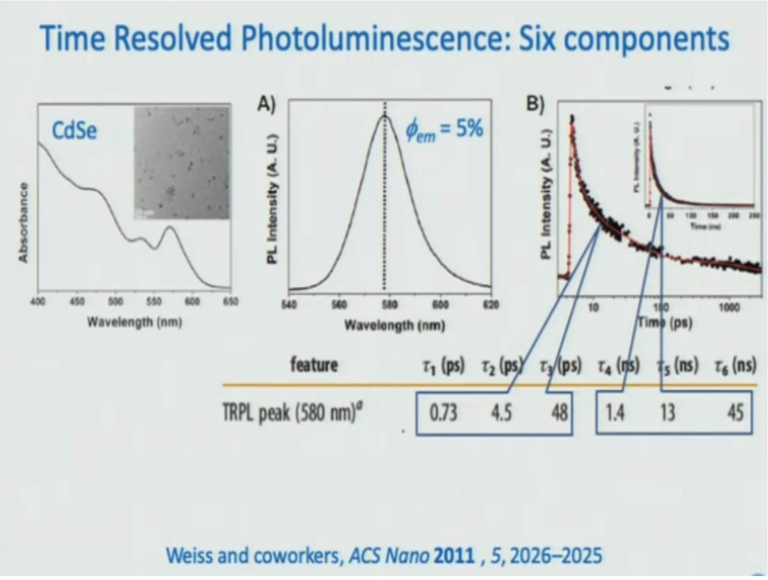
Ultrafast Processes in Chemistry
Prof. Anindya Dutta
Department of Chemistry
Indian Institute of Technology – Bombay

Module No # 12
Lecture No # 60
Radiative and Nonradiative Relaxation Pathways in CdSe Nanocrystals – Part 1

We are discussing radiative and non-radiative relaxation pathways of semiconductor nanocrystals as we said this is a vast body of literature on this and there are differing opinion as well so the limited scope of this course will not be able to discuss everything that I leave to the interest of few people but what we are discussing now is one single paper published in ACS nano in 2011 by Weiss and her group where they had taken a very rigorous approach towards understanding these rate constants or amplitudes also obtained in time resolve studies of cadmium selenite nanocrystals in particular.

Now what I would suggest is that one should try and see go through the paper that have sited her paper because if you do that you will see that there have been people who have supported this approach there have been people who have opposed this approach. So we are talking about science that is evolving now not science that is established 100 years ago. So to be honest the jury is out but the reason why we still discuss this paper is that this is a let us say this is bold approach but a thorough approach nevertheless to try to understand the temporal parameters obtained in ultrafast studies.

(Refer Slide Time: 01:47)


Time Resolved Photoluminescence: Six components

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

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

So we have discussed this already in the previous module what they did is they worked with 5 nanometer cadmium selenide particles they did worked with little bigger particles as well just to verify whether whatever this say is applicable for another set or not and it turn out that they were applicable this as we discussed is absorption spectrum and we have already talked about what this bands mean this is the most prominent band edge absorption that we get.

And the photoluminescence that we get is more or less mirror image of the band edge absorption quantum yield is only 5%. And then the unique approach of this paper is that when we talked about earlier about this data fitting and all we are said that there if you use a sufficient number of exponentials you can fit even an elephant. So here they have used the large number of exponential functions and as we will see they try to use of all the time constants that they get make sense of all the time constant that they get.

So first of all they perform an ultrafast experiment we can see the full scale here is about a nanosecond and from there they have obtained 3 time constants 0.73 picosecond 4.5 picosecond 48 picosecond. And from TCSPC experiments they obtained 1.4 nanosecond, 13 nanosecond, 45 nanosecond. Point to note is that there are there has been a lot of work on semiconductor nanocrystals where people have done only TCSPC and have happily lived with these 3 times constants.

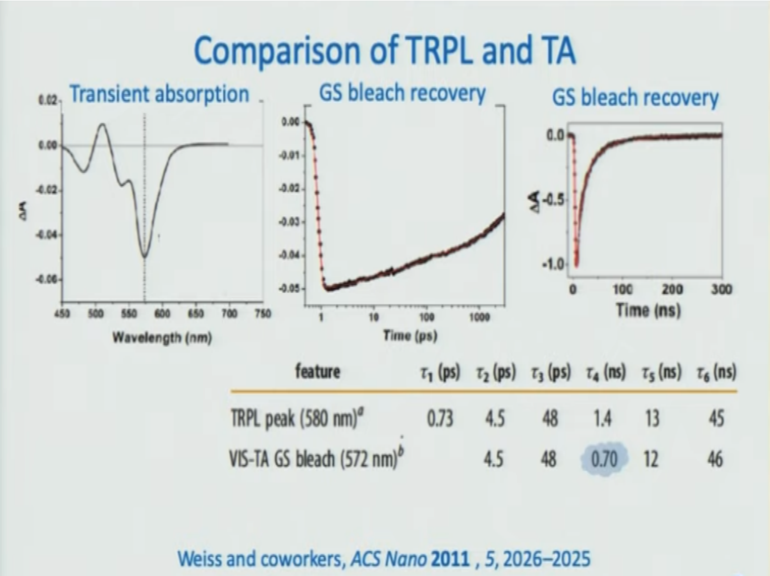
But as is very obvious in this work it is not enough to do this TCSPC one should look at ultrafast time scales as well because as you see. The photoluminescence is decayed to about 10% of what it was at the beginning in a matter of a nanosecond in 500 picosecond it goes down to may be 20%. So there is a very prominent ultrafast component that one cannot neglect of course when you look at photoluminescence perhaps it is a nanosecond component and dominants at least in this steady state spectrum.

Because PL that gets over in 10's and 100's of picosecond do not contribute sufficiently you remember contributing to steady state intensity is Ai Tau i where Ai is normalized amplitude. So it is not only Ai tau i also contributes so if you have 2 tau i's one is 10 picosecond and one is 100 nanosecond that itself is a factor of 100000 / 10, 10000 right and so let us say we have a picosecond component of 90% of the decay's in 10 picosecond.

And well time constant is picosecond amplitude is 0.9 what is amplitude multiplied by tau here 0.9 into 10 picosecond okay so being everything to picosecond so that is 0.9 multiplied by 10, 9 okay. And 10% 0.1 multiplied by 100 nanosecond how much is that? 10 nanosecond that is 10 nanosecond 10000 picosecond so 10000 divided by 9 is how much? Let us say 10000 divided by 1000 so contribution of the long component will actually be 1000 times that of the ultra short component in this steady state spectrum.

Even though it is amplitude is only 10% you can have other examples where you can take this numbers and see that this things actually holds okay. But we digress as a little bit so 3 time constants from ultrafast experiment 3 time constant from the TCSPC experiment.

(Refer Slide Time: 05:47)



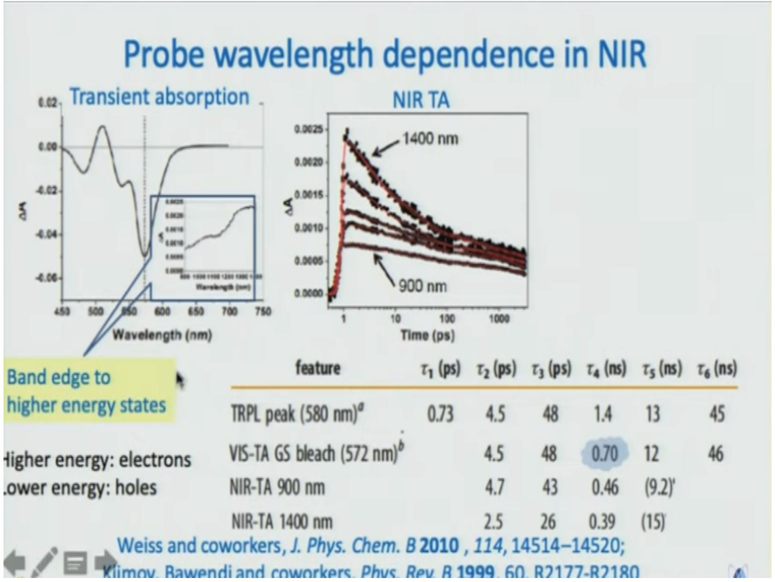
Comparison of TRPL and TA

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

And then they had a visible transient absorption as well in picosecond timescale as well as nanosecond timescale and from their they got these time constant only difference was 1.4 and 0.7 this was the only component it was different otherwise more or less everything was same and that is remarkable. And that is why they what encouraged to prove this further as you see this 0.73 picosecond component does not even show up in transient absorption using visible probe.

(Refer Slide Time: 06:16)



Probe wavelength dependence in NIR

Band edge to
higher energy states

Higher energy: electrons
Lower energy: holes

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
NIR-TA 900 nm		4.7	43	0.46	(9.2)'	
NIR-TA 1400 nm		2.5	26	0.39	(15)'	

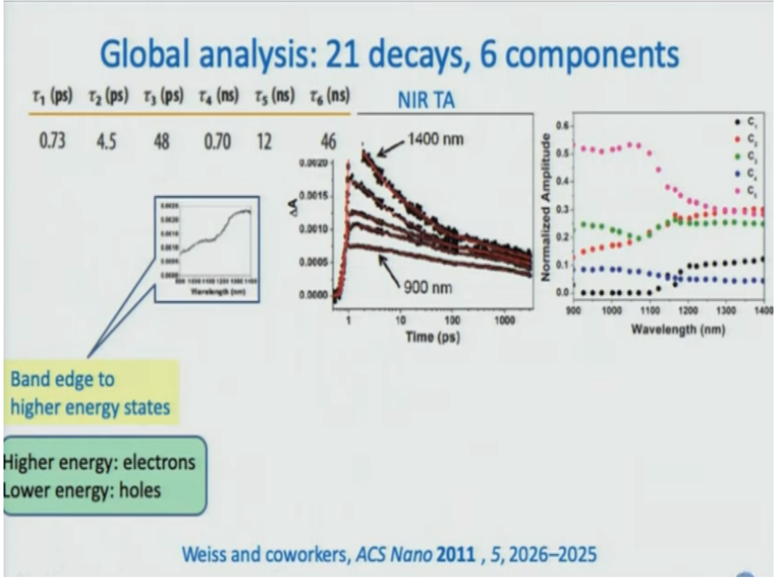
Weiss and coworkers, *J. Phys. Chem. B* **2010**, *114*, 14514–14520;
Klimov, Bawendi and coworkers, *Phys. Rev. B* **1999**, 60, R2177-R2180

It does have indication of showing up when the probe is NIR I think we have discussed all this in the previous module. In NIR you see that as one goes from probe wavelength of 900 nanometer to 1400 nanometer decays get faster and faster and it is very clear that the long time constant decay are all tail matched long time decays are all tail matched in short time the difference is there as you go to the radar side you get the decays becoming faster.

And when fitted just as such this is the kind of data that we had shown you this 4.7 becomes 2.5 but then that does not explain anything. In fact what they also try to do is they try to use things like stretched exponential model but what they found is that even by using stretched exponential model the number of traps that does not decrease so state space exponential model in this case does not teach us anything that is why they embarked upon the analysis that we are discussing now.

So another thing that was known from earlier work of Weiss and coworkers as well as Klimov and coworkers is that if you look at this NIR probe transient absorption this is ascribed to band edge to higher energy state relaxation well higher energy to band edge relaxation or rather I can say this absorption is from band edge to higher energy. How does one goes from band edge to higher energy? One thing is that electrons can go higher up I mean electron might have gone higher up or might go higher up when you excite by the probe or the hole can keep going down or both can happen okay.

(Refer Slide Time: 08:04)



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

So what is it actually? To understand that one thing that is known is that this higher energy side is dominated by electrons lower energy side is dominated by holes that was established in the paper that I have shown. So this seems to be mostly hole contribution because it goes up there so what they did was they had done a global analysis but not really global analysis because that fix the lifetimes they fix the lifetimes because they already see a very good match between PL and transient absorption data for 5 of the time constant.

And this 0.73 picosecond time constant was also well resolved that is why they fixed it but this is one step that can be requested. So did this global analysis and this is what they got all this time constant 1, 2, 3, 4, 5, 6 and then they work with the amplitudes. They plotted the amplitudes and you get this kind of a plot so look at which is C1 out of this you can see the color I hope C1 means the amplitude associated with tau 1 this is also called a1 in later discussion okay.

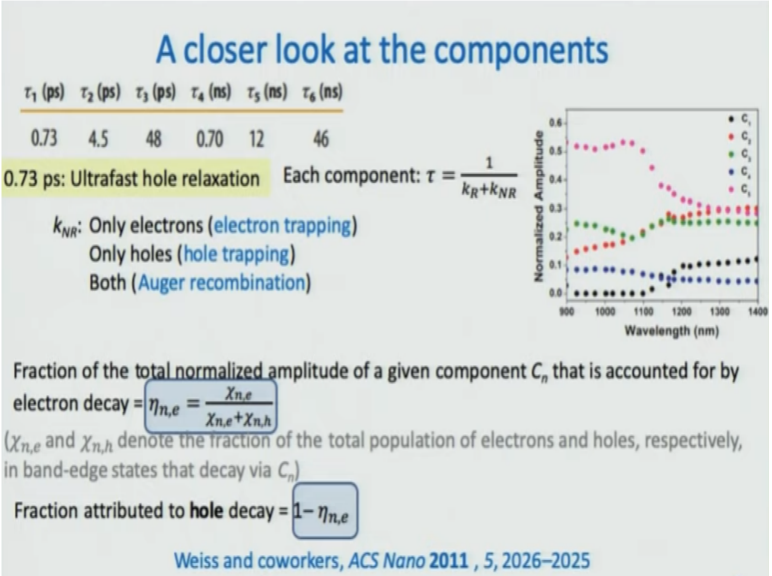
So which one is C1 out of this one right and see what happens to C1? It is not there is S0 and then it goes up in the NIR range and goes to saturation why does that happen because this 0.73 is associated with ultrafast hole relaxation. Remember as you go higher energy to lower energy side in the NIR domain NIR probe domain you get signal that is more and more predominated by holes what all things can happen?

So as you go from higher energy to lower energy side it is dominated by holes right what all things can happen first of all this and then it is important to have this very clear because we need it in the subsequent discussion so you have an electron and you have created an exciton. Now first of all they can recombine right and we will go back to the ground state and that combination is the only process that contributes to emission of light.

We can perhaps have non-radiative recombination also but when an electron hole recombines that is the only time when you get light out of a system that is that clear? Other things can also happen you can have the electron going up the energy ladder you can have the hole going down which also the hole going down means essentially increase in energy right. That can happen independent of each other the electron can go up higher in energy irrespective of the hole right.

Or let us put this I think will all understand electron let us say trapped or hole can be trapped independent of the other carrier. So these are the different things that can happen in trapping process electron and hole one of this is usually effected but in recombination both are involved and that is the process that is that gives you light remember this will come back to this okay.

(Refer Slide Time: 11:40)



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

Each component: $\tau = \frac{1}{k_R + k_{NR}}$

k_{NR}: Only electrons (electron trapping)
Only holes (hole trapping)
Both (Auger recombination)

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

So this 0.3 picosecond component is ascribed to ultrafast hole relaxation. And we will see by the time we have done what that means you understand what hole relaxation means? It essentially means that initially the hole is in one of the lower levels it floats up to the higher level in valence band that is hole relaxation. Electron relaxation means electron is in higher energy level it sinks to the lowest band lowest energy level in the conduction band that is electron relaxation this is hole relaxation.

So this 0.3 picosecond is associated with ultrafast hole relaxation why? Because in NIR in the lower energy side this 0.73 picosecond is absorbed to a greater excite and the lower energy side as it shown is dominated by whole relaxation alright. Then another important thing to remember and we said earlier is that each component is really 1/ kR + kNR every tau every time constant is equal to 1 / kR+ kNR there can be a situation where for a particular component kR is much larger then kNR so you can neglect kNR so we can have cases and we will have a case at least where kNR is so much larger that you can neglect here but those are special cases.

The general case is that every component every tau is 1 / kR +kNR this holes for everything not just nanoparticles. And this is something that somehow we have already talked about this kNR can be associated with electron trapping hole trapping Auger recombination right and kR can be associated with radiative electron hole recombination. So but then how to make any sense of this now we start discussion of this rather rigorous. And sometimes and if possible questionable treatment of the amplitudes that this group had done and I want to tell you by the time we have done what you think of this analysis

And when I say want you to tell me what we think of this analysis do not mean I want you to tell me what I think of this analysis. We should feel free to say that this analysis is rubbish if you feel so this is what they did first of all they define all though not much define straight forward the fraction of the total normalized amplitude of the given component that is accounted for by electron decay they defined to be Eta ne = Chi ne / Chi ne + Chi nh where the Chi's are the fraction of total population of electron and hole respectively in band edges that decay via Cn it is important to understand this statement.

Do you understand what is what they are trying to say what does n denote? Of Cn what is n? What is C? Normalize coefficient amplitude okay and it has also been used as a okay there might be a little misleading what is n? What does n tell you? Which component you are working with? So this 0.73 picosecond component is n = 1 component 4.5 picosecond component for that n=2 48 picosecond n=3 and so on and so forth okay.

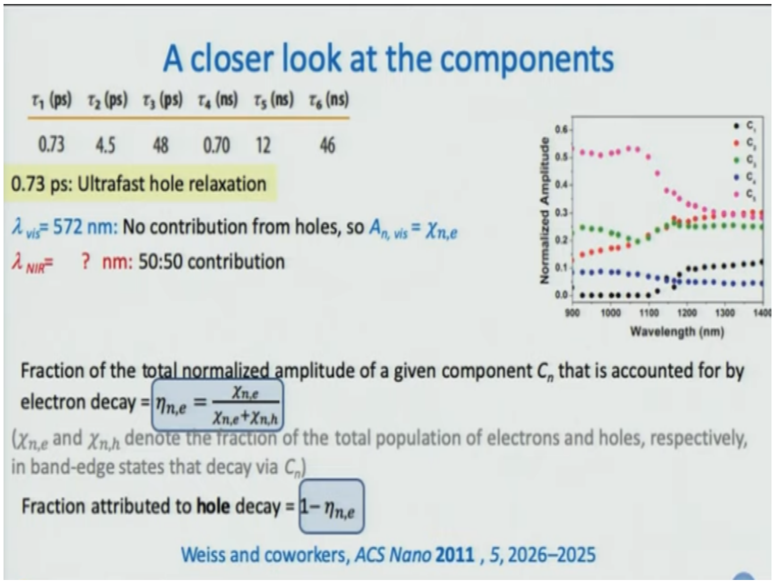
So this subscript of the tau's that are given a the top the subscripts are the n alright now understand what they are saying Chi ne and Chi nh are the fractions of total population of electrons and holes e for electron h or hole in the band edges so in this study we complete neglect things that are not in band edge for now at least in the initial definition that decay via n right. You have say Avogadro's number of electron Avogadro's number of hole right.

Different electron hole pairs will do different things right you can only work with statistics you can only work with fractions that decay by this components or that is all they are saying. And Eta ne is given by Chi ne divided by Chi ne + Chi nh that is very straight forward and of course then the fraction attributed to hole decay would be 1 – Eta ne the 2 Eta's add up to 1 clear what is Eta? It is the fraction of the total normalized amplitude that is accounted for by electrons or hole depending on what subscript you are used are you clear?

Then they started trying to simplify this problem what happens for so one more parameter is there which we have not really talked about there that is wavelength. You are doing transient absorption right? So the different wave lengths are there so is there can you think of wave length where there is no contribution from either electron or hole. If you can do that then the problem become little simpler.

Can you think of a wavelength from what we have seen already probe wavelength where the hole does not contribute I will make things easy higher energy side of course actually let us remind ourselves where do we see the hole dynamics very prominently in NIR right. So if you just go to that visible transient absorption there we will reach a situation where hole dynamics is not even there.

(Refer Slide Time: 17:51)



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 $A_{n,\,vis} = \chi_{n,e}$

λ_{NIR}= ? nm: 50:50 contribution

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

So what they have done is the have taken this position of absorption maximum right what transient absorption minimum 572 nanometer that position they said there is no contribution from holes okay. So An Vis = Chi ne that is starting point they have defined this wavelength to be lambda Vis okay. Of course there is many other lambda Vis why 572 even 500 is lambda is but here they are define is you can treat it as a proper name not as a generic name they are defining 570 nanometer to be lambda Vis.

So An Vis = Chi ne so what they are saying is Chi h Chi nh = 0 for which n? For all n 1, 2, 3, 4, 5. 6 for all the n’s for probe wavelength 572 nanometer which is given the name lambda Vis there is no contribution of the hole that is what they are saying and what is the basis of saying that? The hole dynamics is seen in this NIR okay. Then what they do is in fact you can now take this in any other wave length where you know what is the contribution electron what is the contribution of hole?

So just to keep the calculation simple they have looked for a wavelength where there is 50 50 contribution from electron and hole. How does one find it? That is what we will learn now okay? But perhaps it is better if we take a break and discuss this in the next module from here onwards.