Ultrafast Processes in Chemistry
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Module No # 12
Lecture No # 59
Semiconductors Nanocrystals - Part 2

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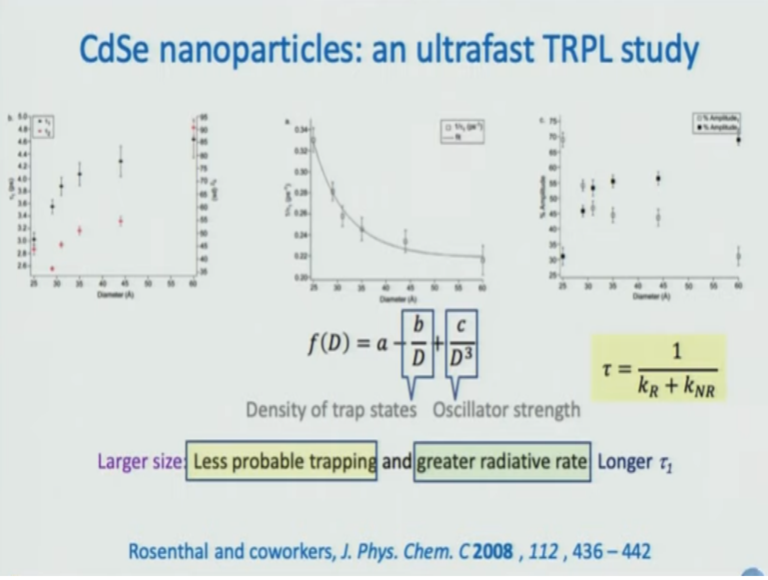

CdSe nanoparticles: an ultrafast TRPL study

$$f(D) = a + \boxed{\frac{b}{D}} + \boxed{\frac{c}{D^3}}$$

Density of trap states Oscillator strength

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

Larger size: Less probable trapping and greater radiative rate Longer τ_1

Rosenthal and coworkers, *J. Phys. Chem. C* **2008**, *112*, 436 – 442

So now in the last module we have started talking about the semiconductor nanocrystals we have discussed Rosenthal's works were they had obtained a bi-exponential decay cadmium selenium nanoparticles and the important thing that we learnt from that study was that the every time constant has a contribution from a radiative part and a non-radiative part. Of course there can be special cases where one of the amplitudes can be 0 I mean one of the rate constant may not contribute as a different issue but the general scenario we should not forget is that every time constant is associated not only just 1 radiative or 1 non-radiative process.

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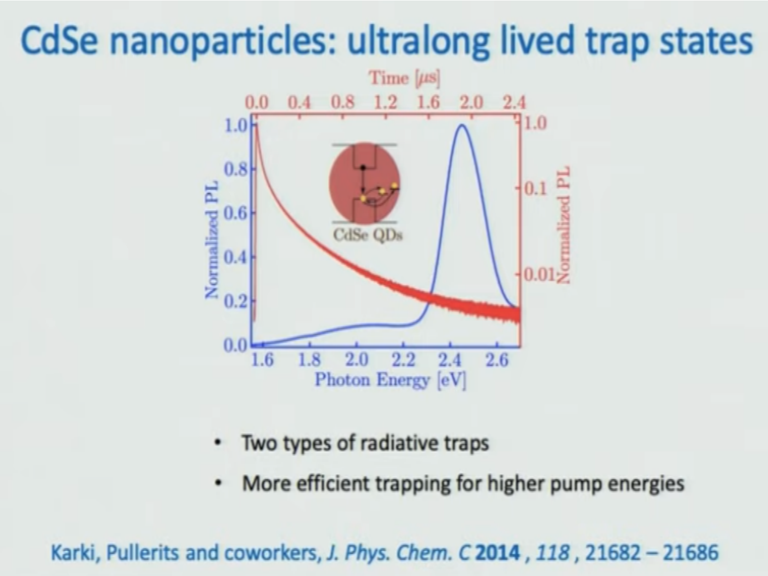

CdSe nanoparticles: ultralong lived trap states

- Two types of radiative traps
- More efficient trapping for higher pump energies

Karki, Pullerits and coworkers, *J. Phys. Chem. C* **2014** , *118* , 21682 – 21686

And we are also said that very often you have ultra-long lived trap states not always you can try and make nanoparticles were this trap states are almost not there but in most of the cases you have long live trap states which is usually hindrance because that would steal from the band edge emission intensity but in some cases trap state emission has been used effectively to make things like white light emitting nanoparticles or well radiomatic nanoparticles which have different kinds of use.

So what is established in this work of Karki and Pullerits and others is that for Cadmium selenide there are 2 types of radiative traps. So it is not a single exponential decay and secondly if you pump with higher energies there is more efficient trapping will not go very deep into this right now but when we talk about multi excitons and all we will talk about effect of pump energy as well.

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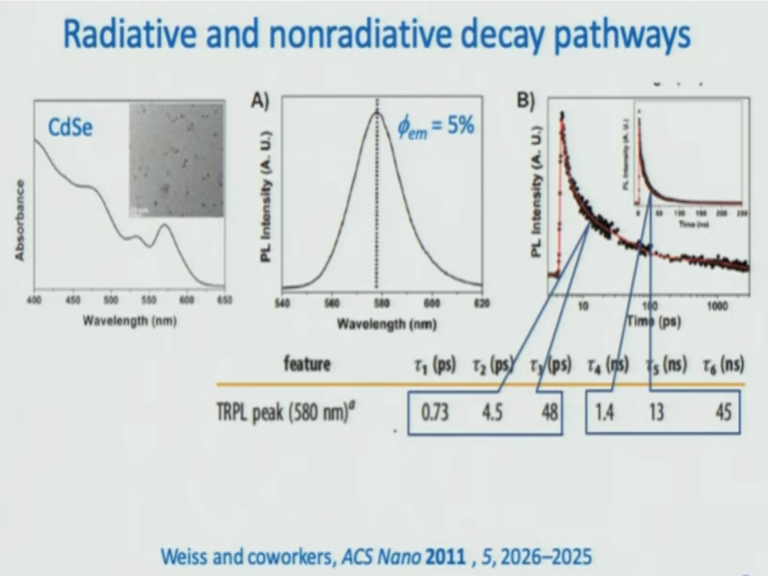

Radiative and nonradiative decay pathways

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

Now let us move on to another piece of work by Weiss and coworkers and here we will not complete the discussion in this module what we will do is we will discuss the philosophy of what they have done and then we will come back in the next module and then discuss the mathematical detail that they have used in the data analysis. So this is the system that they work with Cadmium Selenide nanocrystals once again rather small.

And now we are familiar with this absorption spectrum you can see the band edge absorption you know what it is which electron level which hole level is involved and you can see the other structure very nicely that we had shown earlier in the previous module. And this is the emission spectrum the point to note is that these are nanoparticles were not much of trap emission is there but the emission quantum yield as low as 5% not great as low as 5% because.

If you look at the decays of photon luminescence here you might notice that Weiss and coworkers do not use the term fluorescence and phosphorescence's there in deviation with Rosenthal's assignment. So if you see almost all the PL has decayed within the first nanosecond however if you look more carefully so this is the decay that you get using femtosecond optical gating up conversion. And this insert shows the decay of PL using TCSPC and that goes on for hundreds of nanosecond.

So this is the interesting as well as problematic aspect of working with this kind of nanoparticles you have ultrafast decays you have ultraslow decays and everything means something it is not easy to separate the components and say which means what? And that is what this paper ACS nano 2011 is very useful because it gives you a good idea about what to do this many time constant that you get.

In most of the papers they are dealt with rather sloppy but this is one paper where they had done a thorough analysis of course whenever you do something like this many of the models of phenomenological many of the models are just empirical and can be debated. And that is why so much of work is going on even now because the last word is not really out alright. So let us show you some of the time constants as the got.

So when they look at the time resolved PL peak at 580 nanometer they got a 6 exponentials 3 from up conversion 3 from TCSPC. So you see 4.5 picosecond and 48 picosecond these are in agreement with those Rosenthal's work remember Rosenthal's got bi-exponential decay's for her PL decays femtosecond time regime picosecond time regime they get that. What they get in addition is this 730 femtosecond time scale so this something that one can miss very easily if the resolution of the instrument is not good enough.

And the other thing that they have got and Rosenthal did not most likely because Rosenthal did not try to do a TCSPC experiment and they did is that they got these 3 time constants 1.4 nanosecond, 13 nanosecond, 45 nanosecond. Now there are papers where the ultrafast component is not even considered and this 3 lifetimes obtaining being TCS species quite common and remember this is not trap emission here.

We are not talking about very red shifted emission if trap emission component is there then the trap emission is hidden within the band edge emission itself. So the energy of the trap is very close to the band edge so this is an experiment which is more carefully done and more thorough in which the ultrafast as well as the slow components everything have been considered. But now the question is what will we do with so many components? How does one make sense of this one way of making sense of complicated system is to do more than one kind of experiment.

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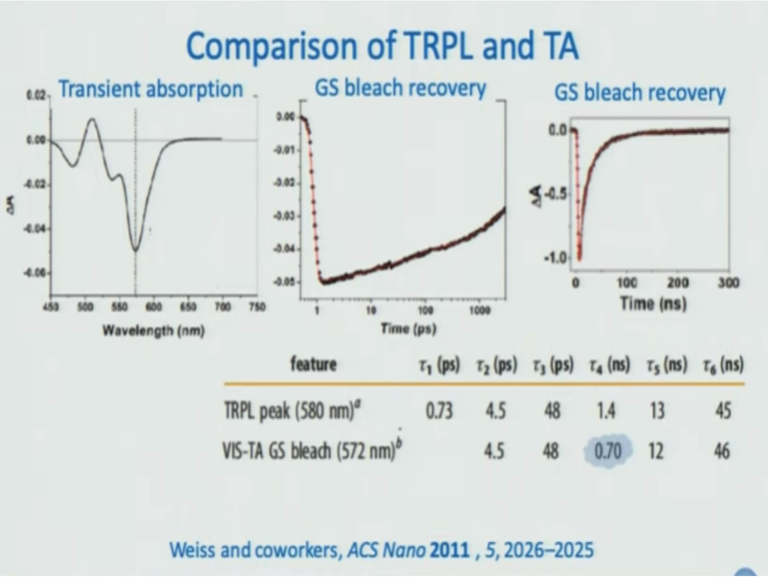

Comparison of TRPL and TA

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 they did transient absorption experiments and compared the results with the time resolve photoluminescence experiments. So this is the transient absorption that you can see again what is this feature? This strong negative feature naturally ground state bleach here you would see some kind of a transient absorption and here again ground state bleach and of course this signal in this entire range is a complete mix because do not forget absorption is not just here it keeps on going up.

So whatever plus signal that you see is really a net signal there is a minus component as well okay. What is a most notable thing in this spectrum I would say the quality it looks like a steady state spectrum absolutely smooth right so it is beautiful. Now so then they looked at the ground state bleach recovery not in picosecond but also nanosecond so they did flash photolysis as well. So as you can see the ground state bleach is not recovered completely within even after 1 nanosecond and this is are major difference between the transient absorption data and time resolve PL data.

Time resolve PL remember was gone in say hundreds of nanosecond hundreds of picosecond well not hundreds of picosecond if you go beyond 1 nanosecond you can see that time resolve PL is almost gone okay. But here you can actually see that the ground state bleach recovery is not complete that means that you do have states that you have do not radiate which are holding either the electron or the hole keeping them separated and not allowing complete recombination and regeneration of the ground state within 1 nanosecond and you get this long component in ground state bleach recovery.

So first of all what is been indicated here is that the nanosecond signal that you get in time is of PL is not rubbish okay. As we know whenever we talk about fluorescence of photoluminescence are very picky we always think that they maybe some impurity and whatever long life time is there perhaps because of small amount of impurity that can happen here also. But what transient absorption looks at is the bulk so you get absorption right.

So if there is very small quantity of impurity it will not show up in transient absorption so from here first thing that we learnt is that long component that was seen in transient in time resolve PL was genuine. Now if you compare the time constants something interesting happens first of all that 0.73 picosecond component does not show up so where is it gone? Secondly you see 4.5 picosecond in TRPL 4.5 picosecond in transient absorption 48, 13 and 12, 45 and 46 amazing beautiful match.

You only think that it is not matching is instead of 1.4 nanosecond you are getting 0.7 nanosecond which may be okay. When you do a 6 exponential fit in all and we stitch together in 2 kinds of experiments 1 out of 6 components going awry is fine alright. So this is what they have got now the problem is where is that 730 picosecond component why is it do not see it in transient absorption? Actually it is seen in transient absorption but not in the visible range of probe.

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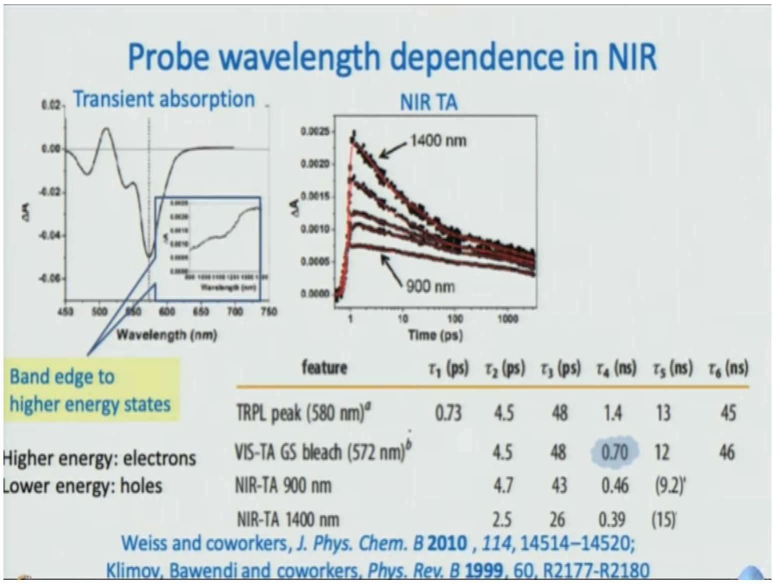

Probe wavelength dependence in NIR

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

So the other experiment that was done is transient absorption but using NIR probe and already there was literature which said that this transient absorption in NIR is due to band edge to higher energy states. In fact one can even guess that you are getting a positive signal so from band edge you must be probing transition of band edge to higher is said that those energy levels are much closer than the band gap that is inherently there that is why it is NIR and not visible.

Now the literature that is existed had established and again for positive of time will not go into how they establish is actually interesting thing to know but it was established that of this transient absorption spectrum the higher energy part is dominated by electron the lower energy part is dominated by holes very interesting papers one should read them okay. And then when you look at transient across the transient absorption band when you plot delta OD versus time this is what you get at 900 nanometer you get this kind of a decay at 1400 nanometer.

Once again remember this Tahara's work that we had shown TL's were matched and at the blue edge of this emission spectrum we could see the ultrafast component nicely this plot is similar is long components are there everywhere but the short components gradually emerges as you go from higher energy side to lower energy side what does that mean? Short component is not there in the higher energy side that is dominated by electron relaxation but it is there in the lower energy side which is dominated by hole relaxation what does it mean?

It means that the ultrafast component that is there is associated with hole relaxation such simple as that. The problem is when they just fit the data simply they did not see that 730 picosecond component 730 femtosecond component they got something like this first 2 if you remember where very nice 4.5, 4.5, 48, 48 what they see is when you go into NIR 4.5 becomes 4.7 to start with which is we can say within acceptable limits and then it becomes 2.5 I am not shown the data in between.

If you read the paper all the data is given and you can see the gradual this decay become faster and faster as you go from 900 to 1400 nanometer. Here we will show you only the 1400 nanometer data here this component is 2.5. And then even tau 3 instead of 43, 48, 43 they are similar it has become 26 tau 4 is actually something like 0.39 nanosecond and tau 5 could not be determined very nicely because in the NIR experiment they did not have flash photolysis.

So this is not a very good fit so what appears from this is that this analysis is not quite right the NIR UV pump visible pump NIR probe experiment. Analysis is not quite right because we expect to see that 730 femtosecond component that it has to be somewhere. In some range it has to be there because it is there in time resolve PL that is not showing up. And this 4 picosecond component that is sort of sacrosanct in our minds that is becoming 2.5 when does that happens?

You know very well that there are 2 components you miss the faster one but the component that you see which should not have become faster appears to become fast when does that happen. When you actually have the slow component but you are not looking for it do you understand what I am saying you have is a multi-exponential decay right you are fitting to a 4 exponential functions.

So it is not very difficult to lose one of the components but then it is there so what it will do is it will show up in some other component. Remember average life time sum over I AI tau I so suppose I fit instead of bi-exponential decay I fit to single exponential decay what will happen? I have bi-exponential decay of course it will not even fit but let us say just to understand the situation that I have a 4 nanosecond decay and I have a 2 nanosecond decay or let us make more realistic 2 nanosecond, 4 nanosecond, 8 nanosecond 3 components are there.

I fit it to a bi-exponential function and usually it will fit may be chi square will be little bad I fit it a bi-exponential function what will happen I will not get 2, 4, 6 I will not even get 4 and 6 perhaps I will get a 3 and 5 or something like that. So because I am not accounting for the genuine short component that is there the other component will also appear to be shorter than the R same is too for longer component okay.

So here is the issue here the important that comes is what we have discussed while talking about data analysis. Data analysis cannot be done blindly you cannot just take whatever come out of the program you have to think that what should be the situation in your system and you have to use an appropriate model okay. So the appropriate model they used was first of all they did what we have discussed towards the beginning of this course they did global analysis.

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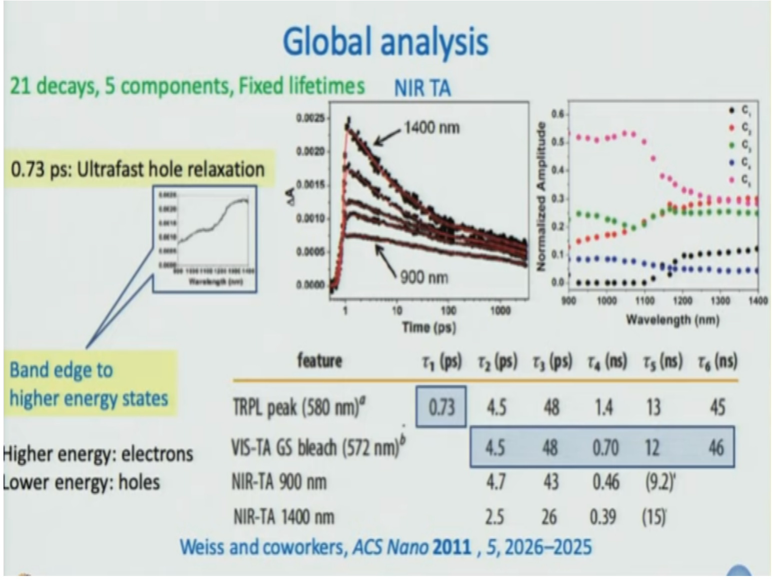

Global analysis

21 decays, 5 components, Fixed lifetimes

0.73 ps: Ultrafast hole relaxation

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

Global analysis across this transient absorption NIR band so they took 21 decays so here the good thing is that you are recording the spectrum right is in principle you can take very large number because you have many pixels there so they took 21 decays and they fit to actually 6 components 5 components is wrong 6 components why 6 components? Because you expect that there are 5 components that you see from transient absorption and a 6 one from your fluorescence well photo luminescence the fit to 6 components this is a mistake 6 component.

And also what they did is they fix the life time and this is where this can be contested one can say why are you fixing the life time vary it globally but they did not do. Instead of so they call it global analysis but what they have really done is that they have fixed the life time. Perhaps because transient data absorption as we know is not as nice as TCSPC data it may not be so easy to do proper global analysis using it especially in NIR but this is what they did.

They fixed the lifetimes 6 lifetimes and they did an analysis so what would change what are the variables here the amplitudes? The amplitudes are the variables so, they got the amplitudes for different wavelengths and they plotted this is the plot of amplitudes versus wavelength. We will focus only on the on C1 and C5 this is C1 right what is C1 associated with? 0.73 picosecond 730 femtosecond so as you see in the higher energy side from 900 to 1100 nanometer that amplitude is actually 0.

Then it rises to some value in the lower energy side remember lower energy side is dominated by holes okay we do not even go into that test lower energy side dominated by holes. So from there what they did is they assigned this 0.73 picosecond components 730 femtosecond component ultrafast hole relaxation okay. And that is only the beginning of this story so we have learnt in this module is that handling data in this kind of situations is the most difficult part of the game recording itself a challenge because you need good data without good data it is useless and that is why it helps they had such a smooth absorption spectrum.

But what you do with that data that is actually what takes maybe 75% of time when you do experiments like this not recoding the data not preparing the sample.

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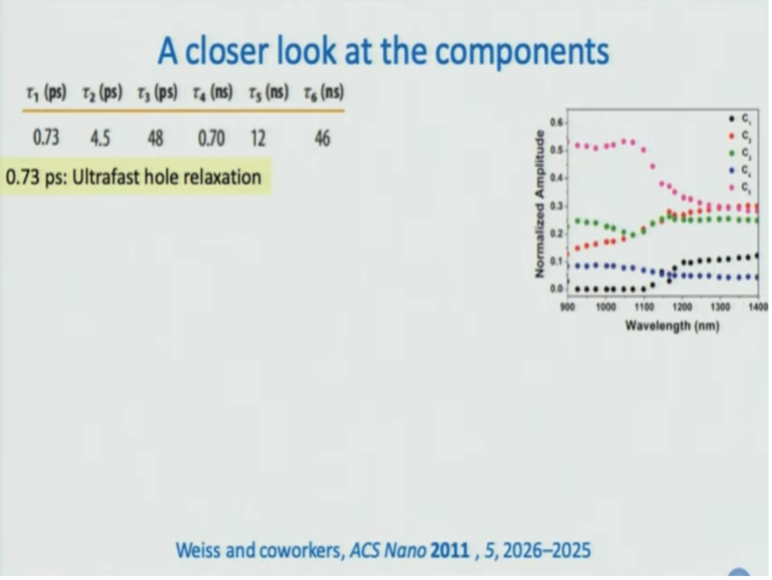

A closer look at the components

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

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

So what they have done so far what we have discussed is that they had fitted their NIR data to 6 components coming from the visible probe transient absorption and PL and from here they have been able to get that earlier elusive 730 femtosecond component is assigned to ultrafast hole relaxation. The next step is a closer look at the component themselves and that is what we are going to take up in the next module.