Ultrafast Processes in Chemistry
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Module No # 13
Lecture No # 58
Semiconductor Nanocrystals – Part 1

Right in the next few modules we want to talk about semiconductor nanocrystals and their ultrafast processes.

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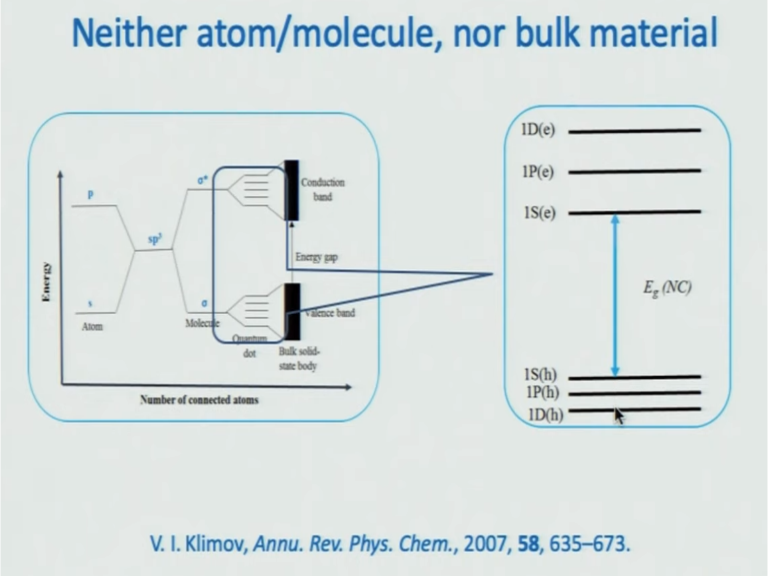

Neither atom/molecule, nor bulk material

V. I. Klimov, *Annu. Rev. Phys. Chem.*, 2007, **58**, 635–673.

So as you know nanomaterials are strange things. They are neither like atoms and molecules nor really like bulk material. As we have studied maybe even in class 11 and 12 in atoms we talk about orbitals discrete energy levels. And then in the first approximation we used them as linear combination either in hybridized or un-hybridized state to generate what are called molecular orbitals when we want to talk about molecules.

Once again in molecules we have discrete energy levels. Now the issue is that more the number of atomic orbitals that is used to generate the molecular orbitals smaller is the energy gap between the bonding and anti-bonding level produced or even if there are several bonding levels bonding molecular orbitals energy gap between them would decrease. Energy gap between the antibonding orbitals would decrease.

So if you keep on increasing the number of atoms like this what would happen is that the energy gaps between the bonding molecules orbitals would keep decreasing to practically 0. So you will end up getting no longer discrete states but continuous bands. And band theory what is used to discuss bulk solids may they be conductors or nonconductors semiconductors whatever. Whether it is conductor or semiconductor or nonconductor depends on what the band gap is.

Now if you think of the reverse process, if you think of taking a solid and breaking it down into smaller and smaller particles what will happen? There will come a time when this continuous bands are no longer going to be continuous. Rather they will break down in to discrete levels. So there is still not be molecules but you will have band structure that will look something like this. So you can also think that there is a sort of band gap but within the band you have discrete energy levels.

And this phenomenon is especially observed when you work with moderate band gaps that is for semiconductor nanocrystals. And these energy levels are designated for further discussion of a designation energy levels one can follow this paper by Klimov Annual Review of Physics Chemistry in 2007. So the energy levels are designated like this the lower ones the valence band the energy level 1S hole 1P hole 1D hole so on and so forth.

In the upper level they are designated 1S electron 1P electron, 1D electron so on and so forth. What does it mean? What it means is that when there is a transition what happens? An electron goes to a high energy level and it leaves behind a vacancy this is something that we know from our understanding of solid-state chemistry or solid-state physics. So the conduction band is always occupied by electrons and the vacancy will leave behind which are called holes are in the lower level. So what happens when a electron goes to higher energy level of course the energy increases. And that transition would require light of higher energy shorter wavelength.

Now what is the meaning of this whole energy level that means the separation charge separation has started in you can think from lower energy level. So the hole is in a lower energy level means that the energy is more. So you can think of molecule you can think that the transition has taken place from a lower energy orbital rather from rather than from the highest occupied orbital. And this SPD this are essentially like term symbol and this stands for the total angular momentum of the particle we are talking about.

We are not going to enter a very details discussion of that because I mean once again semiconductor nanocrystals can be half a course by itself. We really do not have so much time any more we are slowly approaching the end of this course. So let us just taking axiomatically that in the conduction band we have 1S 1P 1D in increasing order of energy of electron. And in the valence band you have 1S 1P 1D in a decreasing order of energy but then do not forget that lower the hole occupying a lower energy level actually means greater energy because that is where the energy has started from.

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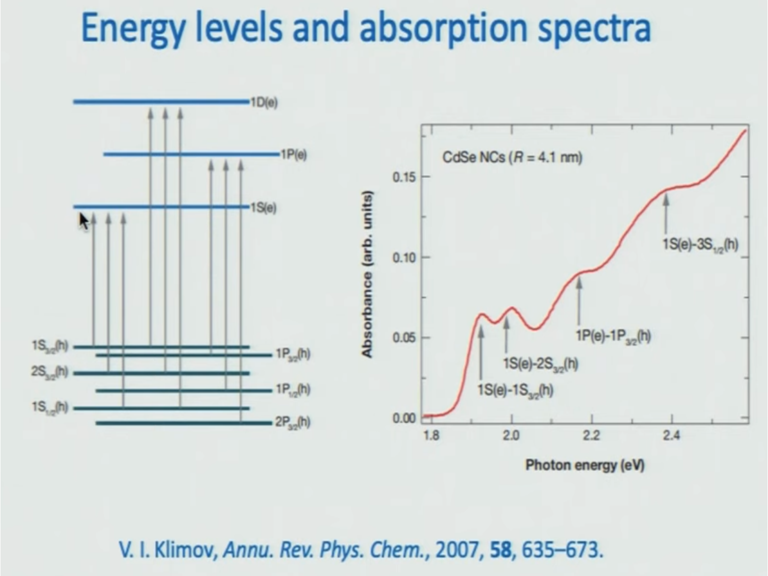

Energy levels and absorption spectra

V. I. Klimov, *Annu. Rev. Phys. Chem.*, 2007, **58**, 635–673.

So if you think of transition between these levels so you can have something like this. Say this one is 1S half once again we will not get into a discussion of what half is but if one knows this total angular momentum and Z component of angular momentum is not very difficult to figure out. So this transition what has happen is that the electron has gone from here to here and the hole is in this level. So this is 1S half hole and this is 1S electron alright.

So this transition would be the lowest energy transition in the energy level that we have drawn here is that quiet clear? If you have some other transition let us say 2P 3/2-hole 1P electron. If these 2 energy levels are involved see it is longer arrow energy gap is bigger. So if you look at the absorption spectrum the lowest energy absorption is and today we are going to discuss cadmium selenide and nothing else.

Many semiconductors are there many studies are there we will only focus on few representative studies on cadmium selenide. So the lowest energy transition is the 1S hole 1S electron these 2 energy levels are involved. And this is how one write it 1Se dash 1S 3/2 h you do not read the dash you just call it 1Se 1S 3/2 hole ok that is designation of the band. The second one is 1Se 2S 3/2 hole that means the electron is still in the lowest energy state in the conduction band but the hole is somewhere here.

So of course, energy gap is larger that is why it shows up at higher energy band as a higher energy band in the absorption spectrum. And so on and so forth you can see all you can designated all this band is a little difficult because as you go higher up in the energy there is also scattering profile and that regenerated transitions so it becomes sort of smooth. But the lowest energy bands are usually visible, and this lowest energy band is called the band edge absorption.

It is called band edge because it is what it is right one end of the lower energy band one end of the higher energy band. That is the meaning of band edge. The lowest energy transition is the band edge transition.

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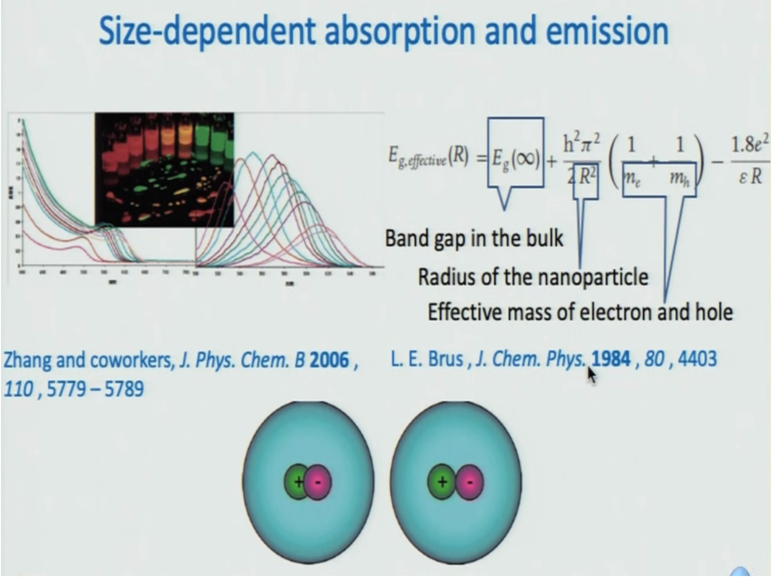

Size-dependent absorption and emission

$$E_{g,effective}(R) = \boxed{E_g(\infty)} + \frac{h^2\pi^2}{2\boxed{R^2}}\left(\boxed{\frac{1}{m_e}+\frac{1}{m_h}}\right) - \frac{1.8e^2}{\varepsilon R}$$

Band gap in the bulk

Radius of the nanoparticle

Effective mass of electron and hole

Zhang and coworkers, *J. Phys. Chem. B* **2006**, *110*, 5779 – 5789

L. E. Brus, *J. Chem. Phys.* **1984**, *80*, 4403

Again it is also well known that if one changes size of a nanoparticle then the color of absorption and emission also change. So this is very common figure whenever anybody does any work on semiconductor nanocrystals you will see this photographs of vials with change in color material is the same only the size of the particle is different. And you see the absorption spectra have also moved towards lower energy as have emission spectra as this size has become larger or smaller.

What happens? So the size increases does the absorption band edge absorption move to higher energy or lower energy? Lower energy why? Because the energy is given by a sort of a particle in a box kind of model particle in a box because you have 1 / R square here but it is a little more complicated than that particle in a box works if you want to just compare different energies. So Eg effective for a nanoparticle of the radius R is given by Eg infinity means the band gap of the bulk solid + h square Pie square / 2 R square multiplied by 1 / me + 1 / mh.

Of course when we have something like this what is this? This the reciprocal of the effective mass -1.8 e square / Epsilon R. So this is the addition R dependence that comes in over and above the simple and particles in a box model. Of course, one can ask what is the particle and what is the box? And there is some confusion often in people mind that sometimes you understand what the particle is but why does a box model work after all we have a spherical nanoparticle at least that what we are talking about right now we are not talking about rods or anything.

Well the particle is the exciton an electron hole pair that moves together tightly bound electron hole pair. And what is a box the size of the box is given by the diameter of the nanoparticle because the way it works the 1 dimensional box model is that see outside the electron and hole considering them to be a particle. The particle always has to be in the nanoparticle it cannot given outside. So the situation is exactly the same as the particle in a box model that we have study in a quantum mechanics.

So it basically means v = infinity outside the particle and it does not matter in which direction there is no Theta Pi dependence. So outside the particle V = infinity particle cannot exist. Inside the particle what you assume here is that the potential energy is 0. Why is potential energy is 0? Because right now we are talking about only one particle only one exciton in a nanoparticle so there is nothing that it has to interact with.

So the idea is that interaction with the lattice and all is completely neglected. So you are pretending as if once you form the exciton remember there is no question of interaction between electron and hole separately that is already accounted for because electron and hole together forms exciton that is why v can be take into 0 and that is why this model is more or less works. So let us just explain the terms this is band gap in bulk as I said already this R is the radius of the nanoparticle.

And this is the effective mass of electron and hole. And now there is another point of confusion that is often there what is the meaning of effective mass of hole? Hole is a gap, but effective mass of hole can actually be calculated and that has been done long before people started even talking about nanoparticles. So that is something that is very well established this is a standard formula by which the effective mass of hole can be calculated fine.

And what I have in this so all this discussion is not from any textbook whatever papers we have been used reference are given on every slide right. Now let us go on and talk about ultrafast time resolve PL study of cadmium selenide.

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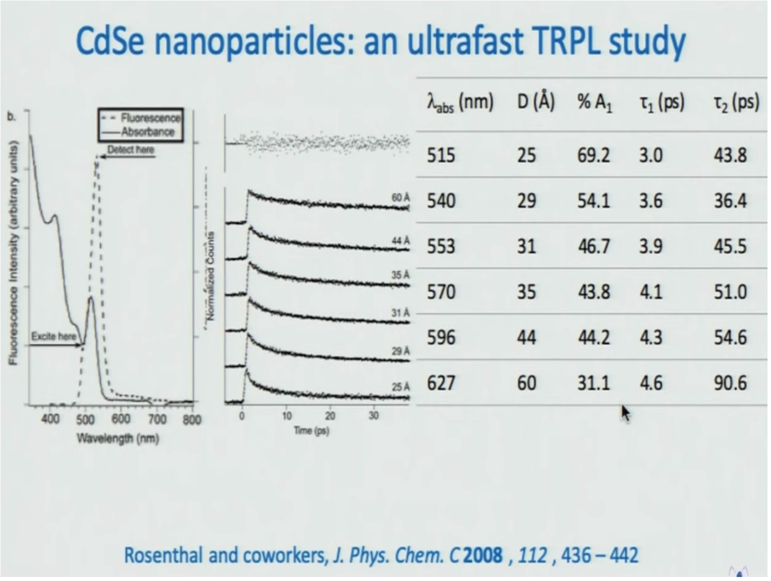

CdSe nanoparticles: an ultrafast TRPL study

λ_{abs} (nm)	D (Å)	% A_1	τ_1 (ps)	τ_2 (ps)
515	25	69.2	3.0	43.8
540	29	54.1	3.6	36.4
553	31	46.7	3.9	45.5
570	35	43.8	4.1	51.0
596	44	44.2	4.3	54.6
627	60	31.1	4.6	90.6

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

This is a paper by Rosenthal and coworkers so here you see well let us neglect that the fact the absorbance arbitrary units is written. This solid line denotes the absorption spectrum. The dash line denotes the fluorescence spectrum Rosenthal as actually called it fluorescence and not photoluminescence because model that they used involve as they going to see singlet and triplet state. That is not accepted universally. People are more comfortable calling this simply photoluminescence because spin states and all may not be easy to incorporate in a system like this.

But for now the important thing for us to notice is that all the emission that is there is a the emission spectrum is a mirror image of the band edge absorption which means that it is completely band edge emission. Now when see exciton formation essentially is generation of the what is called carrier right. The carrier is exciton which is tightly bond electron whole pair. Now when they recombine the excess energy has to be given out.

That energy can be given out in a radiative manner or in a non-radiative manner both actually happen. And we are going to discuss that in a little more detail. So there are several things that can happen before this electron hole recombination is complete. First of all they can just recombine that is one thing. Secondly what can happen is that at the surface of nanoparticles they always defect.

Usually there are defect not impossible to make completely defect free nanoparticles, but it is not easy and you have capping agents and all just to classified the surface. So very often what happens is that either the electron or the hole is trapped by the surface. Some dangling bond at the surface or even sometimes the protecting the capping group capping agent. When that happens of course now see either the electron or the hole is not even there in nanoparticle.

It is separated it is somewhere else it is none other energy manifold. So it cannot recombines so easily. So what will happen then is that you will get a long life time and you will get usually if it is a radiative trap state then you will get red shifted long life time emission. More often they are not trapping is just non radiative process you get non radiative traps and you do not see anything.

The other thing that happen is auger recombination, it means this energy is transferred to a third particle and once again that is going to show up in the dynamics of the recombination. The third thing that can happen pretty much like what happened in the gold is that you have exchange of the energy with this surrounding the excess energy that goes in lattice non radiatively and that would cause a severe decrease in life time as well as your quantum yield.

So what Rosenthal did was that she looked at nanoparticle of different size. So very simple kind of experiment to start with so these are nanoparticles of diameter 25 angstrom to 60 angstrom. So relatively large nanoparticle not really 2 nanometer, 3 nanometer, 5 nanometer not like that. And I do not know if you see it in this decay actually you do right. What happens in 25 angstrom you see a first component? And that first component is not there so much when you go to longer lifetime right.

So this is a summary of amplitudes I have not shown the second amplitude amplitudes and time constants associated with this nanoparticle of different size. What we see is that as of size increases from this diameter not radius 25 angstrom to 60 angstrom well even before going there all this decays are fit to bi exponential functions. There have been more complicated treatment of this kind of data as we will discuss in the next module.

But here Rosenthal group has fitted 2 a biexponential function. And then what they got is they got a very short life time 3 to 5 picosecond and relatively longer but still not enough lifetime that went from 43.8 to 90.6 picosecond. And the percent amplitude of the ultrashort component the picosecond component decreases from 69.2% to 31.1%. So naturally the amplitude of the relatively longer component increased accordingly ok.

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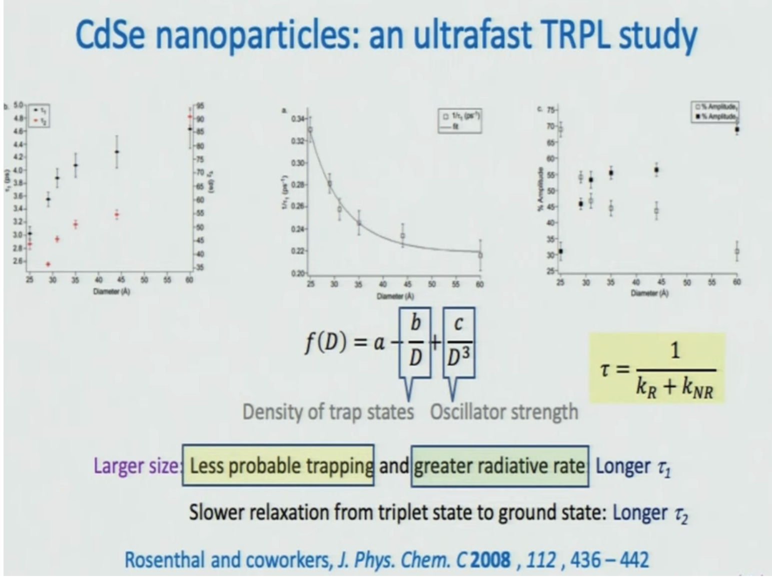

CdSe nanoparticles: an ultrafast TRPL study

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

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

Slower relaxation from triplet state to ground state: Longer τ_2

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

So all this is shown nicely in these 2 graphs the only thing in do not know is that can you see the difference in colors which one is which color? Ok bravo I cannot see it. So what we see is that both the lifetime actually increases as the size of the nanoparticle increases. Naturally this is the 2 axis are actually different this is a shorter life time this is a longer life time. And this is a what we have discussed already. Amplitude of the short component decreases as a diameter increases amplitude of the relatively longer component increases with increasing in diameter ok.

So these are the qualitative trends. the most important inference of this paper comes from the next figure that we are going to see. So what they did was they plotted reciprocal of life time against nanoparticle size. Why would one we interested reciprocal of lifetime? Yea is the rate constant right. And that is what I mean by the time we done this discussion we remind ourselves of something that is actually obvious but something that we tend to forget many times.

So this is the plot and this is the plot for Tau 1 ok the shorter component. 1 / Tau 1 plotted against diameter that of course would decrease because Tau itself increases and this is fit to a polynomial function of diameter. And the best fit is obtained for a function like this a-b / D + c / D cube nothing in D square. D to the power 4 is not required and this is more profound that what it might look like at first glance. First of all what is a? What happens if D = infinity? Second and third term vanish.

Even then this lifetime will be there that is what it means. Rate constant will not become 0 right. Rate constant will not become 0 lifetime will not become infinity. So this finite lifetime will be there that is all it means. And that would be the limit of bulk material. What is this significance of b / D? What is the significance of c / D cube? These are actually important terms because b / D is proportional to the density of trap states. What happens when traps when size increases. What happens to a very fundamental property by which nanoparticles get characterized.

Well many things happen it is not so easy for you to read my minds so I tell you but is quite obvious also. A size increases the surface to volume ratio decreases right. That is something that we all know. The one of the claims to fame of nanoparticle is that for their they were very high surface to volume ratio. Lot of the material is exposed and that is what makes them good catalyst stuff like that ok so that is one thing.

Surface to volume ratio decreases as D increases. So if surface to volume ratio increases then naturally density of trap states also decreases. So this is something that we may not realize if you think only of the surface. You might think that the surface increases the number of surface traps will also increases. Number of surface traps does increase but density decreases right. So this first one is density of trap states and what is c / D cube? c / D cube is something that is proportional to oscillator strength.

What is oscillator strength what does it give us information about? So how strong the transition is what kind of transition? Actually this as well as that but what kind of transition? Radiative transition right absorption can only be only involve photon I guess but deexcitation can be radiative or non-radiative. So once again let us not forget that the oscillator strength is directly proportional to the square of transition moment integral which again is proportional to Einstein's b coefficient.

Einstein's a coefficient is also proportional to a Einstein's b coefficient. Einstein's b coefficient is first stimulated emission a coefficient is first spontaneous emission. So basically, the second term has got to do with oscillator strength that is radiative transition. So what we see is that when the size becomes larger then first of all trapping is less probable because density of the trap state decreases and you have greater radiative rate ok. And this is what is important this fate a term for non-radiative process as well as a term for radiative process.

So let us not forget that Tau = 1 / kR + K NR. So 1 / Tau = k R + k NR. So the rate constant that we get by taking a simple reciprocal is really a some of the radiative rate constant and a non-radiative rate constant. Just because it is 1 Tau we should not think that it is either trapping process or radiative process or something like that. So the point we are trying to make here is that every rate constant that we get every component that we get has a radiative part and non-radiative part.

And this is going to be extremely useful in the discussion that we are going to perform in a next module or the next. And what they had done is they had assigned this ten of picosecond component to a relaxation from a triplet state to ground state as I said this is not accepted by everybody there are other explanation of slower recombination. This is one part of the story.

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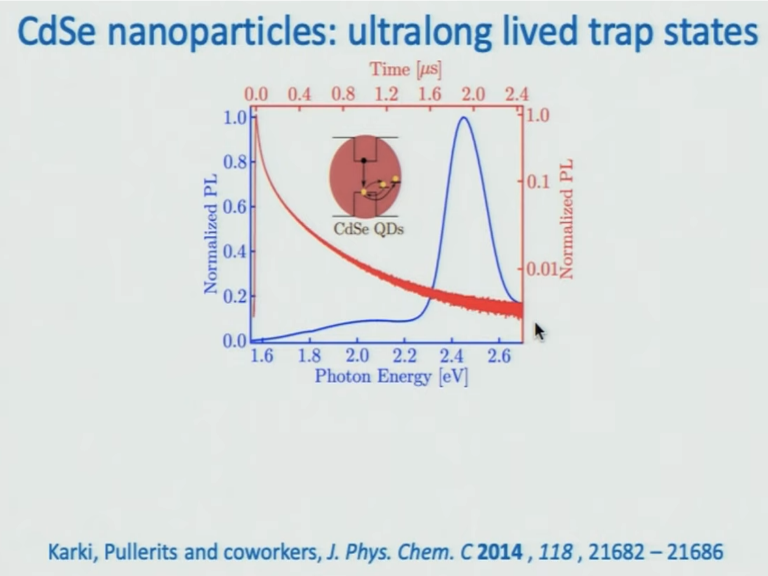

CdSe nanoparticles: ultralong lived trap states

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

The other part of the story is that as you said you can have trapping. And when you have trapping very often you have long x long lived trap state. And this is an example of how long live it can be? In fact the life time can be microsecond. So here in this spectrum as you will understand this is the band edge emission this is a trap emission. So when you record the life time here it is going to be an ultrafast with may be a nanosecond component as you will see in the next module.

If you record the photoluminescence decay here will actually get a long component here you see the PL is not over even in almost 3 microsecond. It is almost 1 microsecond time constant if it is single exponential it never is. But one thing that we need to remember is that total intensity what is the contribution in a multi exponential decay? What is the contribution of each component to the steady state intensity Ai Tau i right? Ai is important.

Here the issue is number of trap state of course is much less. So that is why the total intensity from trap state is very small even though the lifetime is very large. Intensity is less because the amplitudes are very often in 1%, 2%, 5% to which 10% is used ok. This is that is another aspect that you should remember ok. So we will close this discussion and we will come back for the next module which will the little short one and another one which will be long one.