Ultra Processes in Chemistry
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Module No # 12
Lecture No # 62
Multiexcitons in Semiconductor Nanocrystals Part - I

Today we close our discussion on ultrafast dynamics in semiconductor nanoparticles. So far we have been talking about excitons and how they evolve. We have talked about exciton trapping we have talked about the ultra short and ultra long live time constants and we have seen an elegant example where a rather complicated decay has been handled and useful time constants and rate constants have been extracted from there. Today we move onto another phenomenon that is very peculiar and is observed in nanoparticles and that is of multiexcitons.

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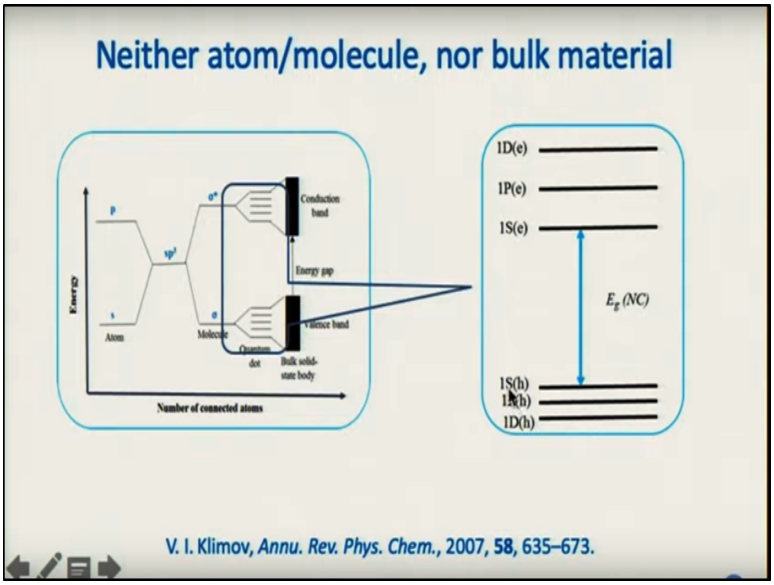

As we have discussed already and it is common knowledge now a days that nanoparticles have bands like in bulk but then within the bands they also have this discrete energy levels. And we have talked about how they are named this sort of NL kind of nomenclature this one well it is easier to go by L. S stands for the angular momentum of the excitons. If it is 0 then the level is designated S. If it is 1 then it is designated P if it is 2 then it is designated D and so and so forth.

The reason why the lower ones are designated h is that after excitation these lower energy levels are occupied by holes and higher ones are occupied by electrons. And the one that is there that is

N that denotes the number of levels of particular kind of angular momentum. For example this is 1S because this is the first level with angular momentum 0. 1P, first level with angular momentum 1 and so on and so forth.

And this review by the way by V.I. Klimov is very instructive what we will do today is we will really gloss over several papers. It is not possible to discuss the vast body of literature that exists in this field but it is important that we individually actually read those papers cover to cover then only we will understand the field.

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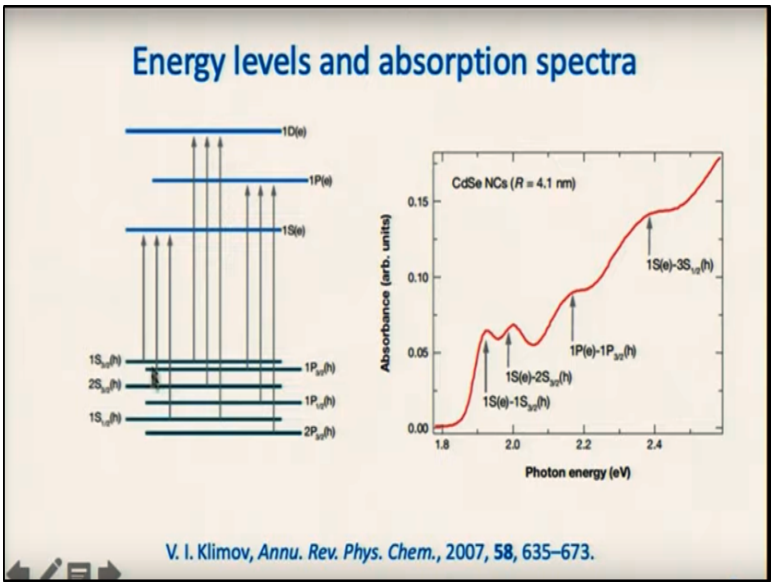

Right, so we have also said that the absorption spectrum in semiconductor nanocrystals shows several features due to different kinds of transition. The lowest energy one is called the band edge transition because it involves the energy levels at the edge of the conduction and the valence bands. However, you can have a promotion from a lower level so after promotion the hole can be left in a lower level and the electron can be in a higher level and so and so forth.

One thing that may be noted is this see we have drawn the, this arrow here from 1Sh to 1Se we have not drawn a line from here well we actually have drawn from here to here as well but the point I am trying to make is that selection rules do hold here as well. And if we do a good experiment if we have a uniform nano particles and if the absorption spectrum is recorded properly then one can see features like this which are very easy to miss because if any case there is a

scattering background that is there. But different in the excitations can take place at energies higher than the band gap as well.

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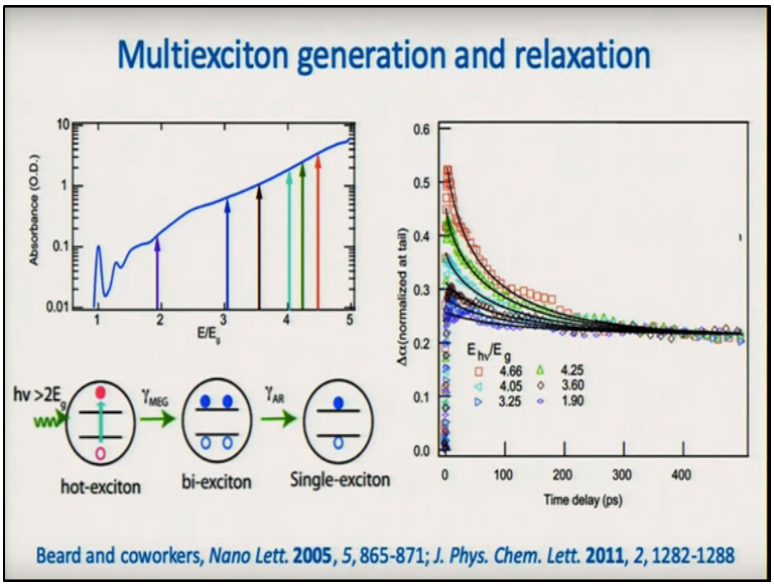

So what we have talked about today really is what happens when excitations is performed at energies greater than band gap. And in this discussion it is conventional to write the X axis as E/Eg. How much above by what factor above band gap are we exciting. That is what is typically used and results are also discussed in these terms that is what we are going to do. So you can say this is the band gap. So this is 2 Eg, 3Eg, 4Eg and so and so forth.

What happens is for that kind of an excitation the electron reaches higher energy level and the hole in the general case would also reside at a lower level. Hole residing at a lower level remember, means that electron has been promoted from a lower level and so energy is more. So to start with what we produced is called hot exciton. Hot exciton means an exciton that has more energy than the band gap. A cooled exciton has energy equal to band gap.

So in this phenomenal work by Beard and coworkers what they have done is that they have tried to explain what happens when hot excitons are formed. In other words they have studied hot excitons dynamics. And a very interesting thing that happens if one uses an excitons energy of more than 2 Eg is that when this electrons comes down to1Se and the hole floats to 1Sh the energy that is involved can be utilized to cause another electron hole separation.

To lead to what is called bi exciton. So bi exciton remember, is within a single nano particle. Within a single nano particle you have 2 electron whole pair instead of one. And when one wants to study this phenomenon one has to be very careful about something. If we use too much of pump fluence then also you can actually generate the bi exciton by the excitation itself. Because every nano crystals is subjected to a lot of photons.

1 photon will cause only 1 transition. But if a single nano particle is bombarded with billions of photons, then it is possible to have more than 1 electron hole pair formation in a single nano particle directly. Even if one uses pump energy of not more than 2 Eg that is the different ball game all together. In fact there is been lot of studies in that as well we are not getting into that for the positive of time.

So what they are also proposed is that after bi exciton formation there is an Auger Recombination which leads to formation of single exciton. So how would this show up and what is the time scale involved? It would show up in transient absorption data like this. And this transient absorption data are again we have encountered tail matching again and again in this course. This transient absorption data are also tail matched at long time.

Well tail is at long time for so that is I am saying tail matching at long time if we sort of the saying the same thing twice. But when the tail match what one sees is, if you look at the transient absorption decays this transient absorption not ground state bleach, ground state bleach is once again is a little different story. What one sees is as you go from 1.9 Eg to say 4.66 Eg excitation energy then we see the emergence of an ultra fast component that gets over by 200 or 300 picoseconds.

That is the time involved in cooling of hot excitons. Formation of bi exciton so and so forth. Or again this is rather complicated dynamics because it is not as if hot electrons are formed and then they cooled down to form single exciton. The intermediacy of bi exciton is always there.

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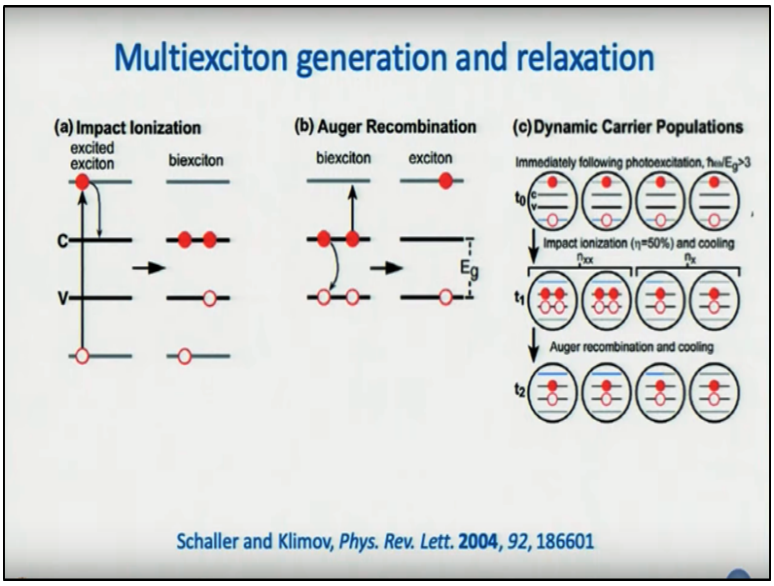

So to understand that one needs to analyze the data very carefully and in this seminal paper of Nozik comes handy. So what Nozik had discussed in this paper, this review, annual Review of Physical Chemistry published in 2001 is what happens after, what is called impact ionization. Impact ionization means what we have said earlier, formation of a hot exciton. And we said the first step is always bi exciton generation. Taking a clue from there, Klimov well Scheller and Klimov did a more elaborate study few years later and these are all very interesting papers.

And these are really papers that push the frontier. This is absolutely new. Novelty is one thing that is not in question in the paper that we have discussed today. So what they have said in that, ok, you have impact ionization and then you can have Auger recombination and then you can have formation of exciton like this. So their model the model that they used was immediately following photo exciton and what they did is? They did photo exciton at more than thrice band gap to ensure the formation of hot excitons.

So this is the model that you have hot excitons that are formed and of course the reality is not this homogeneous also. Because do not forget we are working with femtosecond pulse. There is always a width and there is always heterogeneity. So whatever we talked about here is really an idealized situation. And manifestation of that will also show up in result that we are going to see in a couple of slides.

So what they said is that 50% of this population undergoes impact ionization and formation of bi exciton. Remaining 50% undergo cooling means the energy is given to the latest. No further exciton formation is there. And then these bi excitons also undergo Auger recombination and then cooled down. This is the model they used to fit the data. We are not going into fitting of the data as such. Because if we do then to discuss this one paper then again we are going to do 3 modules like we did it last time.

And now we are almost at the end of the course. Everybody is sufficiently familiar with the phenomena. So we should be able to read this and understand ourselves. But it is the time to consuming and I strongly encourage everybody to read this. Alright now while doing experiments like this couple of things need to kept in mind first of all what we discussed already, we should use a low pump fluence. Low intensity of pump light so what happens in ground state bleach is that you see a rise time in ground state bleach.

So rise time in ground state bleach is something that we may not expect at first thought. And why would there be ground state bleach? You performance excitation population in the ground state get the depleted. So the bleach is supposed to be instantaneous and then it recovers that is associated with the decay. When can there be a rise time in ground state bleach. When post excitation further depletion of the ground state population takes place.

And that is what happening here is not it? While formation of a bi exciton from the bi exciton is formed this is generation of another electron hole pair and this electron hole pair means that comes at the cost of excited state population, unexcited. So we think of how many unexcited nanoparticles are there that number could go down. That is why one sees a rise in ground state bleach.

And if I am digress a little bit this is a phenomenon that is once again definitely not expected in molecules. We have talked a lot about molecules. In molecules one does not expect it. But even in molecules this can be seen. And it can be seen in something that has attracted a lot of contemporary interest. And I am digressing from the nanoparticles for a moment. I am talking about molecules now.

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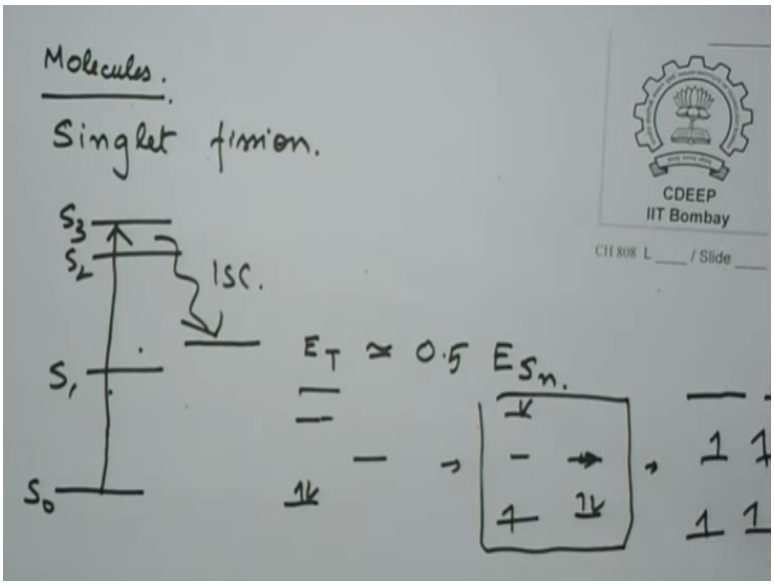

Recently there has been lot of interest in what is called Singlet Fission. Singlet fission means, ok, we have this S0 state we have S1 state we have S2, S3 whatever, to perform excitation to a higher singlet state and this is something that we have seen already when we talked about the Tahara's work. There we could actually see the emission from S2 state in ultra fast time scale. Singlet fission means in case the energy of a triplet state is approximately half of the energy of some excited singlet state.

Of course I am talking about relative energies here. In case this happens then this molecule can undergo what is called singlet fission. Means there can be further excitation to the triplet state, ok this will cool down. Right but while cooling down that energy can be utilized by another molecule to get excited to triplet state and in this molecule intersystem crossing would take place.

In another molecule the triplet state would get populated. Alright you start with the situation like this if I draw simply. This is your ground state configuration, this is excitation to some singlet state which has energy that is double that of your triplet state and then what you have is you take another molecule which is in ground state this combination becomes something like this. Even in this case one can see a rise in ground state bleach. I missed out on this while talking about molecules so I thought that since there is a very similar situation in materials.

It is a good idea to just at least mention it once. Right but now let us come back to the topic that we have discussing. What you have learnt so far is that one can generate a hot exciton by promotion

of the electron to a higher energy state and when the hole is in a lower level per se. That hot electron cooling can generate bi exciton and then the bi exciton can undergo Auger recombination to form regular excitons.

And this would show up in a fast decay in the transient absorption when pumped at high energies. When I say energy I basically mean when pump in pumped at more at shorter wave lengths. I am not talking about pump fluence, let us not confuse pump energy and pump fluence here. When excitation is performed at lower wave lines higher energies then this phenomenon can be seen. That is when you see a fast decay in the transient absorption.

That is when you see perhaps a rise time in the ground state bleach. At lower wave lengths this observation is not there. The question one can ask at this point is so what? This happens, great. So what is the need of getting excited about this? Well this multi exciton generation actually has a rather elegant application and their application is, I am going to excite using 1 light 1 photon and I am going to generate not 1 exciton but several excitons.

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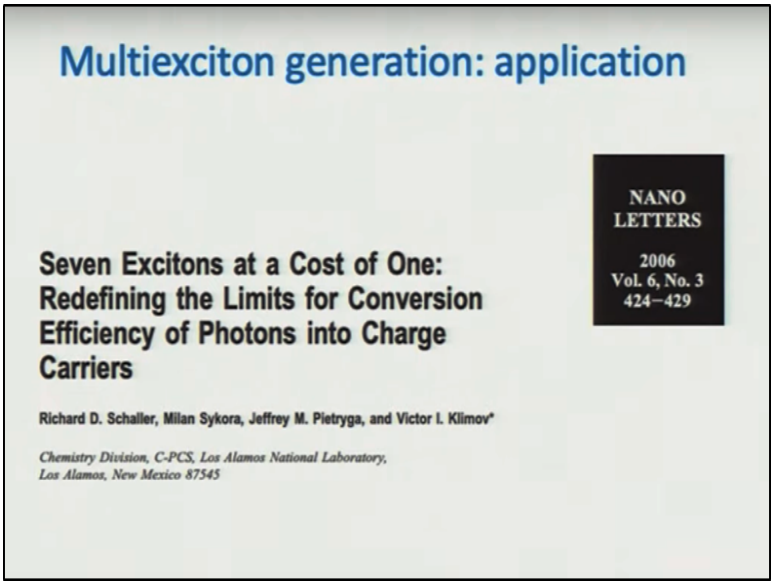

And in fact that is what was shown by Klimov and coworkers in this nano letter papers. That has really made an impact in field. The title itself is such that we have to read that papers if you read the title. 7 excitons at a cost of 1 redefining the limits for conversion efficiency of photon into charge carrier ok, what use is it why should I get excited if I can produce more exciton per photon?

Well I should get excited because one very major application of semi conductor nano particles is in solar cells light harvesting.

So the idea is that, your solar cell should be able to absorb the light from sun and it should be able to generate charge carriers. So more excitons means they we are going to get eventually more charge carriers. In the ideal case scenario from each electron we should get an electron and should get a hole. So if it is possible to harvest the blue part of solar energy spectrum and then if it is possible to generate more charge carriers per photon per blue photon. I am saying blue in a very qualitative manner here. All here mean is higher energy.

Or if it is possible to generate not 2 but 3 or 4 as they have shown here they have generated 7 excitons. So If I can generate 7 pairs of charge carriers then it is great. So that is why this is a rather important problem but how did this people know that they have generated 7 excitons at the cost of 1? That is what we are going to discuss in the next module.