Ultrafast Processes in Chemistry
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Module No # 10
Lecture No # 55
Plasmonic Nanoparticles 1

We have discussed ultrafast processes is in molecules at length not with really at length because it is really fast field we have talked about only some of the processes we have not talked about even things like FET that we promised to discuss and we have not talked about photoisomerization. Ultrafast dynamics in molecules is really a very rich field which has been pursued for long time and there are thousands of good papers that one needs to read.

But then in this course we cannot really go through the entire body of literate that is there in this field. We can only introduce you and then it is up to you to read and learn more. So and we have to finish in a given time frame as well. So what we will do now is that we will keep molecules aside and we will move on to things that are of great interest over the last 20 25 years. So we will talk about nanoparticles today we are going to talk about plasmonic nanoparticles to start with then we will talk about what happens when you break down nanoparticles further.

Is there something between molecules and nanoparticles that is called nanoclusters and today we are focusing on things like gold. When you talk about nanoparticles generally you would be interested either in gold, silver and all this things metal nanoparticles or you would be interested in semiconductor nanoparticles. We have done lot of work on silica as well but for now we will not get into that. So after this we are going to talk about semiconductor nanocrytals solar cells and perovskites.

So for now let us being our discussion on plasmonic nanoparticles what is meaning of plasmon? What is the plasmon can somebody tell me? That is phonon quantum of vibration is phonon see electron is like unit charge right quantum of charge phonon is quantum of vibration photon is quantum of light. Similarly plasmon is also quantum of something what is that something? The name suggest that it is plasma.

Plasmon we are studied from childhood that it is the fourth state of matter plasma essentially means ionized gas. Now here not going to work with gases we are going to work with what happens when you ionized the gases you said electron free. So plasmon is essentially a quantum of free electron that is present mostly on the surface of metals.

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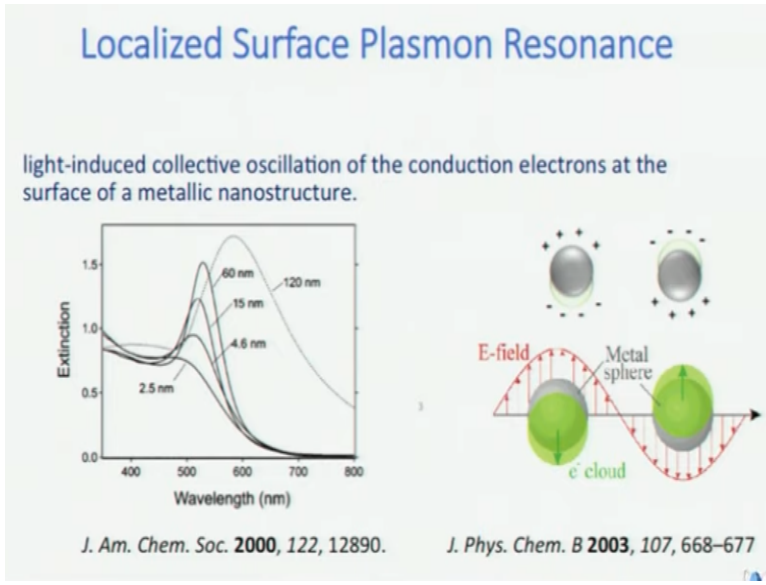

So this surface plasmons have been of lot of interest over the last 25 years or so phenomenon called localized surface plasmon resonance is quite well known. More or less well understood and it is it has been used extensively to do things like augmentation of signals enhancement of fluorescence’s. So you might well I do not think I have mentioned this earlier we have talked about radiative rates and non-radiative rates.

Now generally in whatever molecules we have discussed so far we have only talked about suppression of non-radiative processes so that the fluorescence quantum will goes up. But there is another way of doing it the other way of doing it to play around with the radiative rate of course you understand radiative rate consonant is directly related to Einstein’s B coefficient which is related to epsilon.

So you are basically saying how one can increase epsilon and one way of doing it is by using plasmonics. Joseph Lakowicz has done a lot of work on this started with silver islands and then he worked with silver nanoparticles as well see using it what you will do is enhance kr what happens when you enhance kr? Radiative rate constant fluorescence quantum will goes up right but lifetime goes down. Because do not forget life time is 1 / kr + knr so kr appears in the denominator of lifetime.

So lifetime going down with fluorescence quantum will going up provided no mistake has been made is sure shot signature of what Lakowicz likes to called radiative rate engineering and that is done by using plasmonics. In fact now a days SPR spectrometer is available commercially where one can enhance this signal from weekly emission samples and all. And it is used extensively in things like sensing so that is why surface plasmon resonance is interesting and useful.

So now what where does it comes from will paint a very qualitative picture actually this as a lot of theory that one needs to discuss if one needs to understand surface plasmon resonance quantitatively will not try to do that in limited scope of this course. We will just point you to this picture that is available I think even in Wikipedia. So what happens is in metals why are metals conducting the simplest theory that is used to describe conduction of metals is that of free electron theory right.

So where one says that since the work function is small all electrons are more or less free they can move easily so on and so forth. So what happens is these electrons forms sort of cloud the free electron and then you have a hard core that is the metal nanoparticle noble metal nanoparticle to we are going to talk about gold almost exclusively we will refer to silver and platinum and nickel once.

But in this discussion as well as in the nanocrystal discussion we will talk mostly about gold that does not mean gold is the only thing other metal nanoparticles also give very good surfaces plasmon resonance. So what happen is this is the gold nanoparticles let us say and say this is the cloud of electrons you can think. So this cloud of electrons can oscillate and what happens when they oscillate if the cloud of electrons goes up then in this ensemble the top portion is slightly negative partially negative and the bottom portion is slightly positive so you create a dipole.

When it goes down then the bottom portion is slightly negative the top portion is slightly positive okay. So what you have essentially is you have an oscillating dipole due to the movement you can think of plus this surface plasmon. That is almost always depicted in this manner you see the surface plasmon going down then this side is minus and here the metal of ions you can say or expose a little bit so this side is plus and here it is the opposite phase.

So now what you have is essentially then is that when this surface plasmon going up and down you create an oscillating dipole moment once again let me reiterate that if you are painting an very qualitative picture here. So what happens when you have an oscillating dipole? If you remember what you studied in basic molecular spectroscopy courses why is that polar molecules are microwave ative?

Because the dipole moment rotates this head components of dipole moment fluctuates it goes up comes down to 0 goes to the opposite direction and keeps on oscillating. Here also this oscillating electric field is set up and you can think that electric field can interact with light that is incident on it okay. And that is why there is an absorption remember in the classical picture absorption of light is always associated with resonance between the electric field of light and some kind of fluctuating electric field in the molecule or material whatever it is.

So when the frequencies match of the oscillations that is when the resonance is achieved and light absorption takes place alright. Now this frequency of oscillation depends on several things first of all composition you might thing what am I talking about am I saying yes say gold nanoparticle. So where is composition coming from we will come to that in few minutes geometrical shape. If it says sphere or if it is a rod or if it is a prism we have different kinds of oscillation.

In fact when it is a gold nano prism you can have many kinds of oscillation so you have a really broad surface plasmon resonance. And nature of the chemical environment what do you have around it do you have a coat of silica do you have polymer you have solvent even that is important and we see why it is important? Before that let me show you at least one spectrum of you can this 1 of the earlier works in 2000 19 years ago this is the kind of spectrum that you expect to see in well what we conventional call absorption spectra okay.

So what you can see is at 2.5 nanometer you can see a band forming here 4.6 15 60 nanometer now here the band has become prominent and it is quite sharp right. Then you make bigger nanoparticle when you go to 120 nanometer there is a further red shift and then it becomes really broad for different reasons will not go into that is not really what you want to discuss today what we do want to discuss is what happens after you excite this. So essentially when you excite the molecule this excess energy not molecules sorry a nanoparticle this excess energy in the nanoparticle and it has to equilibrate.

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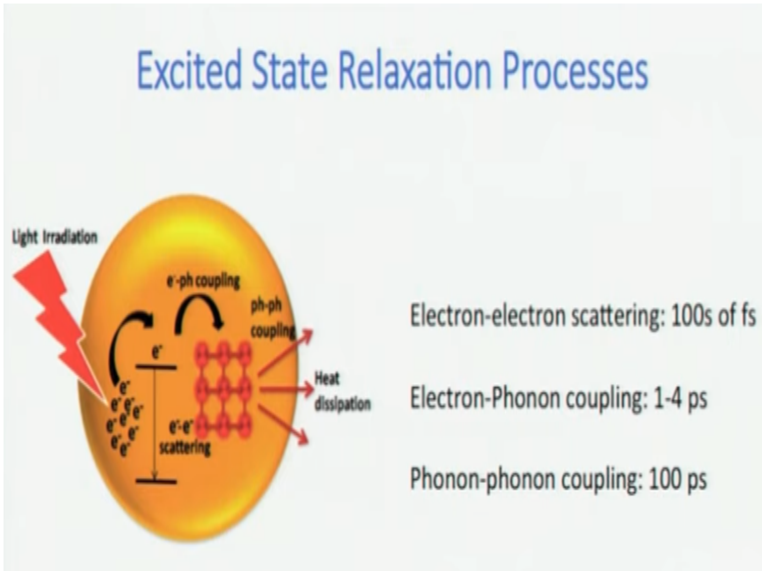

It equilibrates by several mechanism first things happens is fastest one is electrons-electron scattering right so you have this electron here a lot of electrons around you remember it is plasmon right lots of free electrons are there. So electrons-electron scattering gives rise to reinstatement of the ground state if you want to call it that okay the other things that can happen is that you can have electron phonon coupling phonon is basically this lattice vibration right.

When we talk about a solid now you cannot talk about normal modes of molecules anymore you must talk about the vibrations of the lattice as a whole as we have seen earlier in this course many new kinds of vibrations can arise when you have association. Like what happened in water remember what happens in liquid water we did not have just the symmetric stretch and bend in asymmetric stretch.

You also had liberational motion and that too were of different kinds so similarly here in lattice and which is even more associate the system you have different kinds of vibration and these vibrations can be activated further if the excess energy is transfer to them that is called electron phonon coupling. And then what happens is if you remember what happens in water you excite one mode of vibration and then the energy gets transferred to things like libration right the same thing happens in the crystal lattices as well.

One kind of phonon transfers energy to another so that is called phonon-phonon coupling that is how the heat gets dissipated heat means excess energy here gets dissipated okay. I should mention here that for the initial slides I am grateful to my student Bala he is the one who made it is the one who sort of taught us in our group about the surface plasmon resonance stuff alright. So now this electron-electron scattering is the fastest and we will show you some data later that takes place in hundreds of femtosecond that is really fast.

Then you have electron-phonon coupling that takes place typically in 1 to 4 picosecond and phonon-phonon coupling is the slowest step that takes place in 100 picosecond.

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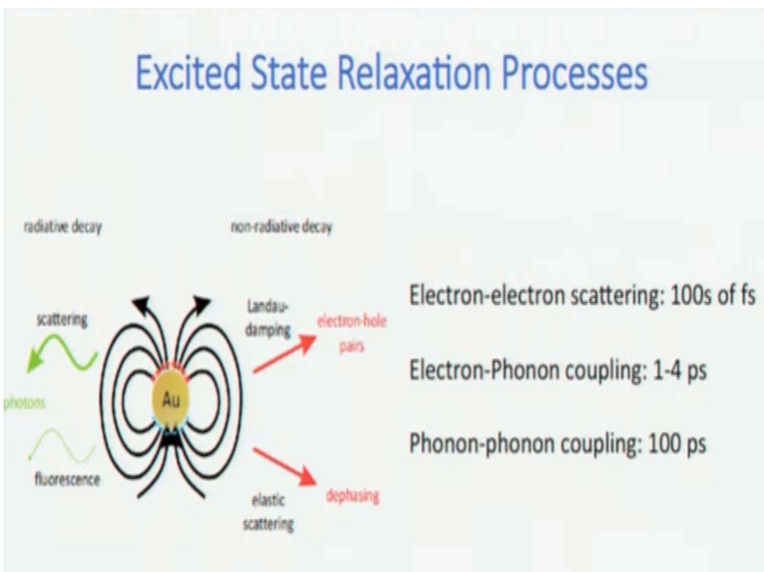

So let me show you another diagram other than this where the relaxation is divided into 2 kinds radiative and non-radiative. The non-radiative processes are essentially Landau damping involving electron hole pairs and elastic scattering which causes dephasing. And radiative decay consist of well scattering photons and there is somewhat you can call fluorescence as well. We are not going to discuss the photoluminescence of gold nanoparticles but I will give you a recent reference at the end this is an interesting thing as come up over the last 5 years or so.

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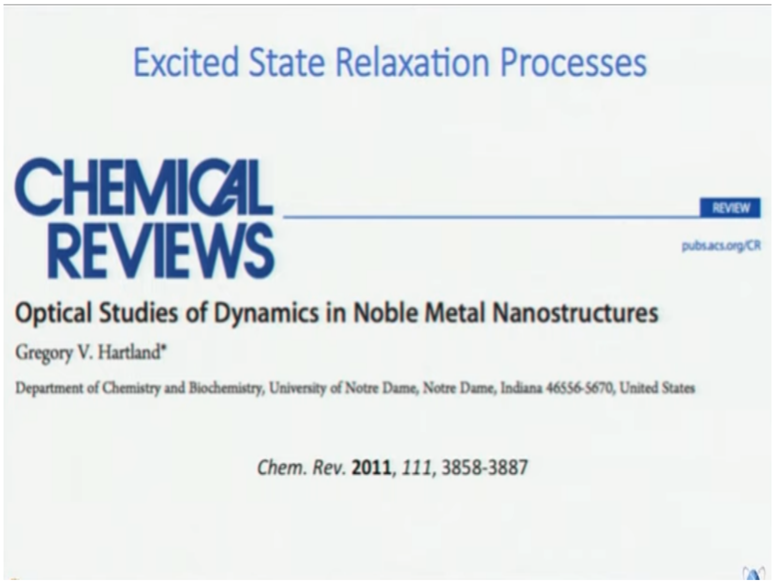

It makes sense to read it by ourselves what we will do is we will mostly present to you literature from this review that was published well 8 years ago this is by Hartland. So let so what this review does is that it discusses in good amount of detail the dynamics post excitation of Nobel metal nanostructure this is one review that i have recommend that everybody should read we are not going to discuss everything in the module today. There will be a lot of things that are left for ourselves to read alright.

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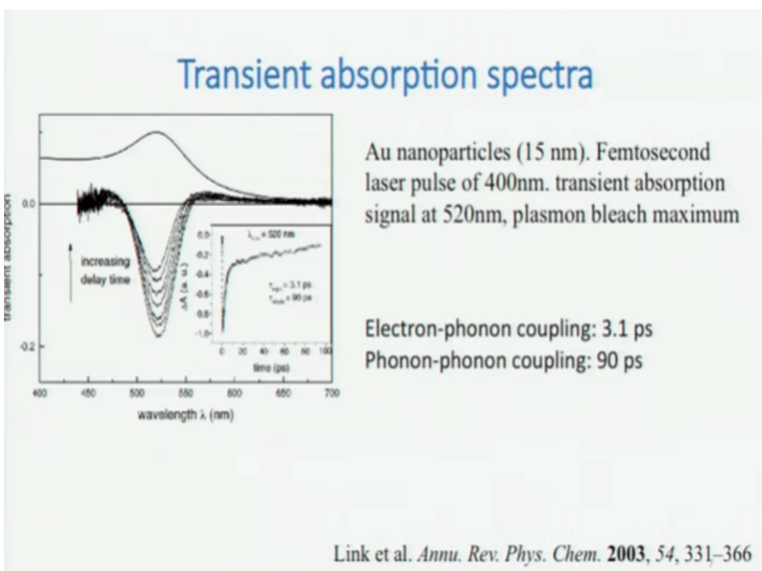

So let me start with by showing a piece of transient absorption data recorded by El Sayed's group Link at that time was a student post doc with El Sayed. So what you see is this one on the top for your reference is the extinction spectrum that I showed you little earlier this is your surface plasmon resonance band. And the main feature the dominating feature in the transient absorption spectrum is a ground state bleach that exactly corroborates with this band.

And what link can El Sayed and other people did was that they looked at the ground state bleach recovery dynamics and they got 2 time constants you can see the trace here 2 time constants 3.1 picosecond and 90 picosecond 3.1 picosecond was assigned to electron phonon component coupling and the longer 90 picosecond component was assigned to phonon-phonon coupling. So what did they not see what is it that they missed they miss something right?

The 3 processes so electron-electron scattering is missed because it is too fast for the resolution of the setup they used. We are going to show you some data there as well. Now this is very important difference between molecules and materials when you talk about material and we want to do pump probe spectroscopy with them some interesting feature arises well you have seen earlier in case of 7 Azaindole also that if you pump at higher energy lower frequencies what happened there?

There was an additional first component due to S2 to S1 relaxation right or due to relaxation of S2 just we can say. So something similar but more prominent happens in nanoparticles because you see the absorption is really a continuum except for that well it is not the continuum but there is a peak and then it just goes up so in principle you can excite in you can pump in many different wavelengths.

But if you pump at high energies not only for plasmonic nanoparticles but also for semi conduction nanoparticles interesting phenomena start showing up especially for semiconductor nanoparticles. So that is what we will discuss in one of the future modules so here what is important is when you want to talk about some time constant you should not forget what the pump power is one thing is you can excite at higher energy the other thing is if you excite by a greater pump power then lot of interaction can happen.

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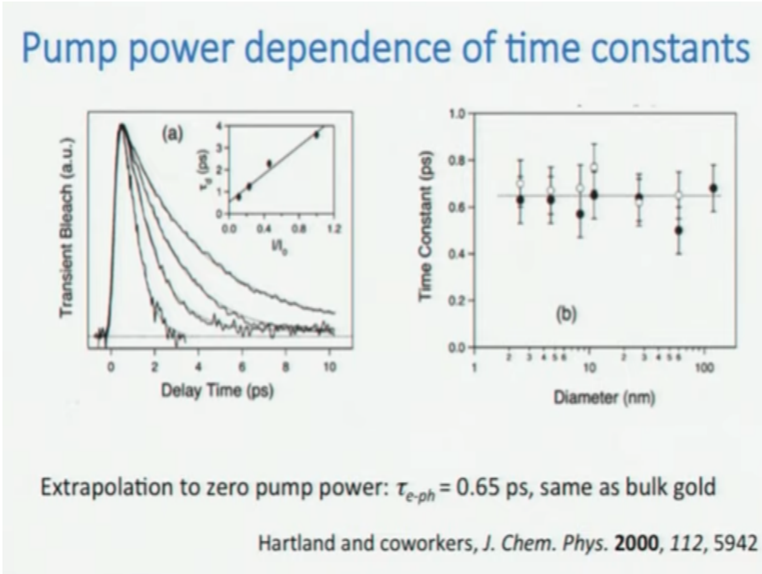

And this is an example of Hartland group as early as 2000 what they showed was that you look at this decays at different pump power the tau the electron phonon coupling time constant actually goes up right that is due to further interactions that are there now what they showed is that first of all if you look at this time constant how do you know what the time constant is? So what they did is in this graph in the insert the extrapolated it to 0 pump power so this is sort of like infinite dilution we must have read right actually you cannot achieve infinite dilution.

But you always extrapolate and find out what it is so by extrapolation they found that at 0 pump power or the electron phonon coupling time constant is equal to 0.65 picosecond which interestingly is exactly the same as what is there for bulk hole okay. With increase in pump power the time constant becomes longer the time constant becomes longer means what? Coupling is more efficient or less efficient? Less efficient why? Because radiative not radiative the rate constant is actually reciprocal of tau right so when you talk about coupling we have to talk about the rate constant.

And then the interesting thing that we showed here is that this time constant they got when they plotted against diameter and again this is a semi-lock plot where X axis is logarithmic so that they can show the data say from 3 nanometer all the way to 120 nanometer the time constant remain exactly the same irrespective of the size of the nanoparticle okay this is one thing. Now let us see an example where the electron-electron coupling is actually observed experimentally this time it is not gold it is silver.

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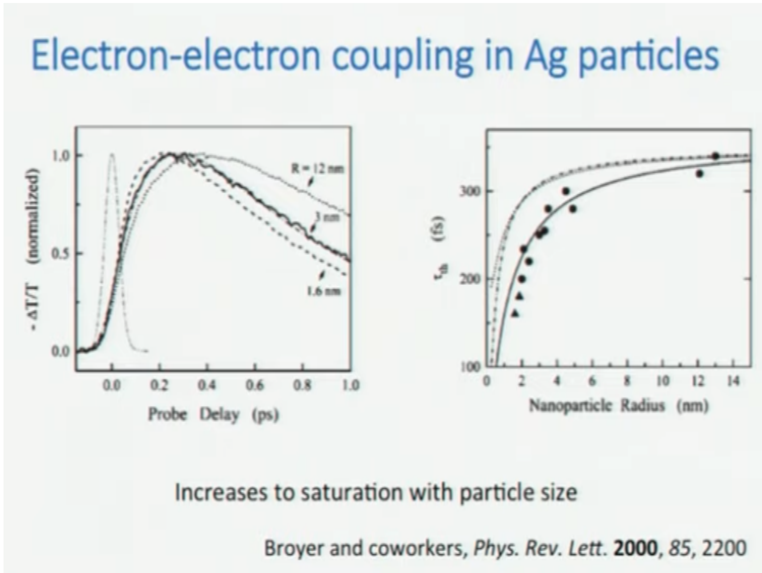

This is the work of Broyer and coworkers once again way back in 2000 here you see what they have done is they have done an experiment at a very good resolution full scale here is 1 and you can more or less understand how many points there are it looks like a straight line is not it a little uneven straight line. So wherever there is change in slope that is the point so there are may be 500 points or more within this 0 to 1 picosecond time window.

And also note the quality it is quality is excellent right? It is a linear scale Y axis is linear their you get this kind of data I mean we do not tell you that excess in picosecond and I will tell you this is TCSPC data you might believe this Xn and data that is why they could get this small time constant. Data quality has to be outstanding if one wants to talk about very precise measurements. So this electron-electron coupling time was found to be where is electron-electro coupling time here you are excited and then see there is a rise right.

Why is there are rise? Because equilibration has to take place among the electrons that are there first you have done quantum of excitation that has to get redistributed among all the electrons before anything else can happen. So that comes up actually as a rise and this rise time is found to increase from say 100 femtosecond to 300 femtosecond the second plot depending on what the nanoparticle radius is.

Right now do not worry what this line is or what is curve is just look at the points remember this is silver and it increases from actually their observation was it 2 nanometer so their about 150 femtosecond time constant was there and it went up to 300 femtosecond and from the data you can see that the trend is there it is not a fluctuation. Once again it is impossible to get believable data I mean it is impossible to differentiate between 300 femtosecond and 150 femtosecond if you do not have data of this kind.

I am sure this was very painstaking experiment especially 19 years ago okay so we have talked about spherical nanoparticles for gold and silver and we have shown you what the electron-electron scattering time is in the last slide and we have talked about electron-phonon coupling as well phonon-phonon coupling is just the longer longest timescales that you have here. So this is where we will end this module in the next module we will talk about what is gold nano rods and composite nanoparticles.