Ultrafast Processes in Chemistry
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Module No # 12
Lecture No # 56
Plasmonic Nanoparticles 2

Right we stopped here in the next module where we showed you the electron-electron coupling time constants for silver particles. Now let us go on and talk about gold nano rods.

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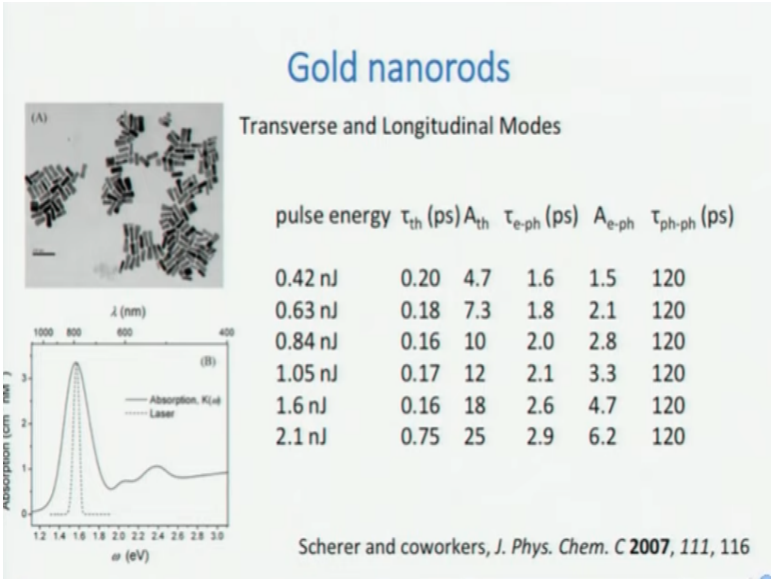

Gold nano rods have a more interesting spectrum as may be expected than gold nanoparticles why because here there are 2 access right. If you if I have a rod then you have a length and you have a diameter okay. So you have actually 2 modes a longitudinal mode and a transverse mode which one will be associated with a higher energy transverse mode. So here you see spectrum from Norbert Scherer and co-workers where you can this is the longitudinal mode it is at about 800 nanometer 1.6 electron volt.

And here you have the transverse mode around 2.4 2.3 electron volt something like 500 nanometer. So 500 nanometer roughly is what you get for the nanoparticles right spherical nanoparticles that more or less matches because of width is comparable the diameter of the nanoparticles that we discussed earlier. And here you see TEM image of this rather good looking gold nano rods. Now

what Scherer groups did was not just regular pump probe spectroscopy but they used heterodyne detection.

We will come back and talk a little bit about heterodyne detection when we talk about surface some frequency generation later. But let me just tell you now that when you do heterodyne detection you can get to know not only about the intensity but also about field. See intensity is basically mode square of field right. So once you take intensity you do not have idea about the sign but when you do heterodyning what heterodyning is will speak briefly little later in one of the later modules.

Then you can actually get an idea of the field along with its sign so it is a more complicated experiment then simple pump probe but the time constant that they got were this. First th means thermalization electron-electron interaction for that you see from 200 picosecond the time constant went up to 750 picosecond as pulse energy went up. And the amplitude went up as well amplitude as gone up here as well electron-phonon coupling time constant goes up from 1.6 picosecond to 2.9 picosecond and phonon-phonon coupling that is not effected that remains 120 picosecond throughout.

So that is what they had observed so this is one thing that when you go to gold nano rod you actually get to see different things and in fact if it is possible to look at the dynamics so question is are the dynamics different for longitudinal transverse mode? That is not answered in this paper they said that is same is it really same is it different? That perhaps is still an open question.

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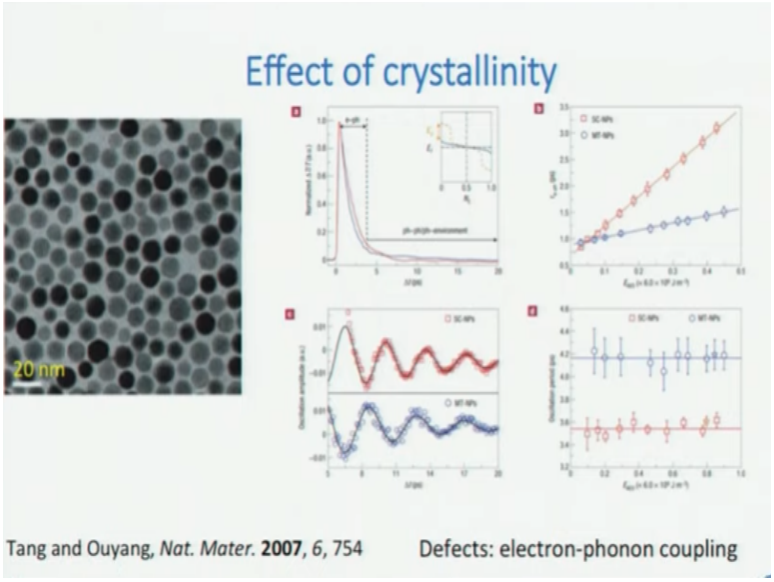

Another rather interesting work that has been done more recently is how are the dynamics effected by how good a crystals you prepare so this is PNS 2007. Here you see the TEM image of the so they basically a made 2 different kinds of crystals and the focus of the paper is really is on preparation which we were not discussing. So prepare the nanoparticles 2 different ways in 1 they got highly single crystals in 1.

And in the other one they get what they called empty crystals where well empty basically let us just say that they are not they are different kinds of crystalline forms in them. So what they see is this first thing is they look at electron-phonon coupling time and hence they work out the well they have actually plotted the electron phonon coupling time constants this one this plot is for single crystal nanoparticles.

This one is for non-crystalline less crystalline nanoparticles okay what do you see for every an X axis is little different from what we are using to use to see it is actually pump power but they have a way of calculating how much of the pump power is actually absorbed by the nanoparticles. That is a to be honest more relevant parameter because not all the pump power is absorbed right so who has said that as you increase pump power the amount of light that is absorbed increases linearly specially for nanoparticles it may not be the case in fact it is not the case.

So they worked out what is the actual pump power that is absorbed that is there in the X axis I do not know if you can read it the figure quality is not all that great. So for every pump power what

do you observe the time constant is larger for the crystalline form than for the non-crystalline form what does it mean coupling is less electron phonon so what they saying is that if you can make a better crystal then electron phonon coupling is less efficient and hence they gone to say that it is defects crystal defects that actually promote electron phonon coupling.

And they have not just done simple transient absorption what you see here is sort of residual remember residual we talked about in TCSPC actual data minus a fitting curve. And if you want waited residual then you have to divide it by square root of Y provided you are doing for photon counting I do not thing they have done that here so you see this damped oscillation.

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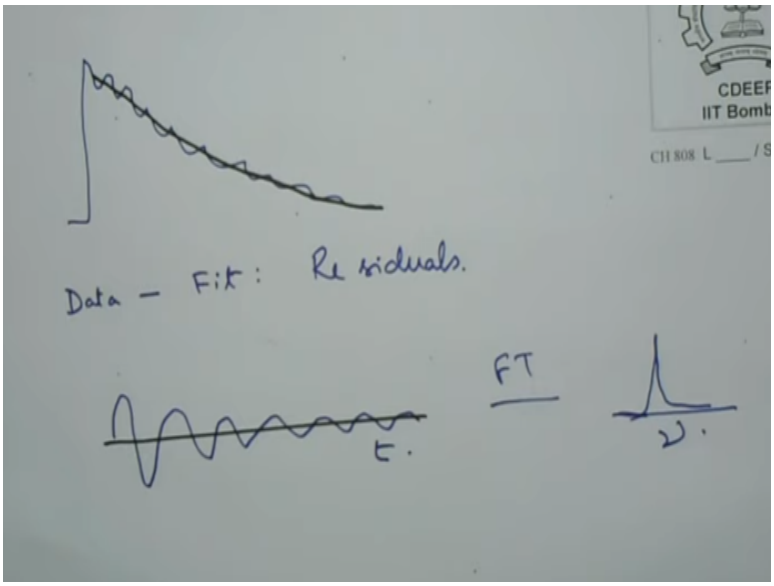

So I hope you understand what this is? Let us say this is your data I have over emphasized the oscillations and let us say this is your fit if you substrate your fit from data then you essentially get the residuals and they would look like this damped oscillation. Now what we have said so far is that this distribution around 2 sides is due to noise but here noise is eliminated completely I think by using a lock in amplifier.

This is a very high quality transient absorption data when you can do that you can see in fact this is not the first time seeing data like this remember Ahmed Zewail's experiment right 1 picosecond periodicity it was more or less obtain by the same way. So you have this from here remember X axis is time so what you have is you have damped oscillation and it is very easy from here to find out the period of oscillation right.

Simple Fourier transform will give you frequency domain data from their you can work out the period of oscillation there are other ways of doing it but this is the simplest way give a fit to whatever number of exponential is required look at the residuals and Fourier transform to residuals to get the frequency domain data from their work out the periodicity. So that is essentially what they have done here you can see this is for black one is for single crystals this one is for non-crystalline nanoparticles and they have been able to work out to the frequencies.

What do you see here? First of all the frequency is remain the same irrespective of pump power absorbed. Secondly which one is higher which one is lower at the SC is higher or lower. So this oscillation period is lower for the SC's then for the non-crystalline forms this also tells you that coupling is weaker so this oscillation is also because of electron phonon coupling right. So coupling between electron and phonon is weaker when you have crystals of better quality.

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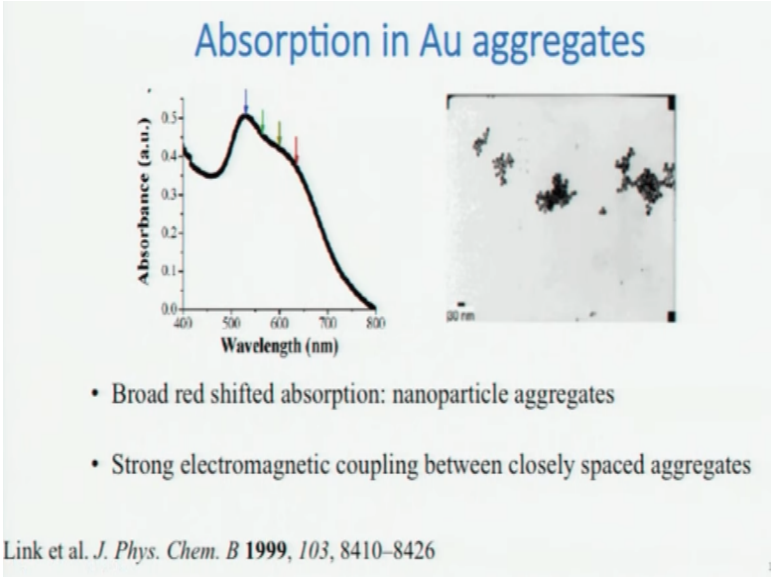

Now let us talk a little bit about absorption in gold aggregates what happens when you do not have gold nano rods at least in this study you can see it is long ago 1999 they did not really bother about crystallinity but what they did is they once again this is Link and El Sayed's paper they prepared aggregates of gold. And what they saw is that immediately in the absorption spectrum is little discertaining to see absorbance Au in this paper of all papers but in absorption spectrum you see that you do not have a single surface plasmon band it is quite broad.

And the idea is that the surface plasmon band comes from different kinds of gold aggregates that is why you do not get nice Gaussian band or anything.

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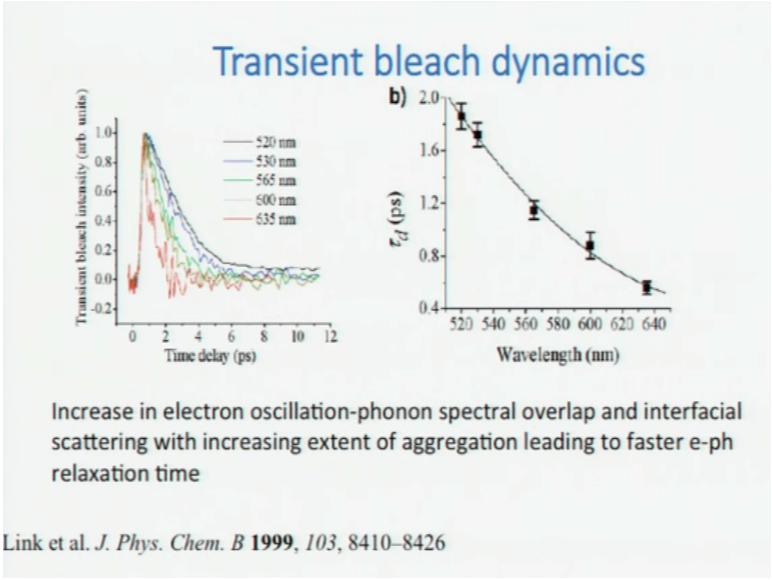

And what they had done is that they had found out the time constant for electron coupling across the spectrum that this decays are all very different the other thing that you can see is that the decays are not good looking. So data quality here is nothing compared to the data quality that we discussed in the last couple of cases but anyway what you see is that is electron phonon coupling as wavelength increases electron phonon coupling becomes smaller.

Now this is a little soppy way of doing things because we know very well that whatever signal we get at whatever wavelength is not from 1 species it is impossible to select 1 species by changing the wave length okay. So is always a mixture but it has been fit to this simple model keeping in mind what had shown you in last module there are 3 kinds of decays but the idea here is that the electron phonon coupling time constant itself is different for different aggregates so it is the mixtures.

So one really needs a little better data analysis for this kind of a thing. So at the moment we are trying to do something similar in related system right. That means it let us move over to multi component nanoparticles remember in the last module we have said that one of the things that thing time constant depend upon is composition so until now composition was a mood question because everything was pure.

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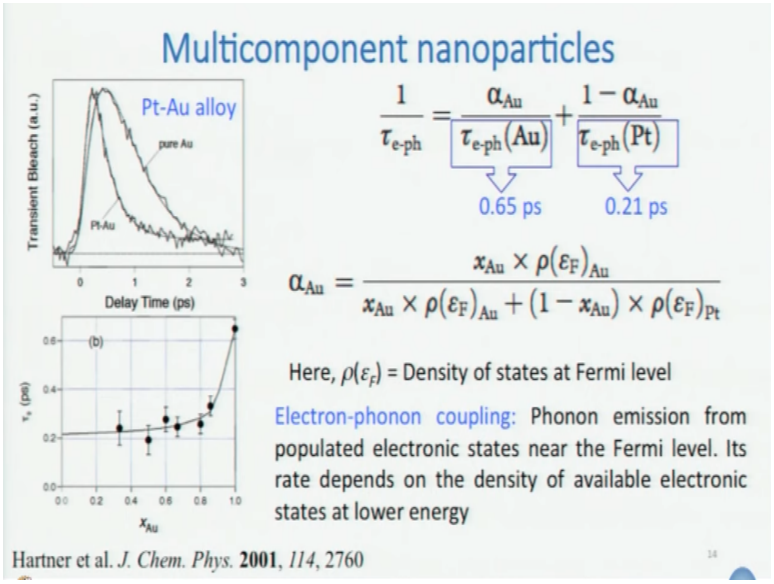

So multi component nanoparticles here we start talking about some platinum gold alloy nanoparticles. You see when you have multicomponent nanoparticles you can think of 2 extreme situations one is alloy that means the composition is homogenous throughout the nanoparticles 5% platinum 95% gold everywhere if you could take samples from different part of the nanoparticles you get the same thing the other is core shell where may be you have a gold core and a platinum shell both are useful in their own ways we are not really talking about the applications here we are just going to see what the time constants are and why?

But both have different kinds of applications okay so what we see here is that the moment you have some platinum the time constant become small right. This first one is the decay this is basically once again looking at the bleached recovery Y axis transient bleach and here it is arbitrary unit because they have been normalized. So this is what you have for pure gold nanoparticle and this is what you have when you have a little bit of platinum in it.

Well if you separately look at and we are going to show you a values of electron phonon coupling times of gold and platinum they not same. So you might think that you keep on increase when you have 5% platinum I will say little bit of difference from gold then when I have 50% platinum I will see more difference right. But actually that is not the case upon plotting the time constants for electron phonon coupling against composition means mole fraction of gold.

What you see is from pure gold to say 10% or 12% platinum there is a huge decrease and then it tappers off okay. The points are experimental data the line is not an arbitrary line I will tell you what it is? But the crux of the matter is this that it is not linear with composition just composition why not? Because so this people Hartner and coworkers worked out this kind of expression 1/ tau eph and why 1 / tau?

Because essentially the rate constant is the more fundamental quantity that is what they are comparing when 1/ tau of electron-phonon coupling for the multi component nanoparticle is equal to alpha gold divided by tau electron phonon gold + 1 – alpha gold divided by tau electron phonon gold what does it mean? If the idea scenario this alpha should have been X mole fraction right but actually it is not this is what it is.

Alpha gold is equal to mole fraction of gold multiplied by rho of epsilon F of gold divided by mole fraction of gold multiplied by rho of epsilon F of gold + 1 – mole fraction of gold into rho of epsilon F of platinum what is this rho? Rho of epsilon F is essentially density of states at Fermi level what is Fermi level? Yes that is right at 0 Kelvin the highest occupied level that is at Fermi level right.

Now so when you have discretization coming in then all this levels are they are actually any closely spaced energy levels that are present their right. So what is the density of those states near Fermi level that is what determines it. Now the values of electrons phonon coupling constant of gold of course is known from previous experiment it is 0.65 picosecond I talked about it earlier and that is for platinum is 0.21 picosecond.

And the issue is this electron phonon coupling is really due to phonon emission for populated electronic states near the Fermi level. That is why it is not enough just to look at mole fraction this density of states of platinum density of states of gold they also have to be considered alright. It is not just how much of gold is there the density of the states are not the same they are different material okay.

So the density of the states is what determines the efficiency of the electron phonon coupling so you have to consider this as well. So this curve that you see here really is the calculated curve from here okay see you know everything is not it you know what the mole fraction is this density of

states is obtained by DFT calculation and electron phonon coupling time are known. So this is the simulation of how tau would change as the function of X keeping into account this equation and you find that the experimental points fall more or less on this simulated curve.

So this is most important take home lesson from this study that for multi component systems you have to consider density of states as well it is not very straight forward. So I hope the message that has come out all this discussion in all this module and previous one is that data analysis in this apparently simple system is actually not simple one is take into account many things then only we can get meaningful data okay.

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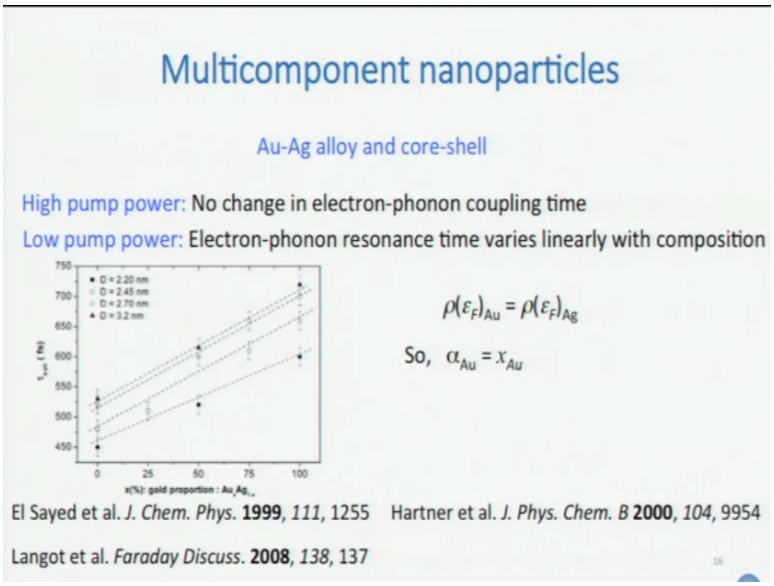

Now let us talk about something else gold silver alloy very widely studied system so they have here there will be many studies right at the beginning when this field open. So here there are 2 examples there are many more one by El Sayed's group one by Hartner's group where they studied gold silver alloy nanoparticles as well as core shell nanoparticles. And what they reported is there is no change in electron phonon coupling time but the problem is that they worked at very high pump power.

So for the next 7, 8 years this was the start of the art that you take this gold silver alloy and core shell nanoparticles there is no change in electron phonon coupling time with anything with composition nothing but then more recently in 2008 there this is faraday discussion paper by

Langot et al where they have shown that this time constants are really linear they have a linear dependence on the pump power absorb.

Problem is after certain range it becomes flat so it does not matter but here you have different sized nanoparticles and for them there is a linear dependence X axis is mole fraction of gold. Remember what happens for gold platinum this process was not linear is not it remember it fell here it is linear why is it linear? What is the difference between gold silver and gold platinum? The difference is that these rows are the same gold and silver they are more alike each other. So alpha of gold is really equal to X of gold go back to that equation that we showed little while ago and plug this value in you will see this.

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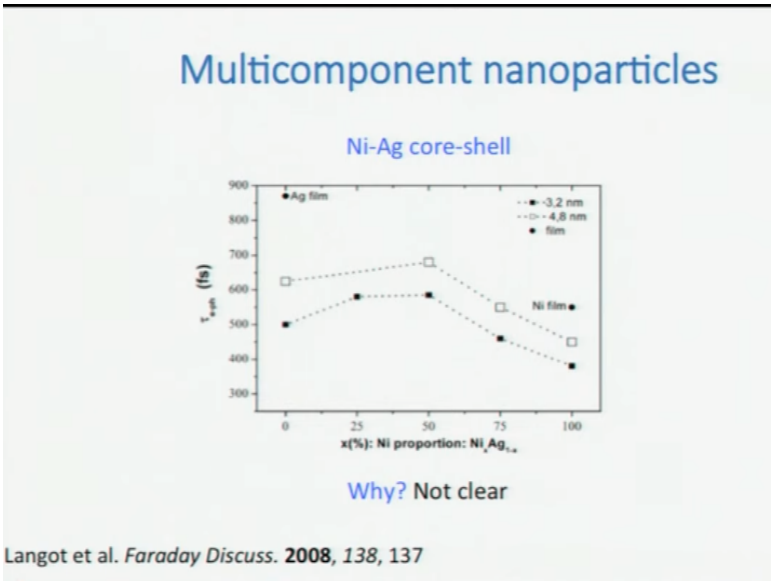

Interestingly it was reported that was Nickel silver core shell nanoparticles you do not get what you get earlier for gold platinum you do not get a linear variation either what you do get is what looks like it goes to a maximum why that happens? At least in 2008 it was not found there have been more studies after that I do not think this question is elucidated completely okay.

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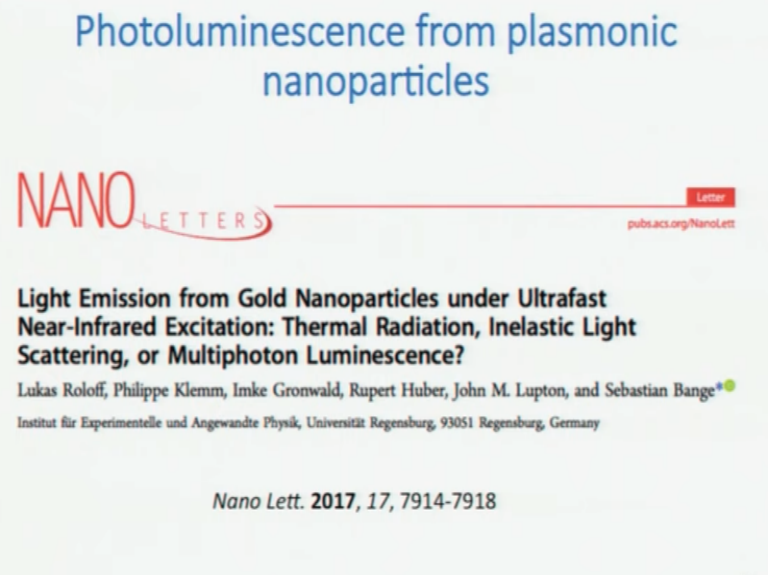

Well that brings us to almost end of our discussion of this Nobel metal nanoparticles the closing note as had said at the very beginning is this that there have been many studies on pump probe of Nobel metal nanoparticles. Roughly it over the last 5 years or so there have been consistent reports of light emission for gold nanoparticles especially when you use ultrafast lasers to pump them.

And this first came up because see gold nanoparticles are used commonly in SCRS enhance the signal so there it was reported that this some extra light that comes this messes up the signal where it that come from? That is when people understood that is not only non-radiative relaxation radiative relaxation is also there and this is now being reported by many workers it is not difficult to miss if you are not careful but for example in this nanoletter paper only 2 years ago they observed this light emission for gold nanoparticle they used an ultrafast NIR excitation and then the question that they discussed was what is this? Is it thermal radiation? Is it inelastic light scattering or is it multi photon luminescence?

Very similar questions were asked by Raman and Krishnan when they observed Raman effect for the first time. In fact to start with they thought that it is feeble luminescence only after they did polarization studies did they understand that it was something very new and that is why Raman effect came into being that was several decades ago what we are discussing now is the slide that is coming out what is it? And so far even in this paper the consensus is that it is actual emission it is not inelastic life scattering it is not thermal radiation it is actually multi-photon luminescence will not discuss this further.

But i would encourage everybody to read papers that have been published in the last 5 years on this luminescence of gold nanoparticles not only gold well Nobel metal nanoparticles okay that brings us to the end of this discussion in the next module we will talk about what happens we keep on making the size smaller and smaller.