Ultrafast Processes in Chemistry
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Module No # 13
Lecture No # 57
Nanoclusters

Ok so we have talked about molecules we have started discussion of nanoparticle we have talked about plasmonic nanoparticles. Now the question that we want to address is there something in between? Something between the molecules and nanoparticles or may be atoms and nanoparticles rather. And what of course when I asked like this the answer is yes. Yes there is something in between and what is in between is right now projected nanoclusters.

Nanoclusters are of course as the name suggest they are conglomeration of not molecules but atoms. And we will talk about what their dimensions are and all about. They are actually you can think that if you can you go on making smaller and smaller nanoparticles they will come a time when there will be a transition between nanoparticle to this cluster of few atoms which you can estimate the number of atoms. Again we are not going to go into preparation we are not going to go into how people know that there are so many atoms and so and so forth.

That I will leave for us to read by ourselves. We will only going to talk about the ultrafast dynamics. But this nano clusters have been have drawn a lot of interest over the last few years because they are the newest kinds of Fluorophores to be honest. And what people have found is that this cluster of atoms that are not covalently bonded in things same kind of atom and that too nobel metal gold, silver, copper coinage metal. So these this clusters conglomerates of atoms sort of behave like molecules as for as spectroscopy is concerned.

And you can use them to make sensors you can use them in fret and you can do a lot of that. So may have been very intense activity especially from labs of fluorescence spectroscopy in the area of nano clusters. And of course, like anything new this also comes with its share of disbelieve and non-acceptance that have been lot of people do not believe in nano clusters. But people will believe far out number people who do not. What we will do is out of this vast body of literature we want to present 2 paper. First is this review which is exhaustive but little old 2013 6 years ago.

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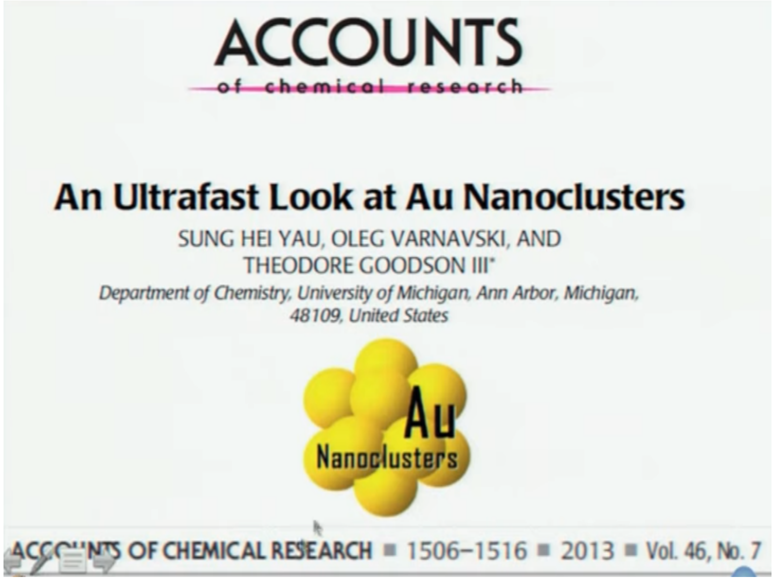

ACCOUNTS
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An Ultrafast Look at Au Nanoclusters

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So at least until 2013 this state of the art of ultrafast dynamics in gold nanoclusters is summarize nicely in this review. Once again we are not even going to talk about silver or copper or anything that is self-study. But if you understand gold nano clusters, I think it will not be difficult to follow the rest. So this is the paper by professor Theodore Goodson 3 the very eminent ultrafast dynamics researcher.

So of course, it is a review accounts of chemical research it does have a papers from his group mostly but other researcher as well. And for whatever reason in this paper in this module I am not written the reference as such at least in the first part. I have written them as reference 9 reference 10 reference 12. Those reference 9, 10, 12 are with respect to this paper accounts of chemical research volume 7 year 2013 page 1506.

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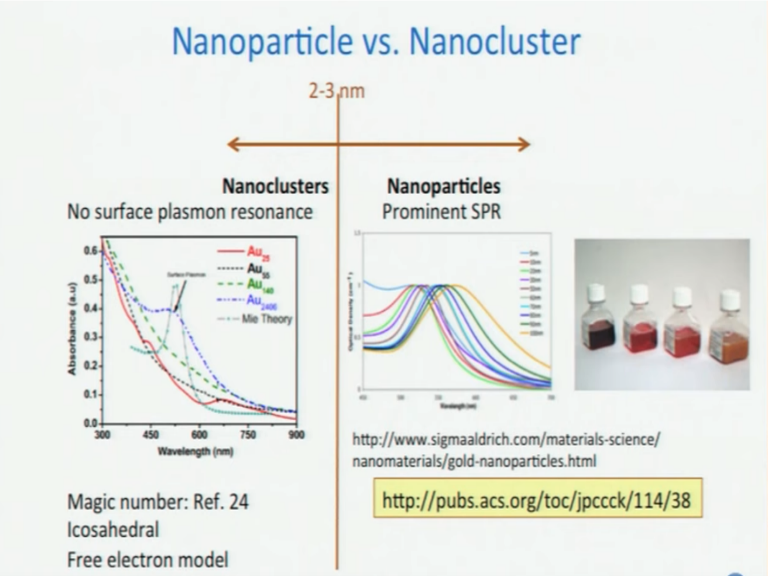

Nanoparticle vs. Nanocluster

2-3 nm

Nanoclusters
No surface plasmon resonance

Nanoparticles
Prominent SPR

http://www.sigmaaldrich.com/materials-science/nanomaterials/gold-nanoparticles.html

http://pubs.acs.org/toc/jpccck/114/38

Magic number: Ref. 24
Icosahedral
Free electron model

Now the things is this is where one usually draws a line between nanoparticles and nano clusters. In nanoparticles we have discussed already your prominent SPR and as the size increases there is a progressive red shift and the color changes as well. In fact this change in color of gold nanoparticles is there even in CBSE class 12 text books now. It has become that common place. Now when you keep decreasing the nanoparticle size what happens?

You see a blue shift progressively and also the peak become less and less prominent because you are getting into scattering regime, as scattering regime. At about 2 to 3 nanometer this peak vanishes. So what you see here is for this 2 to 3 nanometer this is what we expect to see from Mie theory. If you have actually have particles and nanoparticles Mie theory is so that 2 theories of light scattering one is Rayleigh and one is Mie theory. They work in different regimes of particle size.

So Mie theory is still predicts the sharp bend. And what you see here is that if you look at this cluster, I am not going to tell you how this numbers are found. You can read up to yourself for goal 2400 or something. You do see still some surface plasmon band. It is almost gone in the next one. And when you go down to things like gold 25 and all there is no band. So you do not see anything in the absorption. But you do see emission as we are going to show you later.

Now it has been worked out that nanoclusters can be formed of certain discrete number of atoms. You cannot have a cluster of 5 atoms then 6 atoms, 7 atoms, 20, 21 no. There are certain magic numbers and the reason why magic numbers arise is that the basic structure of nanocluster is icosahedral. So of course, when you go down to this clusters of atom symmetry becomes very important. In fact even do not have to go down to atom you can talk about the assemblies of nanoparticles.

So Gilad Haran group as done significant work on spectroscopy assembly of nanoparticle and there symmetry plays a very important role there symmetry and symmetry breaking. Here also symmetry has an important role to play. So they are found to be icosahedral mostly by theoretical calculations. So of course, it is not very easy to see it individual atoms. And what holds here once again is free electron model very much like the nanoparticle. But as we will see nanoparticles are very different animals compared to nanoclusters are different.

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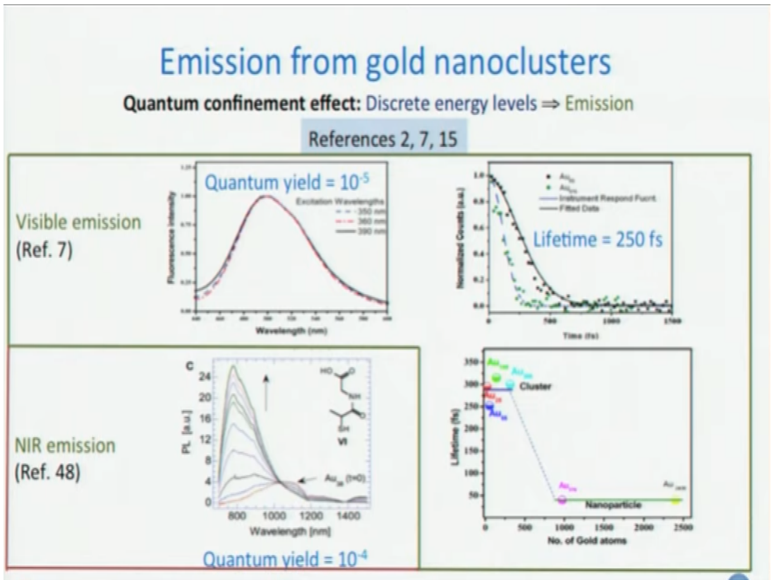

Emission from gold nanoclusters

Quantum confinement effect: Discrete energy levels ⇒ Emission

References 2, 7, 15

Visible emission (Ref. 7)

Quantum yield = 10^{-5}

Lifetime = 250 fs

NIR emission (Ref. 48)

Quantum yield = 10^{-4}

The major difference between nanocluster and nanoparticle it is prominent emission. The previous module we stopped with the comment that gold nanoparticle do have some emission. But then that emission is feeble, and you need to work hard to see that emission. It is easier to miss that emission than to see it. In nanocluster you cannot miss the emission no absorption emission is there. So what you see here is 2 kinds of emission one is visible and the other is NIR.

So in different regions you have 2 different kinds of emission. And if you look in the time domain this comes up very nicely what you see here really is up conversion normalize counts. So you see when you have a nanoparticle then the laser pulse and whatever light comes out from nanoparticle they are completely super impose can you see that these 2. However, when you go down to nanocluster regime then you see the decay here is different from the instrument function ok.

Not very different but different, nevertheless and the lifetime comes out to be 250 femtoseconds once again not very easy to measure unless we are careful. So 250 femtosecond is the lifetime that you observed. And what Theodore group has done very carefully is that they have looked at the lifetime for the different size nanoclusters. And what they establish is the lifetime is around 250 femtoseconds not so easy to differentiate between the clusters.

But the moment you go beyond say 2 nanometer or 3 nanometer there is a drop in lifetime. So this is scattering all the way. So this is the nanocluster nanoparticle divide as far as temporal properties of luminescence is concerned.

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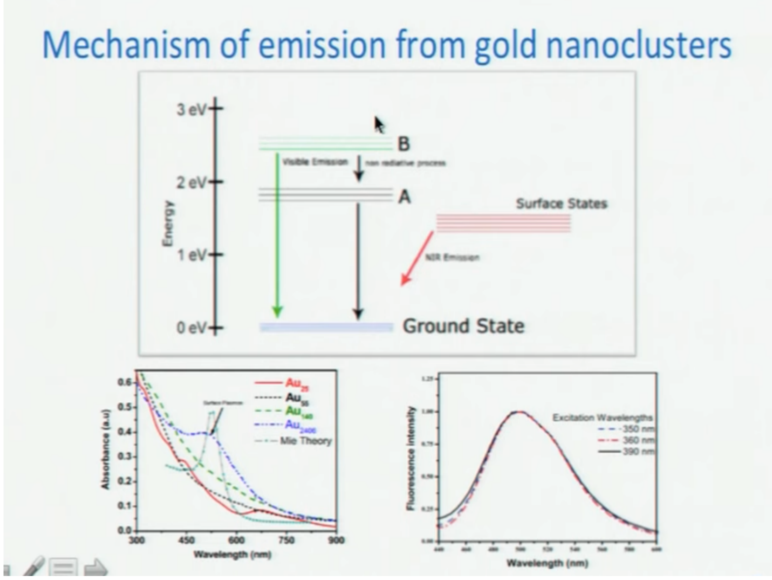

Mechanism of emission from gold nanoclusters

And the mechanism of emission that has been proposed for gold nanoparticle is this. That first of all, you excite and if you excite to higher level then it comes down to lower level pretty much like a molecules this is basically a Jablonski diagram. And you get visible emission from B as well as A. So that would remind you perhaps of 7 Azaindole and then the NIR emission has been attributed to surface states ok. So this is the explanation why you have 1 emission in visible? Why you have another kind of emission in NIR.

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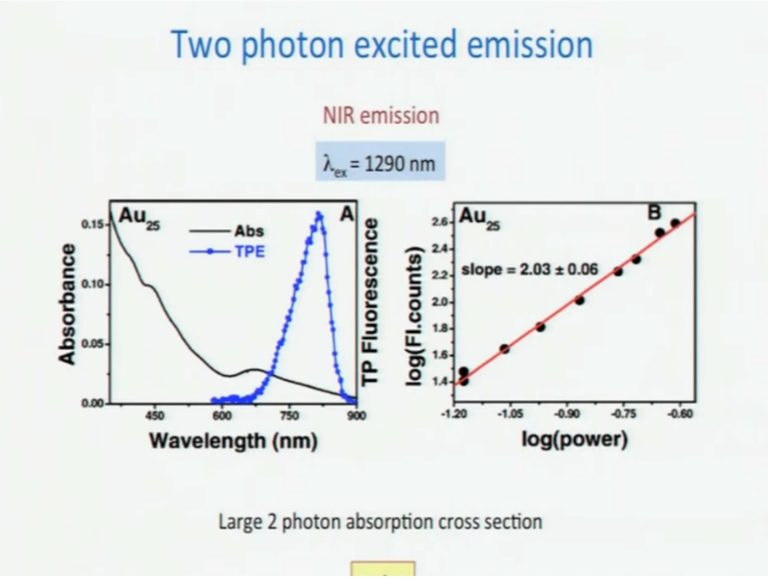

Two photon excited emission

NIR emission

λ_{ex} = 1290 nm

Large 2 photon absorption cross section

Now the other thing that has been done very nicely is 2 photon excited emission. It turns out that these nanoclusters have a large 2 photon absorption cross section. And that is what makes them very interesting and useful from the points of view of say microscopy. Thus the microscopy you do not want to excited 400 nanometer, 400 nanometer will get scattered. If you want to excite at 350 nanometer then you need a different microscopy which cost much more because all optics have to made of quartz.

So 2 photon excitation is the way to go and in 2 photon excitation you see this is the absorption and this is the 2 photon excitated emission and this is for gold 25. As you see excitation wavelength is 1290 nanometer. Exciting by 2 1290 nanometer roughly the state is excited and you can see a nice emission coming from there. And if you plot fluorescence count against power the well log plot if your slope of 2 which confirms that it is really emission arising out of 2 photon absorption, 2 photon excitation.

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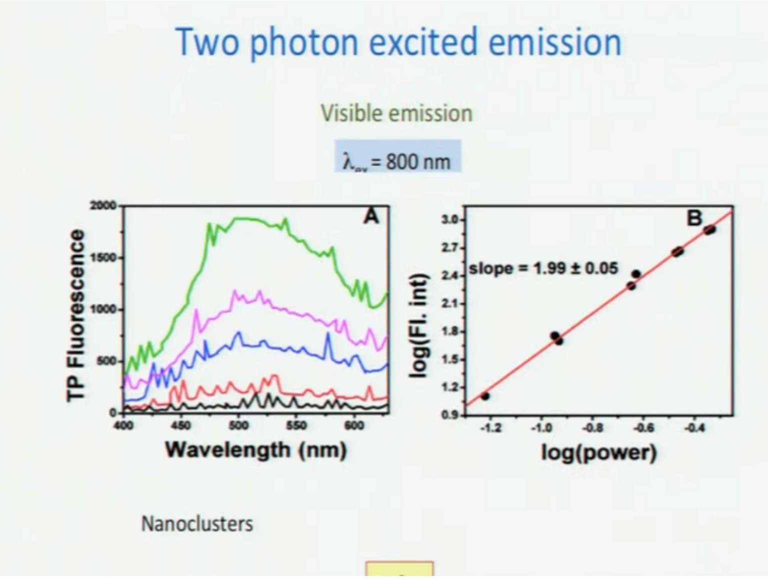

Two photon excited emission

Visible emission

λ_{ex} = 800 nm

Nanoclusters

So this is the visible emission with Lambda ex at 800 nanometer. Once again the slope is about 2 and this is visible emission of another kind of nanocluster. Again with excitation wavelength of 800 nanometer once again you get a slope of 1.94 which is roughly 2. So from all these experiments it is established that 2 photon absorption is the reality and that can give rise to very well that can give rise to fluorescence that you can see.

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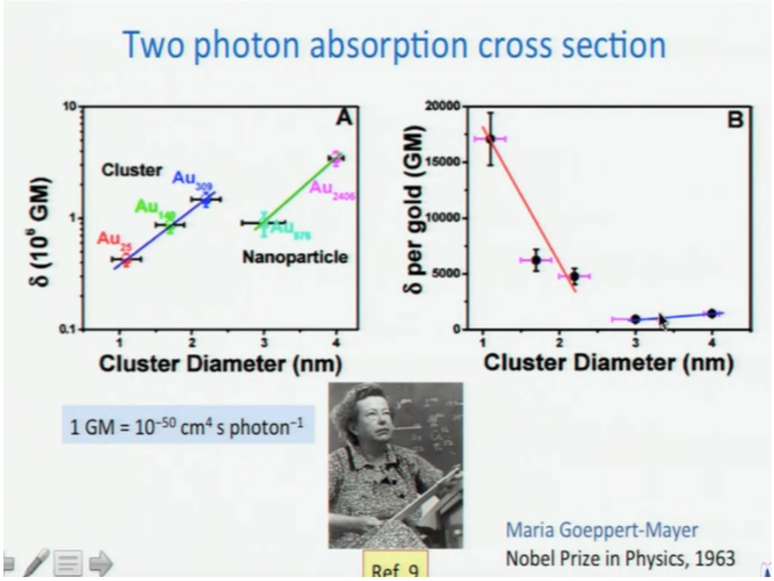

Two photon absorption cross section

1 GM = 10^{-50} cm^4 s $photon^{-1}$

Maria Goeppert-Mayer

Nobel Prize in Physics, 1963

Ref 9

And once again by looking at this 2 photon absorption cross section itself you get a nice distinction between nanoparticles and nanoclusters. And by the way the unit of 2 photon absorption cross section is GM 10 to the power 6. And this GM is for Goeppert Mayer Maria Goeppert Mayer was the Nobel prize winner in physics for her work on nonlinear optics in 1963. This unit is named after her. You see just look at this.

This is 2 photon cross section this you get a linear variation with increase in number of gold in nanoclusters. And then there is a break and then you get another line with little different slope for nanoparticles ok. So this is another evidence that nanoclusters are really different from nanoparticles. And the thing becomes even more interesting when you work out delta per gold atom in GM.

Then you will there is actually no increase. This increase that you see was really a brute force increase an extensive quantity right because the number of gold atoms is increasing. But what you see really is that delta per gold atom decreases as the nanocluster size increases and then when you go to this nanoparticle regime then it is really very small per gold atom because do not forget nanoparticles have many more gold atoms than nanoclusters.

So if you work out the intrinsic quantity then the separation between nanoclusters and nanoparticles is really very good. With that background let me show you transient absorption data.
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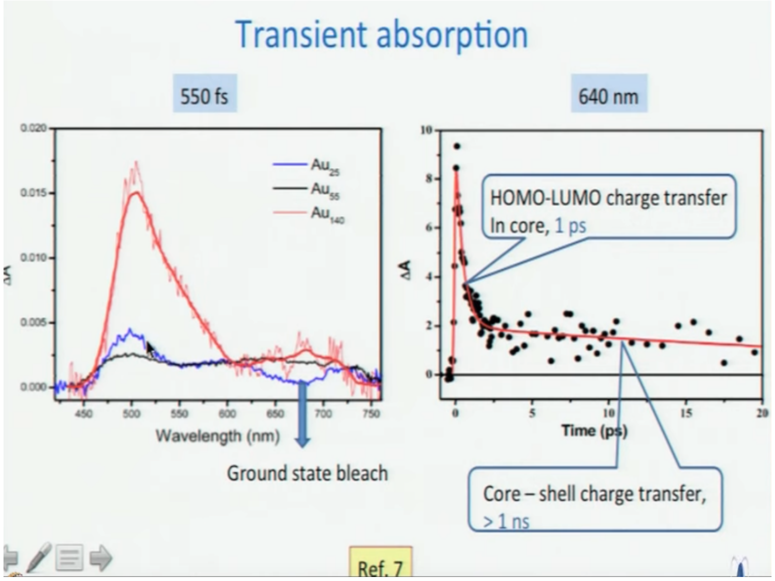
Transient absorption

550 fs

640 nm

Ground state bleach

HOMO-LUMO charge transfer
In core, 1 ps

Core – shell charge transfer,
> 1 ns

Ref. 7

This is what was so this is little old data will talk about new data as well. So here you see there is a ground state bleach. And when you go from gold 25 to gold 55 to gold 140 how does it change? Gold 25 whereas 55 what is the big one 55 or 140? 140 so this size increases this delta A here the transient absorption becomes larger and you see look at the decay HOMO LUMO charge transfer in core that is how it was assigned at that time that was assigned a time constant of 1 picosecond and core to shell charge transfer because what is the core shell all this thing nanoclusters cannot exist by themselves.

You need some kind of the core from polymer or protein using HSA or BSA to make nanoparticle very popular. So some core is there and then like what happened in gold nanoparticles the energy does get dissipated. So this core shell charge transfer is you can think in some way let me just send of the electron phonon coupling right. Not really but more or less so it is basically active species to the environment kind of charge transfer.

So this is how it was assigned initially that there is a HOMO LUMO charge transfer in core and that is associated with 1 picosecond time constant and there is a core to shell charge transfer that give rise to a longer than nanosecond kind of lifetime.

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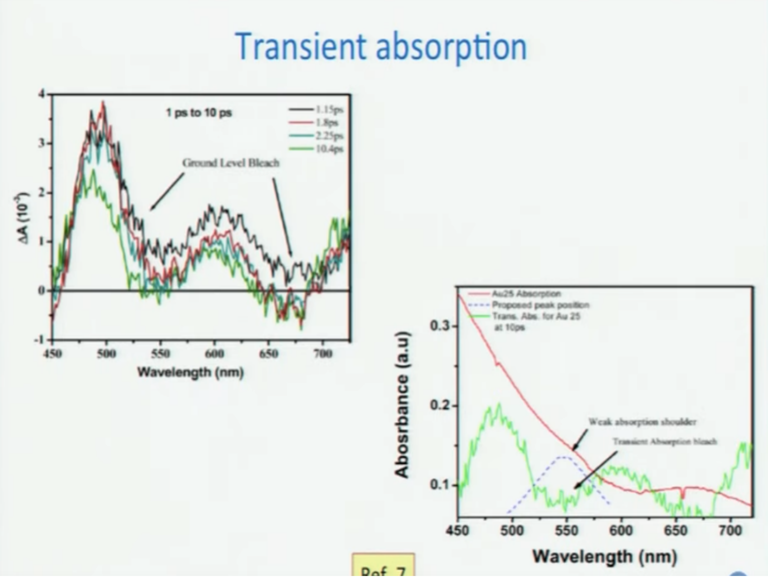
Transient absorption

Now 1 problem that we have and you might remember what we said in the beginning 1 problem we have here is there is no absorption spectrum. So who has said that this is really emission from gold nanocluster and not some impurity? Where you can record excitation no problem. What will we compare the excitation with? How do we know that it is not an impurity? Well transient absorption comes handy there because if you look at 1 picosecond well the earlier transient absorption I showed you was in of 550 femtosecond ok.

But then it is something that goes on for long time so if you look in the 1 picosecond to 10 picosecond regime you see this ground state bleaches that are coming up ok what does that say? It says that at that position spectral position there is something that is absorbing right. So using that the absorption spectrum has been reconstructed and that can be compared conveniently with excitation spectrum ok.

So this is an elegant experiment where transient absorption helps you establish that you are really looking at the thing that you are think you looking at. It is not some garbage right. So this was the state of the art until that time 2013.

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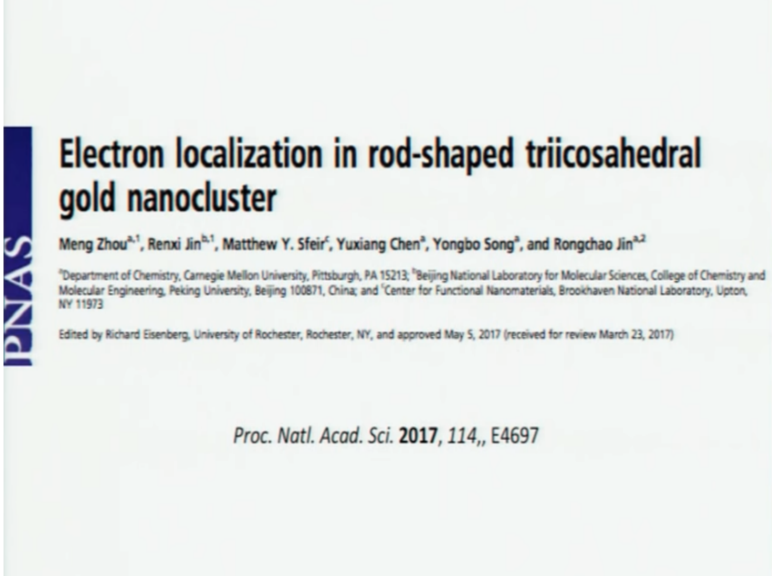

PNAS

Electron localization in rod-shaped triicosahedral gold nanocluster

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Now let me present this paper at least part of it that was published as recently as 2 years ago. So this talks about electron localization in rod shaped triicosahedral gold nanocluster. You might remember that we have said that icosahedral geometry is a reported from DFT calculations right. So this is actually the result.

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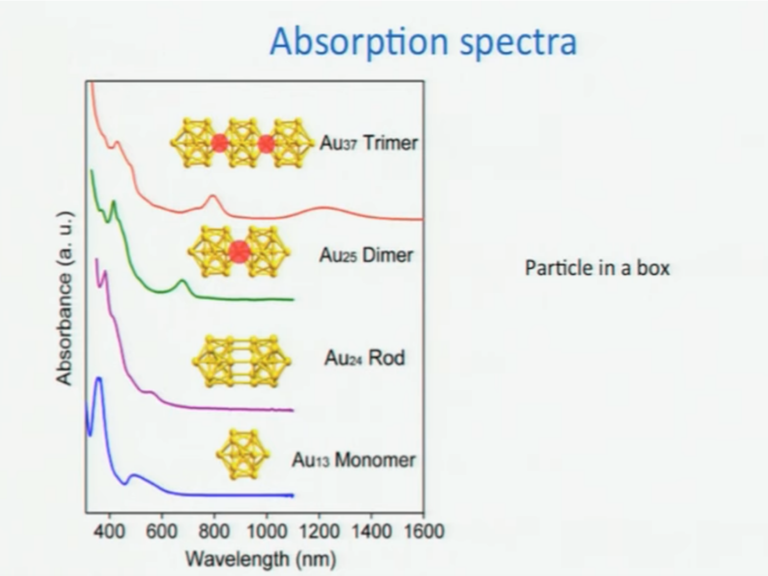

Absorption spectra

Particle in a box

So and this is the origin of the magic numbers also. So what is proposed from theoretical study is that the monomer you need at least 13 gold atoms to get a nanocluster. So gold 13 is the monomer and then you need monomer to join up in different ways to give you other nanocluster which are of different shapes. For example you can have 2 monomer unit coming together to make a rod or they can come together to make a dimer. The difference between this and this is of 1 gold atom. This one and the center is missing for the rod but it is there for the dimer.

Similarly you can have gold trimer were you will have 37 gold atoms. What those red dots are we will talk about little later. And this absorption spectrum can be conveniently discussed like conjugated molecules using particle in a box model because they are not very large ok. So see these are the absorption spectrum you can see a red shift and then when you go to the trimmer you can see something new in the NIR regime. So with this background what has been done is the transient absorption studies have been carried out on the monomer as well as some dimer and trimmer.

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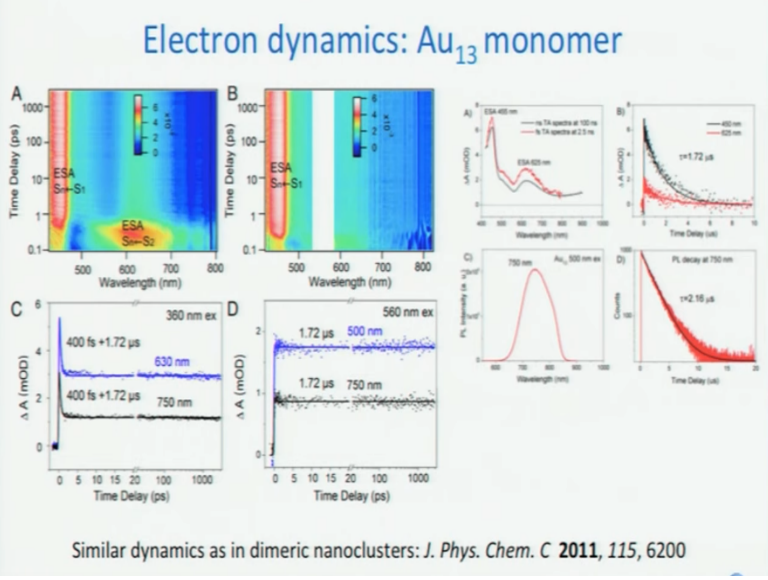

Electron dynamics: Au_{13} monomer

Similar dynamics as in dimeric nanoclusters: *J. Phys. Chem. C* **2011**, *115*, 6200

And this is what you see for the monomer. These are the transient usually we do not show transient absorption like this but they actually are better looking more colorful and since both time and spectral information is there if you know how to read it then it can be more useful. I mean it is same thing you can take sections and compare. But if you are used to it you can just look at this matrix and gets spectral as well as temporal information alright. So let us look at this one.

What they have done is they have used 2 kinds of pumps 2 wavelengths 360 nanometer and 560 nanometers. This first column is for 660 nanometer pump this is for 580 nanometer pump. What do you see here? You see an excited state absorption in that 650 kind of region and here you see ground state bleach. Here of course you cannot look at this region of the spectrum that is why it is white color. And then you see another excited state absorption in the high energy site ok.

So that picture is there and here also but the excited state absorption in the 600 to 700 nanometer region is absent when you excite at 560, nanometer. What does that mean? Well what this means is that when you use 360 nanometer pump and when you use 560 nanometer pump you are exciting to different energies right. And again this should remind us of this 7 Azaindole problem. When they used higher excitation wavelength, they end up exciting S2 and then carefully they tried to decrease the wavelength so that they excite S1 and not S2.

And remember what happed there when we excitation wavelength were varied what happened was that there was initially when excited at higher energy there was the fast component 0.2 picosecond which vanished when excitation was done at sufficiently long wavelength. So here what this tells us as is this. So this one 600 to 700 nanometer excited state absorption this is excited state absorption remember a positive signal.

It shows up only for 360 nanometer pump. That means this excited state absorption is most likely from S2. It is not accessed when you pumped by 560 nanometers and what about this? The higher energy excited state absorption which is absorbed in both that must be due to S1. And the evidence is that S1 is accessed by the lower energy pump as well S2 is not. Secondly what is the energy gap between S1 and some higher energy state and S2 and the same energy state.

The energy gap is higher for S1 right. So this absorption here is assigned to S2 to Sn smaller energy gap longer wavelength smaller energy gap. This one is assigned to S1 to Sn S1 to some higher energy singlet stage. And you see here we have started talking about singlet triplet once again because since it is a cluster you can actually talk about this spin states it is like a molecule. So here you see you get a 400 femtosecond decay and you get a very long lifetime 1.72 microsecond long live state.

At 630 nanometers as well as at 750 nanometer when you pump at 560 nanometer you do get that 1.72 microsecond decay but there is no fast component alright. What is that fast component due to then 400 femtosecond pass it from S2 to S1 that kind of thing. And this corroborated by the long-time pump probe and TCSPC studies. And this year is the emission spectrum which is centered at 750 nanometer ok.

And then they did this experiment on monomer and already there was literature from 2011 I forgot who did this work. There were literature report on dynamics in dimers and they turn out to be the same ok. So monomer dimer is not much of difference is there.

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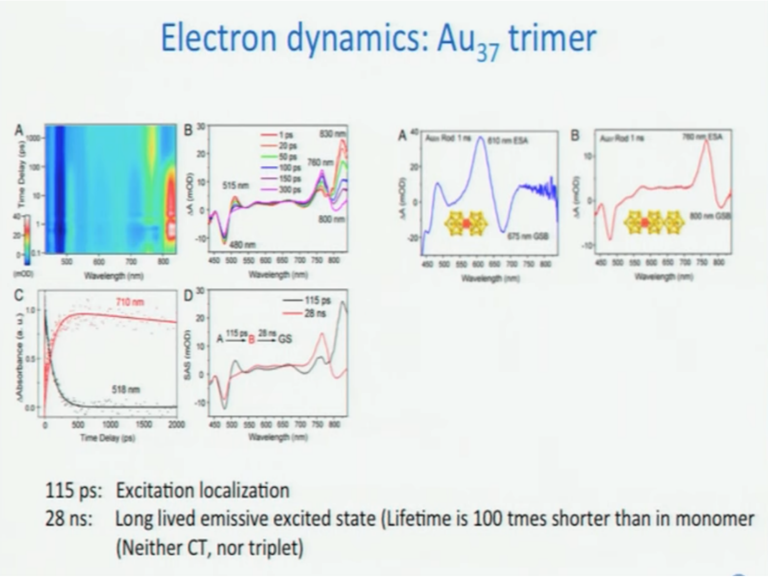

Electron dynamics: Au_{37} trimer

115 ps: Excitation localization

28 ns: Long lived emissive excited state (Lifetime is 100 tmes shorter than in monomer (Neither CT, nor triplet)

Then they moved on to Au 37 trimer and in case you have forgotten how Au 37 looks like? This is what it looks like. Now what do they see? It is better that we look here at 560 nanometer probe you see a fast decay at 710 nanometer you see a rise. And that is associated with 100 this decay and this rise look at the full scale 2000 picosecond. The time constant associated with that is 115 picosecond. So what they concluded from here is that this is due to excitation localization because they have done some calculation right excitation localization means this.

So when you excite initially the excitation is localized over the entire nanocrystal but then they said that it is in another state which is little war in energy which you cannot access by direct excitation in which the excitation is localized that is what is this means. And also they compared the spectra pump probe spectra at long times 1 nanosecond. And dimer and trimer turn out to have more or less similar features I will beat at different wavelength. Now dimer of course has no option. It is known that the excitation is localized.

So what they said is that this is long live species that is there is excitation localized species. So when you excite excitation is delocalized in 115 picosecond post that ultrafast dynamics you get a localization of the excitation and then you get the emission. Also they made an important observation here. The long lived emissive excited state is has a lifetime of 28 nanosecond. So much lesser that what you get for the monomers.

And they did some more studies of what they did is they deoxygenated the sample and there was no change. So they inferred that it is not a triplet state the second state that we are going to buy this 115 picosecond time constant pathway is not a triplet state. They also establish by changing in the medium dielectric constant and all that it is not a charge transfer state.

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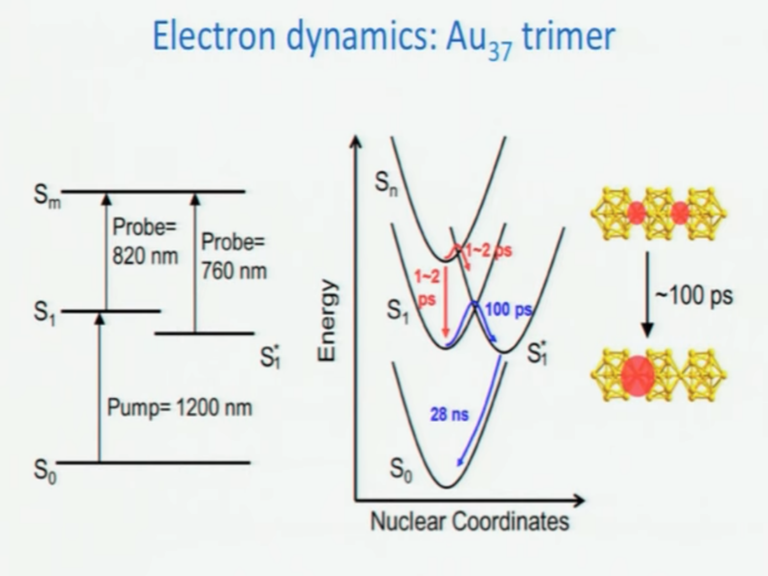

Electron dynamics: Au_{37} trimer

Hence the energetic that comes out is like this. That post excitation initially this is the state that is produced where is the excitation is the localized. Then the 100 picosecond it has to go from here to here. So if you pump at 1200 nanometer as we had shown earlier then you reach S1 by the way this was Au 37 has to be pumped at 1200 nanometer because that is what the band gap is. So this is the probe and here this is S0 if you excite to S2 S from S2 there can be 2 pathways.

Within 1 or 2 picosecond it can be come down to S1 or what the propose was this another state S1 star which is not available by direct excitation and that is ascribed to this localized excitation excited state but a singlet excited state nevertheless. So that has a little lower energy than this S1. You might ask why is it not being called S1 then and why this not being called S2? The reason is the notionally you can call this as S1 you can call this S2. The reason why you preferred to call it S1 star is that you cannot access it by direct excitation.

There has to be this relaxation and localization of excitation before you can get here. So that time is 100 picosecond. So right now this is the state of the art this is how the excited state dynamics of this dimers and trimers and monomer have been discussed but I am sure that is ample opportunity to work in this and it is not as if you have one kind of nanocluster you have same thing the environment is also dependent.

So it is for good reason that there is so much of activity in this area and then as we said it is also useful for microscopy. It is being used as normal fluorophore in many cases. And it is not very difficult to say denature the protein. And then your nano crystal is completely gone. So it can actually be very sensitive to inputs that one may provide. So that is what we want to talk about in nanocrystals in nanoclusters. In the next module we will go on to semiconductor nano to ultrafast dynamics in semiconductor nanocrystals.