Ultrafast Optics and Spectroscopy
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Lecture - 43
Femtochemistry of Nanocatalysis 2

Welcome back to the last module. In this course we have discussed how Femtosecond Pulse can be used to deposit heat energy, in a well defined time window to the metal substrate why do we need that? We would like to initiate a catalytic reaction. So, I have a surface I have now molecules sitting on that surface I know how many molecules what is the arrangement of the molecules on the surface.

Then we will use femtosecond pulse to deposit heat energy within a very short time scale. And then we will monitor how the reactions is moving forward on the surface. So, this is the goal, which we have and, in the surface, chemical dynamic study. And the technique which we are going to use is called two pulse correlation technique which is nothing but a correlation technique.

Correlation technique we have already seen in the context of pulse measurement. It is called autocorrelation measurement cross correlation measurement and. So, similar kind of correlation measurement will use, in the correlation measurement we have two pulses time delayed.

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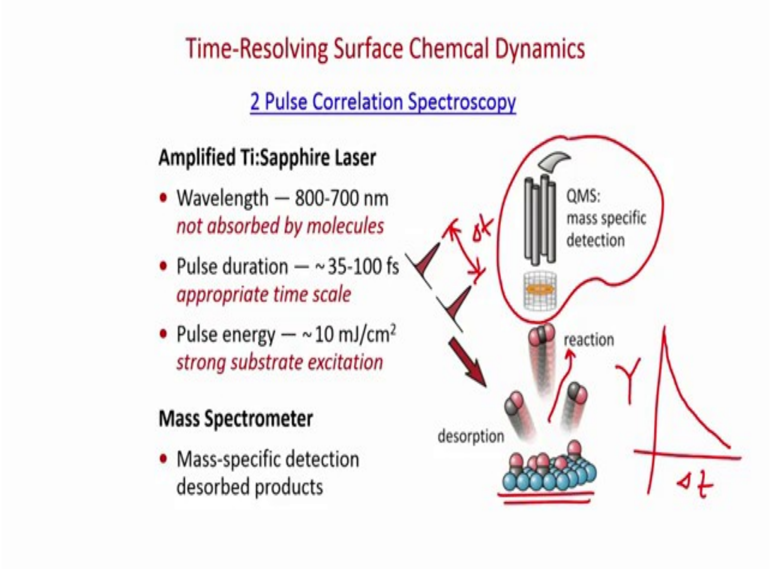

Time-Resolving Surface Chemcal Dynamics

2 Pulse Correlation Spectroscopy

Amplified Ti:Sapphire Laser

- Wavelength – 800-700 nm
  not absorbed by molecules
- Pulse duration – ~35-100 fs
  appropriate time scale
- Pulse energy – ~10 mJ/cm^2
  strong substrate excitation

Mass Spectrometer

- Mass-specific detection desorbed products

Pulses this is the delta t that is the time delivering two pulses. They will be used to deposit the heat energy on the substrate. And this blue colored surface is the substrate surface and the molecules is desorbing from the surface due to this heat energy dis desorption. And that quadrupole mass spec will be used to detect the molecules which is coming out of the surface.

So, this is the basic idea of the two pulse correlation spectroscopy as a function of delay. So, all we are going to monitor is that the yield, the desorption yield as a function of delta t. The desorption yield as a function of time and obviously, desorption yield will decrease as a function of time; because in general it will decrease as a function of time; because.

As when two pulses are overlapped with each other I deposit the energy simultaneously but if the pulse are not separated the pulse are well separated. Then what will happen, I deposit the energy the first pulse will deposit the energy and second pulse will now try to disrobe the molecules from the surface as much as possible. And we will see the dwell effect or the combined effect of pump and probe in the desorption yield.

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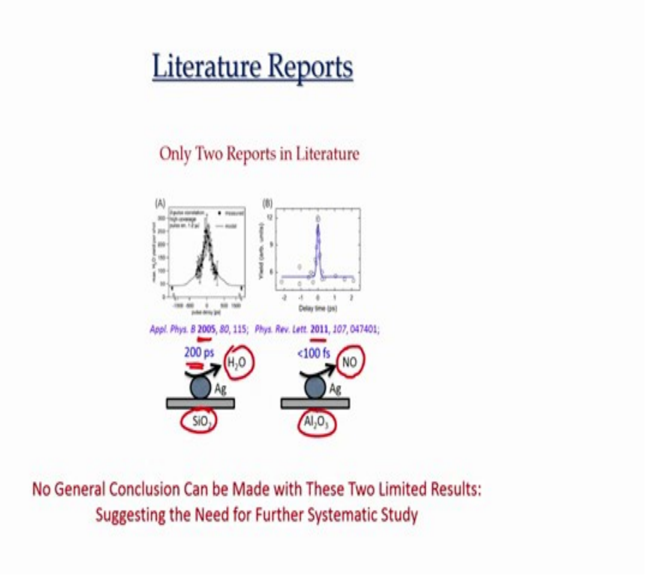

Literature Reports

Only Two Reports in Literature

Appl. Phys. B **2005**, *80*, 115; *Phys. Rev. Lett.* **2011**, *107*, 047401;

No General Conclusion Can be Made with These Two Limited Results:
Suggesting the Need for Further Systematic Study

If we look at the literature, then we find that there are mostly two works which have been documented. And one work was done in 2015 another work was done in 2011. Now, in 2005 and 2011 and in 2005 the work was done based on the water desorption from the silver nano particle.

And it was found that 200 picoseconds of the time scale for the water desorption from silver nano particle. On the other hand if we look at the 2011 work the work was done based on the no absorption from the silver nanoparticles. So, similar kind of nanoparticles was used but the substrate support surface was different. One is silicon another one was alumina.

The support surface are different. So, I have a support surface then I have nanoparticle sitting on it nanoparticle of the order of 10 nanometer probably. And then on the nanoparticle, I have molecules sitting on that molecule surface. And then we use these two-pulse correlation spectroscopy. And it was found that 200 picosecond was the desorption timescale for the water.

And 100 less than 100 femtosecond was the desorption time scale for no. So, with this two information, it is very difficult to get a general conclusion for the femto commissioner of nano catalysis. And with this motivation we started working on it. I started working on this field when I was (Refer Time: 04:53) doctoral fellow in Brookhaven national lab with Nicky Maloney. When and we are continuing it in the in Indian (Refer Time: 05:01) science right now.

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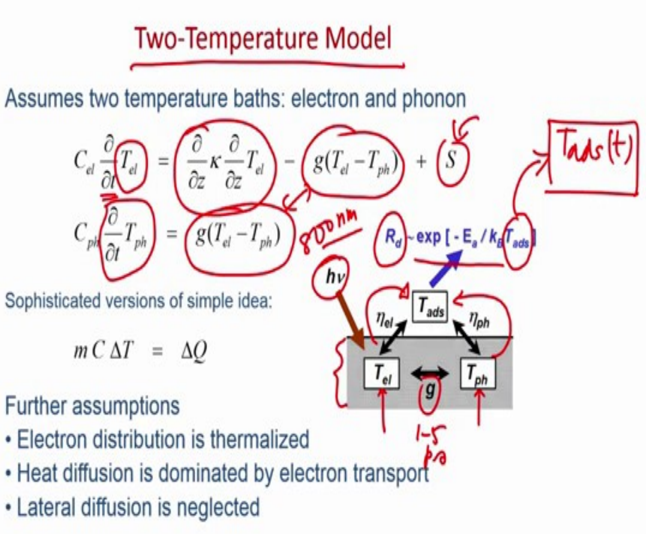

Two-Temperature Model

Assumes two temperature baths: electron and phonon

$$C_{el}\frac{\partial}{\partial t}T_{el} = \frac{\partial}{\partial z}\kappa\frac{\partial}{\partial z}T_{el} - g(T_{el}-T_{ph}) + S$$

$$C_{ph}\frac{\partial}{\partial t}T_{ph} = g(T_{el}-T_{ph})$$

$R_d \sim \exp[-E_a/k_B T_{ads}]$

Sophisticated versions of simple idea:

$$m\,C\,\Delta T = \Delta Q$$

Further assumptions
- Electron distribution is thermalized
- Heat diffusion is dominated by electron transport
- Lateral diffusion is neglected

So we will look at the before you go but one interesting result. We will look at the energy deposition process theoretical a little bit because that will clarify many of our doubts. Theoretically when we discuss heat energy deposition with the help of femtosecond pulses we generally use two temperature model. Two temperature model considers that I have a substrate, this s substrate has to hit baths.

So, any metal I take any metal, I told you that there are two constituents in a metal one is electron another one is nucleus both are present in a metal. So, what I am doing right now, collectively all electrons I am considering as a heat bath as a package. Let us say which can take energy give energy a heat bath; another all phonon are considered to be collectively considered to be a phonon bath.

And that is why we have shown here. Metal substrate is nothing, but a coupled heat bath of electron and phonon. And also I have mentioned that the photon energy will be deposited to the electron first not the phonon; so in the range of 800 nanometer. Now electron will transfer now once we deposit a energy to a reservoir because they are coupled let us say I have two containers attached together.

One container is here another container is here. And they have a there they have they are in thermal contact. Then what will happen in this container when I deposit heat energy you I am increasing temperature. Then due to thermal conduction definitely this heat bath although I am not depositing directly energy to this heat bath it will gain energy.

And it will also slowly increase the temperature how quickly it will increase a temperature? Depends on how quickly it is transferring energy through this partition right this partition. Similarly, I have two heat baths electronic bath and phonon bath they will exchange energy with the help of g; that is the coupling constant.

And once this is and this is the time scale is going to be 1 to 5, picosecond in this time scale this will transfer the energy. So, when they will transfer the energy this energy can go again to the adsorbate bath adsorbate. The all adsorbate can be collectively considered to be an adsorbate bath. Another heat bath and it can transfer the energy.

And electron baths can also directly transfer the energy to the adsorbate bath both is possible. And I will show you how they can differ the behavior of two pulse correlation spectrum. And in the end if I deposit energy sorry if I increase the temperature. Then from Arrhenius equation we know that the rate will depend exponentially with respect to E to the power minus Ea by kT that is an simplest expression, we know this is an Arrhenius equation.

So, what is important to know that, how quickly this adsorbate bath temperature is increasing? That is our goal in this process. And to understand that we what we would like to know how the electronic temperature this electronic temperature as a function of time is. So, this is how electronic temperature is increasing.

Electronic temperature increase will depend on three different factors. We have three different factors one factor is S; S is how what is the rate of energy deposition? So, I have a surface in the surface I have I am depositing the energy continuously. What is the rate of energy deposition? That will depend on how quickly the temperature of the surface will increase.

That is why this is the source term coming from the laser term. When I deposit the energy there are two process which can happen. One process is that in the electronic bath let us say I have a bucket of water, when I deposited energy on the top surface of the bucket of the water that energy will go down slowly defuse the energy.

Similarly, in the electronic bath when I deposit the energy on the top surface this can diffuse the energy. And this diffusion part is governed by this. In addition to that diffusion there is two baths are coupled one bath is electronic bath another bath is phonon bath. So, electronic bath can deposit energy to the phonon bath as well.

And that is the term, which is controlling this exchange of energy between two baths. So, there are three factors which can control the final electronic surface electronic temperature. The first factor is that how quickly I am depositing energy to the surface? Second factor is that once I have deposited energy how quickly this energy is getting diffused?

And third part is that this is the one bath I have, another bath is phonon bath and they will exchange energy. So, electronic bath is exchanging energy to the phonon bath and how quickly that is happening? These three factors is going to control the electronic temperature. On the other hand phonon temperature will be controlled only by this coupling term which we have here also.

This coupling term is nothing but how the energy is deposited from electronic bath to the phonon bath. So, phonon does not have any external source phonon cannot directly interact with the laser pulse. It is taking energy only from the electron bath and that is the only way it can increase the temperature. So, these are the two behaviors.

We have this is the these are two equations, which we have coupled equations with differential equations we have which we have. And they can actually increase the temperature.

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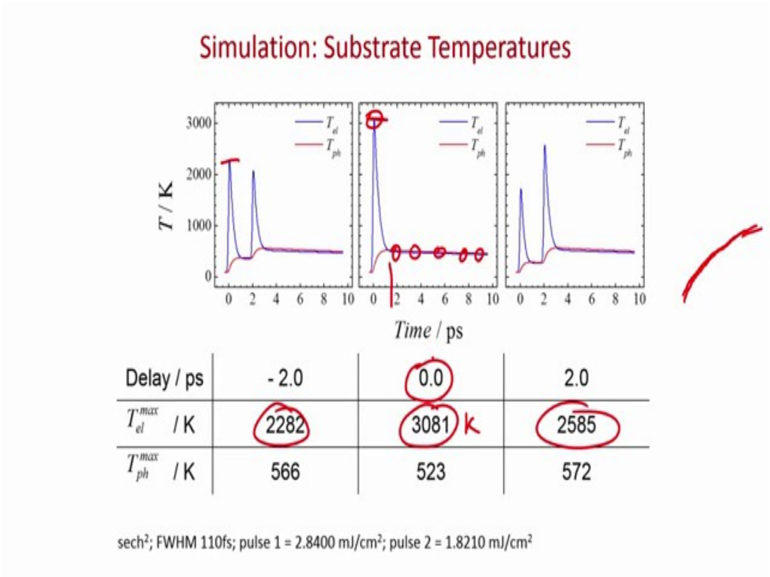

Simulation: Substrate Temperatures

Delay / ps	- 2.0	0.0	2.0
T_{el}^{max} / K	2282	3081 K	2585
T_{ph}^{max} / K	566	523	572

$sech^2$; FWHM 110fs; pulse 1 = 2.8400 mJ/cm^2; pulse 2 = 1.8210 mJ/cm^2

This is an example if two pulses are overlapped together, that is the 0 delay then we see that the maximum electronic temperature is here. This is the maximum electronic temperature. It peaks to 3000 Kelvin temperature its a huge energy transiently we can create 3000 Kelvin temperature. But remember at this 3000 Kelvin temperature, electron and phonon they are not an equilibrium they are out of equilibrium.

That is why you see this part this is out of equilibrium part which means. So, let us say I am trying to melt a metal. I have a metal I increase the temperature, when I increase the temperature electron. Temperature and phonon temperature both are increasing simultaneously in equilibrium with each other. But when you deposit heat energy to the surface; then for the first 1 picosecond timescale up to the 1 picosecond timescale they are in non equilibrium state.

They are not equilibrium why? Because it takes some time to get the as to send the energy to the phonon bath its more like, if I am talking to somebody over phone let us say then I send the message I speak something right now. But it may take some time to reach the destination. And there is always a time delay between these two.

And so this time delay will make that non equilibrium. And that is why although electronic bath having that energy. And it has started and the transferring energy to the phonon bath but to reach that equilibrium between. Equilibrium means maintaining the same temperature for electronic bath and phonon bath.

To maintain that it takes some time 1 picosecond can almost it takes. And then its maintained that the equal temperature journey for both electronic and phonon baths. So, what we see that, the maximum temperature achievable temperature for electronic bath is maximum when they are overlapped together.

But when they are not overlapped together, the maximum temperature has gone down to 2500 Kelvin temperature, this is a big difference now. This suggest that depending on how we are depositing the energy at what delay we are depositing the energy. The peak temperature may vary and if peak temperature is varying then it may affect the adsorbate temperature as well. And adsorbate temperature if it is affecting adsorbate temperature then it can also affect the kinetics on the surface.

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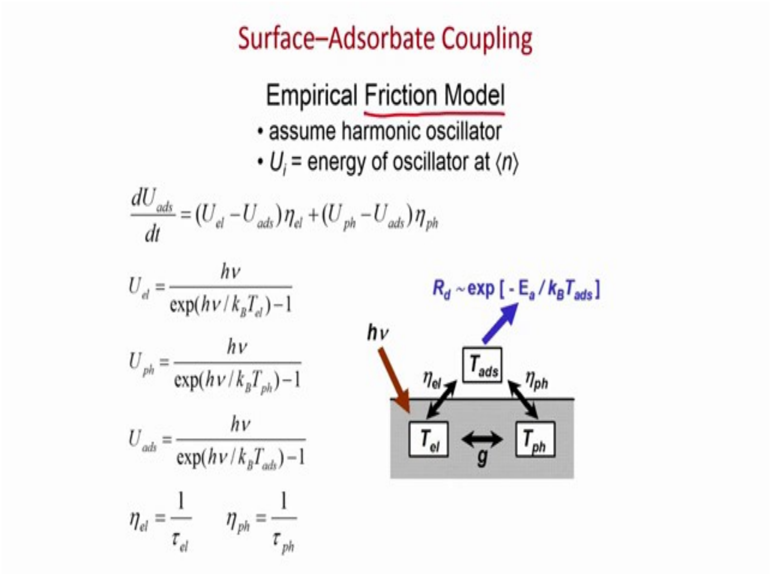

Surface–Adsorbate Coupling

Empirical Friction Model

- assume harmonic oscillator
- U_i = energy of oscillator at $\langle n \rangle$

$$\frac{dU_{ads}}{dt} = (U_{el} - U_{ads})\eta_{el} + (U_{ph} - U_{ads})\eta_{ph}$$

$$U_{el} = \frac{h\nu}{\exp(h\nu / k_B T_{el}) - 1}$$

$$U_{ph} = \frac{h\nu}{\exp(h\nu / k_B T_{ph}) - 1}$$

$$U_{ads} = \frac{h\nu}{\exp(h\nu / k_B T_{ads}) - 1}$$

$$\eta_{el} = \frac{1}{\tau_{el}} \qquad \eta_{ph} = \frac{1}{\tau_{ph}}$$

So, this is the way we are going to perform. And finally, the energy transfer is used as a friction model. This friction model I am not going to go over very rigorously, but what we do is that. We use Bose Einstein distribution for the adsorbate and we check the how much temperature we get for this system.

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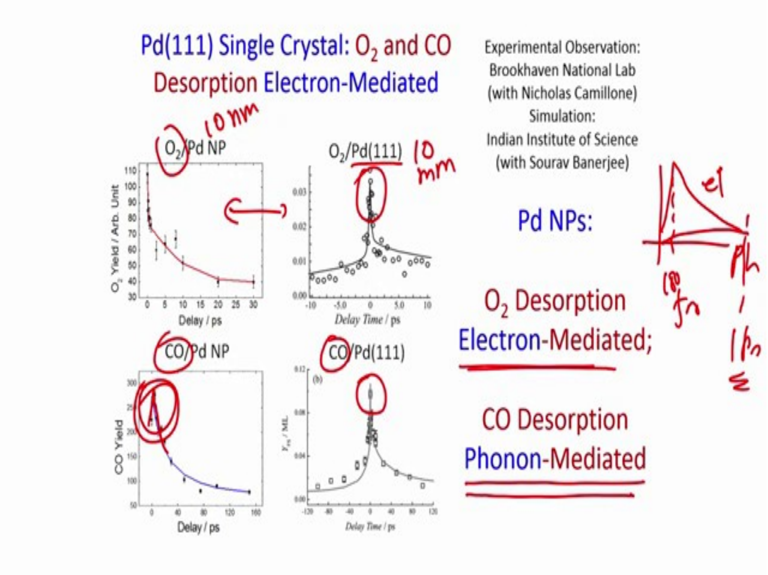

Pd(111) Single Crystal: O_2 and CO Desorption Electron-Mediated

Experimental Observation:
Brookhaven National Lab
(with Nicholas Camillone)
Simulation:
Indian Institute of Science
(with Sourav Banerjee)

Pd NPs:

O_2 Desorption Electron-Mediated;

CO Desorption Phonon-Mediated

This is the example which will go over; this example is very good example although it is not published to work. But this is a very good example to show what might happen when we decreased. What kind of changes one can expect on a nanoparticle surface? When you change the substrate from millimeters millimeter sorry 1 centimeter to the nanometer dimension.

What we see here is that, oxygen desorption from lithium nanoparticle and oxygen desorption from lithium one surface. This is let us say 10 millimeter and lithium nanoparticle is 10 nanometer. So, this is the two different dimensions entirely two different dimensions is it 1 dimension is 10 nanometer another dimension is 10 millimeter. 10 nanometer, we cannot see with our bare eye 10 millimeter, we can see it very nicely.

So, this is the two different dimensions we are talking about but same molecule sitting on that surface same molecule. What we see is that, if we do two pulse correlation spectroscopies then they behave just like similar to the palladium nanoparticle we are sorry palladium 111 crystal. So, bigger dimension and smaller dimension does not have any big difference.

But if we look at CO carbon monoxide, we change the molecule from O2 to carbon monoxide. Carbon monoxide is poisonous molecule, but carbon monoxide is used to synthesize many chemicals. And this is very important molecule for the chemical production. Although this is very poisonous and.

So, if we change the molecule from oxygen to CO on the on this very small dimension and large dimension system. Then we see a big change near the zero delay. Here we have only a decay here we have a increase and then decrease there is a deep here these two difference we see. And these two difference are characteristics of phonon mediated process phonon mediated why phonon mediated?

As I told you that 2 for phonon to reach a particular temperature it takes some time the behavior was like this. We had later on temperature is very quickly increasing and then decreasing and phonon temperature is slowly increasing. This is the way we have seen this is phonon this is electron. So, electron temperature can reach the maximum very quickly within let us say 100 femtosecond let us say this is 100 femtosecond.

But this phonon temperature is 1 picosecond, this is there is a big difference between ad by when electron can reach the maximum and phonon can reach the maximum. And whenever we see a deep near the 0 delay, it in general it points to the phonon mediated process. But if we do not see a deep if see a picoseconds became then it is electro mediated process.

So, what we see is that, if we change the dimension from millimeter to nanometer then oxygen does not change the behavior. Oxygen remains to be electro mediated desorption oxygen shows up electro mediated desorption. But when I changes the dimension from millimeter to nanometer. We see that carbon monoxide is changing the behavior carbon. Monoxide is becoming from electro mediated to phonon mediated question is why? What might have caused that?

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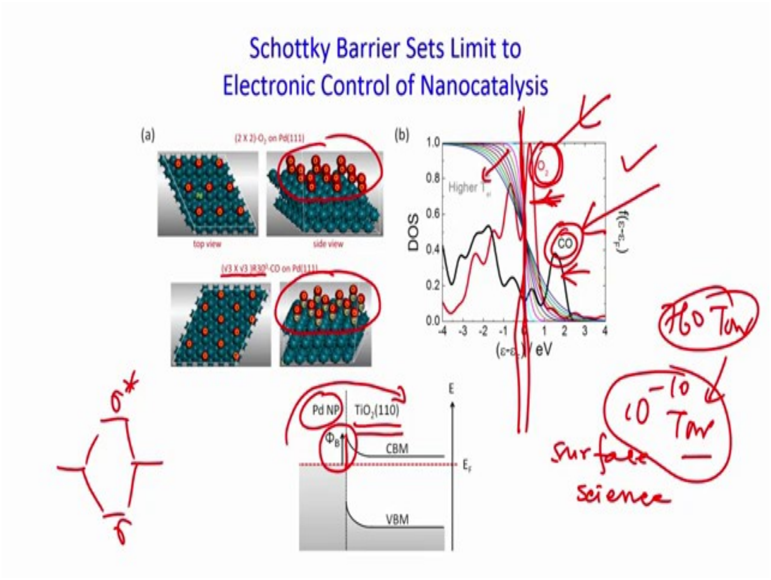

Schottky Barrier Sets Limit to
Electronic Control of Nanocatalysis

So, what we have shown here is that how the molecules are sitting on the surface. This is oxygen molecule sitting on the surface and this is CO molecules are sitting on the surface how the molecules are sitting on the surface. Now oxygen and CO how they should sit on the surface they can differ. And this is for example, root 3 root 3 R 30 degree CO arrangement.

This is surface science nomenclature surface science is a; surface science is a field where we study the structure of the surface under ultra high vacuum under very pure condition. So, that we do not have any impurity on the surface. So, what happens let us say, in this room I have this metal ring and in my ring finger.

And then in this metal if this is a gold metal. So, let us have a go to gold metal in this room because the pressure is so high it is an atmospheric pressure continuously molecules are hitting the surface always. So, its very difficult to have a clean surface empty surface no surface can be made can we kept clean in this step pressure.

So, what I need to do I have to take this sub substrate and place it in a chamber and then pump it down; pump it down what does it mean? I am creating the vacuum and if I create the vacuum of 10 to the power; let us say 10 to the power minus 10 torr. atmospheric pressures 760 torr this is the pressure we have right.

Now, but if I reduce it to 10 to the power minus 10 torr then what will happen the number of collision will be reduced significantly. And I can get 2 to 3 hours not having any depositing on the surface. So, once I have clean the surface under ultra high vacuum then I can keep that surface for even few hours and clean it will not. So, any no molecule will be absorbed on the surface for few hours.

And that is why we can now deposit. If I once I clean the surface I can deposit my own molecule like oxygen or CO. And then I can study it that is why we need this ultra high vacuum to perform the surface size experiment. Now in this experiment sorry in this structure. In these figures we have shown the structures how oxygens can be organized on the surface and how CO can be organized on the surface.

And on the right hand side this figure is suggesting the density of states density of states what does it mean? You can view visualized as a empty state an occupied state in the metal surface. Metal surface does not have a discrete states they have highly densed pack of states. And that is why we call it density of states and CO density of states if we look at CO 2 0.

So, this is the Fermi level of that state this is the Fermi level. So, if this is the Fermi level then what does it mean? It means that oxygen antibonding states and CO antibonding states antibonding with respect to adsorbing metal bond. These states are empty on the at the room temperature. But if we increase the temperature slowly then what will happen?.

Oxygen can be very easily populated oxygen antibonding state. But CO antibonding state because it is high in energy it will not be very easily populated. Antibonding state what does it mean I will view metal adsorbate as a diatomic system. And in a diatomic system we know that in a diatomic system we create bonding and antibonding states.

This is let us say sigma this is sigma star. And demonstration a simple demonstration. So, I have metal surface and absorbate I consider as a diatomic molecule. And then if I somehow inject the electron to the antibonding state, then what will happen it will slowly decrease sorry, increase the bond distance and it will try to break the metal absorbate and that is nothing but desorption.

So, if I have antibonding state very low lying close to the Fermi level, I can very easily access that at the bonding state and I can desorb oxygen very quickly. But for CO its difficult to dissolve; because CO antibonding state is above 1 eV from the Fermi level. And we know that the in a metal semiconductor interface this plenty of nanoparticles are actually deposited on that TiO_2 surface and TiO_2 is a semiconductor.

So, we create a Schottky barrier this barrier is called Schottky barrier and this called the typical Schottky barrier height is 1 eV almost. So, above 1 eV whatever electronic excitation we do that goes to the TiO_2 surface. So, I have this substrate TiO_2 substrate I have nanoparticle sitting on this. And then on this nanoparticle I have molecules sitting oxygen or CO.

Now, what happens when I electronically excite nanoparticle above 1 eV; all the electrons are most of the electrons is going to the substrate not to the adsorbate sitting over here. And that is why I cannot anymore electronically excite CO on the nanoparticle surface. And that is why CO desorption on nanoparticle surface is becoming phonon mediated it is not electron mediated anymore.

But on a single crystal surface I do not have TiO_2 I have only lithium. And I can maintain that high temperature of electronic temperature and absorbate can see that electronic temperature and can it can take the electrons from that. That is why the difference is coming, but for oxygen we see that it is below 1 eV.

So, the Schottky barrier is almost 1 eV and the Schottky barrier will not allow the electrons to go away from the nanoparticle. So, oxygen remains to be electron mediated, but CO remain as CO becomes phonon mediated on the nanoparticle surface. This is called nano confinement effect.

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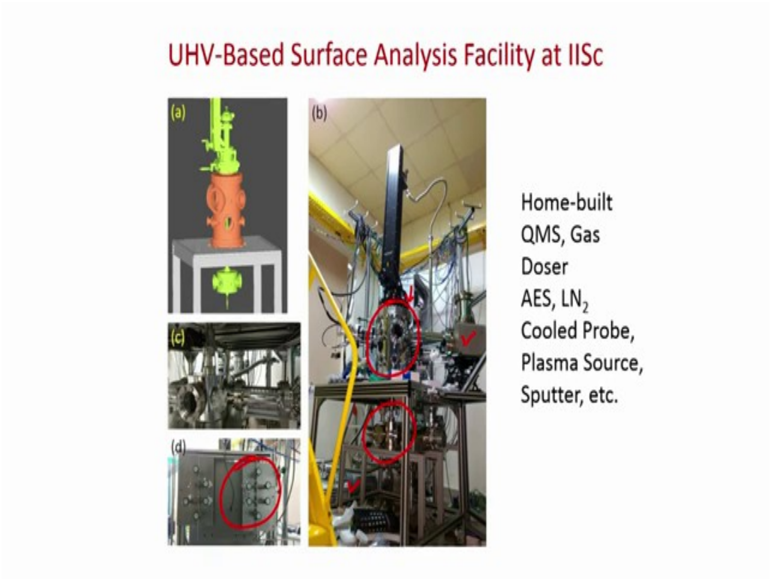

UHV-Based Surface Analysis Facility at IISc

Home-built
QMS, Gas
Doser
AES, LN_2
Cooled Probe,
Plasma Source,
Sputter, etc.

And one can explore different aspects of nano confinement effects with the help of this, the technique which you will couple surface science technique and femtosecond spectroscopy; this is just a image we have taken from our lab instrument. The top part is the surface science experiments we perform.

The bottom part is a cleaning and also transfer of the sample we which we do. And to maintain the vacuum in this chamber we have to use different than upon this called ion pump then there are scroll pumps here. And then there are on the back side in the back side we have the turbo pump. Different kind of pumps we have to use and these are the gas lines which we use to deposit the sorry.

Those the oxygen and CO molecules on the surface. So, these are the this is little complicated the chamber and the analysis procedure. But primary idea of this whole chamber, building whole this chamber building this whole chamber is that to create the vacuum first and maintain that vacuum at the level of 10 to the power minus 10 torr.

So, that one can perform the experiment before we contaminate the surface. Contamination and this in this room temperature will be very quickly within few microseconds will be contaminated. But if we keep it in the vacuum then contamination will not occur. So, that we can maintain the clean surface that is very important.

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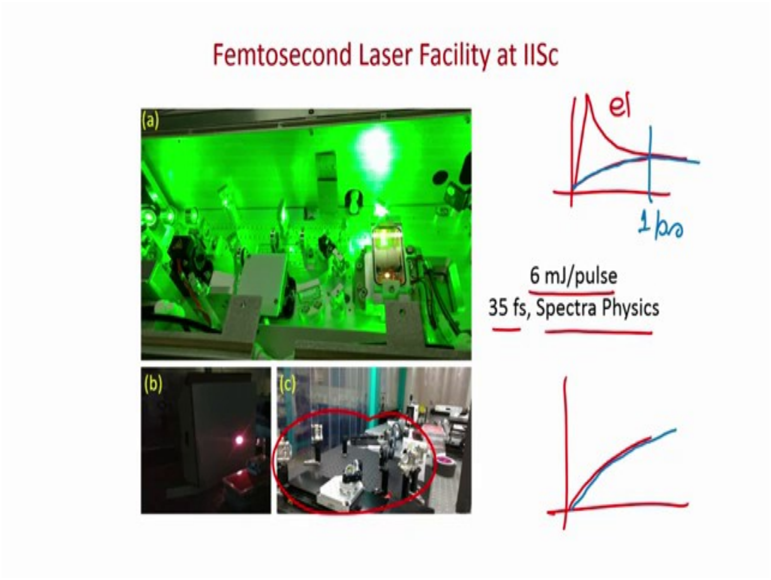

Femtosecond Laser Facility at IISc

6 mJ/pulse

35 fs, Spectra Physics

This is the laser system which we have used in our in our lab. This is 6 mili Joules pulse energy it produces but we do not need 6 kilo Joules pulse energy in our in this experiment 30 femtosecond spectra physics has applied this. And we and this is the pump probe setup which we have in the lab that is a two pulse correlation setup.

So, the bottom line of this whole module is that, we if we want to use femtosecond pulse as a sophisticated heater. Just we want to deposit heat energy, then there are some reservation and there are some advantages. Advantages is that, it can provide the well defined time window for the heat the position.

But the reservation is that there is a time period for which electron and phonon are not in equilibrium that is for first 1 picosecond. And because they are not in equilibrium what might happen is that the hot electron can do some chemistry which is not possible thermally. So, as long as something is going on beyond 2 picosecond or longer than 2 picosecond; one can say that we are following the thermal chemistry pure thermal chemistry.

But if it is going on in the order of let us say 600 femtosecond, it is difficult to judge whether the same reaction will occur thermally or not. Because with the help of femtosecond pulse we have seen this non equilibrium situation where electron temperature is going like this when phonon temperatures we like this way. If I thoroughly heat it then slowly both the electron temperature and phonon temperature will go up together.

I show it with the help of two different color there they are going together. But here they will not go together they will just be in it non equilibrium for a certain time. And then they will be in equilibrium after certain and this time is almost 1 picosecond time. So, for 1 picosecond the first 1 picosecond time scale it can be highly non equilibrium.

So, the interpretation of the data and the relevance to, if you are trying to find out the relevance of this photo excitation femtosecond pulse excitation to the real life catalysis it is little difficult. And we need to understand many other factors to make the final conclusion. With this we will conclude this module. This is the last module in this course.

You have gone over the different modules. I hope you have all of you have enjoyed every session, if you have any correction or if you have any suggestion, please do not hesitate to write to me directly; so that you can improve it for the next year or for future classes. And I wish you all the best for your work in the field of ultrafast science.