Ultrafast Optics and Spectroscopy
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Lecture - 42
Femtochemistry of Nanocatalysis 1

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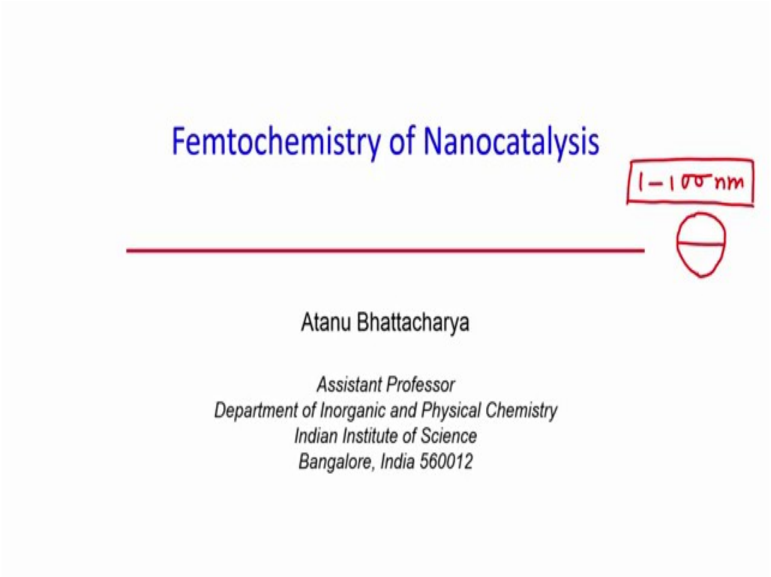

Femtochemistry of Nanocatalysis

1-100 nm

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Welcome to the last module of this course. In this module we will go over an interesting topic Femtochemistry of Nanocatalysis. Femtochemistry of nanocatalysis is all about the movement of nuclei during the catalytic process. This is again going to be based on the research work which we have been performing in institute of science on femtochemistry of nanocatalysis. Nanocatalysis is a catalytic reactions which occurs on nanoparticle.

Generally, when we say nanoparticle; generally we consider it is going to be 1 to 100 nanometer in size. So, if I consider a spherical particle, then the diameter of the particle is going to be in the range of 1 to 100 nanometer. So, if we decrease the size of metal semiconductor or any material to this nano regime, then we observe different interesting phenomena. And in this talk we will discuss some of the interesting information which will come out based on the femtosecond study.

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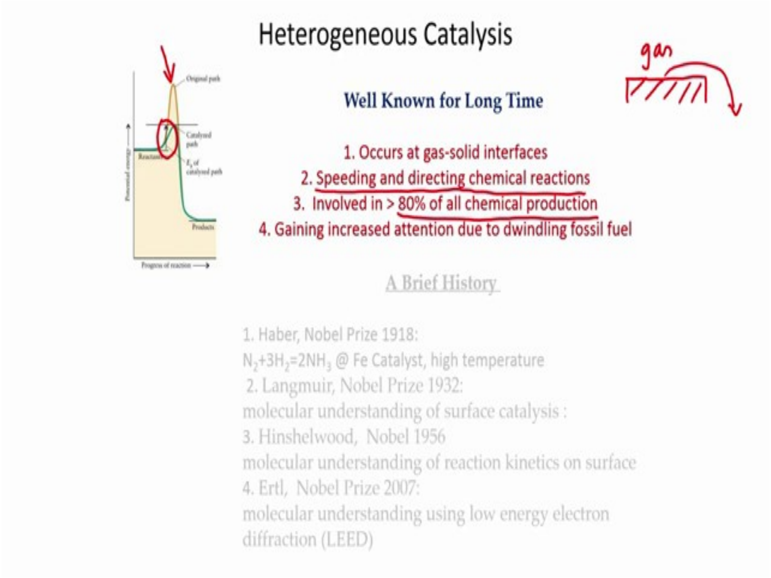

Heterogeneous Catalysis

Well Known for Long Time

1. Occurs at gas-solid interfaces
2. Speeding and directing chemical reactions
3. Involved in > 80% of all chemical production
4. Gaining increased attention due to dwindling fossil fuel

A Brief History

1. Haber, Nobel Prize 1918:
N_2+3H_2=2NH_3 @ Fe Catalyst, high temperature
2. Langmuir, Nobel Prize 1932:
molecular understanding of surface catalysis :
3. Hinshelwood, Nobel 1956
molecular understanding of reaction kinetics on surface
4. Ertl, Nobel Prize 2007:
molecular understanding using low energy electron diffraction (LEED)

So, we will begin with a short, very short introduction to the heterogeneous catalysis. Heterogeneous catalysis is something which is known for a long time. It is actually done on a; in general it is done on a solid gas interface; but it could be solid liquid interface as well. So, I have a solid surface, I have a gas medium; and then at the interface, at this interface some reaction will occur and generally the catalysis, the by definition catalysis will always decrease or suppress the energy barrier.

So, if a particular reaction having energy barrier of this level; if we use a catalyst, what it does; it decreases the energy barrier and increases the reaction rate. So, this is the role of catalyst. And in the end of the reaction catalyst can be recovered as, so that it can be cycled several times. So, it actually speeds up and directs chemical reaction. Heterogeneous catalysis, it more than 80 percent of chemical production, all chemical production actually are based on heterogeneous catalysis.

And, currently heterogeneous catalysis is gaining increased attention due to decrease in fossil fuel resources. So, as we know that we are consuming fossil fuels, coal, natural gas or oil all the time for the benefit of humankind for the industrialization; but at the same time we have to understand that it is finite resources. They are finite resources and we have to improve the procedures by which we can increase the sustainability and for that heterogeneous catalyst is going to play an important role.

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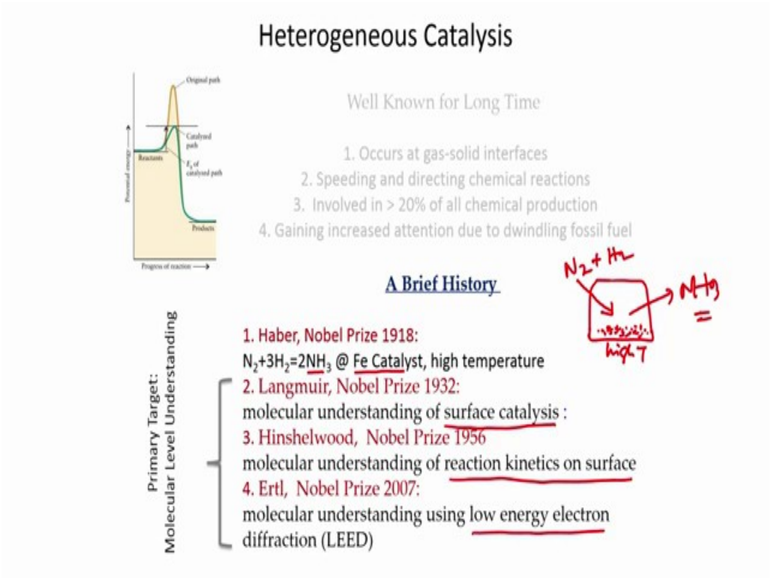

Heterogeneous Catalysis

Well Known for Long Time

1. Occurs at gas-solid interfaces
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A Brief History

Primary Target: Molecular Level Understanding

1. Haber, Nobel Prize 1918:
$N_2+3H_2=2NH_3$ @ Fe Catalyst, high temperature
2. Langmuir, Nobel Prize 1932:
molecular understanding of surface catalysis :
3. Hinshelwood, Nobel Prize 1956
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molecular understanding using low energy electron diffraction (LEED)

Now, this heterogeneous catalysis is known for a long time; it is probably more than 100 years. It may, we may say that heterogeneous catalysis, the idea of heterogeneous catalysis it started with the, this started with Haber ammonia synthesis. Ammonia was synthesized from nitrogen and hydrogen. So, what Haber did at a little high temperature; Fe catalysts, he used Fe catalyst; he actually used many catalyst and then found Fe to be active for this reaction.

So I have a chamber, in this chamber I have now iron part, finely dispersed iron material I have, and then if I inject N2 and H2 at high temperature. So, if I increase the temperature as well at high temperature, then it produces ammonia.

And ammonia is an important product. Ammonia was important product, because ammonia is directly used to synthesize urea and urea is a fertilizer. So, this reaction, ammonia synthesis reaction revolutionized the way we think of cultivation and food production as well, that is why this is a very important reaction and it was discovered by Haber.

And, this discovery was can be considered to be the starting point of the Era of heterogeneous catalysis. Then after we realized that, heterogeneous catalysis could be an interesting pathway and a very important pathway to for the chemical synthesis; fundamentally many scientists started looking at the meaning of different aspects of heterogeneous catalysis. For example, Langmuir; Langmuir tried to understand the surface catalysis fundamentally at the molecular level. Then Hinshelwood, tried to understand reaction kinetics on surface, how the heterogeneous catalysis are going on the surface. And recently Ertl also try to understand catalytic reactions with the help of low energy electron diffraction.

So, there are many scientists, these are the few names I have documented here; but there are many scientists who were involved in understanding heterogeneous catalysis at the fundamental level. So, with this very rich history, the first question comes to our mind; this is already 100 years old subject.

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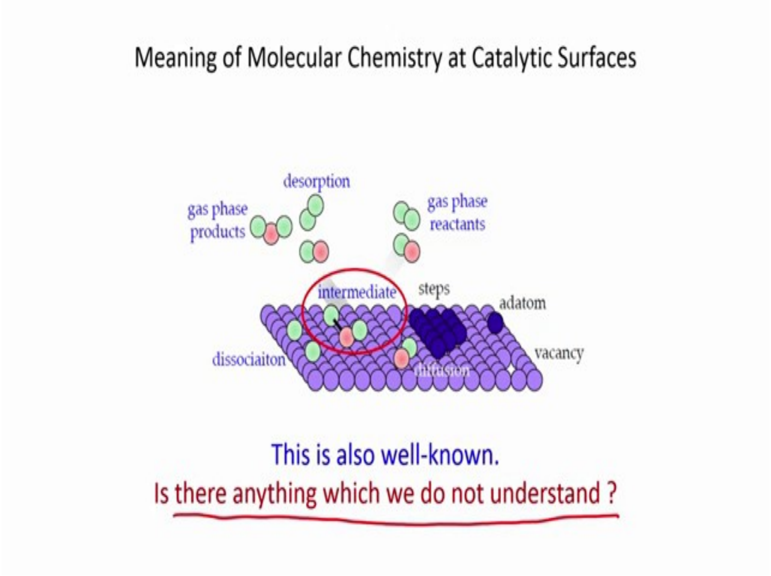

Meaning of Molecular Chemistry at Catalytic Surfaces

This is also well-known.

Is there anything which we do not understand ?

So, what is; what we have understood from this from all the contributions taken from last century. The understanding we have is that at the surface we may have different structures; structures like I can have vacancy, I can have adatom, I can have steps these are the surface structures I can have.

Molecules can be on the in the gas phase and that gas phase molecule can be adsorbed on the surface, they can be diffused also, they can undergo dissociation; and then on the surface it can actually react and form the product and then it can go out of the surface. It can undergo desorption to form the gas phase product. So, many details are now known for the heterogeneous catalysis.

And because they are known and they are kind of an textbook study currently; we all know that heterogeneous catalysis what does it mean, what is the, how catalysts works, and what kind of kinetics it follows many actually are known in terms of class textbook studies. And given this 100-year-old history, the first question is that; is there anything we do not understand currently or what part of heterogeneous catalysis is unexplored mostly. And that is an important question, because if a subject is having 100-year-old history; then question is there any anything we do not understand, or we have some lack of understanding in heterogeneous catalysis.

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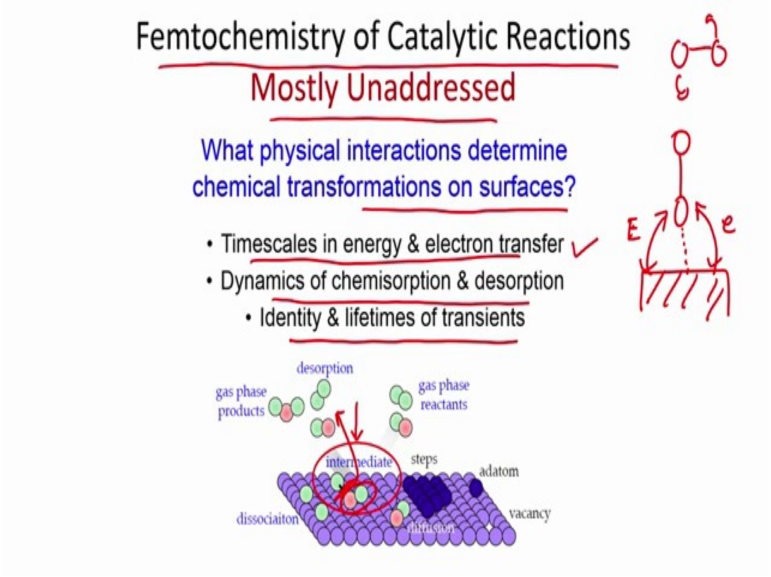

Femtochemistry of Catalytic Reactions

Mostly Unaddressed

What physical interactions determine chemical transformations on surfaces?

- Timescales in energy & electron transfer ✓
- Dynamics of chemisorption & desorption
- Identity & lifetimes of transients

Now in my opinion as I told you, this is an account of my perspective of looking at heterogeneous catalysis; and in my opinion femtochemistry of catalytic reactions mostly unaddressed. Femtochemistry of catalytic reactions, we know femtochemistry or does it mean; we are looking at the chemistry at the level of when the bonds are breaking.

So, if you look at the intermediate, this is kind of a transition state let us say; in this intermediate, the molecule which is sitting on the surface they are breaking the bond. Let us say this bond is broken and then this molecule will be desorbed after breaking that bond. So, femtochemistry; the role of femtochemistry is to capture that moment when the molecules are dissociating the bonds or forming the bond. So, to capture that; and to study the catalytic reaction at that level, when molecules are breaking, molecules are forming on the surface that is kind of a regime where I believe that we have lack of understanding.

So, in other words, if I rephrase the question is that what physical interactions determine chemical transformations on surface, this is an important question which we would like to understand. Timescales in energy and electron transfer, so if I have to give a definition of catalysis; I look at the catalysts, a catalytic process from a energy and electron transfer perspective.

So, I have let us say I have a surface, on the surface I have a molecule sitting on the surface; and in my opinion at the molecular level catalysis is nothing but the energy and charge exchange between the substrate and the absorbate. So, this is e and this is E; capital E is the energy and the small e is the charge, it which is exchanged between the adsorbate and the substrate. So, question is what is the time scale of such energy and electron transfer? That is an important question; then if there is a time scale known, then what is the dynamics, typical dynamics of chemisorption and desorption.

One can say that, when the molecule’s is dissolving, molecule is heavily rotating that can also possible let us say. Question is, do we know what is it, what kind of rotational energy it gains, after it leaves the surface. So, these are the dynamics, dynamical information one should gather. And then identify in life terms of the transients; transients the intermediate, which will not live for a long time, which will be transiently appearing on the surface. And can we capture those structures to identify the transients.

So, these are the important questions and, because catalysis is a big subject right now; it is a really a big subject, because the contribution came from different scientists in this field for last 100 years is enormous. And chemical engineer are working on catalysis, material metallurgy or material scientists are working on catalysis, in organic chemists are working on catalysis, physical chemistry is also working on catalysis.

The part of the catalytic work, catalytic process which we are capturing in this particular module is mostly the very molecular level catalytic process in the ultrafast domain.

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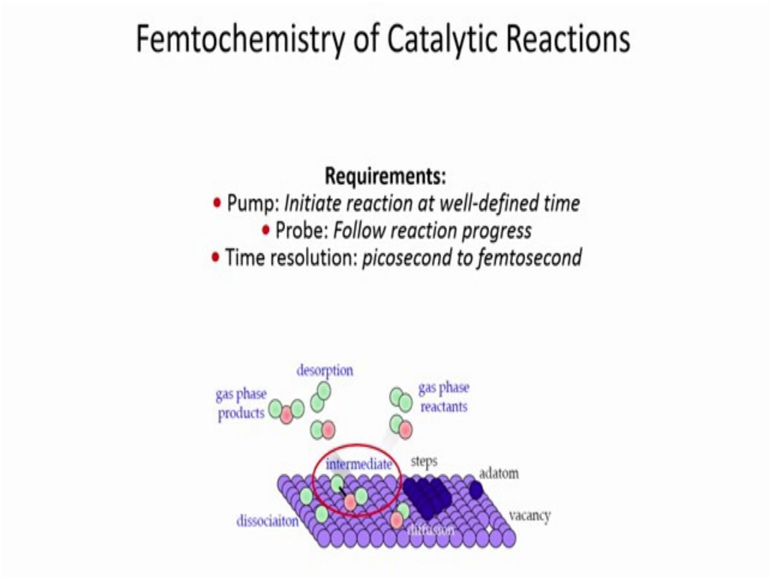

Femtochemistry of Catalytic Reactions

Requirements:

- Pump: *Initiate reaction at well-defined time*
- Probe: *Follow reaction progress*
- Time resolution: *picosecond to femtosecond*

Now, any ultrafast process which we study, we definitely need a pump probe scheme that we have already convinced ourselves in this class. A pump will initiate the process, which means, it will be it will trigger the process; and probe will follow the system or integrate the system to find out how far the system has remembered the initial excitation.

So, let us say I have a molecule, I initiate the process, dissociation process with the help of pump and then molecules is dissociating and my task could be to capture individual frame at different time with respect to the pump excitation. So, this is called pump probe scheme or flash photolysis scheme developed by Norrish and Porter. This pump probe scheme needs to be followed; but when we think about pump probe scheme needs to be followed in catalytic process, we face a big problem and a dilemma.

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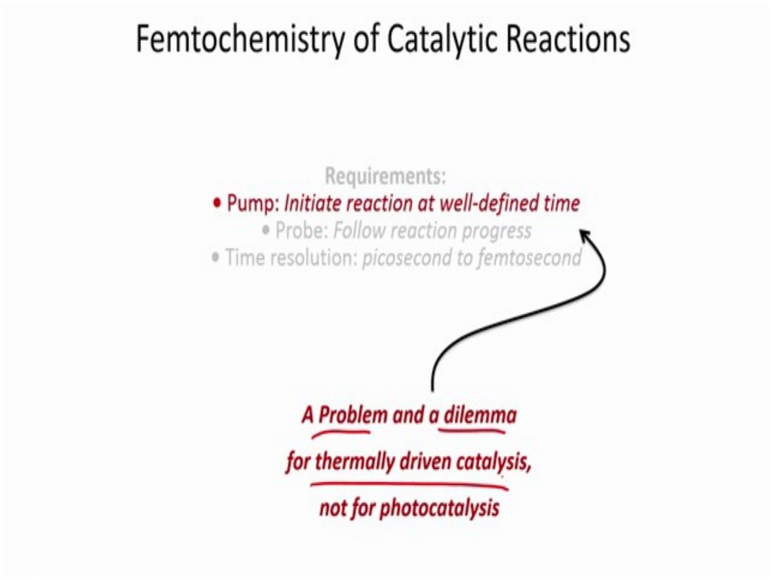

Femtochemistry of Catalytic Reactions

Requirements:
- Pump: *Initiate reaction at well-defined time*
- Probe: *Follow reaction progress*
- Time resolution: *picosecond to femtosecond*

A Problem and a dilemma
for thermally driven catalysis,
not for photocatalysis

The big problem and a dilemma; what is that problem? The problem is that, when we initiate a reaction at a well-defined time. So, pump and probe gives a time window; the capturing time is actually time between the pump and the probe. So, most of the femtosecond laser systems are an optical pulse, and if it is an optical pulse; then I am actually electronically exciting.

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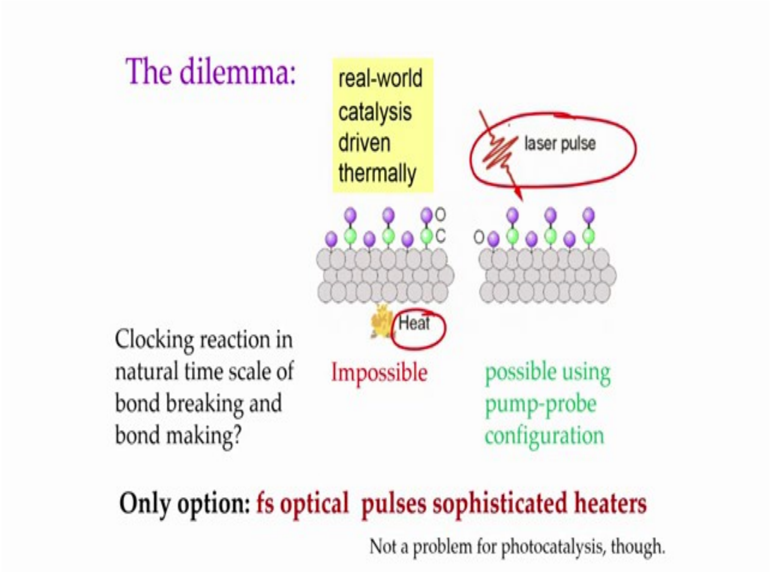

The dilemma:

real-world catalysis driven thermally

Clocking reaction in natural time scale of bond breaking and bond making?

Impossible

possible using pump-probe configuration

Only option: fs optical pulses sophisticated heaters

Not a problem for photocatalysis, though.

Or every optical pulse will create electronic excitation or let us say, vibrational excitation is also possible; but there is a problem, the problem is to be clarified here first. Most of the catalytic reactions is driven using thermal energy currently.

There is another part of catalysis, which is called photo catalysis. In photo catalysis we reduce the reaction barrier with the help of photon energy. So, we electronically excited. So, photo catalysis is acceptable; if it is a photo catalyst, then we can use an optical pulse on one laser pulse to initiate it. But most of the catalytic reactions which are carried out industrially, they are driven by thermal energy; which is nothing but the heat energy.

So, all we need to do is that, when we will use ultra fast pulse; our pulse has to deposit the energy not well-defined time window. If we use a thermal heating, we cannot define the time; at what time we have started and what time we have stopped it. There is no way one can control it; but if we use femtosecond pulse, then we can actually control the time at what time I have deposited the heat energy, and at what time I have to monitor the subsequent reaction. So, this is the whole idea.

And the dilemma comes, when we think about creating heat energy with the help of femtosecond pulse. And how far it is legitimate to consider that; yes, femtosecond pulse will create the heat energy; because if we can create heat energy within that time scale, then we can get the time window and we can deposit the heat energy. So, in the end what is going on, there is a question; question is that pump probe spectroscopy requires clocking a reaction in the natural timescale of bond breaking and bond formation, which is femtosecond timescale, because within femtosecond timescale I have to deposit the heat energy.

Now, if I use let us say any kind of heat like wood fire or anything, I cannot control the heat energy deposition within the femtosecond time scale; it will be always second, millisecond something like that. So, in order to create that time window and deposit the heat energy in a well-defined time window, I have to use femtosecond pulse.

So, the first question is what it does to the substrate? Let us say I have a metal surface, let us say I have metal surface of 10 millimeter by 10 millimeter one metal surface I have. And one femtosecond pulse, one pulse is hitting the surface; what will happen to that surface that is the first question we have. If we look at one interesting example is that instead of femtosecond pulse hitting the surface, we will think about.

If I take a surface, let us say; I take up metal surface, let us say gold surface or silver surface and I take hydrogen atom, I have created hydrogen atom and I am just taking it is like a cricket, I take one ball and then hit the surface. So, I take hydrogen atom, hit the surface; if I keep doing it then what will happen, this surface will be electronically excited, this is exactly what is shown here is called chemicurrent.

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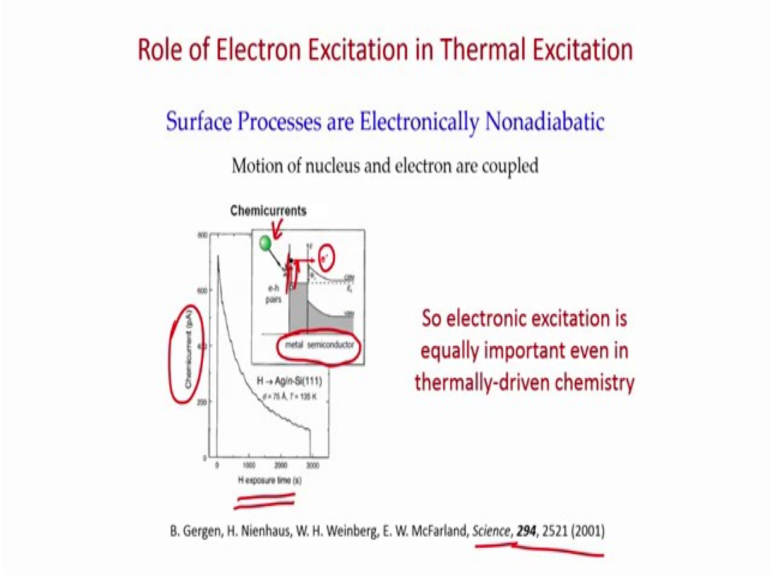

Role of Electron Excitation in Thermal Excitation

Surface Processes are Electronically Nonadiabatic

Motion of nucleus and electron are coupled

So electronic excitation is equally important even in thermally-driven chemistry

B. Gergen, H. Nienhaus, W. H. Weinberg, E. W. McFarland, *Science*, ***294***, 2521 (2001)

So, if I consider this metal semiconductor interface, they have there in this experiment the authors have taken this is the publication they have. The authors was hitting with an atom, the surface of metal surface; and when it is hitting the metal surface, it is actually exciting electron and this electron is coming to this is crossing this schottky barrier, and then they are seeing this electron flow is nothing, but the current and that current they are seeing as a function of hydrogen exposure time.

This is an important observation; what does it mean by this observation? I have hydrogen atom, which is hitting, as slow motion I am just trying to find out one hydrogen atom slowly hitting the surface. When it has hit the surface, then what is going on, there is an electronic excitation going on in the metal surface. So, approaching, hydrogen atom approaching the surface; this is nothing but nuclear motion. This nuclear motion is exciting the electron in the metal surface; which means, electronic is getting coupled with the nuclear motion. And that is why every surface reaction is actually electronically non-adiabatic reaction; electronically non-adiabatic, when we call electronically non-adiabatic, when electronic motion which is naturally they are faster than the nuclear motion.

But, sometimes electron can be slowed down and it can be comparable in the motion with the nuclei. So, there are two particles in any matter, any cons matter we consider gas state, solid state or any matter. There are two-part constituent particles; electrons and nuclei, they are the two constituent particles. Nuclei is heavy, is like an obeys and is a heavier mass. So, that is why it is goes very slowly; and electron is very fast, because it is lighter mask, so it will move very fast.

Now, if something is moving very fast and something is moving very slowly, they will not be coupled, they will never be coupled, their motion will never be coupled; but in order to be coupled with each other their motion needs to be comparable. And this comparable motion will make electron and nuclei both coupled with each other, this motion will be coupled with each other, it is a joint motion.

Now what happens on the surface; if I have a hydrogen atom hitting the surface, this is nuclear motion, this nuclear motion is inducing electronic motion in the metal surface, this may happen only when this nuclear motion is coupling with the electronic motion, they are comparable. So, on the surface it has been found that all reactions are actually electronically non-adiabatic reaction. And, when I have electronically non-adiabatic reaction, then I take this analogy and will be able to find out different processes.

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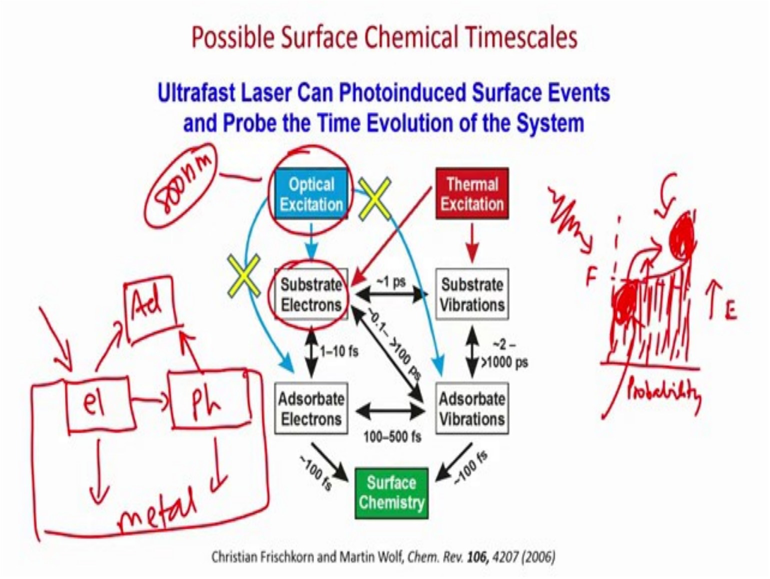

Possible Surface Chemical Timescales

Ultrafast Laser Can Photoinduced Surface Events and Probe the Time Evolution of the System

Christian Frischkorn and Martin Wolf, *Chem. Rev.* **106,** *4207 (2006)*

Processes for example, I can use the optical excitation; I can use the optical excitation, still it is an optical excitation and this optical excitation can excite substrate electron. Because it cannot excite substrate phonon, because generally optical excitation is done at 800 nanometer, this is the substrate phonon can be excited, but we have to go for that terahertz or some other frequency. Phonon frequencies are very very low frequency. So, we have to go for some other regime; optical regime generally in the UV visible IR regime.

And UV visible IR regime if we use, they will never excite the phonon, they will excite only a substrate electron; because we have let us say Fermi level distributions like this, this is Fermi level distribution of a metal. And this is the Fermi level, let us say this is at a particular temperature and this is energy and this is the probability same. So, this is for metal distribution, this is the Fermi level. Now, what might happen; this is the unoccupied state, this is the occupied state that is why this is occupied, these are all occupied with a lot of electrons, let us say more than amagat a number of electrons are occupied by all these states that occupied.

Now, what happens when femtosecond pulse interact with this electron, suddenly chunk of electron, this chunk of electron will be excited to the unoccupied state, this will be going to the unoccupied state. And this can happen at any frequency, because this energy does not need to be always single photon process, it can be multiple in process as well.

So, electrons are in inner metal, when I have a metal surface and when I have a pulse hitting the surface always that optical regime, in the optical regime we are exciting electrons. And those electronic excitations will now transfer their energy. So, I have now coupled heat bath; I have electronic bath, a metal surface can be viewed as a coupled heat bath. All electrons collectively electronic heat bath and all phonon considered to be phonon at the ionic core, all phonon are collectively called the phonon bath let us say, and they can excite energy.

Now, I have initially deposited energy in the electron bath of the metal; this electron bath of the energy in the electron bath will be transferred to the phonon. And then electron can directly transfer to the absorbate, and absorbate or phonon can directly transfer energy to that absorbate. Or electron can transfer to the bulk or phonon can be transferred to the bulk of the metal surface. So, this is the metal part, this part is metal part.

And this is more a commonly accepted processes in the surface; how the femtosecond pulse is interacting with the metal surface. Now, as we have stated already that the substrate electron will be excited not the phonon with the help of optical pulses; that can transfer energy to the substrate vibration, that is the phonon vibration, adsorbate electron can be excited directly, and then absorbate vibration also can be excited.

And they can be coupled, every process are coupled, highly coupled and it is very difficult to say which one will be initiated after what; they can be overlapping in terms of time. And in the end, once we have deposited energy to the adsorbate electron or adsorbent vibration; then we observe the surface chemistry, because surface chemistry is nothing but the chemistry going in the molecules which are adsorbed on the surface.

So, I have a surface, on the surface there are molecules sitting on this and as long as we have energy in these absorbate, this absorbate will react; but first deposition of energy is going on through the substrate, because it is more like you can view it like a ocean of electron. A big ocean you have and absorbate are nothing but few couple of boats floating on that ocean. So, anything which is hitting the ocean first, it will hit the water of the ocean, it will not hit the boat; and then boat will slowly gain the acceleration or whatever the agitation from the ocean surface, it is more like that.

When I have a metal surface, microscopically they have lot of electrons; I mean amagat number of electrons are sitting on that metal surface. So, when optical pulse and then there is a adsorbate sitting, adsorbate are also sitting there; but absorbates are more like few boats on our ocean. And then optical pulse is hitting it, it will only see the electrons of the metal and that is why substrate electron will be excited first with the help of the photo excitation.

Now, these are the processes we have and thermal process on the other hand, this is the thermal excitation which is used in the industrial catalytic processes. Now, if we look at the thermal process, then we see that the thermal process is also exciting electrons; this is thermal process, thermal process is also exciting electron. And this is very unique in terms of molecular chemistry. In a molecule when you say that, we are hitting the molecule, we are increasing the temperature of a molecule, we never say that we are undergoing electronic transition; it is only vibrational transition we undergo for a molecule. So, that is a substrate vibration.

But on a surface, when you heat it up; if I take a metal and try to increase the temperature, I am actually increasing; I am electronically exciting the system as well. So, both electronic excitation and vibrational excitation going on simultaneously when we increase the temperature of a metal; but for a molecule when you increase the temperature it will never undergo electronic transition, it will only undergo vibrational transition.

So, initially vibration was like this and after depositing heat energy; if we heat it up, if we increase the temperature then vibration will be much faster. So, we are vibrational in exciting molecules; we will never electronically excite a molecule with the help of thermal energy. But on metal surface we actually do both, because they are coupled with each other; that experimental results we have already shown. That if I take a metal surface, and if I take a atom and if I hitting the metal surface like this way, just like cricket, playing cricket then what will happen in the substrate I am exciting electrons.

So, this is very unique and I repeat this of a statement; in a molecule when I increase the temperature we never electronically excite a molecule, we only vibrationally excite a molecule. But in a metal surface when we increase the, when we deposit the heat energy, when you increase the temperature we actually undergo both electronic transition and vibrational transitions. And this catch, this little information will be helpful for us; because now we can connect the real life catalysis and the femtosecond laser induced catalysis.

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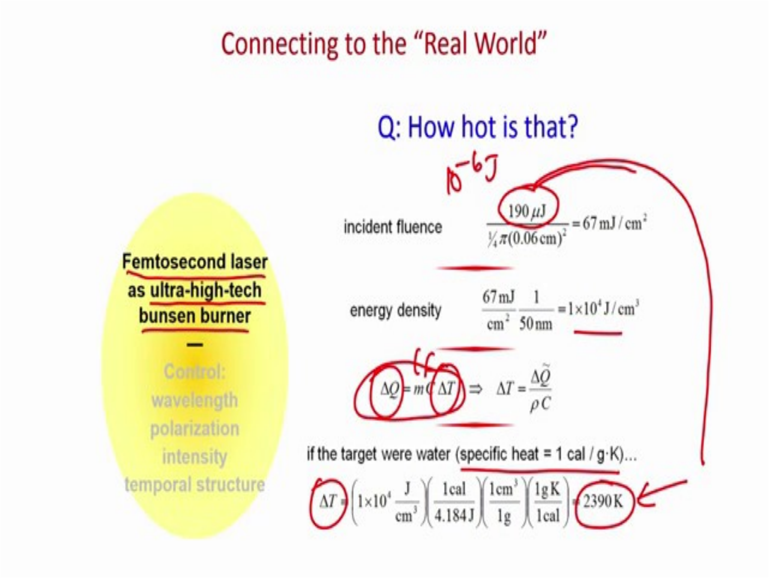

Connecting to the "Real World"

Femtosecond laser as ultra-high-tech bunsen burner

—

Control:
wavelength
polarization
intensity
temporal structure

Q: How hot is that?

$10^{-6}J$

incident fluence $\frac{190\,\mu J}{\frac{1}{4}\pi(0.06\,\text{cm})^2} = 67\,\text{mJ/cm}^2$

energy density $\frac{67\,\text{mJ}}{\text{cm}^2}\frac{1}{50\,\text{nm}} = 1\times10^4\,\text{J/cm}^3$

$\Delta Q = mC\Delta T \Rightarrow \Delta T = \frac{\Delta\tilde{Q}}{\rho C}$

if the target were water (specific heat = 1 cal / g·K)...

$\Delta T = \left(1\times10^4\frac{\text{J}}{\text{cm}^3}\right)\left(\frac{1\,\text{cal}}{4.184\,\text{J}}\right)\left(\frac{1\,\text{cm}^3}{1\,\text{g}}\right)\left(\frac{1\,\text{g K}}{1\,\text{cal}}\right) = 2390\,\text{K}$

So, in the end what we see that, the femtosecond laser is behaving just like an ultra-high-tech Bunsen burner, this is the way one of my advisors in Brookhaven National lab, used to call it is a Bunsen burner. So, in this talk, we have never actually discussed, in this class we have never discussed that how femtosecond laser can be used in micro machining or micro or making a hole.

If we increase the temperature; so basically if I take metal surface and if we direct the laser beam to the metal surface, at a particular intensity it can actually drill a hole. And drilling that hole can be very very controlled; that is why micro machining can be done very nicely with the help of a second laser. And what is the basis of this micro machining? It is the heat energy deposition. So, that is exactly what we are going to do here, we want to deposit the heat energy.

And question is how much how hot it can be; I mean that is an important question. So, if we consider 190 micro Joule per pulse energy that is the very nominal energy, most of the ultrafast laser laboratory is using that 190 micro Joule per pulse energy. If we take that energy and if we focus that beam; then what will happen? Looking at the energy density and then if we focus that beam in an water target; water is like H2O water; if we take the water target, then specific heat of water is 1 cal per gram per Kelvin.

So, if we take that and then if we use this Delta Q m C T that is the very 12 standard equation; which we know that in order to increase the temperature you need heat energy.

So, this is the heat energy deposition, this is the temperature jump you have. And mass and C are known that is why one can actually do that calculations; and finally, one gets that, with the help of 190 micro Joule pop house energy, as I told you this is a very nominal energy this energy can go to milli Joule, can go to Joule even, right now.

But if we take micro Joule, which is 10 to the power minus 6 Joule per cell; then we can increase the temperature by 2000 Kelvin temperature; 2000 Kelvin temperature is a huge change in temperature. Most of the metal will melt above this temperature, in this temperature; because most of the metal having melting point temperature near about 1700 to 1800 Kelvin temperature.

So, if we go to this temperature, this temperature jump can be achieved with the help of very very low energy of the femtosecond pulse. So, say, it is a big hitter which can deposit heat energy to the system and it behaves like a Bunsen burner. But the problem with Bunsen burner, you cannot control the energy; at what time I want to give the energy and then stop the energy. This time duration cannot be controlled with the help of Bunsen burner.

Just like a gas lighter, if you know in our at home, in our oven when we lit the gas; then we know that it is ignited and the flame we see, the blue colored flame we see. But can we control that, can we say that I will turn on the blue color flame for 1 femtosecond; no, it is not possible, I can turn it on and then turn it off quickly manually and that will probably give me 1 second duration. So, I can heat a particular substrate with the help of a gas lighter and the knob, turning on the knob for 1 second; I can do it on off, this duration can be one second at the best.

But, what I need in this process, in the to explore femtochemistry of nanocatalysis; I have to deposit that energy, heat energy for let us say 100 femtosecond, 10 to the power minus 15 second and that is possible with the help of this femtosecond pulse. And we see that femtosecond can actually deposit huge amount of heat energy with the help of very nominal pulse energy, and temperature jump can be of the rough 2000 Kelvin. So, with this idea that femtosecond pulse can be used for the deposition of heat energy, we will move on, we will go, we will learn to pulse correlation spectroscopy in the next class.

We will stop here and we will go over the rest of the slides in the next class.