Laser: Fundamentals and Applications
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Lecture - 37
Laser Induced Chemistry and Ultrafast chemical Dynamics

Hello and welcome back. So we were discussing about the application of lasers in chemistry, laser induced photo chemical processes and we were particularly talking about unimolecular laser induced reactions.

So, I will start with another example. So in the last class we stopped where we discussed about the conversion of this 7 the hydro cholesterol, to drive it pre vitamin d 3 and its conversion to finally d 3.

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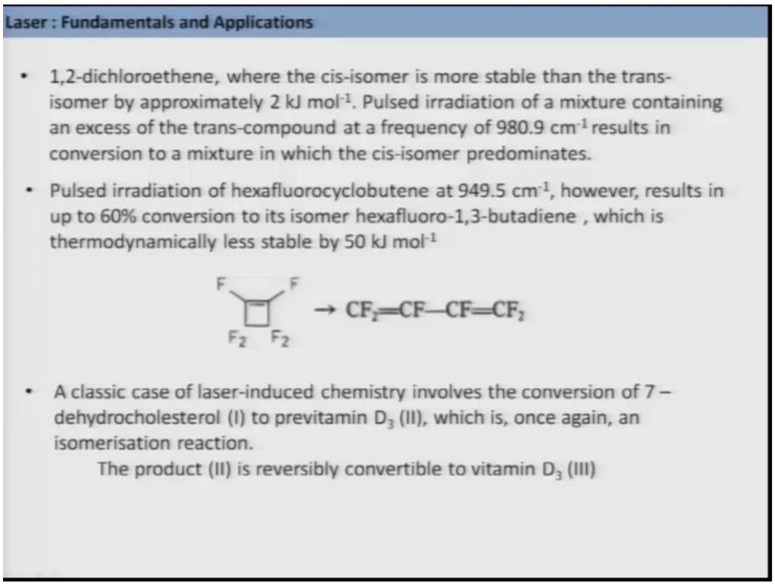

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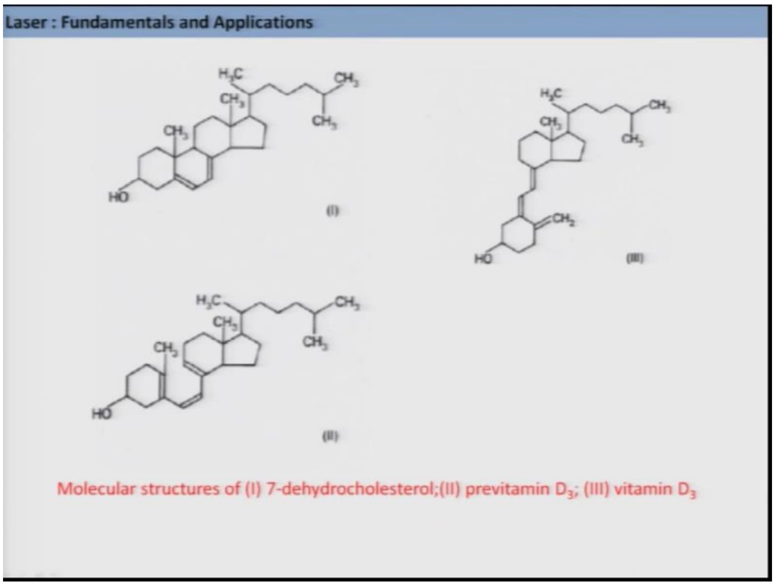

And these are the chemical structures of those 3 molecules.

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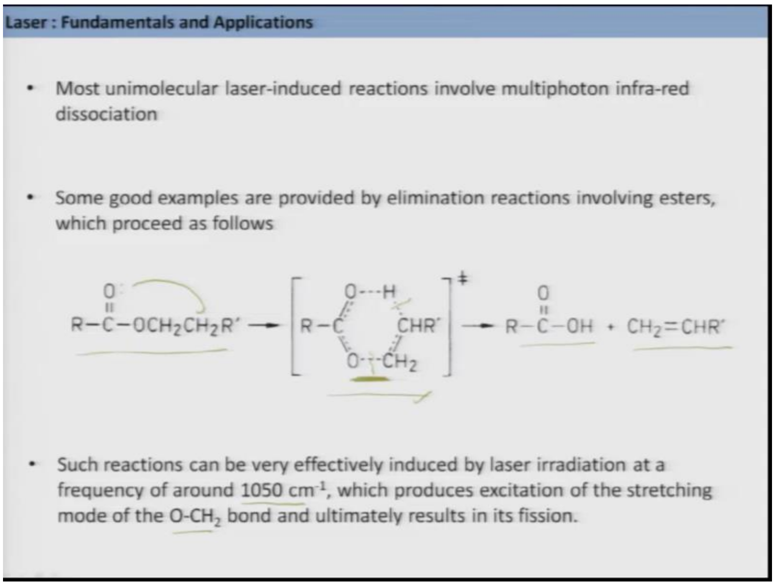

Now most unimolecular laser induced reactions involved multiphoton infrared dissociation. Let us get some good examples, so one good example is the elimination reaction involving esters which process as shown in this scheme. So, you have an ester, so it is like C double bond O and O R, are is an alkyl group, and this is the transition state.

So, when you know excite this molecule by laser of particular wavelength it you know goes to the excited state and the excited state structure is something like this, which is a transition state or here I will call it like a intermediate, and here what happens this you know essentially this part is going here right. So, this oxygen lone pair it can actually attack here and you get something like this structure and in the next step what happens this hydrogen is abstracted by this OH then this bond is broken right and this bond is also broken and this becomes, C double bond O and this is what we get, we get an acid and we get an alkene.

So, this is an elimination reaction and this is an example of an unimolecular reaction induced by laser, and not only that this particular reaction is achieved using multi photon excitation and this you know yield and selectivity of this particular product using the multiphoton excitation is really, really high and that is why one need to really care about the laser induced chemical reactions and this is of tremendous importance in industry as well.

Now, such reactions can be very effectively induced by a laser frequency of around 1050 centimeter inverse, which produces excitation of the stretching mode of O CH 2 bond. So, C O stretching that is specifically this bond I am talking about. So, it excites this one so if you know remember this potential energy diagram. So, essentially you are having this multi photon transition and then ultimately go here.

So, what it does it you know effect is the vibration of the C O bond and after some time the C O bond goes. So, far that that they are no longer within the same molecular and that is what exactly is this reaction you get C double bond O instead of this alkyl group attached to this oxygen, and you know that is what is the whole mechanism.

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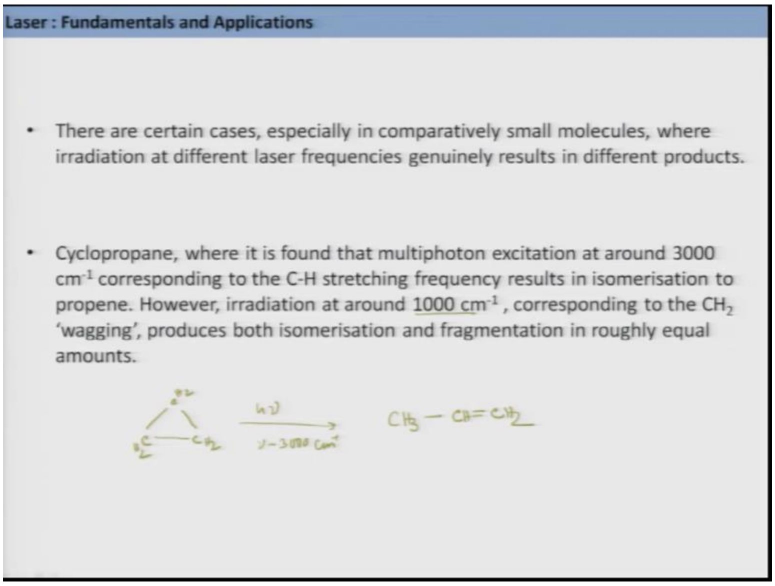

Now, there are certain cases especially, in comparatively small molecules where irradiation at different laser frequencies generally results in different products. So, which is you can understand how important that can be a cyclopropane which is like this. So, the cyclopropane, where it is found that multiphoton excitation at around 3000 centimeter inverse corresponding to the CH stretching frequency result in isomerization to propene.

So, if you excite it by you know photon where nu is approximately 3000 centimeter inverse this will lead to the stretching of CH bond and because of that you end up getting propene, which is CH3 C double bond C this ok. So, now that is for this 3000 centimeter inverse, but if you irradiate at around 1000 centimeter inverse corresponding to the CH2 wagging.

So, we were talking about the CH stretching now if you talk about the CH2 moiety. So, you have essentially C and H and H right. So, this one this movement is known as wagging and that produces both isomerization as well as fragmentation in roughly equal amount. So, some amount you will get this propene which is isomer also you can, you know break into products like you know methane and you know ethylene stuff.

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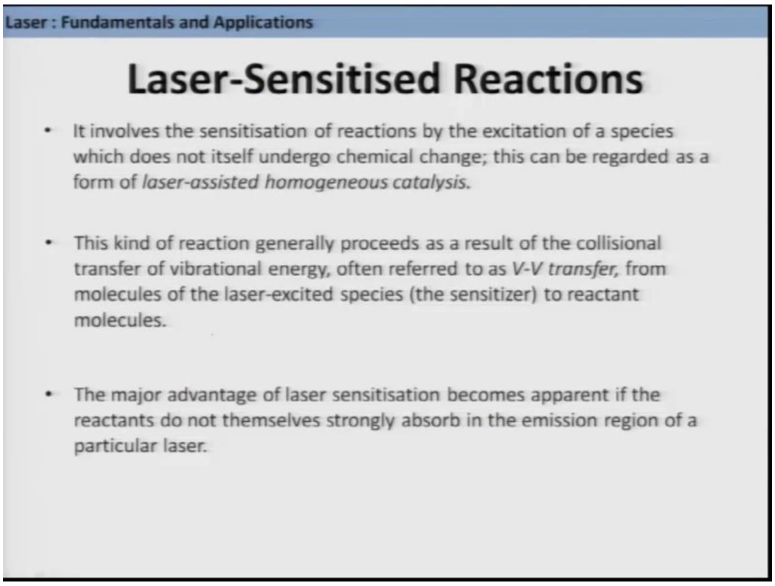

Next we will look into the laser sensitized reaction, which is you know really, really important not only in chemistry, but also in you know medical sciences. So, this laser sensitizes reaction it involves the sensitization of reactions by the excitation of a species which does not itself undergo the chemical change.

So, this can be regarded as a form of laser assisted homogeneous catalysis. Now this kind of reaction generally proceeds as a result of the collisional transfer of vibrational energy often refer to as vibrational, vibrational transfer from the molecules of the laser excited species that is a sensitizer to the reactant molecules.

So, if I put it in a nutshell then what it is? Then I have some molecule which takes up the light energy from laser and then gets excited, now this guy does not do anything other than transpiring this energy to another molecule, which is the real reactant and then it you know proceeds toward the overall reaction.

So, this guy again comes back and then again do that job which is pretty much similar to you know a catalyst the role of a catalyst that is played in a homogeneous catalytic reactions, and the advantage of this laser sensitization is it will be clear if the reactants do not themselves strongly absorb in the emission region of the particular laser, this is you know quite easy to understand.

So, it is the photosynthesis which will absorb and not the reactants. So, reactants are kind of transparent to this laser wavelength that is being used, so if you do not use that light no reaction will process you know happen, once you use the particularly laser frequency this photosensitizer will absorb go to the excited state transfers its energy and the reaction will proceed.

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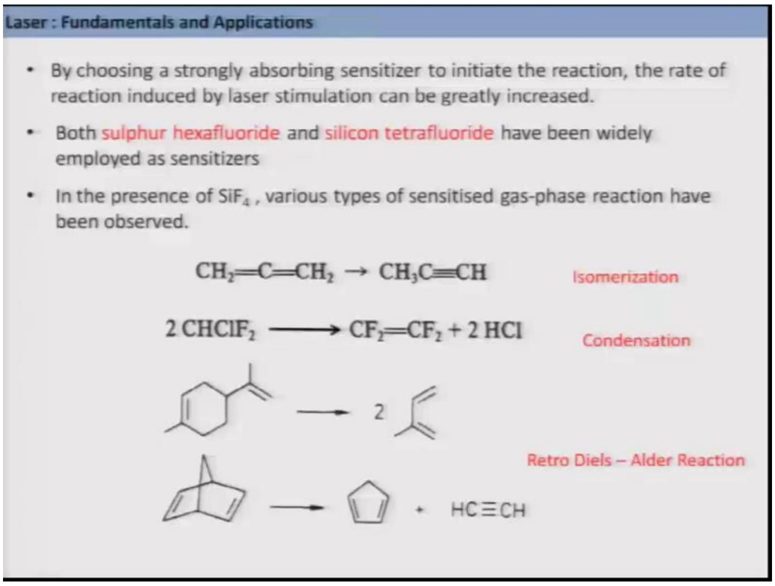

If you can choose a strongly absorbing synthesized to initiate the reaction the rate of the reaction induced by laser stimulation can be greatly increased, now a couple of sensitizers which are widely used is sulfur hexafluoride or a SF 6 and silicon tetra fluoride or SIF 4.

In the presence of this silicon tetra fluoride various types of synthesized gas phase reactions have been observed one example is here. You have an allene molecule here and this allene is you know isomerized into this propyne or methyl acetylene. And then, if you take this chlorofluoromethane and you excite it you know, you excite the sensitizer SIF 4 by a suitable laser light, then you get this reaction where two molecules of HCL comes out from this reaction and this is known as a condensation reaction chemistry and the next two examples, are essentially the example of Retro Diels-Alder Reaction.

So, you essentially excite SIF 4 and SIF 4 transfers energy to this molecule, which then breaks apart into you know two molecules one is diene and another is diene file as they call it in chemistry.

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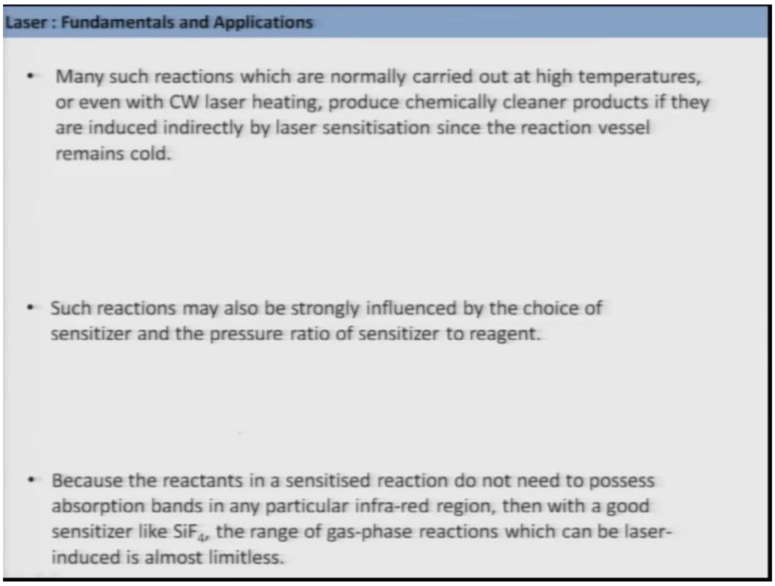

And many such reactions, which are normally carried out at higher temperature, so this you know Retro Diels-Alder Reaction that I talked about the opposite to that has Diels reactions you require lot of heat, in order to you know get this reaction going.

So, you know mean this is kind of reaction which normally carried out at high temperatures or with you know using a laser heating process, when you use laser it produces chemically cleaner products, if they are induced you know by a sensitizer which absorbs a laser light, because you really do not you know you know produce heat due to this you know in any way during this reaction sensitized by say SIF 4, and such reactions may also be strongly influenced by the choice of synthesizer of course, and the pressure ratio of sensitizer truly agent.

So, these are two important things that people should keep in mind while proceeding for a chemical photochemical reaction initiated by the laser light absorption of a sensitizer, because the reactants in a sensitized reaction do not need to process posses absorption band in any particular infrared region, then with a good sensitizer like SIF 4the range of gas phase reaction in which can be laser induced is almost limitless, that is a biggest advantage because I, you know when I use a photosensitizer and if I have a good photosensitizer, then I really do not care about whether my reactants are going to absorb in the particular you know laser wavelength or not this is really a big advantage, and which is provided by the existence of a photosensitizer like silicon tetrafluoride or sulfur hexafluoride.

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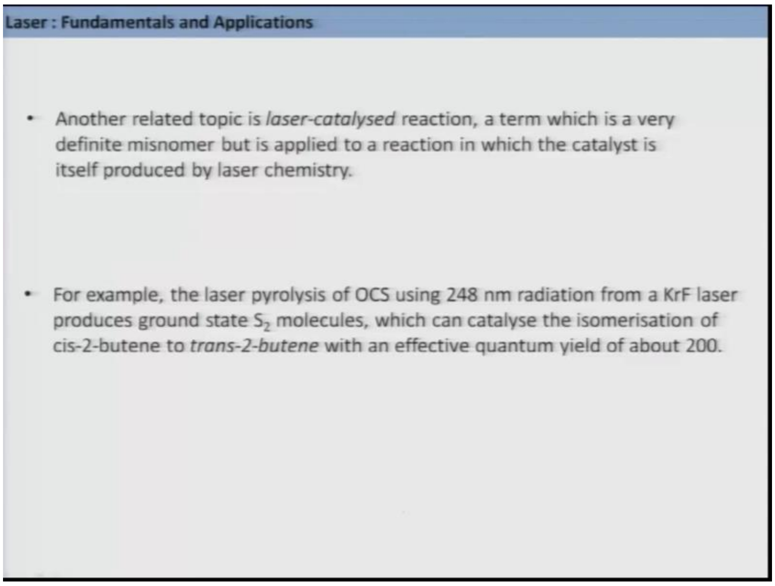

And another related topic is the laser catalyzed reaction this is a term, which is a very definite misnomer it does not need to be you know mistaken, but it is applied to a reaction in which a catalyst is itself produced in laser chemistry.

One example the laser pyrolysis of OCS using 248 nanometer radiation from a krypton fluoride laser, produces ground state is two molecules which can catalyze the isomerization of cis 2 butene to trans 2 butene with an effective quantum of about 200, which is a great amount. So, here you can see that the catalyst itself can be produced by a chemical reaction.

So, it should not be confused with the direct you know catalytic reaction, but actually the catalyst is being produced by the laser excitation and then that catalyst you know helps one reaction to precede this getting this s two molecule otherwise is very, very difficult ok.

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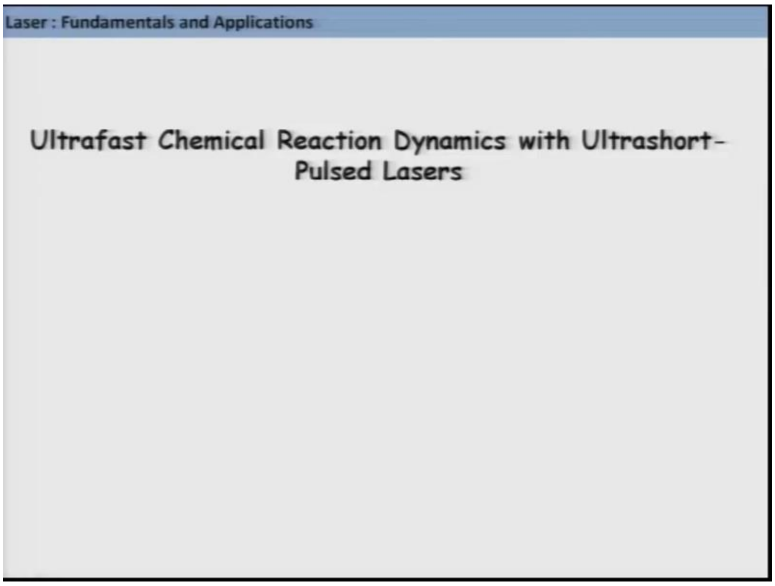

So, having discussed about those you know laser induced you know chemistries. Let us now draw our attention into another domain where laser is used to prove you know chemical reaction or you know very fast processes going on due to a chemical reaction. So, we will be talking about ultra first chemical reaction dynamics with ultra short pulse lasers.

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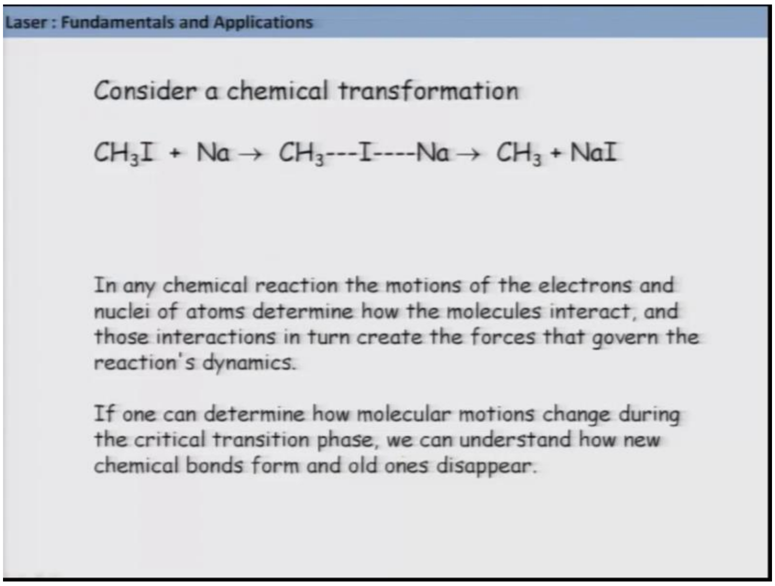

Now first let us consider a chemical transformation, which is given here on the screen is a methyl iodide reacting with sodium and ultimately CH3 radical and sodium iodide.

Now, I have two molecules and from there I generate another two molecules. So, the initial reactants and the final products the number of 4 and none of them are identical right. So, then there must be something happening some intermediate is being formed or the transition state are is being formed, how does the transition state look like how the transition state is evolved and from transition state how the product is evolved that one needs to understand this is of a fundamental interest and this is tremendously important, if we really want to you know understand the chemistry really well.

Now, in any chemical reaction the motion of the electrons and nuclei of atoms determine how the molecules interact, as I was saying and those interactions in turn create the forces that govern the reactions dynamics. Now our aim is to determine how this molecular motions change during, the critical transitions phase from reaction to product and we can understand how new chemical bonds are formed and old ones get broken.

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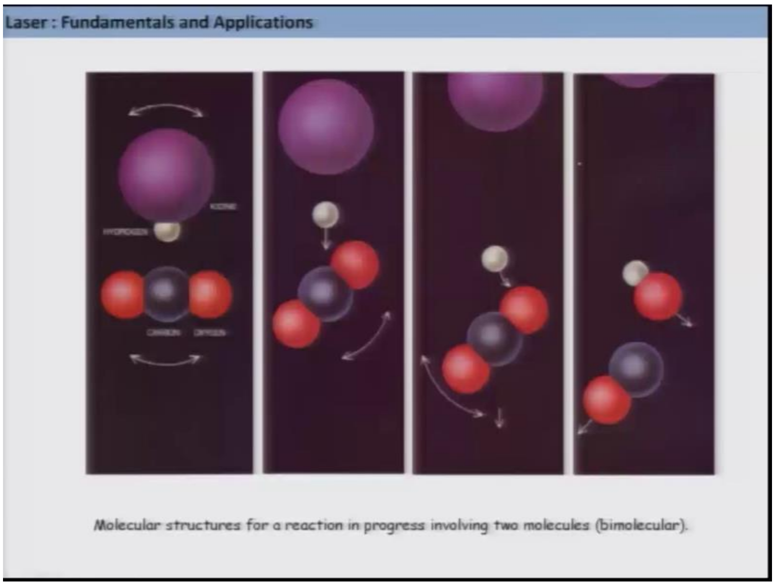

So, if this is the aim then we are essentially looking into something like this. So, here you have you know some snapshots, which are taken from some simulation result.

So, if you have a hydrogen iodide reacting with a carbon dioxide then how it reacts. So, the molecules they orient themselves in a particular configuration and then you know approach of two atoms you know toward each other happens and then detachment of certain part and formation of the new bond, and that is what is the final product?

So, here like you can see this hydrogen iodide that bond distance is altered and it goes and attacks this CO2 molecule and then CO2 orient itself in such a way, that this you know hydrogen is you know it attacks the oxygen molecule of the carbon and then it takes away the oxygen with it and then carbon is left with only one oxygen.

So, now this is from a simulation now, this is a by molecular process now how do I really visualize this one that is something which we would like to know.

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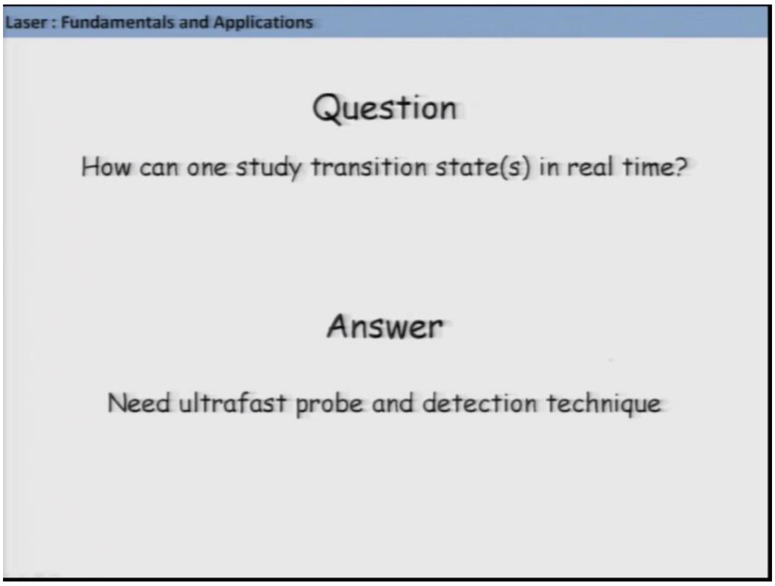

So, our question is how can one study the transition state in real time, now the answer to this question is that we need ultra-fast probe and ultra-fast detection technique.

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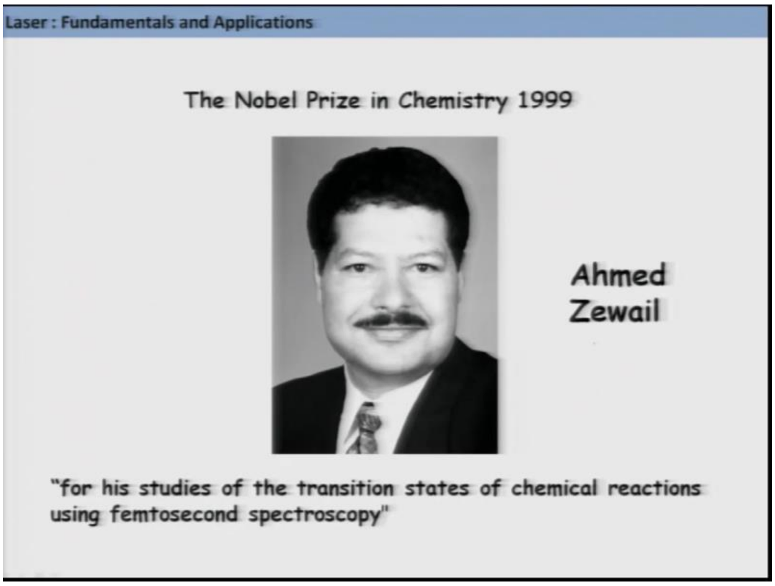

And this is the work, which you know which got process Ahmed Zewail the nobel prize in 1999 in chemistry, for his studies of transition states of chemical reactions using femtosecond spectroscopy.

So, he used ultra short pulse laser to do spectroscopy to find out ultra fast processes happening in the in chemistry that is how the change transition state evolves.

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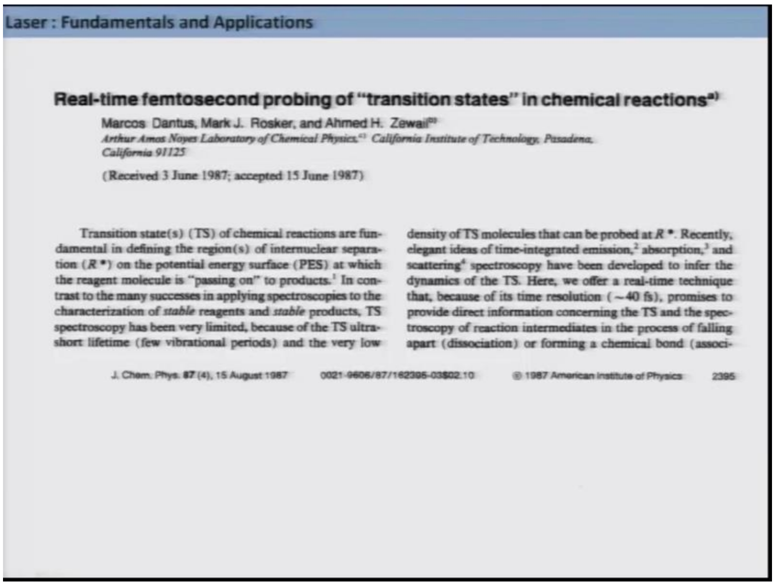

And just for your information you know this is the first paper that he published you know in this direction some more.

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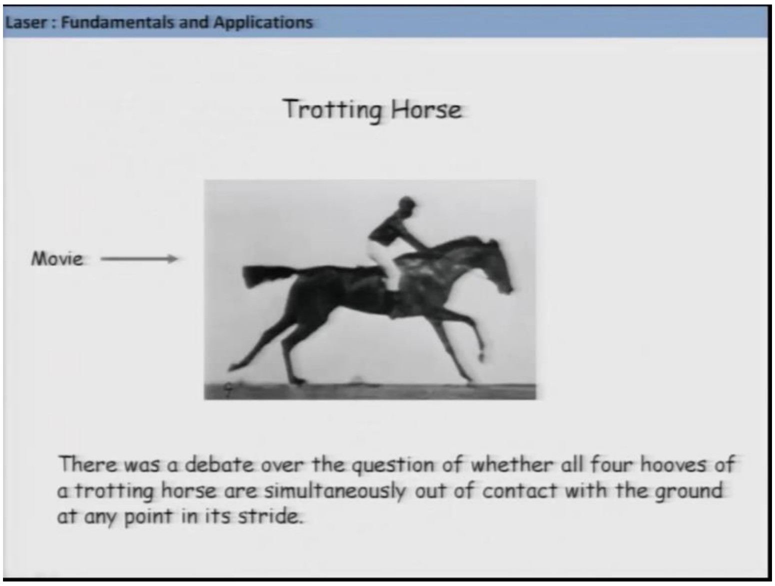

Now on your screen you can see there is a video of a horse you know trotting. So, while the horse you know executes a trotting motion a lot of question was there like is there any moment when all the four hoops of the horse are above ground a lot of debate was going on, and people did not know the answer because there were no so, fast camera that could you know give you the answer.

So, this answer was given by you know at some point of time by doing photography at a real fast scale and in one of the snapshot, it was seen that yes literally all the four hoops lie above the ground at one particular time. So, this answer could be given because there was a technique developed, which could take snapshots of any you know, object in moving condition or in motion in a much faster rate. So, this is something known as stereoscopy.

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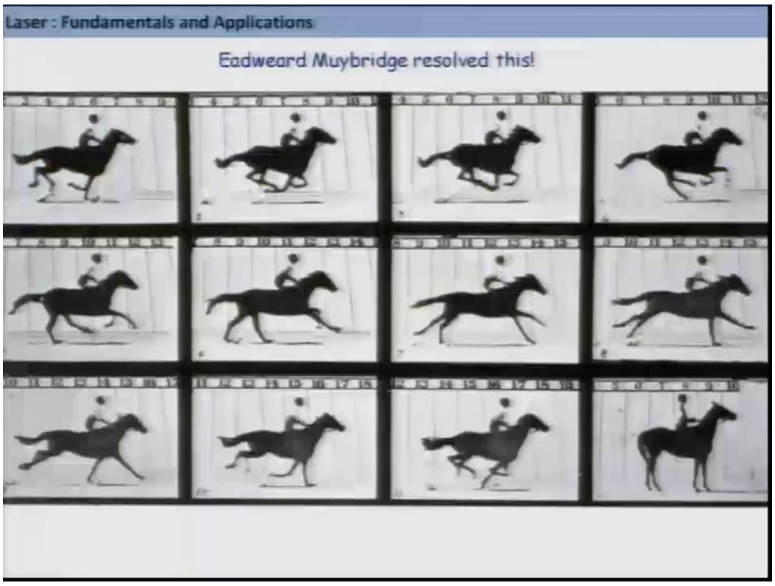

So, you hear the person who actually resolves this problem was named is Muybridge and he took this photographs.

So, you can see that there are individual photographs taken during the horse trotting and they were taking so fast at that type you know point of time and if you look into each individual frames, you will see at one particular frame all the four hoops are above the ground level. So, you know like if you look into this particular one you can see all the legs are above the ground.

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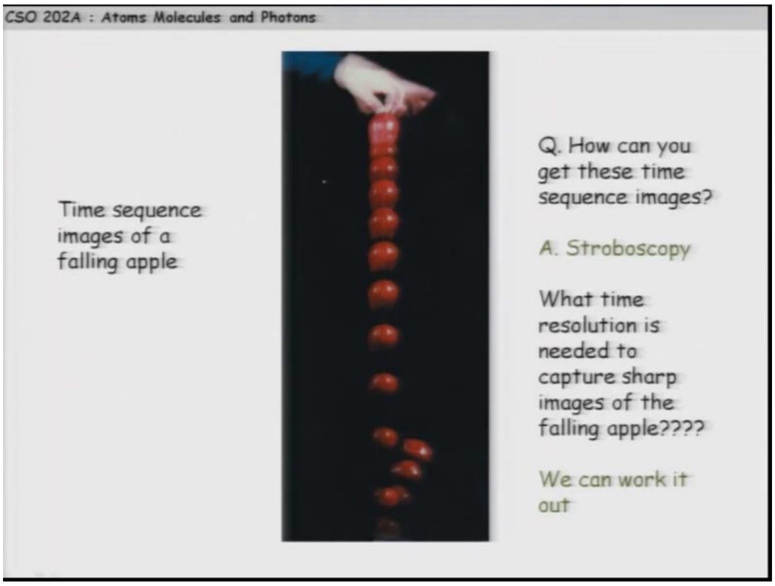

Now, similarly if you take an apple and just you know leave it, it will fall now how actually it is falling at different, different you know falling stage you know how it is oriented if you want to know that you really need you know, to you know take snapshot at a much faster scale or you need to take the you know photographs of the apple which is falling by flashing the light at a very first scale and then you know taking the image and this is known as stroboscopic.

Now, how fast you should be able to you know you should take the image how will you know. So, that can be very easily calculated, because you know suppose an apple is falling that what speed it is falling what is the distance between the you know stationary state and then when it reaches the ground and you know how long it will take to fall down.

So, if you want to take at different, different time scale you can easily figure out you know how fast you should take because you also know about the acceleration. So, you can essentially take a photograph like this which is essentially the time sequence of the image of the falling apple.

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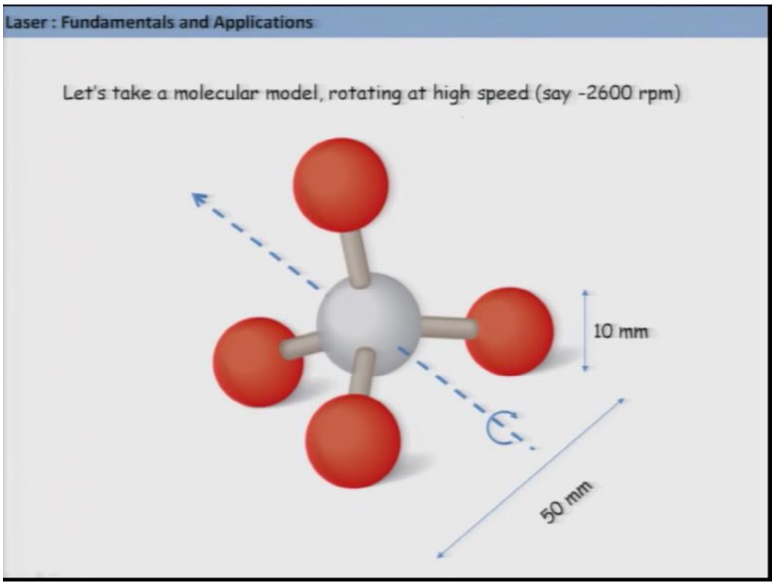

Now let us consider a real you know chemical problem, where you have a molecule and let us start with a molecular model. So, suppose you have a methane molecule and this essentially not a molecule, but you take it as a molecular model now this molecules real molecules they rotate they executes rotational motion right.

So, this molecular model also we can rotate and if we can rotate it very fast say for example, 2600 rpm, how will it look like to you, you will not be able to differentiate between you know different atoms there you will see something really fuzzy you may not be able to understand that this is a molecular map, when you know model having four balls and sticks you will not be able to you know guess that.

So, now suppose you have a you know diameter for this you know red balls and then the distance between two successive balls is given then you can actually calculate you know.

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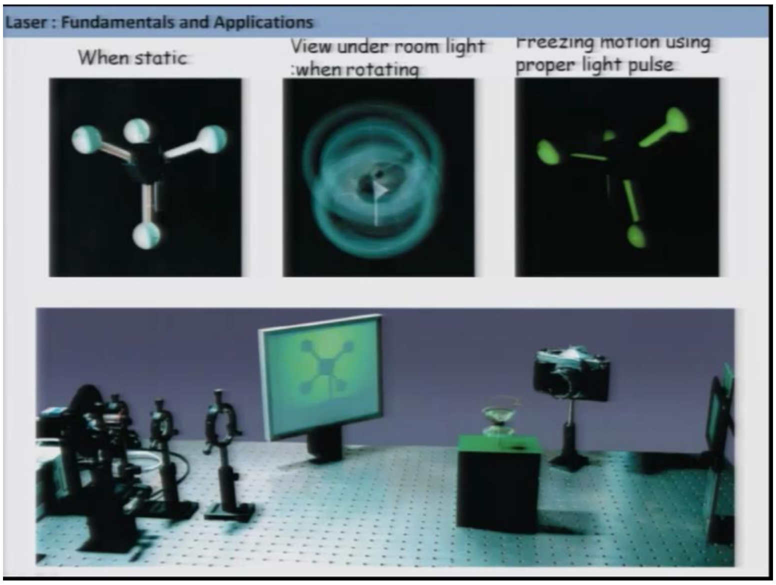

What should be the resolution of your light flash? So, that you can take the image at a as if the molecular model is stationary, so this is the image of the stationary model and when you allow it to rotate it appears like this this is a real image of a rotating model. So, you can immediately figure out that this is totally fuzzy right you cannot figure out whether there is a molecular model or there is you know something else.

Now, if you can really come up with a short pulse light how short we can work it out then you can actually freeze the motion correct. So, if you know flash it worship very short time scale and you can detect that. So, while it is rotating it has its own speed, but if you can come up with a much you know similar you know speed of this flashing then you can freeze this motion in space and you see something like this.

So, this was under room light and this figure on your right is under a proper light pulse. So, this is exchange exactly the experimental geometry one can think of that this guy is making a rotational movement here and the light is being you know sent to this guy and then there is a blocker here and the camera sitting here takes the picture.

So, if this light pulse is fast enough then or short enough; sorry, then you can freeze this motion and you can get an image like this.

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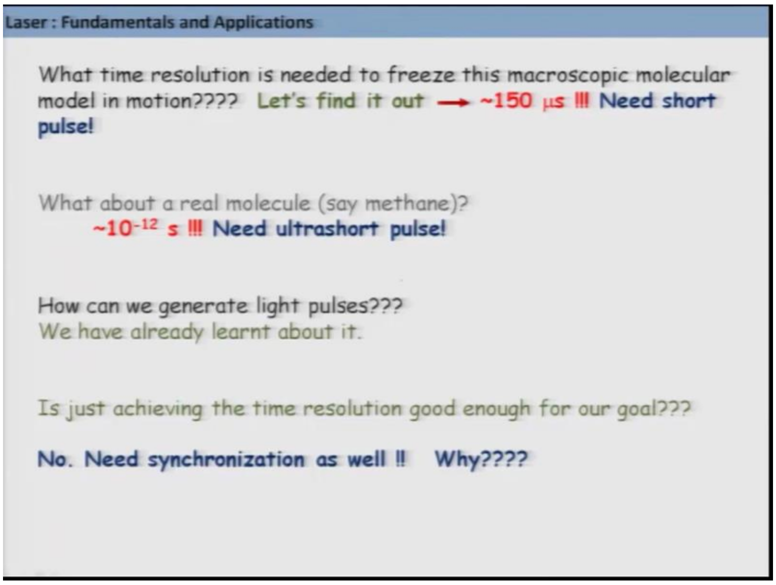

What is a time resolution that you will need, it is needed to be something like 150 microseconds, so it need to be short, now this is about molecular model what about a real molecule say if you take say methane essentially. So, this timescale that you need to freeze the motion in space is approximately a picosecond.

So, that is an ultra-short pulse, so how to get that ultra short pulse we know about that we can prepare a mold lock laser and we can get the short pulse ultra short pulses you know picosecond and beyond we can go up to femtosecond quite you know easily.

Now, is it only about creation of a pulsed light source ultra short pulse light source no we also need to synchronize this you know pulses with this molecular motion ok.

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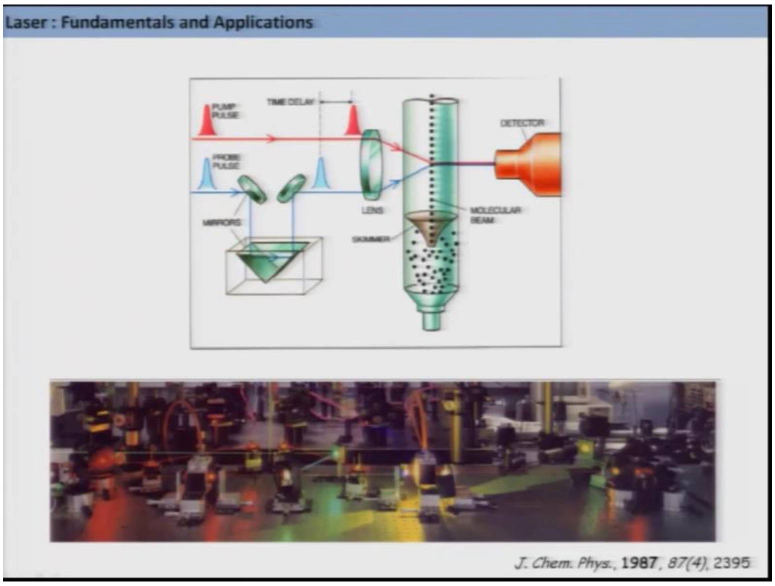

So, one needs to do a proper arrangement of doing the experiment as was done by Ahmed Zewail, where you have one pulse which excites the molecule and in the second pulse probe that excited state. So, essentially if you are you know trying to figure out what happens between this CH3 I and sodium. So, how the transition state, so you create that you know molecule in the excited state, so the transition state is created and then how it evolves with the time you come with a second pulse.

Now, this second pulse if you come at the delay. So, essentially what I was drawing earlier like you have a potential will you are exciting it here. So, you are creating the transient state that is slowly evolving. So, when it is here you come with the probe then when it is here you come with another probe, another, another you take the whole snapshot up the transition state as a function of time and that is how you do that by choosing a proper time delay between the pump and probe.

So, this is the pump probe set up that Ahmed Zewail actually used. So, you can use this pump probe technique involving ultra short pulse laser you can really study a fairy you know or you know ultra short chemical processes, it can be bond baking, it can be bond making, it can be you know bond reorganization this isomerization, it can be a change in the conformation.

So, various things are possible to be studied one can study all these different, different processes which happen in very short time scale as sort as picosecond or femtosecond level and these are all now possible all these studies are possible, because I have pulse laser not only pulse laser, but pulse lasers with ultra short timescale.

So I hope, I could show you certain examples, of you know lasers in spectroscopy and you know the in general the affect the application of this laser spectroscopy in understanding several you know chemical processes. So, this that is all for this particular lecture and let us meet again in the next class.

Thank you very much.