Rate Processes

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Module No. # 01

Lecture No. # 30

Ultrafast Process (Contd.)

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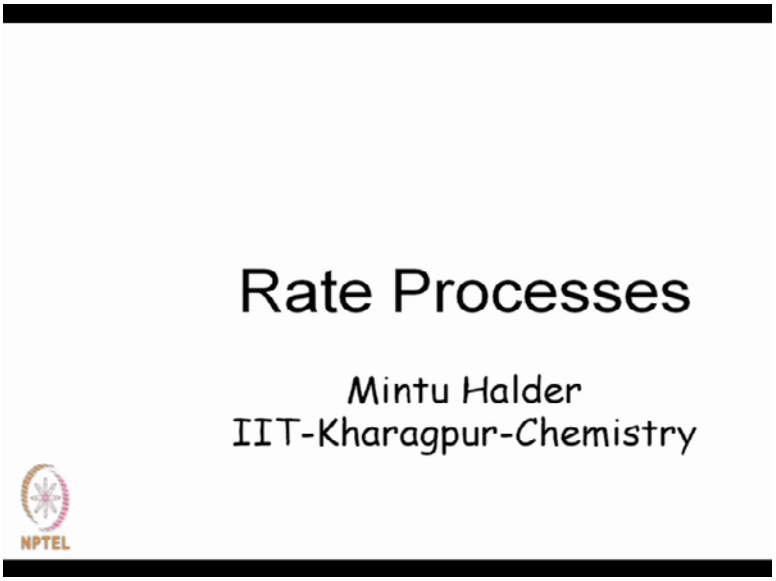

Good morning everybody, we are back with rate processes. In our last lecture, we talked about the ultrafast processes in chemistry. Now, these ultrafast processes, are you know are very important in many respects. So, some of the, I mean, you know putting of this ultrafast process is very important, in respect of the fact that it gives us a new insight on the understanding of chemical reaction, specially proving the transition state of reaction.

On that ground, we discussed many techniques of which one is Pump-Probe technique, which is the modified version, I mean the faster version of this Laser Flash Photolysis. We also try to give the outline of how this transition state can be proved using ultra short laser pulses.

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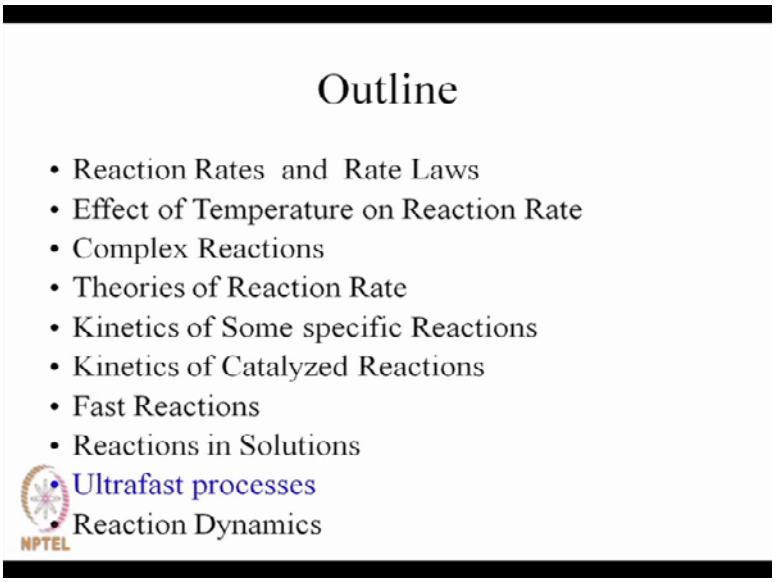

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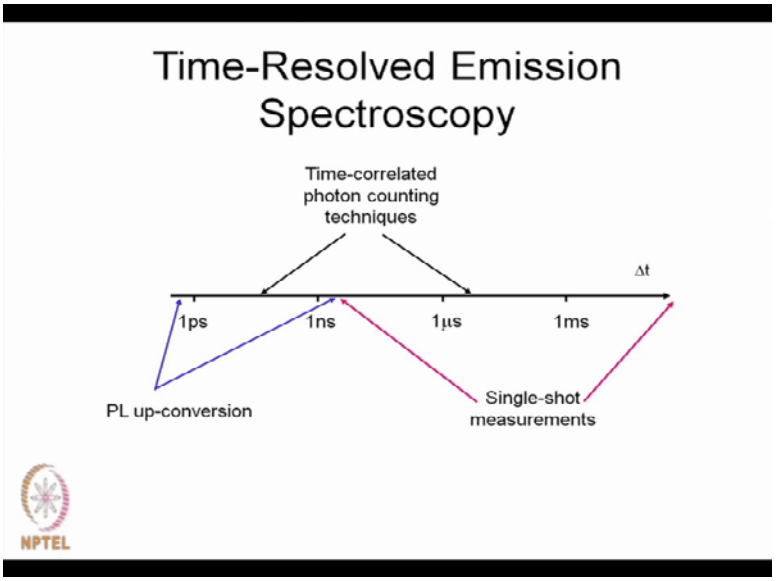

So, today will still continue with this and under the heading of Time-Resolved Emission Spectroscopy, talked about that it is a technique, which is called the Time-correlated single photon counting technique, which is based on counting of photons and immediately after the excitation pulse enters into the fluorescent sample that starts some process, that may be photo-physical process, may be some photochemical process. Photo-physical process may be like; I discussed this solvation dynamics, dynamics of solvation on how these solvents are oriented around this transient dipole that is created as a result of excitation, I mean, excitation by photons of appropriate frequency. So, this

technique t c s p c or time correlated single photon counting technique, that has this span around you know in between 1 picoseconds to several nanoseconds, and even above 1 nanosecond as well like say tens of nanoseconds we can do that.

The single-shot measurement that is another way of looking into the ultra faster or may be faster processes. Of course, that does not go into ultrafast region, single-shot measurement that is you shine with a single-shot of laser pulse, single-shot of laser, and then you measure the emergent light, that is emergent probe light or maybe you measure if any spontaneously emitting light is coming out of your solution. In case of time-correlated single photon counting methodology, there you excite your sample with brief pulse of radiation and you know this spontaneous emission is coming out of the solution or that emission may be coming out of the solution due to some chemical reaction as well.

There is another technique which is called the Up-conversion technique that I also talked about, which is basically some frequency generation technique where you generate, you amalgamate two frequencies, in as specific you know, through a specific media that is showing non-linear optical properties. So, exploiting the non-linear optical properties of certain materials, we can join two photons to generate one photon and by some specific or using some specific protocol, we can find out the time dependence of your sample decay. How this sample is decaying? As a function of time, so these are the ways that you can do time-resolved emission spectroscopy.

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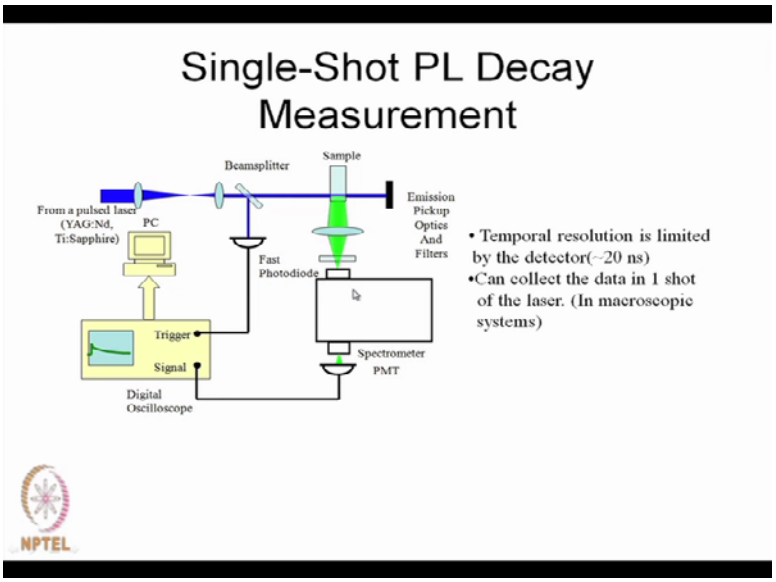

Single-shot photo luminescent measurement, which is temporal resolution is limited by the detector, which is of the order of say 20 nanosecond, and can collect the data in 1 shot of laser, in macroscopic systems. Now, here you have got the photo luminescence decay measurement, what is happening that is you shine; you get here to use a pulse laser that is N D YAG laser or may be titanium sapphire laser. Then you collimate it, then with the help of a beam splitter you have a fast photodiode, which triggers your digital oscilloscope, and may be a very little percentage of this laser light, maybe it is a blue, say it is a blue lasing light, so may be 1 percent or even less than that is directed to your fast photodiode; it is responding very fast.

The moment light is falling on the photodiode, it gives a triggers pulse, which triggers your oscilloscope, digital oscilloscope, and the remaining 99 percent of your laser light, which is falling on the sample and then the emission is collected at 90 degree, because if you collect the emission and this is called dump; that the excess of lasing light, which is coming out of the solution in this side, is a absorbed by some material, some medium, so the excess light is not going somewhere else, because that may create some hazards.

That is why it is dumped and if this luminescence is collected by optics at appropriate type, so that appropriate optics has been used up, so then it is collected by a spectrometer. So, spectrometer and then the outgoing light from the spectrometer is collected by a photomultiplier tube, which may be generally the detector is of temporal resolution and could be of the order of nanoseconds. So this, I mean photomultiplier signal, is fade into digital oscilloscope. Now, the oscilloscope collects the signal but the point is that the moment this fast photodiode receives a signal from the beam splitter, then photodiode puts a trigger on to the oscilloscope, so that the oscilloscope is ready.

So, after this trigger is on, may be this oscilloscope remains on for may be several microsecond, so between the trigger and may be say after up to 100 microsecond, this oscilloscope is ready to receive any signal and if any signal is coming out of the PMT, then this digital oscilloscope digitizes that signal and it shows on the display, so it is a typical decay profile, so typical luminescence decay profile.

So, this temporal resolution is limited by the detector and it can collect data in one shot of the laser, but the thing is that the digital oscilloscope, whatever the signal it is collecting over here, can be fade into a p c, for further processing of the data. Suppose, in

the one shot, if your signal is not very smooth, if it is noisy, then you may average that signal for maybe, I mean this decay, may be for 100 shots, may be 50 shots, may be 25 shots, and depending on how good is the signal quality. If the signal quality is very high then may be in one shot it is ok.

So this is the way, you can also collect a fast decaying profile. So, fluorescence profile you can collect and this fluorescence profile may be correlated with some photo physical phenomenon or may be some photochemical phenomenon, because that fluorescence, may be this green fluorescence say whatever you are getting or whatever is coming out of the sample, may be due to a photo physical process or may be due to some chemical process as well suppose because of some chemical reaction photon is liberated, so that photon and how this photon is changing its intensity as a function of time that we can measure.

The use of the spectrometer and usefulness of the spectrometer is that you can resolve these emission into a number of frequencies, because it may not be a single frequency that it is giving. Sometimes, and in most of the cases, the fluorescent material they have they have a broad emission band, so you can collect emission as a function of different wavelengths. So, may be at one wavelength the decay profile is different from the other wavelength. From that some complicated reaction or complicated scheme can be probe into. So, that is a typical diagram for a single-shot photoluminescence decay measurement.

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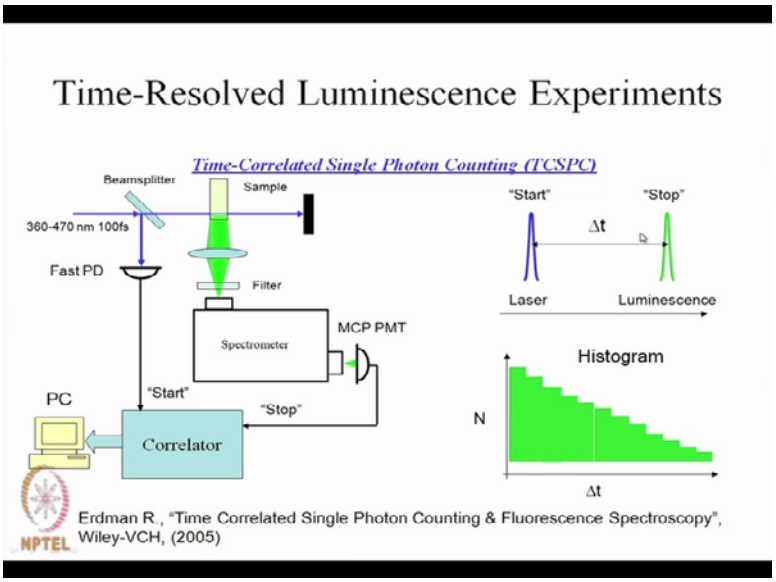

Next is time-resolved luminescence that I told you as you know by time-correlated single photon counting that is a basic apparatus you have got, may be about 100 femto second pulse, may be 360 to 470 nanometer, 100 femto second pulse, with a help of beam splitter, a fast photodiode as you know this. May be 1 percent of this laser light is directed to the fast photodiode and the remaining 99 percent is fade into sample, and then here the same it is collected, and in this case, the thing is that our detector is a different kind of detector. It is not a simple slow detector as I talked about here in photomultiplier tube.

It is a special kind of detector called MCP PMT, so micro channel plate photomultiplier tube, so it has got a time good time resolution, in that case the detection, the time resolution is not that much limited like the earlier case, so it can give good time resolution and here the spectrometer again is used over here for resolving your emission as a function of different emission intensity, as a function of different wavelengths.

You can measure the decay profile in terms of a histogram, as a function of time, which is number of photons that are collected at different time gap. So, here what happens that the moment laser falls on the beam splitter, it triggers a photodiode, and then a signal is fade into this, it is called the Correlator, and fade into this box and so this is ready to receive the another photon from the MCP PMT. The moment MCP PMT receives another photon then its stops, so number of photons that is received in between this is now converted, and then it is fed into a personal computer, and histogram is generated. So, this is basically a decay profile. So, this way you can do the time-correlated single photon counting measurements.

This is another fast technique. So, by this you can you can prove many things, like solvation dynamics. If this dynamics of solvation is not like in a 1 or 2 femtosecond or may be 100 femtosecond, then you can easily do that. May be if its time resolution is about say 40 picoseconds, say 20 picoseconds, then you can do quite a fast process or processes. So, this way you can do time-resolved luminescent experiment like single-shot. It is not a single-shot one but it is a different way that you find out the correlated photons. You collect the, measure the, number of correlated photons, that you are getting which is called the time correlated single photon counting.

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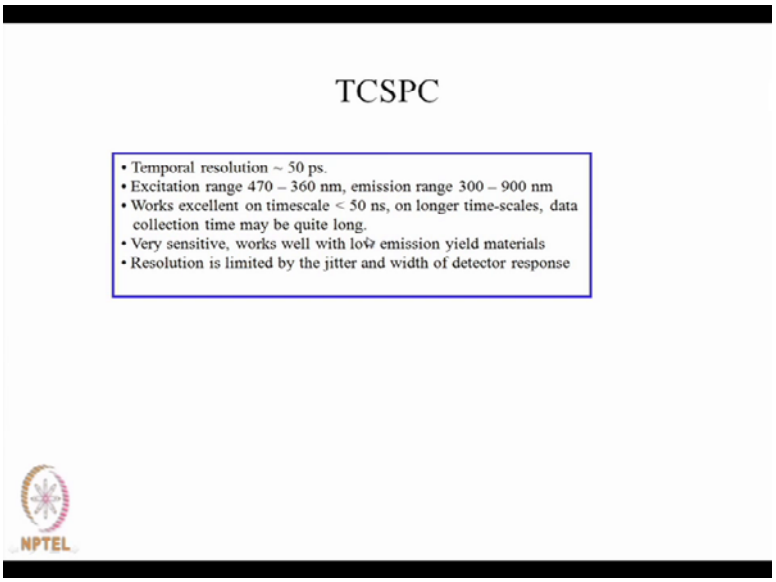

So T C S P C is temporal resolution is of the order of 50 picoseconds, and it is not that much limited like single-shot photoluminescence where 20 nanosecond resolution, but here its temporal resolution is 50 picoseconds, and its excitation range can be 470 to 360, emission range can be 300 to 900, and nowadays different sources are available, by which even you can excite a little longer frequencies, I mean wavelengths, and works excellent on time scale, which is less than 50 nanosecond and on longer time scales. Data collection time may be quite long, sometime it may quite long, because you have to collect the data for a longtime, because you have to shine your sample for a quite longtime, and you have to collect those single photons that is coming out of your sample, by the help of this fast detector.

So, a collection time may be very long depending on whether it is weak fluorescent material or it is a strongly fluorescent material. It is a very sensitive apparatus and works well with low emission yield materials. Resolution is limited by the jitter and width of the detector response. So, there are other factors which may complicate the issue of the time resolution, so that we are not going to discuss over here, but may be some other factors are important like as I told you like jitter and the width of detector response.

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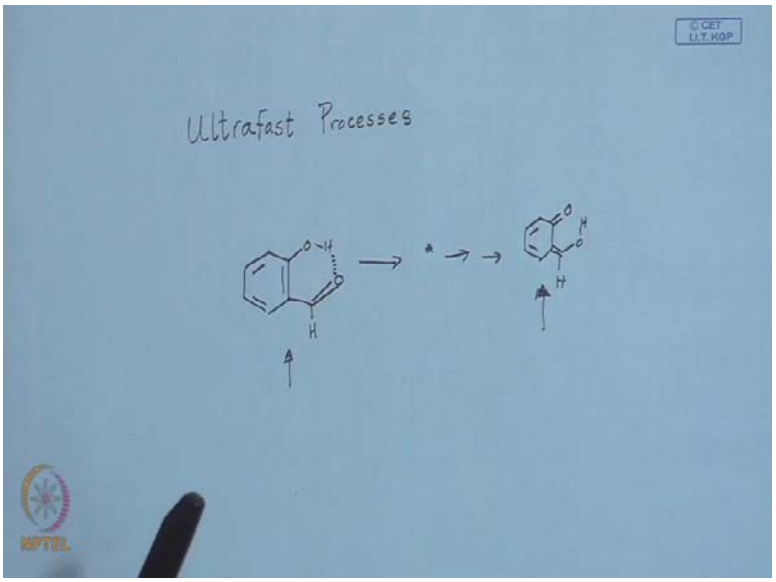

This T C S P C is another very nice technique by which you can probe this very fast processes like a solvation dynamics, may be excited state intra molecular proton transfer reaction, like suppose you have got a species say like something like this, say hydroxyl benzaldehyde, like this. So, this makes a hydrogen bond over here. At ground state there is a hydrogen bond, but in the excited state what happens is that this proton, I mean this proton is transfer from here to here, which is called the excited state and it is through intra molecular hydrogen bond, so excited state intra molecular protons, so you can probe this process.

This is a very fast process. So, you excite, then you generate your excited state specie, which is denoted by star and then in excited state the acid base properties differ considerably than in the ground state. So, it snatches this proton and thereby may be this species is generated this way and this. So, you can probe this process because this is a tautomer and this is your normal. So, tautomer and normal can have different absorption wavelength or may be fluorescence wavelength, so you can monitor for this species or may be for this species, and with function of time, you can monitor the intensity of your fluorescence or may be the absorption intensity is changing as a function of time. So, if you want to monitor by fluorescence method then may be t c s p c will be one of the best options to look into this excited state intra molecular proton transfer process and that is that is a fast process.

So, that is one very important use of this technique. So, fast processes like this atom transfer or proton transfer that can be probed by this ultrafast technique. So, we can follow the rate of this transfer of this proton from one atom to another, and what are the factors by which this proton transfer can be or may be this atom transfer can be modulated that you can also follow, by changing may be the solvent, or may be introducing something else, may be putting of this system into some, say may be in micelle environment or may be in cyclodextrin cavity, or may be somewhere else, so that how the environment can affect this proton transfer process that we can follow, with that it becomes extreme faster or may be it becomes slower, we can we can look into that.

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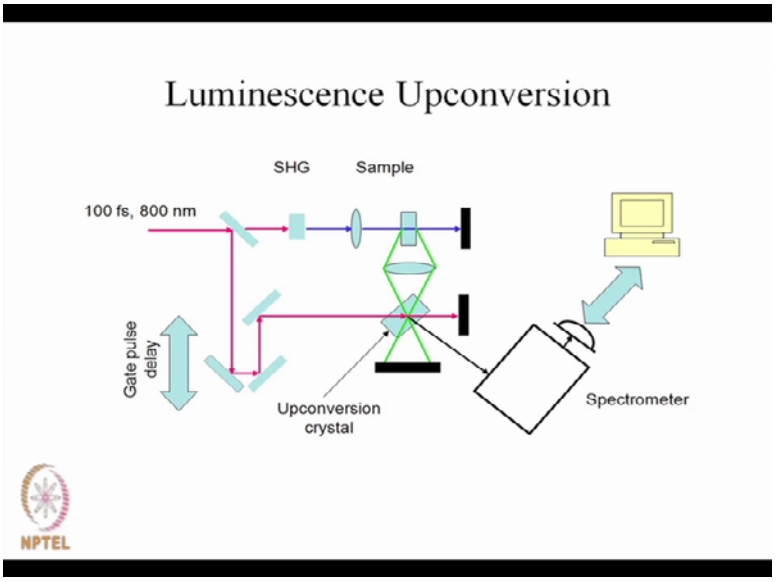

Luminescent Up-conversion, as I told you, I have given you a brief idea that again in this case, say, your using say 100 femto second, 800 nanometer red light, from your titanium sapphire laser, and then it is divided into two parts. One is directed this way and which will be used as a gate pulse and the other one portion is fade into a second harmonic crystal. Second harmonic crystal, basically generates the second harmonic that is 2 photons of same frequency, these 2 are amalgamated and that is also a non-linear process, so you have to focus this 800 nanometer beam tightly on to this S H G crystal, so that the output will be blue one.

Then with the help of a lens, you can let this light to fall on the sample in a more tightly, so that the luminescence is coming out of this sample, so it is a luminescence sample, and this luminescence sample, I mean the luminescence is again collected with the help

of a lens and then it is focused on to another up conversion crystal that is again a non-linear crystal, and that has to be put on to your this crystal at a specific angle. Not all angles will do your business or your job. So, then this is focused on to here and this gate pulse is then allowed to fall on this focused point, so that these two frequencies will make a mix and thereby generating a mixed frequency, I mean an up converted frequency.

This side these 2 are the dump that is excess light will be dumped and may be at a specific angle this is collected. At a specific angle this up converted light is collected, and collected by a spectrometer, and then it is the detector, and then this detector signal is you know detector signal is into a digitizing system, may be a P C. Here, your luminescence contains a number of frequencies. What will happen is because it is not a single wavelength, because a emission is a different combination of frequencies. So, you will be getting a number of frequencies over here and then this as it is fades into this spectrometer then you collect your signal.

Now, the thing is that how to generate your time axis, because this spectrometer what it does is basically collecting the signal or the time integrated signal, because you remain may be at a given a time point, and allow the spectrometer to collect the signal and integrate for longtime, so that your noise is minimized and then that signal number or signal intensity information is fed into the computer, so that you generate a point, that is signal point, corresponding to a signal, but how to generate your x-axis? In that case, in the same way as we talked about for pump-probe that you use a retro reflector, I mean pair of mirrors, and so here the optical path traveled by rate and the optical path traveled through this. When these two exactly match or exactly equals then it is your time 0 and then you progressively delay or advance this gate pulse to generate your time axis, so that ultimately you generate decay profile like this.

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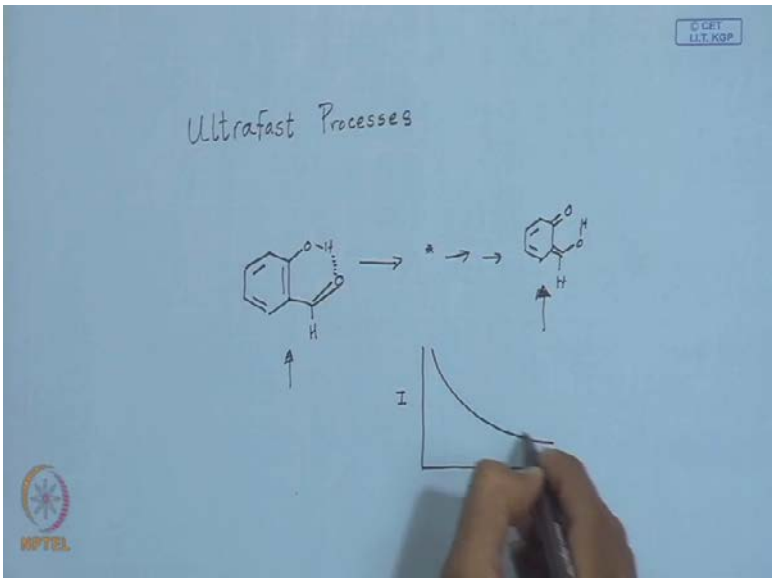

So, it is your delay and delay corresponds to the delay between your gate and the up, which is fluorescence, and this is your fluorescence intensity. So, you collect it and then you fit with some mathematical formula, so that you can find out the kinetics of the decay, I mean, decay kinetics that is the time required for the intensity to drop down to some value or may be it can give rise to some rising signal as well depending on the on the system of interest.

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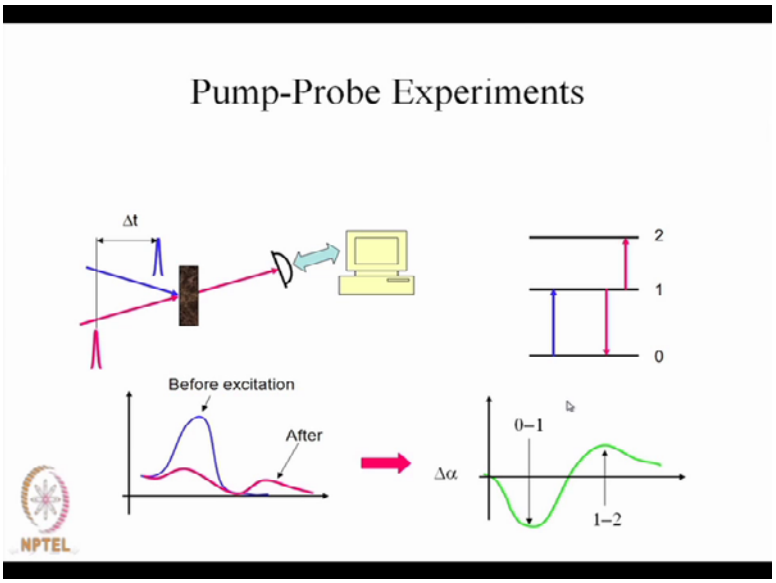

Pump-probe, as I told you that pump-probe is another way of looking into non-linear processes, as I already have talked about. Pump is like basically, you pump over here, and then maybe you can probe from here to here; there is an absorption process or maybe emission process. So, there are various complications may be there which we are not going to discuss in detail.

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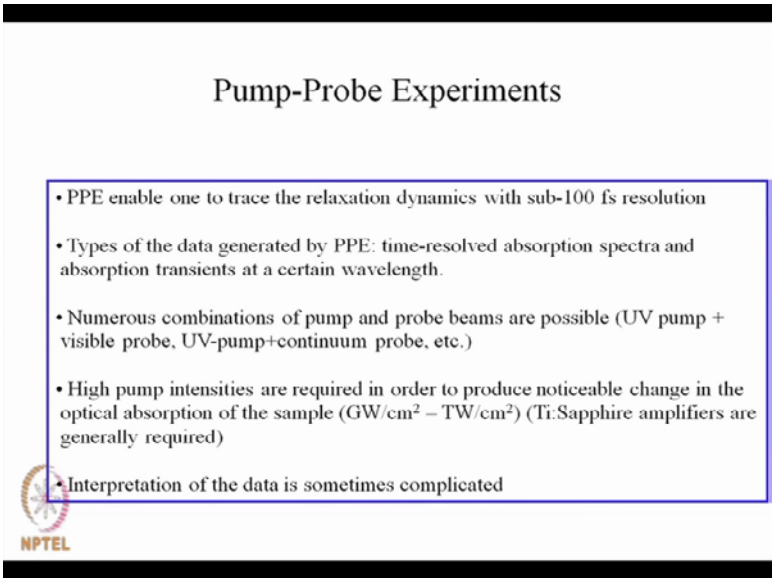

Basically, pump-probe experiment and in pump-probe experiment it enables one to trace the relaxation dynamics with sub-100 femtosecond resolution. It has got a quite good resolution.

The type of data generated by pump-probe experiment is time-resolved absorption spectra and absorption transients at a certain wavelengths. So, these are the type of data that is generated by pump-probe experiment. Numerous combination of pump and probe beams are possible. UV pump, visible probe, as I told you, it may be one color or it may be two colors or in one case UV pump visible probe, in another case UV pump continuum probe, may be blue pump, blue probe.

The beauty of this method is that since you are using the shot pulse, therefore, it is you know frequency resolution is not that much. So, it is more dispersed, so bandwidth is more, because by time wise it is short, but its bandwidth is more. So, it enables one to measure different wavelengths as well. High pump intensities are required, in order, to produce noticeable change in optical absorption of sample, giga watt or terawatt. Now,

Ti-Sapphire amplifiers are generally used and sometime your interpretation of data is complicated, because of the processes that are going on in the sample after your photo excitation or after pumping, the sample could lead to complicated photo physics or may be could lead to complicated photochemistry.

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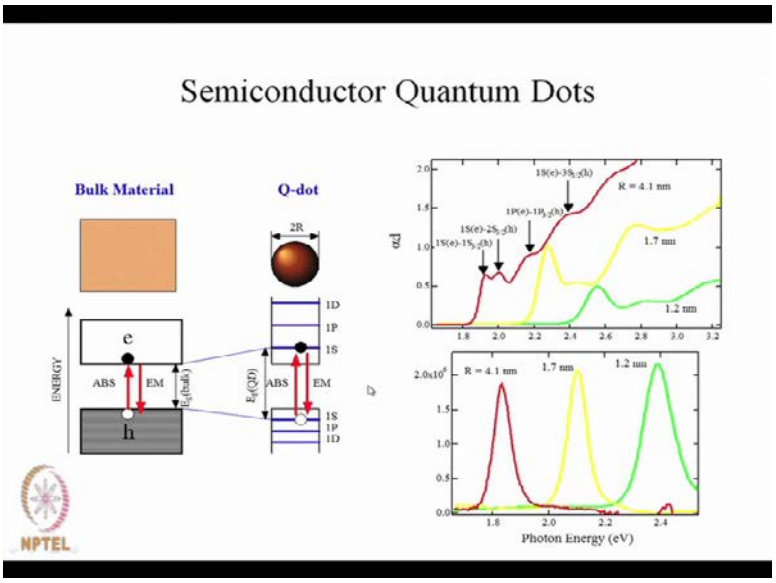

You can use you know this ultrafast techniques to probe into semiconductor quantum dots. This semiconductor quantum dots are between bulk material and atom. So, interesting photochemistry, I mean interesting photo physics or may be photochemistry can be looked into by this ultrafast process. So, that is another possibility.

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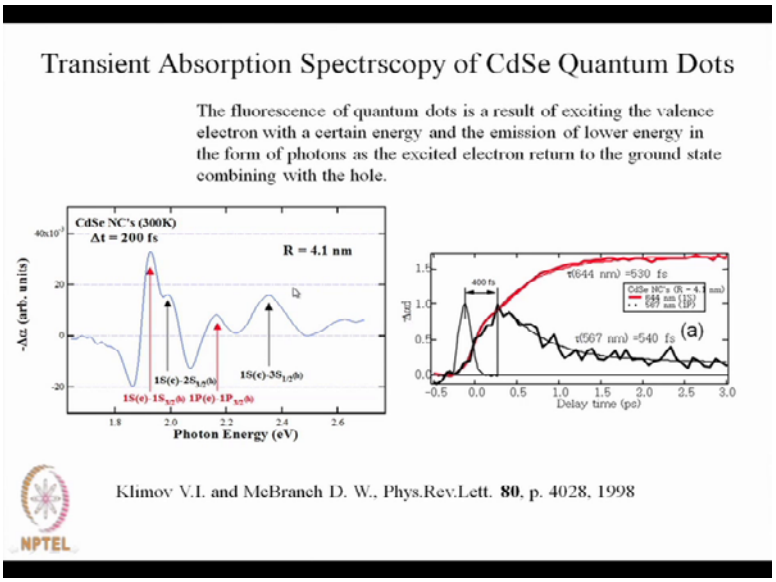

This is a typical transient absorptions spectroscopy for cadmium, selenium, quantum dot taken from this reference, so where you can see in one case, just I am giving you the typical idea that this transient absorption spectroscopy can also be used for this quantum dots, because quantum dots are nowadays very hot topic. So, you know this a nanotechnology, advancement of nanotechnology and nano-material research is a very interesting field nowadays.

Using this transient absorptions spectroscopy, we can look into various photo-physical or may be photochemical aspects of this material. So, it has got a tremendous application. Here, again I mean these guys put some time-dependent behavior which, right now we are not going to discuss in detail but, that can be can be useful.

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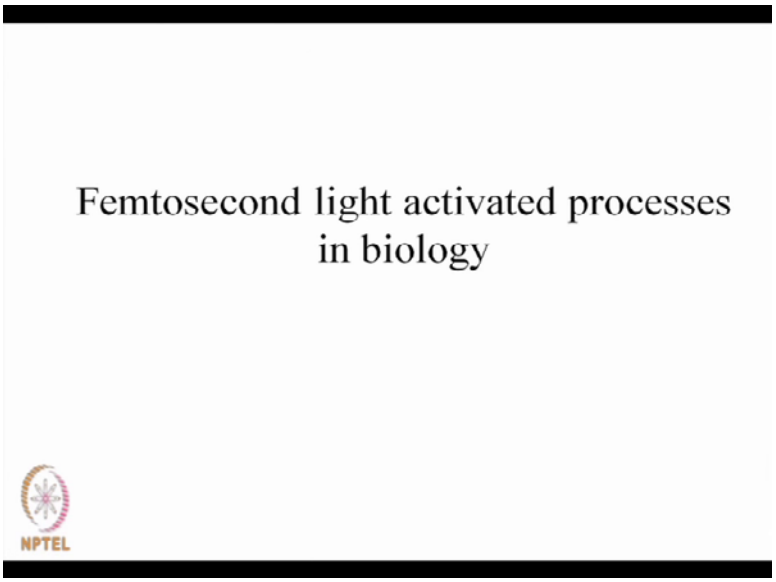

Next, we will look into this femtosecond light activated processes in biology or may be biochemical systems.

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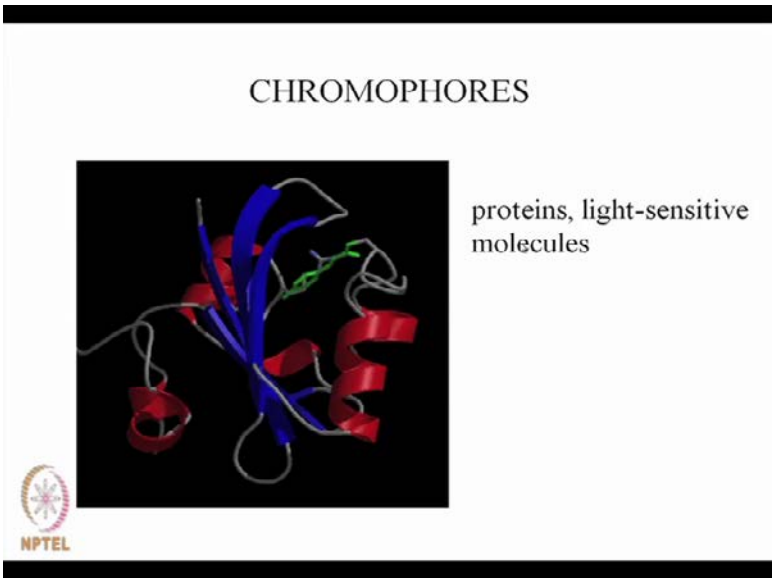

These are proteins. In this case, Chromophores; Chromophores could be proteins, because these proteins have many Chromophoric groups and may be light sensitive substances, light sensitive molecules, can be Chromophores as well, because you know proteins contain amino acid residues.

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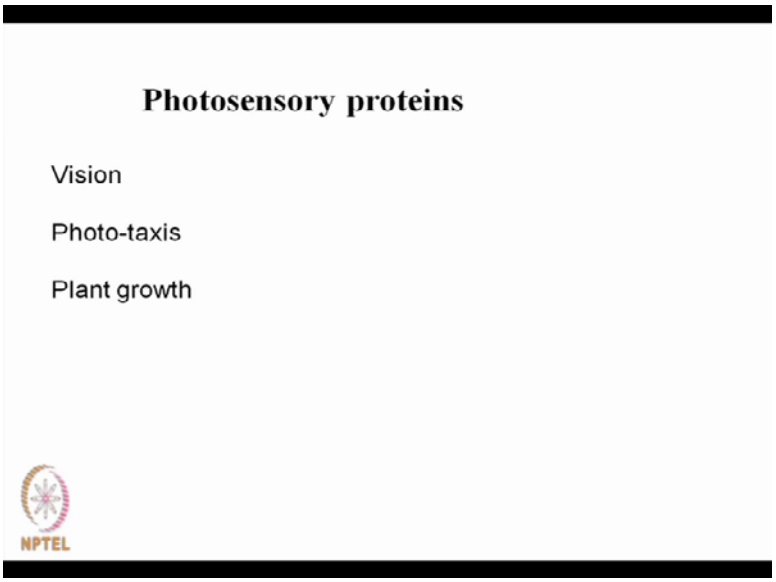

It may be aliphatic amino acid or may be aromatic amino acids. It may contain chromophoric groups like the group which is available with tryptophan, may be tyrosine, so chromophores available over there. So, protein itself can act as chromophore that if you shine with radiation, may be of appropriate frequency, it will emit. Like if you excite a protein sample containing tryptophan residue, with a 295 nanometer of light, so that 295 nanometer of light selectively excites this tryptophan residue and thereby emission is generated, emission is coming of the sample.

And may be probing that emission and probing the emission characteristics of that protein, we can look into various aspects of proteins like binding or may be reaction, so that we can probe, whether this protein is unfolding or whether it is refolding, because if a protein is unfolding and if your tryptophan residue is coming from inner, may be hydrophobic core to the outside, solvent exposed situation like water, then its emission is tremendously reduced.

Therefore, by looking into the emission intensity of your tryptophan residue, as a function of time, we can probe this folding dynamics, folding kinetics, we can probe in to. Therefore, this is very important that if using time-dependent behavior of protein fluorescence and sometime it happens in femtosecond time scale as well. Not only in slower time scale but also in femtosecond time scale, so in femtosecond time scale, lot of interesting things may happen and that can give us important information on what is going on, immediately after photo excitation, may be some breakage of bond, may be

some restructuring, may be rearrangement within the molecule, within a molecular system and that we can follow with ultrafast spectroscopy.

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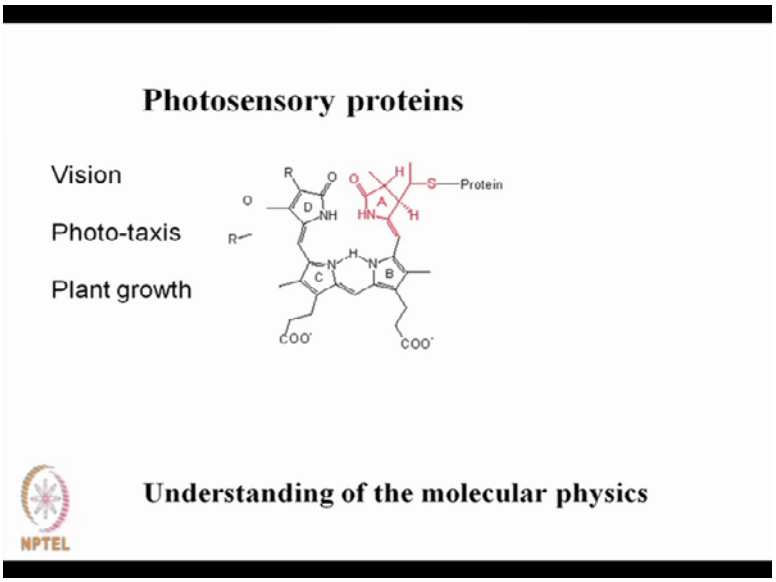

Now, photo sensory proteins like which are responsible in vision, that is we can look, we can see, so there is a mechanism; photochemical mechanism, photochemical reaction going on the moment light falls on our eyes, so photo sensory proteins are important and then photo-taxis, plant growth so these are really important.

These are light driven processes, light driven rate processes. So like light falls on something, on some molecule, then it does some chemical reaction, and in product of reaction may lead to some something new. Maybe, that leads to some output like vision, maybe photo taxis, maybe a plant growth. So it is a typical structure of this photo sensory proteins, I mean a domain, a part which is photosensitive, which has got photo sensory property.

Understanding of the molecular physics behind these phenomena like vision, photo taxis, and plant growth is of immense importance. So, what is the molecule.. I mean we wanted to know the physics at the molecular level and also the rate process involved over there. What are the exact rate processes that are going on? What could be the mechanism of such an ultrafast process? So this is very important.

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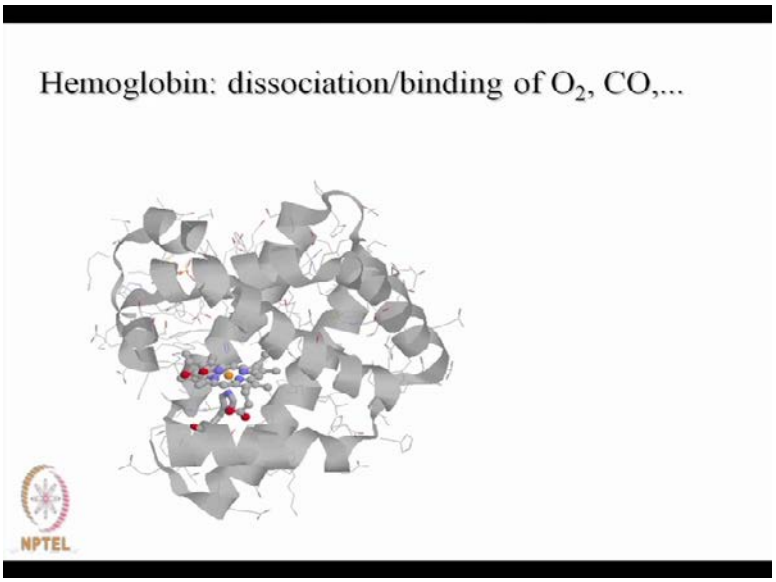

Like as I told you this dissociation of hemoglobin.

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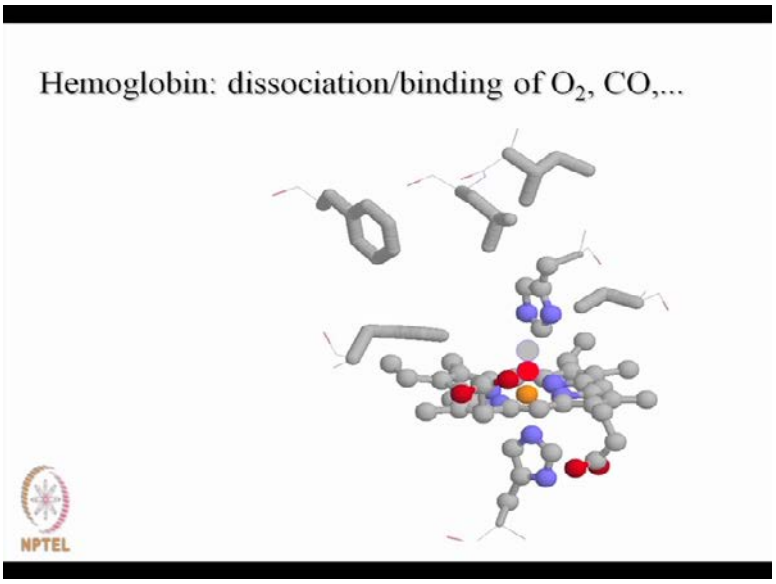

Like dissociation of, I mean, hemoglobin, oxygen bound or maybe when oxygen leaves.

Ligated hemoglobin then when gives this oxygen to your cells, then dissociation of this hemoglobin oxygen bond, I mean, the iron oxygen bond is dissociated, so, how this is occurring, I mean, in time scale, what is happing? So, this can be can be probed into by the use of this ultrafast spectroscopy. Like, I give you one example, in the last lecture

that carbon monoxide binds with hemoglobin giving rise to carboxyl hemoglobin and that particular material is very stable.

Now, the moment you shine with radiation of appropriate frequency, then this iron carbon monoxide bond, is broken and this carbon monoxide will tend to go outside the protein matrix. Whether it is really going outside the protein matrix or not that you can probe. So, using ultrafast processes, I mean ultrafast spectroscopy, you can do this, do this way, I mean you can look into the exact processes or the inner mechanism.

Light is falling, then it is detached, and then it is going outside your protein matrix or maybe outside your central metal. This is your metal. Initially, this was maybe carbon monoxide, the light falls and then it dissociates. So, what is the dynamics? I mean, how this is coming out? Is there any specific channel by which it is going out or maybe it remains over there for a long time?

So, photo-physics of that, I mean probing of the photo-physics of that process could be very interesting and can give us enough information about what is exactly going on and also doing some mutational studies over here, maybe, you mutate some of the residues, along the channel, through which it is migrating from one region to another.

If you mutated maybe, few amino acid residues along the path of this out going ligand, if you mutate then maybe you change the barrier; barrier that this molecule is facing while it is coming out or maybe it is trying to rebinding or trying to rebind with this iron. So, that maybe affected, so by doing this biochemical modification, maybe mutational modification, of this protein pocket, you can gain enough insight onto this rate process, which is going on inside this cavity, inside this hemoglobin, when carbon monoxide is bound or when you shine with radiation, it is detaching.

That is one very important topic but we are not going into much detail of that. Just I wanted to give you the idea, use of idea of how this ultrafast spectroscopy and you know probing of rate phenomena can give enough understanding of the nature of the bond or nature of bonding that is there and you know further like as I told you over here about the path it is taking after the reaction is proceeding. Whether this is going this way or may be the other way round.

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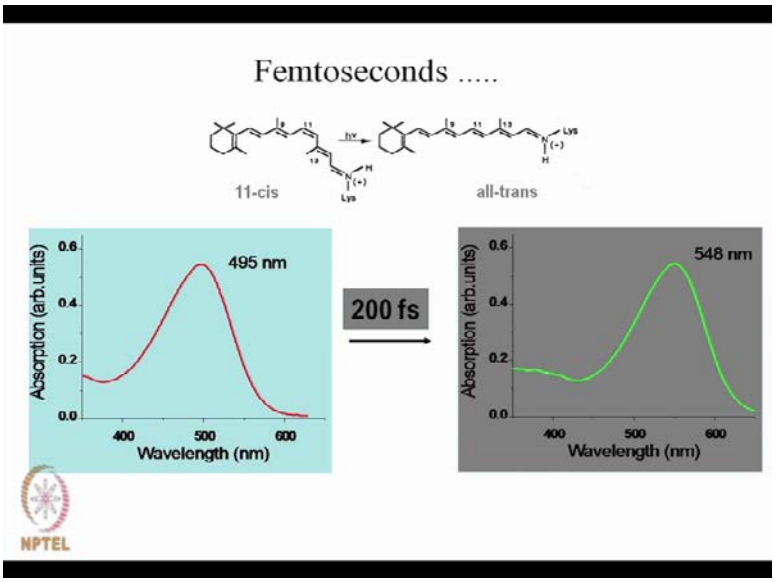

Another thing is photochemistry of vision. So, it is basically retinal; 11-cis to all-trans retinal. What is happening that if you shine with radiation of h nu, then you see a rotation about this bond that is 11-cis and here all-trans. So, you shine with radiation then maybe a partial single bond character comes in and then rotation about this bond occurs leading to this structure so that is the key ingredient for our vision; this retinal 11-cis to all-trans retinal, and if you look into the absorption spectrum then one will absorb at a different wavelength than the other one. In certain period of time, one is growing, after say 200 femto second; one is growing from the other. What is happening that if you probe into this particular region say 495, then with time we will be seeing that it is decaying, I mean, it is reducing and this is growing.

By looking in to this decay kinetics or maybe rise kinetics or growth kinetics, we can follow the exact time dependence of the process, and that is possible if you use ultra shot laser pulses, maybe 10, 15, femtosecond pulses. In that case, you can probe this processes as fast as several hundreds of femto second, maybe may be 50 femtosecond to maybe 200 femto second or like that.

Employing this femtosecond spectroscopy, we can again, as I told you in connection with carbon monoxide dissociation in hemoglobin, it has been found that after dissociation it tends to rebind. It has got a rebinding kinetics and this rebinding can be altered by mutation. So, it has got two options. It will rebind and maybe it will leave the cavity, I mean, the pocket, this hem pocket. The point is probing into this things will

again will give us enough insight onto the process. Here, we see you see that when you shine with h nu then this bond, the double bond character is lost so that rotation about this single bond, I mean this would be single bond will lead to this all-trans.

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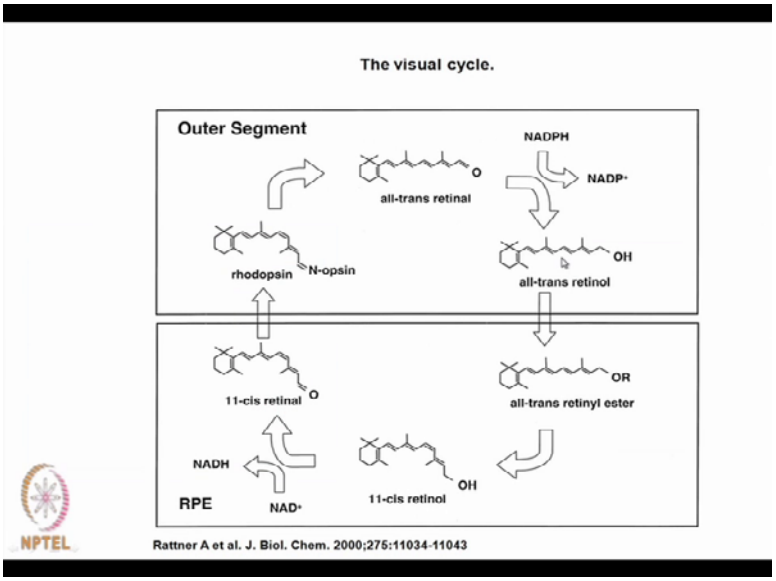

What is the actually scheme? Scheme is like this that 11-cis retinal, then through this schemes, I mean, through this various steps, it is again converted to retinol and then retinol to retinal. So, what is happing is that 11-cis retinal, then rhodopsin, then it is going to all-trans retinal, then involvement of NADPH to NADP plus, it is giving rise to all-trans retinol, then to all-trans retinyl ester, then 11-cis retinal.

It is the visual cycle and it is taken from this reference. It is a complicated event involving many things. In principle, using a femtosecond spectroscopy you can see this rate process, because the ordinary conventional kinetic measurements you cannot see, because it is several femtosecond processes. Remember, femtosecond is minus 50, 10 to the power minus 50. So, how can you do it in a laboratory using a pipette or burette or maybe some titration. It is not possible, because it happens the moment it is falling. To us, it is like that. The moment it is falling, it is happening. The moment the photon is hitting, it is happing.

So, it is very fast. It does not take or give any time. So, how can you see it? How can you look into this very fast process? That is why the importance of this ultrafast spectroscopy. Ultrafast spectroscopic technique is that you can see because of the advent

of this ultra shot laser pulses, you can see this, you can visualize and you can monitor it, you can, in principle, see it experimentally that it is converting from here to here. That one substance is growing, another substance is decaying. So, substance growth and decay, these are complimented; is a complimentary even. That is why it is very important, this ultrafast application of this ultrafast laser spectroscopy is very important, specially probing into this ultrafast step processes, which using conventional techniques like stuff flow, maybe plug flow, may be relaxation mechanism or maybe pump-probe like flash (( )) you cannot see.

That is why it is very important thing, that is, this ultrafast spectroscopy is important in probing into this ultrafast rate processes. The protein environment controls at which bond the chromophore will turn, whether like here this star and here this rotation will take place or in some other point or at some other point.

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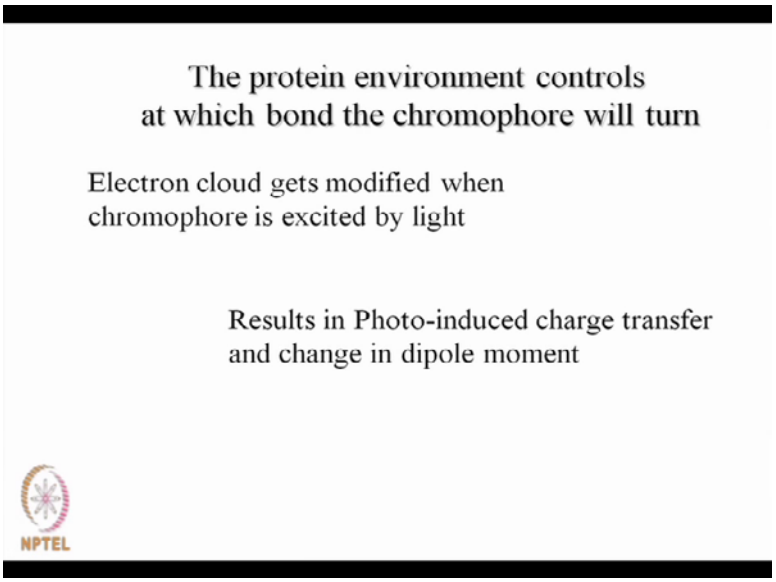

Now, because of this when you shine with radiation, the electron cloud, because it goes into the excited state, goes to the excited state. So, electron cloud, I mean, electron distribution is different from that of the ground state, so electron cloud is getting distorted as the chromophore is excited with light. This results in photo induced charge transfer. When you shine with radiation, there is another possibility is that electron cloud when gets modified, it results in photo induced charge transfer and change in dipole moment as it happens in case of solvation dynamics.

In case of this visual cycle that which bond will turn, means which bond will rotate, that is dictated by via your protein environment at the same time, you have to remember that because of your photo excitation, electron cloud gets distorted, so maybe there is a possibility of charge transfer as well. So, in there is a possibility of charge transfer, means generation of a dipole moment, generation of a dipole, or maybe change of a dipole. So, when there is a change of dipole then what do you expect that particular dipole will tend to gets solvated.

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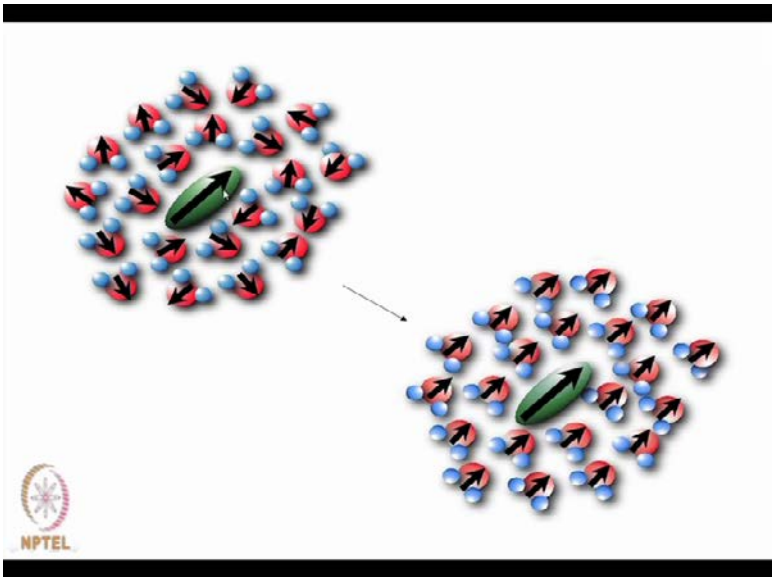

So, there is a schematic that has already shown to you. Your dipole is here, because of photo excitation, the dipole solvation is possible, and immediately after photo excitation what happens is that these dipoles are at the ground state, and this is your ground state configuration of the solvent dipoles. The moment it is excited, the solvents, the solvent molecule still remain in the in the Franck-Condon configuration.

For Franck-Condon configuration means that it is still to get relaxed. The moment it is generated it will start to rotate to give you the stabilized geometry. So, it will take time and after some time the system will be solvated in such a way that it has got some lower energy. This way you can also follow solvation dynamics in protein environment. So, how this? This water is, maybe bound to protein molecule or maybe bimolecular, bound protein, bound water or bound solvent. So, how this solvents will respond to a newly formed dipole, because of photo excitation.

You can follow the dielectric response of the protein environment so that you can get information on the pockets of the protein concerned. So, that is why this ultrafast spectroscopy in that respect it is important.

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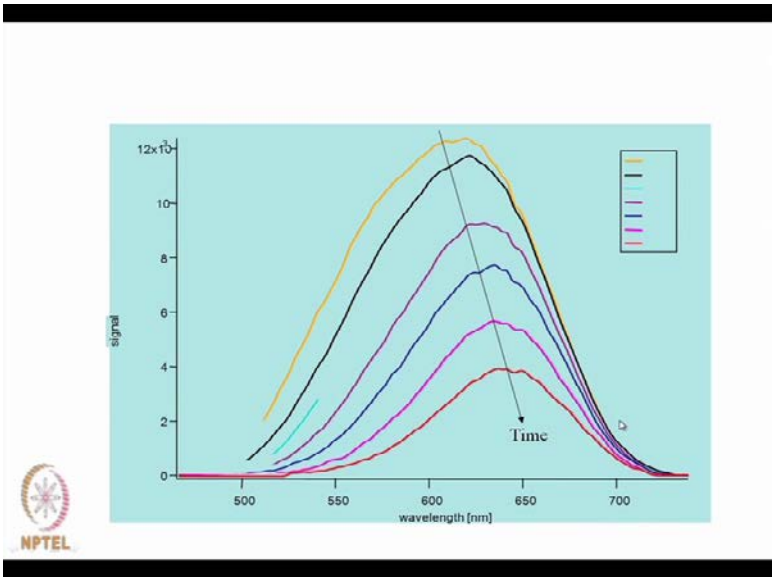

It is time dependent stop shift. What we have learnt over here? In ultrafast we have given you the idea of this various techniques in faster and ultrafast time scale, and then its application probably, maybe, in semiconductor, we just have not elaborated it, but it can be used in materials research as well. Then femtosecond, in terms of femtosecond, in a application of femtosecond spectroscopy, in light activated processes. This light activated process are very important in biology, especially which, another important aspects is that light activated, maybe, you may have some chemical substances, which are at room temperature, I mean, in normal situation, they are not doing anything.

But if you excite with light, it show some antiviral activity and again those antiviral activity, antiviral substances, light activated antiviral substances like hipericin, hypocrellin or many other substances.

So, they will tend to kill viruses showing some antiviral activity. How this antiviral action is happening or what is exactly happening immediately after photo excitation to this molecules? What rate processes are involved that you can probe? In the same way, we also have given you the idea of this visual cycle use, you know what is happing in the

visual cycle or means how you can probe into the cavity of some protein like hemoglobin carbon monoxide complex.

So, what happens when you shine with carbon monoxide? Whether it detaches? If it detaches what happens? So, these are the aspects that we have try to give you the idea but, not exactly in detail because of the limitation of the scope. That maybe you can if you want to know more on this, you can consult any standard text or maybe text book on femto chemistry application, maybe application in femtosecond spectroscopy in biology, femto biology, femto chemistry, femto biology or maybe application of ultrafast spectroscopy in materials research that you can consult.

There are plenty of texts books available in literature, may be internet resources are also available. So, I guess that is all of our ultrafast processes as for as introductory things are concerned. We are not going to detail in to these things. In the next piece of lecture, we are going to take up a molecular reaction dynamics.

So, molecular reaction dynamics, it is basically in this case again, we will recap some of our old parts of this lecture series and we will try to have a link with the modern understanding of reaction dynamics with chemical kinetics, what we have learnt so far. I mean, how these concepts of molecular reaction dynamics can be translated into the reactions or maybe into the aspects that we tried to learn so far. That will be taken up, that is concepts and applications. Those things will be taken up in the next lecture with the heading reaction dynamics. Till then,

Thank you.