Rate Processes

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Lecture No # 29

Ultrafast Process (Contd.)

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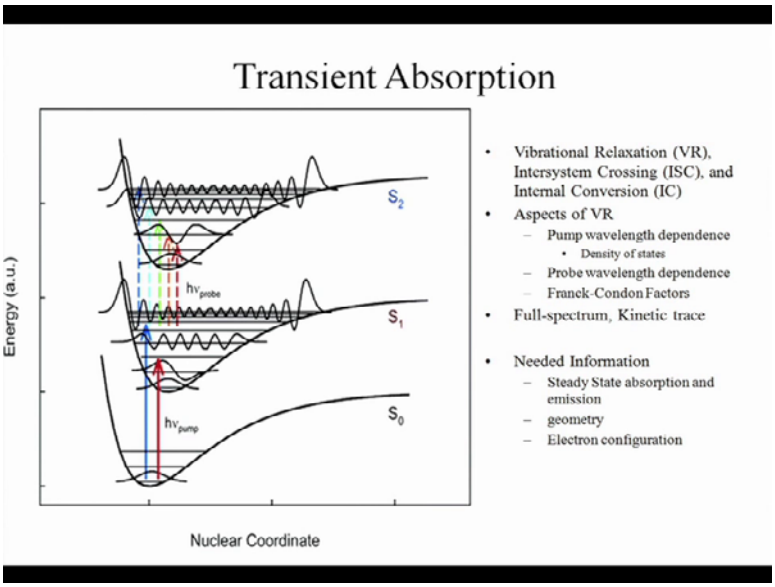

Hi good morning everybody. We are back with ultrafast processes, now in the last lecture we talked about this pump-probe technique. Now this pump-probe technique is similar to laser phosphatases, but only difference is that it has got faster time resolution. So, this pump-probe technique is basically a transient absorption technique where you generate transients by the help of a laser pulses and then you probe with a second light source. So, here this is a typical example this is your s 0 state low lowest in electronic state this is s 1 I mean next lowest then s 2 and so on. You know these are the vibrational ladders and vibrational function that is like this and the probability is shifting to the extremes of vibration I mean this ladder.

So, what you do is if you pump-probe means you pump it is an electronic spectroscopy again. So, you deal with electronic flask of course, vibrational levels are involved

vidronic may be. So, that is you pump with red photon then maybe you are exciting summer over here, you pump with a blue photon energy more you are exciting at some higher energy. So, your system will be either over here or over here depending on depending on whether I know you are using high energy or low energy photons. So, the movement it is here then you has another pulse which is called the probe pulse and this probe pulse is basically as I told you that white light. White light means you have got the option of selecting different frequencies.

So, you choose different frequencies like blue then green then red or in between frequencies so; that means, you can probe this process that is from here to the upper states. So, that you can get information of the of the positions of various levels and also immediately after excitation what is happening whether this is coming back to here or it is doing something else. So, that basically the population of the state you can monitor as function of time end also as a function of frequency of your probe. So, various processes may happen after excitation it is vibrational relaxation may be it is here. So, it relaxes to the lower level, it is called the vibrational relaxation say from 1, 2, 3, 4 say it is excited to 5 th ladder it will come back to the less ladder of s 1.

So, it called the vibrational relaxation may be inter system crossing to s 1 to say t may be internal conversion from a s 1 to s 0. So, all these things an aspects of vibrational relaxation is pump wavelength dependence probe wavelength dependence will also be there and then Franck Condon factor these are all inter. So, that we may not able to talk more in detail we can get the full spectrum of this substrate of this species or may be can be get the kinetic traces will give you the idea. Whether a new species is generated or a species is generated from one to another may be you will be getting at one wavelength you will be getting a decay another wavelength.

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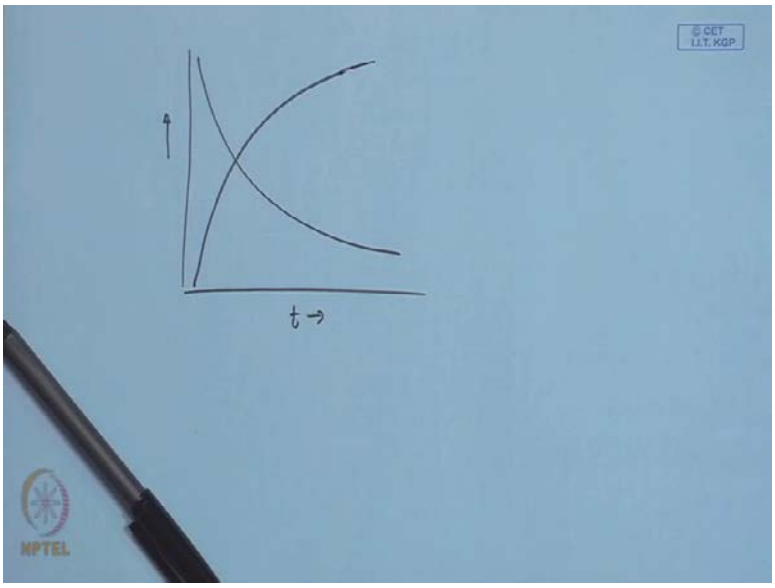

You will be getting a rise like this say with time may be one wavelength you will be getting decay another wavelength you will be getting rise. So, from this you can find out the mechanism you can this will give you. These numbers will give you the idea what is exactly going on and at what rate this is going on this decay process or this rise process or growth process. So, that this kinetic traces are very important. So, ultrafast spectroscopy transient absorption will give you that information. So, it is a very important technique.

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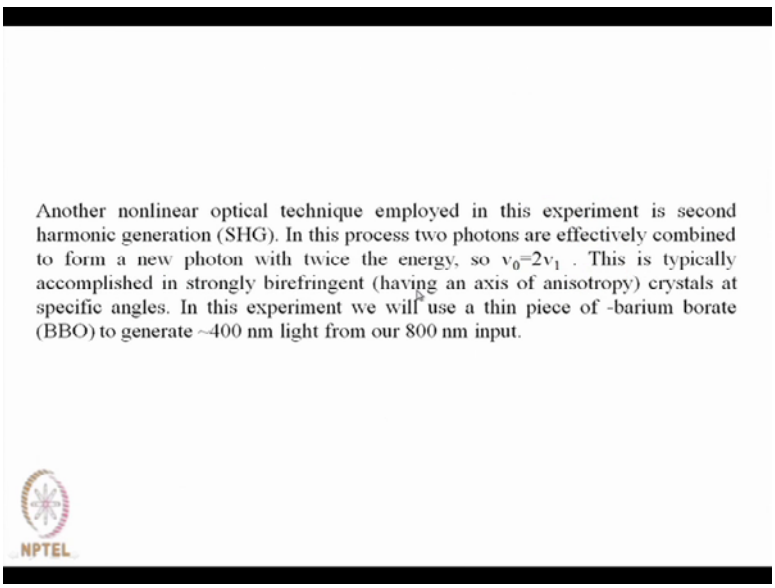

So, these are the things that we can know follow another non-linear technique employed is the second harmonic generation. In this process two photons are effectively combined that is amalgamated to form a new photon with twice of the energy and this is called up conversion although it is exactly double. The energy means it is second harmonic, but broadly it is called the up conversion that is energy is a lifted this is typically accomplished in a strongly birefringent medium having an axis of an isotropy like beta barium BBO crystal. So, a v beta barium borate and a like those BBO crystal or may be other crystals as well having this geometry. So, in this experiment we use in generally use a thin piece barium borate BBO to generate 400 light from 800 nanometer input. If we have 800 nanometer, we can generate 400 nanometer light.

So, it is basically 2 nu 1 giving rise to nu 0, but maybe it is nu 1 plus nu 2 giving rise to another frequency having which is higher than both and that is called the up conversion frequency up conversion. That is also another useful technique for studying this very first processes, very first may be physical, may be very first ultrafast chemical processes.

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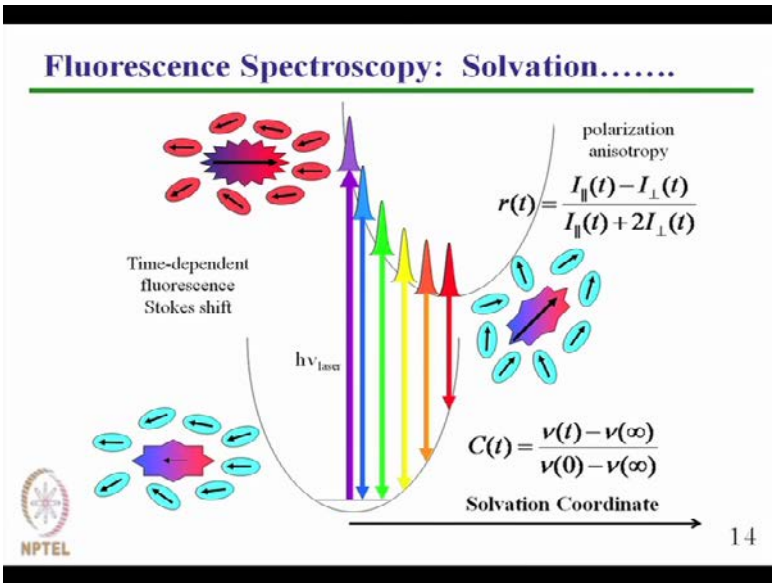

Next we will move on to another important trope topic solvation dynamics. What is this solvation dynamics? Now it is a very important experiment by which we can follow this dynamics of solvation kinetics of solvation how solvation is going on with time. So, basically you know you have got a sample I mean say you have got a dimolecule. So, dimolecule means it has got some absorption bent. So, absorption then it absorbs at the

absorption bent, if you shine with light it absorbs energy and it goes to excited state. Now the thing is that if it happens like as follows that you have got initial dipole movement may be like this much dipole movement is the product of charge and their separation.

So, in the excited state may be it is electron distribution changes such that dipole movement becomes more say initial, it was like this then it becomes like this. So, dipole is changed also it may. So, happen that direction of the dipole is also changed. So, there is a huge change in say dipole movement between the ground state and the excited state then what will happen. So, the ground state this molecule with lower dipole is solvated by solvent molecules may be water may be other polar molecules. So, it remains solvated now. So, these dipoles are oriented in a manner that it is this I mean water dipoles or may be the solvent dipoles are oriented in a manner that it is stabilize the energy of the system.

So, it is lowest in energy then you shine with radiation so; that means, you have got this low stable solvated then you know a level which is not at all solvated excited. So, it is called it is your Franck Condon excited state which is not at all solvated and may be dipole is increased. So, you see that here initially the molecule is there it is solvated in a definitive fashion, now you excite over here. So, it is energy is more and dipole may be in a reverse fashion dipole may be in a reverse fashion. So, what is going to happen for that dipole is increased then it is called the system has changed it is polarization state of polarization. So, these dipoles will tend to reorient themselves I mean the solvent dipoles will tend to reorient themselves in a manner in a manner that stabilizes the system that is this will solvate this will solvate this one was originally solvated now it will solvate.

So, this will solvate and that solvation will take some time because solvation will recurs, suppose your dipole is oriented this way. So, say this is your delta plus side. So, these delta plus side is you know this delta plus side and this delta plus side or maybe if it is minus side whatever it does not really matter means may be this is delta plus, this delta plus. So, they will repair same sign it is better to say same sign. So, dipole movement is dipole is oriented this way and this dipole is oriented this way. So, they will repair each other. So, it will tend to reverse it is orientation that is this will be preferably in this side and this tail will be in the other side.

That means, they are required to orient this way that orientation takes time that orientation takes some time therefore, what is going to happen what we can observe means if we have you know efficient spectrograph and if we can record the time dependent transients then we should be able to find out a how much time that these solvent molecules will require to stabilize the system. So, what is happening that you shine with violet light or the blue light? Then it is progressively stabilized energy stabilized initially it is at some high energy level and then as progressively they rotate the overall energy changes. So, this dipole is stabilized, it is energy I mean it is solvated. So, this electronic state is solvated means, it is energetically reduced.

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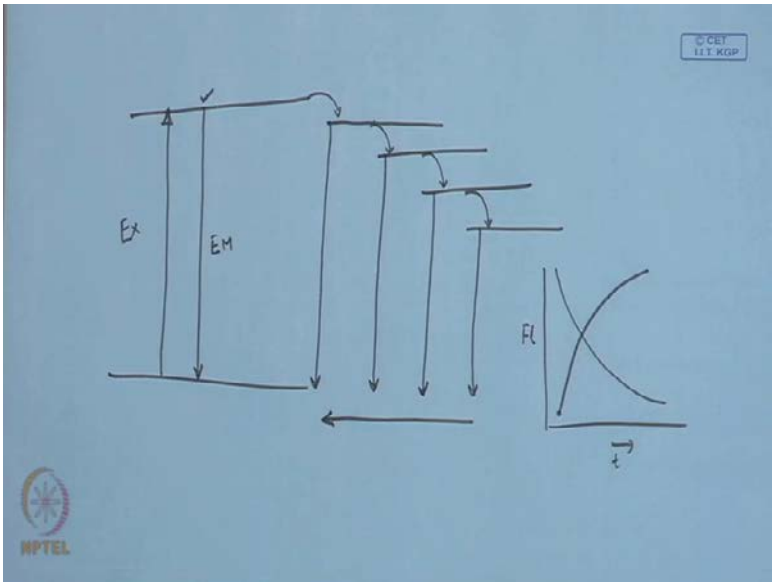

So, what is happening that you shine with radiation you generate this state and then gradually you have these levels. So, with time this level is stabilized from here to here means a little change in solvation state. Another solvated state and these are may be all non radiated processes. So, you have got excitation you may get emission from here to here, this is also emission. Now, can you tell what the difference between all these emissions is? What is that I guess you are that difference are that this length is more than this length than this than this. So, energy gap is more here than here then here then here. That means, corresponding frequencies will be more I mean this way frequency will be more frequency will be more so; that means, your emission spectra will show a time dependent.

You know stokes shift means it is maxima emission, maxima is changing with time why that is changing because of the solvation the levels are gradually solvated therefore, basically this much of stroke shift you may observe in your emission spectra. So, if you take the emission spectra as a function of time then surely you expect a rate shift in the emission spectra rate. So, what do you expect that you may expect that in the blue side? Blue side means this side of your spectrum there is decay and the redder side, because it is generated from here to here. So, red side you will be expecting a growth because at t equal to 0 that is immediately after execration. You have got only this level this state not this state you allow sufficient time or sometime then this solvated, I mean unsolvated one or may be. This one will be transformed to this slowly to this level.

So, if you plot this intensity or I mean frozen intensity as a function of time for the blue side and for the red side you are you may expect there is a decay and there is a growth decay why because this species are generated from here to here. Therefore, it is decaying to this and this species was not there at 0 time that is why 0 time it is 0. So, this way you can follow the dynamics of solvation that is by monitoring the time dependent fluorescence stokes shift you can follow the solvation dynamics of solvation. That is the kinetics of the process that is how you know this system is solvated.

So, that gives you a great deal of information about the directed behavior because the movement you generate a dipole or you change a dipole of the system then it is dielectric properties is also getting affected. So, that is dielectric dependence time dependent dielectric properties that you can follow that is how this solvent molecules are solvating from this. You can get important information about the solvent properties what are the components of solvation whether this is the principle mode of solvation, I mean principle I mean only rotation is there any translation component or may be some other modes by which this dipole can be solvated. So, that those information are you can get. So, that is following these rate processes that is rate of solvation you can follow the dielectric dependence dielectric behavior.

So, that is a very important part and also you can follow the polarization, how this is orienting, reorienting that you can follow by measuring the polarized fluorescence. Polarized fluorescence means you follow the fluorescence intensity at two different linearly two planes. One is perpendicular component and another is the parallel component and see how this is changing with time. So, that will give you the idea of how

the solvent molecules are reorienting and also how this probe molecule is also reorienting. So, from this by noting this polarization behavior like you think of your polarimetry time dependent.

Polarimetry kind of that will give you the idea how that is changing I mean this solvent molecules are rotating or this probe molecules is rotating with time that is also another rate process, I mean whether there is any viscous drag force. So, that will give you the idea of viscosity that is facing by the probe molecule. So, following ultrafast processes I mean ultrafast fluorescence we can gather information about the micro viscosity of the medium that is the viscosity. That is the bulk viscosity that we do in our you know find out in our laboratory (( )) that is the bulk viscosity microscopically. What we know it is a microscopic one, but what is in microscopic sense that is you know immediately in the neighborhood of your molecule, that is dictated by the very nature of the interaction of the molecule with your with your solvent molecule.

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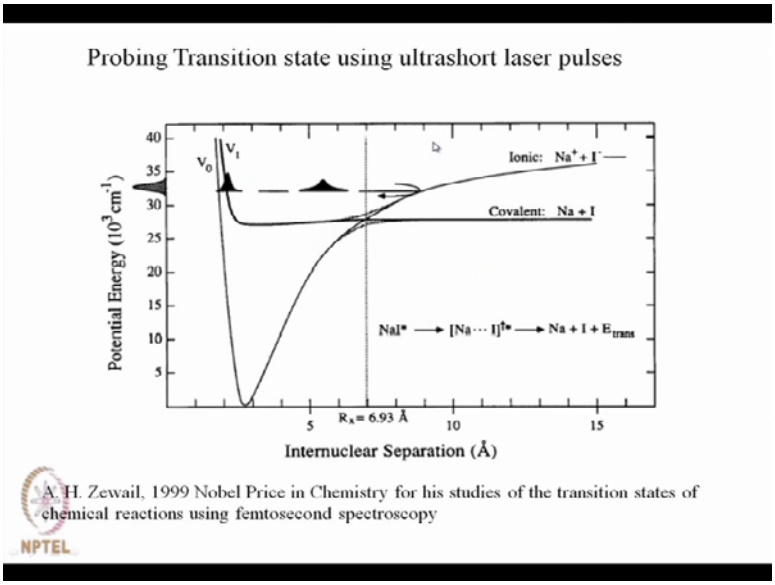

So, that is reporter for micro viscosity. So, you can find out that also from following ultra fast spectroscopy there is another very important that is as I told that in the last lecture that with advent of ultra short laser pulses. We can probe the transition state, now for this A. H. Zewail in 1999 he was awarded Nobel Prize in chemistry for his studies of the transition states of chemical reactions using femtosecond spectroscopy I am giving you just one example. That is the sodium iodide decomposition, now what you have seen that

the signal, but what he has his group has monitored have been found to have some oscillations for the sodium iodide decomposition reaction and that has been interpreted, has been found to be the real gas from other experimental data.

That it is disexperiment demonstrating correctly the observation of this observation of this dissociation of sodium iodide and this dissociation, because of this dissociation you are absorbing this oscillation and signal. So, how this is happening that sodium iodide has got two potential energy surfaces one is ionic another is a covalent and there is a crossing. Now you when you excite your sample with a lizard then may be may be you excitements you generate the wave packet and this that wave packet will go back and forth this way in the ionic potential energy surface and here you see there is a close you know appearance of another level that is your covalent.

So, may be what is happening that the movement it is coming over here it may pass from this level this to this level this covalent and may be it will pass out of this attractive ionic potential energy surface and giving rise to giving rise to decomposed sodium and iodine sodium metal and iodine via the sodium iodide some transition state.

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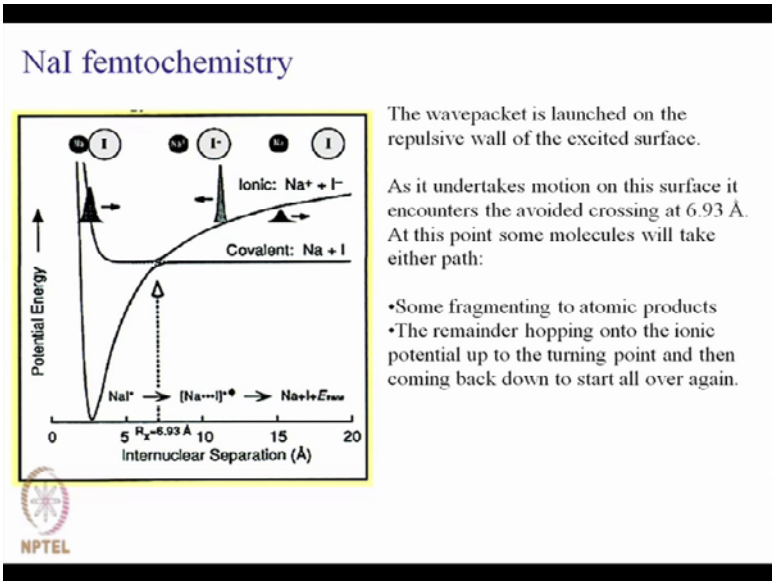

So, this has been done by ultra short laser pulses now. So, what is this sodium iodide femtochemistry? Now first what has been done you see as I told you that there is a I mean there is a crossing. So, maybe you generate your wave packet may be somewhere over here which is located on the covalent surface may be. So, wave packet is launched

on the repulsive wall of the excited surface somewhere over here. So, your sodium iodide is over here. Now as the sodium iodide has been launched over here that is wave packet that is means you can think of your wave packet.

You can represent your molecule in terms of your wave packet which is combination of various frequencies, now this wave packet will move back and forth over here on the ionic potential in the surface and as it undertakes motion on this surface it encounters the avoided crossing at 6.93 Armstrong. So, here some are over here, if it passes I mean if it encounters at this point this system has got two options, one option is either it will remain over here in the attractive potential in the surface or it will move onto this covalent I mean this side. So, what is happening that in if you record the signal, and then you will be getting some oscillatory behavior?

So, here it is bonded it is the intermediate one may be transition state and it is fully dissociated fully dissociated may be covalent I mean sodium dot or sodium metal and iodine atom. So, there are some fragments to atomic products I mean like this these are the atomic products and reminder is hopping into the ionic potential surface this is your ionic I mean basically there is a crossing. So, this is your ionic potential surface this is your covalent potential surface into the ionic potential up to the turning point and then coming back down to start all over again I mean it is going back and forth.

So, doing the same motion, it is moving to and forth this motion. So, some fraction will passed to this level and this surface and some fraction will go back to your to the another round trip excretion. So, basically sodium iodide excited it is a transition state and then sodium plus iodine plus translation irons energy.

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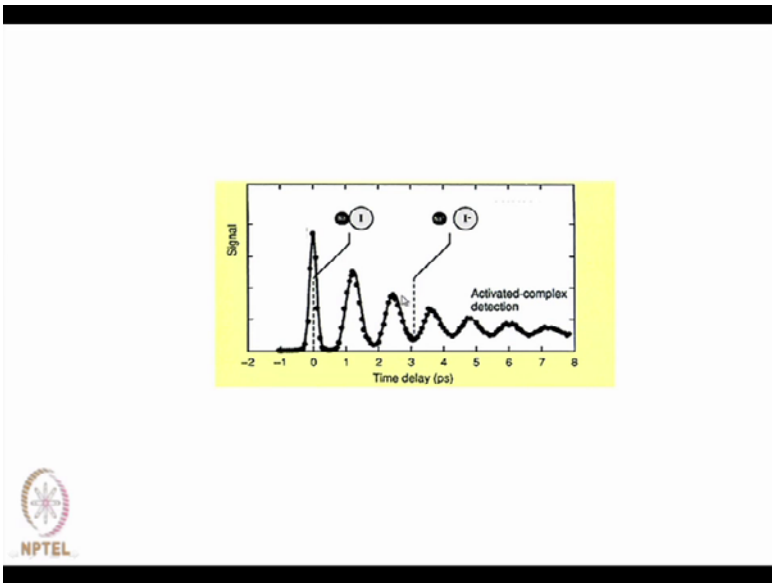

So, what is happening the signal it is maximum then minimum then again maximum then minimum again maximum, minimum, but you see it is gradually decreasing why gradually decreasing you see maximize is decreasing that is mode of sodium iodide is has passed into a passed into this (( )) I mean covalent surface. So, when it has started that is this wall inner wall it is sodium iodide its intensity is maximum then some portion has passed into this giving rise to dissociation products. So, remaining will again go back to here, but with less population therefore, it is intensity will be less again some portion will go out its intensity will be less. So, this way and this curve is minimum in the minimum signal corresponds to sodium plus iodide minus. So, this way with time this is decaying.

So, does through this experiment I mean it was for the first time demonstrated using sodium iodide, I mean using femtochemistry that decomposition of sodium iodide to sodium iodine occurs via an intermediate. Where this intermediate is stretched a little bit and from that it is dissociated to your dissociated sodium and iodine. Because of this whenever it crosses over to your covalent potential energy surface and it is I mean there is no attraction. So, just they will pass I mean they will separate. So, this is the first demonstration and if you want to know more on this if you can go through this A. H. Zewail website you can read this I mean you know many of his works on this topic.

There are plenty of examples and details of these particular I am just giving you the overall idea just a brief idea that a using femtochemistry I mean using ultra short laser pulses we can see indeed we can follow the transition state. So, that is the usefulness of this. You know transition state it is called the transition state spectroscopy. So, it is a very useful you know technique by which you can probe the transition state and we and here we have taken the help of means these two potential in surface that. Since they are crossing therefore, certain percentage is going out certain percentage is just going tunneling out to the covalent potential energy surface and thereby giving rise to your signal.

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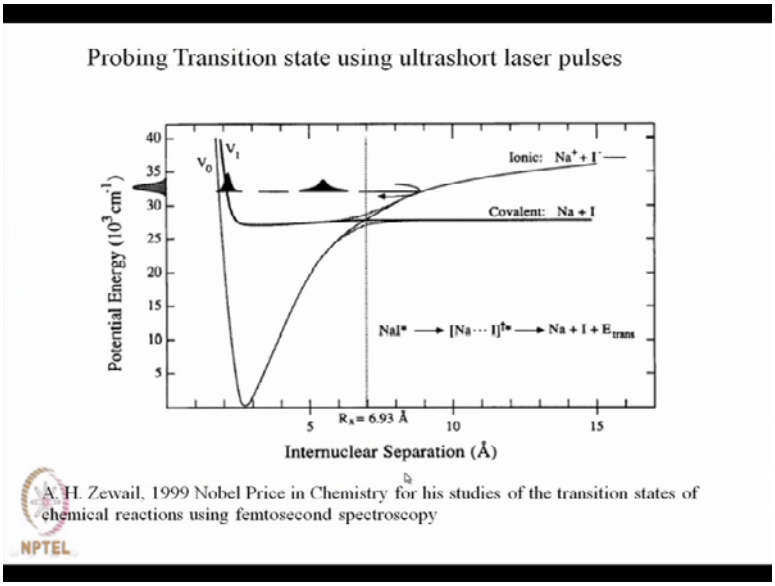

So, here at the 0 time maximum signal then it is coming this way the movement it is coming it has got the option to pass on to this certain fraction is here. Again it is coming back, but with less population I mean this wave packet is lower in height therefore, it corresponding signal will be less. So, this way that the thing has been explained and it has been found that other numbers generated from this experiment matches with whatever has been with explanation.

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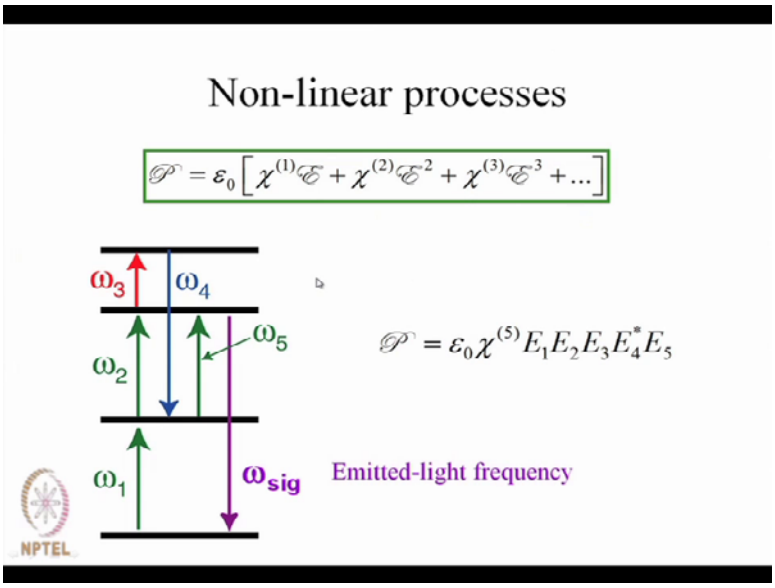

Now, again let us come back to non-linear processes because non-linear processes are very important especially in chemistry non-linear optics. So, and also non-linear optical material these are of material usage here. Now this expression has already been a told earlier that this is the polarization, this has got the fast rate time second order, third order and so on. You see it is a two photon process and if the intensity is high then two photon process means omega 1 and omega 2. They will combine to give another one this is called your frequency up conversion two frequencies combined to give you another frequency.

If omega 1 and omega 2 these two are same then it is called your second harmonic generation. So, using second harmonic generation various things can be done, but that I am not going to talk about. Suppose we have got a bi-photonic absorption and followed by another probe. So, you can follow after bi-photonic absorption the faith of this state although originally with low intensity like you cannot reach this level with sufficient population therefore, using lasers and by the use of bi-photonic absorption. You can follow the dynamics of the upper limits as well which is very important not only the ground state, but upper states are sometime very important for chemistry may be the movement. The third button is here you can follow this emission from this between these two.

So, depending on how many photons you are using whether it is a bi-photonic process or it is a monophotonic process this is very very important like fluorescence of conversion it is another technique it is like your similar to a photon amalgamation. So, in that case you have got your signal I mean you have got your sample you have got your sample.

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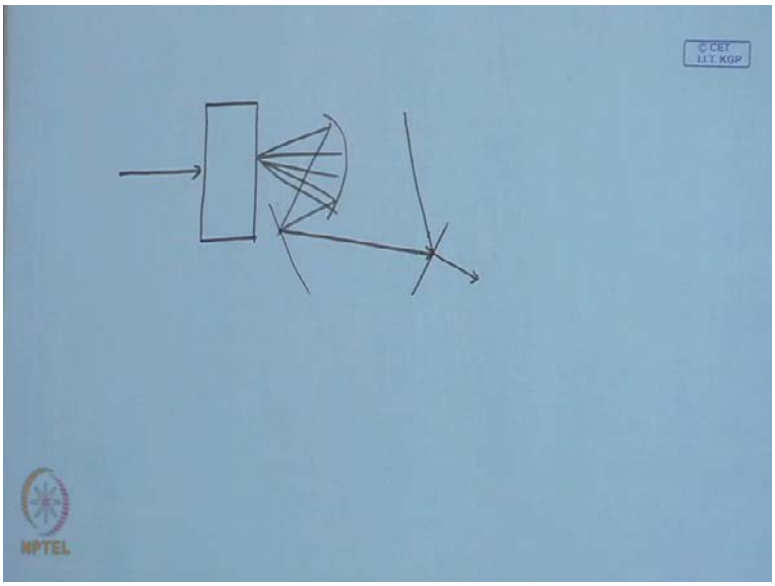

So, when you shine it with light your fluorescence is coming out you collect the fluorescence, it is collected and then it directed to the crystal. So, another crystal, but a second beam is also allowed to fall on. So, it is focused at that point I mean this crystal and because of this non-linear effects these two photons are combined to give you give you the third photon and you monitor this third photon as a function of time means in the same way. We do pump-probe here also similarly you generate your time axis by changing the optical path between this excitation source and portion of your excitation source which is fade over here and there by you generate the fluorescence decay curve as a function of time. So, you can follow the fast process as a function of time that is kinetics of a decay that is of whether is ultrafast decay. So, that is also very very important.

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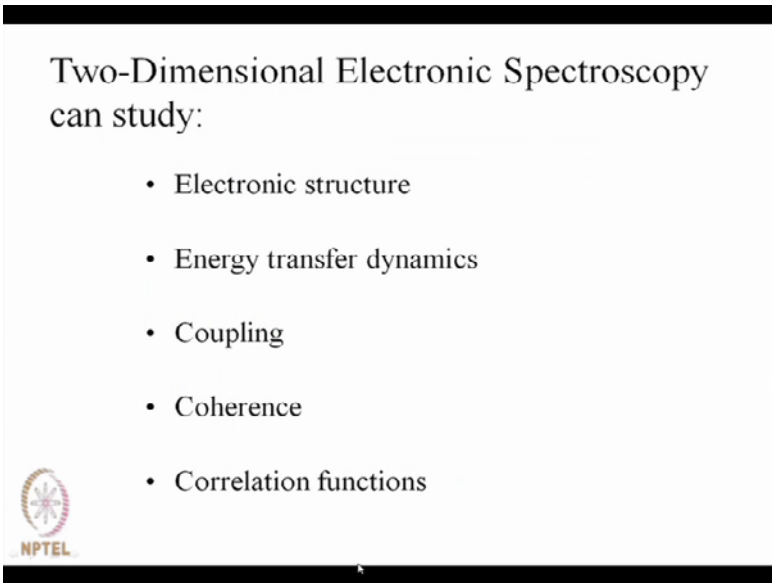

So, there is another thing which is called two-dimensional electronic spectroscopy which can study electronic structure energy transfer dynamics, how this energy transfer is occurring with time coupling coherence correlation function. So, although these are not the topic of discussion, but two-dimensional electronic spectroscopy is another important topic of discussion.

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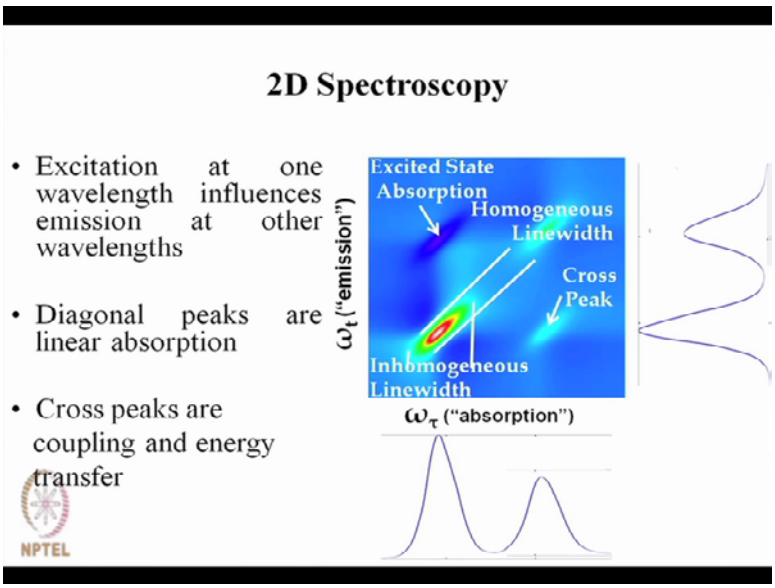

So, like in this case excitation I mean in 2 D spectroscopy excitation at one wavelength influences the emission at other wavelength and diagonal picks I mean this side your

emission and this side is your absorption. So, diagonal peaks are linear absorption and cross peaks are coupling and energy transfer. So, you can follow both from 2 D spectroscopy, if there is any energy transfer. So, this is your diagonal peak these two are cross peaks coupling and energy transfer or diagonal. So, you can follow this coupling and energy transfer. So, this is another and of course, it is time as a function of time, we can follow therefore, if you do (( )) spectroscopy you can follow both linear absorption also coupling and other phenomena.

So, this is very important. So, this is you see this is your absorption this is cross peaks excitation absorption this is cross peaks this is a typical example I mean it is not something it is just a typical example. So, many things can be done excitation absorption how this is happening how this excited species is absorbing, that is important. So, let us go back, what we have been talking about it is the whole thing let us try to summarize, but when it is ultra fast process there are many techniques to follow what is pump-probe another is fluorescence up conversion. These are I mean two parallel ways of doing ultrafast spectroscopy and of course, if it is a multicolor experiment that is you pump with blue light and you want to probe with say red light it is called the two color experiment.

Sometime it is a one color experiment that is you pump with blue and pump with red, I mean blue. So, depending upon whether it is a one color experiment or two color experiment it is named, but generally white light is used to pump-probe and there are different experiments as I told you that transient absorption and fluorescence up conversion. These are very widely used techniques and of you want to follow this solvation dynamics, one is very important way of doing is fluorescence time (( )) fluorescence.

Which is called the time correlated single photon counting that is generally done may be up to several picoseconds means for detecting components of several picoseconds of course, above that there is nanosecond also, but the movement when it is faster than several picoseconds like say if it is below 10 picoseconds then it is difficult to follow by time correlated single photon counting this is another technique. So, in that case you have to use this fluorescence of conversion sometimes UV up conversion is also needed in the species is having a specific way in that the up converted beam may be or may not

be in visible range you may need to the conversion, but the thing is that this up conversion technique a by using up conversion technique.

You can follow processes I mean very fast processes like solvation dynamics it another technique as I told you stimulated emission is another following stimulated is also important. That suppose in the excited state the species gives you stimulated emission, which is emission, is stimulated by your excitation source. Then this kinetic this stimulated emission gives you much more exciting information. So, not only just following fluorescence kinetics stimulated emission kinetics is also very important and most importantly. Now a days these solvation dynamics has been employed in many systems.

You know starting from micelles may be reverse micelles may be room temperature ironic liquid I mean this is a new types of solvent green solvents. So, I mean green chemistry starts from I mean it is low in the pressure and these are called green solvents. So, chemistry in these green solvents is really interesting. So, and also if you look into the literature you will be finding plenty of papers, plenty of observation that are reported almost every day that dynamics of solvation is different in this (( )) compared to bulk solvents or may be micelles.

So, study of this salvation using ultrafast fluorescence spectroscopy gives us lot much information about the varying nature of the solvent and the factors that are responsible for solvity certain iron or may be certain dipole. So, certain dipole or certain iron how they are the solvent and what are the components, whether solvent motion data in motion or a motion of collective other motions are important and there are many theoretical studies also going on. So, studying or study of solvation dynamics gives us not only just gives us the information on the dielectric polarization, but also on the behavior of this solvent molecule towards some dipole and also this micro viscosity.

So, that you I mean that micro viscosity can be followed by following the polarization and isotropy. That is you do polarization experiment like it is like you just think of this polar metric experiments although it is different, but similar to that. So, that is very very interesting. So, ultra spectroscopy gives you lot many information. So, polarization gives know how this solvent molecules and this dipole is reorienting with time. So, that is also a kinetic process that is also time dependent thing, time dependent process and also most

importantly the probing of transition state. So, that and the most powerful application is the probing of transition state and for which professor Zewail has been awarded Nobel Prize.

So, in that way it is success of it is one of the most important discover that we can follow the transition state. So, spectroscopy can give you I mean help you or you can it can help to visualize the transition state. There are plenty of examples that you can finding in literature about this probing of transition states, I mean not on transition state and similar oscillatory signal that is observed not only in this sodium iodide case, but also in biological cases another important aspect of this ultrafast spectroscopy is that you can follow ultra fast spectroscopy means ultra fast electron diffraction or may be x ray diffraction can give you idea of how you know a migrating from one position to another.

There are many reports available in literature that supposes if all of you have heard of this mioglobin or hemoglobin. So, it binds carbon monoxide, now if we shine with ultra short laser pulses then this carbon monoxide is detached from this iron center and then after detachment it travels around within the protein matrix. So, how this carbon monoxide is travelling within the protein matrix and that you can picture using the help of x ray diffraction that time result x ray gives you means, gives you the probable position of this carbon and oxygen with time.

So, how this is carbon monoxide is transported immediately after this flask that you can follow. So, that is another success of ultrafast spectroscopy. So, in the next piece of lecture we will take up that issue that is ultra fast I mean how ultra fast spectroscopy can be used to follow many biological processes like our vision what is; that means, whether we can follow it ultra using ultra fast spectroscopy, what is actually happening over there? What is the active molecule that is responsible over here? What is time dependence how it is evolving with time at what rate? Whether it is very fast or it is not that much fast.

So, these are the questions that still remain that are other applications other interesting and important application of ultra fast ultra fast spectroscopy that is I mean how these ultra fast processes can be probed that is ultra fast processes like the sodium, iodide decomposition or may be your carbon monoxide detachment from mioglobin. This is happening at some ultra fast timescale. So, how it is means it is position is changing,

whether it is changing or not those we wanted to look into. So, this much for today, in the next lecture we will pick up some of the remaining issues related to ultra fast spectroscopy and of course, ultra fast processes. So, till then thank you.