Advanced Chemical Thermodynamics & Kinetics
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Lecture – 40
Reaction Dynamics: Femtosecond Pump Probe Spectroscopy

Hello my name is Shaina Darvija, I am a PHD student at IISER, Mohali. As a part of the course Advanced Chemical Thermodynamics and a Kinetic. We would like to demonstrate how to capture ultrafast processes which are typically occurring on a time scale of picoseconds or sub picoseconds. In order to this, we are today here at ultrafast dynamics lab which is supervised by Doctor Arijit K De. The current research activities which are carried out in our lab include studying the energy transfer dynamics in molecular aggregates, solvation dynamics and starting the ultrafast processes which are occurring in the analogues of light harvesting complexes. Like right now, we are starting systems like quantum dots and fluorescent proteins.

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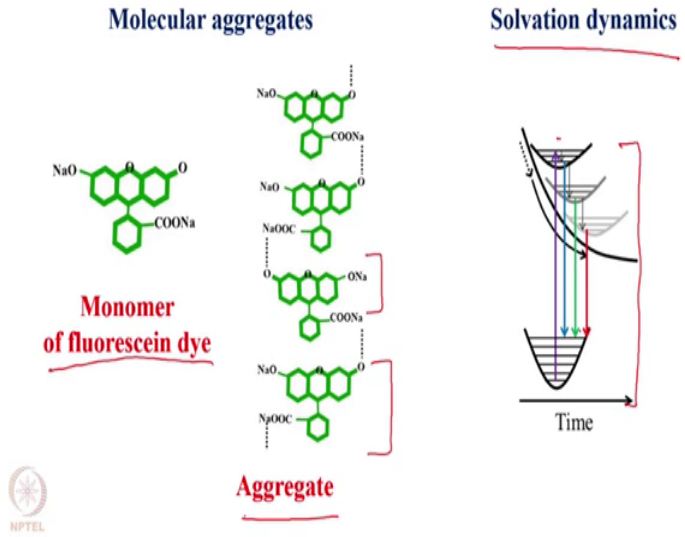

As I told previously that there are different kinds of, research projects that we are carrying out currently in our lab. This is the first system that we are studying. So, this is a monomer of a dye which is called fluorescein and this is an aggregate. So, currently we are studying how molecular aggregates are found and then we are studying them

spectroscopically. So, these are the aggregates which are formed, because of non covalent interactions between different monomer units.

The other process that we are studying currently is called solvation dynamics. And suppose the system gets excited to some level and then there is solvent rearrangement around that and the emission spectrum then shifts to higher wavelengths.

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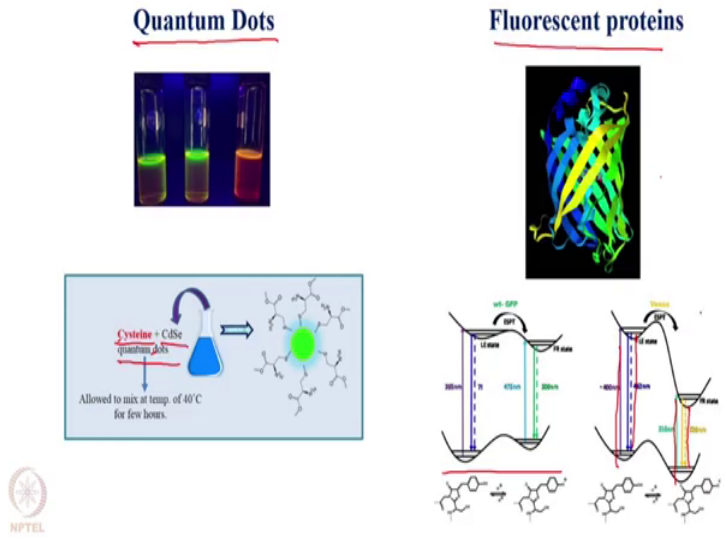

The other recent project being carried out in our lab is based on semiconductor nanoparticles which are called quantum dots and quantum dots we are synthesizing. And then we are studying their applications and artificial light harvesting systems like solar cells. So, then the quantum dots are which are made up of CdSe and are functionalize using cysteine and then they are allowed to mix up for a 40 degree celsius and then that properties are being monitored spectroscopically.

The other projects that we are doing is based on fluorescent proteins, which are we are using as analogues of pigment protein complexes which are present in plans. So, right now what we have studied is a protein called venus and we have been trying to point out how, why some of the fluorescent proteins exhibit dual emission kind of behaviour? So, excitation from a state leading to emission and then excitation of the other form of chromophore leading to another emission; while there are some which can be categorised as the original natural wild type GFP, which do not exhibit any dual emission kind of behaviour which and we are trying to point out the reasons.

So, this is a hypothetical model which depicts that this dual emission kind of behaviour depends upon different nature of the potential energy surfaces. In order to study the processes that I told about, our lab is equip with different instruments which includes a titanium sapphire laser which gives a 1 kilohertz output pulses with a pulse width of about 50 femtoseconds and a non collinear optical parametric amplifier which is capable of generating different wavelengths of light whenever required.

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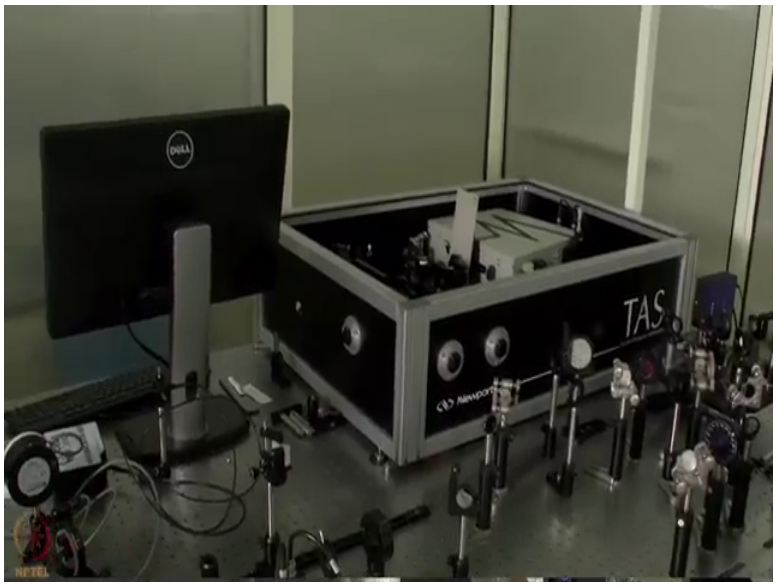

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We also have an apostrophic pulse shaper which is capable of generating complex pulses from an input pulse. It is also possible to change the phase of the pulses and also it is possible to generate a train of pulses using this.

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We also have a transient absorption spectrometer which is used to spectroscopically study ultrafast processes. Today will be demonstrating the photochemical processes which are occurring in a dye which belongs to the class of organic dyes called sainels and this dye is known as IR 140.

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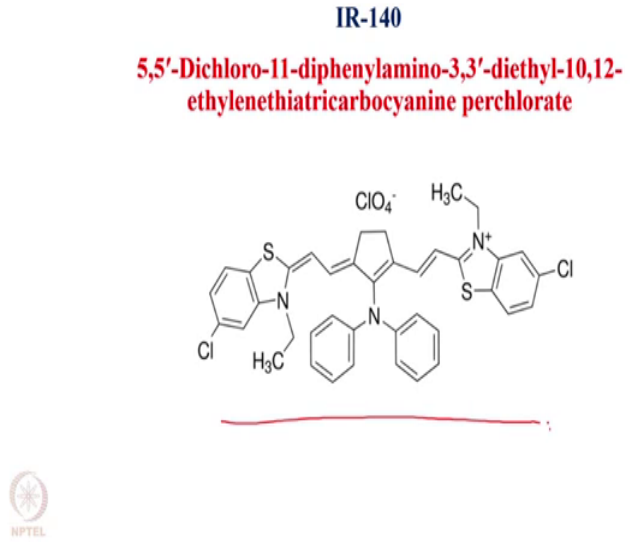

This is the dye IR 140, which we are using today in order to carry out the pump probe experiment. And this is the structure and the common name of this dye called IR 140. We will be doing this using a technique which is called pump probe spectroscopy. We will be using an 800 nanometer pumpers and an 800 nanometer probe pulse. For this dye called IR 140, it is possible to study different photophysical processes like a ground state bleach, excited state absorption or a stimulated emission using pump probe spectroscopy.

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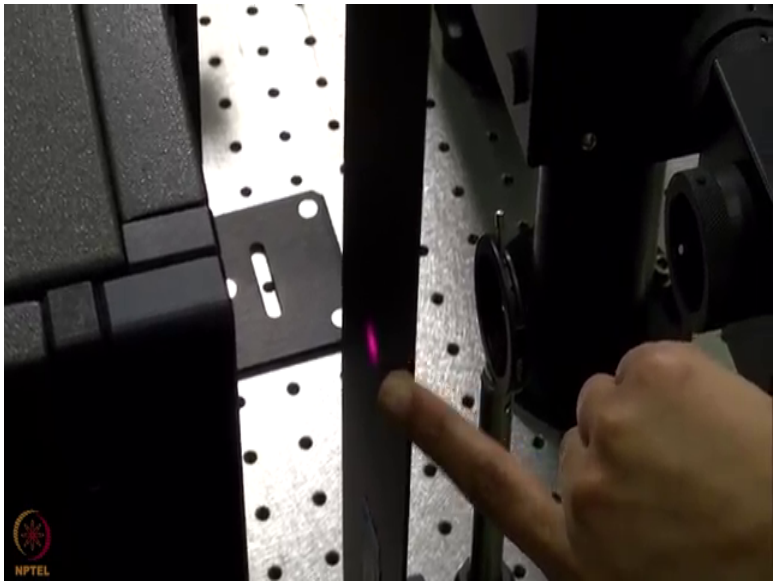

This red dot is the laser output beam that we are getting; it has 1 kilohertz repetition rate and the central wavelength being 800 nanometers. Then the beam is directed through a path, the path traced is like this. It is first hits this mirror and after passing through a series of mirrors it finally, is made incident on a beam splitter, which split the output into two parts. The one being with higher power is the pump pulse and the one with lower power is the probe pulse.

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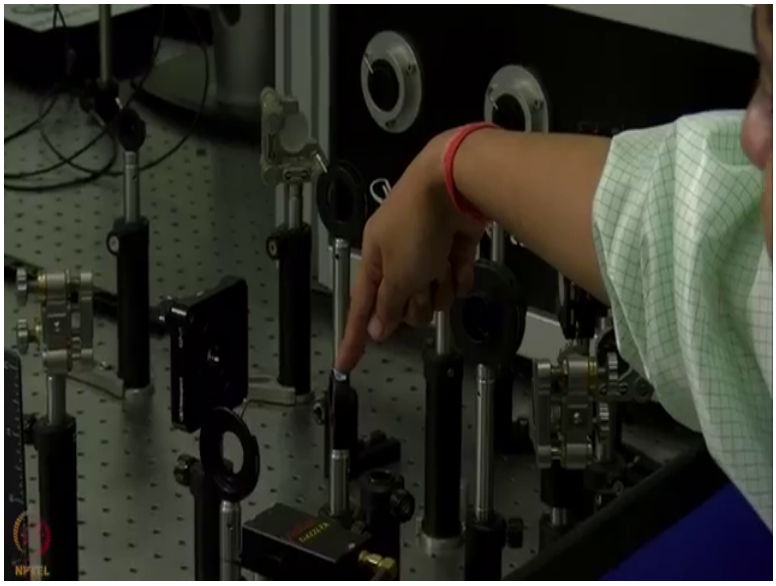

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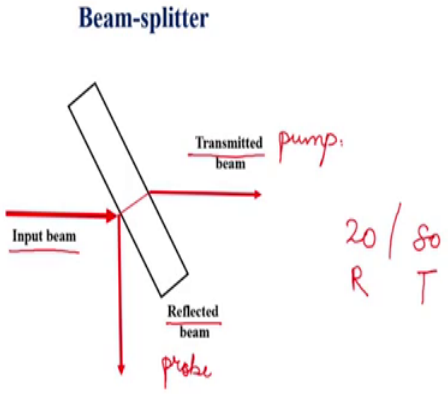

The following diagram shows a Beam splitter where there is an input beam which is incident on the Beam splitter. And then it gets split into two parts one is a reflected one, the other one is a transmitted one. So, here the one we are using is a 20, 80 kind of beam splitter, where 20 percent of the beam intensity is reflected and 80 percent is transmitted. And the one which is reflected will be using as the probe beam and the one which is transmitted will be using as pump.

So, the pump will be of higher power and the probe will be of lower power. Up to now, we got an idea about what all equipments we are using and the part traced by the beam on the table. Now my lab mate Pankaj will explain how pump probe spectroscopy works its set up and the analysis part. Hello, myself Pankaj, we I will now proceed with what Shaina told and the perform a pump probe which the spectroscopy experiment on IR 140 dye.

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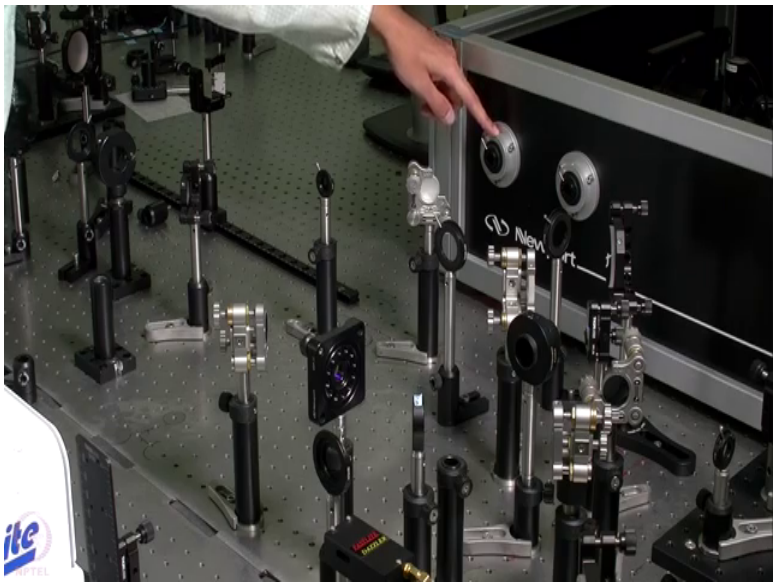

The beam after being incident on the beam splitter is split into two parts, one being transmitted which is of higher power serves as a pump beam and traces this part and is made incident on that transient absorption spectrometer through this iris. While, the beam which is reflection by our beam splitter is of lower power and serves as a probe beam for our experiment and is made incident on the transient absorption spectrometer through this iris.

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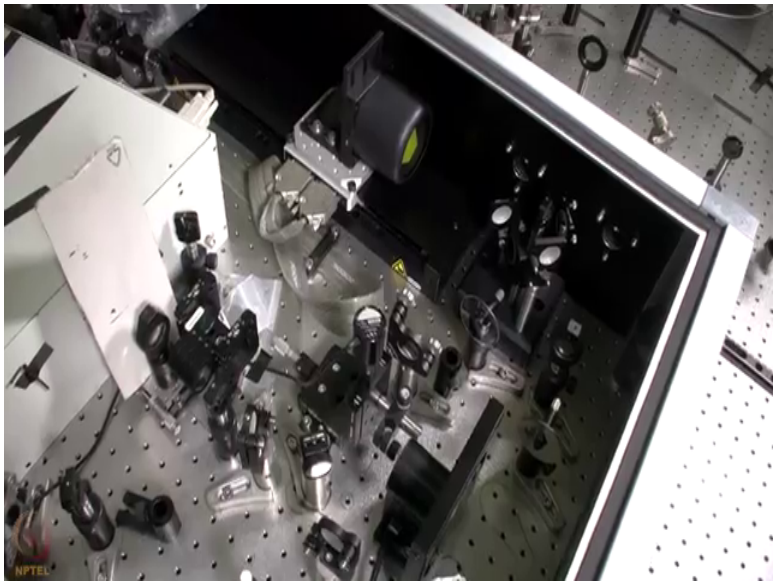

So, the pump and probe pulses after entering that transient absorption spectrometer to two different paths the pump takes this path. And after passing through a lens and the mirror is passed through a mechanical chopper which rotates at a frequency of 500 hertz. So, that it blocks every alternate pumpers as our laser beams are coming at a repetition rate of 1 kilo hertz and then is reflected through this mirror to the sample.

While our probe pulse take this path, and is made to incident on a delay line which consist of a retro reflector. Now, this retro reflector most with the speed given by us such that each step taken by this retro reflector, release the probe pulse with respect to the pump and we can trace the effect of pump at e delay of the probe pulse. Now this probe pulse after being reflected by this retro reflector takes all this part and is also incident on the sample. So, the pump and the probe pulses after taking their respective paths are made to overlap inside the sample.

Now, we need to assure that our pulses is overlap is temporally and especially at inside the sample. So, for that we have two tuning mirrors in the pump, pump by which we can move the pump beam with respect to the probe beam and can assure there especial over lab inside the sample. Now after passing through the sample the pump beam is blocked behind the sample. And the probe beam which also consist of the signal is made to travel all the way up to the spectrometer through the indicated path.

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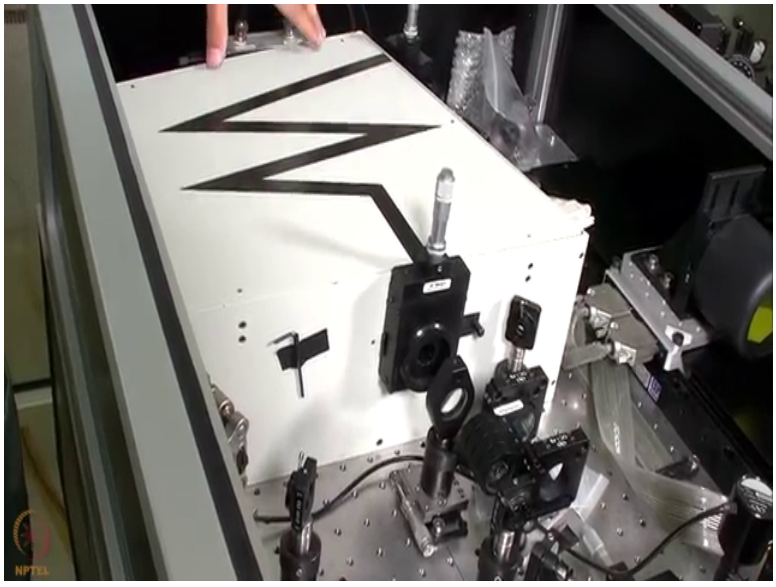

Now, this is spectrometer consist of a grating which is used to spectrally resolve the signal and contains us CMOS camera which collects the optical signal. Now this CMOS camera is then interfaced with the software and then the signal is collected. So, now the signal collected by our software is a differential signal which is based on the transmission of power probe when the pump is on and when the pump is off.

We collect the signal in differential mode, because we want our probe to probe the effect of only pump. We do not want that the, the effect of probe alone. So, we subtract the signal of the probe when the pump is chopped with the mechanical chopper. So, that is why we are blocking every alternate pumpers with the mechanical chopper.

Now, this delta OD or which we call as the differential signal can correspond to different photophysical processes such as the excited state absorption, stimulated emission and the ground state bleach. Now we can also differentiate between these processes using our delta OD. Now, this delta OD will give different sign for different physical processes and we know that our excited state absorption has a sign opposite to that of ground state bleach and stimulated emission. And hence, we can discriminate between these processes from our signal.

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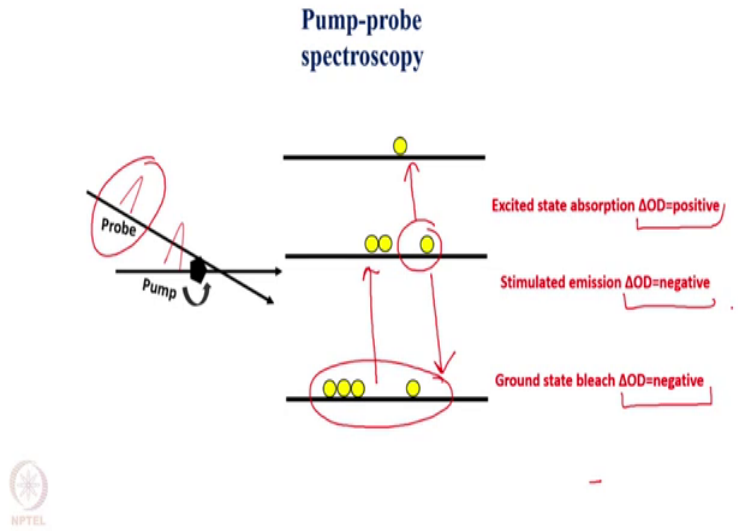

So, to explain how does a pump probe spectroscopy work we will be using a three level system in which there is some population in the ground state. So, the first pulse which,

we call as pump pulse arrives. And the thus, some of the population from ground state is excited to the first excited state.

Now after certain times which we can see here, a second pulse which we call as probe pulse arrives. Now, this probe pulse initially has some delay with respect to the pump pulse. Now it can monitor the processes done by pump pulse. So, it can either do a excited state absorption and further excite the population from first excite state to a second excited state. It can also do a stimulated emission in which it can stimulate the population from first excited state to the ground state itself.

It can also do a process known as ground state bleach, in which some more population from ground state is excited to the first excited state. So, these all processes are there in a pump probe spectroscopy. And this is how a probe probes the different processes done by the pump. Now, we can see that we have written here that the sign of delta OD is positive. The sign of stimulated emission and ground state bleach has a negative symbol or sign. We will explain what is the origin of these signs.

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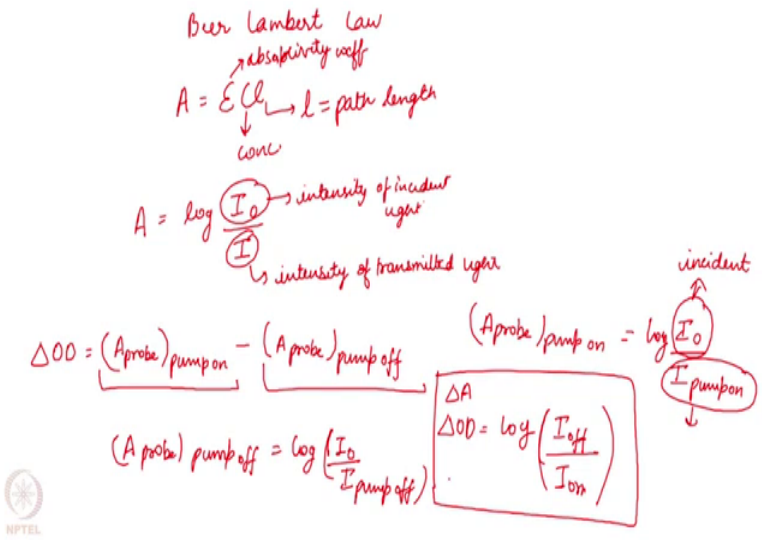

As we know, from our Beer Lambert law A is equal to epsilon C l, where epsilon is the absorptivity coefficient of the dye and the study. C is the concentration of the dye and l is the path length of the (Refer Time: 12:16). Also A, A can be written as or absorbance can be written as log of I naught by I where I naught is the intensity of incident light, I is the intensity of transmitted light after passing through the sample.

Now, what we are calculating in foot pump probe spectroscopy delta OD which is the absorbance of probe when the pump is on minus absorbance of probe when the pump is off. So, we can write the absorbances for these two individual processes. So, absorbance of probe when the pump is on can be written as log of I naught upon I when the pump is on.

To this I naught is the original intensity of probe or incident probe. And this is the intensity of probe after passing through the sample. And absorbance of probe when the pump is off can be written as log of I naught by I, when pump is off. So, in this way, we can write delta OD as log of intensity of probe when the pump is off divided by intensity of probe when the pump is on. So, this is the final expression of delta OD or delta a which we have.

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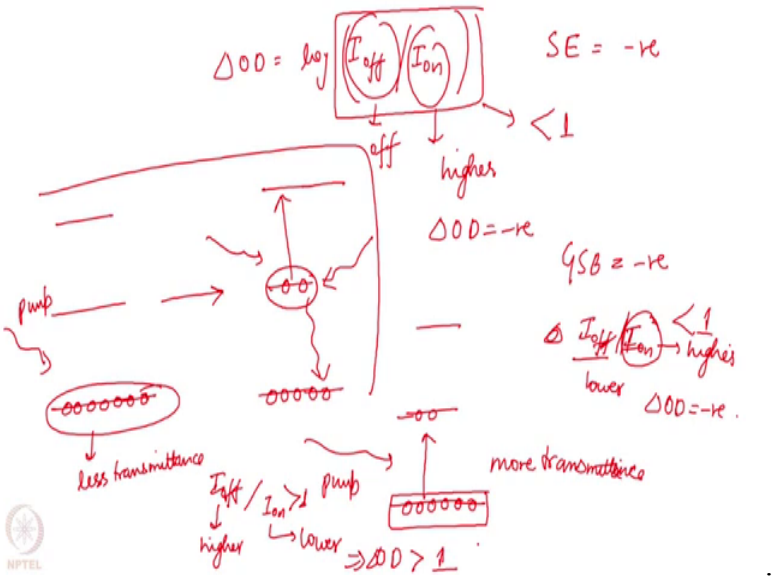

Now, we will start with why the sign is negative for stimulated emission? So, for stimulation emission as we can see that if we have a three level system and there is some population in the ground state. So, to stimulate a population from excited state, there should be some population in the excited state which can only be created when there is a pump. So, when we sign a pump on this, there will be some population in the excited state with the probe can now stimulate to the ground state. Now, the intensity of probe when the pump is on will be higher, because the probe is now transmitted much more,

because the photons transmitted in the direction will be the total photons contained in the probe plus the photons emitted due to stimulated emission.

So, the intensity of probe when the pump is on will be higher as compared to the intensity of probe when the pump is off. So, we can see that these whole value will be less than 1. So, we can see that delta OD will be negative for delta. Also we have, we know that for ground state bleach, we get delta OD as negative. So, for this also when we sign the pump, the population on the ground state has been depleted, because of which now the probe will be absorbed less for this probe for this process.

If we do not have any pump in the system then there will be higher population in the ground state due to which the probe will be absorbed much. So, because of in this case the probe will be absorbed less so, will be transmitted more. So, in this case also we can see that so, this I on is the intensity of probe when the pump is on. And we can see that probe will be transmitted more when the pump is on, because it is absorbed less. So, this is higher and this is lower so, this value again less than 1, so, delta OD here will again be negative. Now for excited state absorption, there should be always there should be some population created in the first excited state by the pump.

So, the picture can be seen at same like this. So, there is some population in the first excited state. So, for the excited state absorption, the probe should excide this population further to a higher level. So, we can see that now the probe will be absorbed much when the pump is on, because this population is created only when the pump is on. So, in case when the pump is on, there will be some population in this state. And now with the probe will be absorbed more for this process. So, the intensity of transmitted probe will be less in this case that is when the pump is on.

So, we can write it here. So, this will be higher oh sorry, this will be lower in this case and this will be higher. So, this value will be greater than 1 which we can see from that the delta OD value will be greater than 1.

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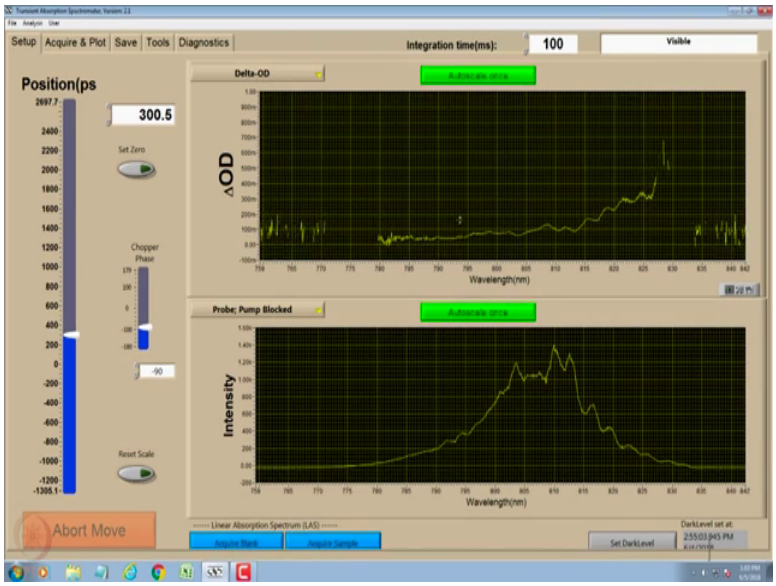

Now, from the window, we can see that we have different types of plots in the software. So, this down plot shows us the spectrum of our probe pulse and how the intensity of the probe varies at different wavelengths. And the top plot shows how the delta OD changes at different wavelengths. So, what we need to do is, we need to do I scan to do the time resolved dynamics of our system.

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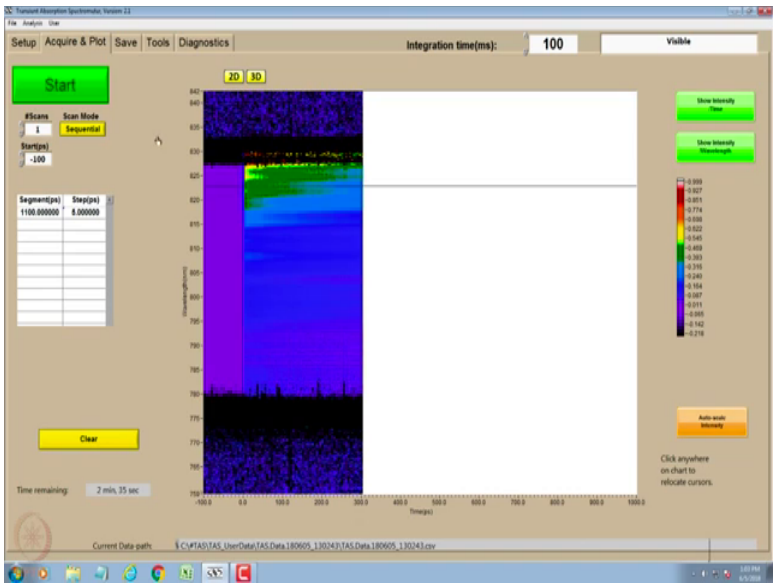

So, we give a starting point of for dye scanning and we give an endpoint for a scanning and we define at how much steps I, we should move dye scanning. So, for scanning we

have contour plots in which one of the axis shows the wavelength, while other axis shows the time which is in picoseconds which corresponds to the delay taken by our delay line or our probe pulse. Now, as we scan across different delay line, we can see that in intensity versus time plots, we can see a decay of intensity with time delays.

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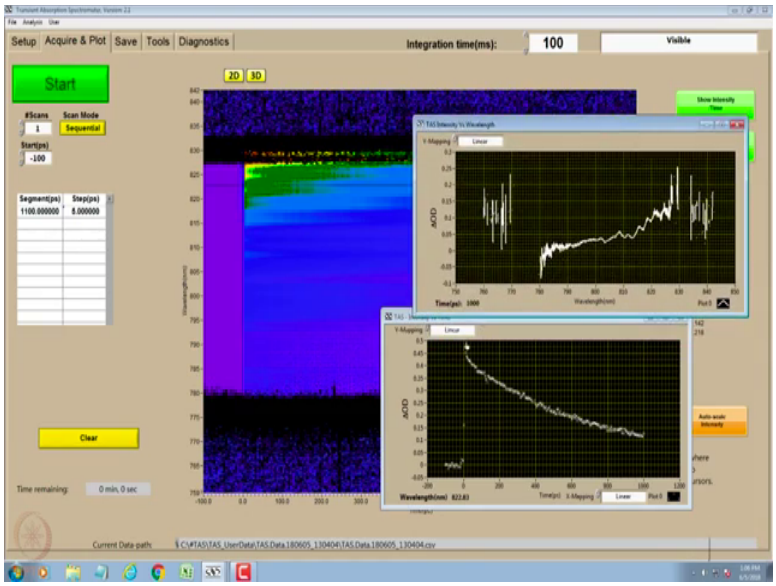

Now, as a way scanning is complete, we can see that the signal height decayed a lot over time. Now we see in the plot that there is a raise in the signal. So, this sudden raise is due to the exact temporal overlap between the pump and the probe pulses. Now also in the contour plots, we could see that there is sudden change of colour in the intensity plots. So, this colour change maps with this raise in the spectrum. Also we can see that at a particular time how the spectrum of our dye looks like? So, if we change the time we can see how the spectrum evolves with time. So, at different time intervals which we are changing from this axis this vertical line which we can see, our spectrometer can be seen different at different time intervals.

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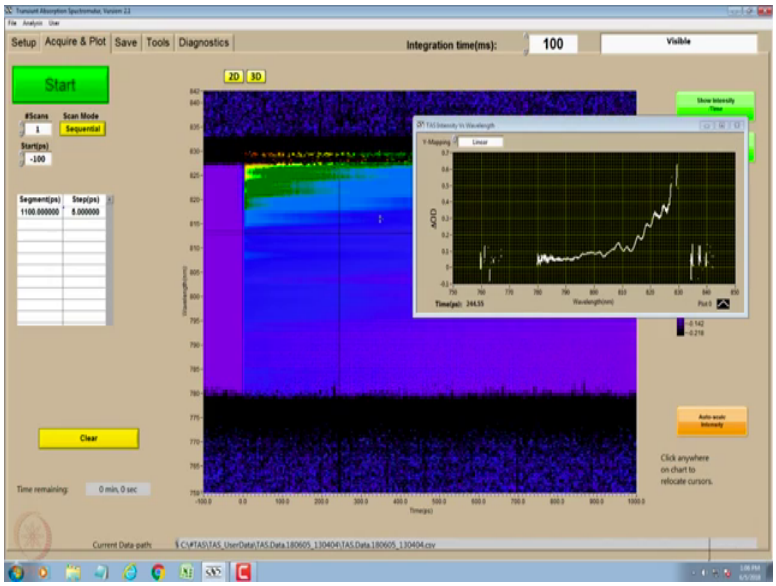

So, this from the intensity versus time plot, we can see that there is a decay in the signal. And when we fix with decay in an exponential equation, we will find the time constant which will corresponding to the life time of the system under a study. So, in this way we are able to time resolve the dynamics or life times of various physical processes during pump probe spectroscopy. We hope now, you have some idea about instrumentation, how pump probe spectroscopy works the setup and the analysis part and this is how we are studying our systems.

Thank you.