Ultrafast Optics and Spectroscopy
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Lecture – 25
Measurement Techniques in Ultrafast Spectroscopy

Welcome to module 8 of the course Ultrafast Optics and Spectroscopy. In this module, we will go for different measurement techniques employed in ultrafast optics and spectroscopy.

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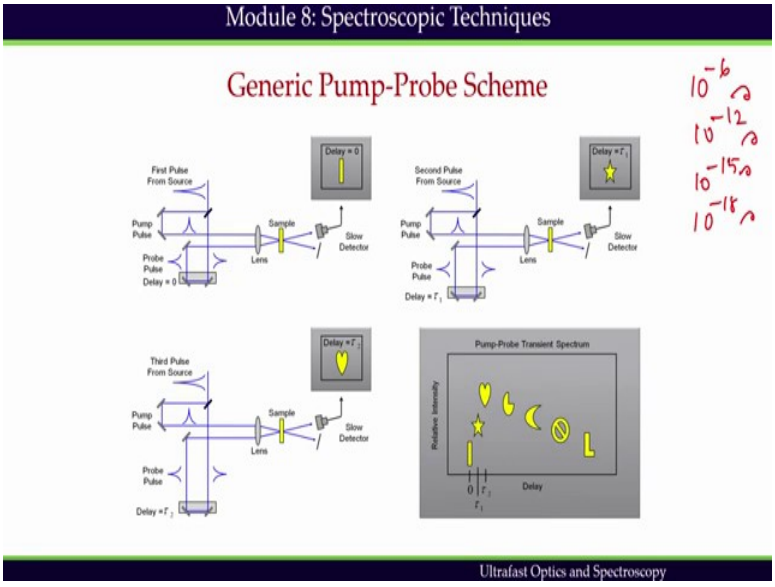

Using ultrafast spectroscopy, one can capture chemical and physical events in a very rapid time scale. The first introduction of this spectroscopy technique to chemistry came with microsecond, which is 10 to the power minus 6 second microsecond resolution with the development of flash photolysis. Later, the time resolution was improved to picoseconds, femtosecond, and to attosecond. Numerous ultrafast measurement techniques have been have been developed that is for.

We will begin with a generic pump-probe scheme used in time resolved experiments. In this scheme which is shown here a pump and probe pulses, pump and probe pulses are generated from the same parent pulse in a pulse train originated from a source. So, let say I have it just like the pulse measurement techniques we have seen.

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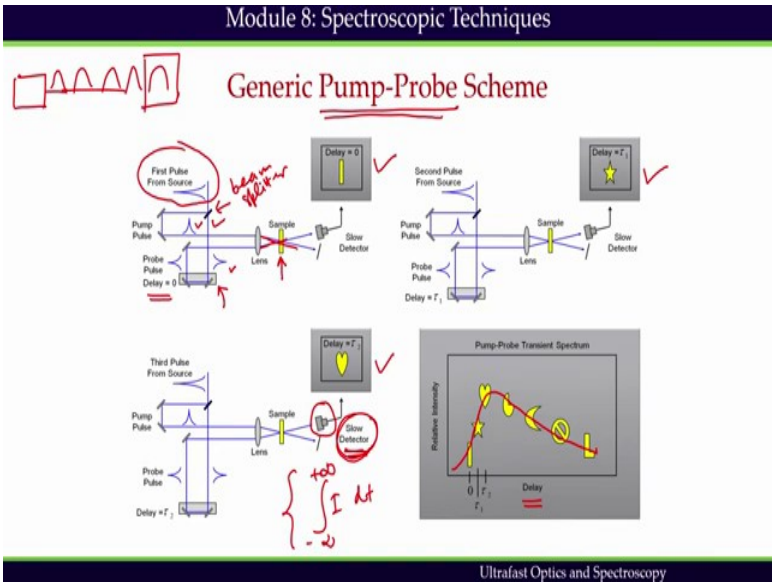

This is the pulse coming out of the source; we can use a beam splitter. And we can generate two different pulses this one and this one and we can introduce a delay between two pulses with this delay stage. Here we note that the pump and probe pulses are not two different pulses in the pulse train. When I have a source we have a pulse train a train of pulse is coming out of it. When we talk about pump and probe scheme, it is not the delay between two pulses coming out of the source or two different pulses in the pulse train.

The pump and probe has to be prepared from the same pulse coming out of the source, and then we split them with the beam splitter, and then we induce a delay between those two dotted pulses. When probe pulse at a variable time delay interrogates the system exited by the pump pulse, it sees different time evolving nature of sample, so that pump pulse will induce the excitation in the sample. This is pump pulse, and act different delay, when the probe pulse will interrogate the system, it will see different behaviour of the sample.

And this time evolving nature is manifested here by different shape of the sample, let say sample shape is changing. It is a hypothetical idea to understand the basic understanding of the pump-probe scheme, we are assuming that the pump pulse is inducing or change in the sample and the change is manifested by different shape of the sample. So, what will happen at this delay, probe pulse will see a particular shape, at this delay probe will

see a particular shape; and at this delay probe will see another shape. And as a function of the delay, if we plot, what is observed by the probe pulse, it looks like this.

And this is the basic idea of pump-probe scheme. We have already in the pump-probe scheme, an ultrafast pulse is used to excite the system, and the second pulse which arrives at a variable time delay is used to probe or integrate the system to find out how for the system has remembered, the excitation by the first pump pulse. The probe pulse can integrate the time dependent and time induce changes by monitoring samples absorption, reflection, refraction index, ionization, fluorescence and etcetera. Temporal evolution observed by the probe pulse is schematically depicted with different shapes here for demonstration.

Shall we note that the pump-probe scheme is an all optical scheme, involving a slow detector? So, we have to understand that the detector finally, which we are using is a slow detector, and nothing wrong in using slow detector because at a particular delay we can wait for very very long time to collect the total signal. So, slow detector will always find out time integrated yield minus infinity to plus infinity. And, even if we wait for this long time, it does not matter because at a particular delay we have to collect the total signal, then we change the delay.

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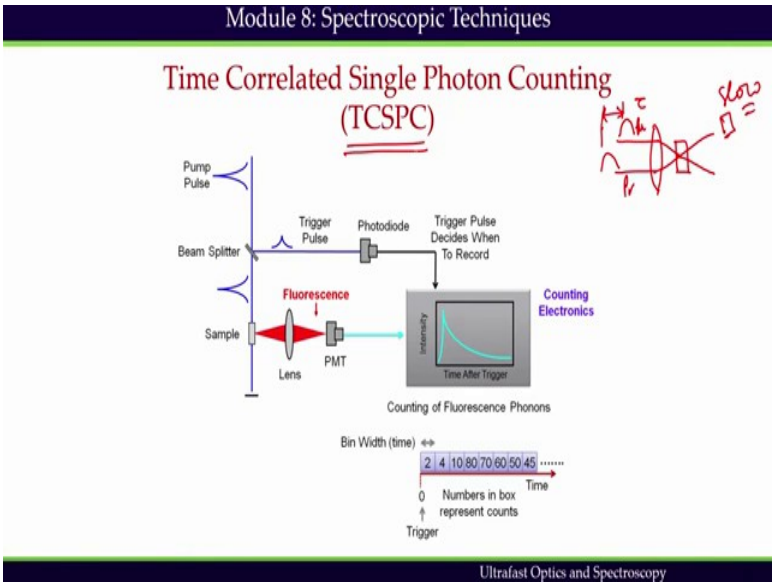

Next we will introduce a few common measurement techniques. We will begin with the time correlated single photon counting which is based on detection of fluorescence from

electronically excited state species using a time sensitive photo detector. So, as I have mentioned previously that the pump-probe scheme is a all optical detection scheme, where I have two variable pulses interacting this pulse.

This is the time delay between two pulses; we call it tau[τ]. And finally, this is let say pump, and this is probe. And finally, we have to use a detector and this detector is a slow detector. So, this is all optical schemes for the pump-probes spectroscopy, but in time correlated single photon counting, it is not an all optical scheme.

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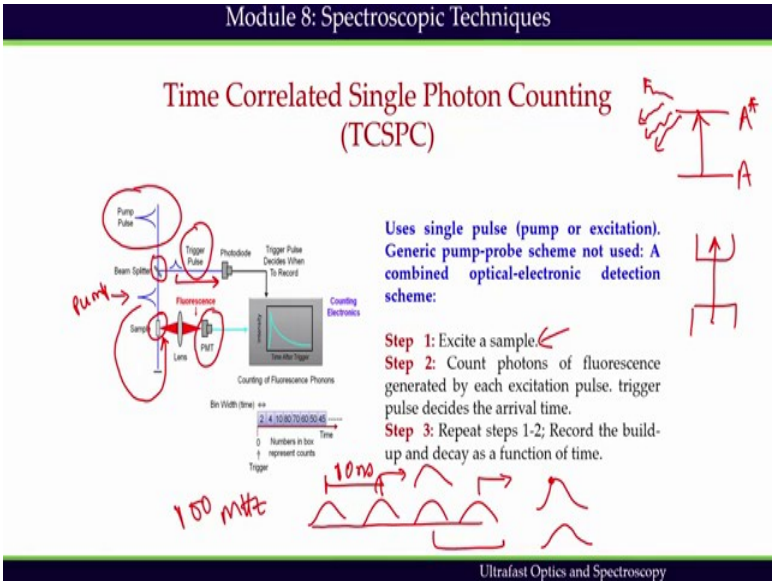

In this scheme, what we do not use pump and probe two different pulses. In this scheme we use a single pump pulse excitation pulse. We use the beam splitter to split the beam, very TCSPC, technic uses only single ultrafast pulse as pump or excitation. So, this technique does not follow generic pump-probe scheme. It employs the combined optical electronic detection scheme and follows following steps. First we have to excite the sample. And the sample is excited with the pump pulse. This excitation can be electronically excited state for a particular molecule or it can be an excitation through the bands.

Excited samples spontaneously emits fluorescence from the excited states. The moment I excite this molecules they will emit fluorescence. And our task is to record the fluorescence with the help of photo sensitive detector such as PMT. Then we have to count photons of fluorescence generated by each excitation pulse. Start this counting at a

certain time interval, it is called beam with of counting electronics relative to the time of arrival of the excitation pulse at the sample. It is called trigger pulse which can be used from this by splitting the beam. So, one beam is we are splitting this beam, and one of the beams is used is direct to the photodiode to trigger or tell the electronics at what time we should start recording.

And then this pulse will excite molecules or specious in the sample, that sample will emit fluorescence and will start collecting the fluorescence. A very small portion call trigger pulse of each excitation pulse is picked up by a beam splitter and sent out to a photodiode to create an electrical signal that decides time zero. Then arrival times of fluorescence photons are measured electronically with respect to this zero time. Therefore, TCSPC uses purely electronic detection scheme this is why time resolution of the experiment does not directly depend on the optical pulse duration rather it depends on the response time of the counting electronics such as multi channel scalar card and the photo multiplier tube.

Typically time resolution of several ten and hundred picoseconds is achievable with photo multiplier tube coupled with multichannel plate, and fast counting electronics such as multichannel scalar card or digitizer. Here we must note that the fluorescence time scale has to be longer than the pulse duration, and an also the response time of the counting electronics. Each excitation pulse induces fluorescence generally ultrafast laser source produces train up pulses, and as a result each pulse will induce fluorescence in the sample.

Therefore, temporal separation between excitation pulses determine by the reputation rate of the laser must be longer than the fluorescence lifetime. So, what we are trying to specify here is that from a source we have train of pulses. And for each pulse we get certain fluorescence signal. And if the fluorescence signal so let say this pulse has created this fluorescence signal and this pulse is creating again the fluorescence signal this pulse will create a fluorescence signal.

And if each pulse is giving us fluorescence signal, then temporal separation between excitation pulses must be longer than the fluorescence lifetime, so that no molecule in the sample stage in the excite state when the second pulse arrives at the sample. Typically Ti sapphire oscillator exhibit a repetition rate on the order of 100 megahertz which

corresponds to an inter pulse separation of 10 nanosecond. So, if it is 100 megahertz laser system, then the separation typical separation would be 10 nanosecond typical separation between two pulses in a pulse train will be 10 nanosecond.

And in this situation, if the fluorescence lifetime is longer than 10 nanosecond, then we have to use a pulse picker to step down the effective repetition rate of the excitation laser. The basic idea is that next pulse should not see any excited molecule in the sample when it is interacting with the sample to give the fluorescence. So, this is all about time correlated single photon counting process.

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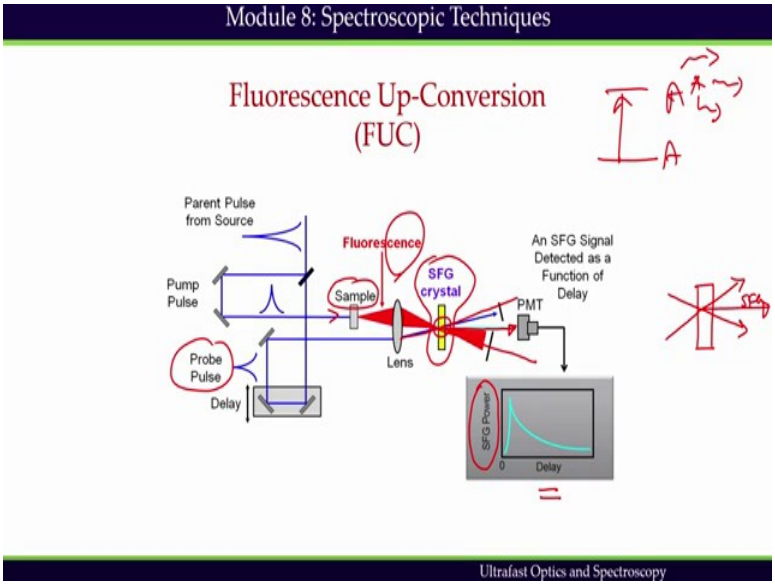

The next technique which we will discuss is fluorescence up-conversion. Similar to TCSPC, fluorescence up-conversion technique can be employed for a system, which gives fluorescence such as organic die. However, this technique does not use electronic detection scheme just like the one which we have seen in TCSPC, whether this technique uses an optical detection scheme or variation of or a variant of the pump-probe scheme.

In this technique an excitation pulse is used to excite the sample to the electronically excited state. So, this is the excitation pulse and is exciting the sample to the excited state. And obviously, as a result sample give fluorescence, this will emit fluorescence, this incoherence fluorescence beam is then directed this fluorescence beam is directed to a non-linear crystal, where it is mixed with the gate pulse which is the probe pulse it is mixed with this probe pulse or the gate pulse.

And due to this mixing we create sum frequency generation. And we remind our self what does it mean by sum frequency generation, if I have beam coming like this beam coming like this, then due to non-linear effect, we get sum frequency generation along this line and that is why fluorescence beam is coming along this way, gate beam is coming along this way, we have sum frequency generation along this way.

So, we get sum frequency generation as long as fluorescence exists. If fluorescence does not exist, we will not get sum frequency generation signal. And then what we plot is the SFG yield as a function of delay total SFG yield at different delays. This technique is called fluorescence up-conversion technique.

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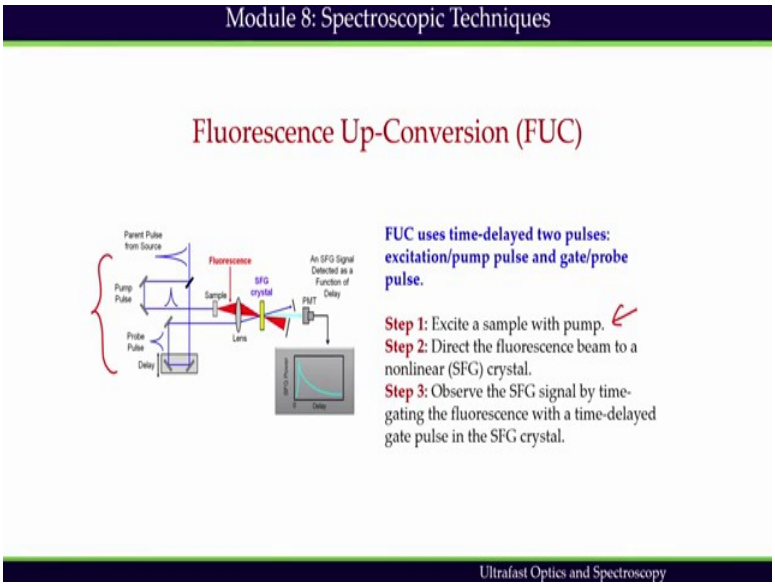

Next we have given the steps which next to be followed in fluorescence up-conversion technique. Fluorescence up-conversion technique uses time delayed two pulses which we have already seen. One is called excitation pulse; another one is called gate pulse or probe pulse. First we have to excite the sample to the electronically excited state as a result the sample will provide incoherence fluorescence.

Fluorescence emission is incoherent emission is not like stimulated emission. Then direct the fluorescence beam to a non-linear SFG crystal observe the SFG signal by time getting the fluorescence with a time delayed gate pulse or probe pulse in the SFG signal. So, these are the three steps which need to be followed in fluorescence up-conversion technique.

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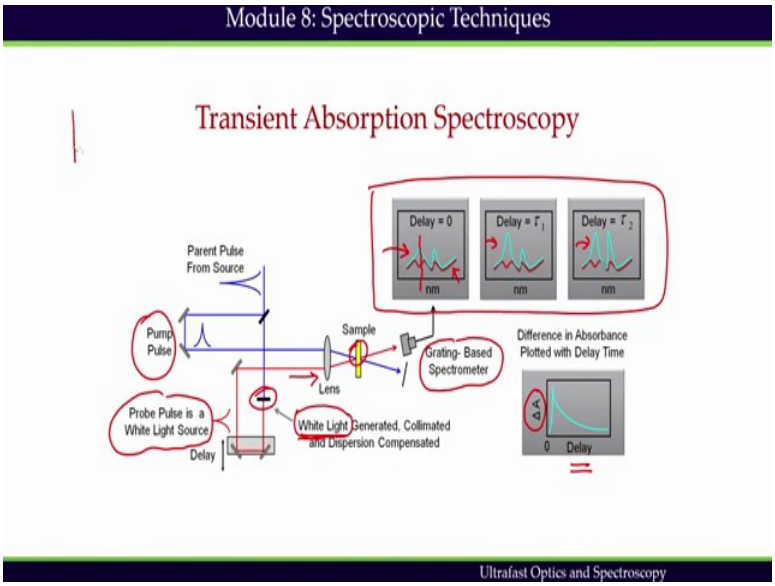

We will now discuss transient absorption spectroscopy. The basic idea of transient absorption spectroscopy is that one ultrafast pulse is used to excite a system of interest a simple pump pulse is exciting the sample, and the second pulse which arrives at a variable delay time this pulse used to observe the absorption of the transient species created by the pump and that is why the probe pulse which we use definitely will time delayed, it will be time delayed with respect to the pump pulse, but the probe pulse has to be a white light pulse, so that I have a broad spectrum to observe the absorption spectrum of that transient species.

Transient absorption spectroscopy employs pump-probe scheme in which time evolving absorption spectrum of an excited sample is monitored using a continuum white light probe pulse. A broadband white light probe pulse can be generated using self phase modulation. Here in this figure, in these three figures, we show the changes of the absorption spectrum at three different time delays between pump and probe pulses. This red spectrum represents, the absorption spectrum recorded without pump pulse.

So, the probe pulse is with the help of a spectrometer, and the probe this white light probe pulse we can record the absorption spectrum first. Finally, pump-probe transient is recorded by plotting the difference obtained with and without excitation pulse, and absorption at a certain wavelength as a function of time delay. We can see here that at a particular delay absorption is changing in different delays absorptions are changing. And

if we monitor at a particular wavelength, the difference in absorption and we plot delay as a function of delay, then we get the transient signal.

Here we may ask an important question using conventional grating based spectrometer for which response time of the spectrometer is equivalent to the response time of the electronics. We can also monitor the changes in the absorption spectrum. So, instead of a pump-probe configuration, one could also think of like this.

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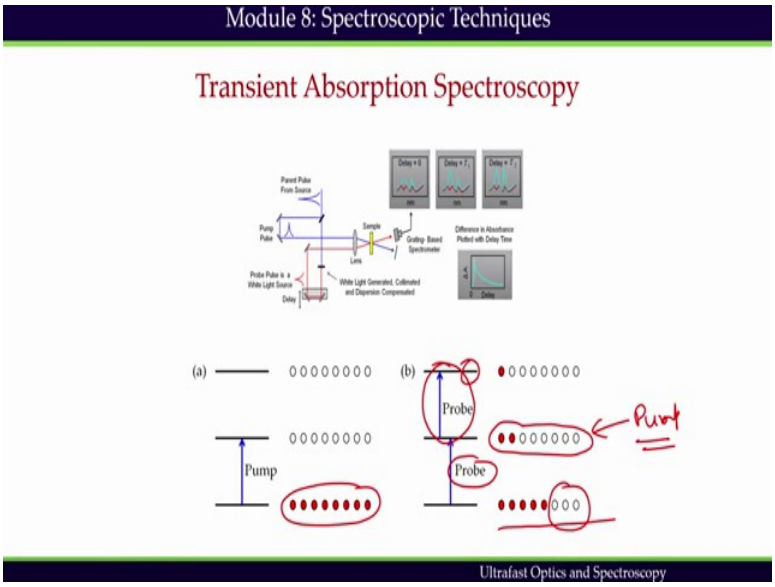

The transient spectrum obtained at a particular delay between pump and probe contains contributions from various processes. First there is depletion in the ground state population due to there is a depletion of the ground state populations. So, pump can deplete the ground state population. And due to this depletion, if the probe pulse is trying to probe it, the transient spectrum obtained at a particular delay between pump and probe contains contributions from various processes.

First there is depletion in the ground state population. So, if pump is acting on the ground state, there will be depletion in the ground state population. The pump pulse excites a fraction of ground state population to the excited state, decreasing the number of molecules in the ground state that is why we have depletion. Hence, the ground state absorption in the excited state sample by the probe if the probe is trying to probe the ground state absorption, then we see a deep or less absorption by the probe.

On the other hand, if the probe pulse is in the resonance with the allowed high lying excited state like this like the one here, again in the absorption may appear because this absorption will occur only when I have a population in the excited state and that can be created with the pump pulse only. So, there are many processes may be involve in the transient absorption spectrum.

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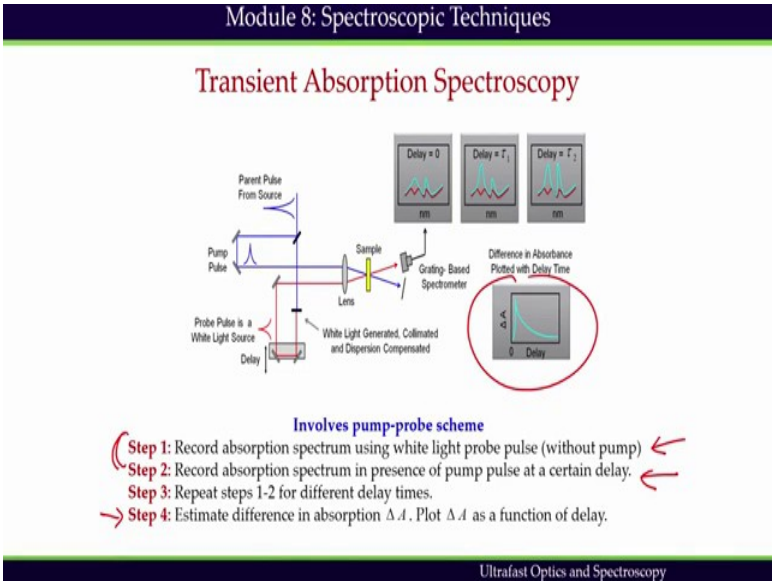

In this technique, first we have to record the absorption spectrum using white light probe pulse without the pump. Then we have to record absorption spectrum of the sample using white light probe pulse in presence of the excitation pulse. This is recorded at a certain delay time between pump and probe pulses. Then we have to repeat these two steps for different time delays.

And finally, we have to estimate the difference in absorption delta a calculated with and without pump at a specific wavelength for different delay times. And finally, we have to plot delta a as a function of delay time and we get this transient spectrum.

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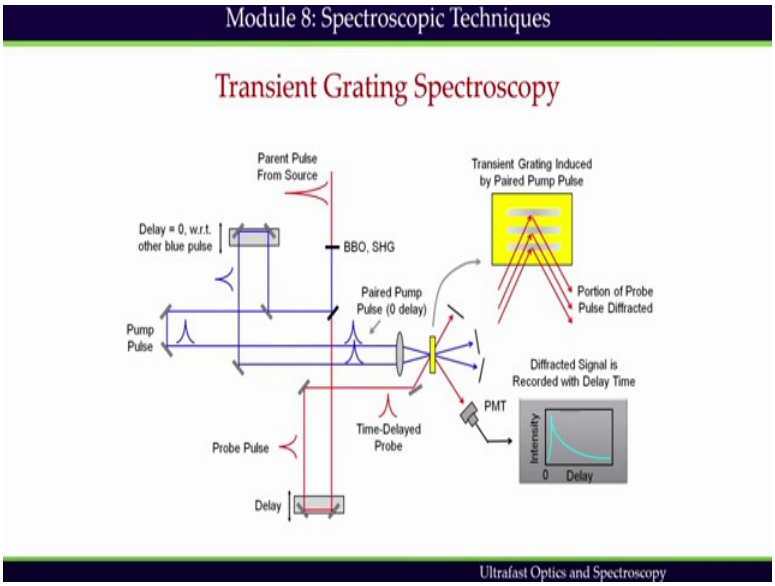

Next we will discuss transient grating spectroscopy. The transient grating spectroscopy which is also known as laser induced dynamic grating is a time resolved spectroscopic technique based on third order non-linear optical response.

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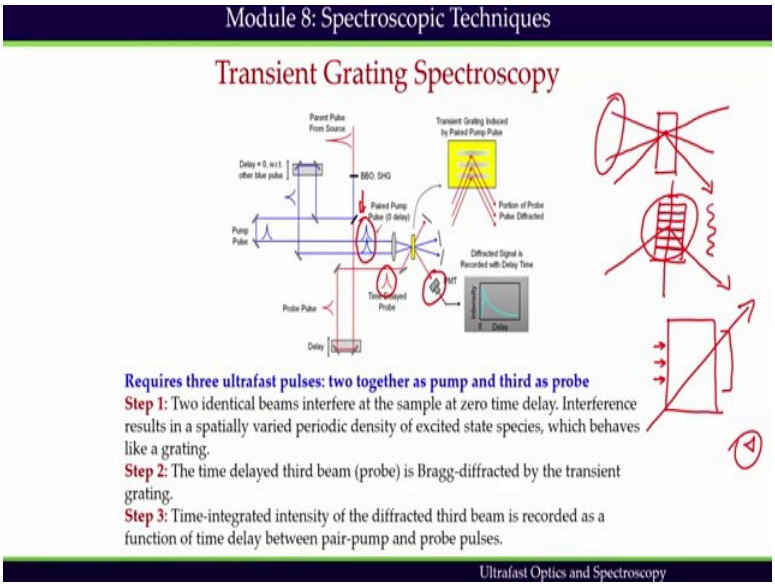

The technique is following. We use two identical pulses. These two identical pulses which are kept at zero time delay. Interfere at the sample with an angle 2 theta[θ]. So, let say I have a sample and two identical pulses are interfering. And due to this interference in the sample, due to this interference, we get spatially varied periodic density of excited

state species which behaves like a grating or transient grating. So, due to this due to the interaction of these two identical beams in the sample, the sample behaves like a grating.

Then the time delay third pulse, this pulse is time delayed with respect to the paired pulse is this time delayed third pulse is Bragg diffracted by the generated transient grating. This will be diffracted back. And in this technique, we monitor the time integrated diffracted signal of the third beam. So, it is quite clear that in this technique, we see the diffracted beam as long as this transient grating is present in the sample.

And the transient grating is nothing but a variation of the excited state species density in the medium, and this variation occurs due to an intensity variation like this along this direction. So, what happens effectively I have a sample due to the interaction of these two identical pulses at time zero delay, we create excited state species in this regime, excited state species in this regime, excited state species in this regime, excited state species in this regime and this white regimes are representing the ground state species.

And the third beam time delayed beam is then getting diffracted because of this transient grating. And this diffraction is possible only when I have this excited state species in this regime. If these excited states are decaying to the ground state, then we are erasing this grating and if the grating is missing then there is no scope of getting diffracted beam. So, we do not see any diffractive beam. And by this way we will be able to measure the excited state dynamics and also diffusion kinetics as well.

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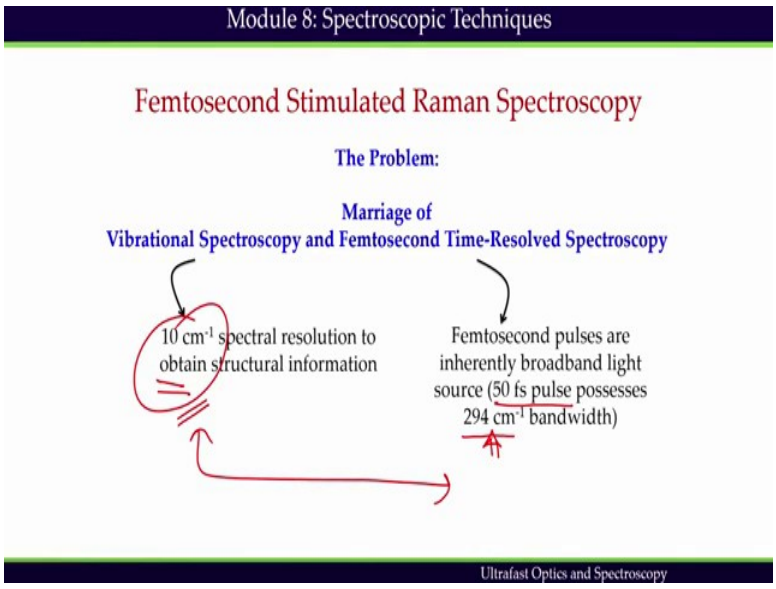

Next we will discuss femtosecond stimulated Raman spectroscopy. Chemical transformation of formation or breaking of chemical bonds. Hence to understand the mechanisms and dynamics of the evolution of structure of reactant into product, we can propose to use vibrational spectroscopy techniques with femtosecond time resolution to follow the temporal evolution of vibrational modes which are responsible for the structural change.

For an example, in a simplest form, one can monitor temporal evolution of a stretching mode to follow bond breaking or bond formation in a reaction. However, marriage of vibrational spectroscopy with femtosecond time resolved spectroscopy possesses a fundamental challenge originated from time energy uncertainty. One must achieve at least 10 wave number spatial resolution to obtain structural information using vibrational spectroscopy.

So, I need 10 wave number resolutions to obtain the vibrational spectrum. On the other hand, femtosecond pulses are broadband light source. And let say we have taken 50 femtosecond pulse definitely it should have almost 300 wave number bandwidth. So, with the help of a light source having 300 wave number bandwidth will not be able to measure a vibrational spectrum with 10 wave number resolution. It is impossible. Femtosecond stimulated Raman spectroscopy is an ultra fast spectroscopic technique that provides simultaneously high temporal and spectral resolutions by passing this problem.

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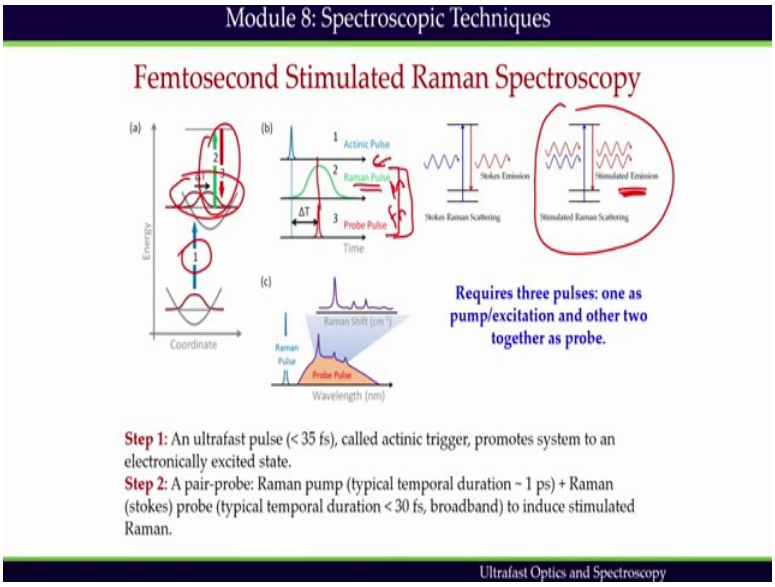

And what is this technique? In femtosecond stimulated Raman scattering a picosecond Raman pump pulse and a femtosecond broadband continuum probe pulse are incident on a sample simultaneously with zero time delay. So, this Raman pulses, Raman pulse and probe pulse, they are kept at zero delay. These two pulses drive Raman transition stimulated stokes emission which is shown here. If the difference of the frequencies of the two pulses matches the molecular vibrational frequency of the sample, we get this stimulated emission. Raman game spectrum is generated only during the time that Raman probe pulse is on the sample.

And thereby less than 100 femtosecond time resolution can be obtained using femtosecond stimulated Raman spectroscopy. On the other hand, the full Raman vibrational spectrum over a 3000 wave number (Refer Time: 34:17) can be obtained using this spectroscopy technique. However, pulse duration greater than 1 picosecond are necessary for the coherent Raman pump beam for this beam to achieve good spectral resolution.

So, here what we have done is that we need a long pulse picosecond pulse which is called Raman pulse, and a short very short pulse probe pulse. And combination of these two pulses, we get stimulated emission, Raman scattering. Raman probe signal is detected using a spectrometer and it is not time resolved, this is why femtosecond stimulated Raman spectroscopy provides resolution which is independent of time bandwidth product of the femtosecond pulses. It depends only on the bandwidth of the Raman pump and the resolution of the spectrometer, so this one and the resolution of spectrometer.

Following techniques are followed an ultrafast pulse which is called trigger, initiates photo physics or photochemistry of a sample in solution by promoting the system to an electronically excited states. So, this excitation is electronic excitation from ground state to the electronic excitation excited state. This excitation is followed by probing the excited state system using two pulses these two pulses overlapped in time which means that these two pair pulses are kept in delta t[Δt] 0 delta tau 0, one of them is called Raman pump pulse with temporal duration 1 picosecond and another one is called Raman probe pulse with temporal duration less than 30 femtosecond broadband.

This pair pulse probe induces stimulated Raman scattering and this is why a gain is observed in the Raman probe beam.

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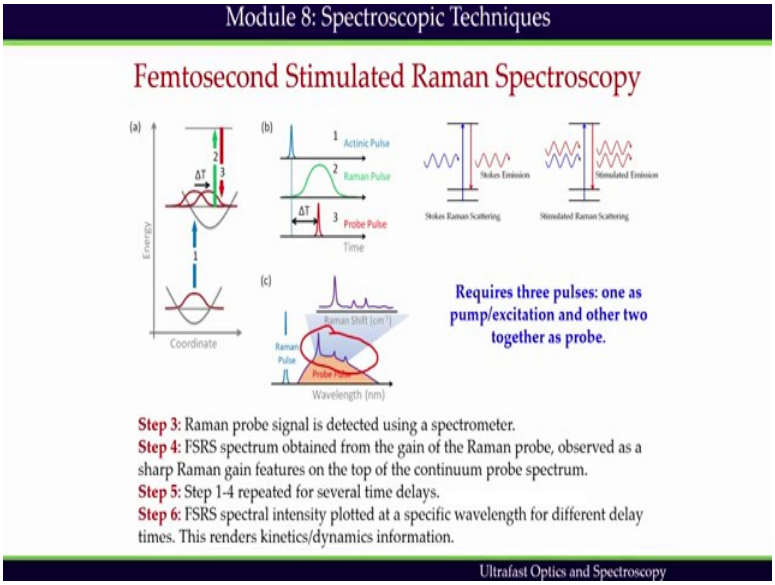

Raman probe signal is detected using a spectrometer then, finally, femtosecond stimulated Raman spectrum is obtained by determining the gain of the Raman probe pulse throughout its spectrum by taking the ratio of the probe spectrum when the pump is on and off. This is observed as a sharp Raman gain. So, we get a sharp Raman gain feature on the top of the continuum probe spectrum.

Femtosecond stimulated Raman spectral intensity is plotted then at a specific wavelength for different delay times and we get the transient signal. So, by this technique, we can study excited state dynamics while monitoring different vibrational modes during the dynamical process.

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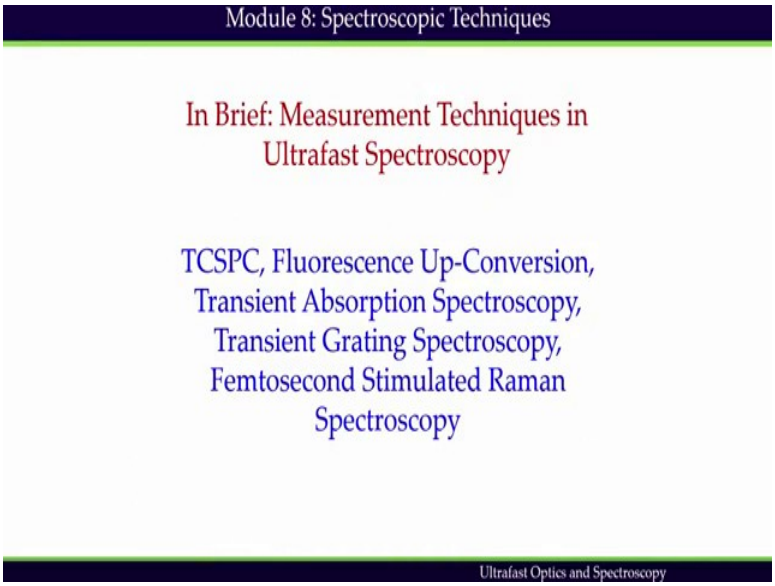

With this, we have come to the end of this module where we have discussed different measurement techniques used in ultrafast spectroscopy. We have discussed time correlated single photon counting technique, we have discussed fluorescence up-conversion technique, transient absorption spectroscopy, we have discussed transient grating spectroscopy and femtosecond stimulated Raman spectroscopy.

We will meet again for the next module.