Ultrafast Processes in Chemistry
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Lecture # 14
Fog Lab

In the last three modules, we have discussed femtosecond upconversion spectroscopy, femtosecond fluorescence upconversion or femtosecond optical gating fog. Today, we have come to the lab, and we are going to show you an actual fog spectrometer, and you will see how the data is recorded. But before we do that, let us to capitulate what we have done in the class. I will first show you a diagram of the system, then we will go to the instrument.

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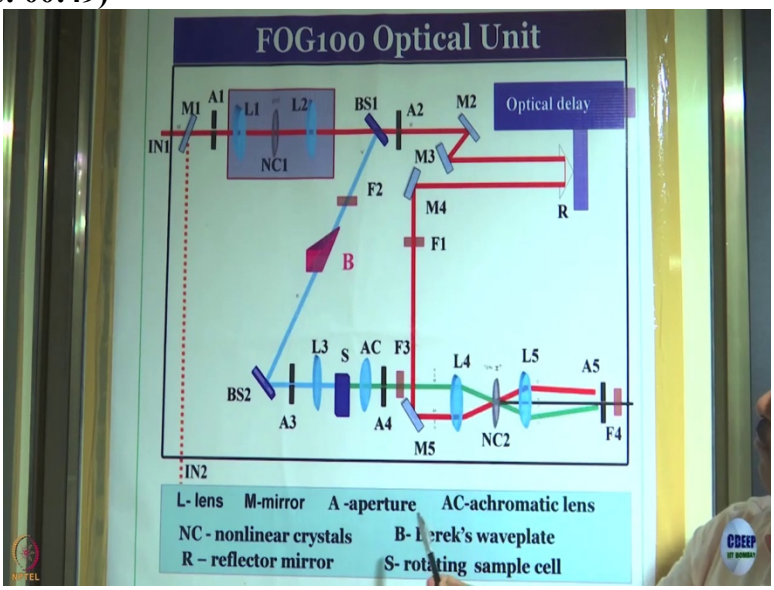

So you might remember that this is the layout of our optical unit for the fog spectrometer. The spectrometer we use in our lab has the name fog 100. It is from a company called CDP Corporation, which is based in Russia. So, just to remind you, what we have here is that we have red light, nominal, 800 nanometer, but in our case tunable from 690 nanometer all the way to 950 nanometer from a femtosecond pulse titanium Sapphire laser.

Later on in this course, we are going to open up the laser that is used as a light source for this instrument and we will show you what is in there. But let that be the story for another day. And let us wait until we discuss the operation of a titanium Sapphire laser in class before we come back

and show you the laser for today. We just take the laser as a light source, 100 femtosecond pulses 80 megahertz repetition rate.

This light source passes through an aperture and is focused by this lens L 1 onto a non linear crystal NC 1 here we typically use beta barium borate BBO crystal, and by focusing the red light onto the nonlinear crystal 1, second harmonic generation takes place and we generate blue light. Now in this region, you have red and blue light that is there are mixed together. Since you focused you go to have a diverging beam here.

The diverging beam is captured by another lens L 2, which is placed in such a way that the focus of L 2 is at NC 1. Then the mixture of red and blue light goes and hits a beam splitter VS 1 here, red light goes through and blue light gets reflected to something called berek wave plate that every show you do light goes and hits another beam splitter through which any residual red light is dumped and the light blue light itself is reflected, this light is focused by another lens L3 onto the sample.

And as you are going to see, the sample that we use is mostly liquid sample, which we rotate all the time so that it is not destroyed by these femtosecond pulses. We are also going to learn later on how much energy per pulses there. Then, from the sample fluorescence is collected by another lens goes through a long pass filter F3 which blocks the excitation blue light, but passes the fluorescence light this fluorescence light is focused by a lens L 4 on to another nonlinear crystal which we call NC 2 or as we have discussed in class, the sum frequency generation crystal.

So this is one part of the story. The other part of the story is that the red light that passes through BS 1 hits a mirror M2 another mirror M3 and then gets retro reflected to a mirror, M4 to M5, from M 5 it is Focused by the same lens as the one that is used to focus fluorescence light onto the same nonlinear crystal NC 2. So, here what you have is a sum frequency generation, you remember this is called gate light the red light, let us say that has omega 2 frequency.

Let us say omega one is a frequency of the fluorescence, I do not exactly remember whether you use omega 1 omega 2, but I think you can understand. So, what happens here is that omega 1 +

omega 2 sum frequency generation takes place and it is this sum frequency that is made to go through another filter which in this case is a short pass filter passes only UV and we have calculated in class how UV is generated here and this UV goes from monochromator and then to our detector.

So, the way it works is that this retro reflector is mounted on optical delay, optical delays essentially a 1 foot long screw which is moved. So, the screw is moved to a particular position, then intensity of sum frequency is recorded, then it is moved to another position, intensity of sum frequencies recorded. And this is how the entire map of fluorescence decay is generated by plotting intensity of sum frequency against the delay time.

And as you might remember, we had said that since the intensity of the gate pulse is constant and intensity of fluorescence falls off with time, intensity of the sum frequency, its product of intensities of omega 1 and omega 2 the intensity of sum frequency actually provides a measure of intensity of fluorescence light, the intensity of gate light is constant. So, when we plot that against delay time, we generate the fluorescence decay with femtosecond time resolution.

And while calculating this time resolution I've roofed up a little bit because I have taken frequency of the velocity of light to be three into ten to the power ten meters per second actually it is three into ten to the power eight meters per second. So, crux of the matter is if you move this through in with microsecond resolution, then you can obtain time resolution in femtoseconds. So, that is a recap that we wanted to provide. Now, let us go and see the spectrometer.

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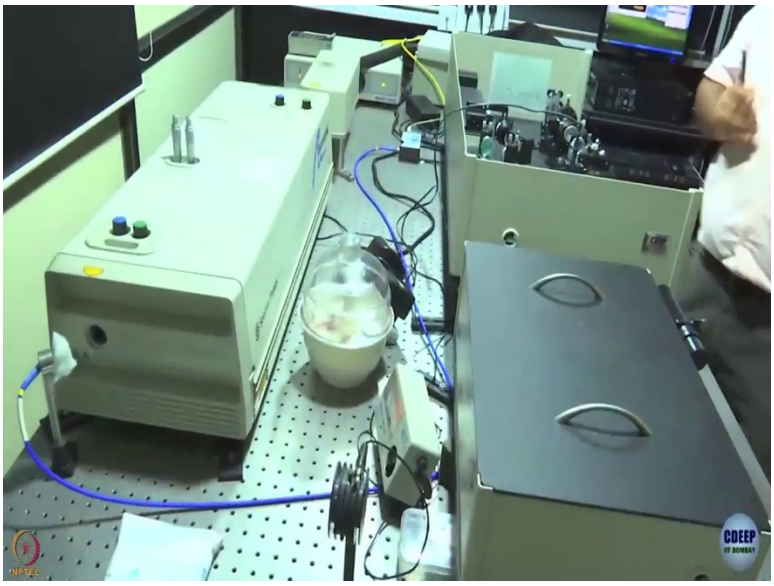

Alright this is the optical table on which our femtosecond optical gating experiment is done. This here is a femtosecond laser. In our case, it is a tsunami laser from new port it is quite old. The other laser that we have not shown you yet I think is much compact. But what tsunami does is that it provides 800 nanometer light with 100 femtosecond pulses at 80 megahertz repetition rate. So that light you can hardly see it comes here hits this mirror comes here goes to this optical unit.

Which we are not going to discuss because we are not talking about third harmonic generation. From there it goes into the spectrometer. This is a spectrometer fog 100 where the experiment is actually done and for your benefit, what I will do is I will remove all this so that you can see a little better.

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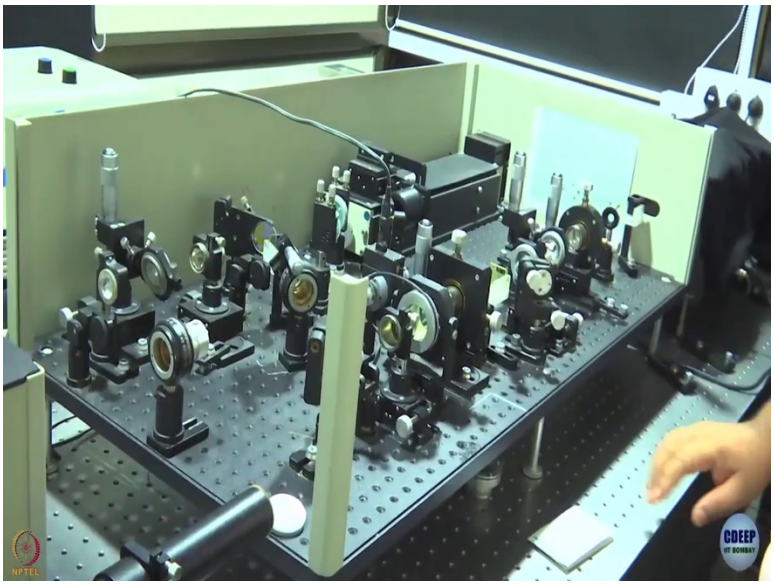

This here is the optical unit remember where laser light is supposed to come from? It is supposed to come from this direction. Now let me show you the red light if you can see. You see the red spot of light. That is the output of the titanium Sapphire laser. To your eye. It seems that it is a light that is always on but actually it is not. We have hundred femtosecond pulses there and the pulses are coming at a repetition rate of 76 megahertz too fast for our eyes to make out the pulses from each other. That is why it looks like continuous wave.

So this comes here. This is the lens that, for dramatic effect, let me do something else. Let me block this or maybe not, this is the lens that focuses it on to. Ye, that is better focus is it on to this nonlinear crystal. And you can already see some blue light coming out from here as you see, the intensity of blue light is something that depends on how I turned the crystal. You see the blue light got brighter .

And if I turn the other way, it is going to get dimmer and dimmer. So these crystals are angle tuned as you are going to study perhaps later on, you can actually change the angle of the crystal by using this micro meter screw head and that is what is going to affect the efficiency with which second harmonic is generated. Now, this slide, you can only see blue light here because it is so bright, and our eyes do not see red light all that well.

So this blue but actually it is a mixture of red and blue. So that comes here on to the beam splitter, this is the beam splitter. So if I hold the card here you can see the red beam once again. That is because the beam splitter has deflected most of the blue light and has transmitted the red light. I have always been talking about the blue part first. So for a change, let me talk about the red path to start with.

Remember this is the gate light the red light, it hits the mirror M2 M3 and go straight this here is the retro reflector. You can see the spot here. This is a retro reflector and this thing that you see and you see better when we turn the lights on. This is a retro reflector remember, and it is mounted on a 1 foot long screw you cannot see the screw because it is inside when we show you pump probe later on, we will actually be able to see it.

And what this retro reflector does is that retro reflector can move all the way from here to here, we will just move it once and show you see, this is computer control. Your TA just clicked the mouse, and now you see the retro reflector is moving back. And as you understand where it moves back, this red light here is undergoing a longer path. So this is how we can actually change the path length of the red light red light, which as you know by now is called the gate light.

So, now we are going continually just to show you, but actually we go in steps, we go step by step, and then we stop at every step and that is where the measurement is made. So you have seen this through now, let us get back to the demonstration of the light path. We have taken the retroreflector back here, this is the incoming beam and the outgoing beam comes from here on to this mirror. I think you can see the spot on the card here.

So, it hits this mirror here, this mirror if you remember is called M4 this is M2 this is M3, this is the retroreflector R, this is M4 from M4 it comes to this mirror M5 and from M5, it goes to this lens, which focuses it on to this crystal, this crystal is the NC2 Crystal, the second nonlinear crystal. Let us turn on the lights so that you see the components once. So to repeat. This one is M2 M3. That retroreflector R,M4, M5.

This is the lens L4 which focuses beam onto this nonlinear crystal NC2. And from there, the output is collected by this lens here, this lens is L5 go straight, you see this has opened all the way this piece of optic here is a short pass filter, it allows you we like to go through but not visible light. So, you understand this is the part of the sum frequency as well as will show you this here is the monochromator.

As I told you, there is an old machine, she has developed some light leak. So, you have covered it with black cloth and this is what contains the photomultiplier detector. So, what we have showed you now is the path of the gate light. Now, let us talk about fluorescent light, I show you the path first, when the light is on, then we will switch the light off and show you the light will show you the fluorescence.

So now remember, this is beam splitter red light has gone through, and blue light has been reflected in the path of blue light, we use these pieces optics, which are called neutral density filter. The reason why we use them is that you do not want to put too much of sample on too much of light on your sample any way to get destroyed. So from there, blue light comes in this thing you see is called berek wave plate.

Because as you remember, you have to maintain magic angle polarization. If you are wrong there your decays are not going to be correct. So this is what is used to measure polarized to maintain polarization. This is a second beam splitter, which reflects blue beam and transmits the red beam. The Blue Beam is collected by this lens inside the cylinder is a lens and is focused on this sample. The sample we have is a liquid sample.

So what we have to do is we have to keep rotating it so that the laser light does not hit the same spot again and again. Well if it does, then your sample is going to get spoiled. Fluorescence there is collectined by a lens are kept inside this cylinder goes straight and passes through this filter, which is a long pass filter cuts out blue light and transmits fluorescence light then the sources light falls on the lens L4 you might remember L4 from our previous discussion of part of the red light.

L4 focuses the fluorescence light and remember as well as the gate light on to NC2 the nonlinear crystal sum frequencies is generated here, collected by the lens here go straight and we have discussed the detection part already. So, this these are the components. Now, we are going to turn off the light and show you the fluorescence and as well as the sum frequency now that the light is off, you can see blue light once again here.

Blue light comes here remember, it is collected by this lens and is focused on to the sample. The moment I remove this barrier, you see the fluorescence of the sample yourself. And that is because now you are using a standard sample which is very highly fluorescent. There you go. The bright light that you can see is that of the fluorescence and from this side if you look, you can actually see a spot that is brightest.

That spot is where the blue light is focused. And that is why the florescence from that spot is what we are actually collecting. Then everything else is a glow rising from there. Now remember the path once again, the fluorescence is collected by this lens go straight. If I put in my card here, you can see blue light as well as the fluorescence. Now we do not want blue light that is why it goes through this long pass filter as we have discussed and after the filter.

If you put in the card, you see now there is no blue light. You see that? I put it here, you see a blue sharp spot almost at the center of the spot that you see for fluorescence when it goes to the long pass filter That long pass filter does not transmit the blue light anymore, but fluorescence goes through and here florescence looks like a big spot size of which is determined by the diameter of this lens. Then what happens it goes here and on this lens L4 now you can see both.

You can see the sharp red light which is gate light, and you can see the fluorescence light as well as a big spot. Both our focused now, now if you see if I go more and more towards NC, you can see the spots are coming together and they are becoming smaller. They are becoming smaller because they are getting focused and they are focused on this nonlinear crystal. Now what I have done is I have intentionally detuned the crystal here to show you what happens after the crystal.

Let us go back once before the crystal you can see the gate light is towards me and the blue light is away from me. From the direction in which you are looking red light is towards your red towards your right and the fluorescence of light is towards your left after the nonlinear crystal, the directions have reversed because they have crossed here. So the in a perfect alignment, they would have met exactly at the nonlinear crystal.

Now what I want to do is I want to generate sum frequency to do that I have to angle tune this crystal and you will see sum frequency coming out as blue light. Actually it is UV but when it hits the paper, it looks blue. You, there you go. In fact you can tell by eye by and large and but later you have to use the detector. You see you see this sharp blue light coming out. That is actually not blue.

It is UV, but UV light excites collagen molecules in paper and that is what gives you a blue color to your eyes. Now is this light that goes through here of course you can see everything. But if I could put the card after the short pass filter, you will see fluorescence gets cut out, gate light is cut out, only this UV light which shows up as a bright blue light. That is the only thing that goes to the detector.

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Now we are going to acquire data. You see our computer screen. And there, I will draw your attention to the panel on the top left. There you can see 2 readings. On top you see something like 28,998.84 femtosecond that is the delay that we have given to the gate light. It looks like a

ridiculously long, large number. But that is because we are writing it in femtosecond. We wrote it in picosecond. It would not look as bad.

But then the point is that we actually have this kind of accuracy that we can go to the second place of decimal of femtosecond and the bottom panel where you see a number that is fluctuating slowly. Saw 350 now it is 373 Little later it was something else 415. That is the output of the photomultiplier tube. And that number is proportional to the intensity of the sum frequency light. And we are going to show you first, of course, you cannot see me now, but I will tell you what I am doing.

First of all, I am going to block the fluorescence light. So see now count is something like 364 or something. Now I have blocked the fluorescence light, and immediately the count starts falling. It is 292. Now at 60, so it is going to go to almost 0. And we are using a slow acquisition time that is why you still see some counts. Otherwise you have seen nothing, so the count becomes almost 0. When you block the fluorescence like that is one part of the story now have unlocked like and you can see the count growing again after are 2 or three readings since we are using a 5 because again into a 5 second integration time, it takes a little bit of time.

But we are back to where we started from 358. Normally this count is much higher. Now our instrument is not in very good alignment. Normally this count would be something like 80,000 or so. Now next I am going to block the red light of block the red light now and you will see this count falling once again, sees started falling already 294 from 300 something now it is 9. So what does that mean? The signal goes when you block red light, or you when you block fluorescence light.

This is what confirms that it is actually sum frequency signal. Because if you block 1 light, and the signal does not go, that means it is some kind of a spurious signal. Next, what we are going to do is we are going to record a decay, which means we are going to change the delay and we are going to record the intensity of sum frequency as a function of delay time. So now see we are recording the data. And now, the time delay is such that we have not reached time 0.

So you would not be able to see that the data is being recorded point by point. And you can see some fluctuation in data, there is a noise that we are talking about the data you do not get the same value for all measurements even when the counts are actually close to 0. So at times 0 what happens is there is a jump and the decay the signal goes up and it decays from there.

Now you see that there has been a jump, which means that we are now close to time 0, and what was looking like signal to you a little earlier. You can see now that it is actually nothing but base line it is 0. You might be a little confused. By the way acquisition is being done here. The way this program is written is that the x axis keeps changing, and keeps getting expanded as you record. So that is why what look like full scale now is no longer full scale is getting smaller and smaller. Now we have these times 0.

And that means that signal is actually there and you see that there is a jump. Now you are going to see the decay of the signals. And in fact, for the sample that we have, it does not decay too much. It actually has a nanosecond lifetime. But this, whatever once it decays in our time acquisition, you are going to see it here. In fact, now that we have shown you time 0, what we will do is we stop this acquisition and we show you a data that we have recorded previously and you should be able to correlate that with this 1.

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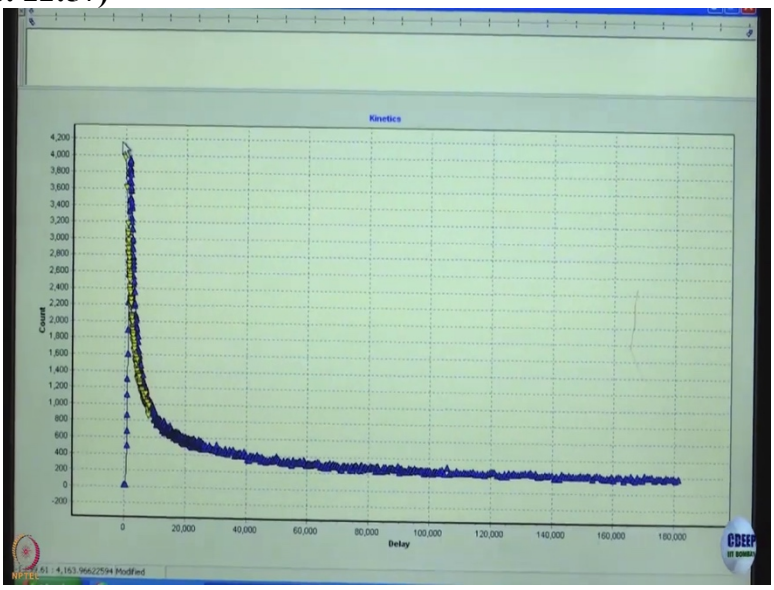

So this is what you see here is a decay that is recorded by the method that you saw y axis is actually intensity of some frequency x axis is delay. So, this as we said earlier is essentially a map of the

fluorescence decay that the sample has so, to conclude this discussion, we are discussing the lecture, how florescence up-conversion technique gives you a femtosecond time resolution. And here today, we have given you some glimpses of how the experiment is actually done.

So, the only thing that remains for you to be to go to a lab and do the experiment yourself. We conclude this part of the discussion now, and later on. After this, we are going to move on to our discussion of how lasers work because as you understand lasers are the central tool for any kind of ultrafast spectroscopy that we do. And once we are done with the discussion of the theory of lasers will come back to this lab will open the laser for you and will show you what there inside.