Ultrafast Processes in Chemistry
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Lecture # 12
Femtosecond Fluorescence Upconversion 2

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We are discussing Time-Resolved Fluorescence up conversion technique and once again let me state that the slides are all from Sobhan Sen of JNU. So, this is where we are stopped in the previous module. And what we have here is.

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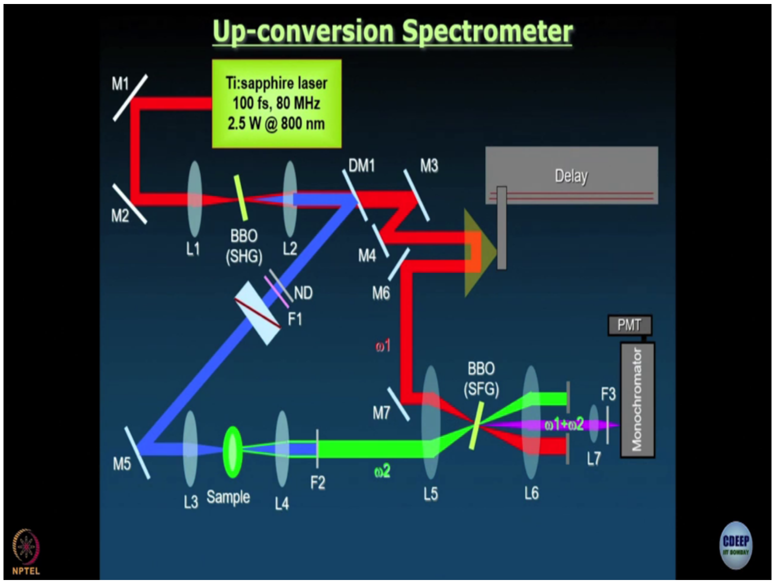

We have a schematic of the optics that are there in upconversion. Now, we want to use this use some animation to show you how the decay is actually recorded. Now, before that let us just quickly remind ourselves what we have. You have a titanium sapphire laser right now you do not have to worry about anything else. But typically we have 100 femtosecond pulse we have hundred femtosecond pulses at 80 megahertz then this is directed into the spectrometer. This is the part that we had discussed earlier.

The spectrometer a lens L 1 focuses the red light on to the second harmonic generation crystal and the Second harmonic generation crystal that is uses typically BBO crystal, what is BBO? Beta barium borate , that is usually the nonlinear optical material that is used everywhere now, then what this one does is that it converts some of the red light into blue light, both are collected by this lens. So, see the thing is in order to get the best result you have to focus your light, but then the output of that is a diverging beam.

You cannot work with the diverting beam, you want to collimate it. So, this combination of two lenses one focusing lens and one collecting lens is ubiquitous when you work with optical instruments, why do we need to focus because let me write now, rather let me draw what we had discussed in the previous module without drawing anything, I think it is better to draw otherwise, it may not be very simple to visualize is that we said let us say this is the ground state of your BBO or whatever it is.

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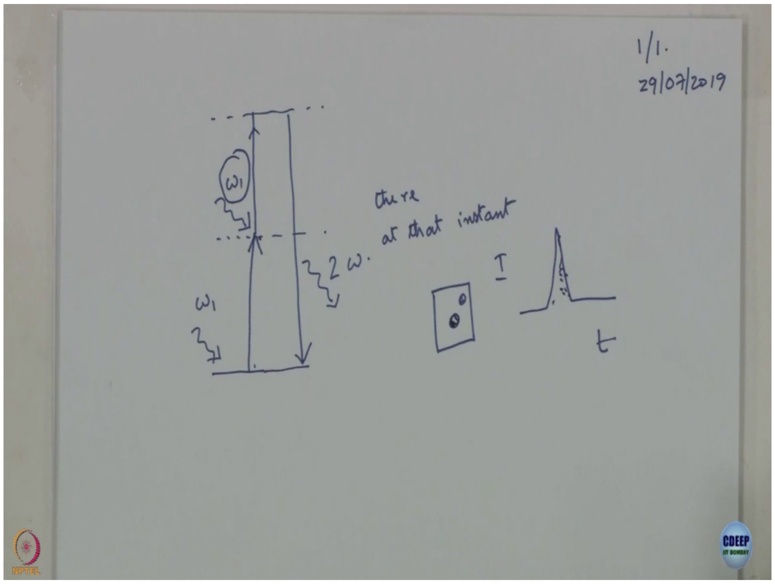

So, first you have this first photon coming and it is omega 1 in keeping with the terminology we have used it causes the promotion and usually the promotion is not to a stationary state, it is to virtual state we have discussed that already. For second harmonic generation, you require the presence of another photon omega 1 which promotes the system to another virtual state. And then as you said there is no memory. The system is here it does not remember whether it came there one step or 500 steps.

So, the light that comes out is like this two omega this is second harmonic generation put very, very simply for you. Now, for this to happen, what is the requirement, the requirement is that when you promote up to here, another photon must be there. And when I said there, I might clarify a little bit saying the second photon must be there and must be there at that instant this is a cross section of your crystal and let us say you have promoted to this virtual state at this spot.

It makes no sense if you have another omega one available here has to be here. It makes no sense, the second omega 1 comes two years after the first 1 are 2 years of course is an exaggeration, it must be there at that instant. That is why, first of all, you have to focus using the optics that we have shown earlier. So that you have a lot of photons here. And when you use a pulse, this is a typical shape of a pulse intensity versus time, all the energy is packed in this short time.

So, within this hundred femtoseconds, you can expect that there will be a large number of photons that will be there to serve as a second one. Right? That is why it is convenient to get second harmonic generation if your laser is pulsed, so this is why we need to focus as well. Now, let us return to our presentation. So this lens collects it straight this is a diachroic mirror dm, is dichroic mirror Blue Light is sent in this side. And if your alignment is perfect, then it goes as a collimated beam, it goes to some other optics.

we have discussed neutral density filter, indeed, what this is will come to this in this module or the next, then you have M5, which is actually another dichroic mirror. Residual red goes this way, blue light goes here again you have a lens which focuses the light onto the sample. And one thing I forgot to say in the previous module is that if you are working with liquid sample, then you want to rotate it so that the same point does not get illuminated always.

And if it is a solid sample, then you want to translate it. And typically translation is like this. There is a name for this kind of a scanning what is it called? It is called raster scanning right? You go like this in the same spot is never hit by like twice so, possibility of damage is minimized. So once again we have this familiar focusing and collecting optics arrangement. Once again, if your alignment is perfect, then what comes out of this lens is a collimated beam.

But in this collimated beam it is nothing, it is anything but monochromatic. You have blue light as well as fluorescence and in fact blue light is more intense. That is why you use f2 which, if you remember is the long pass filter which cuts out the blue light. The excitation light laser light allows only fluorescences to go through and then this lens focuses it on to the second sum frequency generation crystal.

Here what happens is on the other arm, red light which is called gate light, omega 1 as we have put it goes to this mirror M3, then into M4, hits the retroreflector it turn back and the retroreflector is actually mounted on a 1 foot long screw, which is which can be moved using a, what is called a step motor step motor means something that does not turn continually, but goes in steps. So if you step motors are quite common in day to day use.

They are used in printers for example, if there are many other applications. So from M6 it goes to M7 same lens is used to focus it on to the sum frequency generation crystal. If everything is perfect, then you get omega 1 + omega 2 sum frequency and then you detect this sum frequency. And here when I say everything is perfect, what does it mean? One very important parameter 2 parameters.

One is that both the spots must have been focused, both the light beams must have been focused on the same spot. And you understand why the diagram we drew a little while earlier. The 2 lights have to be spatially overlapped otherwise you cannot combine if one spot is here one spot is here how will they combine. second thing that we have not discussed so far because we are going to have a little more discussion when we talk about talk formerly about nonlinear optics is that the phase angle of this crystal has to be right.

So, basically, sum frequency is very strongly dependent on the angle of the crystal with respect to the incident light, it typically works in a very narrow range of orientation. So, what you do is in order to get good sum frequency generation are good second harmonic generation you have angle tune the crystal. Turn the crystal until you get good sum frequency or good second harmonic, right. And you detected.

Now, we come back after 10 minutes of recapitulation of what we said in the previous module, we come back to the question we asked what does all this have to do with femtosecond time resolution. Remember we are doing this because you cannot have electronics that can do a real time femtosecond measurement. All electronic components have the response time, which makes him slow and micro second is something electronics can handle quite comfortably, not femtosecond.

So essentially we are trying to overcome this limitation of electronics by using something that is faster than anything else. If you leave out things like Tachyon and human mind, what is the fastest thing you know, especially as a spectroscopy course, light, right, light since Electronics is too slow, we have to use the fastest thing at our disposal. That is light to get the resolution. What I do is first of all, I will draw and then we are going to show you animation. So let us go back to the drawing board.

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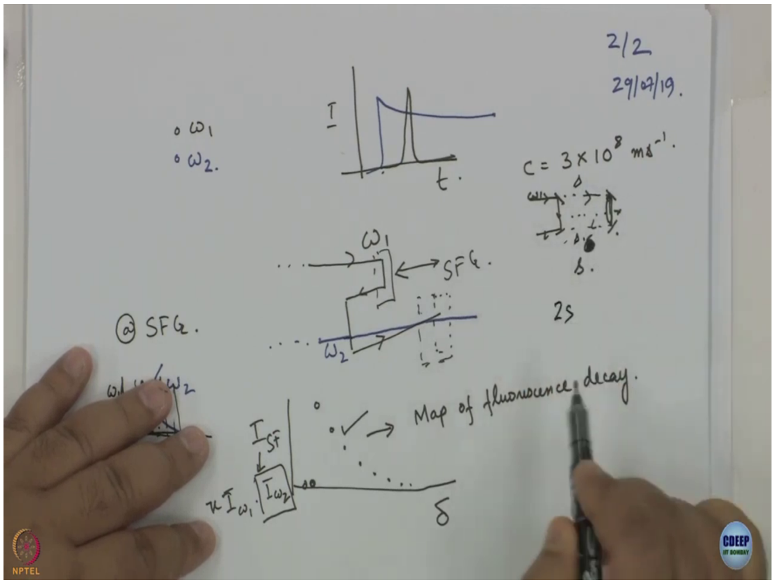

Let me draw omega 1 in blue, omega 2 in blue and omega 1 in black. Right. Now, if I want to plot intensity versus time for omega 1, what does it looked like? Intensity versus time plot of omega 1? Something like this. It is a pulse of finite width hundred femtosecond or whatever. If I want to make the same plot for omega 2. What would it look like? Fluorescence decay, right? It would go up and come down something like this, it can come down completely it can be incomplete whatever it is. Now see, if you go back to the schematic of the instrument, what we have essentially is that drawing it very simply, this is your omega 1.

I am not drawing the bits of optics and just drawing the path. One thing I cannot avoid drawing is the sum frequency generation crystal. What about omega 2 well, there is some path before this. And omega 2 also has some path before this and then it comes straight. Better overlapped with omega 1, exactly at SFG which it doesn't. so what I will do is I will just make this. In real life I cannot do it would better fall on the same spot. Now see omega 1 has traveled some path omega 2 has traveled some paths right.

And if you remember, omega 1 retroreflector is mounted on a one foot long screw. Which I said is operated by a step motor which can move forward and back. What does it mean? That means, omega 1 has a variable path length omega 2 has a fixed path length and I can move omega 1 so, that the path difference between omega and omega 2 can be altered All right. Let us say, the path difference is something like this and this is at the crystal right at the sum frequency generation crystal, the path thing is such that this is a scenario.

Remember, Black is omega 1 blue 1 is omega 2 I will not tried that anymore. Now in this situation do you think there will be any sum frequency generation? Ye, omega 1 has come too soon, omega 2 is not even there. So there will nothing right. So if I now want to plot intensity of sum frequency as a function of I will write delta, what is delta the path difference what will the intensity be 0.

You might see where we are going because we have done a very similar discussion when we talked primary well in a very hand-waving manner when we talked about pump probe spectroscopy earlier on same thing. Now suppose I change the path length of omega one and it comes here. Path difference is smaller will I get sum frequency generation here No. So, once again sum frequency intensity is 0. Now, suppose it has come here now, this is the best possible situation.

So, what will happen to intensity of sum frequency provided the angle is right. It will go up, it shoots up. Now, if I change the path length of omega 1 a little more and bring it here then what will happen intensity of omega is same intensity of omega 2 has fallen off exponentially or whatever and intensity of omega 1 + omega 2 intensity of sum frequency, what will it be it will be something like intensity of omega 1 multiplied by intensity of omega 2, and there can be some factor kappa.

So, what we are doing here is that always intensity of omega 1 is constant, but intensity of omega 2, first of all is 0, then it rises sharply to some value, and then it falls off. So if you keep changing the path length, what will happen is intensity of sum frequency will also change accordingly. So if it comes here, even though intensity of omega 1 is the same. Intensity of omega 2 is a little less.

The fluorescence has decayed a little bit will come down accordingly. If you keep on changing the path length, then the intensity of sum frequency will fall off. And it is important to understand that the shape of this curve is exactly the same as the shape of the decay of omega. So what we have generated here is a map of the fluorescence decay.

We have generated a map of the fluorescence decay and here it is important to not get confused about 1 point. The way it works is that the screw moves so the retroreflector moves and as long as the retroreflector moves no measurement is done. Then it stops at some particular position delta 1 it stays there for some time, half a second 1 second 2 second 5 second, whatever you set it to be that is when the measurement is done all right.

So, two things, first is movement of the retroreflector, second is actual recording or intensity of intensity, they do not take place simultaneously. When one happens, the other does not. So, when we make a measurement actually, then everything else is fixed. Because we are not moving, delta 1 value is fixed. So, we are making essentially a steady state measurement. And we are integrating for 1 second 2 second 5 second, whatever.

So, the good thing about this is that you do not need a fast detector. We are actually get off using relatively inexpensive simple detectors like regular photomultiplier tube which you would use in a steady state fluorescence measurement, because you are performing steady state measurements here and that is the beauty of the technique. Using what is at your disposal, the fastest thing at your disposal that is light.

Just by moving this retroreflector a little, you are giving different path difference. And that is what can give you femtosecond time resolution. Before coming to that, let us show you the animation. All right, this is your back to the projection once again. So this is what it is. And remember what we are doing now is this the same diagram that I just drew. Red is omega 1 green is omega 2 what you are doing is essentially is that you are changing the delay like this.

And therefore, the path differences are changing omega 1 samples different parts of the decay. And that is how the plot is generated. And it is important to understand that what you generate is the map of the fluorescence spectrum. And this is exactly why I do not try to use my presentation. I like to use Sobhans because it takes a lot of time to make animation like this it but now, that you have seen the nice presentation, it is important to go back to the chalkboard once again and see whether what I see makes sense what I say makes any sense or not.

So let is go back and do a little bit of calculation once again. Right? You told me light is the fastest thing that we have right. What is the speed of light? 3 into 10 to the power 8 meters per second. What does this mean? The rule of thumb that I like to use is light travels 1 foot approximately 1 foot in 1 nanosecond. So that is what it means, how much does the translation stage have to move. If I want to give if I want to change the path length of a difference by 1 femtosecond, it is very simple. Let us say. So this is your retroreflector this is omega 1. I am saying that I move it to this position.

And then I am going to neglect this part. Of course, the only thing that matters is this length. So suppose a move it by delta. Rather, I move it by 's' it is better, right? In class 19 physics also we say distances is 's' so move it by a distance 's'. what is the change in path length? Well, what is the change in time involved? If I move it by 's' by how much is how much more distance is light moving S while going S while coming so 2 S.

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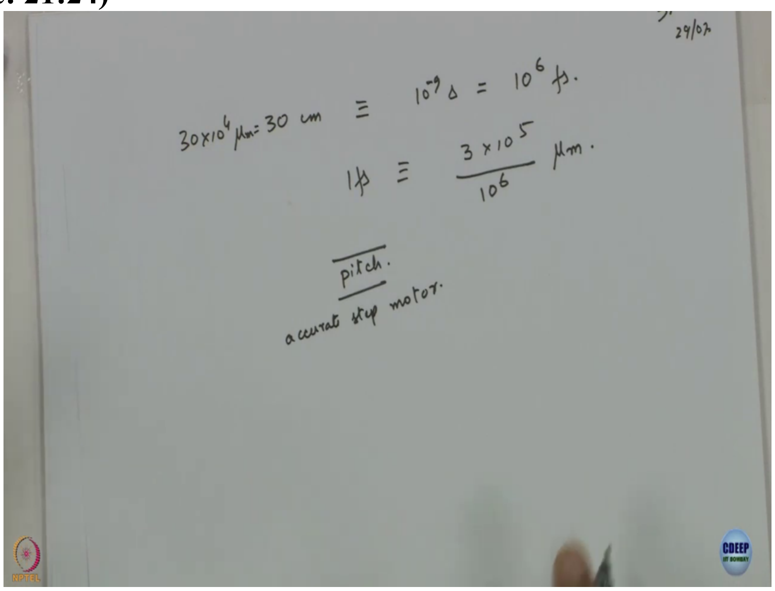

30 centimeter is equivalent to 10 to the power 9 Second how many femtoseconds is that 10 to the - 9 seconds, 10 to the power 6 femtosecond , how many micrometers is centimeter? 10 to the power 4 right 4. So 30 into 10 to the power 4 micrometer is equivalent to 10 to the power 6 femtoseconds.

So if I want 1 femtosecond that will be equivalent to 3 into 10 to the power five divided by it 10 to the power 6 micro meter and that is equal to 2 S. So, from here you can see what it will be something like 1 micro meter or something like that. So, basically you have you must have the precision of moving this retroreflector by micron is it possible because you use a screw it is very easy to get a pitch of less than a millimeter and it is not difficult to move it by a fraction of a degree.

That way you can get femtosecond resolution. So, this is how femtosecond time resolution comes. What do you need? You need to have a suitable pitch of the screw and you need to have a step motor That is sufficiently accurate you should be able to move in milli degrees, something like that, that is not very difficult to get. So this is how you can get the femtosecond time resolution

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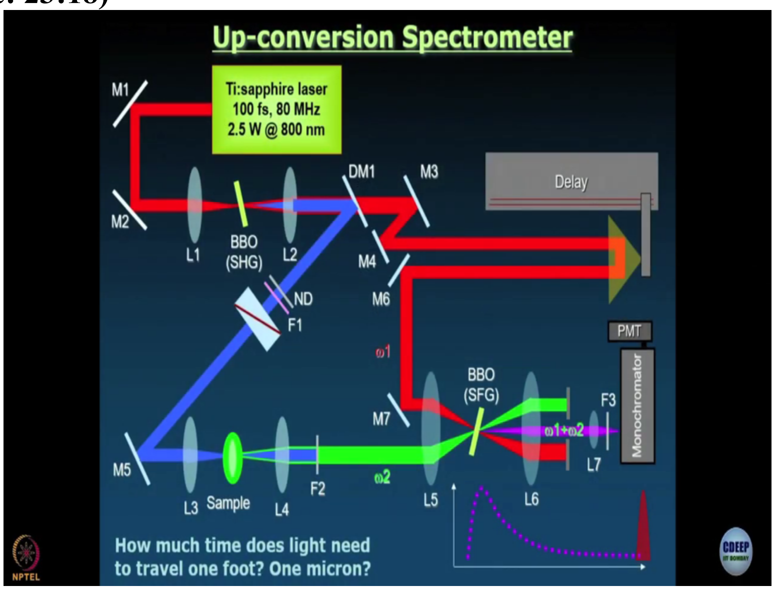

This we have already answered and I think now you have understood how we get time resolution here we get time resolution because we can move this retroreflector in very small steps. So, we can actually give very small differences in path length and then we make a steady state measurement. Now, you might remember that I told you that we use lenses to focus but there is a better way of doing it.

The reason why I said it is that again we are going to elaborate upon this point in 1 of the later modules. When short pulse ultra short light pulses go through any dispersing medium, they get broadened and in fact, it is used to our advantage in some application later on. But then if you want to make a measurement with a very good time resolution, you laser pulse, and everything else must be very short. So then you cannot use any optics through which the light goes, you have to use all reflective optics.

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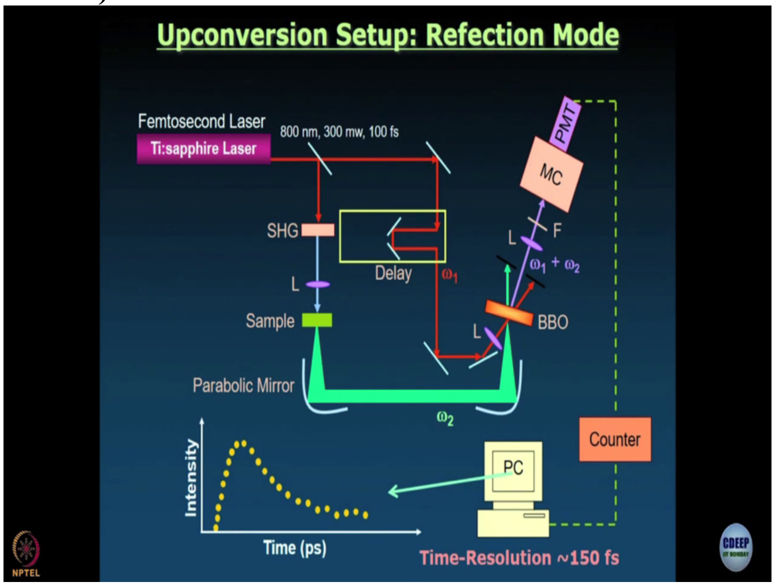

In that case, what you do is, in fact, even here to focus the light on second generation you want to use instead of a lens, you want to use a curved mirror. And then actually even this is not correct. You do not want to use a lens here. You replace all the lenses by parabolic mirrors like this. That gives you better time resolution.

Typically in our instrument, we have 100 femtosecond pulse coming out of the laser. But when we measure instrument response function, it is no longer hundred femtosecond. It is close to 300 femtosecond. So if you do not want that, if you want that your Suppose you want to use a 50 femtosecond pulse, and you want your instrument response function to be no more than 75 to second, then you want to use all reflective optics like this. In fact, initially, everybody made all reflective optics that did not use lens for the fear of losing out and resolution.

The problem here is that to get the first signal, if you build your instrument, and you do it with parabolic mirror, getting the first signal is a complete nightmare. It is much easier to use a lens because with the lens you have only one controller move it forward or backward. And you already know what the focal length is. So you already know the approximate position. It is much easier to get the first signal when you set up the instrument using a lens. That is why usually, people are happy sacrificing some of the time resolution by using a lens because that would give better collection efficiency right.

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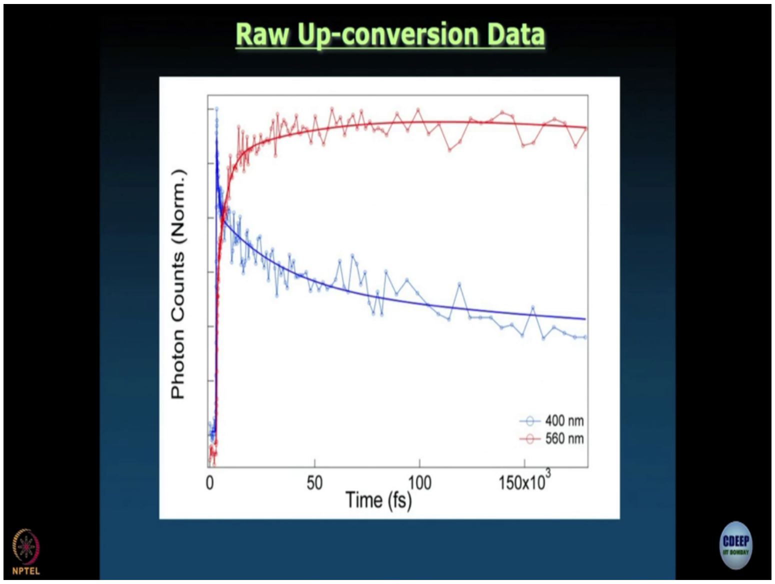

Now, this is an example of upconversion data. You can see this is the data and this is a fitting curve we talked about fitting curve in the previous module. And you might be able to recognize here that the data quality here is definitely not as good as what we get in a TC SPC. This TCSPC gives unparalleled data quality is why it is so popular worldwide. But then, if you want better time that you have to use something like up conversion, you can also use something else called streak camera. We will talk about it in very brief.

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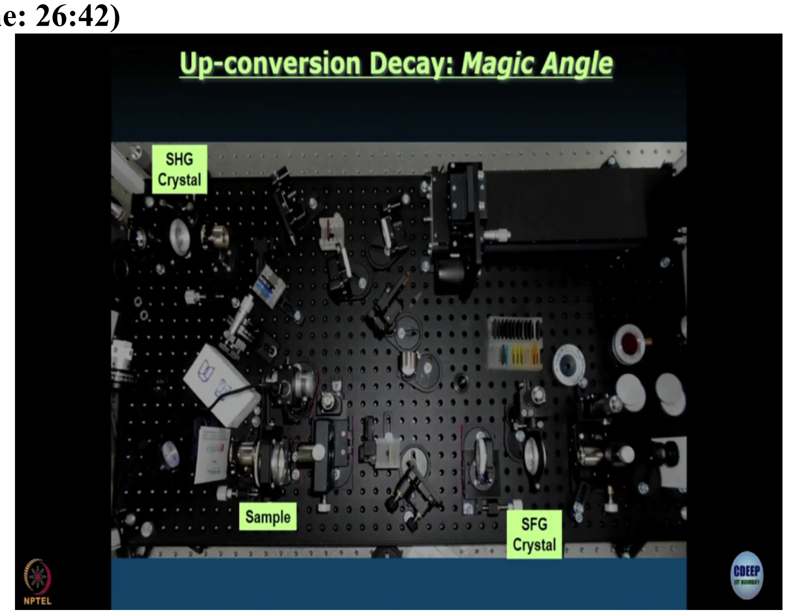

Next point of discussion is why do you want to take care of polarization and what are the things that can go wrong in an upconversion measurement, that is what will take up in the next module.