Ultrafast Processes in Chemistry
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Lecture # 11
Femtosecond Fluorescence Upconversion 1

So far, we focused our attention on a time correlated single photon counting, which allows us to make measurements of lifetime from 100 of picoseconds Well, maybe 10 of picoseconds if you have a very good instrument, like we do, and up to say hundreds of nanoseconds. In some cases, you might be able to go beyond that as well. Today, we talk about technique, which allows you to go down further to hundreds of picoseconds at least, if not better. And this technique is called time resolved fluorescence upconversion or

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Time-Resolved Fluorescence Up-conversion Technique

Sides, Courtery:

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The name I like better is femtosecond optical gating the reason why I do not like the fluorescence up conversion is that there are many people working in the area of material science who want to make up conversion materials, materials in which the 2 photons of smaller energy would join up to give you 1 photon of higher energy. And the moment they see fluorescence up conversion technique, they come and ask me, is it possible for us to test our samples on your equipment.

Of course, it is not possible to test their sample or equipment. So I like femtosecond optical getting better, just to avoid trouble. But then fluorescence up conversion technique is an absolutely valid commonly used name. And we will see where this term of conversion comes from in this technique, and how is it that we get accuracy in time up to femtosecond scale. Before proceeding further, it is important to point out that none of these slides are made by Me, I do not know how to make such beautiful slides.

They are all prepared by my colleague for the Sobhan Sen from school of physical sciences, Jawaharlal Nehru University. He has kindly agreed to allow me to use the slides as many times as I want, wherever I want. So let me start thanking sobhan, for these slides that were made with a lot of care as you will see. So first of all, let me show you a photograph of upconversion spectrometer.

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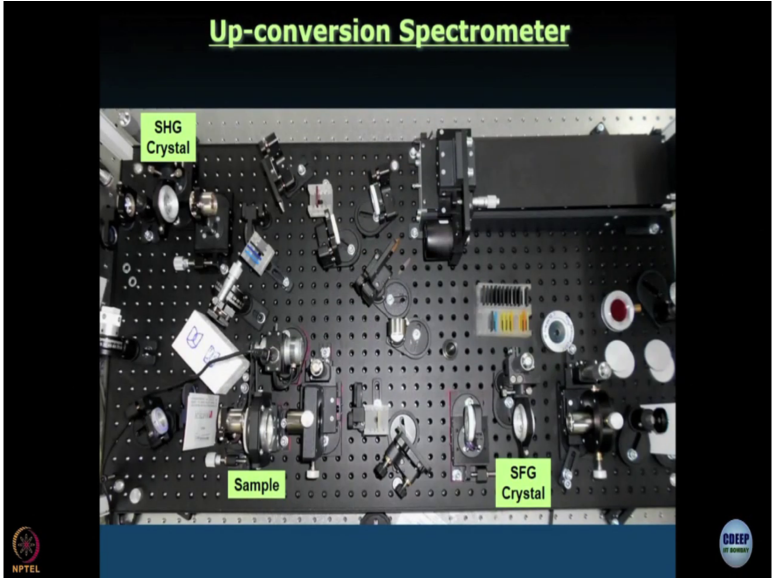

Up-conversion Spectrometer

This is what it looks like this is actually a photograph taken from top. This is not our instrument. It is the instrument that is there in JNU you but then our instrument is pretty much the same. And next day, we are going to go to the lab and we are going to show you our instrument in real time. And we will show you how the data is recorded. So the idea is in this module, we are going to tell you and try to make you understand without actually going to the lab how the data is recorded and what are the underlying principles are all and next day.

You will come to the lab and you will see what exactly is actually done. So what you see here is this black flat surface with a lot of holes is a breadboard. And if you go to any optics lab, you will see breadboard like this. In fact, if you look carefully, you will see that this black surface with holes is sitting on a shiny surface with holes. There is an optical table top of the top of the optical table. And the reason why we have so many screws the so many holes there is that it is possible to use bolts and screws and fix pieces of optics on this surface.

Now whatever you see here is a piece of optics. It may not be very clear from this photograph because it might be for many of us that we are seeing such apparatus for the first time. But when you go to the lab and we see everything in front of our eyes, I hope it will become clear today is exercise is going to help us understand things that are there as well. To start with, let me try to give you from this figure a description of what is there in the spectrometer.

So, first thing that you have is what is written as SHG Crystal SHG means, second harmonic generation crystal, we are going to have a couple of modules on nonlinear optical on nonlinear optics later on, and there will learn that there are materials that allow 2 photons of the may be the same energy they may be different energy, but they allow 2 photons to combine and produce a photon of larger energy. It is pretty much like 2 drops of water falling on a table coming together and forming a bigger drop.

It says that the drops here are not drops of water, the drops of energy drops of light, but not everything allows combination of photons. There are very stringent conditions that have to be satisfied for a material to act as a nonlinear optical material and it that in itself is a very active field of research. So, without going into that, at this time, just believe me when I say that the first thing we have here is a second harmonic generation crystal, what is the purpose we will see in a while.

Now, why are we saying second harmonic, because in this crystal at least, what happens is you make incident laser light nominally of 800 nanometer, but whatever laser light you might want to use, and 2 photons of the same laser join up to produce a photon or double the energy this photon or double the energy that is called second harmonic or if I put it in another way, suppose the frequency of the incident light is omega.

Then 2 photons of frequency omega join up to produce another photon of 2 omega. This 2 omega is a second harmonic of omega. It is as simple as that. So what we do here is that you make incident this red light, which is from a laser in our case. It is a femtosecond pulse titanium Sapphire laser. Later on we will have occasion to talk a little more about what is that in the laser and how femtosecond pulses are produced.

For now, let us just accept that this red light is the output of a femtosecond pulse, second harmonic femtosecond pulse titanium Sapphire laser, and a wavelength of this laser that the one that we have can be tuned from 700 nanometer to 1000 nanometers or so. Let us say that this light that we are showing you here, is has a wavelength of 800 nanometer wavelength of 800 nanometer it is not very difficult for you to work out what the frequencies because frequency and wavelength and rated by lambda nu equal to c.

Now what happens in the second harmonic generation crystal is that, as I said, 2 photons join up to give you one photon. So suppose I am using 800 nanometer light, what will be the wavelength of the sum frequency photon, this one is very easy, it is going to be half 800 by two 400. But while doing this thing, please remember one thing that you have to add frequencies not wavelength is actually a reciprocal state.

So, the right way of doing it is to convert whatever you have to frequency at the frequencies and then go ahead you see when we talk about sum frequency generation later on, rather than second harmonic generation that will become a little important. Second harmonic generation is easy, because the wavelength of the output is just half of the wavelength of input light. Now here, let me tell you something it is a little easier to produce second harmonic of femtosecond pulse is a short pulse lasers.

Why because when you do second harmonic generation what are you doing? The first photon takes the material from its ground state to what is called a virtual state. Virtual state is a non-stationary state associated with the lifetime of 0 and it is usually described as a linear combination of these stationary states of the system. So, requirement for second harmonic generation is that you take the system from the ground state to the first stationary state then there must be another photon of the same energy which will take it to another virtual state.

So, first frequency takes it to an energy of say, new well stating energy in terms of frequency omega, second 1 second photon also of omega frequency takes it to a virtual state whose energy gap between whose energy gaps with the ground state it is equivalent to a frequency of two omega. And now there is no memory the system does not remember that it had gone up into steps and it cannot stay in virtual state for any finite amount of time.

So, it has to emit a photon and comes down and since the energy gap between that virtual state and the ground state is equivalent to frequency of two omega, it actually emits a photon of two omega and that is what you see as the sum frequency or in this case, second harmonic, it may be a little difficult to follow it in this way when I speak but then later on when we talk about nonlinear optics will actually draw diagrams and then I hope it will be a little easier.

For now, all we need to understand is that this red light falls on the second harmonic generation crystal SHG crystal and blue light is produced. And what you have seen is the path of the blue light. I will go back a little, and I will show you the part of the blue light. But before that, let me tell you, you could see what happened? Blue light gets produced here at this second harmonic generation crystal, it hits. What we have here is a dichroic beam splitters means it reflects one color and transmits another color.

In this case, you use a dichroic beam splitter, which reflects blue light, but transmits red light. It could be the other way around as well. You have dichroic beam splitters of both the variety. Then, having been reflected from this dichroic beam splitters, the blue light comes to another dichroic beam splitter. This one dumps the residual red light, residual light goes through and blue light gets reflected in this way where it gets focused on the sample which is kept here, by a lens, that is the path of blue light.

And just show you the animation once more blue light is produced at second harmonic generation crystal is the first beam splitter the second one and now is focused on to the sample using a lens. In our case we use a lens but there is a better option as we will come to later on. Now, then, the sample fluoresces and this is why you need blue light as we have discussed in one of the first modules, fluorescence spectrum always comes at a lower energy compared to the excitation light unless you have an upconversion material.

but normally when you talk about normal fluorescence, emission always has emission is always in a lower energy, because you cannot have more energy than what you put in unless something like this is going on, that is where you need blue light. Because suppose you excite using 800 nanometer light, where is it going to emit? The only hope is an IR. In fact, materials, everything and IR are very useful, but most of the things do not most of the things actually emit in visible range, sometimes in UV range.

So, for that, you need higher energy light, and that is what is produced by the second harmonic generation crystal. So, red light second harmonic generation crystal, gives rise to blue light that is deflected through a lens on to the sample and then from the sample, you get a fluorescence that is shown by this line. Now, fluorescence occurs in all directions. So, fluorescence of light is sort of light the light that comes out of the regular lamps that we have, it is in all directions and what we do here at that we collect the fluorescence by using this lens.

So you can understand this is a sample this is a lens. So the only fluorescence it can collect is something that comes from this point on the sample on which the excitation light has been focused and is within this solid angle that can be captured by the lens. So, here something that becomes very important is numerical aperture. The issue between the focal length of the lens and the diameter of the lens.

If you are focal lens is large, in this case, is it good or is it bad? Do I want to use a large focal length lens or a small focal length lens? Definitely small focal length lens. In fact, there are instruments in which they use a microscope objective. You want the lens to be as close to the sample as possible, because the further away you go more is the loss of light. If you are here then you are catching this solid angle. If this is suppose this is your lens cross section of your lens, you keep it here. This is a solid angle that you catch.

You go here, this line goes in this direction this way goes in this direction, so you end up catching a much smaller solid angle. That means light collection is less efficient. And fluorescence in any case, the number of photons emitted is not all that great, especially when you are talking about femtosecond timescale, your lifetime is small and what we learned in the previous module is that lifetime is proportional to the fluorescence intensity phi f is equal to kr into tau.

So small lifetime would usually imply a small quantum field as well. Now out of that, if you are going to reject most of it, then what will you see? So that is why you want to capture as much of the solid angle as possible. If you can capture 360 degree there are possible if you could capture 180 degrees it would be great, but one it is not possible. So you want a lens with high numerical aperture.

So that you can go as close as possible and capture as much of the fluorescence light as possible. Are you clear about that and the other thing that is also implicit here is that the sample is kept at the focus of the collecting lens. That is the configuration for best collection. So you told me you do not want a long focal length lens and we discussed why do you want a small, wider lens or do we want a narrower lens.

I mean, diameter of the actual optic, should it be small should be large, it should actually be as large as possible. But there is a practical problem to that. Because your focal length is small. If you want a very large lens, there is going to be a very huge curved surface like there cannot be very large actually. So there is a limitation. That is where numerical aperture is the quantity that determines what kind of lens you are going to use.

So let us see what is happening here. We have some labels here, omega 2 is the frequency of fluorescence. As we are denoting here, what is omega 1, we will come to that shortly. So this fluorescent light is captured by the lens with small focal length. Then here we have a filter. What is the purpose of this filter, you see you are doing a collinear collection, you are collecting in the same direction as the direction of propagation of the incident light.

So of course, there will be not only this fluorescent light, a lot of excitation light will also be there in the same path, but then you do not want it because if excitation light gets into the detection channel, then your instrument is going to get messed up. So you want to cut out an excitation light. Let and you want only the fluorescence light to reach wherever it is going to reach later.

So now tell me, how do I cut out the excitation light and allow only fluorescence to go through? What should I use? I we should use a filter. That is right. What kind of filter a filter that cuts out high Frequency high energy, short wavelength light and transmits low frequency, low energy, and long wavelength light? What is that kind of filter called? It is called a long pass filter that is right. So, in equipment like this, you have to actually use this many different kinds of filters.

Here, you use a long pass filter, and the purpose of the filter is to cut the excitation light while allowing the fluorescence to go through. Here, if you look carefully, you will see there is another something here also you have some filters. These are a different kind of filter. They are called neutral density filter. What is the meaning of a neutral density filter, something that ideally cuts down a lot of the light going through irrespective of wavelength?

So if you plot absorbance, or rather plus percentage transmittance against wavelength, then you expect to see a flat line. In case of neutral density filters, a flat line that is a 50% 20% 10% 1% depending on your need. Why do we have neutral density filters here, because we do not want too much of light to fall on the sample using 100 femtosecond pulse. So, that is putting a lot of energy in to the sample in a very small time sample is going to burn.

That is why you always want to work at minimum excitation energy possible. If you put in more excitation energy, perhaps we will get stronger fluorescence, but that comes at a cost and the cost is a sample might get damaged. And if you are not careful, you might not even understand that your sample is getting damaged. So the problem with that is that once we are done with this discussion we can come back to it the problem with that is you are actually get incorrect result.

The lifetime record can actually be different from what it is. That problem is not there in TC SPC. First of all, not much of damage is there if you use diode lasers and all secondly, it does not matter if the sample degrades even during the experiment, unless another fluorescence is produced, lifetime will remain unaffected. Not so enough conversion not so in optical getting. In this case, if the sample degrades, even if it becomes something and then your measurement can be affected.

And we will discuss why once we are done with the remaining part of the experiment of the discussion. So what do we have? We have this fluorescence going through the long pass filter, then that cuts out of the blue light, only fluorescence that goes through here you have a lens, perhaps you will understand better when we show it to in three dimensions next day, here you have lens and this lens focuses the fluorescence light on to another nonlinear crystal.

But here you see this one was a SHG crystal. The first one the second one is called SFG crystal was here it means sum frequency generation crystal not second harmonic generation crystal. Why do we need on nonlinear crystal? What is it doing there? What is the function? How does it we will come to that shortly. But for now we need to remember that this is a sum frequency generation crystal.

And you see here when I say long pass filter, you might actually have to use a different filter for a different sample. That is why in this kind of an instrument, you always need a set of filters what you see here, you can see some color there, they are all colored glass, a set of filter, mostly long pass, which allow only the fluorescence like to go through but actually not all long pass some short pass filters also there will come to that alright.

So are we all ok with this path, fundamental, red light, getting frequency double producing blue light, which is directed onto the sample focused on to the sample, then fluorescence light goes through a long pass filter, whereby the excitation light is eliminated, and then the fluorescence is focused by a lens on to a sum frequency generation crystal are you with this arm, but this is only one arm of the instrument, only half of the story.

The remaining half of the story and that is where omega one comes in, is in this site. Remember what is this optical is it a plane is a simple mirror. It is actually a dichroic, right, and dichroic reflects blue light and transmits red light. What you see now is a path of the red light which is omega 1 it show you the animation once again but then I am afraid I cannot speak fast enough to keep up with the animation.

After all we are trying to animate light which is the fastest thing in the universe. So, let us see. So red light goes through the dichroic it is a mirror another mirror goes to retroreflector comes back. See I could not keep up with it. So now let me try to do it in a static mode. So this is where your red light goes through. Where is it produced is produced in the laser outside the spectrometer.

It is there if you see carefully you can see 2 beams, one blue and one red. That red light goes to the dichroic hits this mirror, comes back and here you have a retroreflector means it can even be a pair of mirrors. Something that turns light back, light does an about turn at the retroreflector what we have in our lab and in these instruments, which are marketed by CDP Corporation.

What they always have is they have a three sides of a cube front coated with gold, there is some advantage with having three sides of a cube. The advantage is that the light that comes out from the retroreflector is exactly parallel to the light that goes in. That helps it alignment. So light goes in like this, it will come out like this. If it goes in like this, it will come out like this. So, having a retroreflector which is three sides of a cube helps us in the alignment a little bit.

But after that, again you have another mirror which takes the light to this mirror, which focuses it through the same lens on to the sum frequency generation crystal and we are saying that this red light has a frequency of omega one. And this light also goes by the name of gate light. Remember one of the names is femtosecond optical gating, this omega one serves as the gate. Before going any further, let us make sure that we have not forgotten.

What kind of a light is that red light? Is it continuous or light or is it pulsed light? It is pulsed right. Remember is the output of a femtosecond pulse titanium sapphire laser. It is a pulsed light, its full width half maximum of the pulse would be something like hundred femtosecond in our case it can be even smaller, pulsed light omega one is pulsed. So, what does it look like if the x axis time It looks something like this What about omega 2? If I look at it in time domain.

What is the time evolution of omega 2 it's a fluorescence right? So, it is a decay. This is a point that we are going to come back to shortly right. But before that, let us think in a little simple manner not worrying about time at the moment. Now, you see what we have done. We have focused light of 2 different frequencies omega 1 and omega 2 onto the sum frequency generation crystal. What should happen? It is a nonlinear crystal.

It is called sum frequency generation crystal. So, it would better give rise to sum frequency was the meaning of sum frequency omega 1 + omega 2. So, there is sum frequency is generated here and actually it is this sum frequency that is detected, how do we ensure that after here what we have not shown is we have a monochromator like the ones that we have discussed earlier while talking about steady state measurement,

but generally here you use a double monochromator there are 2 gratings those you need very high precision in this case and then your regular photomultiplier tube or some other photodiode detector, like what you have in your fluorescence spectrometer. So, you are going to see omega 1 + omega 2 and if you just measure the photo current out of the photomultiplier tube, then you can get an idea about the intensity of the sum frequency omega 1 + omega 2.

But what does all this have to do with femtosecond time resolution femtosecond optical gating? We understood the optical gating part perhaps because we said that there is omega 1 light is called optical gate. But why is it called a gate and we have understood femtosecond up conversion because here we are doing a upconversion. So this crystal is also called the up conversion crystal but how does that give us femtosecond time resolution.

That is what we are going to discuss in the next module. Before that, let us do simple arithmetic. I am 800 nanometer light right that is omega 1. And 600 nanometer light here of course fluorescence is broadband. Let us we are focusing on 600 nanometer fluorescence light. So, what wavelength is obtained upon mixing 600 nanometer and 800 nanometer light. can we work it out.

Of course, when we go I can do the little bit of mental arithmetic it is a upconversion right. So, you have to add 600 + 800 1400 nanometer is the wavelength of the are we going to get 1400 nanometer when we combine 600 and 800 nanometer light in sum frequency duration crystal why not go see 1400 nanometer is actually lesser energy then both 600 and 800 hundred right and let us not forget that when you so go back to the fusion of drops analogy.

When 2 drops fuse 2 drops of water the masses add up when 2 drops of light when 2 photons fuse Energy is should add up right. E equal to h nu or equal to h c by lambda. So, what you need to do is E1 + E2 you cannot do lambda 1 plus lambda 2 right. So, E1+E2 would be h c 1 by lambda 1 + 1 by lambda 2 you cannot add lambdas just like that you have to add frequencies.

So, who can tell me what is the wavelength will obtain when we mix 800 nanometer with 600 nanometer? It worked it out I do not think you are so good at mental arithmetic that you will be able to do it just like that I am not what you actually have to use is 1 by lambda equal to 1 by lambda 1 + 1 by lambda2. So, if you do not believe in digging LC lambda and all it is 600 + 800 divided by 600 800. But reciprocal of that it is it turns out with 344 nanometer. Now tell me this C 44 nanometer light is it you is it visible is it ultraviolet is it infrared what is it? UV right.

So, now suppose your 800 nanometer is a nominal value for omega 1, if omega 2 is less than 600 nanometer it will be even more high the energy. Sum frequency will have even higher energy more into UV, what is the best case scenario? If this is 800 the second one can be at most 800 actually cannot it has to be longer than 800 nanometer right. So, if you did 800 nanometer, know what I was saying? It can be anything actually because you are excited with 400 nanometers. Sorry, my mistake, but suppose it is 800nm, then it will be 400.

So, typically well the point I am trying to drive it is that now when you choose the monochromator and you choose the detector you want a monochromator and a detector that worked well, in the ultraviolet range. We have not had the scope of discussion the blazing of monochromators unless you are using monochromators that use your holographic grating, they are usually blazed at some wavelength or the other that means they are the optimized the performance is best at that wavelength if you have grating that is blazed at 600 nanometer.

That means, you will get maximum light coupling of 600 nanometer. If you have something that is blazed at 300 nanometers, that is what it means, so typically, and same is true for detectors. You do not have one ring to rule them all usually. So you have a detector that works well in a particular range. So when you do the upconversion measurement, you might think that you need a red sensitive detector you do not. Because you are looking at sum frequency, higher energy will always need a higher energy. You need a detector that works well in UV region.

So that is another point to remember that you are actually detecting UV. So the instrument would better be such that it can detect UV nicely. But we are still not answered the question Where is femtosecond in all this? Where is the question of getting that is what we want to do in the next module. When instead of using the photograph, we are going to use the schematic and we will show you where femtosecond time resolution comes from.

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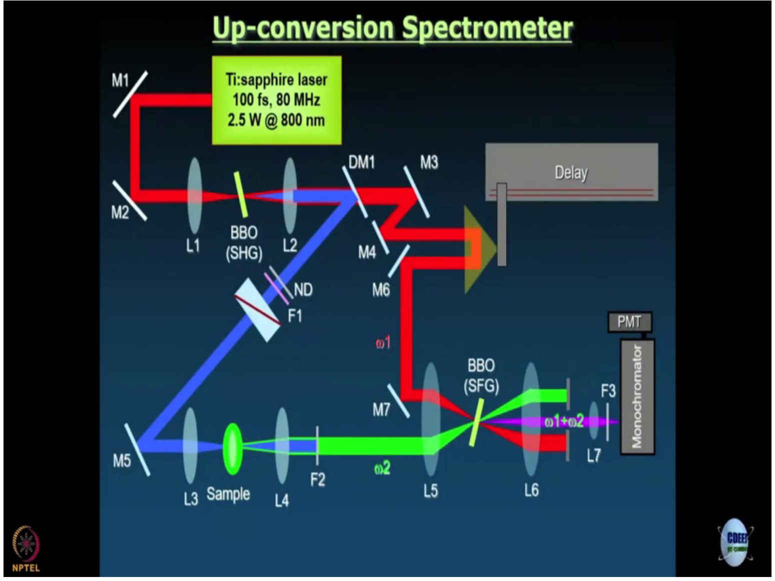

Up-conversion Spectrometer