Ultrafast Processes in Chemistry

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Lecture No. 15 Part II
Gated Detectors and Streak Camera

Let us get back to the presentation so using this intensifier, MCP something that is a little more sophisticated.

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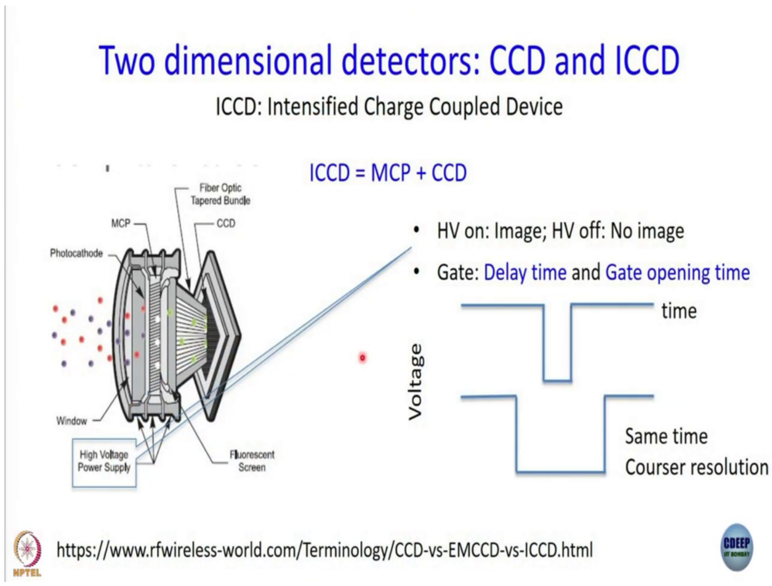

Than just ICCD is often used and that is called a streak camera.

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It sounds strange,camera we are we understand now, because you talked about CCD camera already. What is this streak camera? What is a streak? We will see very soon. But to do that, once again let me draw something before we start presenting this.

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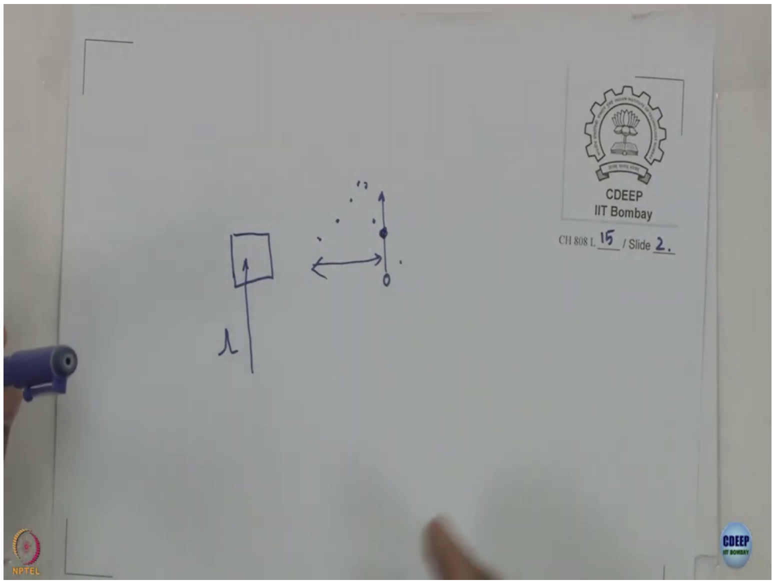

Let us say, element from the top this year is your sample in a cuvette, excite using pulsed light fluorescence goes out now, let me try to draw it in this in this way. Let us say I have some magical power, whereby I can see the photons along this line with very great tempo, time accuracy. What will I see suppose I can make out between photons that arrive first and photons later, initially, the first photon will reach, go back to your analogy of marathon runners, the winners will reach first then the slower ones will reach a little later.

And then we will the photons that are that have been emitted even later when I say slower. I did not mean the photons are running slower. I mean they have been emitted at a longer time post excitation. So suppose I could look at this entire region, then what and I could see photons, then I would see a distribution like this, is not it? This is space. But photons that have been emitted first would have reached here, photons that have been emitted after some time would have reached here, photos that have been emitted even later have reached here, and so on and so forth.

So, does this not look like a fluorescence decay? And is that not the histogram that we have been trying to construct all along? Do you understand what we are saying? Suppose I have a slit here at this point, then, first, the photons that have been emitted shortly after excitation will reach followed by photons that have been emitted a little while later, and so on and so forth. So, this is basically a depiction of the same thing. We have some kind of a slit here and what arrives there is not a bunch of photons altogether, but a distribution of photons, so forth.

So photons in band three would go in first, the little strange way of drawing it, but then I have taken it from this paper I would have written one first two second three third but where we go with whatever is in there, so photons of band 3 would reach first followed by photons of band 2 photons of band one, and one two three are only three of in principle infinite number of bands that I could draw here. So this is where it reaches this is just lit. And here we have input optics lens or whatever it gets in. And this is the photo cathode.

What will happen this three men number three of photons is going to emit a bunch of electrons. Then mesh number 2 will limit another bunch by mesh number 1 will have it another bunch, as a number of electrons emitted is going to be proportional to the number of photons in each mesh. So, if I could plot the number of photo electrons, then they would have the same distribution as the distribution of photons here are we clear about that now, what happens is this is a photo cathode, this is a anode and this interact thing is inside something called a streak tube.

And until now, we have not told you what the meaning of streak is where does streak come from all of a sudden, we will see shortly. What happens then, is that you use a sort of an oscilloscope kind of arrangement. I think we all have studied how and oscilloscope works in class eleven twelve modern physics. How does an oscilloscope work? What is the first thing that I am not about digital oscilloscopes? Of course, how they work is a mystery to me as well. But good old fashioned oscilloscopes the way they work is maybe I can draw.

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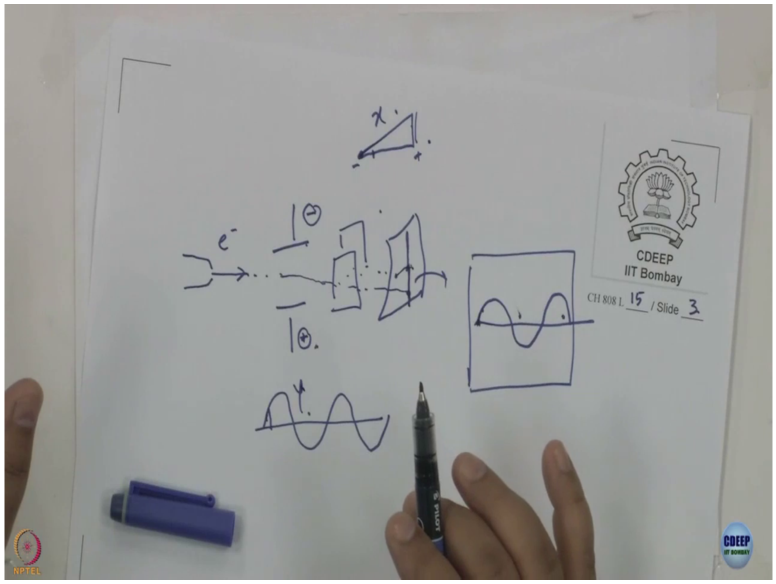

First of all you have an electron gun a electron gun something that is that are very exotic, not very easily found. They are not TV is basically an oscilloscope. Instead of seeing curves, you see people and places and pictures and so on so forth, so basically, you have an electron gun in an oscilloscope and here you have a phosphorus screen. So if nothing else is there, the alignment is as you go and hit the center of the phosphorus screen and you would see 1 bright spot on the screen at the center maybe or the venue center side wherever next what do you have?

You have let us say 2 plates one above one below and these are attached to some high voltage, let us say this is minus this is plus the droplet is negatively charged droplet is connected to the negative end of the power supply, bottom plate is connected to the positive end what will happen if I apply a voltage here this is minus this is plus, so, they should be a deviation this way. So, now instead of hitting the spot at this hitting the screen at the center.

You will see a spot somewhere below if I applied a constant voltage if instead of a constant voltage I applying oscillating voltage like this then what will I see this negative this is positive is first it is zero then the negative the magnitude of negative voltage goes up. So, this spot will start traveling below and then it turns back so it will turn back and go up as well. So you go up and down. So, what you see you see a vertical line clear all of us have studied all this and just revising in case we have forgotten.

So this is what you can see us sign curve generates a line on the oscilloscope screen and that is completely useless, because I cannot really see the curve with the purpose of the oscilloscope is to see the shape of this curve. So, you do that what you do is you apply us another set of plates at right angles. So the initial set of plates was like this. Now the plates are like this. Now what will happen if I apply a voltage here and an oscilloscope, the kind of voltage you apply is a saw tooth voltage?

You start from zero or some negative value goes up and then becomes zero and comes back here. Now, what will happen? Here what will happen is this what itself will be deflected here? Maybe I will draw like this without anything the spot would have been here at initial time along y direction you applied this signal, along x direction we applied this and let us say, this says that this is negative and this is positive. So what will happen at zero time no displacement along Y.

And let us see this voltage is such that the spot is displaced here. After some time has passed, what will happen along Y direction they should be a positive deviation along x direction there should be deviation towards the center. So, the spot will move from here to here. So this way as this so this is always adjusted in a way that is maximum reaches when the spot goes horizontally from here to here. And if you have all the settings right then you get to see this oscillation there is an oscilloscope works.

And that is why it is called an oscilloscope because you can see all oscillations there. So you need 2 pairs of plates 1 vertical, that is where you apply the signal and 1 horizontal that is where you apply the trigger. The trigger is always saw tooth sometimes yourself triggering but that also generates. Why the signal is what you want to see. It is not necessarily that it will be a sine wave it can be something else.alright, So this is an oscilloscope works now.

Let us get back to this so, here what you have is you have this deflection plates pretty much like what you have in the oscilloscope. And the way it is drawn here they are top to bottom vertical like this the voltages that apply there looks like an ogive so what will happen then? So this is color coded 123. So, when three comes, well, it is done in a little funny manner, what you have to think is that you have to go from here to here, because 3 arrives first.

So, remember what is happening, this bunch of photo electrons 3, goes through the slit, at one point of time, bunch of electrons to goes in, at another point of time later. Bunch of electrons one goes in at another the point of time later. So, when three passes, let us say this is a voltage then what will happen? 3 will be deflected accordingly when 2 passes the way we have drawn it we are at 0. So, 2 will go straight with 3 passes sorry 1 passes it is on the other side.

So, to go up all so, what are we doing here we are deflecting, but we are we are sending photo electrons that arrive at different time in different directions, so, effectively if you go from top to bottom, this direction now denotes time. Let us say this is for this is continuous object unfortunately, but let us say this is your slit when this goes in this part the initial part, your voltage is such that it goes here when the middle part goes in through the slit, the voltage is says that will go straight when the end goes in to the slit, the voltage is such that will go up.

So, what is happening photons arriving at the slit at different times are sent in different directions? So, what do you get? Suppose now, you put an MCP here and after that you put a phosphor screen what is the role of MCP simply to increase the number one to 40,000 increase the number of photoelectrons. What are you going to see on the phosphor screen you are going to see the streak, 1 is a point 2 is another point 3 is another point this you understand? How bright will this spot be at 1 how bright will it be at 2? How bright will it be at 3? Depends on number of photo electrons in the band 1, band 2 band three.

So now it is as fast as you can see it. If you have a streak camera, well, this detector part can be open. With your eyes, you can see a streak and actual streak. And the beauty of this is that in this streak, this line is actually the time axis. So you see this shape of photo electrons, x axis is time. Now if you do an analysis of the intensity here, you are going to get exactly the same shape and this axis which is now vertical, that is going to be the time axis. That is how a streak camera works. So what are we not doing here? This MCP we are not really trying to get anymore.

We are not trying to put a whole where what we did in ICCD to route to time result measurement is that we were applying the square pulses of high voltage. We do not do that anymore, MCP is kept at a constant voltage, constant magnification. How do you get time resolution by sweeping this voltage here on the deflection plates, and in fact, this can be done much easily with much greater time resolution That is why a streak camera gives you much better time resolution, then a gated ICCD director. In fact, with a streak camera one can go down to one can measure almost up to 1 picosecond lifetimes.

Is there any question so far? Have we understood how the streak camera works, you get a streak business basically you get a streak on this phosphor and then you capture that image and do an analysis, what is the intensity at every point of that streak? Get a photon of that that gives you the decay. So now once again this foster screen is a square not such a big square, typically of this size. We are only using 1 axis here. The other side is wasted. Can we make use of both the dimensions is the camera actually you can.

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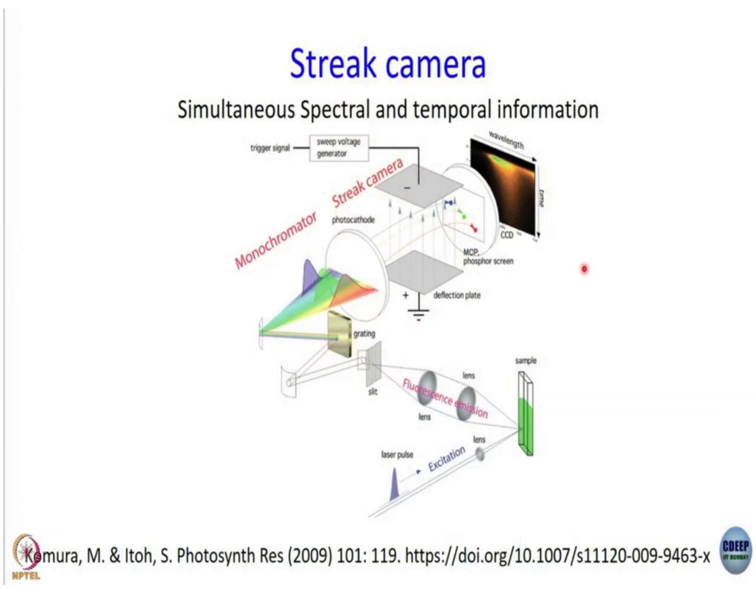

This is one way of doing it I hope you can see the projection. So, this is your pulsed excitation this here you see is a cuvette where your sample is collect and then it goes to a grating this is not a monochromator. Again, this is taken from this paper by Komura, M. & Itoh. This is again a spectrograph basically this exit slit is not there so you disperse. Now see along x axis, you have dispersed right, so you have got the spectrum, along y axis, you are applying voltage you are getting time. So what will you get on the phosphor screen now, you are not going to get one streak. You are going to get an image.

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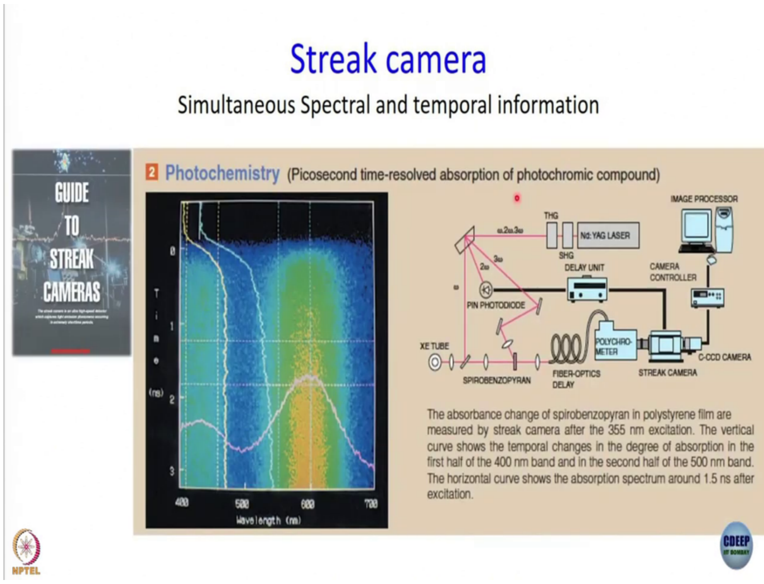

And I will show you an example here. Just look at this image first, then we will say what it is here you see, this axis is wavelength, remember, we are dispersed by using a grating a spectrograph. This axis is time. So if you go from left to right, you see, in case you cannot read, I will read it for you. I mean, in case you cannot read, what is it in here, I do not doubt the level of literacy this is really blurred I can read only because I know what sit in 400 500 600 700 nanometer from left to right you will see this is a spectrum from top to bottom.

What is this? This is time? So, you can see actually it is a high and then it is flat and times that are there are problems I also cannot read what is written there because picosecond or nanosecond I can read 0123 I cannot read whether this one is picosecond or nanosecond I think a nanosecond. So, this is how you can actually use the entire surface of a 2d detector to generate time resolved emission spectra time resolved spectra. Unless they give you the idea that this is useful only for fluorescence experiments because you can read about streak camera from lakowicz book but the reason why I chose this figure.

This there is a book a manual of streak camera I can share it with you this from Himamatsu book guide to streak cameras it is freely downloadable you can download from the net I took the picture from there, this is not time evolution of emission spectra if you look at the setup and you can make out what is there, here you have NdYAG laser, then this is third harmonic generator. So, you generate omega or will omega is already there 2 omega 3 omega then you disperse them.

Three omega comes here, then here, this is where your sample is ok three omega three if you have 55 nanometer pulses are exciting the sample then omega goes here to this XE tube generates white light. White light goes back to you see on the sample you have a pump beam and a probe beam. So what you see here is actually transient absorption. So nowadays for nanosecond microsecond time domain, this has become a more popular technique than using the same MCP.

Because you can see time resolved emission spectra. And if you use a short enough pulse, you do not have to worry about deconvolution or any such thing. So, this becomes very useful. So you can use both the access, and this is not all you can think of doing something else and that is also possible somebody tried it somewhere no, but then that is how it did not work for them. I just draw your schematic to show the other application that might be there. What were we saying? We said that the electron beam gets through.

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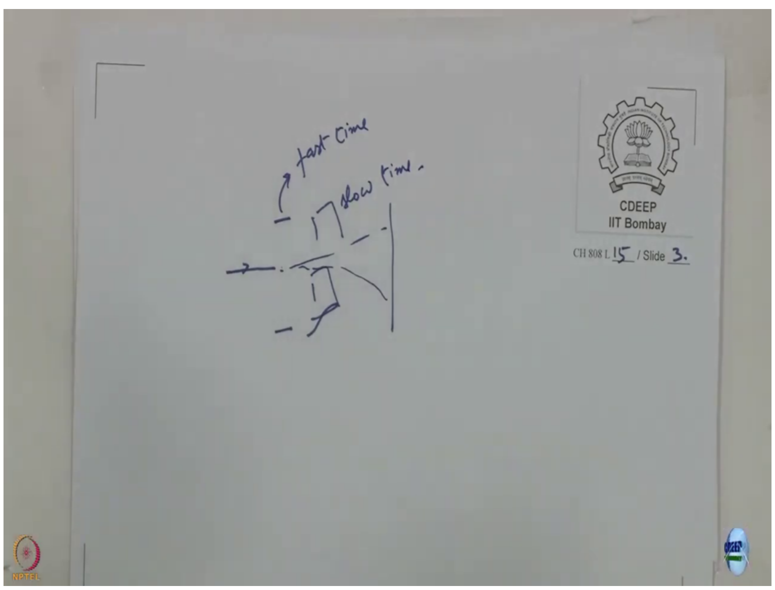

You have this plates and you are applying this kind of a voltage. So, from here you are generating the streak. And then what I showed you earlier is that even before electrons are generated light itself is dispersed. So, this is one thing you could do. The other thing you could do is there suppose you want to look at some kind of a reaction then you can again like oscilloscope have two plates

1 horizontal 1 vertical and this can be the first time axis this can be the slow time axis meaning you apply a voltage here that gives you the dispersion in say picosecond and nanosecond time or whatever it is in the slow time axis.

Let us say you apply a similar voltage but in microseconds or milliseconds then what will happen? You see decays in different time suppose there is a reaction going on. And as a result of a reaction, some new product is formed which has a different lifetime. And you want to follow the kinetics of the reaction using lifetime suppose it is protein folding unfolding, protein unfolding and so whatever fluorophore it is his lifetime becomes small over time, and you want to follow it in milliseconds. What you can do is this one getting one streak can be done in a matter of microseconds.

So, a few microseconds you get one streak and then you apply this voltage on the other axis. The second streak comes above the first streak. And the difference between this streak and this streak is say 10 milliseconds or something or 10 millisecond is too much maybe 100 microseconds. So, what I am saying in 1 microsecond, I get one streak that gives me the decay at certain delay, then I apply a voltage on the other side. So, next thing that will come will come above or below whatever it is, let us say above this one comes, say hundred microseconds later.

So if there is any change in the decay that occurs in these 100 microseconds, you are going to see it. So, you can actually try to follow a reaction by using a fast time axis and a slow time axis. But as far as I know, the lab where I know this was tried out, some of it did not work out, but that might have been for some very different reason. So, what we have discussed in this almost double the usual time module today is that we have discussed how one can use 2 dimensional detectors to make the most of measurements, but then I am sure I have drawn a very rosy picture of streak cameras to you.

In the last 15 minutes, let us end with the discussion of pros and cons nothing in this. There is no free launch. So what is good about the camera what is bad, what is good is obvious. You can get fast measurement along two axis. What is bad? Well, in early streak cameras dynamic range used to be quite poor. Dynamic range means the ratio between the largest and the smallest quantity you can measure. So if you had a biexponential decay, stick cameras were not all that good. But now you can run street cameras in many different modes.

I encourage you to read this book guide to streak cameras, and then you can see how fast the camera can be run in photon accounting mode and so on and so forth. So now time resolution is better and one can actually believe multi exponential decay is on a streak camera. Also another advantage I forgot before I go into the cons in comparison with this TCSPC what is that contributes to this TCSPC full width half max of instrument response function, laser width response time.

And well so these 2 and you can say detector and instrument here, that is not the case because you are applying a voltage, so you can just use the laser pulse to deconvolute. That is one good thing. Now, coming back to the cons, earlier, you had to do this experiment 1 shot at a time. And if you see my 2002 photochemistry photobiology from CAAT, there you can see some decay which was recorded on a very, not so, good the streak camera had burned, but we could get some data you can see that the data quality is nothing like this TCSPC which was then approved data that you get.

But and that is because it was a 1 shot experiment. But now with the advent of Lab view and all that most of the cameras work in simple scan mode meaning automatically you record many data quality and you do everything. So, data quality has become much better than before. Why is it that we do not use it and we have TCSPC we have upconversion and that is true for many labs in India hardly anybody has a streak camera. Why is that so because the cost is for bidding? Cost of streak camera is more or less the same as the cost of your up conversion.

An upconversion gives you better time resolution even though the experiment is more tedious. Here the pro is ease of experiment quickly you can do things and you can do multiple things as well con at the moment, the biggest problem is the cost. So if that is not an issue, streak camera is a fantastic instrument to get and use. So that is what it is we stop here. And then next day, we go back to chalkboard a little bit and we start talking about how lasers work, how you generate pulses an so on and so forth.