Ultrafast Processes in Chemistry
Prof. Anindya Dutta
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture # 06
TCSPC for Picosecond-Nanosecond Time Domain

We have discussed so far in a rather simplistic manner, how to follow the dynamics in femtosecond time regime using pump probe spectroscopy. Now, let us think of a little slower timescale, hundreds of picosecond to nanosecond, but the technique that we are going to discuss is actually little more complicated. So it is, it might be easier if you think start thinking from slower timescale. And then we will understand why we have to do this. Let us say want to follow the dynamics in sometimes scale.

So, the easiest way of doing it is to excite by a pulse and either use a probe or look at fluorescence coming from the sample, look at emission coming up from sample and see how it changes with time. This phenomenon happens in microsecond timescale, then there is no problem because you can see directly on an oscilloscope. We might have occasion later on in this course to discuss very briefly how an oscilloscope works.

But for now let us take a rain check on it. So, an oscilloscope usually does not have enough time resolution bandwidth to give you a reliable measure of times that are down to hundreds of picosecond. Nowadays you do get oscilloscope but then there are issues with it. So you cannot do a direct measurement. When you go down to femtosecond, we solve the problem by using the power of light as we have discussed in case of pump-probe spectroscopy.

We give variable delays but you cannot use the technique if you are talking about hundreds of picosecond or nanosecond, for a very simple reason, what kind of time delays do we have to give suppose I want to measure 10 process that is associated with a 10 nanosecond time constant, 10 nanosecond time constant means you should record at least up to 40 nanoseconds. So 40 nanosecond time delay would work if the light goes and comes back.

So it amounts to effectively 20 feet, you need a 20 feet long transition stage. So, 2 problems with that, first of all, you need a big lab. Secondly, those who have done alignment of even a one foot long transition stage would know how difficult it is. So if you are going to align a 20 foot long delay, then may god help you it is not a good technique anymore and also we record point by point, it will take a long time? So, for this intermediate time resolution, where direct measurement is not going to work and this time delay optical technique is cumbersome.

There is no way other than taking the help of electronics. But then electronics has a problem that the response time associated with electronic components that we are going to use is not in picosecond it is in nanosecond or slower. So, we learned, what we learned is a very elegant technique that uses electronics. But uses a trick to circumvent the inherent core time resolution associated with the electronic components involved to allow us measure hundreds of nanoseconds maybe 10 of picoseconds to hundreds of nanoseconds.

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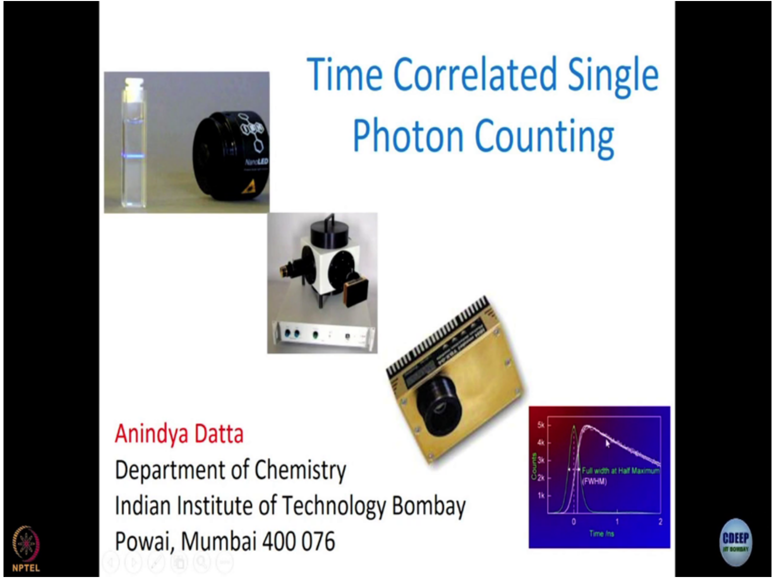

Time Correlated Single Photon Counting

Anindya Datta
Department of Chemistry
Indian Institute of Technology Bombay
Powai, Mumbai 400 076

This technique is called time correlated single photon counting or as it is commonly abbreviated TCSPC what we see here on the slide at the different components that are used in TCSPC. This thing is a pulsed diode laser. And we go to the lab we are not going to show you this will show you a femtosecond pulsed titanium Sapphire laser. But this is something that you can use. And if you do not need too much of timet resolution, these are comparatively cheap and very easy to use solutions for light source.

And you can see the size this would be about 3 centimeter the width is about 1 centimeter compared to that you can see how small the sources are then you need a sample chamber, inside the sample chamber, but you need to keep whatever it is whose fluorescence lifetime you want to record. And then of course, you need a monochromator that is not shown in these diagrams then you need a detector.

What you see here is TBX 04 detector from what is now Horiba, we bought it from some other company at that time, which is the name of features x. So, this is a detector and some associated electronics and when you use this combination you end up getting the decay of fluorescence that look like what is shown in the lower most diagram, this gaussian sort of thing is the laser pulse as the instrument sees it.

And this thing that is there is the fluorescence decay. We might think that it does not look exponential, it does not look exponential because we are showing a rather small time window compared to the decay. So, let us learn step by step. How this technique time correlated single photon counting works and it is important learnt this is because this is now become a very, very commonly used ubiquitous kind of technique. And it is important that we know what to do and what not to do while recording the data and while analyzing it.

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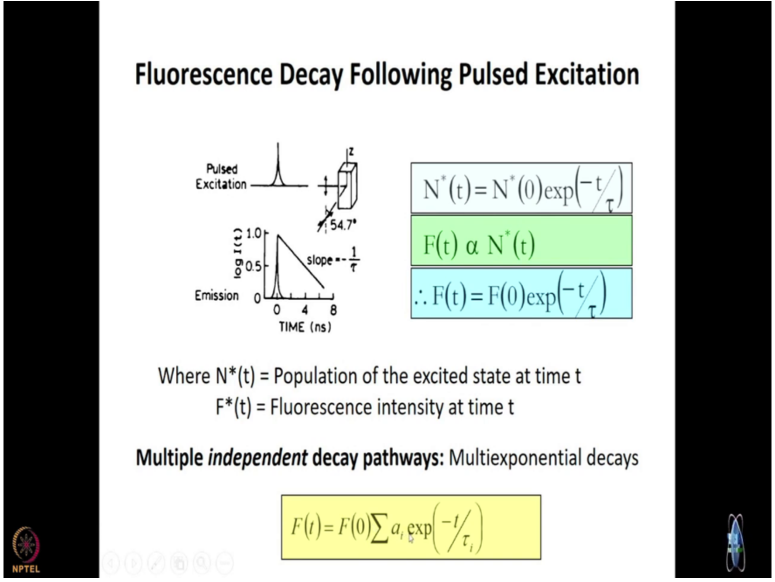

Fluorescence Decay Following Pulsed Excitation

$N^*(t) = N^*(0)\exp(-t/\tau)$

$F(t) \; \alpha \; N^*(t)$

$\therefore F(t) = F(0)\exp(-t/\tau)$

Where $N^*(t)$ = Population of the excited state at time t
$F^*(t)$ = Fluorescence intensity at time t

Multiple *independent* decay pathways: Multiexponential decays

$F(t) = F(0)\sum a_i \exp(-t/\tau_i)$

So this is the basic principle of the TCSPC. Even before going to TCSPC, this is something we have discussed in the previous module in a different way. What we are doing is, we are exciting by a pulse. And then we are looking at the decay the decay here looks like a straight line, because we have assumed a single exponential decay and the y axis is logarithmic. So as we said earlier, in the simplest case scenario, decay of the excited state population is single exponential, because it is a first order decay.

And fluorescence intensity at any given time. If at time, t is proportional 2 the excited state population N* at the same time t. So since N*(t) follows this kind of an exponential variation, we can write a similar exponential variation for fluorescence intensity as well, exactly what we studied in kinetics, there is only one difference in chemical kinetics you would write exponential - kt here instead of that we are written exponential - t by tau.

So this tau is called life time. To put it very simply, tau is the reciprocal of time constant. But then why is it called life time of all things it is called the life time because it is also the average time spent by molecule in the excited state, let us let that be a home work. This is worked out lakowicz textbook and many other places. Please work it out yourself and convince yourself that Tau is actually, the average time spent by a molecule in the excited state that will involve solving an integral working out an integral.

Now, as I said, the simplest case scenario, more often than not, the decay is not single exponential, and where it is not single exponential, the most commonly used model. That is there is a multi-exponential decay where you take a weighted sum of exponential terms. Now, a multi exponential decay would generally fit any decay that you are going to handle, but it is important to not forget that it is not necessary that it is an appropriate decay model for everything.

You might require different decay models. We are going to come back to this issue and show you a couple of examples where a multi exponential decay is not appropriate and you are to use something that is more complicated, like distribution of lifetime or stretched exponential. But let that be the story for another day.

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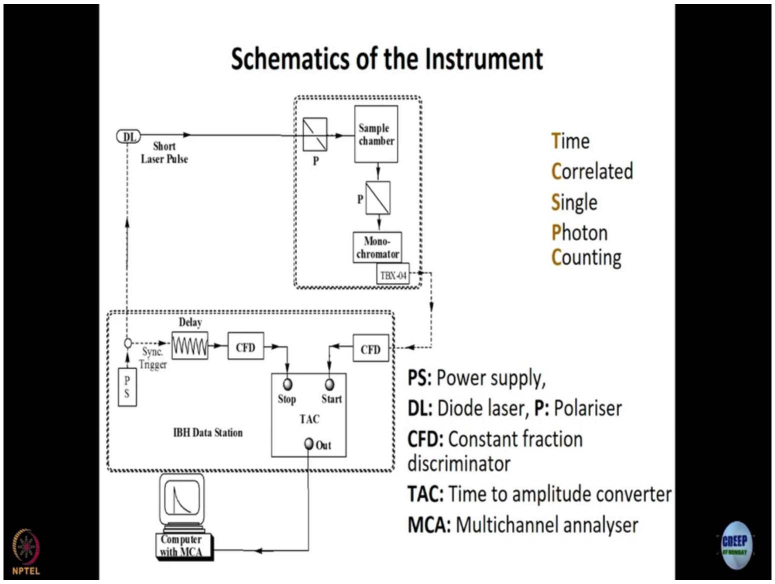

Schematics of the Instrument

Time
Correlated
Single
Photon
Counting

PS: Power supply,
DL: Diode laser, **P:** Polariser
CFD: Constant fraction discriminator
TAC: Time to amplitude converter
MCA: Multichannel annalyser

Now, we come to the schematics of the time correlated single photon counting experiment. And this is where we sort of deviate from a comfort zone of an average chemist and start trying to look inside the black box that the instrument is but if you were to do this experiment properly, it is very important that the instrument is not a black box for you. You need to know unfortunately, the days are gone when you could actually see the components or at least you should know how it works and where the components are.

So the schematics are based on our old diode laser based TCSPC spectrometer, there we had a pulsed laser, DL for diode laser. You can think that is just a pulsed laser, it sends out a short pulse. When you use a diode laser, the output is typically elliptically polarized, which means it is a mixture of horizontal and vertical polarization, not to the same level. But then as we learn later. For our purpose, it is important that we work with linearly polarized like so if we are going to use a diode laser.

Then it is important that you use a polarizer in the path of the light before it goes into the sample chamber and excites your sample. If you use titanium sapphire laser like the one that we are going to show you later on, output of titanium Sapphire laser is already linearly polarized. So this polarized component is not required. In fact, if it is there, then it can be a hindrance, if it is not exactly aligned with the polarization of the light, then the emission comes out.

And as we have discussed in steady state emission experiments once again, you want to record at right angles typically, emission light is made to go through a polarizer. Hold your thoughts on this one, in one of the later modules will learn why it has to go through a polarization. For now, let us just say that for lifetime measurement, what we typically do is we keep the second polarizer the emission polarizer at 54.7 degrees compared to the polarization of the input polarizer. When I said 54.7 degree, I do not mean direction, I mean polarization of the second emission polarizer is said as 54.7 degrees with respect to the polarization of the excitation light and then the emission goes into monochromator and into the detector. So, far it is almost like the arrangement that you have in you are steady state polarization. The difference comes up this what happens is from the detector the electronic signal that is generated goes into something called a constant fraction discriminator the job of constant reflection discriminator is to help us get an accurate timing information will come back to this issue a little later.

For now, let us just assume that the output of the CFD is a pulse, which we can time very easily precisely that goes to the start module of a time to amplitude converter. A time to amplitude converter has at its heart, a capacitor which starts getting charged. The moment a signal arrives at start and keeps on getting charged until another signal appears at stop and where does this signal come from it comes from the power supply of the diode laser, which sends out a synchronous trigger.

Synchronous trigger means the power supply fires the laser and at that instant since upon a pulse of electrons and electronic files that again goes to CFD and goes to stop what does a synchronous trigger signify it signifies firing of the laser. So, if you laser operate set the one megahertz repetition rate which means it gives out 10 to the power 6 pulses per second then for each one of these 10 to the power 6 pulses per second an electrical signal will go out that is a synchronous trigger.

So, the synchronous trigger has the same repetition rate as the laser itself, that is made to go through some cables and all goes to CFD and stops so, now what happens capacitor that is there insight TAC is charged for the time duration between arrival of a signal at start and arrival of a signal at stop and the moment stop comes charging is stopped some charge is accumulated, now it is discharged across a resistance and the voltage across the resistance is measured.

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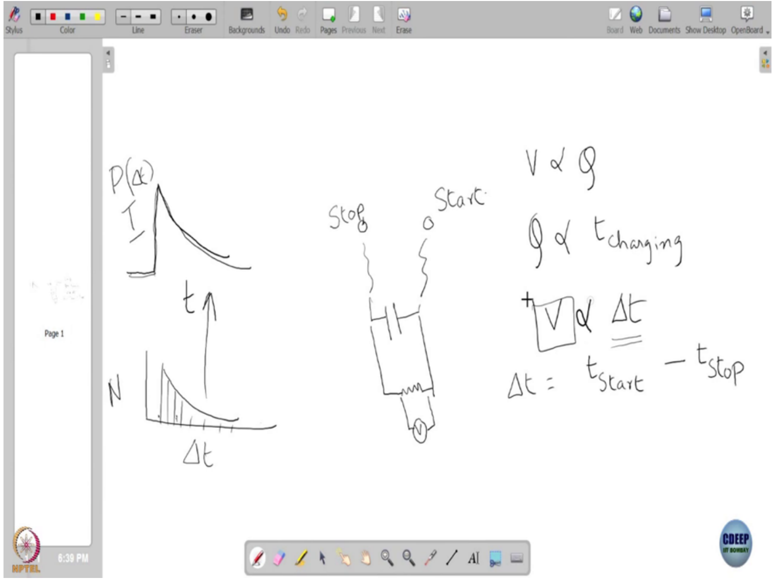

So, if I can try to draw it a little bit. So, what you have is this, let us say this is stop let us say this is start this signals go into starting of a capacitor the start and stop starting of the capacitor when it is stop after that, the capacitor is discharged across this resistance and you measure the voltage across the resistance. So, now see do you agree with me that the voltage that you see is going to be proportional to the charge that has accumulated on the capacitor.

And will you also agree with me, if I say that the charge that has accumulated on the capacitor is proportional to the time of charging, so, I can write it like this. This voltage is proportional to delta t where delta t is the difference in times of arrival at start and stop. Now, it is important to understand what is going on here. So, the reason why we do all this is that we cannot measure the decay directly.

So, we are resorting to a method that is actually probabilistic in nature. So, let us say is the decay of fluorescence. So, if you do the experiment many times what will happen when I say this is the decay of fluorescence, what I mean is that if you take a large number of molecules and performan an ensemble measurement, then population decay is like this if I take one molecule and keep on exciting with the pulse and keep on recording delta t.

What will happen? Will I get the same delta t every time, no right, I will get different delta t's at different time. The basic principle of time correlated single photon counting is that you say that if you take a single photon and plot probability of getting a particular delta t, against number of times it occurs. So, basically we talk about histogram now, we are saying that this histogram has the same shape as the actual excited state decay and fluorescence decay.

It is important to understand this if you understand this, this is very simple. So, what is the working principle of TCSPC is we are going to record this delta T again and again. So, its not a one shot experiment you keep doing the experiment many times and keep recording delta T and what we are plotting essentially is number of occurrences of number of occurences versus delta t so, the delta is 0.

If I get delta t 0 once I started off here, then I get delta t equal to 10 nanosecond, I strike off here. Then again, I get delta t = 1 nanosecond, I put dot here, again I get delta t = 1 nanosecond, I increase the dot by 1 unit. So after a while, what will I get, I will get a histogram isn't it. Something like this as clear about this. So, what we are saying is that if you join the tips of histogram, then you get the same curve as decay of the excited state population, the decay of fluorescence intensity.

So, what is our job then? our job is to perform a large number of experiments and keep recording delta t and keep track of how many times a particular delta t occur. So why is called time to amplitude converter? Because you are actually converting time to a voltage. That is it is called time to amplitude converter. So, from there, it goes to computer with MCA means multi-channel analyzer. It goes into multi-channel analyzers, what is a multi-channel? Multi-channel analyzer is sort of like a digital graph paper.

See what I discussed a little while ago that I want to measure the number of times a particular delta t arrives. If I am to do that manually, what will I do? I will take a graph paper. I will mark of the delta t on the x axis and keep putting dots again one delta t 1 dot same delta t comes again I go up by 1 notch and so on and so forth. I will the histogram computer does exactly the same thing. It has a card nowadays MCA is no longer a standalone instrument MCA means multi-channel analyzer.

So, multi-channel means each channel is a memory location, you can think like that the digital equivalent of a graph paper on a graph paper all those cross lines, are every location you can think of digital graph paper. So multi channel analyzer as all these channels, each of which is in every location. And what you can do is you can record their how many times a particular delta t is coming. So, that is what we do. And thats how we built the histogram, which has the same shape of the decay. So that is how CFD work.

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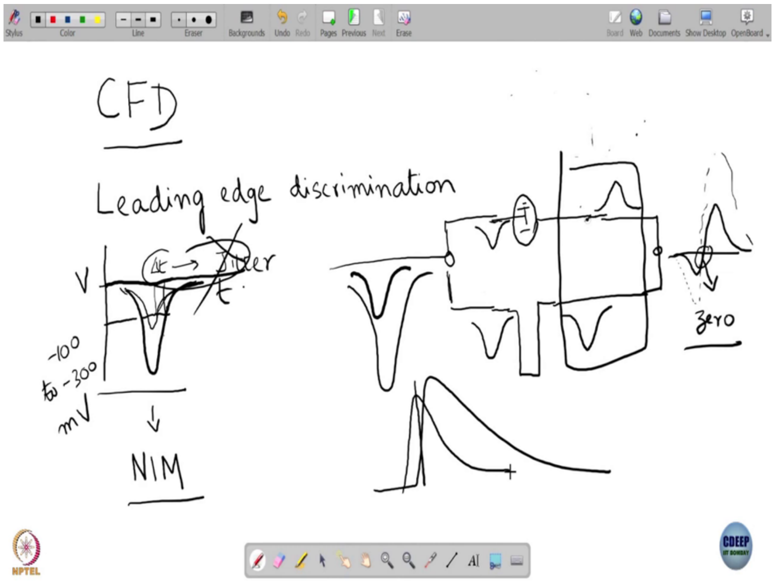

How does CFD work? So, this is how a CFD or constant friction discrimination work before that let us say why do we need CFD in the first place before we go to constant fraction discrimination, let us talk about something that is called leading edge discrimination. See the output of the detector is something like this where this is time x axis and y axis is voltage Typically, this pulse is - 100 to - 300 millivolt that is a maximum ampltitude this kind of pulse is called a NIM pulse.

What is the meaning of NIM nuclear instrumentation module name means nuclear instrumentation module, the thing is, you make many instruments, if every instrument has 1 kind of as a different kind of signal, then it will be very difficult to interface instruments and then only one person can use one instrument that is not a very happy situation. So, some typical patterns of use and NIM is one such kind of pulse nuclear instrumentation module, it is sort of a Gaussian pulse is - 100 to - 300 volt a millivolt in amplitude and other parts that is very frequently used looks like this.

And this site is typically 5 volt can anybody tell me what this pulse is called, it is a squared pulse but it has a name. It is used whenever you use any kind of binary logic any kind of computer, it is called a TTL pulse. I do not know why it is getting written like a stair but anyway TTL is transistor logic. So this is basically we know very well that computer does not understand anything other than 0 and 1.

There is very computer language is all in binary everything is 0 and 1. So essentially this is 0, this is 1. So sequence of TTL pulse tells the computer what you want to tell it, but here typically we do not use TTL pulse. You see there is a provision of TTL output in most of the instruments. But most of the time, we do not use TTL. NIM is what is used because most of the instruments are actually mounted in NIM bins.

So, it is more convenient to work with NIM pulses. Now the problem is - 100 to - 300 there is nobody has said there is going to be 300 millivolt all the time or - 100 millivolt all the time there is always a fluctuation. So, how will I say so, if you remember the diagram some signal comes to let us say start of TAC, this is very easy to say signal comes but how will the instrument know that signal has come? It cannot see all it can do is it can measure voltage.

So, you can tell the instrument that when that when the value has reached 50 millivolt then you considered that the pulse have arrived. So, let us say this is -50 millivolt. This is called leading edge discrimination discriminate like that, that all this is considered to be 0 here. That is 0 time. That is when we start. But there is a problem with this was as we said just others nobody has said this will be exactly 300. Suppose it is not 300, I will exaggerate a little bit and write like this for the same signal, let us say I have got a pulse like that.

Now, what will happen at this time, x axis is time time remember, value is not 50 millivolt, when at what time this value is 50 millivolt. So, depending on whether I get this big pulse or this small pulse, I will have uncertainty in start time by delta t. This is called timing jitter. Timing jitter is eliminated by taking by using constant fraction discrimination rather than leading edge discrimination. How do we do that? let us take a pulse like that?

So first thing that happens inside CFD, and it is very easy to understand is that you divide the pulse into 2 parts. So, you can think of this pulse as an electric current, is it easy is it difficult to divide in the current into 2 parts? Easy, if you have, if you think in a very gross bulk way, you have some copper wires twisted together, you untwisting that he gives you 2 channels in which electrons can flow and you can have say 20 strands on 1 side and you can have 5 strands on the other side, what will happen, resistance will be different between the 2.

So more or less traction will flow in class 11, 12 with our electricity all of us have been bothered with problems like this how much current will flow in which direction and all that I tried to do anything like that everything became 0. That is a different issue, but here it does not. So, depending on the resistances of the 2 arms, let us say in this arm, I have a larger pulse, in this arm, I have a smaller pulse. Next what we do is let us say I invert this pulse inversion using transistors and all is very easy in electronics.

And let us say to this one I give some time delay, which means I use a longer wire. Now what will happen on this arm will have a positive pulse, on this arm we still have a negative pulse but now, this lags in time okay. Now, let us combine them individually or is it difficult to combine very easy again wind the strands together. Now if we combine what will happen? You have to add up these 2 pulses that give you the output what will the sum look like something like this it will be is 0 crossing pulse.

Now, see, instead of this if I have a huge pulse, what will be the output be something like this amplitudes will change, but 0 crossing point will not change. Now, if you tell your instrument that wait until the signal becomes 0 the first time and then start counting, then this timing jitter is eliminated. This is the advantage of constant fraction discrimination it is called constant fraction discrimination because you are taking a pulse of a fraction of the pulse here and another fraction there to 1 - that fraction there.

So constant fraction discrimination eliminates time in jitter. So what we have learned then is that we can do time correlated single photon counting to record fluorescence decays in hundreds of picosecond to nanosecond time regime, we are not limited by the time response of the electronics here, because we are not trying to actually measure the time we are trying to measure delta t that can be done without much hassle, as I hope you have understood now.

And to measure delta t with precision without timing jitter it is important that we do constant fraction discrimination rather than leading edge discrimination. Once we do that, then we are good. Then we can get a decay like this in the timescale that we want but this is not that we really want this decay is more complicated than what we would have liked it to be, because we are not used a Delta pulse for excitation we have used the pulse that has a finite width that complicates the scenario.

So, in order to make any sense of this curve that we get experimentally, we have to as we learn de convolute and extract the actual decay from the observed decay in which you have strong signature from the instrument that is what we are going to do in the next class.