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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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LECTURE NO. – 04
Time Domain Spectroscopy

Now we move on to our next topic, so far we have discussed frequency domain spectroscopy, now we are going to talk about time domain spectroscopy. Hey, can we begin? Can we begin our discussion now? Right, so what is your idea here? The idea is this, the spectrum that we are familiar with always is something on the Y axis let me write power today against some measure of energy, let's say wave number, right, and for an ideal spectrum is going to be let us say 1 line. Of course if all the spectra in the universe where single lines, it would have been a very precise, what an absolutely boring situation, thank God that not all spectra are single lines, okay.

To understand let us start with this, single line here, what kind of light does it imply? One type, so what do you call it in a little? Monochromatic, so the way I draw it here I indicate a monochromatic radiation, right, single wavelength, single energy.

Now if I want to represent this in time domain and equivalent to presentation when X axis is time, what would it be? Let me call this power at nu bar domain, this I can call power in time domain, what will it be? It will be oscillating electric field, right, yeah, it won't be same power, okay, let me say this is E, what is electromagnetic radiation, an oscillating electric field right, this is not electric field, this is just the intensity, so oscillating electric field you can say it's either a sine wave or a cos wave whatever you want to write, let me draw it as a cos wave, something like this. A single sine or a single cos wave, okay, they're equivalent to each other, is that right? I can draw it either like this or like this, so when I acquire the data I can also try to acquire either like this or like this, how we acquire like this we will see.

But can there be any advantage of the time domain measurement, what would the advantages would be of time domain measurement if you can do it. First of all how do you make a frequency domain measurement, you measure one frequency at a time, if I want to measure a majority in time domain, how will I measure it? Anyway, before going there I think I want to show you something else, so this is what I have drawn on the board as well, right, this is the representation of a monochromatic radiation, let us say I don't have monochromatic radiation, I have two, this is what it looks like, you see what happened? When I've monochromatic radiation then I have a regular sine wave or a cos wave.

If I add another frequency to it what happens is, there shapes in just not a regular cos wave that we know, okay. Why does this plot look like this? Sorry, super position of wave so, right, so let us go step by step then it's right in some regions they cancel and some regions they reinforce, I've drawn cos waves right, so for X = 0 the value is 1, so when values are 1 it doesn't matter on the frequency, right? For X = 0 no matter what frequency it is, the values are 1 that means the waves are in step, they are in coherence, right.

What happens when you go to anytime greater than or less than 0, frequencies are different right? So they now start getting out of step. As they start getting out of step what will happen is they don't reinforce each other to that extent, and there will come a situation where they'll completely cancel each other distractive interference, right, because of this you get a pattern like this, this has a name, what is this called? This kind of pattern is seen in interferograms, okay. If I mix more waves then what will happen? First of all I have to zoom out a little bit, this is what happens, at time zero they reinforce each other, they've added more waves, but then they get out of step faster. Have you understood this? If not, please ask now.

I think of two people running around gymkhana ground, okay. Let us say I run a race with Akansha, right, what will happen? We'll start from the same point then we're in phase, but then Akansha is an athlete I am not, so she is going to go much further, so some path difference will come in, very soon if we keep running for long enough you will see I am at one end of the field, Akansha is on the other end of the field, so if you have waves then the situation would be something like this, say this is me, this is Akansha, okay, so at this point we are more or less on the opposite, diametrically opposite points of the field, right, here you get, if you're waves you will get complete distractive interference, so you will get a 0 here. Then what happens? Then you start getting back in phase right, two people running in the same direction but at different speeds, so when the diametrically opposite then the difference is maximum, when they keep running what will happen is, the faster runner will start catching up with the slower runner, right, that is what happens say here, here you see one maximum close to another maximum here, there again the value will be large.

The moment the value becomes large after that what happen? Again this phase difference starts building, so you develop what is called, if you remember your lessons in sound in physics you start getting a beating pattern, right you get beats, okay.

What happens if the two runners, I find it easiest to understand thinking of runners, these two runners if they run at very different speeds then what will happen? Suppose one person is not running I'm tired to stand, Akansha runs 200 laps, then what will happen? She'll keep catching up with me at regular interval, but suppose you can run at more or less the same speed as her, then what will happen? It's not so that easy for her to catch up with me, right, so what kind of beating frequency you'll get depends on the relative speeds or relative frequencies of these two waves, if they're very close then frequencies are small, if they're very far apart from each other than frequencies are large, right, so this is what happens when you mix waves, so you can understand now instead of this easy diagram that I have drawn, if the intensity is actually something like this, many frequencies are there, what kind of time domain signal will I get? I don't have to follow the sequence, and not everything will have the same amplitude also, can I do what? Yes, see what is the difference between cos and sine just phase difference, nothing else, okay.

So you get this signal like this, at first look it does not look like signal at all, it actually looks like noise, but that is your signal, and this one important thing to understand here, and that is let us take this point in time, this point in time does it have information of this frequency or this frequency or this frequency? Yeah, you just be brave I mean what you are thinking is right, I choose any arbitrary point on my interferogram, time domain signal, does it have contribution from this frequency or this frequency or this frequency, all naturally all, right, and think of the other way around, any point here that has contributions from all the waves, right, actually I'm so sorry, from all the time points, isn't it? So these two are completely related to each other, so if you have frequency domain spectrum you can actually generate the time domain spectrum that's what I did, isn't it? So what I have done here, what I have written here in this slide is essentially spectral information, I've said that I have something that has a frequency of say 10, something that is 11, 12 so on and so forth, I'll just mix, so this is the way in which you can generate the time domain information if you have frequency domain information and there must be some way of going the other way as well, right, and the way you do it I think you know already is by Fourier transformation.

Fourier transformation is the translator between frequency domain and time domain data, right, how it comes we'll slowly come to that also. Is there any question about this so far? This is something we'll come back to once again when we talk about nu bar, so it's important that we understand this here. Have you all understood what time domain data looks like, right, now I can come to the advantages. Is there any question? If there is a question please ask now. No question? Arun? Sure? Okay.

So now see if you look at this and that the first advantage becomes obvious, how do you pronounce this word, name? Jaquinot, I have no idea why that T is there, but what can I do, that was his name, Jaquinot, Jaquinot advantage or throughput advantage. See here when you do frequency domain measurement as we've discussed you have to measure frequency by frequency, one point at a time, here when you do time domain measurement all the colours are going in at the same time, alright, they are generating interferogram that's all. Have I been able to make the point? Right, the entire light goes in, so if the entire light goes in naturally signal intensity is large, so signal to noise ratio will also be better, you just discussed that if signal is large, then signal to noise ratio becomes better.

Now see you measure say from 500 to 5000 centimeter inverse in steps of say 3 centimeter inverse, how many points would that be? 1500, so you have to measure this 1500 points one by one, right, now all the intensity that you collect in this, is going in at the same time when you do a time domain measurement, because you are not using a mono-chromator right, when I'll do, we'll see very soon how the time domain measurement is actually done, but schematically you can think like this, this is your source, again when I say source it can be the light source or it can be an emissive sample, or it can be the light from the light source after passing through sample, transmission. That's just goes into your detector, which is capable of producing a time domain output.

How it produces time domain output is a different question of course, okay, if I do this, is there any need of putting in a mono-chromator here? No right? Because which frequencies are there, is something that I am going to learn when I do a Fourier transformation of that, no mono-chromator, so the entire light goes through, throughput is high, okay, that automatic might mix the signal to noise ratio significantly better than what it would have been if you collect it frequency by frequency.

Have we been able to understand this? If there is a question please ask. So first is Jaquinot advantage, second is resolution, you can actually get a very highly resolved data, how you can control the resolution is something that we are going to discuss in a few minutes, okay, but just believe me on this for now that you get a good resolution.

And third is you are doing this multiplex detection, when you do multiplex detection signal to noise ratio becomes better anyway, these are the advantages, but of course as we have now understood there is no free lunch in the world, it cannot be advantages all the way there is a problem as well, multiplex detection means you're measuring all wavelengths together, so once you do that, that signal to noise ratio remember the discussion we had that comes into play.

Now what is the problem? The problem is this, this is what we want to do, isn't it? I want a detector and I want the detector to give me time domain information. How do I get time domain information? What is the device, now this is something we have studied in 11, 12 modern physics, so you have to tell me, if I want to observe, I've signal that oscillates in time, what is it that I use? I've some photo detector that collects it but then what is it that lets me see that signal. Some signal that changes with time, if you cannot say we'll take help from the in-house physicist but yeah, but you see is a current, suppose I have a signal, I have some light whose amplitude, I have a field which oscillates with time, what is it that I use to see this signal? If I tell you the answer you will of course regret because you know already, Vishnu no? Okay, tell us.

Yes of course I'm definite to the oscilloscope. Oscilloscope, ever heard of oscilloscope? No, acchha ever seen an oscilloscope? Where? Outside the lab. See you people are not 10 year olds, so I will not believe it if you say that you've never seen a good old fashion TV, so the big fat TV remember? What does it have? It has an electron tube, electron gun, which sends an beam of electrons, and then you have 2 plates like this, and you have 2 plates like this, so apply a field here, then the electron beam will deviates this way or this way. Apply this field, vertical field electron may moves up and down, so in an oscilloscope or in a television set what we have is this, we have an electron gun which sends a nicely collimated beam of electrons, okay, and you have a phosphor screen, so the electron beam goes and hits the screen and you'll see a spot.

Now maybe I'll draw it instead of acting out, this is your electron beam, now what you have is you have 2 plates, one like this, let us say this is plus, this is minus, high voltage of course, so that is why you are not supposed to open an old fashion TV, right because that 10,000 volt potential difference is that you don't want to touch it.

And another set of plates is like this, let's say this is plus, this is minus, okay, so this is one set, this is another set, what happens if I apply high potential difference here? Let us say this plate is minus, this plate is plus, then the beam will deviate this way, right.

Now if not, that's all I do then let us say this is the screen, the beam is going to hit here and you'll see a glowing spot here, right, I've to draw 2 dimensional screen also. If I apply a potential difference between these two, then what will happen? Say this is plus, this is minus, then the beam will deviate like this, right. And now they will be, alright, so by applying some voltage on this horizontal plate you can make the electron beam move along horizontal plane, by applying a signal on the vertical plates, sorry potential difference or vertical plates you can make it move up and down, right, that is how an oscilloscope works, okay, so on the horizontal plate you apply what is called the trigger signal, which moves it at a regular interval that gives you the timing information, in the vertical plate you provide the signal let's say an oscillated signal that moves it up and down, so on the screen of the oscilloscope you can see signals like this, okay, but the problem is this.

Let us say we want to do a measurement of some IR frequency, let's take a typical IR frequency, 1,000 centimeter inverse. If this is the wave number 1,000 centimeter inverse, what is the wavelength, and say what's the frequency nu? Nu will be C divided by nu 1 or multiplied by nu 1, that lambda nu = C, so nu/nu bar = C, so nu = nu bar into C, is that right or wrong? Right, so if nu bar is 10 to the power 3 centimeter inverse, C is 10 to the power, centimeter per second, what will it be? 10 centimeter inverse. So frequency is going to be 10 to the power 3 centimeter inverse. If frequency is 10 to the power, sorry, 13 centimeter inverse, if frequency is 10 to the power 13 centimeter inverse, what is the time period? Yeah, I forgot the 3, is 3.3 picosecond, doesn't it? Is that right? 1/3 into 10 to the power -13 that comes to 3.3, 10 to the power -12, so the problem is oscilloscopes are not that fast. It is not possible for you to see 3.3 picosecond kind of signal directly on an oscilloscope, alright, so we need a way out, and the way out is frequency modulation that is what we'll discuss in the next period.

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