INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

CDEEP IIT BOMBAY

MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

PROF. ANINDYA DATTA
DEPARTMENT OF CHEMISTRY,
IIT BOMBAY

LECTURE NO. – 05
Frequency Modulation for Fourier Transform Spectroscopy

In this entire discussion that we've had so far is there in Skoog's book including little more detailed derivation of your Lambert-Beer's law, okay.

So today we continue with our discussion of time domain spectroscopy. We had finished the last lecture stating the advantages and one disadvantage of time domain spectroscopy.

What was the one disadvantage that we discussed? What is the problem with time domain spectroscopy? What is the problem? Remember we talked about oscilloscope and all? Yeah, so what is the problem? Oscilloscopes are not that much accurate. So you are saying not so fine tune, I'll use another word, oscilloscopes are not fast enough. As we discussed suppose we want to look at something like 10 to the power 12 hertz, 10 to the power 12 hertz means reciprocal of that is picosecond, so it is not possible to have an oscilloscope that can give you picosecond time resolution, the problem is time resolution, alright, time resolution not spectral resolution.

We do not have electronics that can work that fast, of course this is surely something that is new for you because most of us would not have studied a formal course on electronics, but every electronic component has it's what is called response time, and that is what determines how fast, what is the fastest signal a given electronic device can actually measure. So it's impossible to have an oscilloscope that measures that fast, so what is the solution to that? The solution in conclusion we have said was frequency modulation.

And today we are going to learn how this frequency modulation is used to generate a signal that our devices can handle. TD in this case means time domain of course as you understand. What is the meaning of frequency modulation? Frequency modulation means I have a high frequency signal, I have to change the frequency of the signal in such a way that I can measure it, but then I cannot just slowdown in an any arbitrary manner, right, I've to generate another signal which is related in some way to the actual signal that I want to measure, okay. If I put it in very, very simple terms what I want to generate is a map of the signal that I've actually have, okay.

You want to know what India looks like, okay, how do you do it? You look at a map, right, but then if the map is drawn to 1:1 scale then you'll need a paper that is of the same size as India, isn't it? That's not such a good idea, so what you do is you draw a scale down map so that it fix an A4 sheet, but then if you take the ratio between say Mumbai and Kolkata in this map, measure the distance whatever centimeter it is, and you take the actual distance in kilometers between Mumbai and Kolkata that ratio would be equal to the similar ratio you'd get for say Mumbai and Delhi, right, so it has to be two scale, they're trying to generate a map here, how do you do it? You do it by an instrument that was well invented actually long ago, and we might have forgotten but all of us have studied it in school once again in physics, so what is, how do you measure the speed of light, everybody knows that light is the fastest thing that we can think of right.

How do we measure the speed of light? If you want to measure our speed while we are running we can do it by a stopwatch. How do I make a stopwatch that can determine the speed of light? How is it done? Does anybody remember? By which instrument do we measure speed of light? Exactly, who said that, and yes, so this is done by using Michelson interferometer, right? Right, it's called Michelson interferometer. So the same instrument can be used, right, kind of in the reverse mode to generate this frequency modulated signal.

So we are going to draw schematic of Michelson interferometer now. Let us say this is the source and once again as usual when I say source it maybe the light source, it maybe the emissive source the sample. I just draw two rays to start with, let's say these are the two rays, as usual you collect it by a curve mirror, okay, but there is no grating, there is no mono-chromator, please remember that, there is no mono-chromator here at all, then we do it in such a way that this year is the focal length of the mirror, sources at the focal length so we are going to generate a collimated beam of light, right. So you get a collimated beam of light.

What you have next is that, there are two arms in Michelson interferometer, one arm contains a fixed mirror, the other arm contains a moveable mirror, before I draw the arm so I'll draw another optical element, this is something that has been introduced to you already, this is a 50:50 beam splitter, a piece of glass or any transparent substance, semi-transparent substance which reflects half of the light and transmits half of the light, so what will happen? 50% of the light goes this way, and it's placed at 45 degrees, so 50% of the light goes straight, okay, so far so good. You might be wondering why we are doing this, we'll see in a few minutes, but have you understood what we've drawn so far, sure? Okay, now here on one arm you have a fixed mirror, fixed plain mirror, and the arrangement is such that this one is that 45 degrees, the beam hits the fixed plain mirror at 90 degrees, so what the beam does after hitting the mirror is that it retraces its part, can we focus here please? It retraces its part, it goes back in the same direction that it came from, alright, so it goes straight.

Of course as you understand when this beam hits this beam splitter, 50% of it is going to be reflected back towards the source as well, right, only 50% will go through. And the other thing I should say here is that this is a very out of scale diagram, the beam is not this fat, we are exaggerating the size of the beam so that we can draw it, if I draw too close you won't be able to see from there, alright, so this is one arm, okay.

And here we have a detector, exactly at the focus of the second curved mirror, I'll just write D for detector, so this light falls on the detector as well, so if you ignore this beam what kind of signal do we expect from the detector? A constant signal, right, and there is no wavelength resolution no nothing, are we clear? Any question? But then we cannot ignore this beam also, what we have on this arm is that, we have a moveable mirror, a mirror that can move back and forth, and once again this moveable mirror is kept so that the angle of incidence is 0, okay. The beam strikes this mirror at 90 degrees, okay, so far so good. So what will happen? Even this beam will go back exactly in the same direction that it came from, when it reaches here 50% go straight, remaining 50% gets reflected, and if your alignment is perfect then I hope you understand that the beam from here and the beam from here become completely super imposed after this beam splitter, are we okay? So it is enough to draw a two rays here, I've made sure that the two parts are exactly the same, right.

Why do we need a moveable mirror? This is why we need a moveable mirror, now see you don't have like one ray of light, to keep thing simple let us consider a monochromatic beam of light to start with, monochromatic light of wavelength lambda.

Now see what we have essentially done is that we have created two different beams of light and by moving the mirror I can change the path difference between these two beams of light, is that right? From here to here to here to here that is one path, and from here to here to here to here that is another part, right, so I can move this mirror to such a distance where this parts are exactly the same or I can move it a little bit so that these two parts are not exactly the same, have you understood this part?

What will happen to the signal on the detector, if these two parts are exactly the same, so two parts exactly the same means path difference = 0, right. So in path difference = 0, and remember wavelength is lambda, then if I plot the power at the detector as a function of delta the path difference, remember what delta is, delta is the path difference between the two beams. When delta = 0, then I'm going to get some signal here, okay, then I keep changing this, what will happen when delta = lambda/2? I've two beams, one go straight comes back, goes down, gets focused on the detector, the other goes up, comes back, gets focused on the detector, between these two beams I've adjusted the path difference delta so that delta = lambda/2, okay.

Let me see, this is one of the waves, one of the beams, right, let us say this is the other beam when delta = 0, this will be the situation right, this is what happens at delta = 0, right, constructive interference, what happens when delta = lambda/2? I'll keep the white one as it is, and maybe I'll use some other colour, what happens when delta = lambda/2? Let us say white one is fixed, but I have moved this other one a little bit, then okay this is zero line, this will be the situation, isn't it? Right, that orange wave that is what we get with respect to the white wave if delta = lambda/2, are we clear with that or not? What do we get in that case? What is the sum signal? 0 complete distractive interference.

So now if you look at the signal when delta = 0 you get some signal when it is equal to lambda/2 then you get 0, what happens when it is equal to lambda? Now you've moved it further, so that this speed has become coincident with this one, again you'll get constructive interference, complete constructive interference, so it should climb to a maximum at lambda.

What about 3 lambda/2? Again it will become 0, what about 2 lambda? Again it will become maximum, so what you get at the detector is an oscillated signal, have you understood this? Now see it's like this, suppose this is how I do the experiment, I fix the delta 2, 0 and keep the mirror there, what will I see? I will only see this signal and nothing else, right. If I keep the mirror the moving mirror fixed such that delta = 0 for even one hour, what was our problem? Our problem is that we cannot place our picosecond, okay, what I am saying now is that when I want to look at this signal here, for delta equal to, any constant value even if I measure for one hour, there is going to be no change in signal for that value, right, so I can sit at this point for whatever reasonable time that I want and get a good signal at this point, okay.

Then let us say, reasonable amount, let us say 5 seconds, I'll do this measurements for 5 seconds and I'll get whatever signal I get. Then I move to this point, see that this point for 5 seconds once again, right, so what I am trying to say is that I can generate the powers at each of these deltas without much problem in real time. Are we clear with that? For the question that might come to your mind right now is that what is the use of this signal? This signal is not really the signal that I'm supposed to see, but don't forget, look at X axis, X axis is what lambda, lambda/2, lambda 3, lambda/2 and so on and so forth, so this oscillation that we have, that is actually related to the wavelength that we are trying to detect, so from here as we'll see once we do the, this little bit of math, we will be able to get a mathematical expression that gives us a way of determining lambda. But have we understood that for each of these points I can do a measurement for as long as I want, alright.

Now let us say of course when we do a measurement like this you do not really, you want to automate everything, right, so what we do is what is done in the instrument is this moving mirror is moved at some constant velocity let us say VM, very easy to remember, V for velocity, M for mirror, okay.

Let us say VM is the velocity of the mirror, okay, and let us say tau is the time for the mirror to travel, say lambda/2, if the mirror moves by lambda/2 what is the path difference that we actually bring in? To get this diagram if the mirror moves by any distance X, what is the consequent path difference delta that we get from there? Okay, multiple choice X, 2X, X/2, none of the above? Yeah 2X sure? First the mirror is here, then it moves here, this distance is X, so while going distance that is decreased is X, but then while coming back also distance that goes down is X, so it's 2X, so tau is the time for the mirror to travel lambda/2 that is the time for delta = lambda, are we clear about that? Time for delta = lambda, right, alright.

So now what is your VM tau? What is VM tau? Lambda/2, right, so let's make tau the subject of formula, tau = lambda/2VM, right.

Now let us say F is 1/tau, frequency that is your 2VM/lambda, agreed? 2VM/lambda, now how is lambda? So on the left hand side we have frequency, so it makes sense to have frequency on the right hand side also, what is this frequency? This F, that is the frequency of this signal, isn't it? Right, don't forget tau is the time for displacement of mirror by lambda/2, that means delta = lambda, so it's the frequency of this signal, F is the frequency of signal.

On the right hand side how do I convert this lambda to nu? But nu is the frequency of light, lambda = C, right, so lambda equal to, yeah, so I can write this as 2VM, if somewhere I've written capital M, somewhere I've written small m, 2VM/C nu, okay. So here right away we have the relationship between frequency of the signal and frequency of light. What was our problem? The frequency of light was too high for us to measure, but now we are going to measure the frequency of signal, not frequency of light that is related to frequency of light by a factor of 2VM /C, and I think I hope you can see the advantage right away, you've C in the denominator.

Do you think VM will be comparable to C? Can you move your mirror at the speed of light? No, you cannot. What would be a reasonable speed of mirror? Let us say, well since I know there is a 3 in the denominator, 3 meters per second, is it possible for you to move the mirror at 3 meters per second? Is that a high speed or a low speed? Akansha? Low speed, 3 meters per second. 3 meters per second, so if this is 3 meters per second then what is F? F is 2 x 3/3 x 10 to the power 8 nu, what does this factor come out to be? This comes out to be 2 x 10 to the power -8, is that right? So see what we are doing essentially is that we are scaling down the frequency to a range that we can see on in oscilloscope that is what we are doing, okay.

So remember what was the frequency that we talked about in the previous class? 10 to the power 13 or something, isn't it? 10 to the power 13 multiplied by 10 to the power -8, how much is that? How difficult is it to separate 8 from 13? The answer cannot be a smile, the answer has to be a number, what is 13 – 8? 5, right? So 10 to the power 5 means what? 10 to the power 6 is megahertz right? 10 to the power 5 means less than megahertz, megahertz we can handle, it's not difficult to measure megahertz or kilohertz using regular oscilloscopes, and you understand that if I move the mirror even slower, then what will happen? Then the scaling factor will become even smaller, instead of moving 3 meters per second, if I move 3 centimeters per second, again I will scale down by 10 to the power 3, 10 to the power 2, right, so that way you see you can scale down any signal, no matter how fast it is, to something that you can measure. This is the fundamental principal of measuring signals that are very, very fast.

See now our lab for example we try to determine life times that are down to 10 to seconds, 10 to the power -15 seconds, impossible, cannot do it in real time so use more or less a same technique by changing the time delay between 2 pulses of light in order to get that kind of time resolution, if you cannot do it by electronics you have to use something that is faster, and the fastest thing that you have at your disposal is light so that is how you can scale down the frequency to a measurable limit and this is how you can generate a signal that tells you what the wavelength it is that you are measuring.

How do I get resolution? We've not discussed it yet, now tell me when we talk about frequency domain spectroscopy we said that resolution is determined by how many lines they are on the rating? How small the state width is and so on and so forth. In this kind of a measurement what is it that will give me resolution? What do you think? What you people think? Let see if you can get this. What do you think, look at the experimental setup, think what we are doing and from that try to tell me what is it that gives us resolution here?

Sorry, proximity of the beam splitter to the source, do you think that will give you resolution? So well, actually there is a valid point but that does not give you resolution, that gives you accuracy, what you're saying is if the, see there is nothing in this world is perfect, right, so you'll make a nice curve mirror, fine, and you think that it gives you a collimated beam, if you go say from the earth to the moon then that beam will, you'll see it's not collimated really, it is a little diverging, usually little diverge or converging, so what you're saying if it is closed, is that what you are trying to say one then? If you go close then you assure that it is parallel, well that gives you accuracy not resolution. If you make it parabolic it can increase once again light gathering power but that will not give you resolution, she is asking about spectral resolution, yes, well of course we've not gone there yet but what you do is, this is time domain spectrum, from there you go to frequency domain by Fourier transform.

In this, how do I ensure that this spectrum has enough resolution so that I can see all the lines? Okay, what is the meaning of resolution here that means it should be more points on this spectrum, maybe that's the hint, speed of the mirror what will it determine? Actually you measure slower, let's say take a same travel of the mirror, generally in commercial instruments you cannot change the travel, in fact all this comes as a black box, right, so length is same, now if you cover say 5 centimeter distance in one step, that is one situation and you cover 5 centimeter in 50 steps which one should be better? 50 steps should be better because see resolution here would actually depend on resolution here, how many points, so I have drawn it as a continuous curve, it's not a continuous curve right, actually what you are doing is you are changing delta and you are building this curve point by point, isn't it? Is that right? So more the number of points on this curve, better it is, so one thing you can change is you can have a bigger travel that will give you better resolution, the other you can think you can do is you can travel at small steps that will also give you better resolution, well, bigger travel is little easier to do.

No, I just make the path bigger that is very easy. So these are basically tubes right, so I have a long tube, actually bigger tube, bigger tube, bigger travel is what gives you better resolution, okay. If I just increase the distance with same velocity I'll have more points, so essentially you don't want to stop, see if this curve you stop at lambda that is one option or you can go all the way up to say 10 lambda or 20 lambda, if you go all the way up to 10 lambda, 20 lambda it is better or more 200 lambda, okay. So travel delta, total delta that is what determines resolution.

Okay, right, so this is the situation if you have a monochromatic light. What happens when you have polychromatic light? Remember we discussed in the previous class, what happens when you have polychromatic light, you get these interferograms, remember our old friend the interferogram, so if it is polychromatic light then actually the signal looks like that, okay. Does it still work? Does it still work? Yes, it does, because in this case here also you generate an interferogram that looks somewhat like that and they're related by what is called Fourier transformation.

Prof. Sridhar Iyer

NPTEL Principal Investigator
&
Head CDEEP, IIT Bombay

Tushar R. Deshpande
Sr. Project Technical Assistant

Amin B. Shaikh
Sr. Project Technical Assistant

Vijay A. Kedare
Project Technical Assistant

Ravi. D Paswan
Project Attendant

Teaching Assistants

Souradip Das Gupta

Hemen Gogoi

Bharati Sakpal
Project Manager

Bharati Sarang
Project Research Associate

Nisha Thakur
Sr. Project Technical Assistant

Vinayak Raut
Project Assistant