One and Two Dimensional NMR Spectroscopy for Chemists
Prof. N. Suryaprakash
NMR Research Centre
Indian Institute of Science – Bengaluru

Lecture - 9
FID and Fourier Transformation

Welcome back all of you, In the last class, we discussed about the phases of the RF pulses and what happened to the magnetization by applying 90 degree pulse along X axis, Y axis and how we detect the magnetization, how we can take the magnetization, we can make it completely precess about a particular axis like XZ plane or YZ plane like that. You can make it to precess in a particular plane, completely by 360 degree. And then when we applied the 90 degree pulse, we also discussed.

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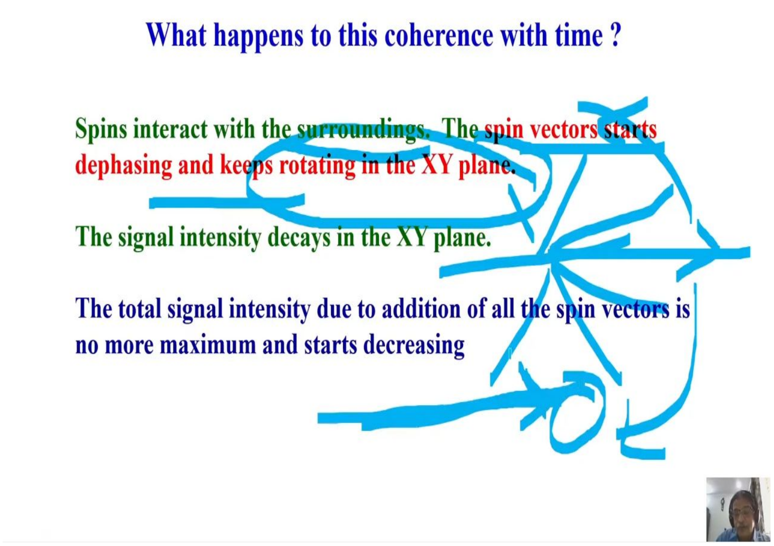

I said, initially there is a statistical coherence, temporary statistical coherence of all the magnetic moment vectors, which get aligned along the detection axis, in which you are detecting, where you are kept your receiver. Now, what happened to this coherence with time, that is what we started discussing. That is where we ended the last class. The spins interact with the surroundings, the spin vectors start dephasing and keep rotating in the XY plane.

What happens as soon as you bring all the spin pockets, along Z axis to X axis like this, initially there will be like this. Then one will start like this, one will start like this, they will start moving like this. Slowly, they start moving like this. These spin starts moving like this. Faster moving and slow moving components get call. When, all these spins are aligned around this axis where you have kept your receiver initially.

Immediately after applying the pulse, the signal intensity is maximum. But what happens as you go with time that we will see, Initially where all the signals, all the magnetic moment vectors are here, it is a vector co addition. So there is a maximum intensity.

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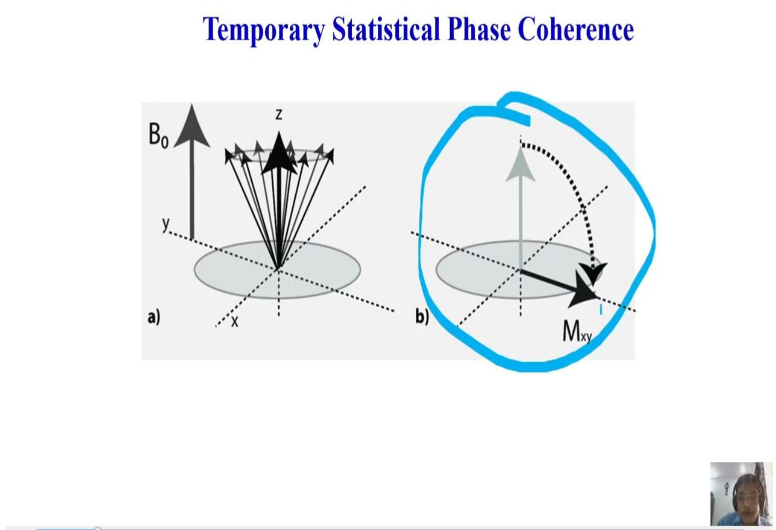

That is fine. Now this temporary statistical coherence is created like this, by temporary coherence, all these vectors are here, but they are independent magnetic moment vectors, but you have created the coherence by 90 degree pulse.

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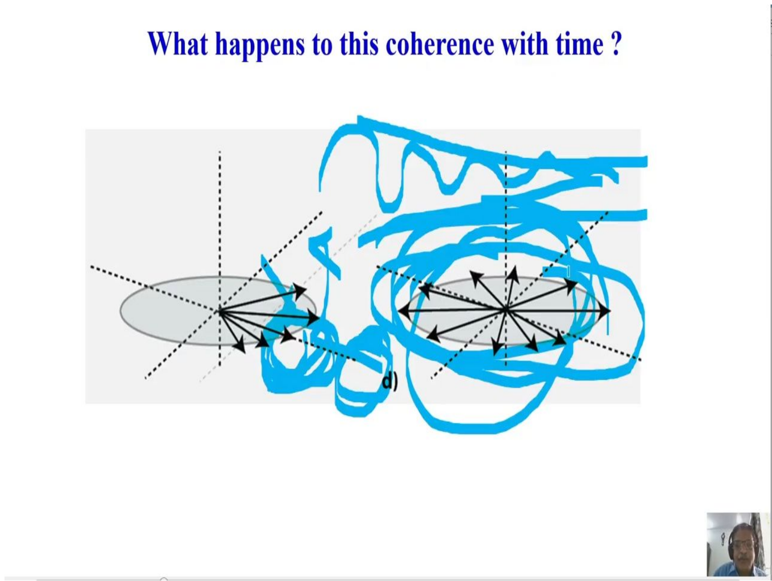

So what will happen? With time they will start decaying like this. That is what I said. So initially, they will move like this, some of them will move like this. And slowly after some time, there is a complete decoherence. Now, if I have my detector here, receiver is here, the magnetization is not full now, because different components are there, then you have to resolve a component along the X axis and Y axis and you will get only magnetization, pertaining to this component along this axis.

So the sum of vector addition of the components is not maximum. It has to come down. So it is intensity will decay. But it undergoes dephasing continuously like this. Afterwards, it is completely dephased. That does not end there, this process keeps on going, the dephasing, the spin starts moving like this. They move like this, and then come back and go like this. These spin move like this and go back and move like this.

This dephasing continuously we will be going on. It is an oscillatory function; understand dephasing is an oscillatory function, at the same time that intensity, the signal intensity, because of the vector addition will become less, less and less. So, the intensity is maximum and then starts decaying like this in an oscillatory fashion. This is what we discussed the wave pattern, we discussed earlier, which you can represent in a circular manner.

Exactly like this, it is an oscillatory function and also getting damped with time, it is a decaying function. This follows exponential again and the time which requires for these spins to completely undergo dephasing is called T2, it is a type of relaxation. The spins are relaxing in the XY plane. The complete decoherence means it is relaxing, thetime required for this is called relaxation time, this is also called transverse relaxation time or in other words, also called spin-spin relaxation.

Why it is happening? Why they are decaying? Why undergo decoherence? Because the spins are interacting with the surroundings. As a consequence, we lose phase coherence that is what is happening. So, this time required for this to interact and to lose complete coherence is T2 that is in the order of few milliseconds to seconds.

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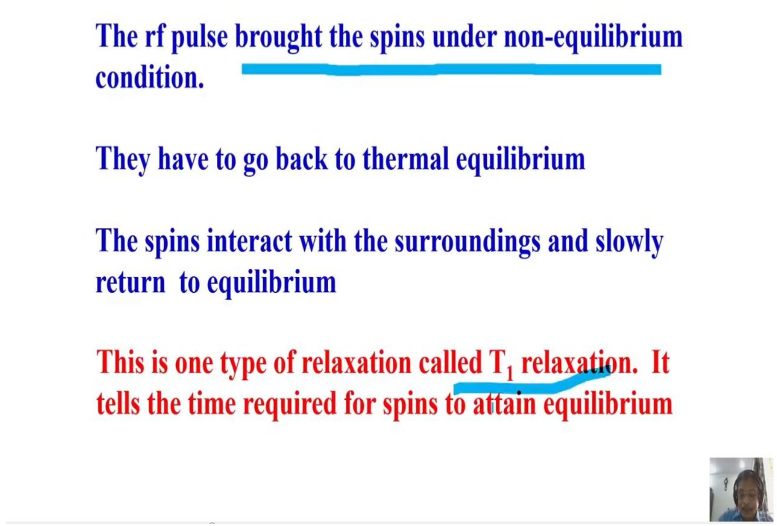

Now what is happening? The spins are undergoing decoherence, but where are they? If it has to go back, signal is still there, but ensemble average , we can take the average of the vector addition completely, we discussed random phase approximation, vector addition is 0, but the magnetization is still there, but it cannot stay there, it has to go back. Its original position was Z axis, it was along Z axis, by applying the pulse we brought it to X axis.

That means we perturbed the system, system is in a non-equilibrium state, the spins which were in equilibrium, we created a non equilibrium condition, they want to still go back and attain equilibrium. Again, this is another type of relaxation, that spins which were disturbed slowly relax and go back to the Z axis. What is the process involved? Again it is the interaction with the surroundings, The interaction with the surroundings for that process of decoherence and for this are different.

Understand, so the time required for this to slowly come back and completely reach the thermal magnetization which was there before the application RF pulse , along Z axis, is called T1, T1 is the relaxation time, also it is called the growth along Z axis, it is also called longitudinal relaxation. Z axis growth, longitudinal relaxation. it is called growth along Z axis, longitudinal relaxation or in other words, this is energy exchange interaction. It gives energy to the surroundings, giving its energy. And what are the surroundings; it is a lattice, that is why it is also called spin lattice relaxation. So slowly spins return to thermal equilibrium.

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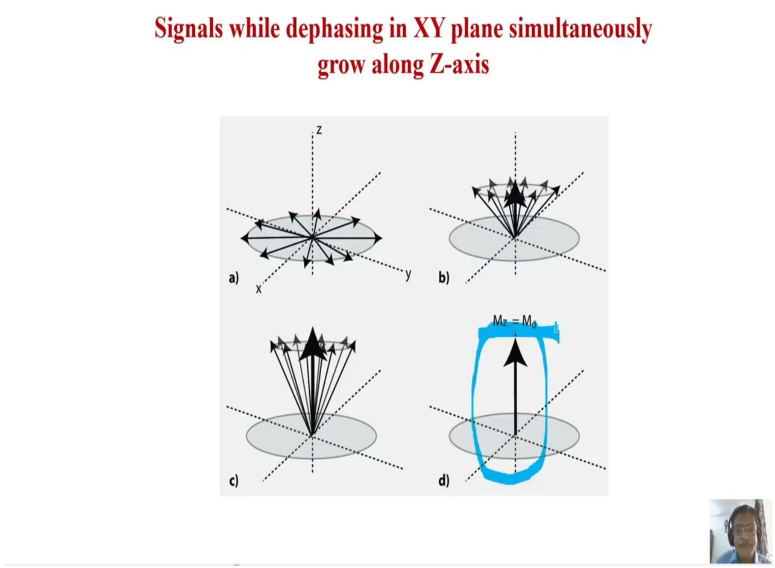

And after time constant T1 and come like this. First we brought and they started undergoing decoherence. Here T2 was there and simultaneously. Let us see the vector components here. Take the addition of these along Z axis. The total sum of the vectors addition, all of them if you add up, this magnetization is this much, but now you see whereas lot more components are present here. We keep adding the intensities going up, now vector addition is more.

Magnitude of this vector addition is much more than this one, see this arrow which is much smaller, I will clear it you can see, this arrow; black arrow thicker one, This intensity of magnetization was much smaller, now it is much bigger. And after some time, what happens, slowly, we reach thermal magnetization, MZ which is going to be M0, which was what it was before the application of RF pulse, this is the magnetization that was before the application of RF pulse.

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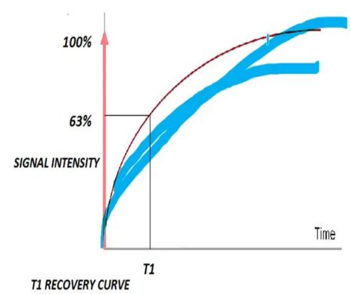
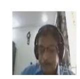
After sufficiently long time, the entire magnetization would be along Z-axis (exactly equal to before the application of rf pulse)





So, this is what happens and the growth again follows an exponential. Similarly, when we saw the decoherence, the decay was exponential, similarly, growth is also exponential, very interesting thing.

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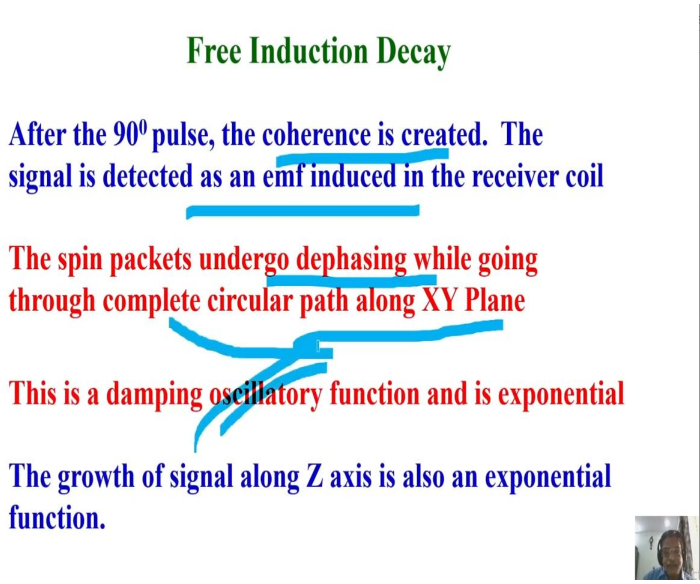

So, now, both these phenomena happen simultaneously, they are not exclusive processes. In reality, when you want to detect the signal, this is what we are doing, we start collecting the signal after the application of 90 degree pulse, create the coherence, coherence starts undergoing dephasing, and decoherence takes place and signal decay along the XY, at the same time inducing emf in the detector, in the receiver, and also undergoing damped oscillation, an exponential decay is there.

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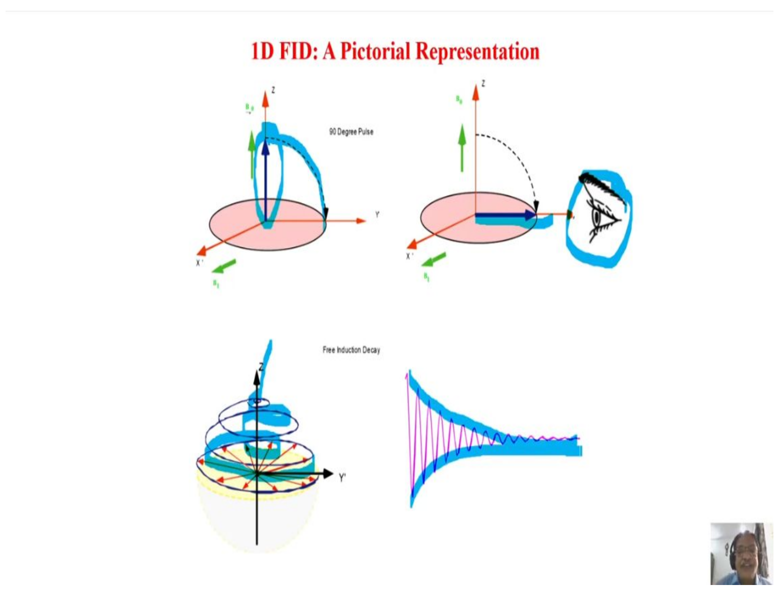

That is what is we are going to collect. That is called free induction decay. Remember I gave an explanation for what is free induction decay earlier. This is exactly what it is. I just gave a expansion for what is free induction decay, the word, what is F, I and D, but this is what is really happening. Pictorially all these concepts what I explained was for you, T1 and T2 is like this, thermal equilibrium magnetization is along Z axis.

Apply a 90 degree pulse bring the magnetization here, temporarily there is statistical phase coherence, and this is my receiver and slowly phase decoherence takes place. At the same time, they start growing along Z axis like this. The magnetization start growing along Z axis, while decaying simultaneously in the transverse plane. It grows along Z axis, decays in the XY plane, and the decay follows an exponential like this and oscillatory decaying function. This is the free induction decay we detect. You understand? This is what you do in your NMR experiment always.

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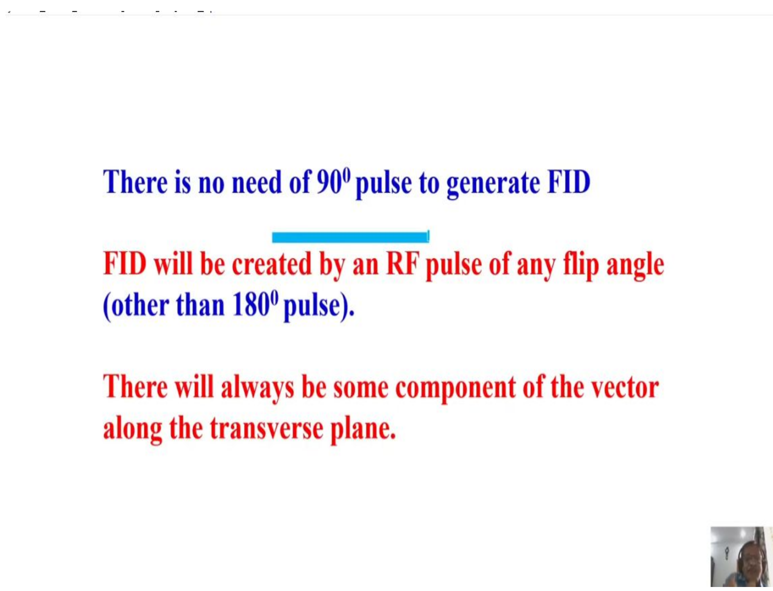

Now, the question is, you may ask me, we applied 90 degree pulse and brought the magnetization here to Z axis, should I have to always apply 90? what happens? If I apply 180 look at, if I apply a magnetization here, 180 degree pulse, I discussed about the pulses and phases earlier you know, I bring the Z axis magnetization to minus Z, but while my detector is still here.

When the magnetization was along Z axis in the equilibrium, I did not see any signal, same way when it comes to minus Z axis you will not see any signal here, 180 pulse make the signal 0, we will not see any signal. I will increase further, I will take it here, you will see the signal, but in the opposite direction. See this is the way, you can collect the free induction decay. That is what I am going to explain now, about the phases of the signal.

I told you about the phases the RF pulses. Now we will discuss about the phases of the signal. So it does not mean necessarily you have to apply 90 degree pulse, I can apply 45 degree pulse here. Then what happens? if I apply a 45 degree pulse here, I have to resolve this components into and cosine and sine components, and you are going to get detect this signal. see here, I will erase it, I have a magnetization here.

Now, I take the projection along this axis and this is a component you detect. The intensity comes down if you use less, instead of 90 degree pulse. If you use less than that, 45 degree, what you detect? Magnetization Quantity is now less, intensity is less, you get less signal intensity. Maximum signal intensity is only at 90 degree. You see what happens if I apply 5 degree pulse or 10 degree here, how can this be 10 degree? Now, I take the component along this axis, see this is very small angle , very small magnitude compared to this.

So, lesser the pulse angle what you apply, you will get less signal. 90 degree pulses is the one which gives you maximum signal. Please remember that. So 45 degree also you can apply, no problem, but only thing is you have to take projection of that along the axis in which you are detecting the signal. That is the amount of magnetization we detect, that is all.

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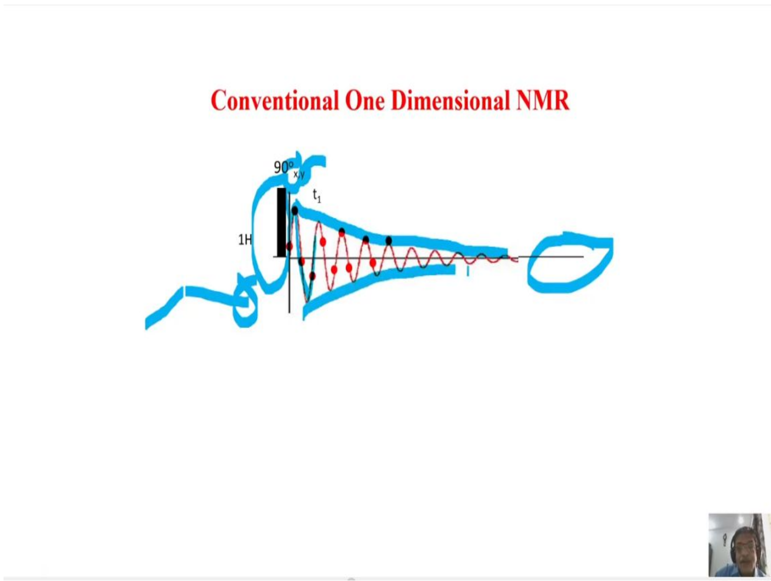

So, in conventional one dimensional NMR this is what we do. And exactly what we do is this. Apply a 90 degree pulse and then put your receiver here, in the X axis, bring from 90 degree X axis or Y axis does not matter, if you have apply along the X axis, you will bring along Y axis, whatever. So, you know how to understand this from right hand thumb rule. Then I start collecting the signal in the other axis. I am applying along X axis, and I will shift along Y axis, start collecting the signal.

And I digitize and collect like this. It is an exponential decay and oscillating. What we will do is, this has the all the frequencies present. I am showing you only one frequency here. But in reality it is not one frequency, which I explain to you when you understand Fourier transformation theorems. There are a number of such FIDs. So, many frequencies are present, each of them will be oscillates at its own frequency.

The oscillation frequencies are different. So, let us say I have 50 peaks in the spectrum, that 50 FIDs like this, they are all superimposed then it looks like an interferogram. Here it is easy. If there is only one frequency, what I will do is, I will measure this and this, I know this is lambda, I can get the frequency, easy. But I have 50 peaks, I will give you, you will get an interferogram, thaen how do I know what are the frequencies present in that.

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It is not possible to identify like that. You cannot distinguish all the frequencies. But, of course, what I want to tell you is the signal we are going to detect in NMR. After all those things, we make some manipulations in the electronics and the signal we are going to detect will be in the audio frequency range. Even though all the operation frequencies everything is in megahertz, the final detected signal, by using electronics we do something, and remove the megahertz component. We detect only frequency in the audio frequency range.

Now, let us say there are 50 frequencies and 50 sounds, different sounds are made, it is because it is audio frequency my ears cannot distinguish all the frequencies, I do not know. If one person talks to me in one frequency, I know what it is. If there are 50 people talking simultaneously at a time with different frequencies, I do not know what it is.

So, how do I understand? this is a mathematical problem? This signal which is collected in the time domain, if I want to know what are the frequencies present in that, we will do a mathematical operation called Fourier transformation, which was given by pioneer in that area Jean Baptiste Joseph Fourier, who gave this idea called Fourier transform. It is a mathematical tool, to do this mathematical operation on this time domain signal, and convert it to a frequency domain signal like this.

Now, when I do Fourier transformation, it tells me what are the frequencies present. How many peaks are there? I know. That is what we have to do. Basically, this is what you do. Basically, what you do is you collect a signal like this, all these things you will not know the technician will do for you. Put this sample, he will give some commands and collect the signal, he will type a command to do the Fourier transformation, computer does the job and you see the output like this, frequencies.

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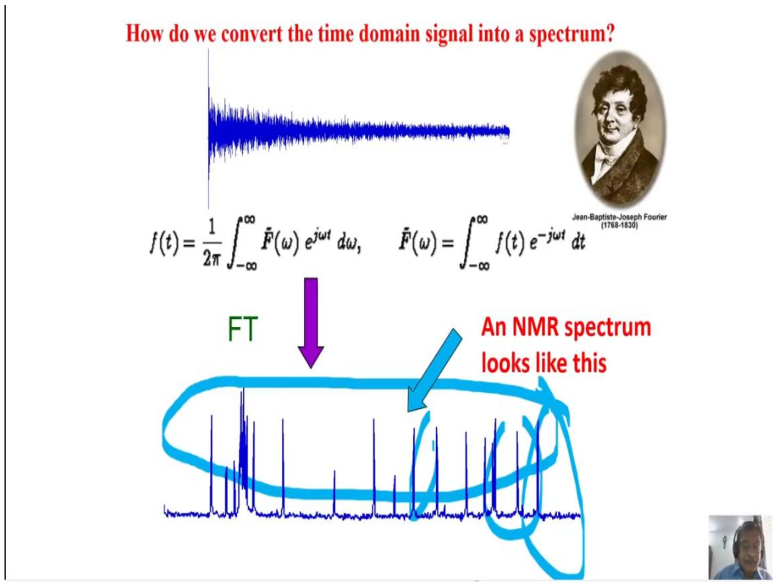

And this is literally what we are going to see. When we do the Fourier transformation, this is an equation for Fourier transformation, it is an integral function. If there is a time domain signal. This is the time domain signal, I can convert to frequency domain. I can do the inverse also, I can get the time domain signal, if I have a frequency domain signal. So, this time and frequencies are called Fourier pairs.

If I know time domain signal like this, like this, what I can do is, I can do the Fourier transformation and then get the frequency domain spectrum take this. Take the time domain component to frequency domain components like this. Convert time domain to frequency domain, they are Fourier pairs. Suppose we are not satisfied with this, I do reverse Fourier transformation, inverse Fourier transform, then I get this time domain signal.

So, these type of operations can be done either way. This is a reversible operation, can be done, I can collect the signal in frequency domain, take in to the time domain, do this one, or if I do not want I can take it back to time domain. So, these both inverse operations are possible, they are Fourier pairs. This is all what you do in your NMR spectrum in the day to day life, the routine NMR spectrum. This is what you are going to get understand. Do send the pulses, collect the signal and do some mathematical operation. Finally, what you are interested to see are the peaks, how many peaks are there? Then you starting interpreting, depending on the frequencies present, what is this peak, what is this peak? to get the information about your molecule. That is what we are going to do.

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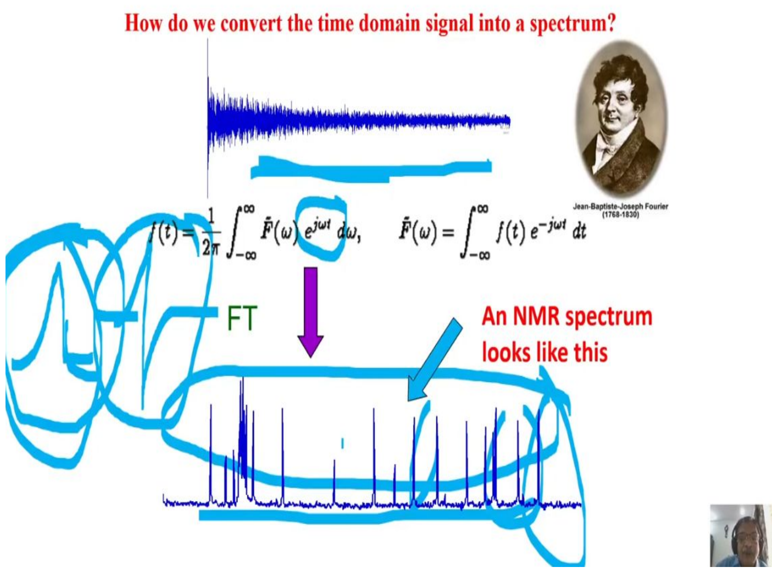

Now, after introducing Fourier transformation, I will tell you something about signal phase. Remember all those things, I hope you understood I know. I applied a 90 degree pulse, brought the signal along the X axis this is called MX component, the magnetization along X axis, my detector, my receiver is here. Now what is the type of signal I am going to get? But I wanted to tell you one important thing I forgot.

When you do the Fourier transformation, the Fourier transform gives you a real and imaginary peaks, it is like that you get cosine and sine components, both will be there. When you have exponential here, I can resolve them into cosine and sine component right. So, cosine component is called a real component, sine is imaginary. When you do the Fourier transformation and the phase correction etc, you get a peak like this, this is called absorptive type peak or you can get peak like this, this is called dispersive type peak. This is because of the imaginary part, this is because of the real part of the signal, when you do the Fourier transformation, this is what we always see here. But this is also present, imaginary component is also there. This is a dispersive signal, but we do not worry because we can get everything from here.

We want only absorptive part, and the difference is this and this is out of phase by 90 degree. Real and imaginary parts are out of phases by 90 degree, it is like cosine and sine, they are out of phase by 90 degree exactly. This is what I wanted to tell you, please remember. After the Fourier transformation of the time domain signal, we are collecting the signal like this. This is the real part, it is an absorptive type signal. In the imaginary part, the dispersive type signal is present, we are not collecting that.

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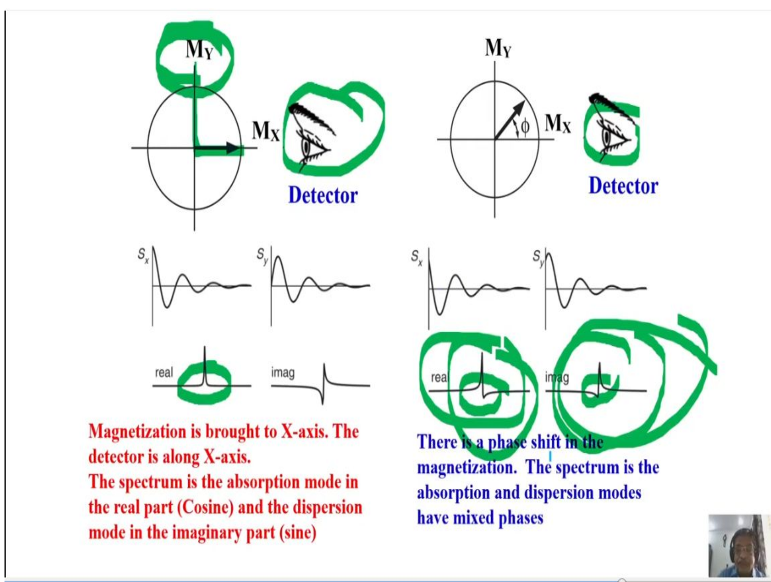

So with that we will go back to the idea of what is signal phase? I told you now the signal is brought to the X axis and we collect the signal, start receiving the signal. There is a maximum signal here now, real part is like this, cosine starts with a maximum amplitude because cos 0 is 1 and then goes like this, maximum amplitude. This is a cosine part and you see the real part is an absorptive type signal now, it is exactly on the X axis.

And the imaginary part should be exactly here. So you get imaginary part, which is a sine part. Starts with origin 0, and you get imaginary signal like this. Are you with me, I hope you are understanding what I am trying to say, this is the real part. And this is the absorptive, real part of the FID, this imaginary part, real part gives you absorptive type signal and this is dispersive type signal. So, now, let us see what happens if I asked the question should we have to apply 90 degree pulse to get FID, you can have different also what will happen then? first thing, magnitude of the signal is less, because now I resolve in to only this component and this component and detecting only this component, so signal intensity is less compared to this, fine. That is one thing, what next will happen? Look at this. Now, there is a phase difference if it is exactly here, And the imaginary is exactly at the Y axis and the phase differences is exactly 90, real and imaginary, but now, it is in between. It has a mixed phase, phase for this is mixed, it has a mixed phase. So, it is not pure real or pure imaginary, or pure absorptive and pure dispersive peak. Look at the real component, the real component is not to pure absorptive and the imaginary part is not pure dispersive. So, this is what happened?

The real part is not pure absorptive and imaginary part is not pure dispersive and there is phase error here. You look at the bottom here, there is a phase error. This is what is called a perfect signal without any phase error, here also, here to here there is a phase error, that is all what happens. when you apply pulse of any phase of angle to collect a free induction decay, one thing is signal intensity is less and secondly we get mixed phases.

So this is what you understand. Pulse phase is one thing signal phase is one thing, signal phase depends upon where is your signal, and where you are detecting, Where is your receiver, signal phase depends upon where you have positioned your receiver. suppose if I have positioned my receiver here, in this case, what will happen? Same signal, I positioned my receiver here, instead of here, then this imaginary part will be real for it and the real part will be imaginary that is all.

You understand, it depends upon where you have kept your receiver. This is why signals phase is very important, it is also called the receiver phase. These things are very, important in NMR. The more often we play with these things, signal phase, pulse phases are important in designing new sequences. Please understand these things, and as a consequence I tell you this is what it is. Now

I am sitting here and they have a mixed phase like this, there is a phase shift in the magnetization. As a consequence, real and imaginary parts, a lot of phase shifts, that is what you are going to get.

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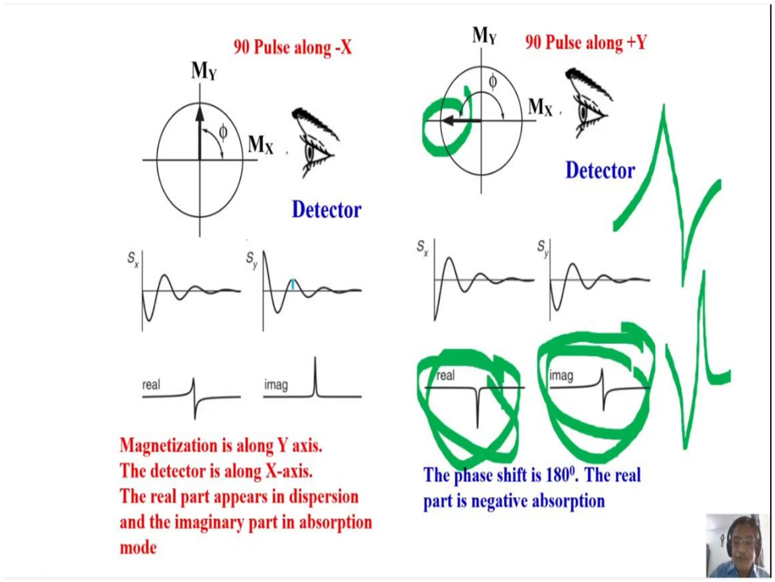

Let us take another example. What happens if the magnetization is here, exactly what I said here? In the previous example, instead of putting the receiver here, I put the receiver here. Alternately, I put the magnetization here and put the receiver here. What makes no difference? Now I am asking the same thing I am doing here. I am putting my receiver here. I am looking for the component of the magnetization along this axis, but the real magnetization is along this axis.

Because I have applied pulse in such a way I brought in magnetization to MY, Y axis. But I have not changed my receiver, receiver position is here. so what type of signal you are going to get. The real part is now out of phase by 90 degree, this is where I have to detect the real part, but it appears to be out of phase by 90 degree. what is happening, the real part appears like imaginary or dispersive peak, it appears like imaginary and the signal is dispersive. The real part of the signal is dispersive type.

What about the imaginary part? Imaginary part of the signal appears to be real and the spectrum is like absorptive. It gets interchanged, you understand, the same thing I said. If I sit here now, the same receiver I will put here, what will happen? There is no change at all, real phase is this, imaginary phase is this. they get interchanged. The real and imaginary gets interchanged depending upon where you are going put your receiver, in this case.

These are all the things you should understand, what is the signal phase or when you want to identify, find out what is the signal phase, you should know, where is the receiver and it is put in which axis. And then, which is the phase of the pulse, phase of the pulse decides, which axis you are bringing the magnetization. And where you have put the receive, which axis you have put the receiver tells you which signal you are detecting. Whether, you are detecting real signal or imaginary signal, that is, dispersive or absorptive or mixed phase.

Now, let us take the example like this. I have put the detector here, my receiver is here, my magnetization is brought to this axis, this is X, this is minus X. I have brought the magnetization to minus X axis, what happens? you are sitting here. Look at the signal, what happens, you are seeing the signal like this.

That means real part appears to be real only, but it is negative in maximum, signal intensity is negative maximum. Same there is no difference. The imaginary and real part remains same, but only thing is real part is negative maximum. When signal was here, it is positive maximum, when signal is here it is negative maximum. What about the imaginary part? Exactly same, it should be opposite, there is no difference at all, the real and imaginary remains same, but only thing signal phase is instead of positive you get negative for real and imaginary also gets phased 180 degree like that. Phase gets changed for imaginary also by 180 degree. In fact what happens if this is the type of signal you are going to get in one case, in another case we are going to get signal like this. When it is out of phase by 180 degree, for this case, this is the type of signal you are going to get. You understand. The signal phase also now we understood. How you have to design the phase of the signal that depends upon where you have put your receiver. OK, the real phase is negative absorption, negative maximum, you are going to get an imaginary phase like this. These are all the things I wanted to tell you about signal phase, I hope you are all with me and you have understood. Today we discussed a lot about free induction decay, relaxation T1 and T2. How the magnetization undergoes decoherence? How it decays in the XY plane, i.e. the transverse plane, how it grows along Z axis, I said both of them are exponential functions. One is a decay function and other is a growth function. Decay function is referring to transverse decay, decay in the transverse plane. Growth pertains to growth along longitudinal axis, i.e. along Z axis and you collect the free induction decay, which the oscillatory damping function as a function of time. You will have to do Fourier transformation to find out the frequencies. By doing Fourier transformation you know when you are collecting the signal. Accordingly the Fourier transformation has real component and imaginary component both, real part give you absorptive signal, imaginary part give you dispersive signal, and depending upon where is your receiver you have different types of phases of the signal. This is all I wanted to tell you today. Next I will discuss something about spectrum and line width.

So, I think if I start that and then I have to introduce to you something about selection rules, etc. It will take some more amount of time. So what I will do is, I will stop for the day. We will come back tomorrow. And tomorrow we will see more about the spectrum, transitions, what are the selection rules, what happens to the energy levels for homonuclear case, heteronuclear case, how do you get transitions, all those things we will discuss in the next class.