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,
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Lecture no. – 57
FT-NMR: 900 Pulse

Before we start talking about FT-NMR as such, let us remind ourselves of something that we learnt a little while ago, there is a population excess in the lower energy state, right, and the population excess is not much.

Here we have done another calculation for 9.5 tesla, 9.5 tesla is a magnetic field for 400 megahertz, okay, for that also it turns out to be 1.000064 pretty close,
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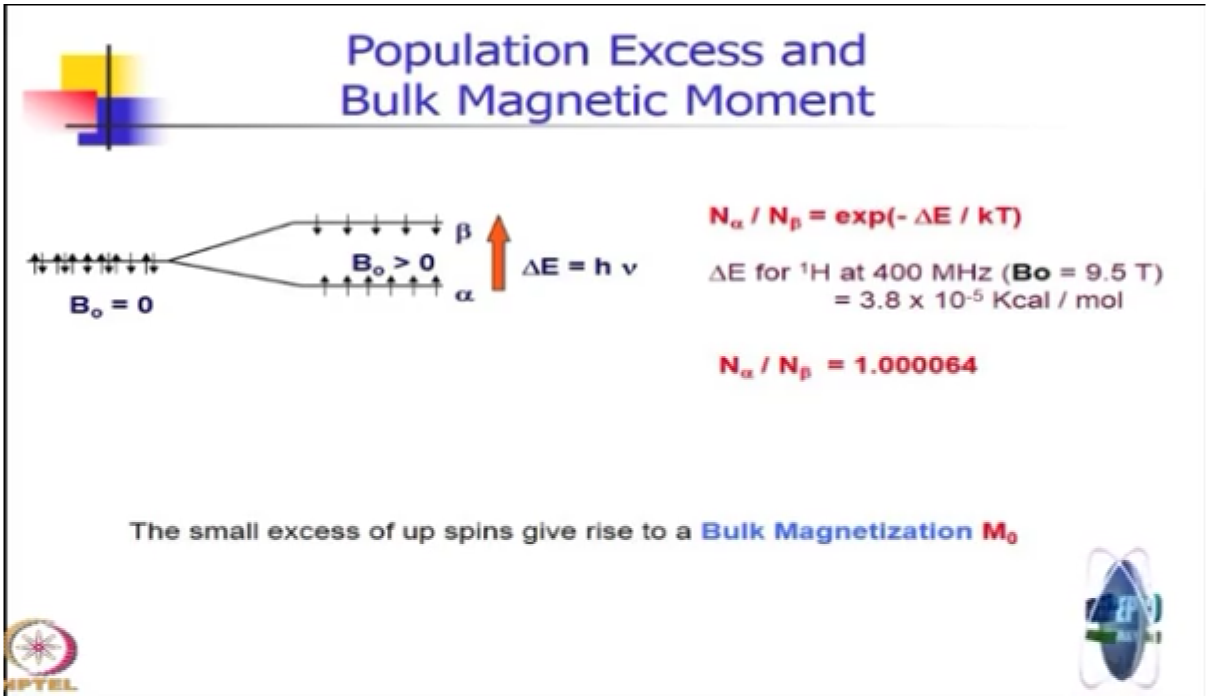

so there is a small but finite excess of alpha spins over beta spins, okay and if you remember the alpha spins are what up spin or down spin? Up spin right? Theta is well-defined, phi is not well defined, okay. So the conventional way of depicting the situation when we have many many spins is you draw many arrows pointing upward with same value of theta but different values of phi, so you draw the arrows distributed along a cone, okay, this is a depiction for alpha spin, this is the depiction of beta spin.

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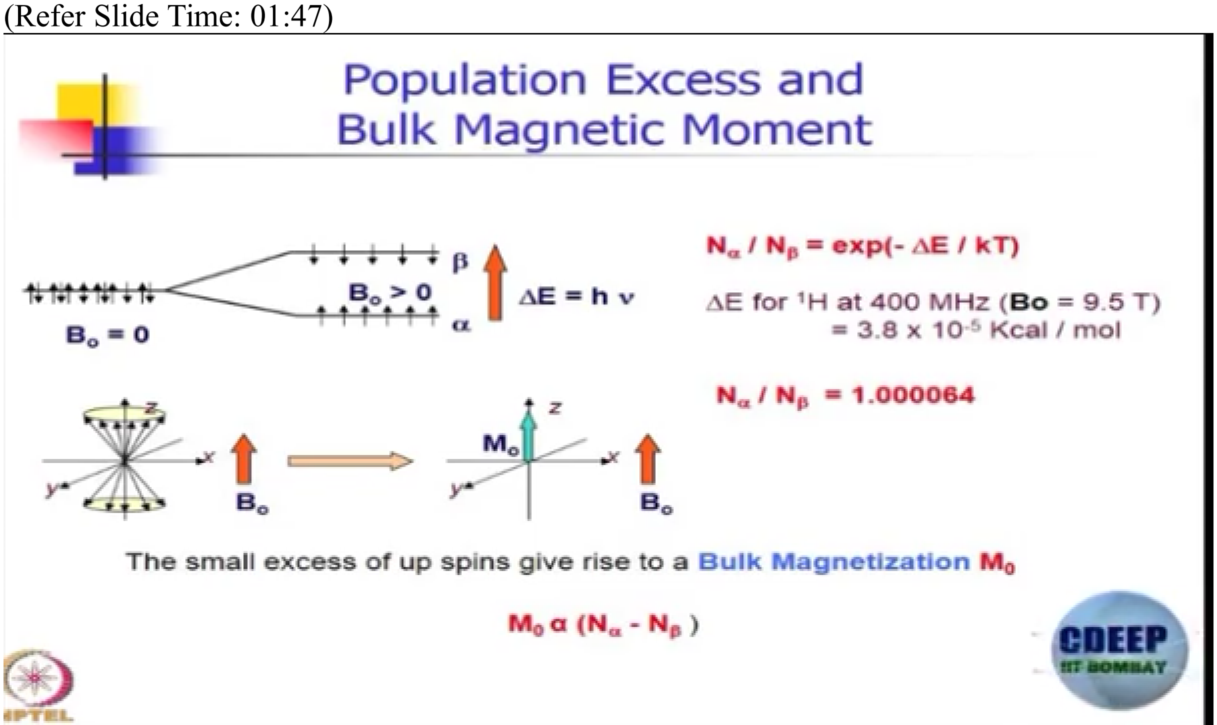

And since you have more alpha spins than beta spins you end up having what is called a net magnetic moment or bulk magnetization M0, okay. You just take the vector some and everything, these are the alpha spins, these are the beta spins, since phi is not defined they are distributed all over the cone with the same value of theta, so if you have say 1 million arrows pointing upward then you have a little less than 1 million arrows pointing downward, so the vector some points upward, okay, and that is what we designate by this thick arrow, right, this thick arrow here M0, bulk magnetization.

What is the color of this arrow? Anyway in the next slide I've change the color so it doesn't matter, so I hope you understand at least pictorially what bulk magnetization is, it is a net vector sum of all the magnetic moments that are there, accha what would happen if we had exactly the same number of nuclei alpha and beta spin, bulk magnetization should be 0, right.

Let me think of another situation,
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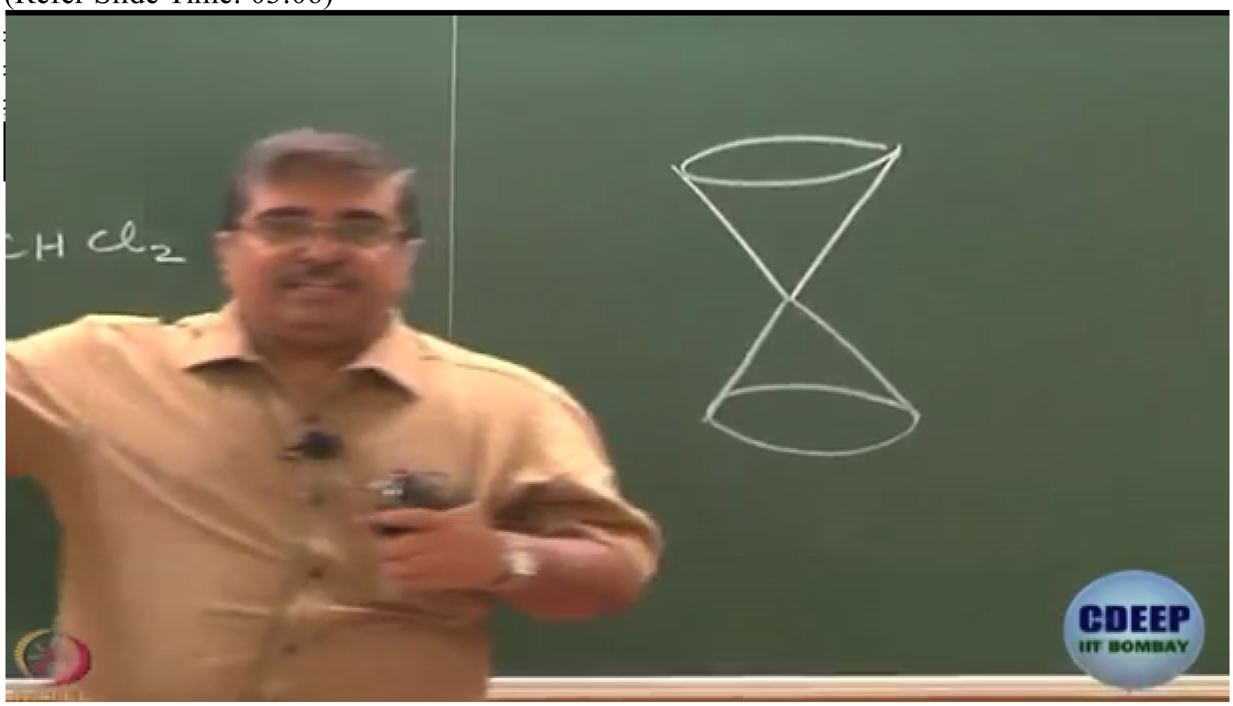

so the way we have drawn it there the vectors are uniformly distributed over the surface of the cones right, let us say by some means I have created this situation, same thing here,
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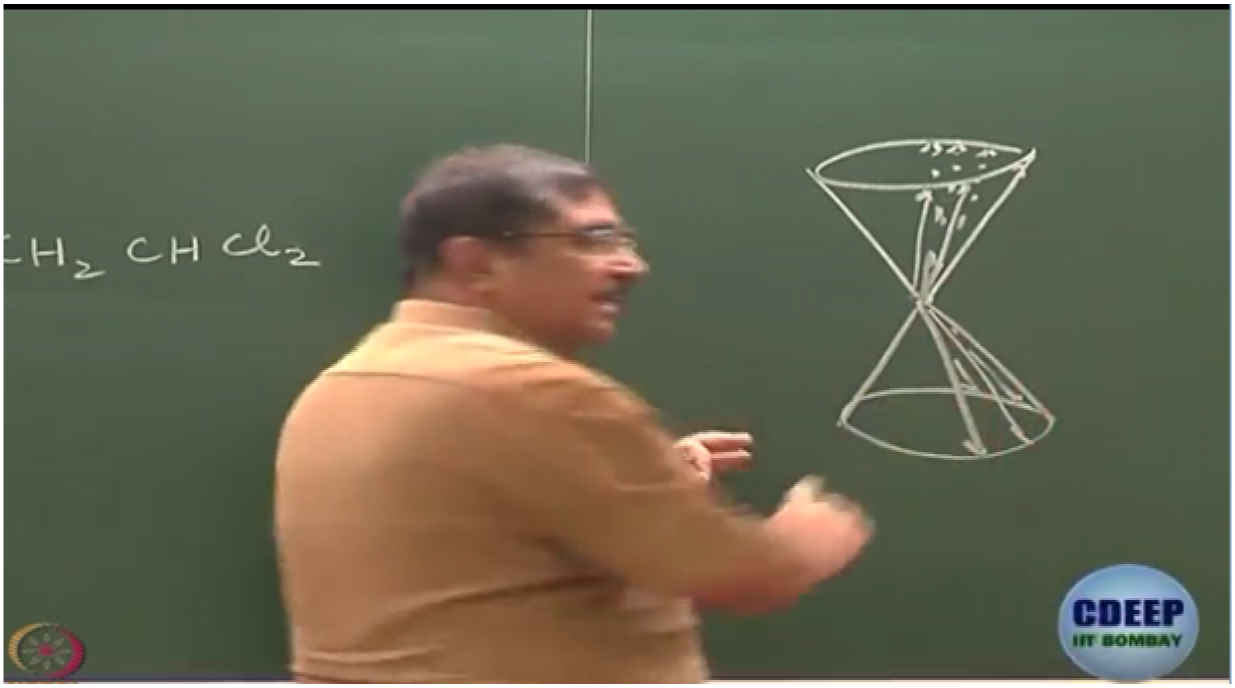

by some way my distribution is no longer uniform, but it is skewed in one direction.

Now how will the bulk magnetization be affected? What is the vector sum of all these small little arrows? So what I am saying is now if you look from the top, so this is where all the arrows are,
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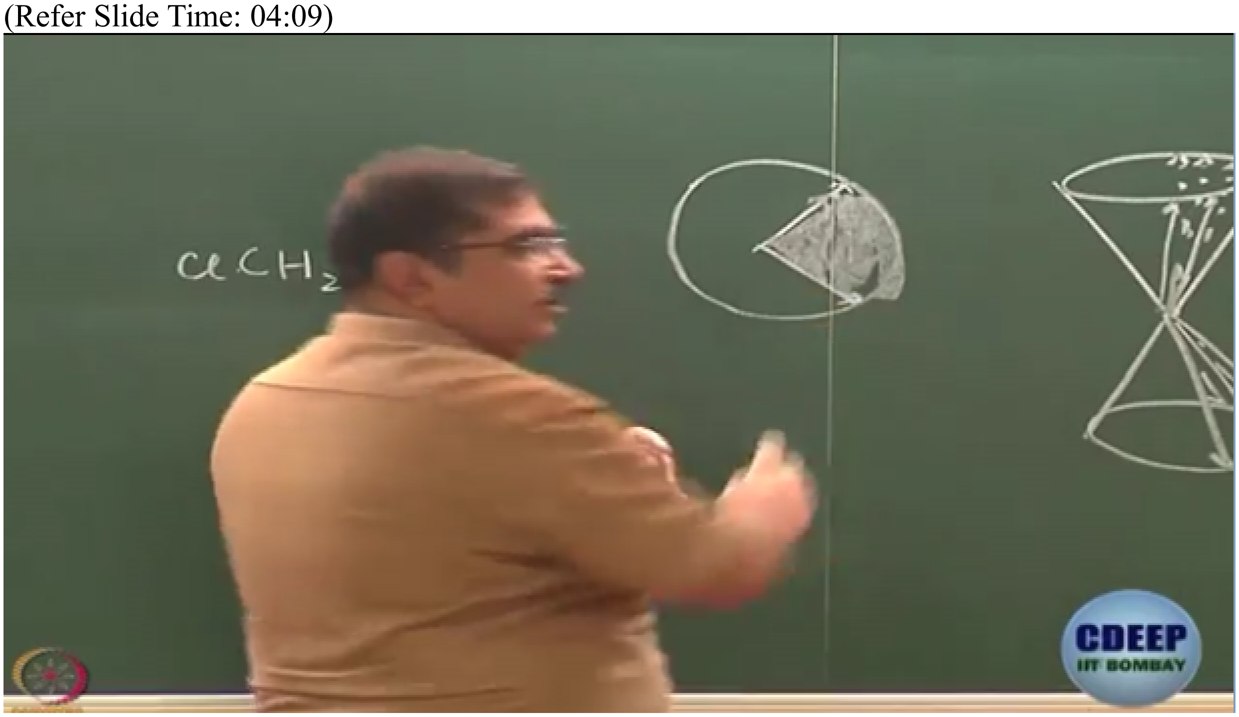

so there is some limiting range of phi, right? Arrows pointing up as well as arrows pointing down are all restricted within this what I can call delta phi.
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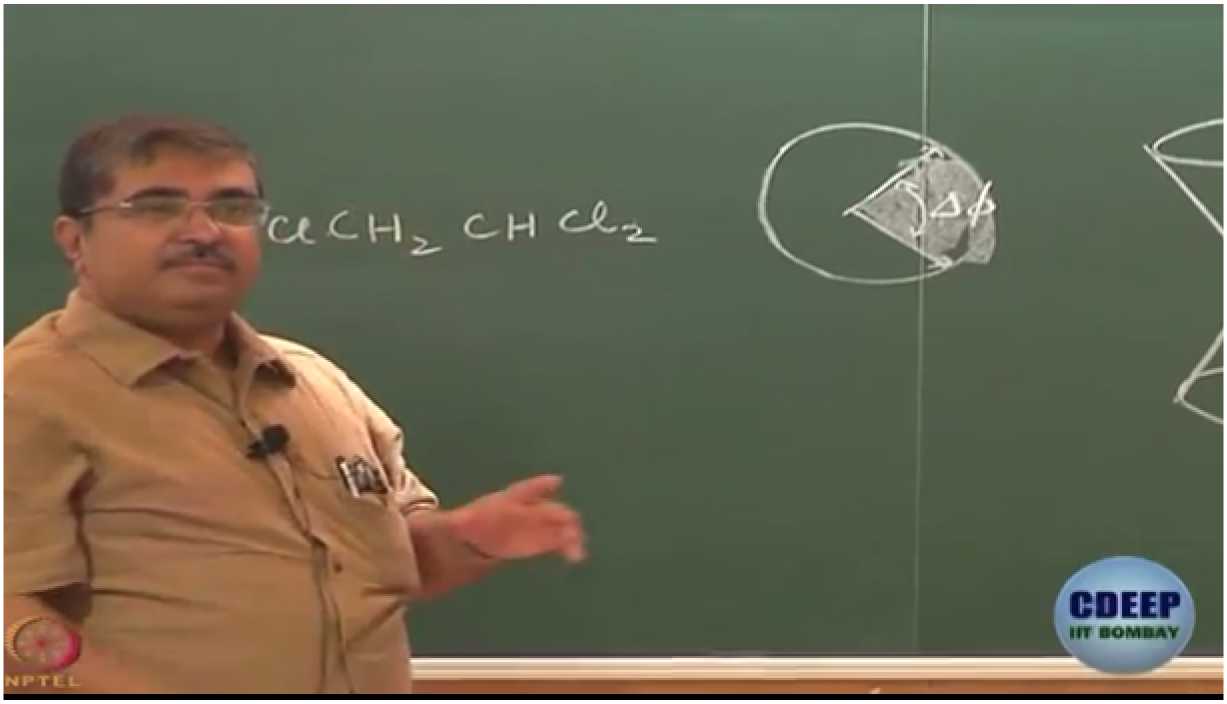

What will the vector sum be? Yes, so all are oriented this way so vector sum will also point that side, right, so the vector sum will be something like this, agreed? Agreed? So let us see why that is important? Let us see why that is important, alright.

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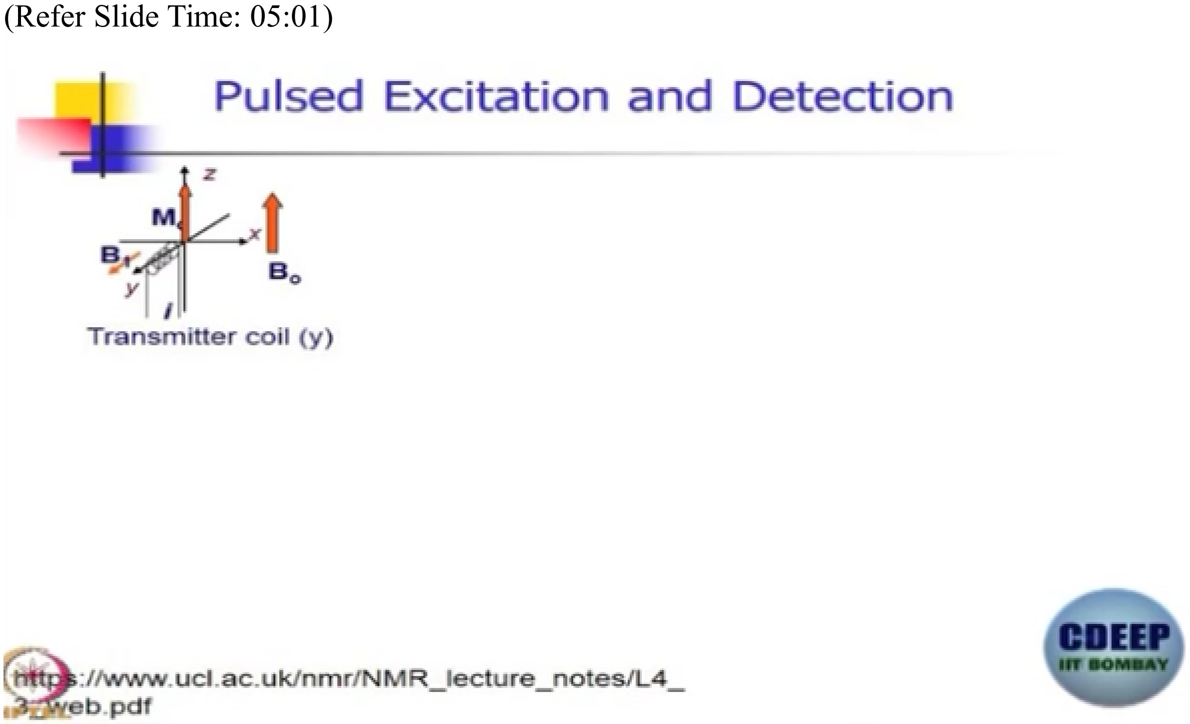

Now let us try to understand how we can perform an NMR measurement using not continuous wave radiofrequency, but rather pulse radiofrequency and remember unlike our earlier discussion in NMR we are using not the electric dipole moment, but magnetic dipole moment, so it is a magnetic component of the field that is important, okay, electric field is not as if it does not interact with magnetic field, but there is a factor that makes that interaction must must smaller compare to magnetic field, magnetic moment interacts, alright, that being said this is the situation, now it's important to understand the layout of FT-NMR instrument.

So what you have is this, let us say this magnetic field is applied in the vertical direction that is let us say we call that Z, okay, as you have told me already when I have a magnetic field along Z direction, bulk magnetization will also point along positive Z direction, agreed with that?

Now the question is what is the orientation of the radiofrequency coil? So the coil in that case placed perpendicular to the direction of the magnetic field, okay, so let us say it is placed along Y. What is the advantage of placing it in the perpendicular direction of the magnetic field? Does the magnetic field have along Z, have any component along Y? Magnetic field is applied along Z, does it have any Y component? No right, so your, well as you will see the detector will also come along ZX, so what we do is we have our magnetic field source of radiofrequency and detector in three perpendicular directions, so none of these directions have a component along the other, that makes the, that minimizes the interference of one with the other, okay.

Now what we do is we apply the radiofrequency along Y, alright. What happens when we apply radiofrequency? Don't forget this bulk magnetization is there when there is no radiofrequency but there is a magnetic field. If there is no magnetic field, will I have a bulk magnetization? No, right, because alpha and beta will have the same energy, the bulk magnetization arises out of application of the magnetic field, now that is understood bulk magnetization is already there, it is bigger, the arrow is bigger if the magnetic field is bigger, smaller if magnetic field is smaller.

Now along Y I apply the radiofrequency, so what I'm saying essentially is that this magnetic field due to the radiofrequency is along Y direction, now what will happen? Now what will happen? Think of the classical picture, don't get into quantum mechanics here, think of the classical picture, what happens when you have these magnetization vectors, right, at an angle to the field, remember what happens to the spin angular momentum? In the classical picture it précises around the access of the magnetic field, right, agreed? Now this bulk magnetization is the vector sum of all these angular momenta that are there, I've applied a magnetic so as long as only B0 is there, there is no problem, because B0 and bulk magnetization M0 are aligned with each other.

When I apply B1, B1 is the magnetic field associated with your radio frequency, then what happens? This bulk magnetization vector is perpendicular to B1, right, should it not start precessing? Right, whenever there is an angle like this it precesses, right, now the angle is 90 degrees so it should precess like this or this might be a little easier to understand, this is B1, this is bulk magnetization when we started the experiment, so it will start precessing, agreed? Sure? Can I go ahead? Yes.

Yes, hold on to that question, we'll come to that as well, for now thus actually an excellent question and that is something that has to be taken care of in NMR measurements, but the way it is taken care off is elegant, we'll come to that. For now so what she is saying is that the moment its starts rotating now it is no longer aligned with B0 as well, so it should precess this way as well, is that right? So now we have kind of normal modes of precession, okay.

But for now let us not consider that we'll come back to it a little later, let us only worry about B1, so it rotates with respect to B1, now see you know about Larmor frequency, whenever you have a frequency you have a time period, what is the relationship between frequency and time period, and what is time period? Yeah, time period yeah one cycle right, time required to complete one cycle, so when we have a frequency in fact we will do that calculation once we have discuss the entire experimental setup, so sometime is required for this bulk magnetization vector to do a full circle and comeback to its original position, as you'll see that time is some 100 femtosecond does so, sorry 100 microsecond does so.

So now if I know that time by calculation what I can do is the moment bulk magnetization turns by 90 degrees I can stop B1, right, can I do that? This is B1, perpendicular to the board pointing towards you, this here is the bulk magnetization vector, what we are seeing is when we apply B1 it's starts precessing around the axis of B1 what we have shown as Y axis here, okay, it takes some times for it to do a full circle, if you know that time then what we could do is the moment it turns by 90 degrees I could turn B1 off, okay,
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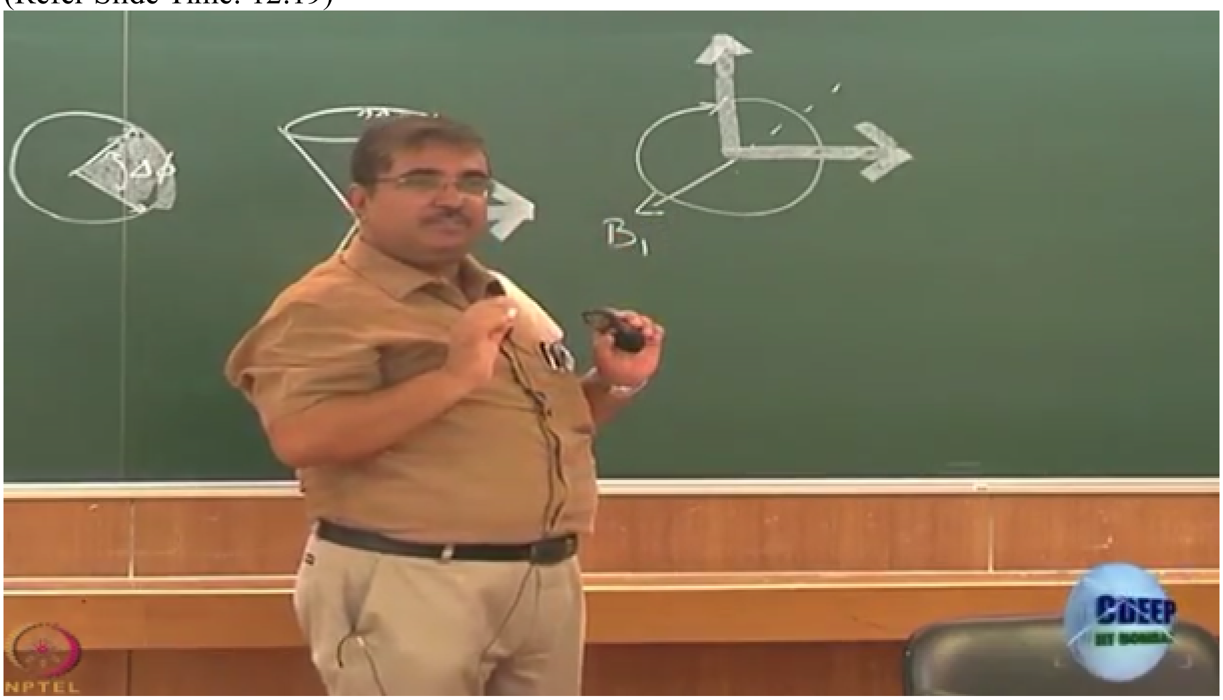

as you will see the time involved here is microsecond, and we have already studied femtosecond, we are not scared of microsecond anymore, microsecond precession is very easily achievable using regular electronics, okay. Do you agree? So I turn on B1 precession begins the moment it turns by 90 degrees bulk magnetization I turn B1 off, what have I created then? In terms of the radiofrequency I have used a pulse, is that right? I have used the pulse of radiofrequency and the duration of the pulse is what is required to turn the magnetization vector through an angle of 90 degrees with respect to B1, this is called a 90 degree pulse.

So how many of us have studied this earlier? Have we studied 90 degree pulse and all earlier? No, so something that is new and something that is not chemistry, so it's very easy it's not difficult but it might be something that we are not used to thinking about, so that's why I want to go slow, I want to make sure that all of us are on the same page, you can study this part from these, from this link but this is discussed qualitatively

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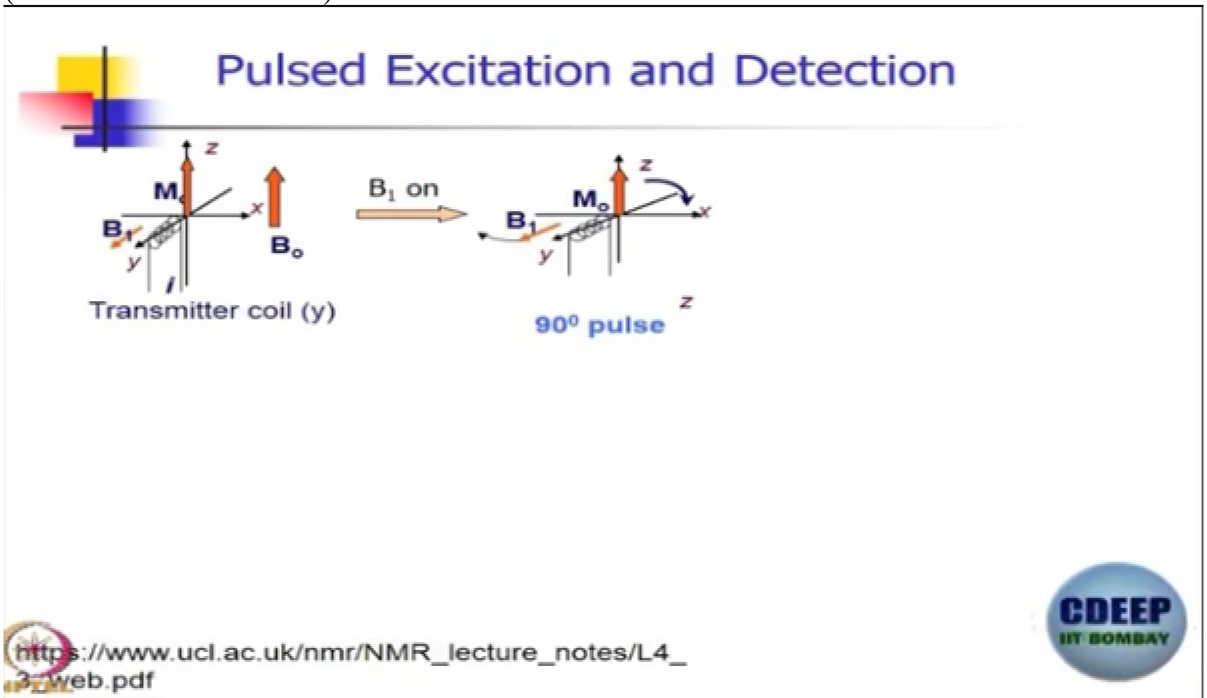

but elegantly in Atkins physical chemistry as well as Banwell book, so you should read it this evening.

Until now have we understood? Have you understood what a 90 degree pulse is? If not you have to say, so see you understood this picture I hope right, so I have a magnetic field and to start with when I have not applied radiofrequency, I have bulk magnetization in that same direction. Now in 90 degrees I apply a magnetic field another, another one, how do I apply the magnetic field? By turning on the radiofrequency, radiofrequency in electromagnetic wave so it has an oscillating electric field and oscillating magnetic field associated with it, here I am using only the magnetic field, now okay, so I apply radiofrequency in such a way that the direction of its magnetic field is perpendicular to the original position of the bulk magnetization vector which is the direction of the applied magnetic field, the big one, alright.

Now see, I have a magnetic field in this direction, and I have on the net angular momentum vector in this direction, should there not be precession? Agreed with precession? You have studied precession earlier, NMR, precession means movement like this, (unknown language) so if you turn a top how does it move? It usually doesn't move just like that, isn't it? Usually when you let go of the top it's at an angle, so this is how it moves, isn't it? It moves about it axis, but the axis itself moves like this that kind of a motion is called precession of motion, okay, so whenever you have a vector, angular momentum vector perpendicular to the applied field, then what happens is that it undergoes a precessional motion, this comes from classical mechanics, okay, so it will start rotating, and you can think that if the B1 is on then this bulk magnetization vector will go around in circles in a plane that is perpendicular to the direction of B1, have you all understood this part now? Any questions so far? Any questions so far?

So what I am saying now is that I do not keep B1 on forever, I keep B1 on only for the time that is required for this magnetization vector to turn through 90 degrees, and then I turn it off, understood? This is B1, this is bulk magnetization vector you expect it to turn around, my hand cannot go around in a full circle unfortunately, but you expect it to keep turning around right, so what I do is I keep B1 on only for the time that is required for this bulk magnetization to turn through 90 degrees, and the I turn off the field, okay, so by that what I have been able to do is I have been able to turn this bulk magnetization vector through 90 degrees, this pulse of radiofrequency is called a 90 degree pulse, understood so far? Why? Will come to that the moment, but first we must understand what's going on, Abhishek understood? Okay.

So now what is the advantage of turning this bulk magnetization vector through 90 degrees? See initially the bulk magnetization vector is along Z, and the detector is actually along X, this here is your detector,

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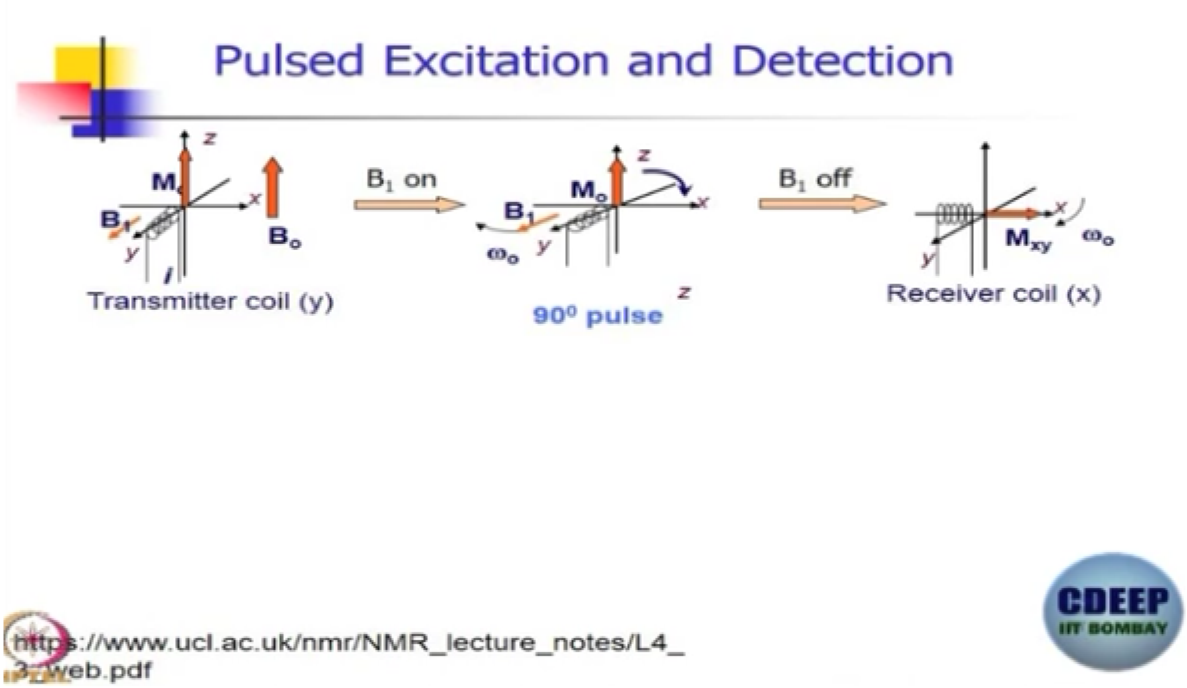

so as you understand there is no component of M0 along the detector that is along X, so initially when you have not turned on the light your detector does not get any signal, but now that you have applied the 90 degree pulse you have brought the bulk magnetization vector into the XY plane right, in fact the way I have drawn it here ignoring Shubhna's question for the moment is that I have brought it on to -X direction or maybe +X direction if I simply place the detector here instead of here, okay, so now I'll get a signal, okay, so the way I have drawn it the signal should be large negative signal X axis is time, alright, so this is our 8^{th} other wake up now things will get excited, so this is what you have done, this is your M0, you applied B1 turned it through 90 degrees and turn B1 off, okay, now what is the situation? You still have the big magnetic field, don't you? You still have B0, and you have this bulk magnetization at 90 degrees that's not a happy situation, what does this field want to do? It wants to bring it back, right, this B0 field wants to bring this M0 bulk magnetization vector back into an alignment, perfect alignment with itself, but then don't forget that there will also be precessional motion, isn't it? So one thing is it has to come back to its original position, the other thing is it tends to precess.

What will the net motion of this M0 vector be? This is one component, it has to come back to its original position, the other component is that it should go around the B0 axis, so what will be the net sum of these two kind of motion, this is one, and this is one, what is the net sum? It should spiral back, isn't it? Something like this, right, this is where it is, it stars spiraling back, okay, until it goes back to the right position.

As its spirals back what kind of a signal do you get in this detector? The way I have drawn it the initially prepared situation gives you maximum negative signal, if it turns by 180 degrees then you should get maximum positive signal, right, so if you ignore this component if you just consider the circular motion in XY that component, then what kind of a signal do you expect? An oscillatory signal, right, but then you don't have only that you also have this vector going up, as it goes up what happens to the X component? It decreases initially MX = M0.

Finally MX is 0, so in the course of this precessional, well spiral motion what happens is the X component also decreases steadily, so if you ignore that, consider only the circular motion then it is an oscillation, if you consider the fact that it's also going back to the Z direction which causes a decrease in the component of the signal, then what kind of an oscillation will it be? It will be a damped oscillation, right.

So what I am saying is this is what we expect if only circular motion in XY plane takes place,
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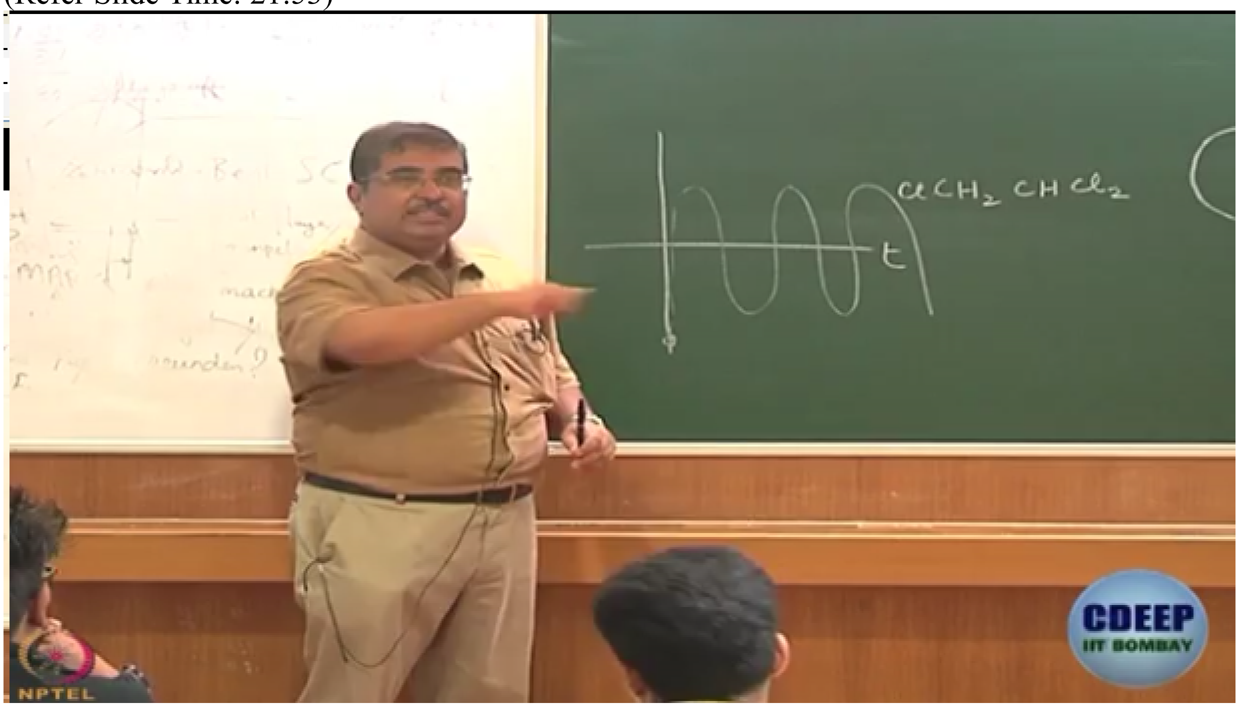

okay, and this is what you expect if you consider only the fact that the component of M0 keeps on decreasing with time, so the signal will actually look something like this, a damped oscillation. Have we understood?
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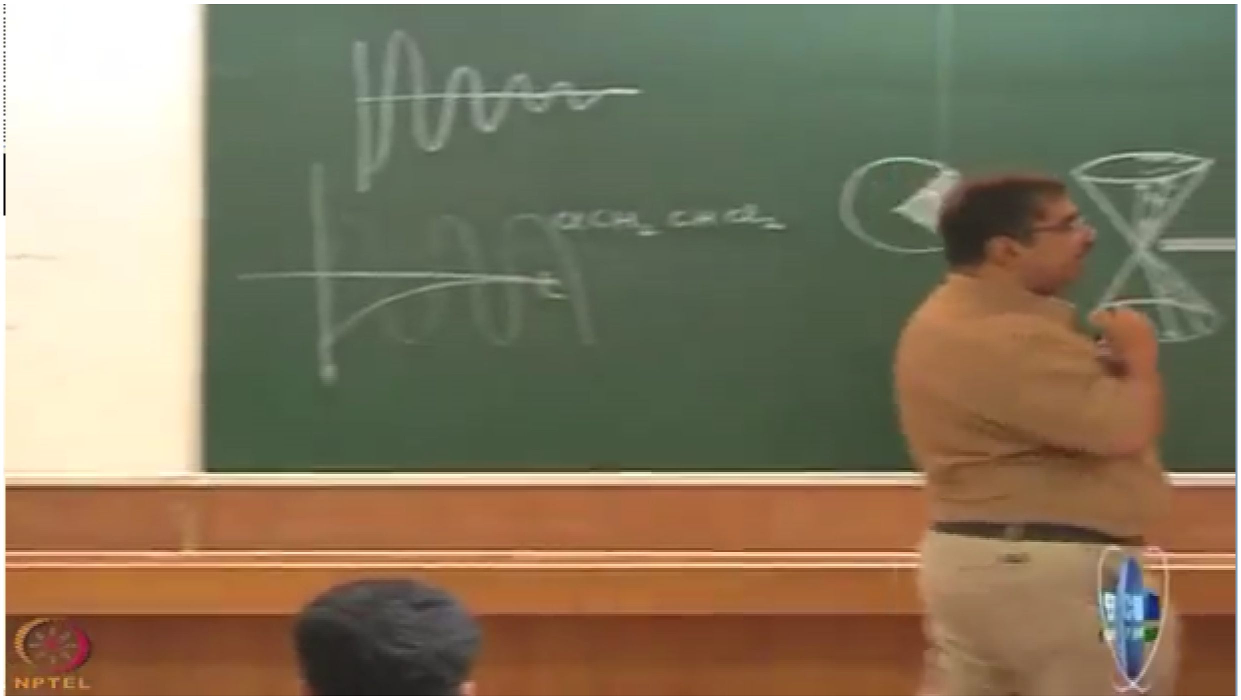

Have we understood is there a question? Sure, so this is what the NMR spectrum looks like,
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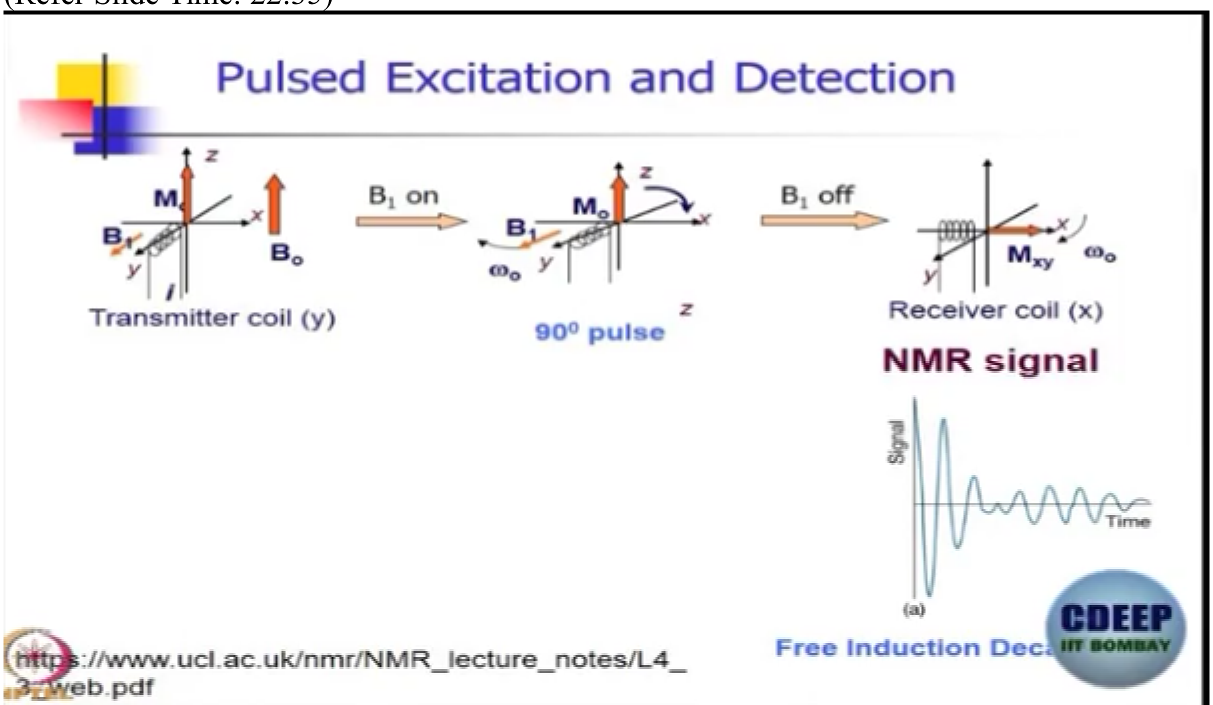

it is called free induction decay if you talk to people who work with NMR they keep talking about something called FID, perhaps some of them have forgotten even what FID means it means free induction decay, okay, this is free induction decay.

And then when you Fourier transform it what you get is, you get the NMR spectrum as we know it, this is how you perform pulse NMR measurement by applying a 90 degree pulse. Please ask questions if you have any at this stage, this is really very different from what we study in chemistry courses. Question? Okay, yeah, free induction decay, yes, so I think what you are trying to say is suppose we have more than one kind of proton then what will happen? Hold on to that I'll show you an actual free induction decay of our old friend ethanol. Yeah, then of course well otherwise what will happen is, remember your time resolved signals that we talked about earlier, what happens when we have more than one wavelength? We get a interferogram, right, so we'll get a interferogram.

We will show you the interferogram for ethanol at least, but before that question or no question so far, if not I'll raise a question now, now let us try to answer what Shubna had asked, that's a very valid question, the question is this you have B1, you have B0, initially this is your M0, right hand is magnetic, left hand is your magnetization vector, what we are saying is when you apply B1 this is how the magnetization vector turns, but that is not a complete picture, that is not a complete picture at all, the complete picture is that you have B0 as well, so one component is this, fine, because of B1, the other component should be something like this, so what we are saying is it comes down on the X axis it does not, what it should do is it should come down like this somewhere, somewhere other than X axis, is that your question? Right, that is taken care off by using what is called a rotating frame of axis, something like this.

So B1 is not in one direction, of course I cannot move the detector along that will be too much, so still you have to do some correction later on, so this is called a rotating frame of reference, so just look at the last one you see this line, the radius it is rotating right,
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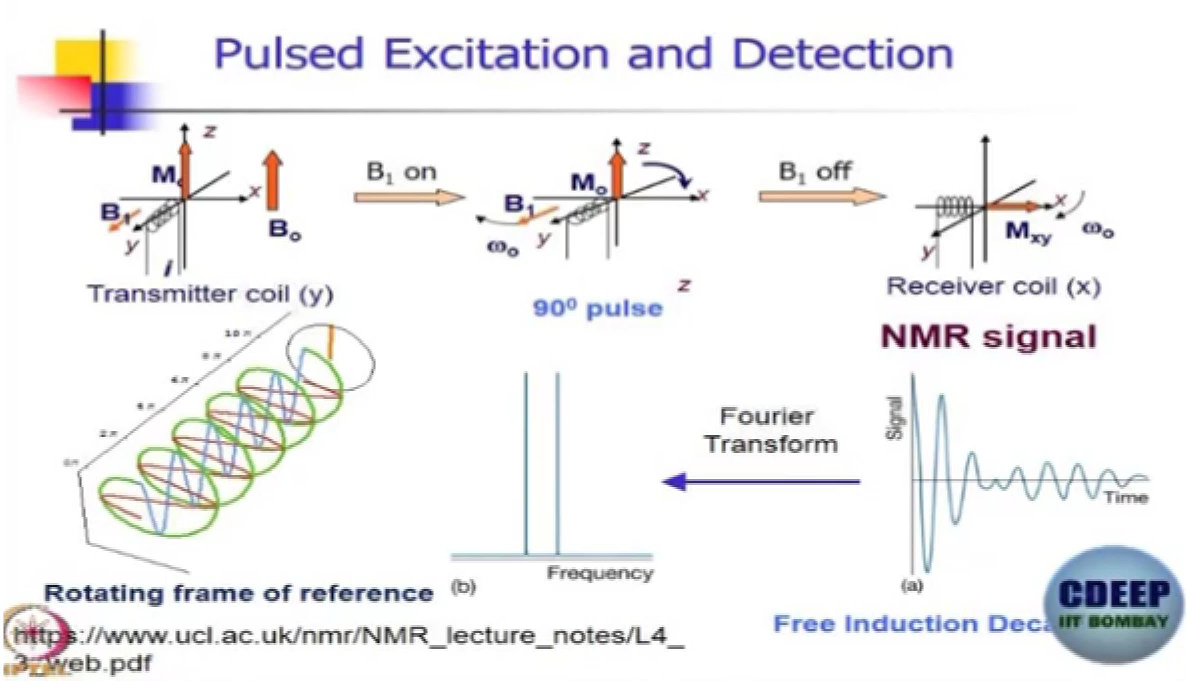

that is your B1, that is B1. So B1 also rotates in such a way that it exactly corrects for this kind of motion, okay, so whatever component M0 has for rotation about the B0 axis, Z axis is exactly offset by this B1 also running away from it, okay, so if the frame of reference itself rotates then you can say that even if it comes like this by the time it comes down to 90 degrees it is at 90 degrees with respect to B1, right, so think of that old fashion record player you can see, suppose there is a point on the record player he missed his voice, you just think of that dog, right, sound of dog is rotating, right.

Now if you jump onto, and if you are sufficiently small and you jump on to the record player itself then what happens? You rotate along with the dog, then you don't see the sound of the dog rotating anymore, that is rotating frame of reference, that is what is used in NMR spectroscopy, and that is something that we can do very conveniently because we are using light, we are using radiofrequency, right, so it is very easy to produce what is called circularly polarized light.

Circularly polarized light is produced by what is shown here in fact I have cheated a little bit, this figure is taken not from a context of NMR but it is taken from a website where they talked about circular dichroism CD spectroscopy where circularly polarized light is actually used, so the way you produce circularly polarized light is that you take plane polarized light, I think all of us now what plane polarized light is, you take plane polarized light in two different directions and they have to have a certain path link between them, if you do that then this is the picture, you see two colors here, waves of two colors they are the two plane polarized light with the certain phase difference and the resultant field actually goes around in circles, this is called circularly polarized light, so in FT-NMR what you use is you don't use any radio wave, any radiofrequency, you do not use plane polarized radiofrequency rather you use circularly polarized radiofrequency so that you have a rotating frame of reference in order to have a fissile measurement of this 90 degree pulses, of course one thing that we have not address is that we are rotating the field of light, fine, we are not rotating the detector, so for that some correction is done. Have you understood so far? If so, we will stop here today, please read this part this is not always easy to understand. And tomorrow we'll see how we can use different kinds of pulses to study something extra.

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