# INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

## IIT BOMBAY

## NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

## CDEEP
## IIT BOMBAY

# MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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## Lecture no. – 59
## FT-NMR: Relaxation Phenomena

So when we talk about NMR spectroscopy it is not just the spectrum, you can also measure some kind of dynamics. I hope you are now familiar with what relaxation is, I talked about time resolved spectroscopy earlier we said that you excite with the pulse, then excited state population is created, then when the light goes off the excitation population decays, and the normal equilibrium situation is rescued, this phenomenon is called relaxation, alright.

In NMR also you have relaxation processes I'll not go into the detail of what this relaxation times tell you, a preliminary discussion is available in Banwell's book, I'll request you to read it, that why we want to study relaxation phenomena,
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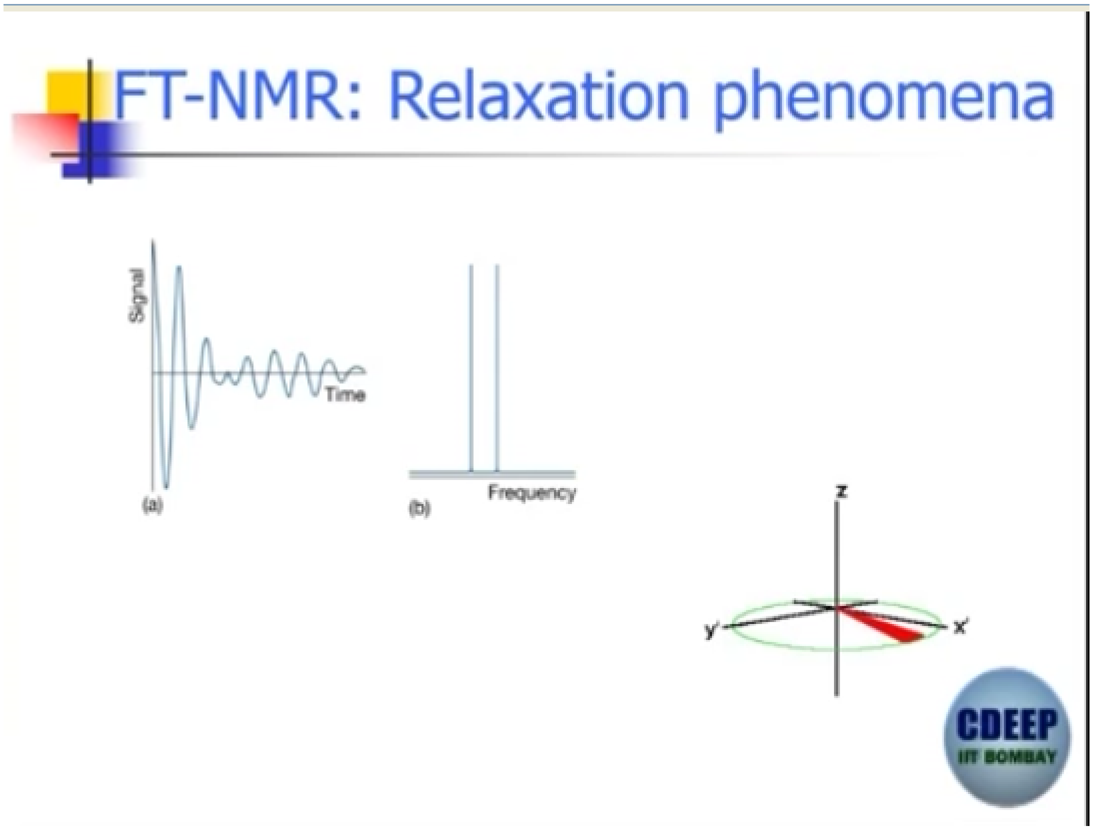

## FT-NMR: Relaxation phenomena

but what we'll try to understand is how we can record the relaxation times. To do that we first have to recognize that there are two kinds of relaxation,

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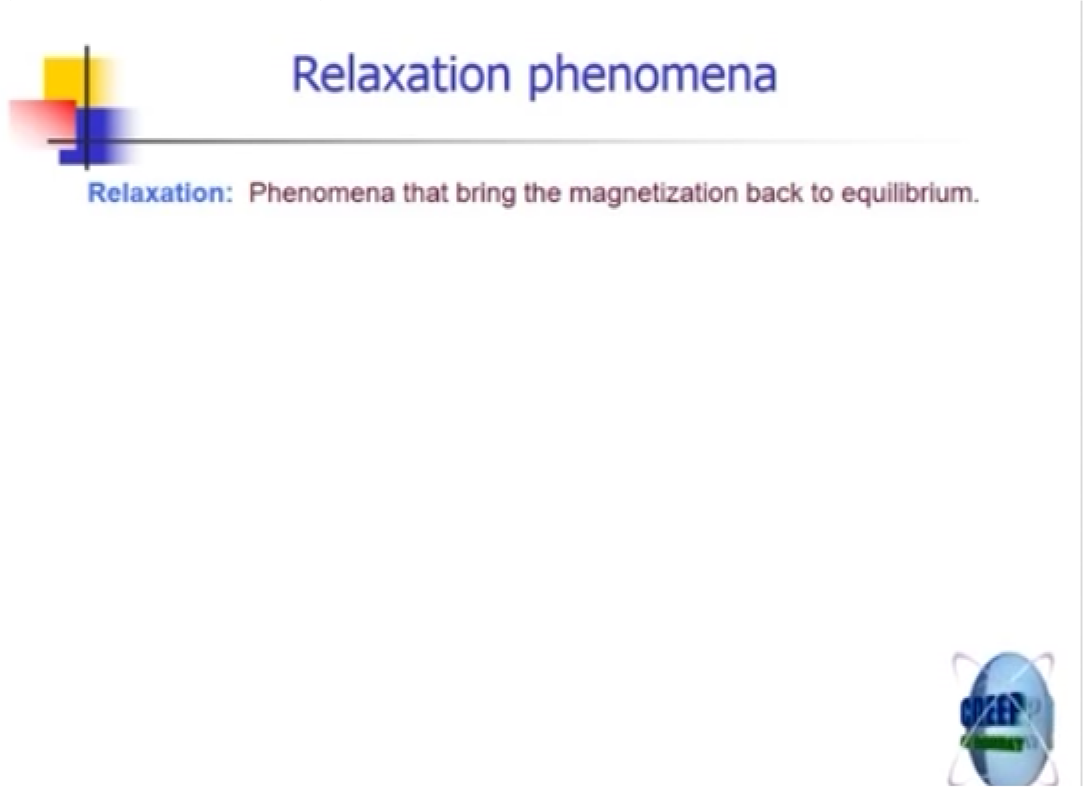

## Relaxation phenomena

**Relaxation:** Phenomena that bring the magnetization back to equilibrium.

so some of us I know have studied NMR already, can you tell me what are the two kinds of relaxation that we need to discuss in NMR spectroscopy? Spin-spin relaxation and spin lattice relaxation.

Spin lattice relaxation is easier to understand for me, what it means is this, we've put in some light and we've done spin flipping, so now your system that you are studying that has some excess energy, okay, if you has to come back to ground state then one way it can do, so is by giving away this excess energy to the lattice, right, this is spin lattice relaxation, and this is also called longitudinal relaxation.

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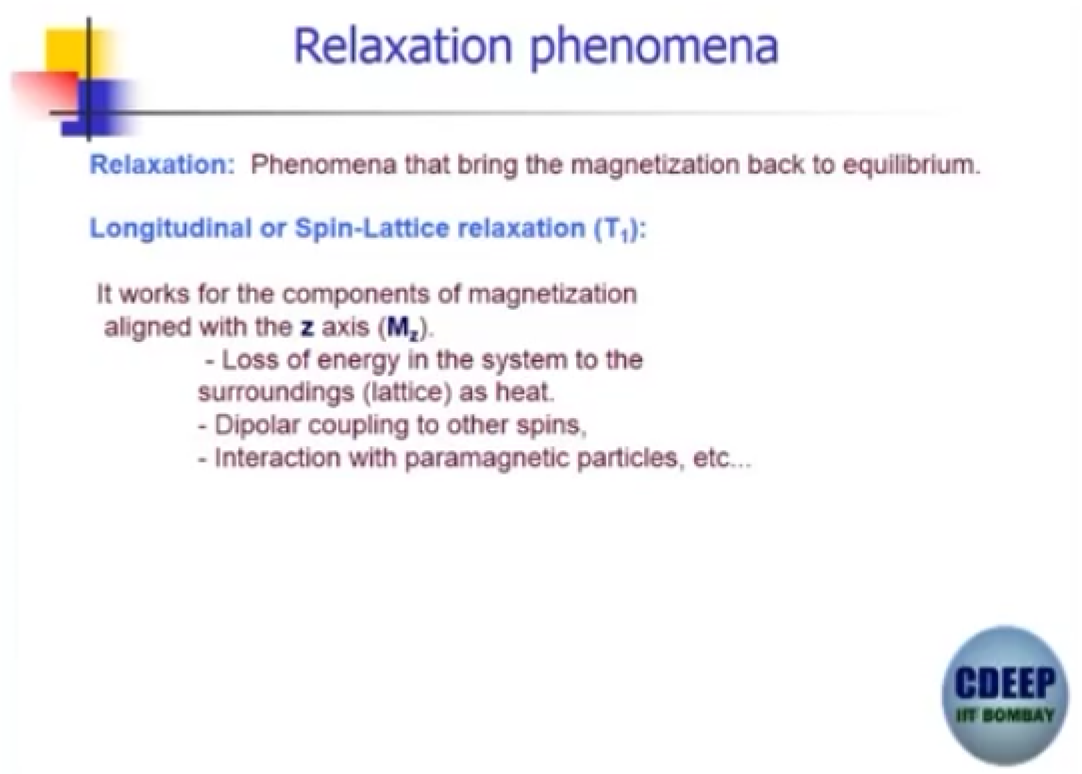

## Relaxation phenomena

**Relaxation:** Phenomena that bring the magnetization back to equilibrium.

**Longitudinal or Spin-Lattice relaxation ($T_1$):**

It works for the components of magnetization aligned with the **z** axis (**$M_z$**).

- Loss of energy in the system to the surroundings (lattice) as heat.
- Dipolar coupling to other spins,
- Interaction with paramagnetic particles, etc...

Why is it called longitudinal relaxation? Because the phenomenon is something like this, this is what you start from M0, okay. Let us say we have given a 180 degree pulse, then it would just turn like this, this is a high energy situation, so the way it comes back from here to here is by giving away the excess energy to the lattice, so as it gives away excess energy to the lattice what will happen to the length of this vector? It will become smaller, right, so it becomes something like this after sometime, after some more time it becomes like this when, after some more it become 0, then what happens?

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Does it stop when the length of the vector is 0? Is that the lowest energy situation? No right, what is the lowest energy situation? This is the lowest energy situation, so after this what happens is this vector starts growing in the positive direction, so going from here to here this is your spin lattice relaxation, okay,

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longitudinal because this change takes place along the direction of the applied magnetic field.

We’ll come to how it is measured, in fact the answer is already there in front of you, but before that let us try to understand what is spin-spin relaxation, and to understand what is spin-spin relaxation

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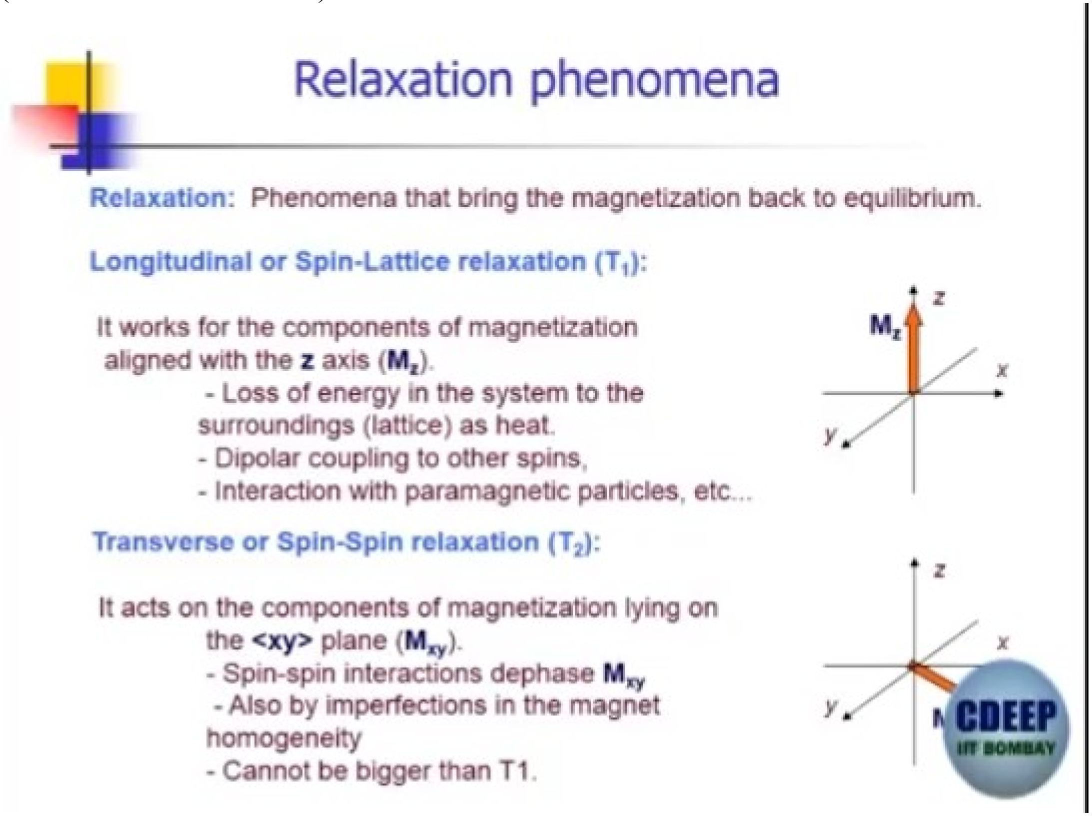

# Relaxation phenomena

**Relaxation:** Phenomena that bring the magnetization back to equilibrium.

**Longitudinal or Spin-Lattice relaxation ($T_1$):**

It works for the components of magnetization aligned with the **z** axis ($\mathbf{M_z}$).

- Loss of energy in the system to the surroundings (lattice) as heat.
- Dipolar coupling to other spins,
- Interaction with paramagnetic particles, etc...

**Transverse or Spin-Spin relaxation ($T_2$):**

It acts on the components of magnetization lying on the **<xy>** plane ($\mathbf{M_{xy}}$).

- Spin-spin interactions dephase $\mathbf{M_{xy}}$
- Also by imperfections in the magnet homogeneity
- Cannot be bigger than T1.

I’d like to remind you of a diagram that we’ve drawn yesterday, when you apply 90 degree pulse, you told me that, okay I’ll draw this by a dash line, this is the original direction of M0,

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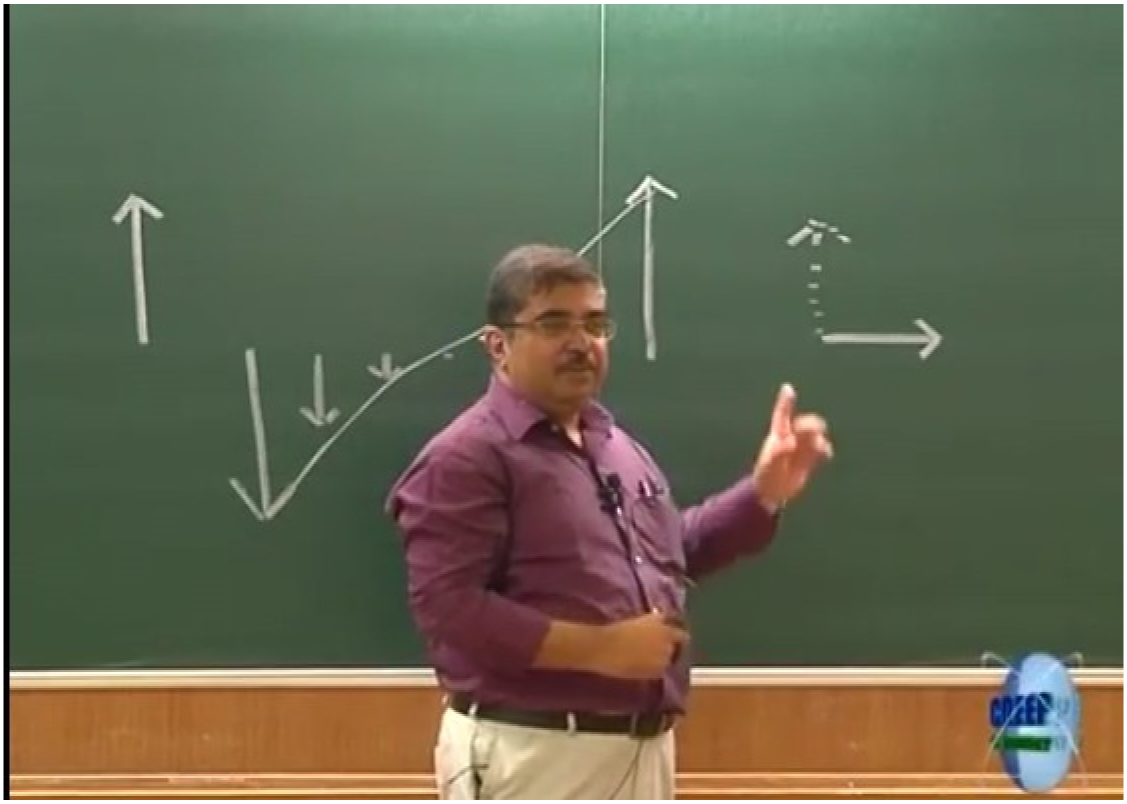

when you apply a 90 degree pulse we said that it turns by 90 degree, but yeah it turns by 90 degrees, but one thing that we said yesterday is what is the meaning of this bulk magnetization turning by 90 degrees, after all it is a vector sum of all the spin angular momenta, isn't it? Right, we understand the situation when it points upward, it means that all the spins upward as well as downward are distributed equally along all the 5 values, but if this is the situation then we said that it essentially means that we have a bunching of spins, instead of this now we have something like this,

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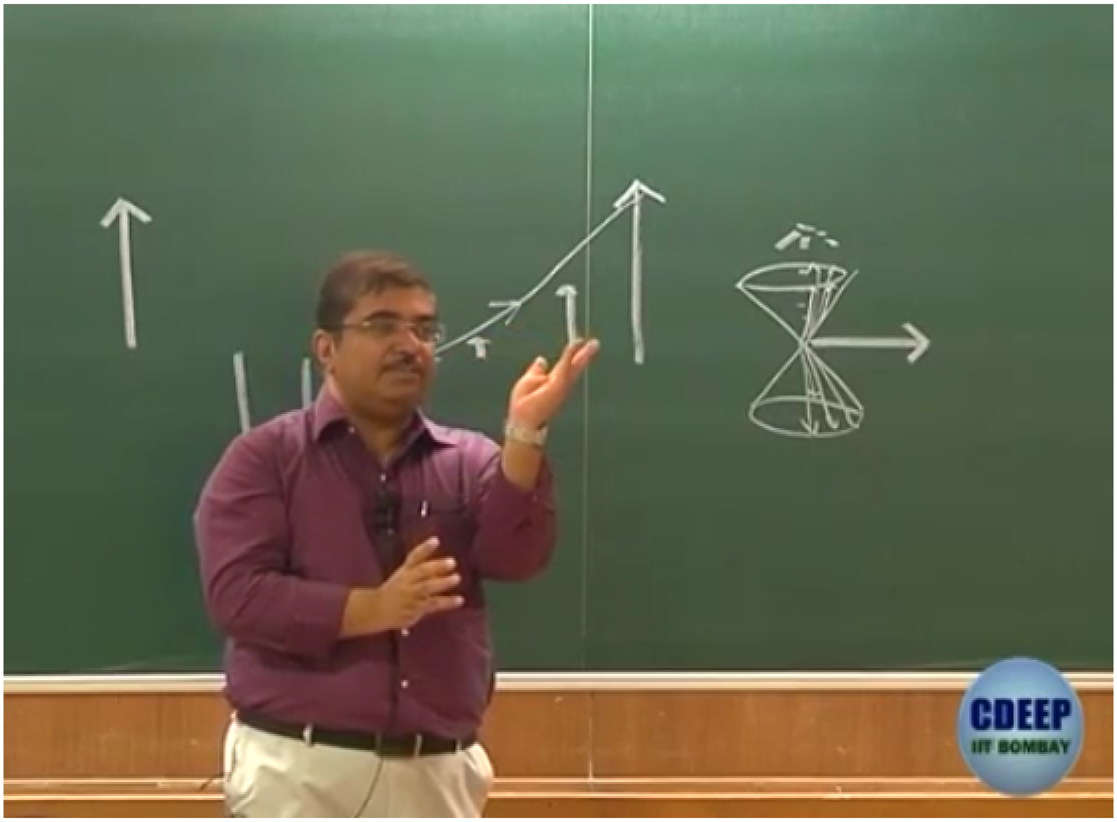

the up spins kind of get restricted to a range of 5 values, same is true for the down spins, this phenomenon is called bunching, if that happens then only can you have this M0 pointing 90 degrees with respect to the direction of the field, poking a little bit 90 degree pulse in a stomach, yeah.

Okay, do you understand bunching? If I look down from the top then what will it look like? All these spins are confined in this kind of a region, do we agree with this?
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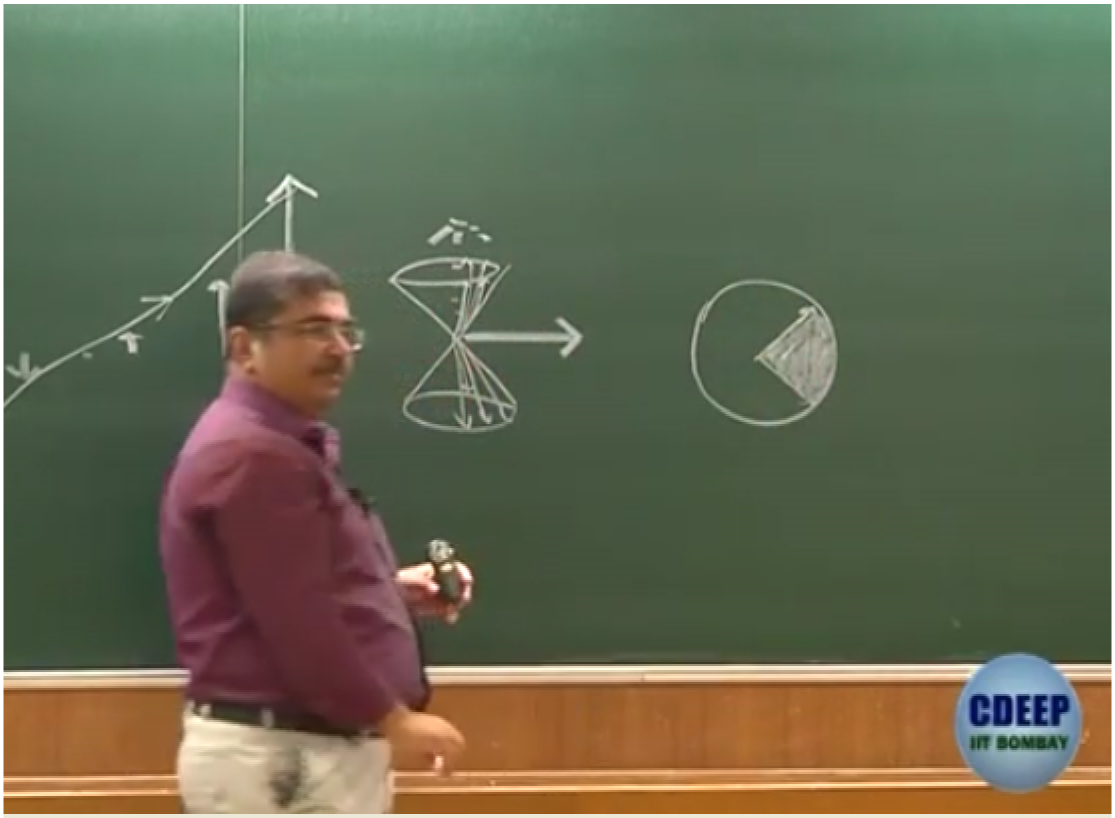

Have we understood? If not, this is the time to ask, this is the only difficult part of today's discussion. Do we understand spin bunching? Yes, when we apply the 90 degree pulse? We apply the 90 degree pulse and so we are only thinking of the resultant right, now what I'm saying is now that we know that the resultant points at 90 degrees think of the components, clear? Any other question? Yes, what is that is what? This, this we have finished discussing, this is longitudinal relaxation. Yeah, it is the measurement of resultant aspect yes, so what we are saying is that this change in the length of the vector that is all that happens, the direction of the vector is always along Z direction, pointing up, pointing down that's the only difference, in all these situations the spins are actually distributed uniformly over all 5 values, otherwise the resultant cannot be along this or this direction. These are the result, the spins of the individual nuclei, right, so if they are uniformly distributed then what will happen? The resultant will point in Z direction, if you have more spins pointing up then the resultant will point up, if you have more spins pointing down then the resultant will point down, that's all, so all we are saying is that this length keeps decreasing, decreasing, decreasing become 0 then increases in the other direction, but at no point of time in this situation is this uniformity of distribution of the nucleus spin angular momenta disturbed.

Unlike the second case where by applying 90 degree pulse what we do is, we cause the spins to get located within a range of 5 values, so entire cone is not occupied anymore. Have you understood? Any other question? Yeah.

What do you mean cone also rather do? Cone is not there, the cone is kind of the locus of each vector you can think, there is no real cone there, we are drawing the cone so that we understand that, that is the theta value. Oh what you are saying is that, it can rotate like this? So we've done a bunching, the whole thing can rotate that's what you are saying. Yes it can, yes it can, we'll come to that.

Right now we are talking about an instant, okay, we'll come to that, that will give rise to something called anti-bunching we'll come to that. Not anti-bunching well yeah, just hold on a moment we'll come to that. Any other question? If not, let us try to see how you can measure these different kinds of relaxation. Of course see when relaxation happens it's not as if spin-spin relaxation gets done, then spin lattice relaxation begins or the way around, the two kinds of relaxations takes place at the same time, but then these are the two orthogonal coordinates of relaxation, so what we try to do is we try to design measurements which will give us an idea of spin-spin relaxation, independent of spin lattice relaxation and the other way around.

So first we'll discuss how we can find out the time required for spin lattice relaxation. The way it is done is by using a sequence of pulses,
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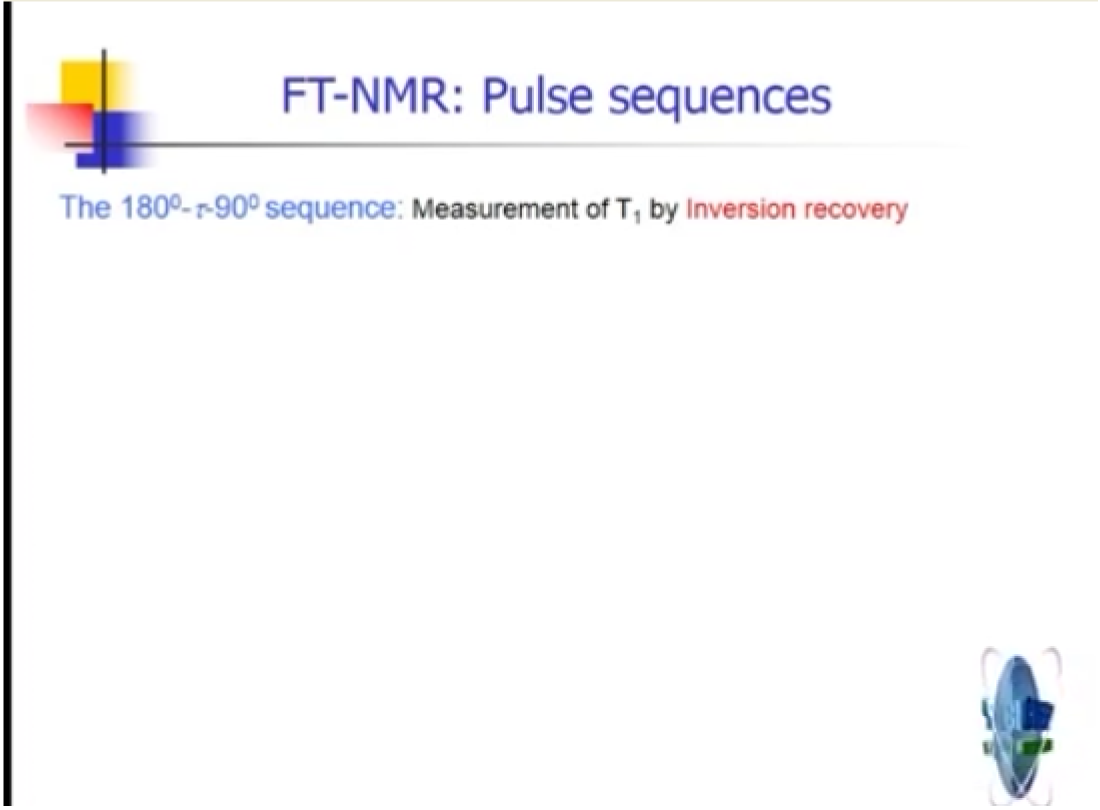

FT-NMR: Pulse sequences

The $180^0$-$\tau$-$90^0$ sequence: Measurement of $T_1$ by Inversion recovery

and this experiment is called 180 tau 90 sequence, 180 is how many pi? Pi, and 90? Of course pi/2, so it's also called pi tau pi/2 pulse sequence, and see this is what it takes us, that this is what teaches us how powerful the technique of pulse NMR is. If you did CW-NMR, first of all your spectra would not be half as good as the spectra that you get from the FT's, and also you'd be limited to recording just spectra, you cannot talk about time, you cannot talk about dynamics, but if you use pulses then by varying the pulses, but varying the sequence of pulses you can get some extra information, and what we are going to discuss in the next 20 minutes or so is only the tip of the iceberg, only the beginning, the simplest measurements you can do by using pulse sequences.

Modern day NMR spectroscopy of complex systems is all about designing pulse sequences that can give you information that you cannot get otherwise, it's about correlation experiments 2D NMR experiments and so on and so forth, and NMR people you know are very good at acronyms, so you might have heard about things called cosy and rosy NMR, have you heard of cosy or rozy? So it's an acronym I've forgotten what it is COSY, everything is in capital letter, so this is a different pulse sequences, and that gives you, so you require this to understand the structure of complicated big molecules, and cosy and rosy if you thought they were funny let me tell you there is also a pulse sequence called enact, I think there is a pulse sequence called New York, New York or Chicago I forgotten perhaps Chicago. And the all kinds of strange names are there for pulse sequences, so we will look forward to the day when one of us will come up with the power sequence, I'm sure that can happen sometime, but for now we restrict ourselves to the very basic discussion of 180 tau 90 and then we will talk about 90 tau 180, what does it mean? What it means is simple, you apply a 180 degree pulse, wait for some time tau then apply a 90 degree pulse, but why will you do that? That's what we have to see.

So okay, let's just neglect that line and go back to the pictures, another 90 degree pulses required, okay. So what happens when you apply 180 degree pulse?
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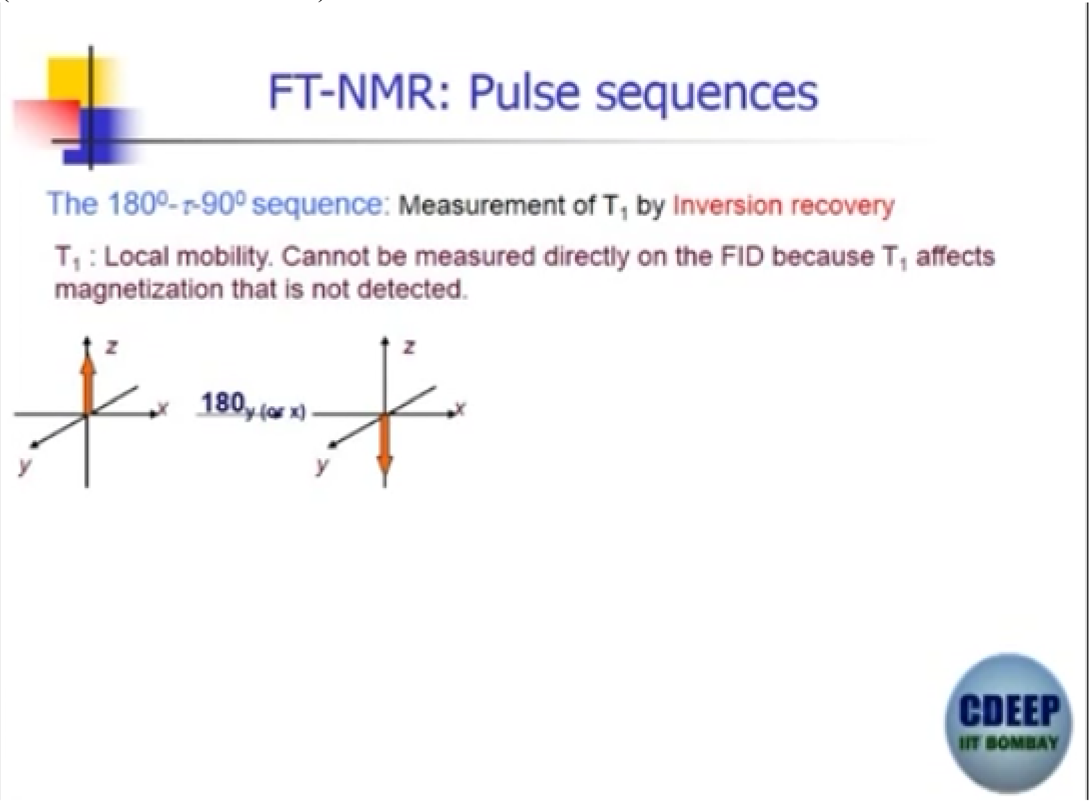

FT-NMR: Pulse sequences

The 180°-$\tau$-90° sequence: Measurement of $T_1$ by Inversion recovery

$T_1$ : Local mobility. Cannot be measured directly on the FID because $T_1$ affects magnetization that is not detected.

And also well one thing I forgot to say is I think we have realized by now that the only difference between 90 and 180 degree pulse is the time for which the radiofrequencies kept on that's it, it is not as if that we have to have one radiofrequency and then another radiofrequency no, one single source single frequency just the time, keep it on for 25 microseconds, it's a 90 degree pulse, keep it on for 50 microsecond it's 180 degree pulse, it's as simple as that, so what you do is you apply a 180 degree pulse.

What happens when you apply 180 degree pulse? You create this kind of a situation, right, it points downward, then what you do is of course when you apply 180 degree pulse, can you see each?

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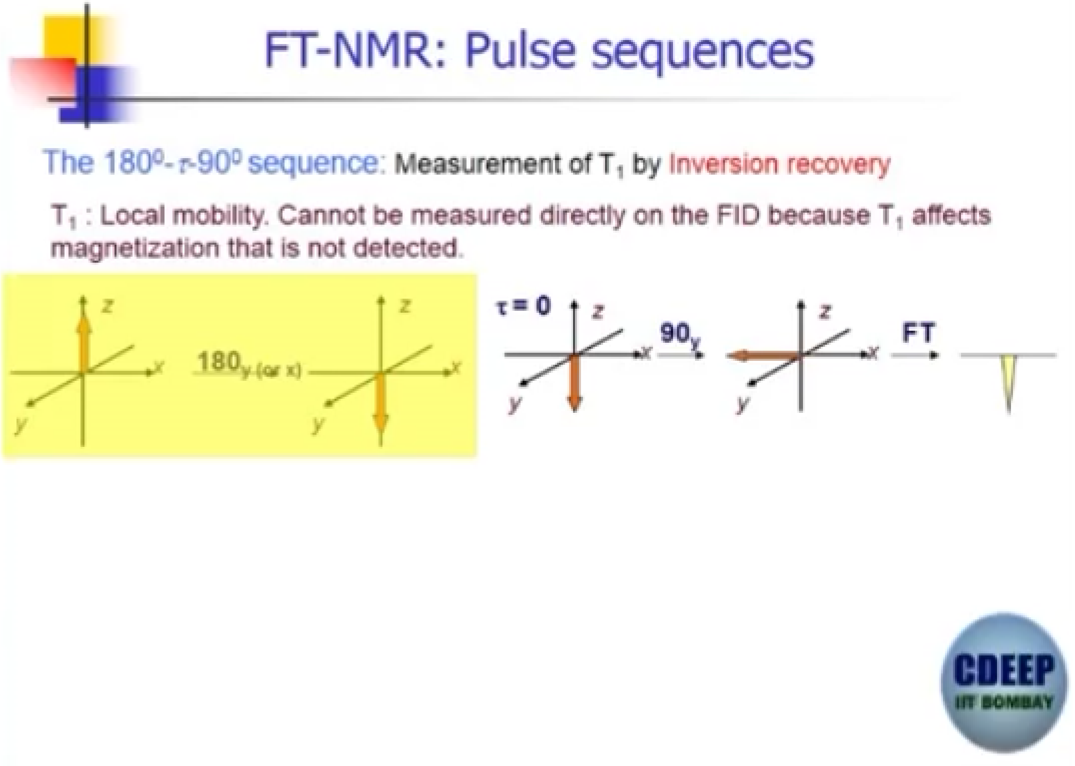

## FT-NMR: Pulse sequences

The $180^0$-$\tau$-$90^0$ sequence: Measurement of $T_1$ by Inversion recovery

$T_1$ : Local mobility. Cannot be measured directly on the FID because $T_1$ affects magnetization that is not detected.

Can you detect or see it? No right, because this is 0, this is 180 and your detector is somewhere in this direction or this direction, so this and this the M0 vector and the detector are at 90 degrees when you apply 0 180 degree pulse, so it is not possible for the detector to record M0 when you apply 180 degree pulse, so what do you do? What do you have to do to record the 180 degree pulse? Apply a 90 degree pulse right away, right, apply a 180 degree pulse it turns around immediately apply a 90 degree pulse, now you get this M0 in the same plane as the detector, and then you get a FID from there you can generate the spectrum, okay,

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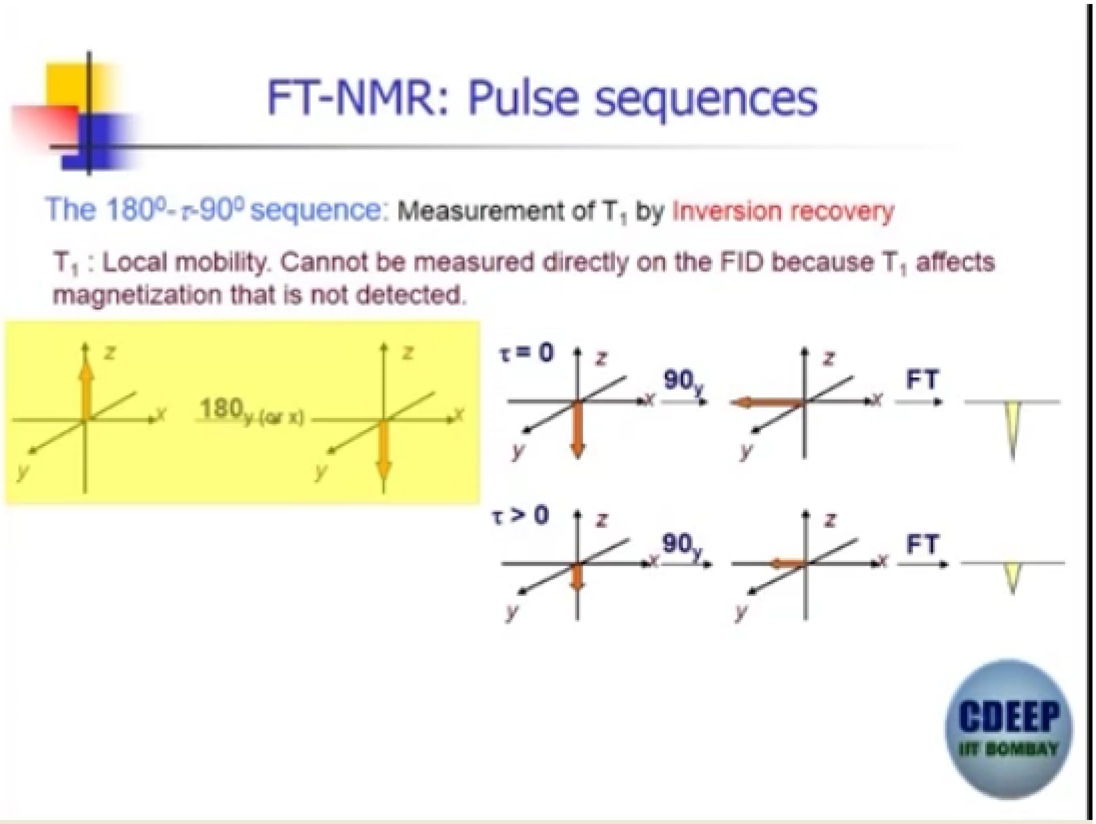

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The $180^0$-$\tau$-$90^0$ sequence: Measurement of $T_1$ by Inversion recovery

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and in fact if you are careful then you can even say whether the spectrum is pointing upward or downward, 180 degree pulse M0 pointing downward that should be your negative spectrum, alright, understood? So this is the first measurement that tells you what is the magnitude of M0 when you give 180 degree pulse?

In the next experiment what you do is you wait for some time, apply a, so this recording is done, then again you apply 180 degree pulse, this time you wait for some time tau, okay, what happens in this time tau? You have turned it by 180 degrees if it has to relax, it has to relax only by spin lattice relaxation do you agree with that? Because there is no inhomogeneity in the distribution of spins at the moment, right, spins are all situated uniformly along those two cones that we've talked about, the only thing is that instead of pointing upward the resultant is pointing downward, understood, and that's not a happy situation, that's a high energy situation, so the relaxation that takes place can only be that some spins flip from beta to alpha, as spins flip what will happen is that the length of the M0 vector pointing downward will become a little less, so I hope we are convinced now that if we apply a 180 degree pulse wait for some time tau then the only kind of relaxation that can take place is actually spin lattice relaxation, okay.

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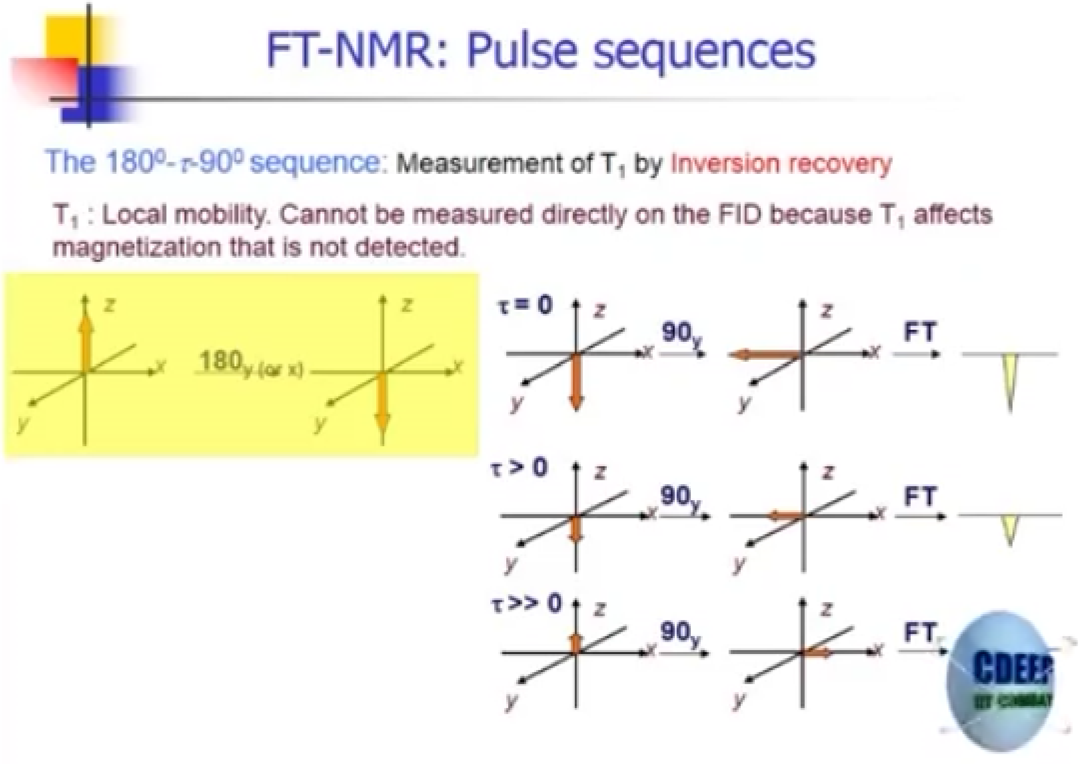


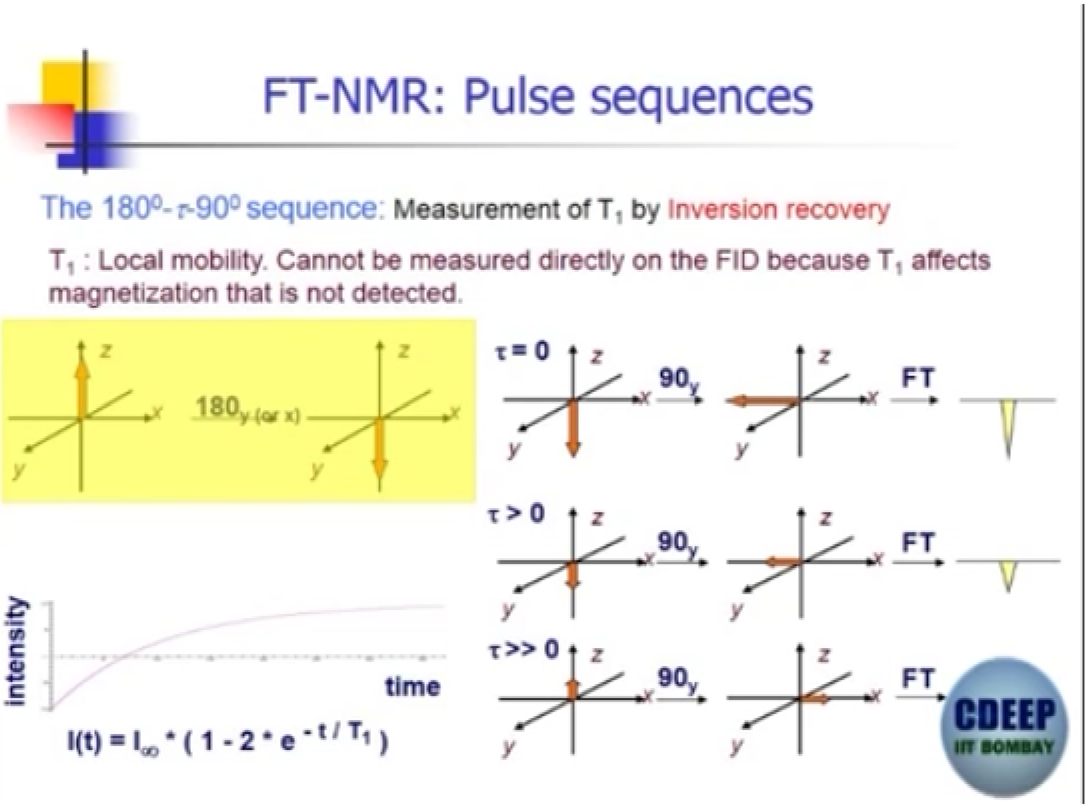
## FT-NMR: Pulse sequences

The $180^0$-$\tau$-$90^0$ sequence: Measurement of $T_1$ by Inversion recovery

$T_1$ : Local mobility. Cannot be measured directly on the FID because $T_1$ affects magnetization that is not detected.

Now what you do is wait for some time, and apply 90 degree pulse, then again you will get a spectra, how will this spectrum be different from that spectra? Spectrum should be same but the size should be smaller right, you should get a less intense spectrum in the negative direction, okay.

Now we are coming to the answer of the question you were asked. You keep on doing this, you keep on using this 180 tau 90 sequence of pulses by progressively increasing the value of tau, then what happens, if you increase a tau a little more finally it will flip, so you go from this situation to this situation to this situation to this and this and this and finally that, okay, so this is what you get. So now if you plot the intensities area under the curve is fine or even the height is (Refer Slide Time: 17:13)



## FT-NMR: Pulse sequences

The 180°-τ-90° sequence: Measurement of $T_1$ by Inversion recovery

$T_1$ : Local mobility. Cannot be measured directly on the FID because $T_1$ affects magnetization that is not detected.

$I(t) = I_\infty * (1 - 2 * e^{-t/T_1})$

fine, if you plot the intensity as a function of time this is what the curve will look like, okay, that curve is fitted to an equation, I at time T = I infinity multiplied by 1-2x E to the power –T/tau 1, T/T1, using tau in the different context so I'll see T1, okay.

Let us see whether it makes sense, what is the magnitude of I0? What should be the magnitude of I0? Just put 0 here, what do you get? –I infinity, does that makes sense? What is I infinity? I infinity is the intensity of the spectrum at infinite time, right, equilibrium situation, so at time 0 that means at the instant where this 180 degree pulse has been applied, height should be the same in magnitude but oppositely direction, so you apply, you put T = 0 you get –I infinity, so does that makes sense for time T = 0?

What about T = infinity? What will this E to the power –T/T1B when T is infinity? 0, at that time what is I(t)? That is equal to I infinity, right, and what is this T1 then? T1 is the time constant that you get for this variation, so this T1 is your spin lattice relaxation, so what we have done in this case is that because we have applied 180 degree pulse we have eliminated the possibility of this clustering off spins, spins are always homogeneous, so the only kind of relaxation that can take place is spin lattice relaxation, longitudinal relaxation, we measure it by applying 90 degree pulses and by doing this 180 and 90 degree pulse application with progressively increasingly gap between the two pulses, okay, so all I have to do is turn on the radiofrequency for 50 microsecond, sorry yeah 50 microsecond and immediately.

So basically in the first experiment you keep the light on radiofrequency on for 75 microsecond and record the spectrum, in the second experiment keep the light on for 50 microsecond, then wait for whatever time you want to wait for tau, and then turn the light on once again but this time for 25 microsecond, record the spectrum, this is what you do just keep changing the time between the two pulses, the time for which the light is off between these two times when it is actually on, this is your 180 tau 90 sequence and this is what enables you to record to measure spin lattice relaxation time without having to worry about spin-spin relaxation time.

If there is a question this is the time to ask, do you have questions? Yes, first we employ 180 degree pulse, sorry can you say that again? Yes 5 values are evenly distributed. So what she is saying is when you apply a 90 degree pulse, then that time we are disturbing the situation, right, we are actually making the pulses the vectors bunch in one direction, but see it does not matter because at that time what do we do? That is the time when we record FID, right, so we are not trying to find out the time constant from the FID itself, all we are using the FID for is to record the spectrum, right, so spectrum, when the moment you record the spectrum what you get? You get time independent data, remember what we have said that each point in time has information about all frequencies, each point in frequency has information about all times, so it’s basically an integral of time, if you remember what Fourier transformation is, is integration of time, so it does not matter.

Okay, so one question that kind of arises from here is that when we record spin lattice relaxation time, isn’t it to enough to see how the amplitude of FID decreases with time, but we’ll come to that, before that is there any question on spin lattice relaxation? Any other question on spin lattice relaxation? Question? Answer? So now before we go on to spin lattice relaxation, let us just remind ourselves of the FID, what you could think is, yeah is there a question? Was there a question?

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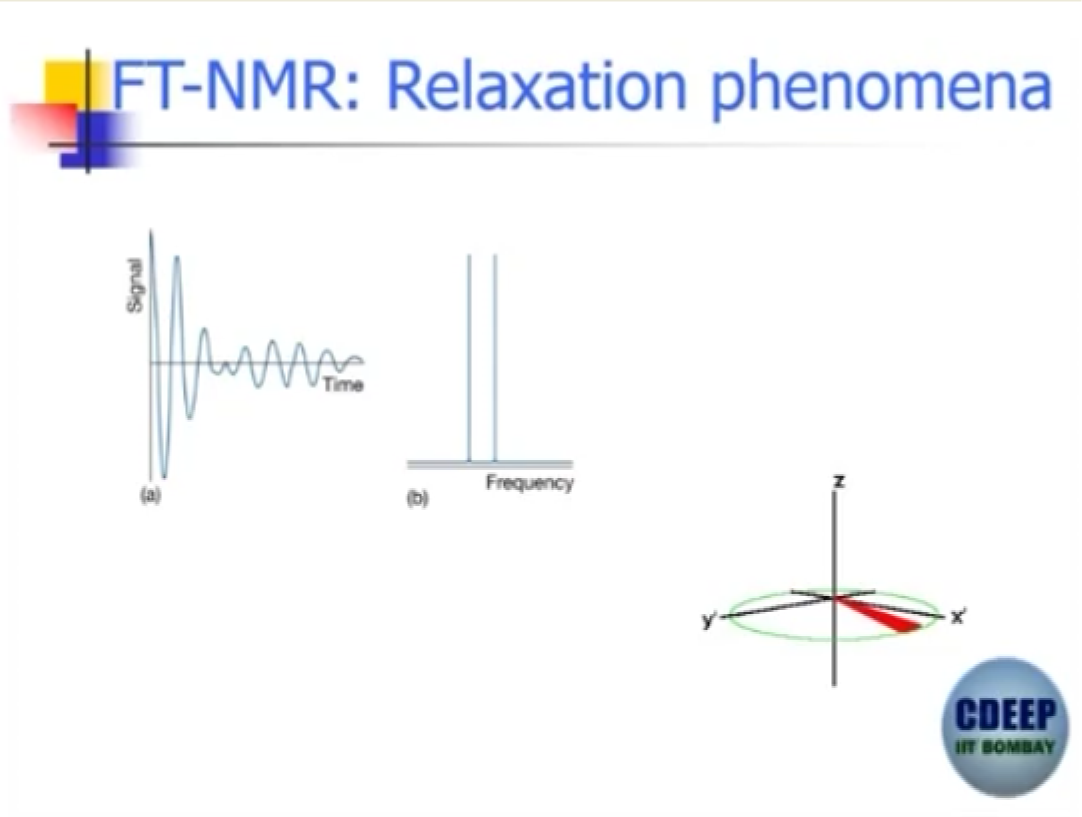

FT-NMR: Relaxation phenomena

What you can think is that you have this bunching that happens periodically, if I just join the maxima I'm going to get a decay curve, is that spin lattice relaxation time? That decay curve doesn't give me spin lattice relaxation time. The answer of course is no, so why do we get this kind of a picture? Why do I get periodic strengthening of the signal, so what is called waxing and waning, in the language of sound, isn't it called waxing and waning? So why do we have periodic reinforcement and then periodic destruction of this side, what is the reason for that?

Why do I not have a smooth decay? So why do I have this going down going up, then going down going up, what is the reason for that? The reason for that if you remember is the occurrence of multiple frequencies, okay, see if I go back to the example that we had used at that time just imagine Akansha and me doing a running this around gymkhana ground and let's say we don't tire, we keep on running for very large number of laps at the same speed, but it is not difficult to understand that Akansha speed will be much more than mine, so we start off at the same point that is when the signal has the maximum, then after a while since she runs much faster than me she will catch up with me once again, so as she goes away from me then you can think the signal is going down, then what she starts catching up with me signal goes up again, when we are at the same point then the signal is maximum, right, that is why we have this going up going down kind of thing, because there is, with time you have constructive interference going on to destructive interference, going on to constructive interference and so on, so the reason why you have this is because you have different frequencies, okay.

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## FT-NMR: Pulse sequences

$90^0$-$\tau$-$180^0$ sequence:

Measurement of $T_2$ by Spin echoes

But that is what we are not talking about when we talk about this transverse relaxation time, so you understand that is actually a problem when we want to record transverse relaxation time, because you are going to have this waxing and waning simply because of presence of different frequencies, and also because in magnetic field is never completely homogeneous, so you have to kind up eliminate that, the way we eliminate that this is a smart trade to be honest, so what you do is this, so this is what is actually done, now see we are looking down from the top you can see that this is X axis,

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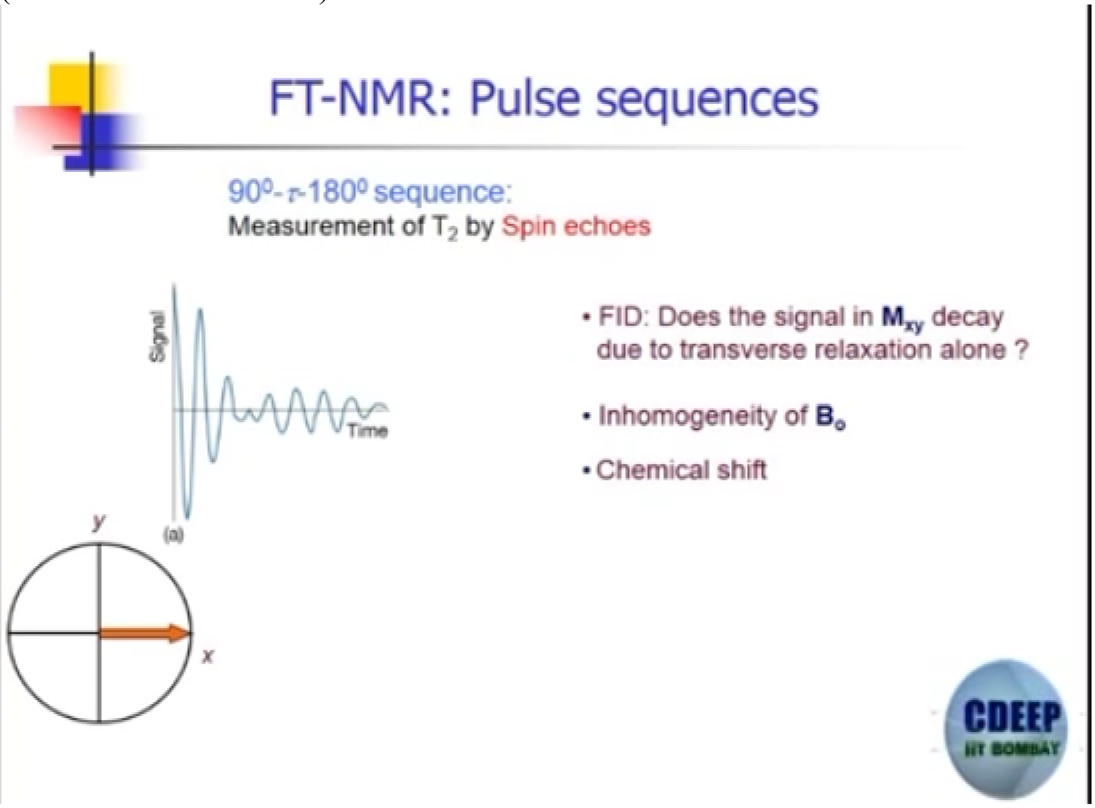

## FT-NMR: Pulse sequences

$90^0$-$\tau$-$180^0$ sequence:

Measurement of $T_2$ by Spin echoes

- FID: Does the signal in $\mathbf{M}_{xy}$ decay due to transverse relaxation alone ?
- Inhomogeneity of $\mathbf{B}_o$
- Chemical shift

this is Y axis, Z axis is pointing towards you, so you actually look down from the top, this is the situation when you apply the 90 degree pulse, right.

What happens if you wait for some time?

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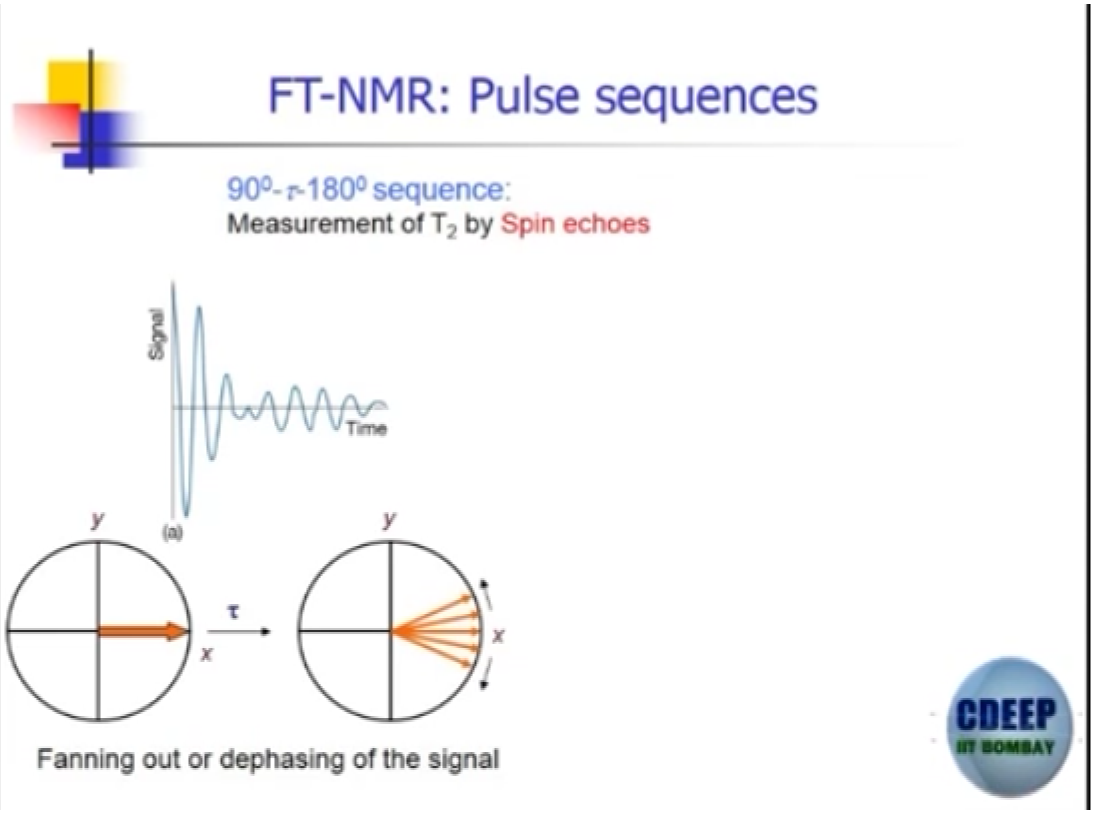

FT-NMR: Pulse sequences

$90^0$-$\tau$-$180^0$ sequence:

Measurement of $T_2$ by Spin echoes

Fanning out or dephasing of the signal

This is what happens, right you apply the 90 degree pulse you have this kind of bunching, then what happens is the spin, the nuclei, what did we say? What is the meaning of different frequency? Nu L, L is for Larmor right, that is the precessional frequency in classical sense, so we have this different kinds of nuclei with different chemical shifts which precess with different frequencies right, so there are nuclei for which the precession is faster, there are nuclei for which and when I say nuclei I just mean protons for now, for which precession is slower, so what happens is first you have a bunching like this, then faster nuclei lead and slower nuclei trail, okay, so what you have is you have this kind of a fanning out or de-phasing of the signal, do we agree?

And what is this de-phasing due to? This de-phasing is due to the difference in chemical shifts of the nuclei that are present in my molecule. Have we understood de-phasing? If not, this is the time to ask. Have we understood de-phasing? Okay.

What is the difficulty? Think like this, let us say I have only bare protons, no nucleus only bare protons, there is only one kind of frequency, if I apply a 90 degree pulse what will happen? You have the spins like this, right, now all this spins will keep precessing about the magnetic field right, but when they precess this will always have the same phase difference with this at all times, but then now think that I don't have bare protons, I have ethanol or ethanol something, so CH3 protons have a different precessional frequency than CH2 protons, one is faster one is slower, so what will happen is well rotating these will lead let us say, and these will trail, so slowly we have a fanning out of the spins, so you start from this situation and after sometime the situation becomes this, fanning out has taken place because this nuclei are precessing you can

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think, well the vectors are precessing at different speeds.

If you allow more time then what will happen? Something like this,
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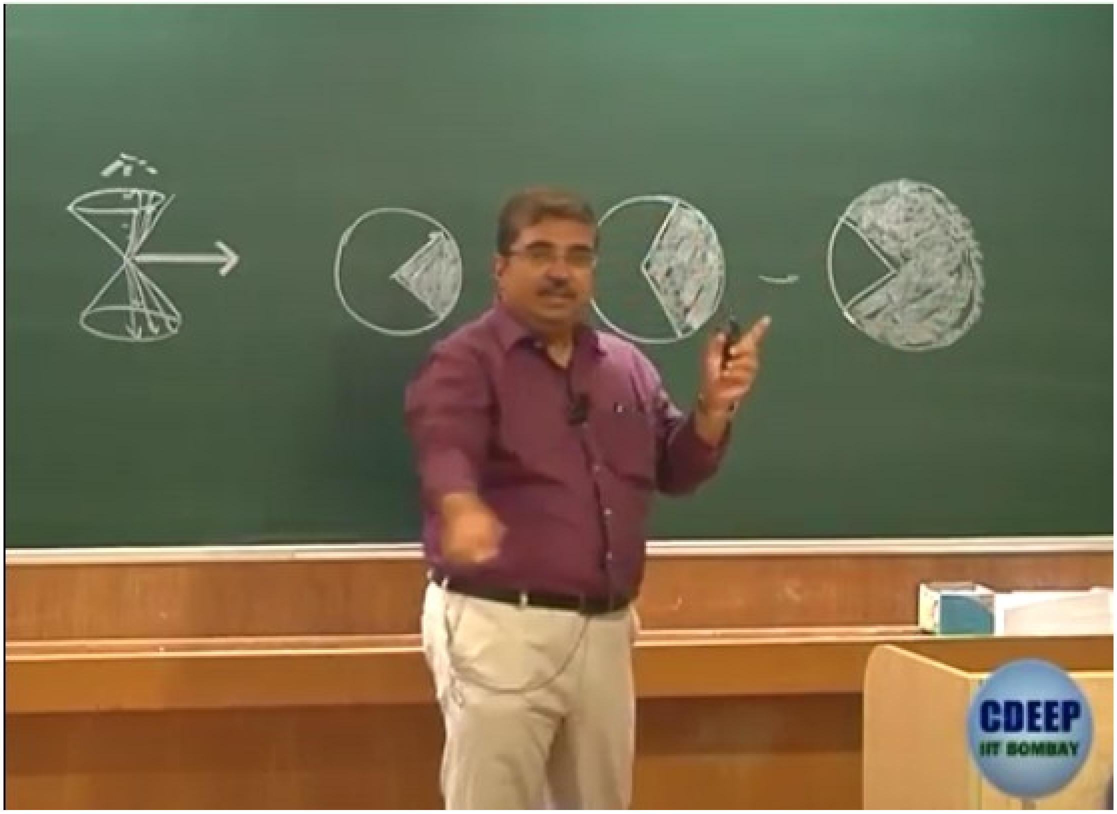


faster nuclei will move much forward, the slower nuclei will keep lagging of course all this is happening in the rotating frame of reference, and if you allow enough time the nuclei will now be distributed uniformly along the cone once again simply because of difference in chemical shifts. Divya had you answer, are we okay with this, what I am saying?

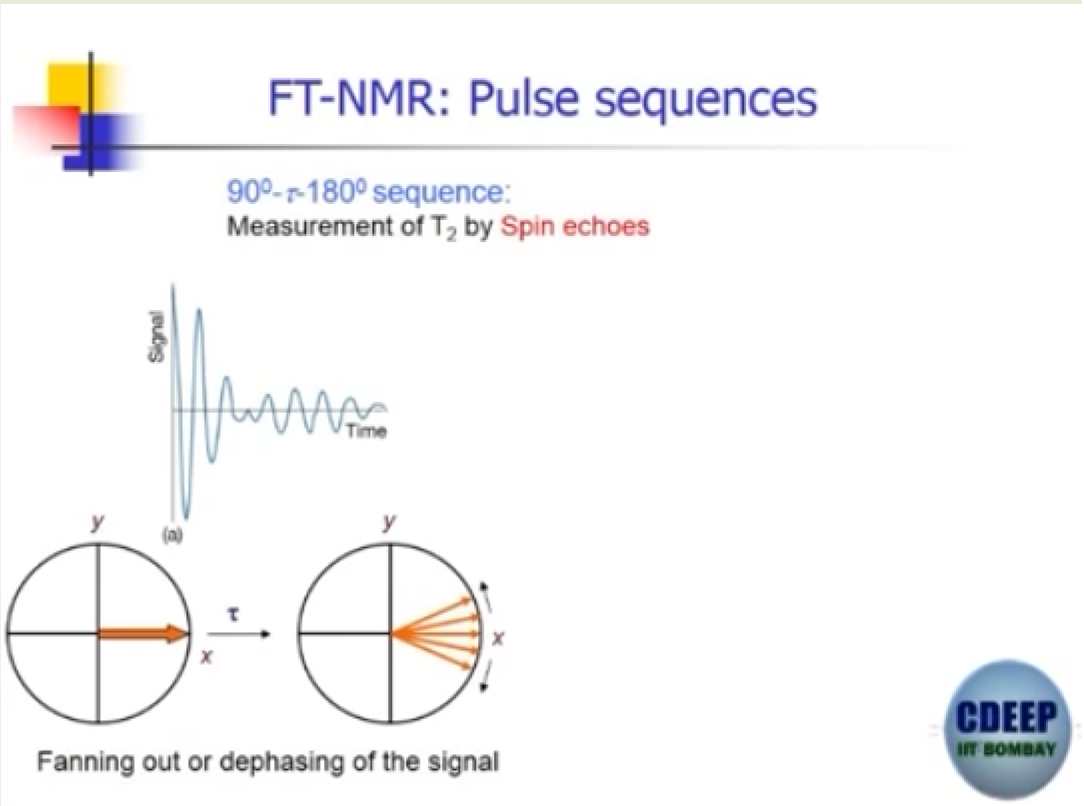
Now let us say I don't give so much time, I wait for some time and I apply a 180 degree pulse, I apply 180 degree pulse, what is the direction along which I'm applying the pulse? This is X direction, this is Y direction, right, let us say Y is the direction along which B1 is, that's what we started discussing, right, X is the direction along which they have the detector, Y is the direction along which we have the magnetic field of the radiofrequency.

So now after allowing for some time, allowing for some bunching, for some anti-bunching, now if I apply 180 degree pulse what will happen? There will be a flip, tell me in this situation let us say this is the direction of rotation, which one is faster this nucleus or this one? This is faster, this is slower right, and now I'm applying B1 in this direction.

Where will the slower nucleus go? Here or here? Here or here, here? Does anybody think it will go here? Let us draw it, so see even though we thought we are done with symmetry we are not, what am I doing? I'm doing a C2 operation, don't forget, so this is the direction of B1, this you can think is, this is the axis along which I do a 180 degree rotation, this is the vector, I do a 180 degree rotation with respect to this, let's do it, this is the vector, this is the axis of rotation 180 degrees, if it turns 180 degrees it goes here, isn't that right?

See this is important to understand, this is a very common mistake that we do, we think that when we do a 180 degree rotation it goes from here to there it doesn't, that would have happened if this was the axis of rotation, but this is the axis of rotation, so this is your 180 degree rotation, understood? Do you understand what am I saying? This is a kind of rotation that I have, okay.

So now don't forget this is the direction in which this entire bunch of spins is rotating now,
(Refer Slide Time: 31:49



FT-NMR: Pulse sequences

$90^0$-$\tau$-$180^0$ sequence:
Measurement of $T_2$ by Spin echoes

Fanning out or dephasing of the signal

precessing by themselves because of the presence of B0. Now I apply 180 degree pulse along Y, and that gives me this situation.
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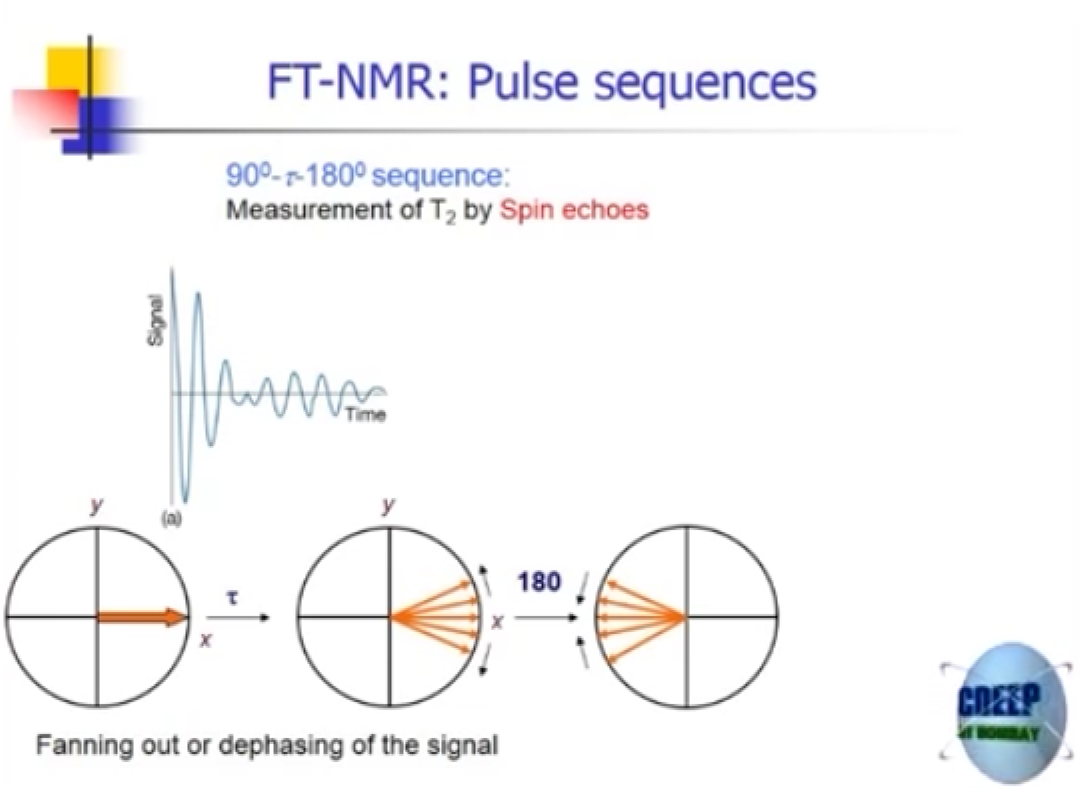

## FT-NMR: Pulse sequences

$90^0$-$\tau$-$180^0$ sequence:

Measurement of $T_2$ by Spin echoes

Fanning out or dephasing of the signal

Now does the direction of precession about B0 change? It doesn't, right, right B1 is off, so direction of precession about B0 still remains the same, in this situation what happen? The faster nuclei were running away from the slower ones that is why you had de-phasing. When you apply 180 degree pulse, direction of rotation remains the same, now what happens? This is slower nucleus, this is faster nucleus, this is slower nucleus, this is faster nucleus, direction of rotation is the same, so before applying 180 degree pulse the faster nuclei were running away from the slower nuclei that's why you had de-phasing, after applying 180 degree pulse the situation changes.

Now the faster nuclei start chasing the slower nuclei, what will happen then? Eventually you are going to have bunching once again, so do you understand? This is actually a trick, how far have you understood? Do you have understood the 180 degree pulse? This is the situation right, which one is fast, this or this? Right hand, my right hand is the vector corresponding to faster nuclei, this is slower nuclei, how are they rotating? Like this, then I apply 180 degree pulse, direction of rotation doesn't change, still like this, right, so what happened was faster nuclei moved away from slower nuclei that was de-phasing, turn by 180 degrees now faster nuclei start chasing slower nuclei, so eventually they are going to catch up. So I think we'll stop here.

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