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. – 60
Inversion Recovery and Spin Echo

We are discussing spin relaxation,

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and we are trying to understand how to record the times required for relaxation. And while doing that what we have discussed so far is that you can think of two mutually orthogonal modes of relaxation, one is longitudinal and the other is transverse.

Longitudinal means the excess energy that is there as a result of absorption of radio frequency is given away to the lattice, this is called spin lattice relaxation, since this mode of relaxation involves interaction of an individual spin and the surroundings there should be no interchange of energy between two individuals spins, so this is spin lattice relaxation, and the other is that more highly energetic nucleus can give away the excess energy to a less highly energetic nucleus, so this redistribution among spins can take this, this is called spin spin relaxation.

And as we have discussed earlier the reason why we call this longitudinal and well not latitudinal sorry, transverse mode of relaxation is that when, well what we have said is that the magnetization vector, bulk magnetization vector M0 is the vector sum of all the spin angular momenta. When the spin angular momenta are distributed evenly along the cone, then the resultant has to point either upward or downward right, so when there is no light it has to point upward, when you have given sufficient amount of light it can point downward, so if it goes from downward direction to upward direction that can only happen by giving away excess energy to the lattice, however any amount of exchange of energy among spins should result in this wiper kind of movement of M0, so what we have said is when we apply 90 degree pulse the M0 vector point in one direction like this, perpendicular to the direction of the applied magnetic field, and that is a result of the spin angular momenta preferentially pointing in that direction, so bunching.

So if now they get spread over all over again that is spin spin relaxation and that causes a transverse relaxation like this. So we have already discussed what is called the inversion recovery technique, I don't remember if I use this term, did I use this term in the last class? So that is the reason why I decided to put it in the title slide so that there is no way to forget once again.

So inversion recovery is essentially, actually I'll need that one later on, I don't need all this at the moment,
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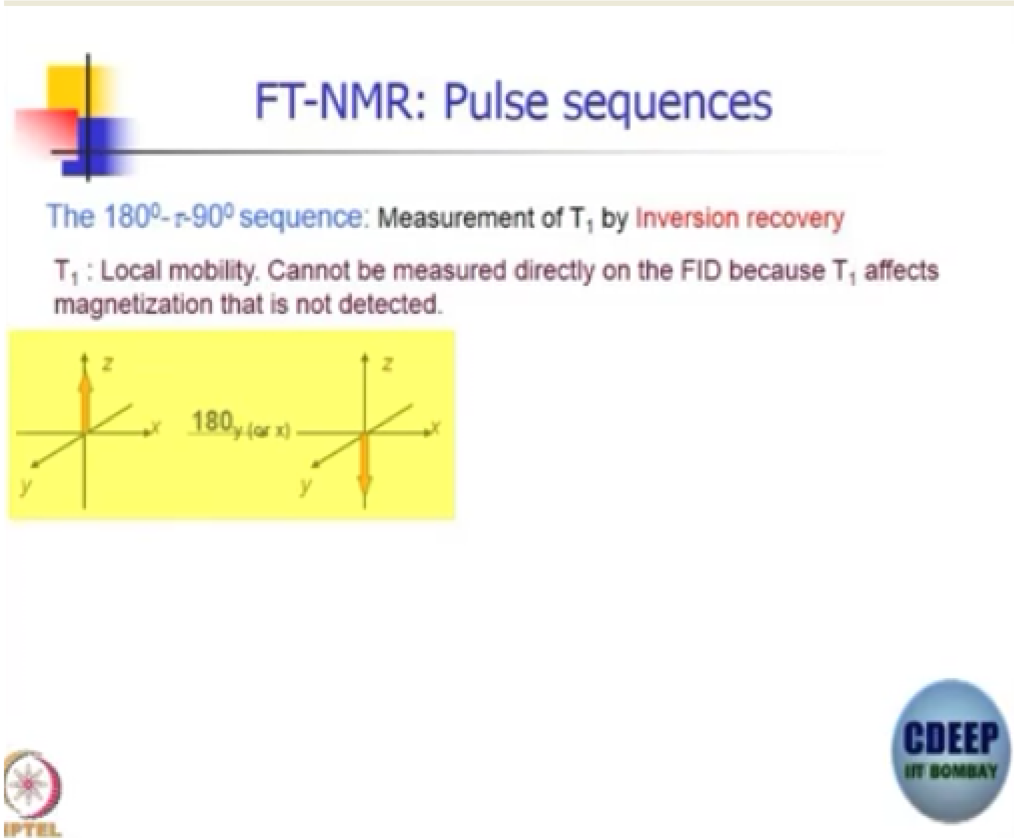

but actually it was written there maybe I forgot to say, inversion recovery means we apply 180 degree pulse, right, and let it relax.

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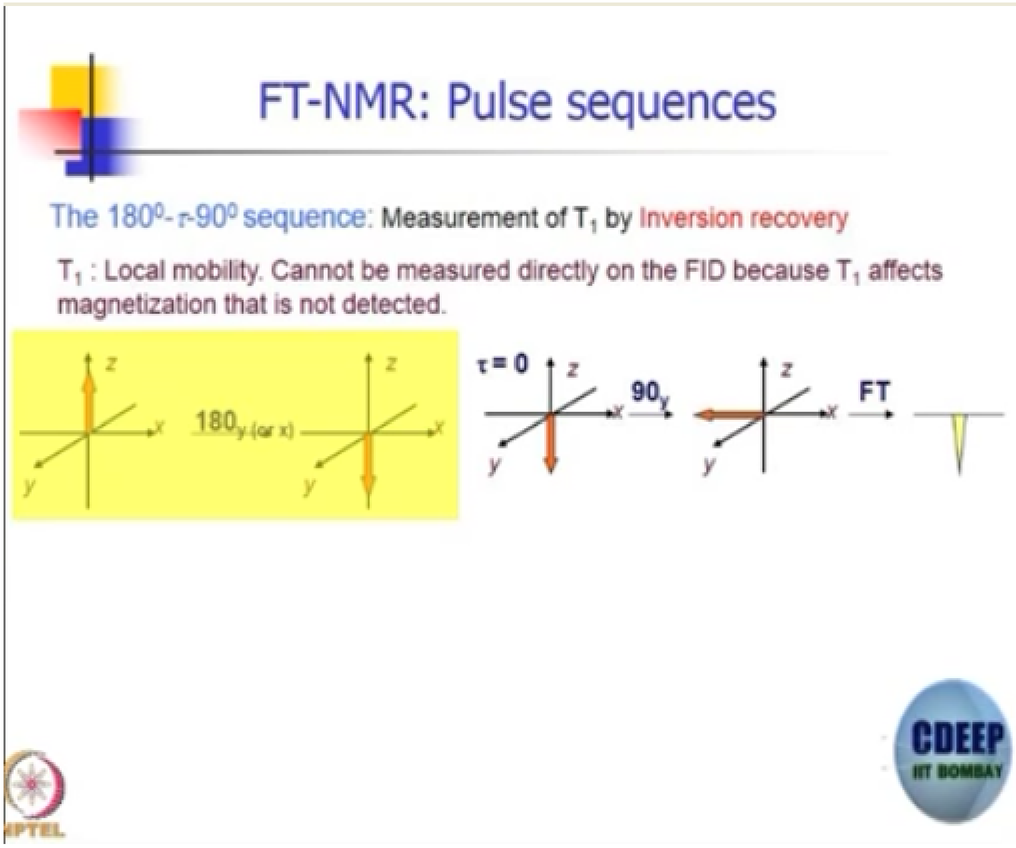

And what you do is at particular time intervals you apply an 90 degree pulse and record the spectrum, initially the spectrum would point downward, as you keep increasing the gap in time between the 180 degree pulse and the 90 degree pulse, what would happen is, this magnitude of this spectrum pointing downward would keep on decreasing becomes 0 and then turn the other way around. And if you now joint the tips of the spectra or if you take the area under the curve along with sign and plot, then that plot will follow an equation like this where T1 is your spin lattice relaxation time, this is called inversion recovery because first you invert and then you see how this inverted M0 relaxes to its original position, how it recovers its original position, it's called inversion recovery, so the pulse sequence is 180 tau 90 pulse sequence and the process is called inversion recovery, this is something we have discussed in the previous class anyway.

And we started discussing was the other sequence, 90 tau 180, when you do 90 tau 180 then what happens essentially is you get an idea of the transverse relaxation time, and this is a little more complicated and therefore little more interesting than inversion recovery technique.
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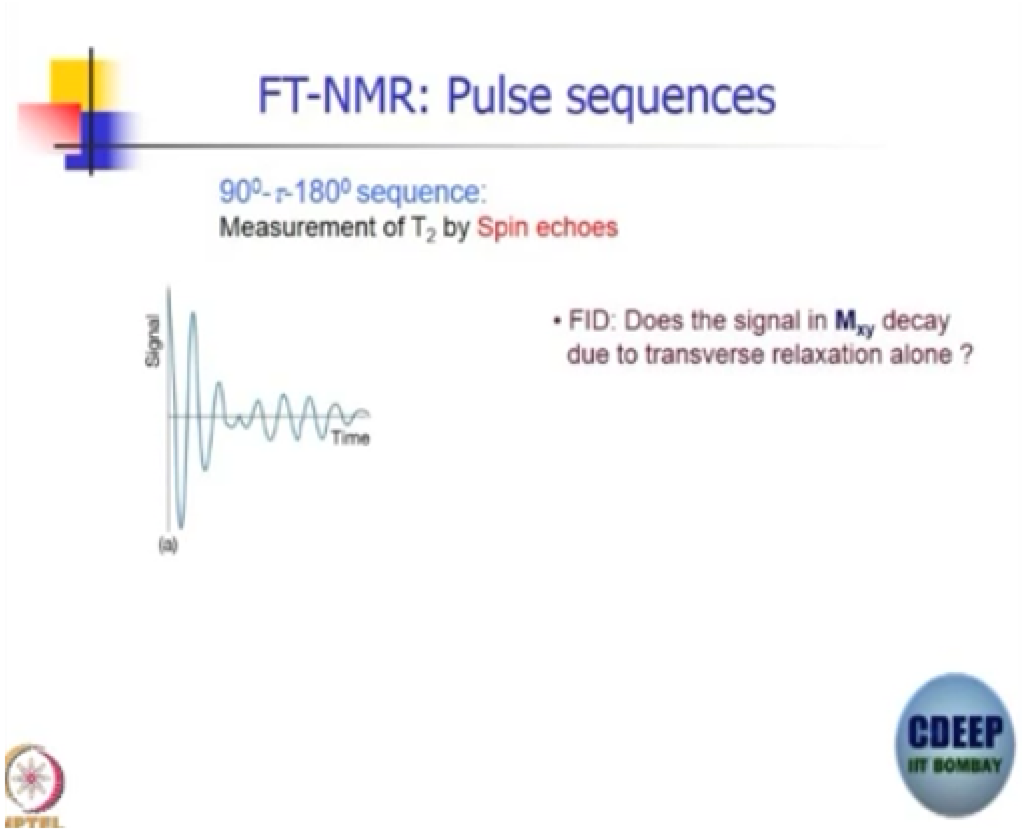

So what we said is this that if you just look at the FID, you can think that I'll, as we have discussed earlier this is going to be periodic function multiplied by an exponential decay, so that exponential decay is that spin lattice relaxation time, this is the question we had started with and we have said it is not, because the decay that you see is not just you to transverse relaxation time, that decay also happens because the magnetic field that you employ is not completely homogeneous, it also happens because there is chemical shift, so different nuclei end up experiencing different amount of magnetic field.

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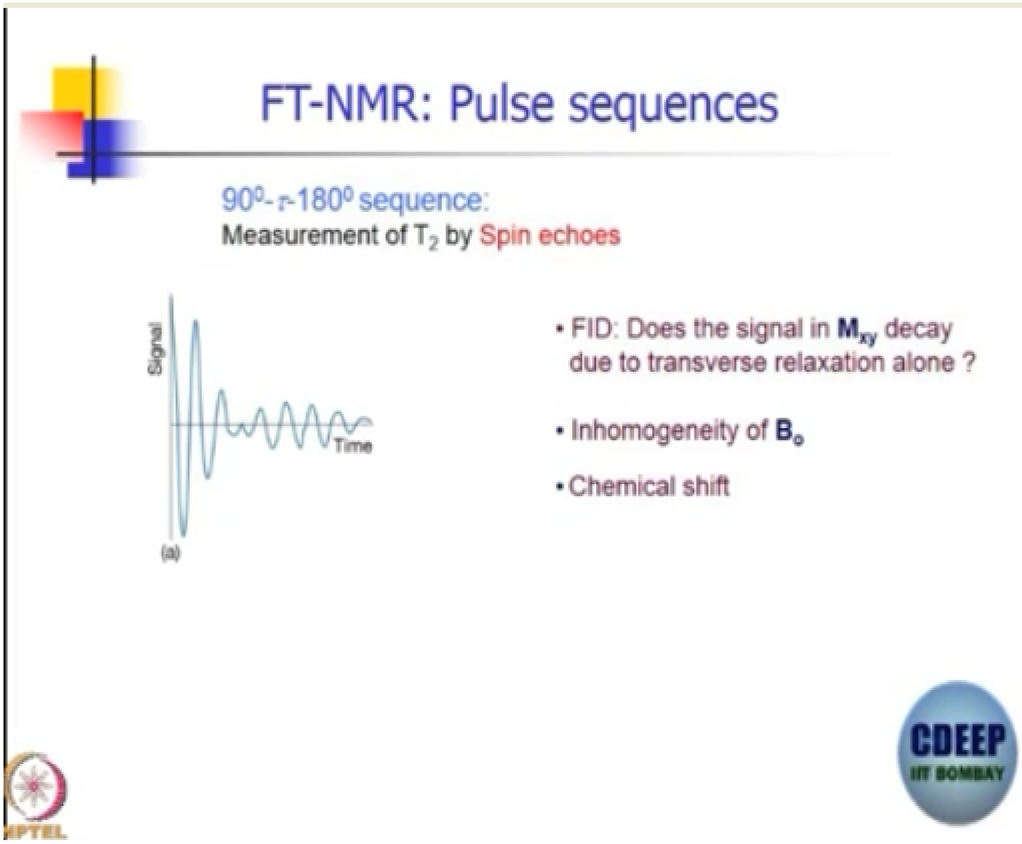

And as we have discussed earlier different amount of magnetic field means what? Different values of Larmor precession frequency, so essentially what we are saying is even if there is no transverse relaxation if you can think of hypothetical situation like that even then due to inhomogeneity of magnetic field and due to difference in chemical shifts the angular momenta actually precess with different speed, so you have slower nuclei and faster nuclei as we put it, so what will happen is faster nuclei will move faster eventually there will be a uniform distribution along the surface of the cone, okay, and that is why you get this decay, it is not just transverse relaxation. So if that is the case, if there are three factors contributing to the decay, transverse relaxation inhomogeneity in magnetic field and difference in chemical shifts, and if I want to specifically get information about a transverse relaxation, what do I need to do? There are three factors contributing to the decay, the first is transverse relaxation or spin spin relaxation, the second is inhomogeneity in magnetic field, the third is chemical shifts, difference in chemical shifts.

Chemical shift I already know right, from the NMR spectrum itself. Inhomogeneity in magnetic field there is no point in knowing, we are interested in the molecule not the instrument, so what I am really interested in at this point of time is this tau T2 spin spin relaxation time.

What do I need to do if I want information only about T2, and not the other 2? Inhomogeneity in magnetic field and chemical shift, I have to somehow eliminate their effects, right, okay, so we have to eliminate the other two, that’s how we can, that’s the only way in which we can hope to get T2, how do we eliminate? This is how, by using not one pulse but a sequence of pulse. So first of all now when we draw this remember we have discussed this yesterday anyway, but I don’t think we completed the discussion and also it is better to discuss this twice, first time we might not understand so we will discuss it once again today.

What is our point of view here, what is our perspective, along which direction are we looking? If we draw the diagram like this, Z direction right, so X and Y are written here isn’t it,
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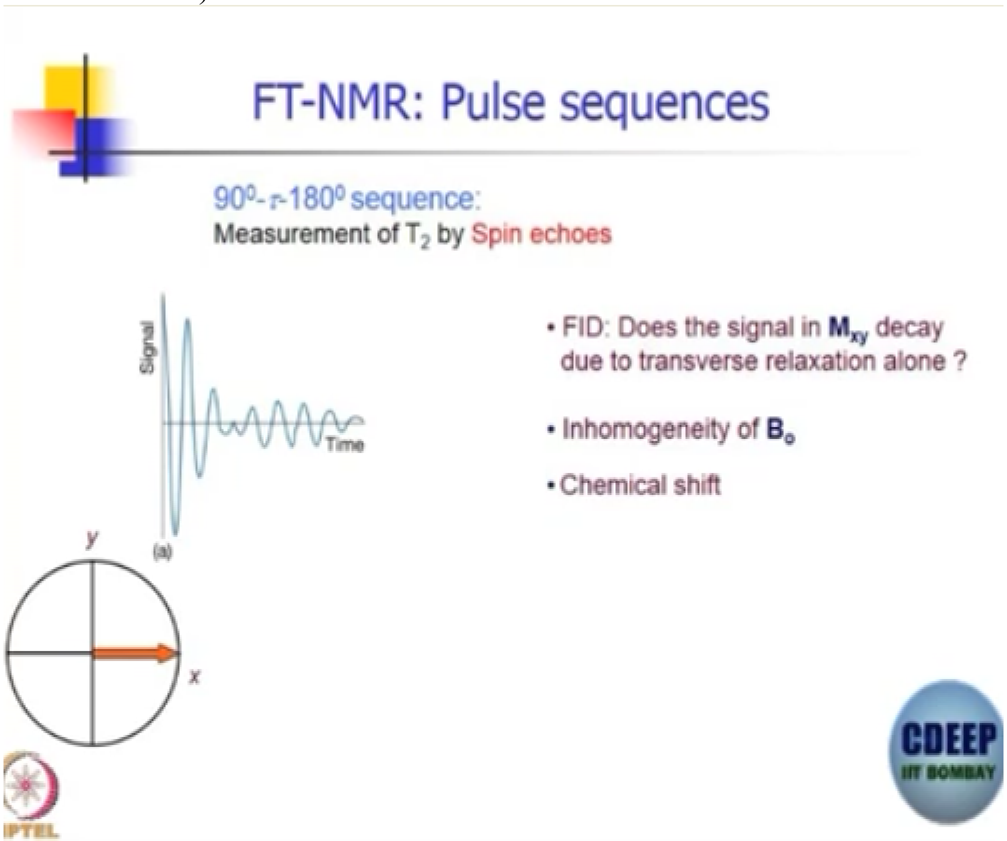

so this is the XY plane, we are looking down up on the system from Z direction, and what is Z direction? Oh this is very fundamental we know but let us make sure we know, Mayuk what is Z direction in this case? That everybody knows, in this context maybe we are talking about NMR spectroscopy, and when we are talking about pulses and all, Z direction is a direction of what? Yeah, they applied magnetic field right, that’s what you said, didn’t you? Do you know when you cover your mouth while speaking? When you are telling a lie, yeah, I mean we cover our mouth when we try to tell a lie or when we are not sure about what we are saying, is that right? Okay.

So Z direction is a direction of the field, okay, we are looking down from the top, so the perspective has to be very, very clear in order for us to understand. What is the direction of B1? So we are looking down from B0 direction, right? What is the direction of B1? B1 is the magnetic field associated with the radio frequency, what is the direction of B1? Why? This is a direction of B1, okay, this is where our detector is, so what we have shown here is that we have applied a 90 degree pulse okay and M0 has gone from here to here, right.

Now if you allow some time what will happen? After applying 90 degree pulse, if you just let the system be for a while, then what will happen is what we discussed the last day faster nuclei will lead and slower nuclei will trail, okay, so you are going to have de-bunching or de-phasing or fanning out, okay, and that will cause a decrease in the signal, will it not? Do you agree that will cause a decrease in the signal? When?

Now let's try a different orientation, this is your Z, this is whatever it is, so when we have more spin pointing in one direction, then this is the direction of M0,
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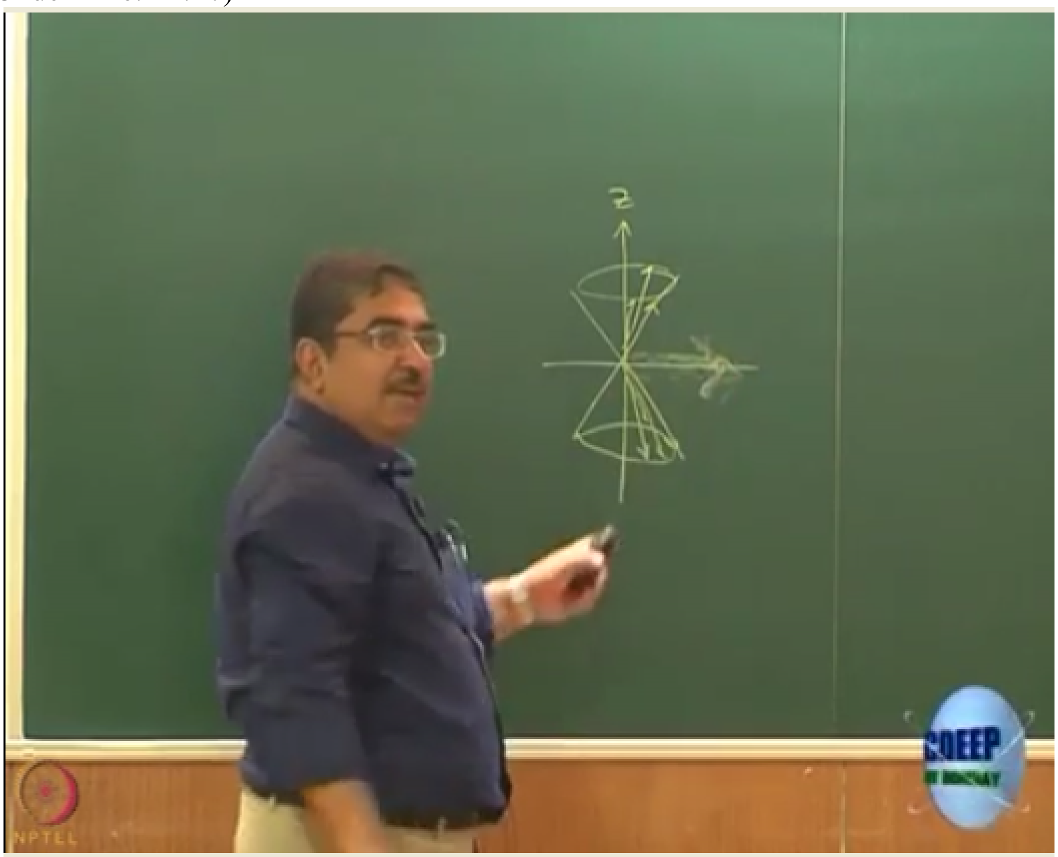

that's what happens when you have applied the 90 degree pulse. Now what I am saying is that, so this is the range of I in which the spins are all located, now when de-bunching takes place, de-phasing takes place, let us say this is what has happened, now this is the range over which the same number of spins have, will redistributed.

What will happen to this magnitude, will it be the same, will it go down? Will it remain the same, will it go down? Will it go up?
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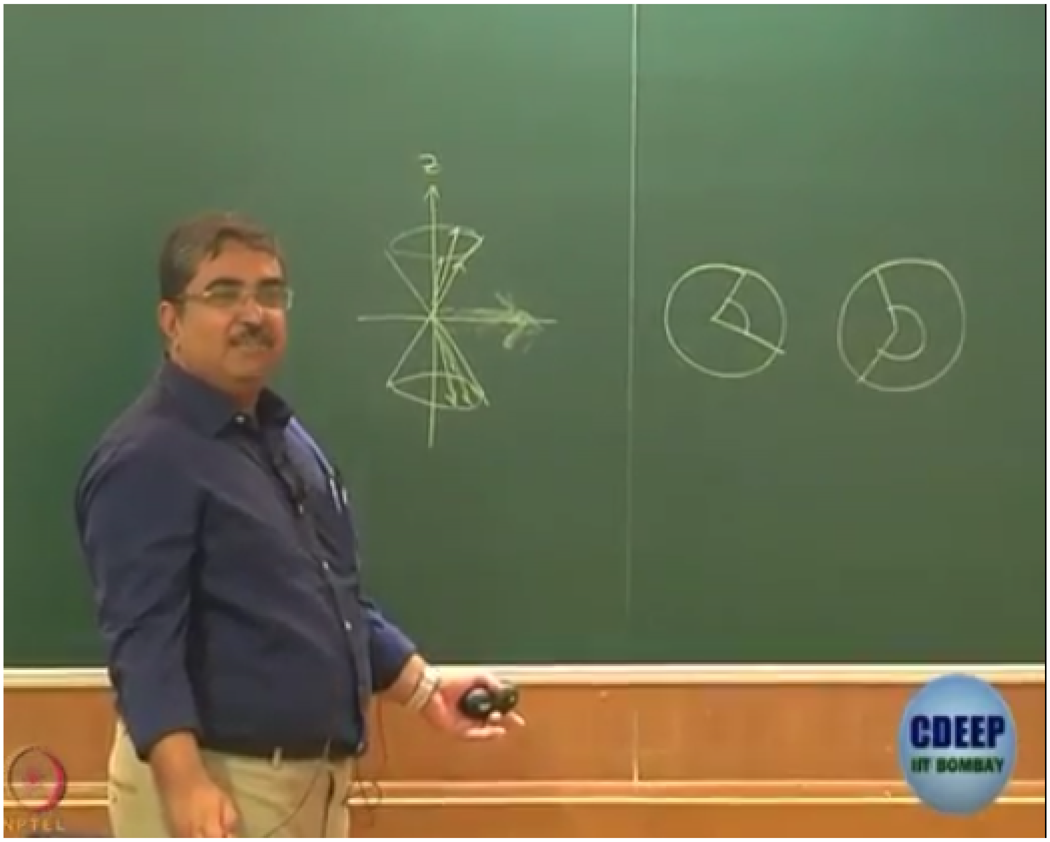

Or we all convinced that it will go down? Let us say I have 4 spins, 1, 2, 3, 4, vectors some of that, right, now I have the same 4 spins one is in this direction, one is in this direction, one here and one here, I hope it is not very difficult to see that if this is the vector sum, in this case vector sum will definitely be smaller, because some are actually getting subtracted, right, so it will become smaller, and this is a hindrance, right, because this decrease that has taken place, has taken place not because of transverse relaxation,

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but because faster nuclei have gone a little further than the slower nuclei and of course the frame of reference is a rotating frame of reference, let's not forget that, do you agree that the signal will go down over sometime?

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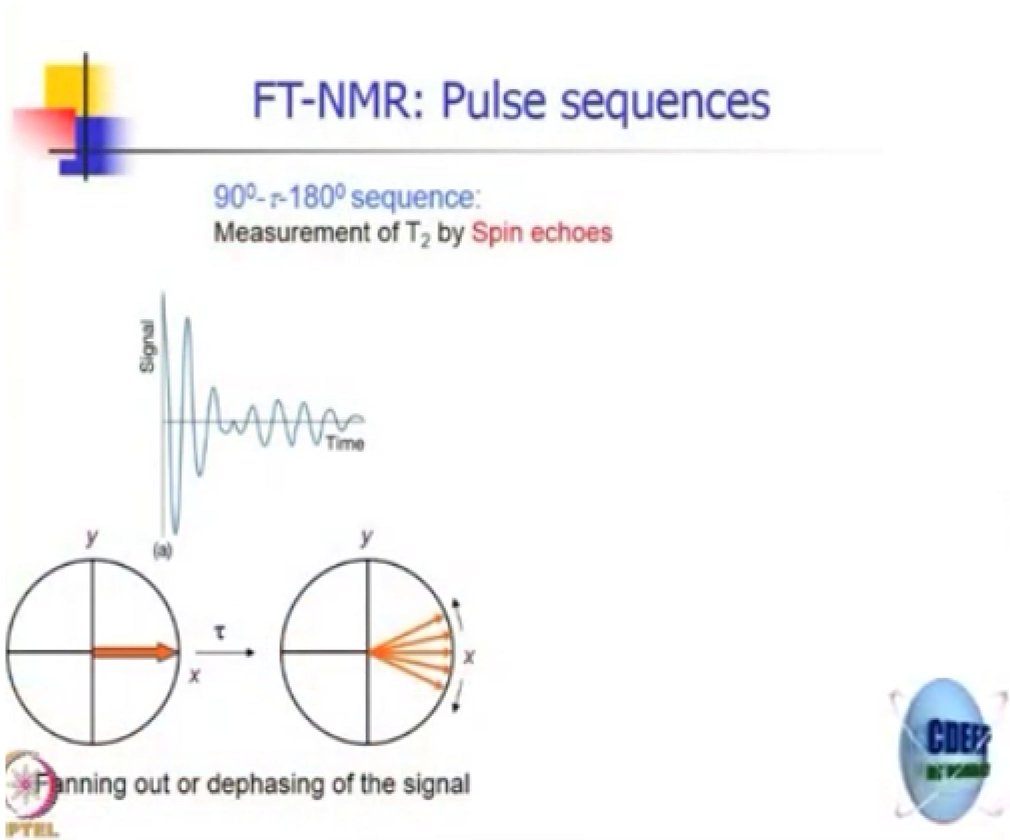

Now what we said is we apply a 180 degree pulse, along which direction do I apply the 180 degree pulse? How do I apply the 90 degree or 180 degree pulse? Do you actually use a magnet? Kajol? How do I apply the 90 degree pulse anyway? We have done some calculation right, 25 microsecond, what was the 25 microsecond? Yeah 90 degree pulse, what did we do for the 25 microsecond? No, easier than that as usual, Keerthi, what did we do for the 25 microseconds? Tetra magnet was on, which electromagnet? This electromagnet, Z direction no, okay this theta less, B1? The light was on, radio frequency was on for 25 microsecond, we keep the light on for 25 microsecond, if I keep the same light on for 50 microseconds what happens? That becomes a 180 degree pulse, right, Shoaib? So what I do is I apply a 180 degree pulse, and the reason of so much of dramatics over the last 3, 4 minutes is that we should not forget along which direction we apply the 180 degree pulse, why? Very good, why?

See if I apply 180 pulse along Y, what we've discussed the other day is that it is like C2 operations, it's like opening a door basically, think of this door, okay, think of that door, if I off course I cannot open it more than 90 degrees that's the different issue, but if I could open by 180 degrees would that sign come down or would it remain at the top? It would remain at the top, it's just that from this side of the hinge it should go to that side of the hinge, so when I apply 180 degree pulse whatever arrow is there on the top comes here, it does not go there this is the classical configuration that we always have, let us make sure we don't have it this year at least.

This is the direction, let us say this is Y or maybe we have already said this is Z, so this is Y, okay, this is one of the vectors, so you turn by 180 degrees it goes there, are we all clear with that? It's a very simple concept but it's important that we have no confusion about that, are we clear? Jaswinder clear? Very good, can we go ahead?

So here what we've said is that these are the faster nuclei, these are the slower nuclei, this is the direction of rotation, clockwise, we apply 180 degree pulse after waiting for a time tau, this is what happens, direction of rotation remains the same, but now that ship and submarine game has taken place, the faster nuclei now starts chasing the slower nuclei, right, then what will happen?
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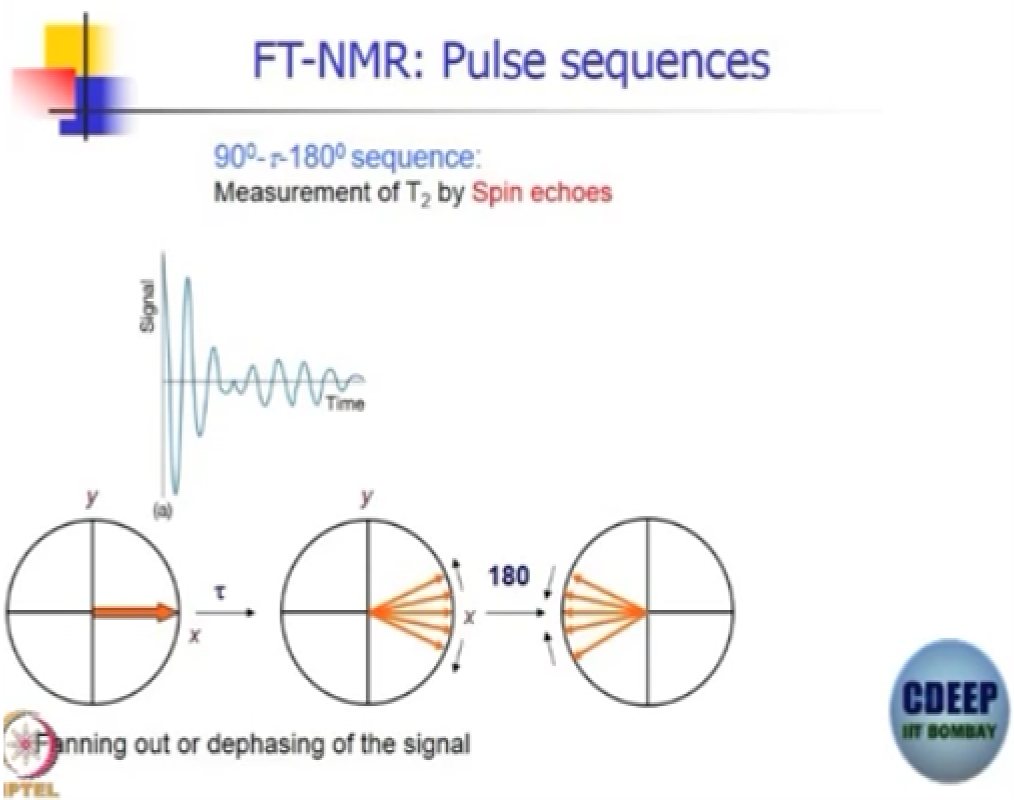

If the faster nuclei chase slower nuclei of course they are going to catch up, right, so if they catch up, when will they catch up? I had allowed for a time tau two laps between the 90 and 180 degree pulse, and this is the time for which de-phasing has taken place.

When will exact rephrasing take place? Yeah, same amount of time, yes, same amount of time, so now let us think like this, what do we expect? Let us say this is time, and this is signal intensity, I'll just write signal S, alright, so this was the signal, this is when I applied the pulse it went up, then over a period of time what will happen tau? It'll go down, okay, now I apply 180 degree pulse, what will happen? It will go up again, so if this is tau then I wait for an amount of tau, I expect it to go up all the way, is that right? So if I keep doing this experiment again and again, what do I expect? I expect the signal, signal goes down for tau, then wait for another time period tau, it should go up to the same value, then start again, instead of tau use two tau or something, signal goes up once again, so what we expect to see is that we expect to see the signal going up periodically depending on what values of tau we use, do we agree?

But do we agree completely? I'm happy that you agree, but I would be happier if you did not agree completely, why does it go up? Why does the signal go up periodically? Because you are exactly compensating for the de-phasing that have taken place, so you have accounted for two factors here. The first factor is difference in chemical shifts because of which nuclei move at different speed. The second factor is inhomogeneity of the magnetic field because of which these vectors move at different speed, wasn't there another factor? Okay, maybe I'll just show you later, so there was the third factor remember, we've talked about three factors that cause in decrease of signal, one was inhomogeneity in magnetic field, one was difference in chemical shift, what was the third? Third was transverse relaxation, by doing this, by applying this 180 degree pulse, can we compensate for transverse relaxation? We cannot, right, we cannot.

So what will happen essentially is that this signal will not go up all the way, it'll be a little less than the initial signal, and this difference is due to transverse relaxation and transverse relaxation alone, in this case it will be a little less, even less, and so on and so forth.
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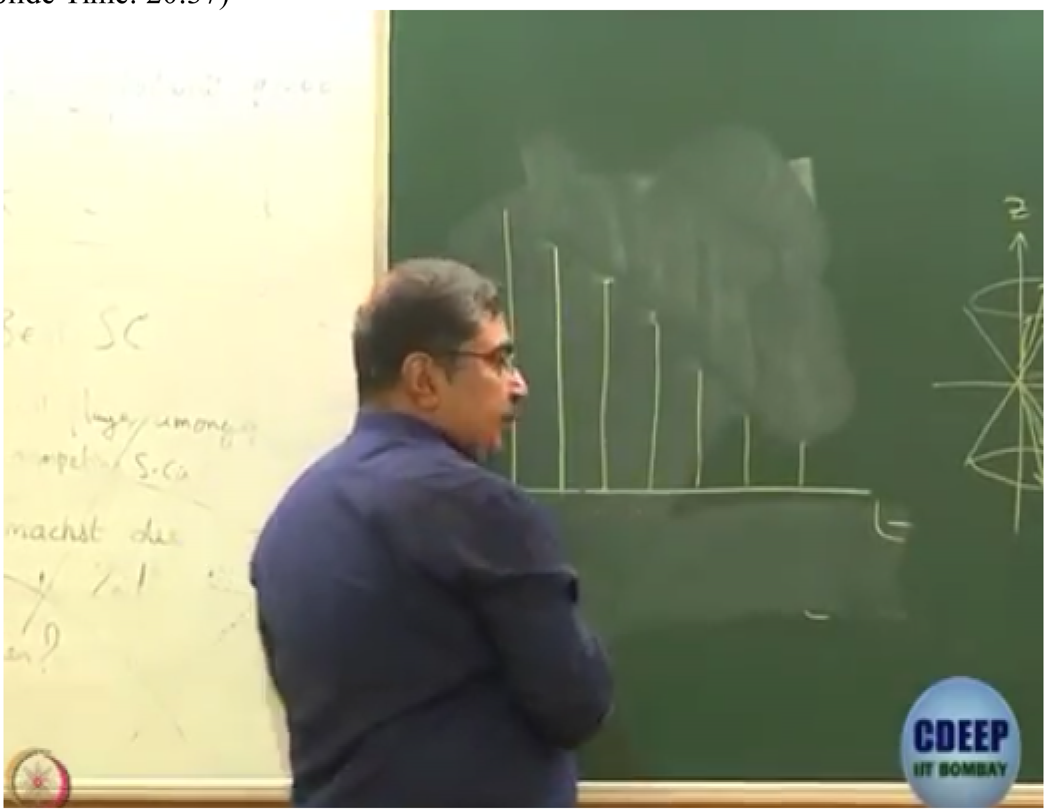

It's actually this is the kind of signal that you get when you use a 90 tau 180 sequence, okay this,
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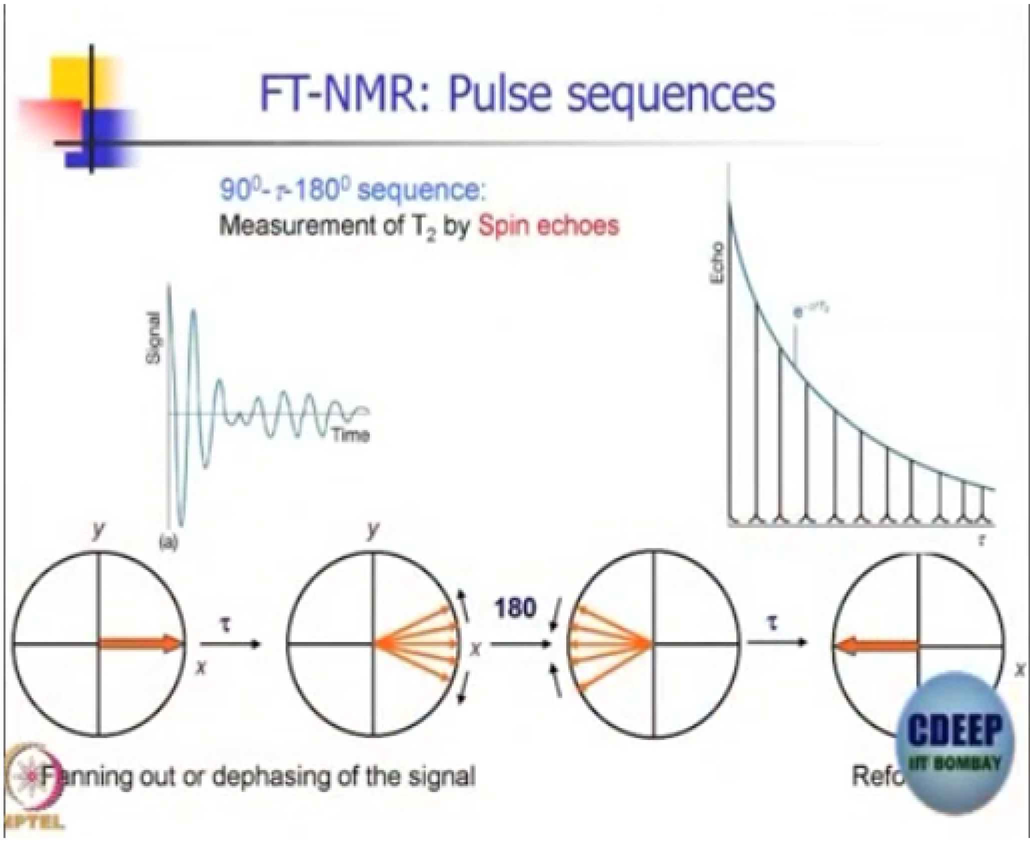

and in each step the decrease in the signal is purely due to transverse relaxation.

So now if I join the tips, then I'm going to get some kind of a decay, that decay is due to transverse relaxation, the simplest case scenario you can fit it to an exponential function, the time constant that you get is the transverse relaxation time. What is the technique I told you? It's called spin echo, right, do you understand why it is called spin echo? We have studied echo in physics, and if you have gone to hill station or some such place we've heard echo our self, how does echo work? Yes, but do we hear it in the same intensity? No, intensity keeps going down right and in fact sometimes what happens is first you hear a higher intensity, then it falls off, why does it decrease? Why is it that echo does not stay there all the time? So how? Because the rock that is there that absorb some energy right, so now see if you could measure the intensity of sound and just plot, what that would give you is similar kind of an exponential decay perhaps that would give you an idea about absorption of this sound by the rocks, okay, similar thing happens here, this is called spin echo technique.

And the reason why we have to use pulse sequences is that we have to eliminate the other two factors if you are going to talk about transverse relaxation and transverse relaxation alone, right, if there is a question this is the time to ask. Do you have a question? If not let me tell you that this is the beginning of some other technique as well, it is called photon echo technique, we have talked about this ultrafast processes and all, and the technique we discussed is the simplest of it, simplest of the technique that are there transient absorption, but then for more involve calculations similar kind of technique exists for photon echo as well, so professor Graham Fleming of Berkeley was one of the pioneers in photon echo spectroscopy, and it is inspired from the spin echo of NMR.

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