Advanced NMR Techniques in Solution and Solid-State

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Module-34
T1 Relaxation Mechanisms and T2 Relaxation
Lecture – 34

Welcome all of you. Since the last class we have been discussing about relaxation; why last class, since the last two or three classes we discussed a lot about relaxation mechanisms, relaxation phenomena. I introduced T1 and introduced what is the concept of T1 especially spin lattice relaxation, how the spins lose energy with the lattice and what is the mechanism of relaxation, what are the fluctuating fields, what is the frequency of the fluctuating field.

We discussed a lot about the spectral density function, correlation time tau c; how they are related and also correlation time depends upon the size of the molecule, varieties of things we discussed and we understood lot about relaxation phenomenon, mechanism of relaxation like dipole-dipole interaction, chemical shift anisotropy interaction, quadrupolar relaxation, spin rotation relaxation, etc. These are the various mechanisms that aid relaxation, especially spin lattice relaxation which makes the spin to go back to thermal equilibrium. Then I introduced what is called as spin lattice relaxation; sorry spin-spin relaxation which is again nothing but dephasing of the magnetization vectors in the XY plane, bring the magnetization from Z axis to XY plane, instantaneously there is the phase coherence.

All the magnetic moment vectors are aligned in the particular axis. Bring the magnetization by applying 90 degree pulse from Z to X axis. All of them are along X axis all the nuclear magnetic moments spins, but because of the local fields fluctuating fields, the spins will start dephasing. They will lose coherence, phase coherence; slowly they will start losing phase coherence, go around in the XY plane.

And if we take the vector addition of all those things, as time passes by the intensity of these vector addition of the total magnetization keeps coming down, coming down. After a particular time when the spins completely fan out in the XY plane, there is complete decoherence and if we take the vector addition of all these magnetic moments you will not see any signal; it will be 0.

And this is the time which is required for the complete decoherence of the magnetic moment vectors in the XY plane, called spin-spin relaxation time. The time required for that is called spin-spin relaxation time; that is what I said. Now I also said for small molecules T1 is approximately equal to T2 and all those things.

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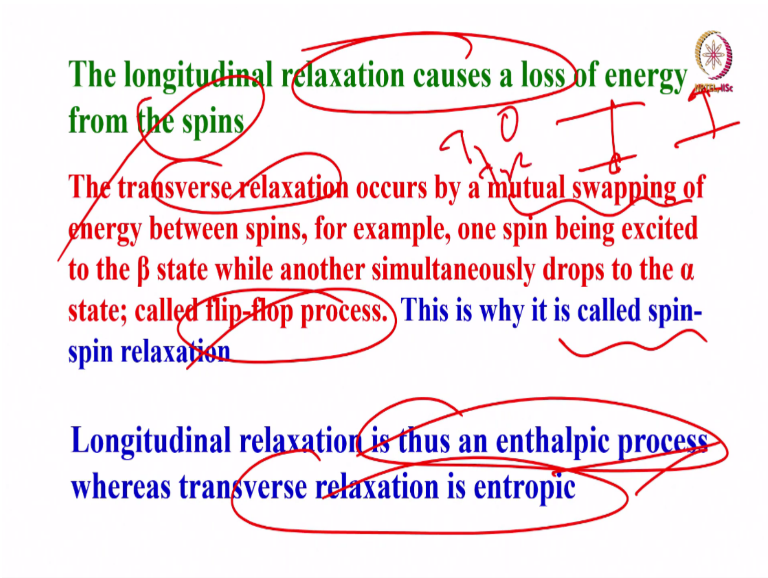

Now we will continue further today. The longitudinal relaxation causes loss of energy from the spins to the lattice, the transverse relaxation occurs by a mutual swapping of the energy between the spins. For example, one spin in the excited state can come to beta state, while another drops to the alpha state. You see one spin, let us say, from alpha can come to beta from beta it can go to alpha.

See it can happen simultaneously mutual swapping of the energy between spins can take place. One spin being in the beta state can go to alpha state, alpha to beta state can happen. This is called flip-flop process. Flip and flop simultaneously spins from alpha can come to beta; then another spin because of this interaction can go from beta to alpha. And this is why it is called spin-spin relaxation.

One spin aid in other spin to undergo relaxation, this is called a flip-flop process and it is called spin-spin relaxation. Longitudinal relaxation is thus an enthalpic process; whereas transverse relaxation is a entropic process. Please remember this is entropic process longitudinal relaxation is an enthalpic process. And of course you know what is enthalpy everything, you would have understood, there is no point in going with the details of that. At least remember T1 is an enthalpic process and T2 is an entropic process.

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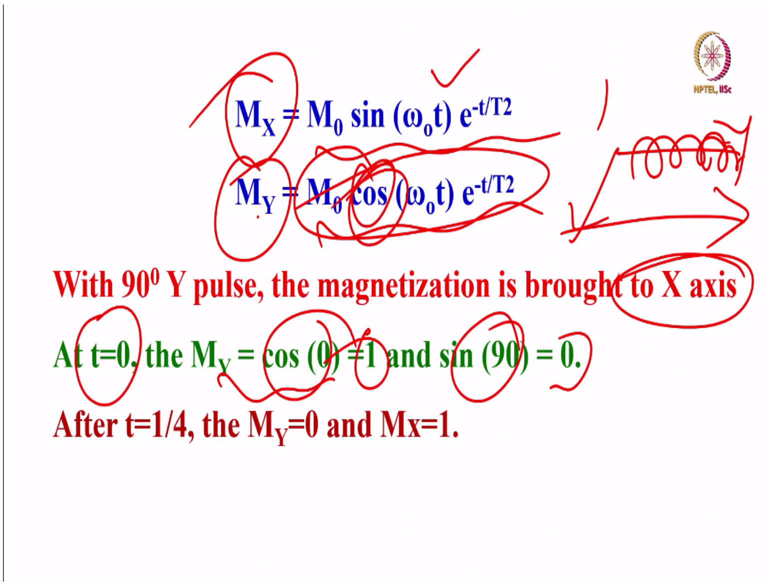

So, now you can work out the decay of the magnetization in the XY plane. We can have two components sine component cosine component; and Mx and My component I consider, and M0 into sin of omega 0 t into e to the power – t / T2 and M y is a cosine of it. And of course depending upon where you are keeping the receiver. If my receiver is along X axis, then this will become cosine if the receiver is along Y axis this will become cosine; does not matter so depends on the convention.

In this case receiver is along Y axis this is Y axis and this is X axis taken; so this is M0 cos omega 0 t into e - T2. This is where My component this one is Mx component. So, with a 90 degree Y pulse the magnetization is brought to X axis at t = 0; My = cosine of 0 at t = 0. So, cosine 0 = 1 and sin 90 is 0. So, only one component is present My component is present immediately after t = 0 that means my receiver is along Y axis you get maximum signal.

And there is no other component at all because sin 90 is 0; and after certain time what will happen other component starts developing; they will also start coming up. After time t = 1/4 the My component = 0 and Mx becomes 1; we will work out from this equation by simply plugging in the values; it is a simple number, simple arithmetic you can do.

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The $e^{-t/T2}$ represents the fanning out of each vector in the XY plane

Time (t)	Amount of coherence left (%)
$t = T_2$	36.8
$t = 2T_2$	13.5 %
$t = 3T_2$	4.99 %
$t = 5T_2$	0.007 %

And you will see that e to the power of – t/ T2 represent the fanning out of each vector in the XY plane. So, it decays exponentially, that is what I said. The magnetization growth along Z axis is also exponential; the decay in the XY plane is also exponential. That is given by 1 – e to the power of – t / T1, it is e to the power of – t / T2; it is a decay. Now again put this value here let us see what happens, if we put t = T2 now 36.8%, but earlier it was 1 – something was there it was 63%.

Now it is, t = 2 if you put it here, you will find out it is going to be 36.82; and t = 2 T2 is like 13.5%, t = 3 times T2 is 4.99 after 5 times T2 it is 0.007. See the total magnetization if you take T2 is some value, let us say some 2 milliseconds; then 5 times T2 if you wai,t after 10 millisecond almost entire magnetic moment vectors would have completely undergone dephasing; there is no coherence at all. It is almost zero magnetization there in the XY plane. This is again just plugging in of the number I did that.

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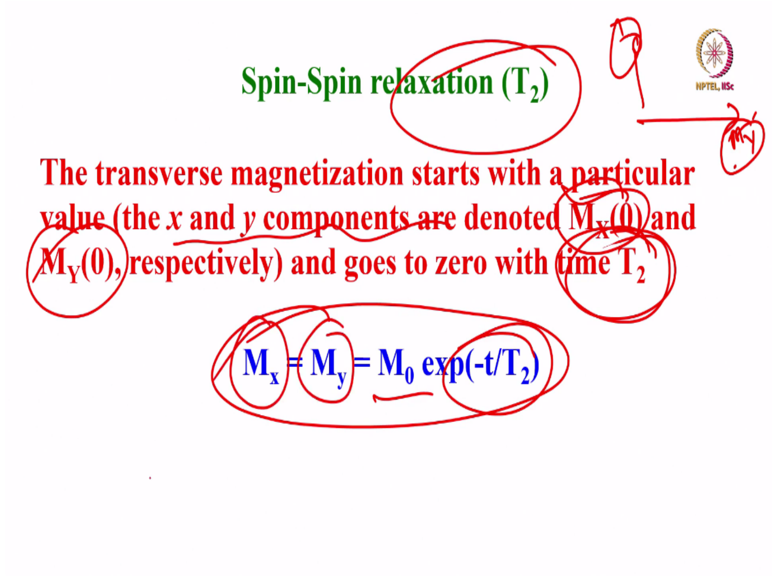

So, more about spin-spin relaxation T2. Transverse magnetization starts with a particular value x and y components denoted as Mx = 0; My = 0 and goes to 0 with time T2 that is what it is. Initially when it come here full magnetization, let us say, this is My is maximum; Mx is 0. After sometime you will see that it starts changing I told you in the previous equation plug it in after 1 / 4 of tau value then this will become 0, this will become maximum.

And undergo rotation like this; and then it goes to 0 completely with a time T2. So, in other word Mx and My can change based on this equation; it is given by Mx = My = M0 into exponential – t / T2. This is an equation for measuring T2; earlier equation was for measuring T1. Here you have to measure Mx component or My component, does not matter and this is given by this equation.

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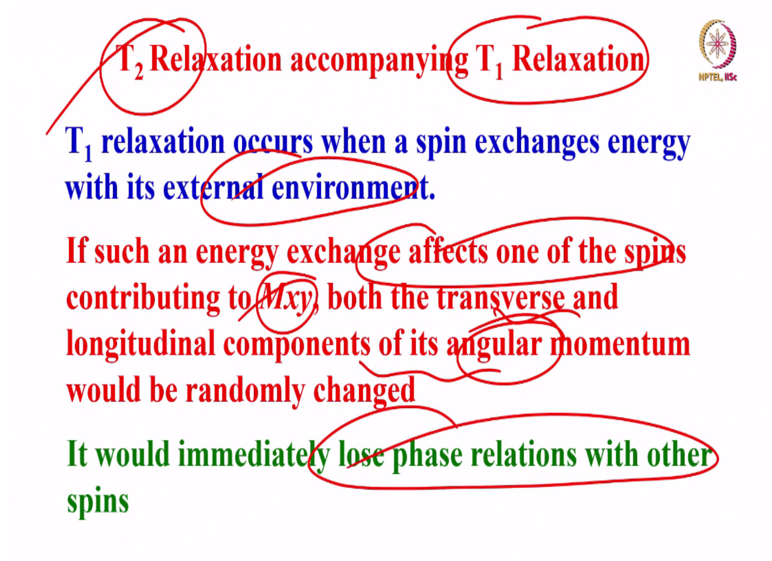

So, T2 relaxation always accompanies T1 relaxation; that is point you must remember. T1 relaxation occurs when a spin exchanging energy with the environment, that is lattice it gives to the surroundings. When it exchange energy with the lattice, with the surroundings; T1 relaxation occurs and if such an energy affects one of the spins contributes to transverse magnetization Mx or My. Then both the transverse and longitudinal components; see angular momentum would be randomly changed, simple logic you understand. T1 is an exchange of energy with the environment. Let us say at that time if one such exchange mechanism affects the spins which is contributing Mx or My; XY component let us say; in which case what happens the longitudinal relaxation mechanism also affects transverse relaxation mechanism.

Both can take place, because some component of the angular momentum gets changed randomly; because of this T2 relaxation accompanies T1 relaxation. As a consequence, it will immediately lose phase relation with other spins.

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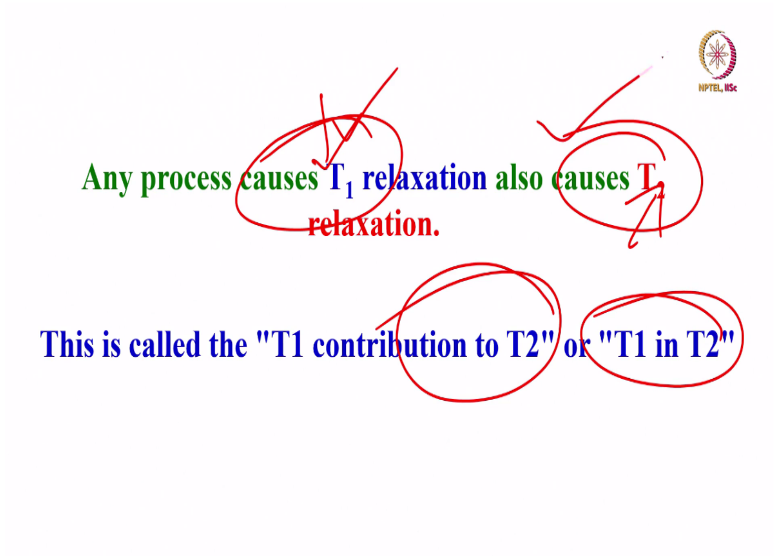

So, any process that causes T1 relaxation also causes T2; that is T1 relaxation and T2 relaxation processes go together. Any process which causes T1 mechanism also causes T2 relaxation. This is why it is called T1 contribution to T2; or T1 in T2; it is a word. Remember this is a definition T1 contribution to T2 or T1 in T2; means any process that causes T1 also causes T2 relaxation.

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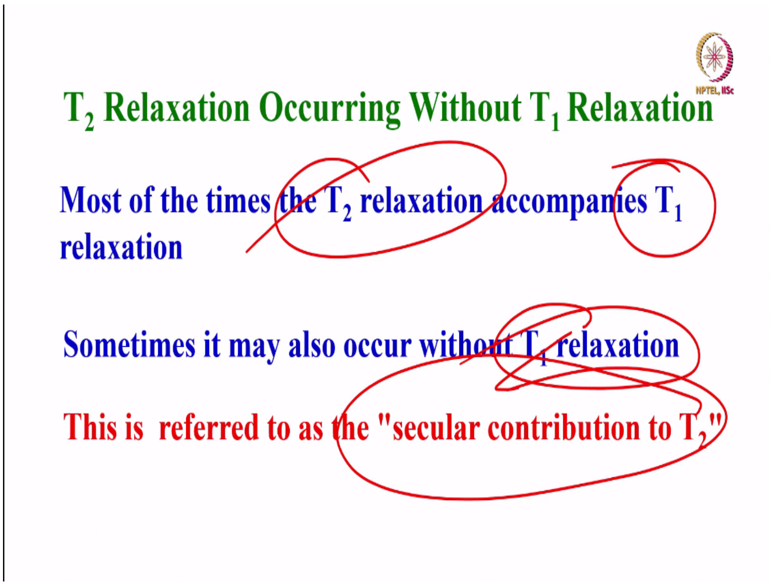

Now you may ask me a question; any process which causes T1 causes T2 that is fine, can there by a T2 process without T1? Can there by a process? All T1 processes will affect T2, I agree, but can there be T2 without T1? Of course most of the time T2 relaxation always accompanies T1, but there are one or two examples. Sometimes it can happen; not always let us not go into the details of this because T1 relaxation phenomena is the biggest and toughest topic to understand in NMR; a lot more to understand, lot more to discuss.

We will not go into the details of that please understand sometimes T2 can also occur without T1 relaxation. Then this is called secular contribution to T2. This is a statement I am giving you just to understand; always in all the book you read T2 accompanies T1. There are examples T2 can also occur without T1; that is called secular contribution to T2; when T2 accompanies T1 it is called T2 in T1.

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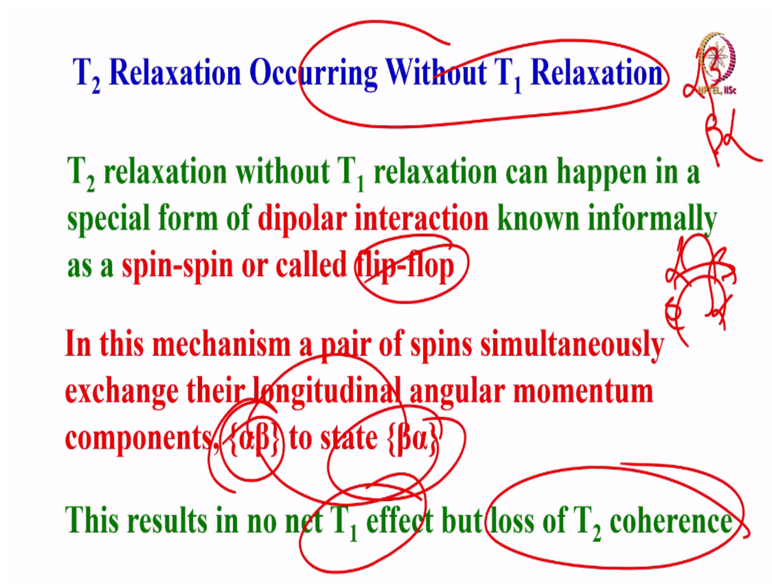

So, now what is that T2 relaxation occurring without T1 relaxation. This can happen only because of one form of dipolar interaction, called flip-flop interaction. The flip-flop interaction is alpha beta spin go to beta alpha state; in which case alpha is going to beta and beta is going to alpha, because alpha is going to beta and vice versa, I said this as flip-flop process; one of the spin flipping process.

Here simultaneously one is going up other is coming down, alpha is going to beta, beta is coming to alpha. This is called flip-flop process. This is called spin-spin interaction, also dipole interaction called flip-flop interaction. This can happen only in such situations. If the pairs of spins simultaneously exchange the energy, the longitudinal angular momentum components like alpha beta to beta alpha states, there will be transition.

This results in no change in T1, but causes loss of T2 coherence. It can happen remember several phenomena I explained today. T2 always accompanies T1, T1 any process which affects T1 will also affect T2 most of the time, but there can be T2 without T1; it can happen one such example is dipole-dipole interaction; where alpha beta spin state changes to beta alpha spin state; it is called flip-flop processes, it can happen that can also cause.

So, T1 process affecting T2, that is T1 in T2; sometimes T2 can also occur, without T1; that is called secular contribution to T1. So, the mechanism for that to occur is flip-flop process.

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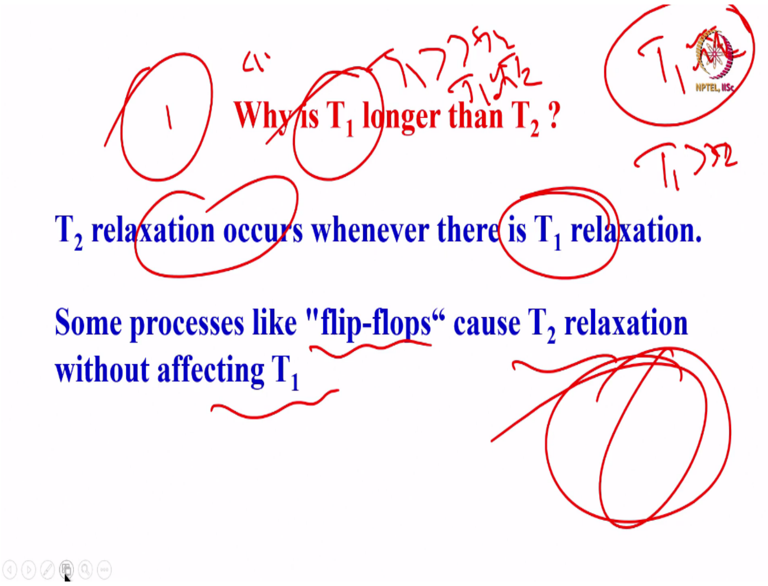

So, next thing is T1 is always equal to T 2 in solution state, I told you approximately and T1 can never be shorter than T2. This is always the case. You will never find situation where T1 is shorter than T2, because spin lattice relaxation T1 is very much greater than T2 or approximately equal to T2 in solution state; that is what I said.

That means T1 relaxation occurs whenever there is T2 relaxation. Only some process like flip-flop cause T2 relaxation without affecting T1. Why T1 is longer than T2? It is a simple logic; unless the magnetization of the XY plane completely undergo decoherence there is no growth along Z axis. XY magnetization unless it decays how can it grow along Z axis? so it has to decay first.

So, for T2 first magnetization has to completely undergoes decoherence, that is why T1 is always longer than T2. Very rarely you will find situation T1 is equal to T2, but it can happen most of the time in solution, but by and large you can always remember T1 is always larger than T2 in solution state. Next we will go further.

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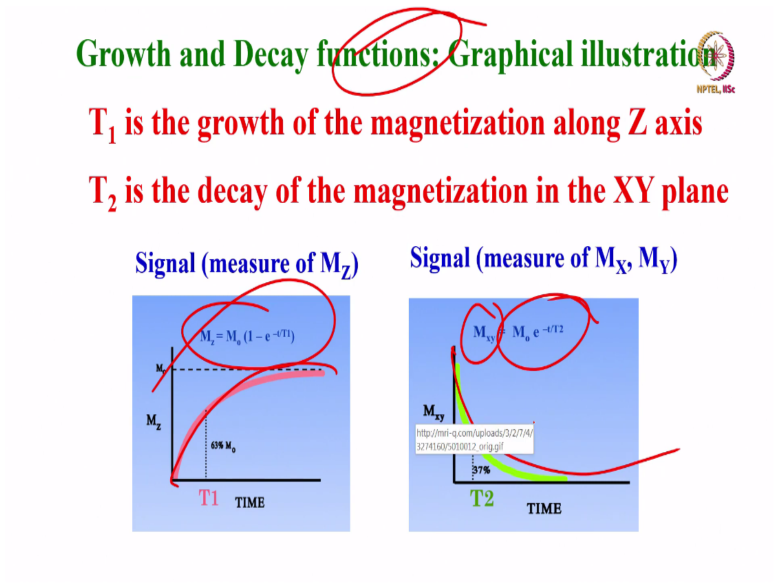

And this is a graphical representation of the growth and decay functions. T1 is the growth of magnetization and exponential it is growing; T2 is the decay of magnetization in the XY plane this is Mxy which decays like this; Mz grows like this, with this term. Diagrammatically both can be shown one is exponentially increasing function other is exponentially decreasing function. Exponentially decreasing function is this one.

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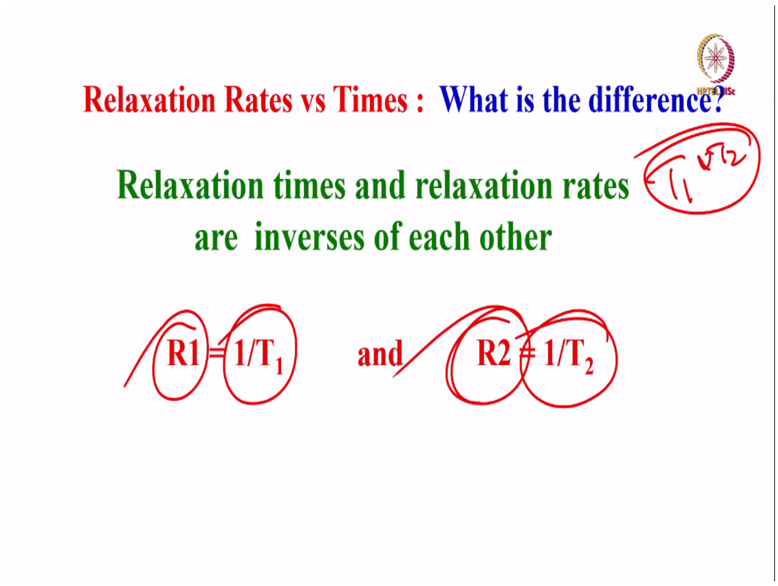

So, relaxation rates versus time if we consider sometimes in some books they use relaxation rates and relaxation times. What is the difference between relaxation time and relaxation rate? Relaxation time is what you are going to measure by doing an experiment T1 and T2 you can measure by doing certain experiments. I will show you how to measure it now, in this class if there is time, I will show you what an experiment we do to measure T1 and T2. And these are called T1 and T2 is called relaxation times.

If I say T1 is 10 millisecond, it the time of 10 millisecond for the spins to lose energy with lattice that is 1. What is the relaxation rate, rate is inverse of this relaxation time, see this is denoted by terms called R1 and R2. R1 is relaxation rate which is inverse of T1 and R2 is relaxation rate is inverse of T2. In some of the biology studies you can see people mentioning in the paper or in books R1 and R2. R1 and R2 are nothing but inverse of T1 and T2, you please remember this.

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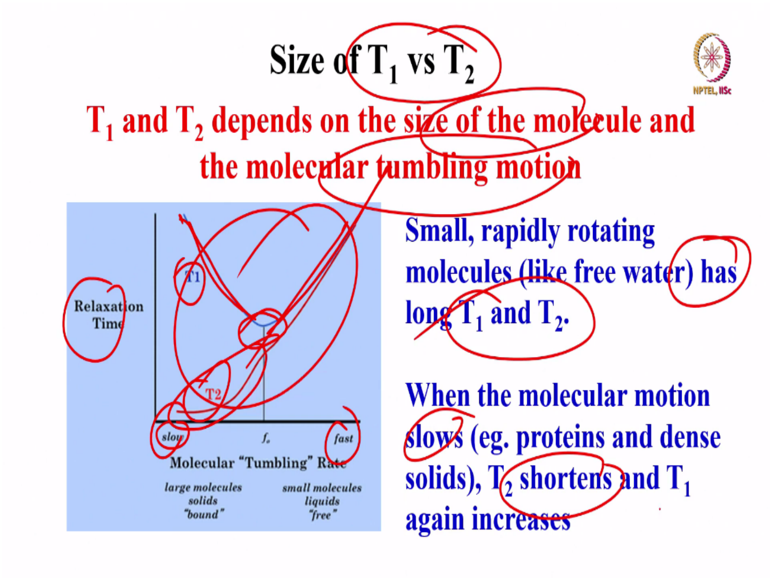

So, now size of the T1 and T2 of course I told you what is T1, what is the size of T1. Approximate value of T 1 in solution state it varies from microseconds to seconds, minutes, hours. And of course this is just a general statement. It is not always true it can vary, it varies from molecule-to-molecule, spin-to-spin, depending upon size of the molecules. And of course and in the magnetic field you are doing experiment etcetera. So, we should have the idea about size of the T1 and T2. T1 and T2 depends upon not only on the size of molecule, but also on the molecular tumbling motion; two factors, it depends upon size of the molecule and on the molecule tumbling motion, both. So, you can see here this is what we saw earlier in the relaxation time if you measure this is T1 and this is T2; as the molecules undergoes slow motion here. T1 is longer as the motion rate becomes faster and faster, it decreases in intermediate regime T1 is very small. Again when the molecular undergoes fast motion it goes up. Similarly T2 it is like this, slow motion T2 is longer as the molecular motion becomes faster and faster T2 becomes smaller and smaller; this is what it is. So, this is slow motion and this is the fast motion and this is how T2 will change this is how T1 will change.

So, when the molecular motion slows T1 shortens, and T1 again increases again. For small rapidly rotating molecule like free water T1 and T2 are very long. So, these are the important things you should know that.

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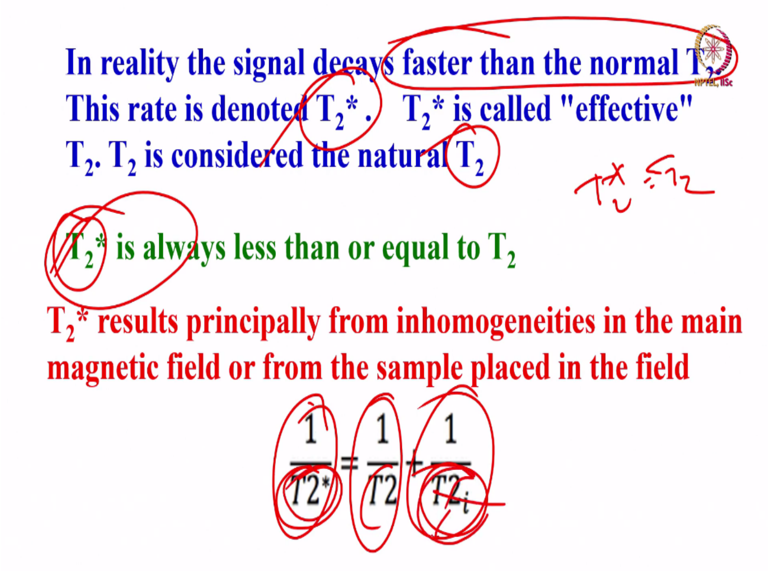

In reality, the signal decays faster than the normal T2. See we say signal decay in the XY plane; that is a T2. Does it comes only because of this spin-spin relaxation mechanism or two spins exchanging the energy? is that is the reason why it is decaying. There can be various other factors which contribute for this. For example there could be magnetic inhomogeneity. Magnetic field inhomogeneity that can contribute for the spins that can also give fluctuating fields at the site of the nucleus, that can cause dephasing.

In reality, the signal will decay faster than the normal T2 because of various other parameters. So, the actual T2 what you measure is not the real T2. So, that is why this is called effective T2 called as T2* ; it is called effective T2. So, this T2 is a normal T2; then how do you get the normal T2 ? when you know T2*. T2* is always less than T2 because it decays faster because of external phenomenon. If there is less external phenomenon there is no disturbance from the other magnetic field inhomogeneity etcetera then what will happen at the most T2* can be equal to T2; it can happen. Otherwise generally T2* is always smaller so then how do you find it what is T2 *? It comes from various inhomogeneity of the magnetic fields when place this sample in magnetic field, so generally T2* is obtained by equation called 1 over T2* = 1 over 2 + 1 over T2$^{i.}$ These are all the contributions from various things what it mentions is the T2* and the actual T2 this is inhomogeneity contributions.

$T2^i$ means contribution coming because of other inhomogeneities of the magnetic field. So, real T2 if I want to calculate you should know T2* and you should know this thing; or we should at least eliminate these terms to get real T2.

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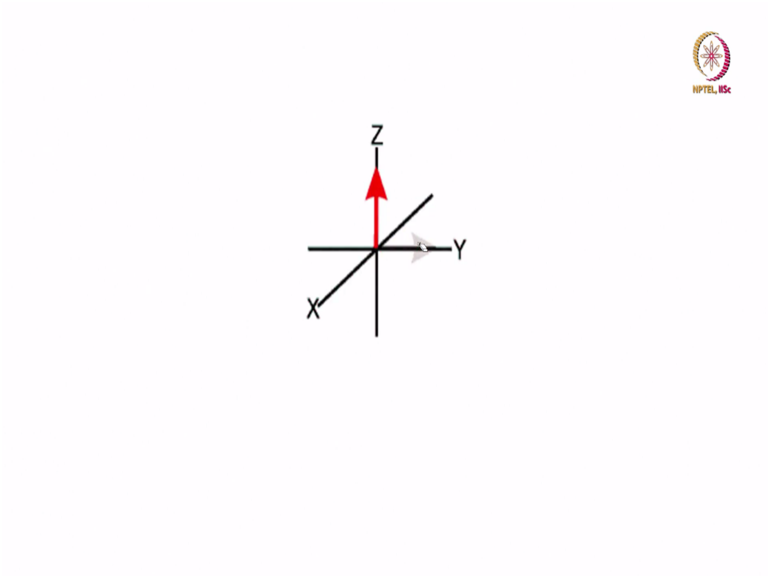

So, this is a diagrammatically what happens for the nuclear spins. You bring the magnetization to XY plane; see what is happening as it comes down it is dephasing in the XY plane. It is coming down in intensity simultaneously it is going up you see what is happening to the magnetization. You have brought to XY plane and then at any given extent of time immediately as soon as you bring it the magnetization is maximum and at any given time keep on decaying in the XY plane and goes along this. So unless it decays completely it cannot go along Z axis that is why I said T1 is always longer than T2. So, this is a phenomenon simultaneously happening; look at it while decaying it is also growing simultaneously.

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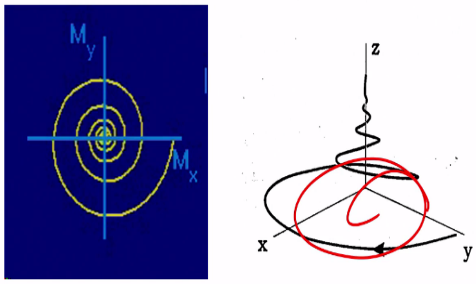
Visualisation of the process of T_1 and T_2



T_1 and T_2 occur simultaneously

These are simultaneous phenomenon. If you visualize a process of T1 and T2 actually this is how it sees, we should visualize the process it appears when it is decaying like this simultaneously it is going up and up; it is like a spiral. If you visualize this thing from the top here it is decaying in the XY plane simultaneously it is going up. It is like you have an umbrella closed and invertedly.

Let us say I open the umbrella first take an umbrella completely open it, spread it along XY plane. Now that means the magnetization has been brought to the X axis and now slowly I am closing the umbrella it will starts growing along Z axis; the vertical component in the umbrella starts going up. Initially it will be spread here and slowly start closing up.

Open and close it is like fanning out the nuclear spins when umbrella is open is when umbrella is completely closed then what will happen magnetization is growing along Z axis. Exactly the phenomenon, when it goes like this it keeps reducing like thi,s like this, like this, like this and then get closed. This is as if spiral is going with intensity coming down in the XY plane simultaneously growing in Z axis. This is how both the phenomena are simultaneously happening and that is how we have to visualize T1 and T2.

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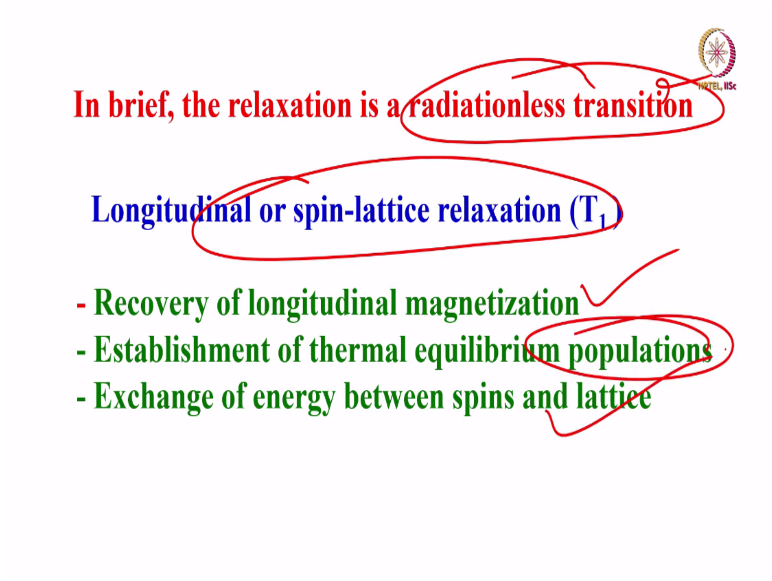

In brief we have discussed a lot about relaxation concepts, relaxation phenomena etcetera. Now let us take some summary of these things and then go for measurement of T1 and T2. In brief, remember relaxation is a radiationless transition; it will not give rise to signal detection. It will only aid the spins to relax; to decay in the XY plane and grow along the Z axis.

We saw it corresponds to energy state of the spins and the lattice, spin in the upper state the come down, then the spins in the lattice lower states will go up, spin in upper state will come down, lattice will go up; all these exchange phenomenon is going on, but then remember it is not giving rise to magnetization for detection. It is a radiationless transition, so relaxation is a radiationless transition. Now what you call longitudinal spin-spin relaxation it is called T1 it is nothing, but the recovery of the magnetization, or establishment of thermal equilibrium of populations and it is a exchange of the energy between the spins and the lattice and the various phenomenon for this thing we discussed.

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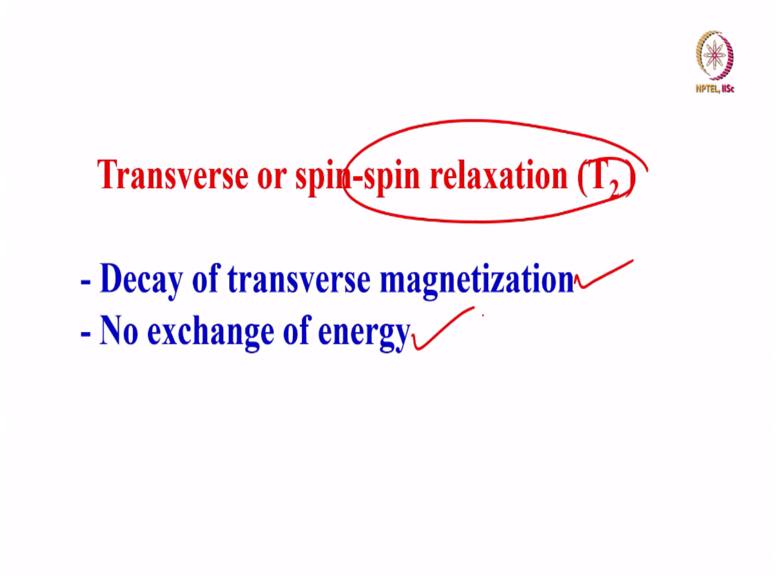

Again transverse relaxation T2. It is a decay of transverse magnetization in the XY plane and here there is no exchange of energy of the spins with the lattice. It can only happen when one spin exchanges energy with the other spin.

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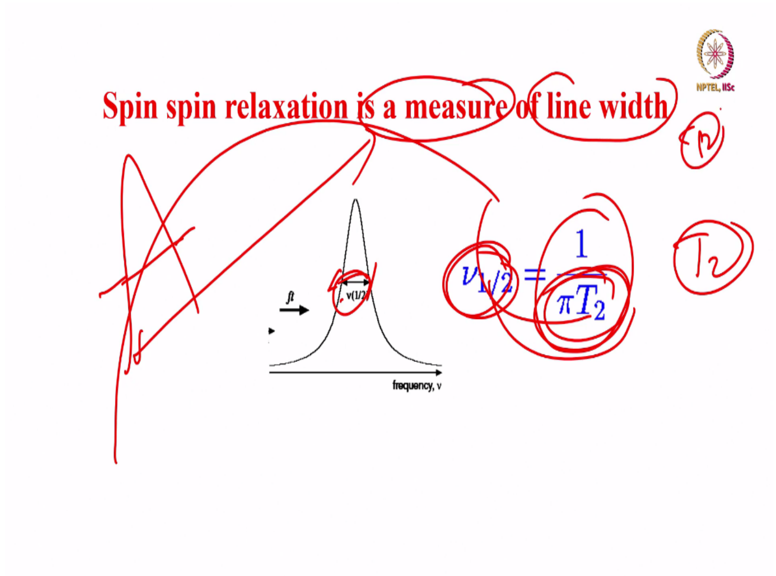

And then if I look at the NMR spectrum very clearly, looking at the width of this peak, I can get a rough estimate of the spin-spin relaxation. The spin-spin relaxation is nothing, but the measure of the line width. See this is the line width of a spectrum, I know what is the line width nu half. I f I know the width of the full width and half height; nu half, this is equal to 1 over pi times T2.

So, if I take a spectrum measure the line width here, and take 1 over pi times the line width then you are going to get T2 approximately. So, the rough guess is you can measure the spin lattice relaxation time by knowing the line width, very easy, very straightforward we are measuring T2, but of course it is the approximate value. If you want to measure accurately you have to remove field inhomogeneity contribution, etcetera there is a complicated experiment one can do. We will come to that later. But this you should remember, in case if you are going to get a very broad signal, obviously it means that T2 is very small, very broad this will bring it down, this will go up; T2 will be very short. Spins are relaxing very fast dephasing very fast in the XY plane. As a consequence, you are going to get a very, very broad signal. T2 is very short means broad signal. This is the important thing you should know.

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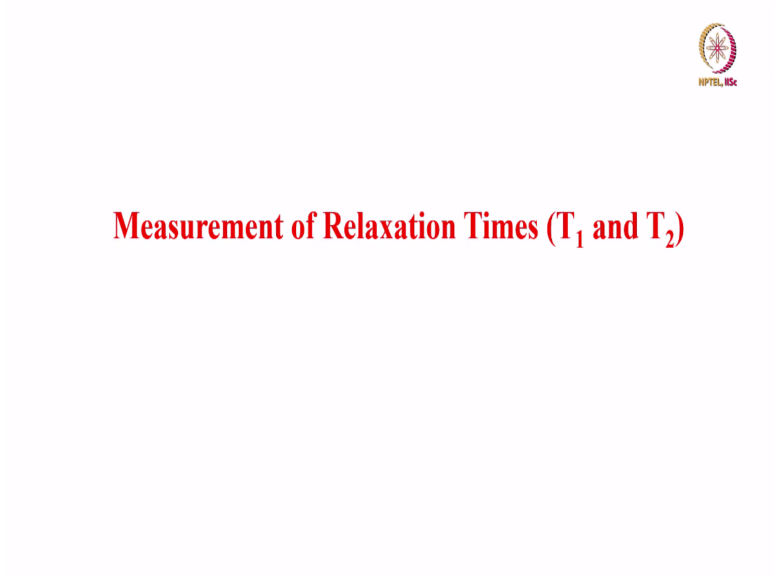

Now we will go into the measurement of the relaxation times T1 and T2. How do you measure these two relaxation times? So far conceptually we understood, approximately we measured what is T2 by looking at the line width; fine, but we have to precisely measure T1 and T2, get accurate values; how do we do that?

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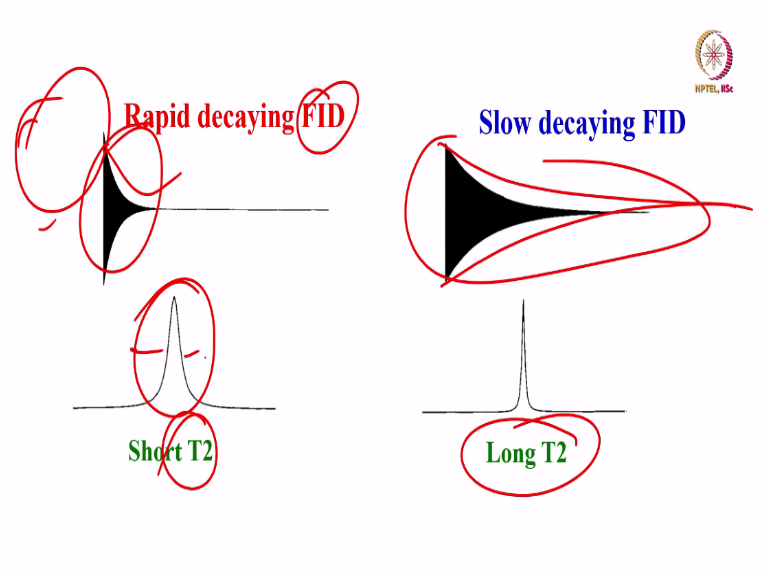

So, before that; I told you T2 is a measure of line width. Now the line width is what it is because of the free induction decay, time domain signal. In the Fourier transformation we understood time and frequency are inversely related to each other; they are related by Fourier transformation. If the signal is decaying very slowly in the time domain, the peak in the frequency domain is very, very sharp. If the signals decays very fast in the time domain, it will be very broad in the frequency domain. This is in the Fourier transformation, when we introduced the theory we understood lot about the Fourier transformation, you please remember, we discuss these points. So, now look at the signal like this; I have two FIDs this is the rapidly decay FID; and you get the short T2, that shows it is decaying very fast; and spins in the XY plane has dephased very fast; that is called short T2. Short T2 means the spins have dephased very fast in the XY plane. Look at this FID this is a long decaying FID, slow decaying; it takes more time to decay means long T2. So, longer the time the spins takes to undergo decoherence in the XY plane, the sharper the lines you are going to get. This thing you should remember. So, that is why looking at the free induction decay you should understand what is the line width. This way I said line width is approximate measure of T2.

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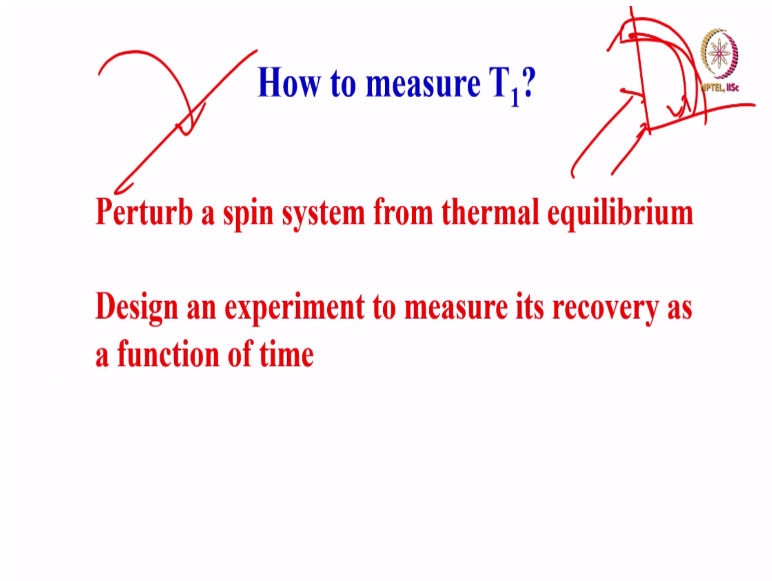

So, now how to measure the T1? First of all, simple mechanism put the sample in this magnetic field, wait for some time to see the signal. Then as soon as you put the sample keep on pulsing rapidly very, very rapidly till you see the maximum signal. It is practically very difficult I cannot do the pulsing so fast and we do not know when you will reach the maximum signal how much time it takes like that. Other way out is to disturb the spin in the thermal equilibrium apply radio frequency pulse bring the magnetization from Z axis to X axis. You have perturbed it and then design an experiment to see how much time it takes to go back; that is the simple experiment. Disturb the spin system, bring the magnetization in the X axis or Y axis, now it has to go back. Design the experiment to measure the time it takes to go back to Z axis to achieve thermal equilibrium.

It has to recover as a function of time; measure this time, measure the time it requires to go back to Z axis, then you will understand, you can measure what is T1.

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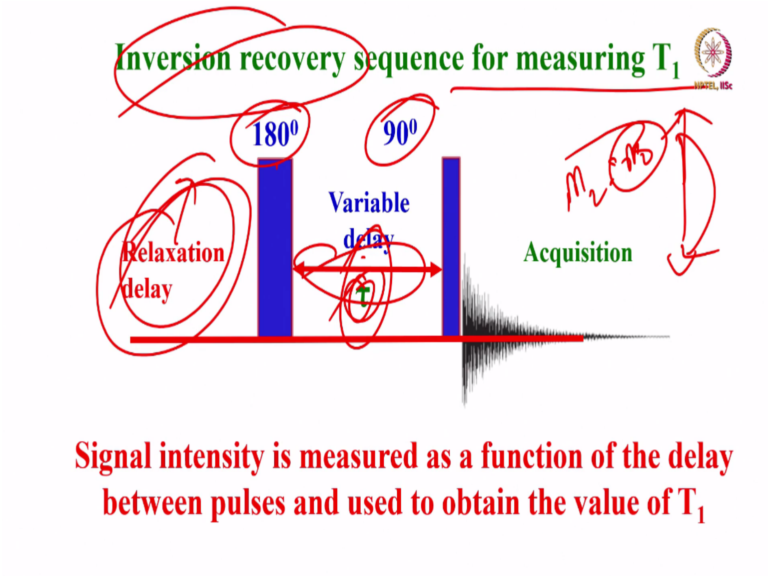

All I do is a simple experiment like this. There are four, five different experiments to measure, viz., progressive saturation, saturation inversion, null method or inversion recovering method, varieties of experiments are there. I am not going to give details of all the different experiments and you can choose experiment depending upon the T1 whether your sample has a longer T1 or a shorter T1 etcetera.

But basically commonly used experiment is the inversion recovery experiment for measuring T1; especially in solution state, which are for short T1; not when the T1 is of the order of days and hours; you cannot do that. There is a different method for that, but in most of the times solution state T1 and T2 are of the order of few milliseconds or seconds you can use an experiment called inversion recovery sequence and measure the T1.

So, it is a very simple two pulse sequence; first pulse is a 180 pulse and second is a 90 pulse. Initially before application of 180 pulse all the spins are in thermal equilibrium, give enormous time, give a delay, make sure that spins attain the thermal equilibrium. And then apply 180 pulse; What does 180 pulse do? Bring the magnetization from Z axis to – Z axis, it will be tilted by 180 degree. Then give some delay and then apply 90 degree pulse, and start acquiring the signal. Now, what you do is; do not do one experiment; keep on varying the delay, N number of experiments we have to do. Every time vary the tau delay and measure the intensity of the signal, and then use these different intensities obtained for different tau values; and then fit to a function; there is a function which I told you M z = M 0 into 1 – e to the power of – t / T1 fitting into that equation you will get the T1 values.

It is a very simple thing because you know tau you know Mz and you should get what is the equilibrium magnetization. Equilibrium magnetization is something a system has attained thermal equilibrium and full magnetization is available and then keep on varying the delay and see that intensity; initially it will be – Z starts growing slowly and after certain time it will again come back to M0; – M z it will become + M z; which is nothing, but equilibrium magnetization M0; then at different values of the intensity of the peaks is fitted into this equation, you can measure the T1 accurately.

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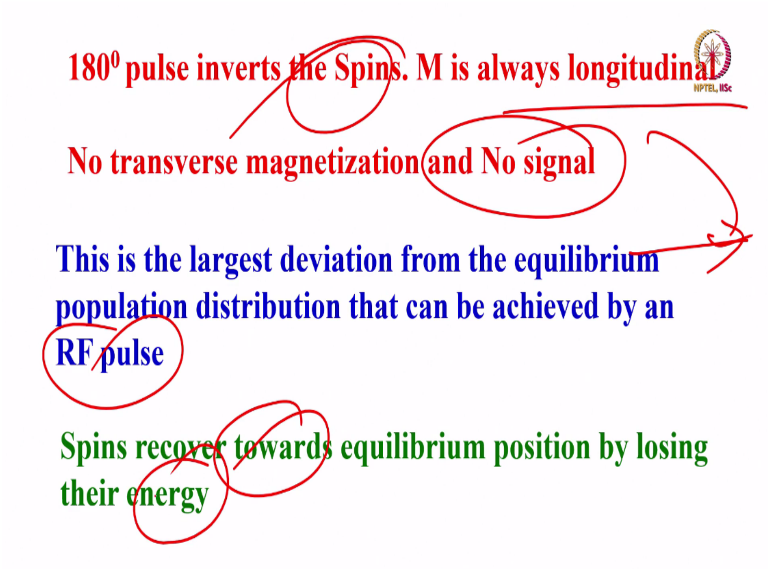

So 180 pulse invert the spins; M is always longitudinal, and no signal initially. It is the largest deviation of the equilibrium can be achieved by the first rf pulse. Bring the magnetization to this thing largest deviation you get signal. The spins recover towards equilibrium position by losing their energy, start going back.

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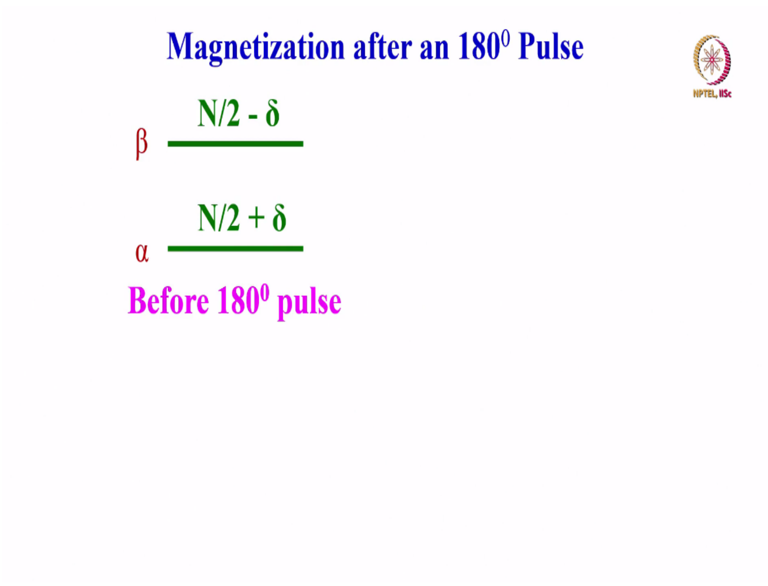

And then this is what I have to discuss something more about what happened to magnetization after spin dropping, I have to discuss. I will come to that later, but remember one thing one experiment, we can design where you have to disturb the spin system by applying a 180 pulse. Bring the magnetization to X axis or Y axis whatever it is depending on where you have receiver.

And then first 180 pulse brings the magnetization to – Z axis; give a delay between 180 and some delay apply 90 pulse and start collecting the signal. Measure the ntensity of the signal as a function of tau value and number of experiments if you do, you fit it into the equation which is M z = M 0 into 1 – e to the power of – t / T1; then you can measure the accurate value of T1.

So, what is happening when you apply 180 pulse, we have to understand by what is called a term called spin dropping. I will come to that, I will discuss that in the next class. So, I will stop today, but today anyway we have understood lot about spin-spin relaxation also. I have told about what is a spin-spin relaxation, mechanism of spin-spin relaxation and in summary we discussed and said the relaxation is a radiationless transition.

In the case of spin lattice there is exchange of energy between the spins of lattice and it attains thermal equilibrium. In the case of spin-spin relaxation it is only between the spins there is no exchange of energy; spin lose coherence because one spins interacts with other spins, because of flip-flop process one spin can disturb the other spin, everything happened both spin relaxation T1 and T2 happens because of fluctuations in the local field.

And T1 is a growth along Z axis T2 is a decay along XY plane both are exponential and then we understood how measure the T1. Simply you have to measure T1 by inverting this magnetization from Z axis to – Z and see how it goes as a function of time. For that a simple experiment can be designed it is called inversion recovery experiment; 180 pulse tau 90 pulse experiment you have to do and measure the intensity of the signal as a function of tau delay. And fit it into the growth function Mz = M0 into 1 – t / T1; that is what we do to get the T1 and how do we do the experiment what happens 180 pulse and how we measure T2, quickly we will finish this in the next class and with that I can go to another topic later. Many other things we will discuss. So, I am going to stop with this thing. I will see you in the next class. Thank you.