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

Lecture – 65
Relaxation Processes – 2

Welcome back. So today let us continue with our discussion on the relaxation phenomenon and how to measure them.

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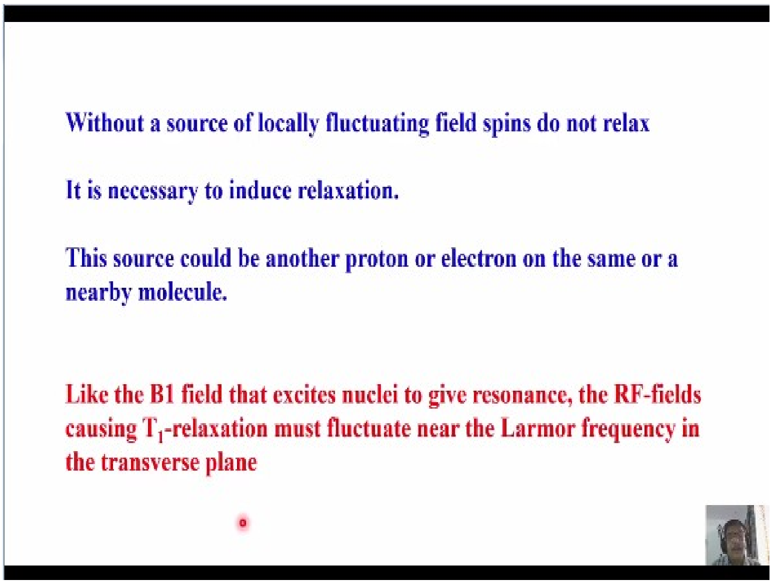

Without a source of locally fluctuating field spins do not relax

It is necessary to induce relaxation.

This source could be another proton or electron on the same or a nearby molecule.

Like the B1 field that excites nuclei to give resonance, the RF-fields causing T_1-relaxation must fluctuate near the Larmor frequency in the transverse plane

And of course, in the last class I was trying to work out and tried to give you the conceptual understanding of what is a spin lattice relaxation. Basically, concept was like this, if you have not followed or if I have missed some points, because I know relaxation is a fairly a tough topic to understand. Let me tell you. Before putting the sample in a magnetic field there is a no net magnetization. As soon as you put the sample in a magnetic field there is net magnetization.

Why this net magnetization came? We worked out taking into account the transition probabilities from alpha state to beta state and beta state to alpha state. And of course, the logic says transition from beta to alpha should be more than alpha to beta, because there are more spins in the ground state than in the excite state. When you put this into this equation and try to understand we found out that at thermal equilibrium $N\alpha = N\beta$. That was not agreeing with the conceptual understanding.

So as a consequence, we brought in the concept of deviation from equilibrium, magnetization deviation from equilibrium or deviation of population from the equilibrium in both the energy states and work out. Then we have understood for the magnetization to attain thermal equilibrium, from deviation to come to the thermal equilibrium, that is, original magnetization; we know there was a time constant called T1. T1 is a mechanism as I said. It is the relaxation phenomena, a time constant, which makes the spins to attain thermal equilibrium, come back to longitudinal magnetization along Z axis. That is why we call spin-lattice relaxation, longitudinal relaxation, attaining thermal equilibrium, thermal relaxation, lots of synonyms are there. Okay, that is what we said. And we also understood because there is more probability of spins aligning in a direction parallel to field, than in a direction opposite to that.

There must be some energy loss in the system. Energy has to be given out. Where does it give the energy? How does it give the energy? We understood the energy is given in the form of a heat to the surroundings? What are the surroundings? Anything other than your observing spin, like any of the surrounding atoms, nucleus, molecules, together the entire external surroundings, we called it as lattice. So it gives energy to the lattice; that is what we said.

So, how does it give the energy? What is the requirement for that? There must be some fluctuating fields whose frequency should match with the Larmor frequency. And this fluctuations should be in the transverse plane, so that it is giving the energy. So, this should match with the Larmor frequency, then the exited been given to the lattice and come down, okay to come to the thermal equilibrium.

Lattice of course, gets energy. When it gains energy; this energy is given to the system in the form of a heat, small amount of heat; which at a body temperatures, this energy, this heat is a much, much smaller than the kinetic energy. Okay. So we can largely ignore. It goes unnoticed and this loss of energy is not recoverable at all. These are the important concepts, I said.

Now I also said there must be a source of fluctuating field, without which spins cannot relax, and the source must be something else. What is the source? The source of fluctuating field must be some other proton, some other electron or any other nearby molecule. And it is necessary to induce relaxation. If there is no fluctuating field spins do not relax, okay, you will understand that.

For example, when we study solids and liquids there is a vast difference in the T1. It is because the fluctuating fields are more and the molecules undergo a lot of motions in the case of solution, thus the T1 is much shorter compared to solids. It is a general statement may not always be true. In solids sometimes the relaxation time can be order of minutes, hours, and days and weeks. Whereas in solution most of the time, relaxation time will be of the order of few seconds or minutes , or few tens of minutes, okay.

So remember when we apply a radio frequency field to excite the nuclear spins we need to have a oscillatory field in a direction perpendicular to it. Perpendicular to the magnetization which is in thermal equilibrium, that is what I said, only then we will perturb the system, okay. See you have to perturb the system to detect the NMR signal, and this perturbation frequency must be at the Larmor frequency. That is what I said.

That is why we apply a radio frequency pulse at the Larmor frequency to bring the magnetization from Z axis to transverse plane. Now similarly, the RF fields which is caused because of the fluctuation here, must also be at the Larmor frequency in the transverse plane, please remember this point.

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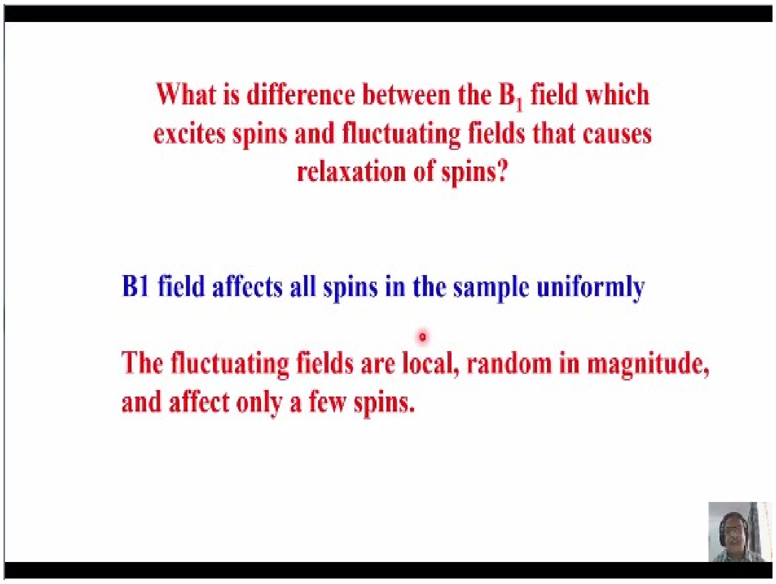

What is difference between the B_1 field which excites spins and fluctuating fields that causes relaxation of spins?

B1 field affects all spins in the sample uniformly

The fluctuating fields are local, random in magnitude, and affect only a few spins.

Now, what is the difference between this and that. The B1 field excites spins, whereas the fluctuating spins relaxes spins. Both we say at the Larmor frequency. What is the difference then? Remember, B1 field is the radio frequency pulse applied to excite the nuclear spins, that is to perturb the magnetization from thermal equilibrium to bring it to transverse plane. Fine. But we also have a fluctuating frequencies are also at the Larmor frequency. This enables the spins to relax.

Then what is the major difference? The major difference is the RF field which you have applied to excite the spins affect all the spins uniformly. Remember the uniform excitation is done by applying the radio frequency pulse. I told you about how to choose a region for uniform excitation, everything. I hope you all remember that. Whereas, the fluctuating fields are local, they are random in magnitude and affect only a few spins. It does not affect the entire system; whereas the B1 field affects the entire spins uniformly. This is the basic difference, please remember that.

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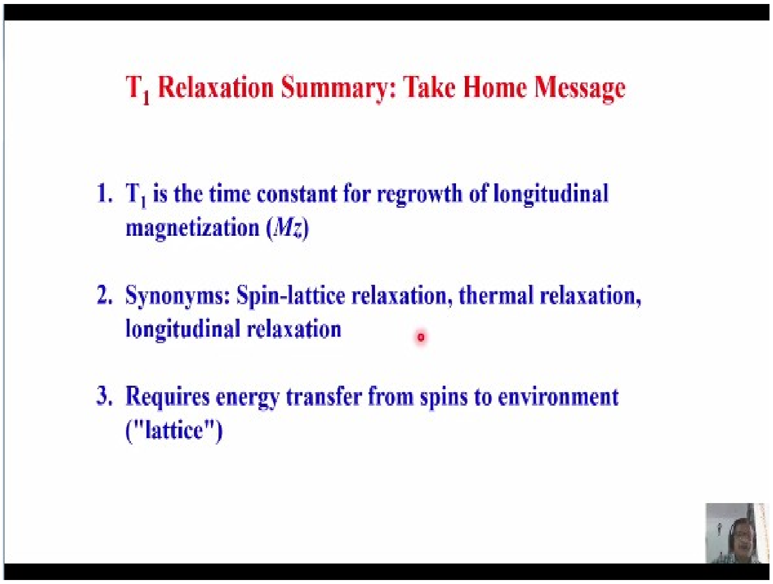

T_1 Relaxation Summary: Take Home Message

1. T_1 is the time constant for regrowth of longitudinal magnetization (*Mz*)
2. Synonyms: Spin-lattice relaxation, thermal relaxation, longitudinal relaxation
3. Requires energy transfer from spins to environment ("lattice")

Okay with this let me give you some idea about the relaxation, T1 relaxation. Some important points for you to take home. One is T1 is a constant; a time constant for magnetization to grow along Z axis. There are several terminologies for this, like spin lattice relaxation, thermal relaxation, longitudinal relaxation, various things. But conceptually everything is same. It is only naming in a different way. And it requires energy transfer from spins to the environment. Anything surrounding that, that is the external environment, is called lattice, okay.

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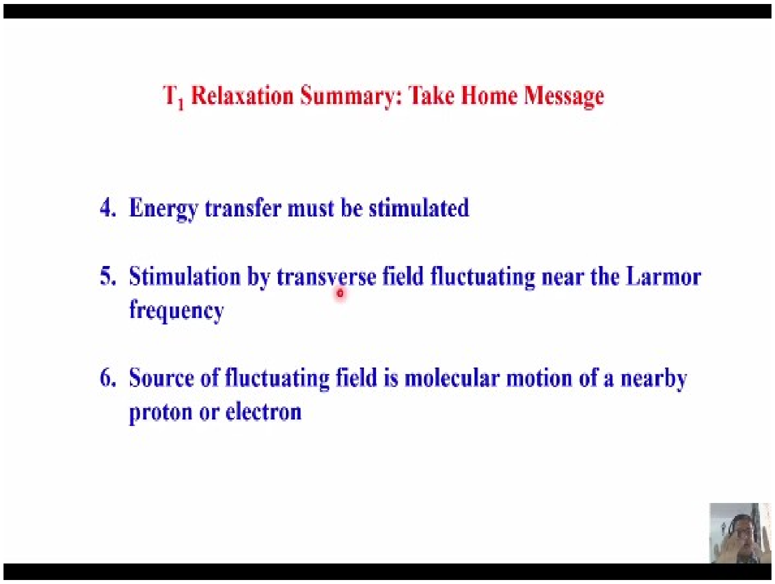

T_1 Relaxation Summary: Take Home Message

4. Energy transfer must be stimulated
5. Stimulation by transverse field fluctuating near the Larmor frequency
6. Source of fluctuating field is molecular motion of a nearby proton or electron

Next, this energy transfer must be stimulated. Spontaneous emission is not possible in the radio frequency region. How do you get this stimulation? It stimulation is obtained by transverse field fluctuating in the Larmor frequency. And what is the source of fluctuating field? It is again the molecular motion of a nearby proton, electron or some other atoms nearby. All this fluctuations gives rise to frequency, which is a Larmor frequency, only then the spins can relax. These are the summary of the points. So, far I was telling you about T1, okay.

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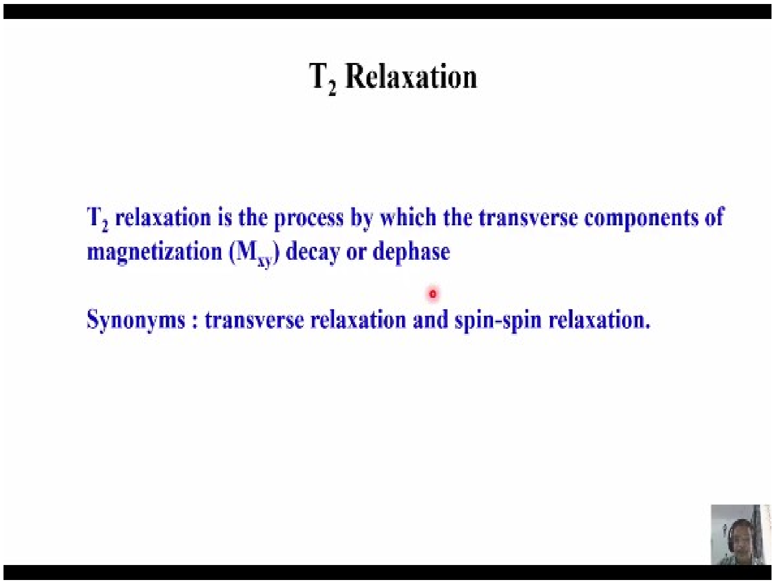

T_2 Relaxation

T_2 relaxation is the process by which the transverse components of magnetization (M_{xy}) decay or dephase

Synonyms : transverse relaxation and spin-spin relaxation.

Let us now go to another topic called T2. T2 is the relaxation phenomena, a time constant. What is T2? Remember, when you bring the magnetization from Z axis to XY plane, we discussed extensively in the earlier classes. Instantaneously when the magnetization is brought there is a phase coherence. All the magnetic moments are along the X axis, along the axis in which we have brought the magnetization, there is a phase coherence.

But then what happens because of various phenomena, the spins start losing coherence, losing phase coherence. So slowly they start moving in different frequencies, some moving faster, some moves at a lower frequency, some moving at a higher frequency. They start dephasing; slowly they start dephasing. When they start dephasing, when you start collecting the signal, if you have a receiver here, immediately there is a phase coherence there is a maximum signal.

When the spin starts undergoing decoherence, the signal intensity keeps coming down. When they completely undergo decoherence, then what is going to happen in the XY plane? There is a random phase of X and Y components. There is a random phase approximation, as a consequence you do not see any magnetization at all. But when it is dephasing simultaneously it is also growing along Z axis; that is what is required and that is a T1.

But for the complete dephasing to take place in the transverse plane, it has a time constant. The magnetization X and Y component decay or dephase with time, that is called T2, a relaxation time. This also is the relaxation process. You understand? This is relaxation is nothing but a dephasing of the spins in the transverse plane; and T1 is growth along Z axis. One is along transverse plane, and other is a long longitudinal axis. And this also has synonyms, you call it transverse relaxation or spin-spin relaxation, does not matter.

So now you know there are two types of relaxations. One, the spins will lose energy from a perturbed state, you have given energy and perturbed it, and then slowly comes back and attain thermal equilibrium; that is one thing, a time constant for it is T1. The spins, which were brought to the XY plane, there was a phase coherence immediately and slowly it started decaying with time and after some time there is complete decoherence, you will not see any signal. That is called relaxation in the XY plane.

This is called transverse relaxation; and it has a time constant called T2. So these T1 and T2 are the two different phenomena. One is a growth function other is a decaying function. In the XY plane, the signal decays, slowly the signal intensity starts coming down as it is undergoing decoherence. But slowly the signal intensity starts going up along the Z axis, because with a time constant it starts coming back to equilibrium. So one is a growth function and other is a decay function.

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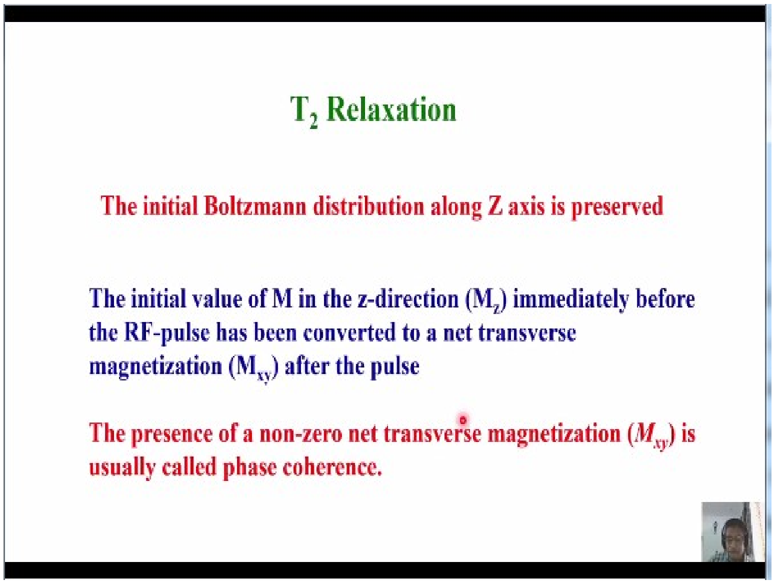

T_2 Relaxation

The initial Boltzmann distribution along Z axis is preserved

The initial value of M in the z-direction (M_z) immediately before the RF-pulse has been converted to a net transverse magnetization (M_{xy}) after the pulse

The presence of a non-zero net transverse magnetization (M_{xy}) is usually called phase coherence.

Interestingly both of them are exponential. One is an exponential decay other is an exponential growth. And after some time the initial Boltzmann distribution along Z is preserved. The presence of non-zero magnetization in the XY plane is called phase coherence. Non-zero net transverse magnetization is called phase coherence.

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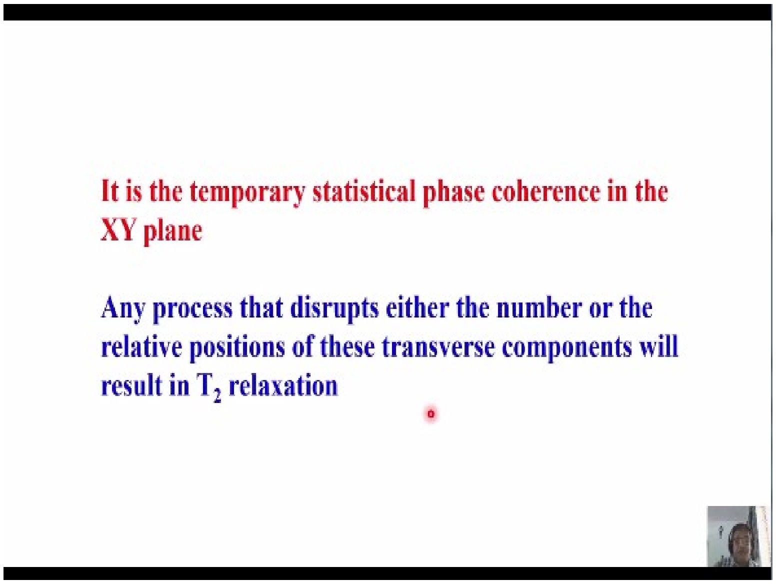

It is the temporary statistical phase coherence in the XY plane

Any process that disrupts either the number or the relative positions of these transverse components will result in T_2 relaxation

And it is a temporary statistical phase coherence. Remember, temporarily there is a statistical phase coherence in the XY plane. And the process which disrupts this phase coherence either the number or the relative positions of the transverse components, will result in what is called T2 relaxation. There can be some number of processes, I will tell you as you go ahead, for the spins to disrupt this type of coherence. okay.

How it disrupts? It disrupts the phases, the relative positions of the vectors. So, it makes them to undergo decoherence. And this process will finally make sure the transverse component undergo complete decoherence, called T2 relaxation.

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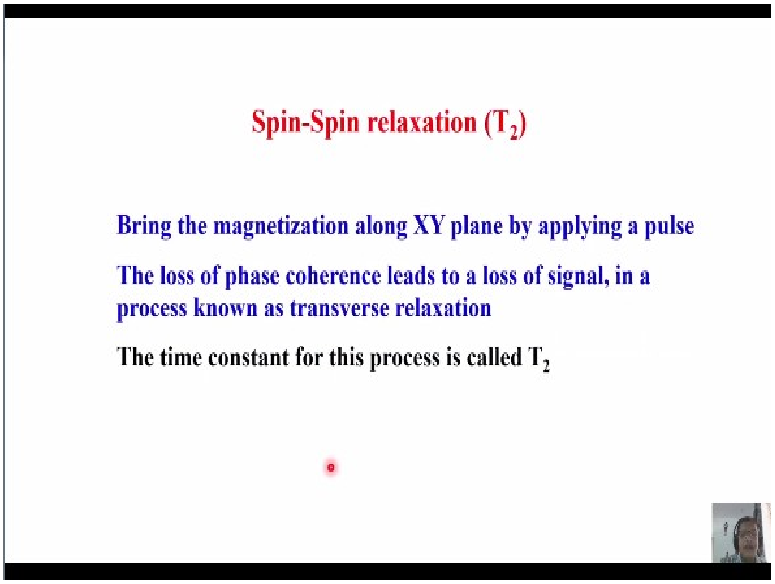

Spin-Spin relaxation (T_2)

Bring the magnetization along XY plane by applying a pulse

The loss of phase coherence leads to a loss of signal, in a process known as transverse relaxation

The time constant for this process is called T_2

So, simple logic is this. Bring the magnetization along the XY plane by applying a pulse. The loss of phase coherence leads to loss of signal, that is what I was telling you. Simple logic, if you do not understand magnetization component etc, bulk magnetization is here brought to XY plane. Instantaneously, there is a statistical phase coherence, okay. That is what I said, remember here. Temporarily there is a statistical phase coherence, and this phase coherence is getting lost by some mechanism. And that time constant required for that is called Spin-spin Relaxation, T2, that is all you should understand.

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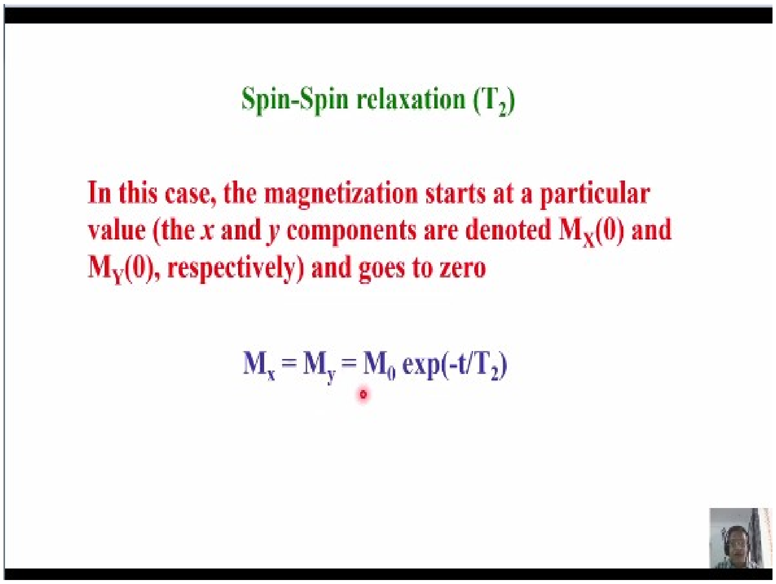

Spin-Spin relaxation (T_2)

In this case, the magnetization starts at a particular value (the *x* and *y* components are denoted $M_X(0)$ and $M_Y(0)$, respectively) and goes to zero

$$M_x = M_y = M_0 \exp(-t/T_2)$$

And as I said, this is MX and MY components; you call it as M0 into this one, a decaying function. M0 is initial magnetization; okay, thermal equilibrium magnetization. And after some time you see that when we give an enormous amount of time, this will go to zero. And then MX and MY, there is no components at all. There is no magnetization. You will not see any MX and MY components of the magnetization.

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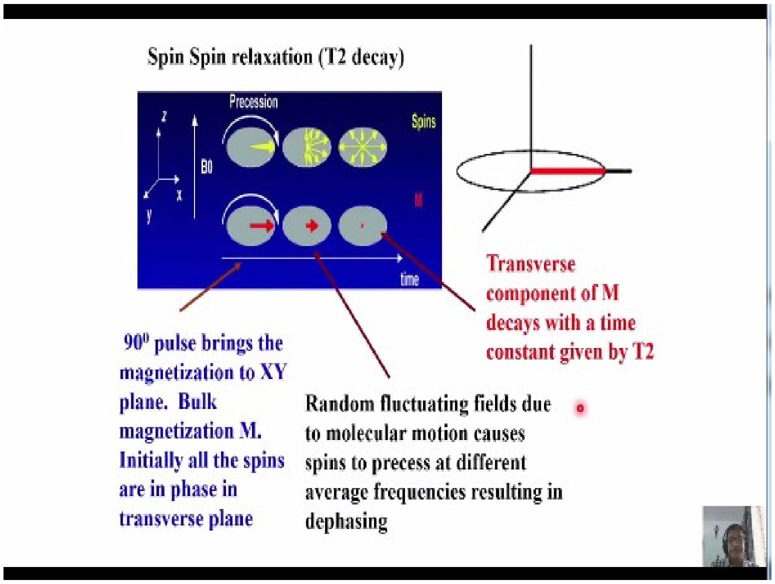

Spin Spin relaxation (T2 decay)

90^0 pulse brings the magnetization to XY plane. Bulk magnetization M. Initially all the spins are in phase in transverse plane

Random fluctuating fields due to molecular motion causes spins to precess at different average frequencies resulting in dephasing

Transverse component of M decays with a time constant given by T2

And this is diagram which tells you how the phase coherence takes place. Apply 90 degree pulse bring the magnetization to this place; and then spins starts undergoing decoherence, here. Initially there is a full magnetization, complete intensity is there. Intensity is maximum at this point because there is a temporary statistical phase coherence. With time slowly the phase coherency is lost, signal intensity starts you losing.

And after some time, it is so happens there is a complete decoherence, there is no signal seen in the transverse plane, there is no component at all. This constant, time constant which makes this component of a magnetization MX and MY to decay completely; or to undergo decoherence completely is called T2, okay. Spin-spin relaxation.

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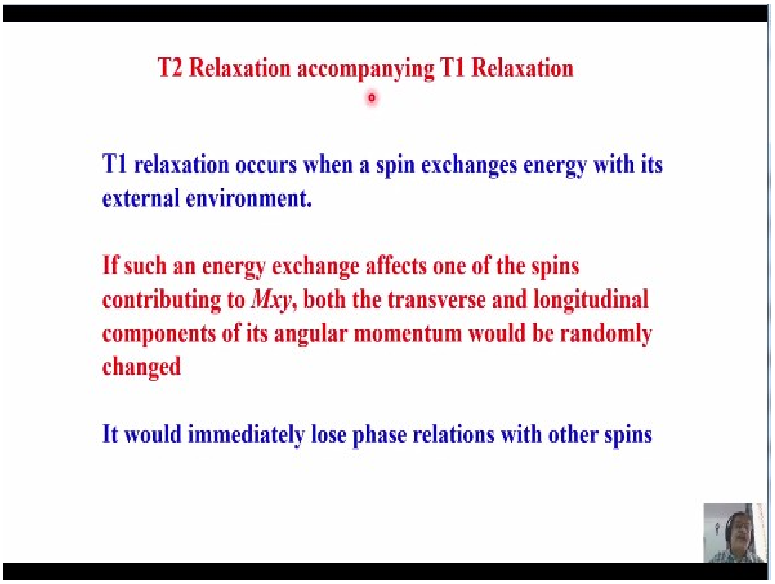

T2 Relaxation accompanying T1 Relaxation

T1 relaxation occurs when a spin exchanges energy with its external environment.

If such an energy exchange affects one of the spins contributing to *Mxy*, both the transverse and longitudinal components of its angular momentum would be randomly changed

It would immediately lose phase relations with other spins

The T2 relaxation will always accompany T1 relaxation. Remember T2 relaxation always accompany T1 relaxation, because T1 relaxation occurs when a spin exchange energy takes place with its surroundings. When such an energy exchange takes place at any time, it affects only one of the spins, any one of the spins, which is contributing to magnetization in the XY plane then you know what will happen? these both transverse and longitudinal components gets affected. They will also start changing, getting changed randomly.

As a consequence, T1 while the energy exchange is going on if affects only one of the spins contributing to Mxy, then it helps in losing phase relations with other spins. So, this also helps in T2 relaxation. So, that means T2 relaxation always accompany T1 relaxation.

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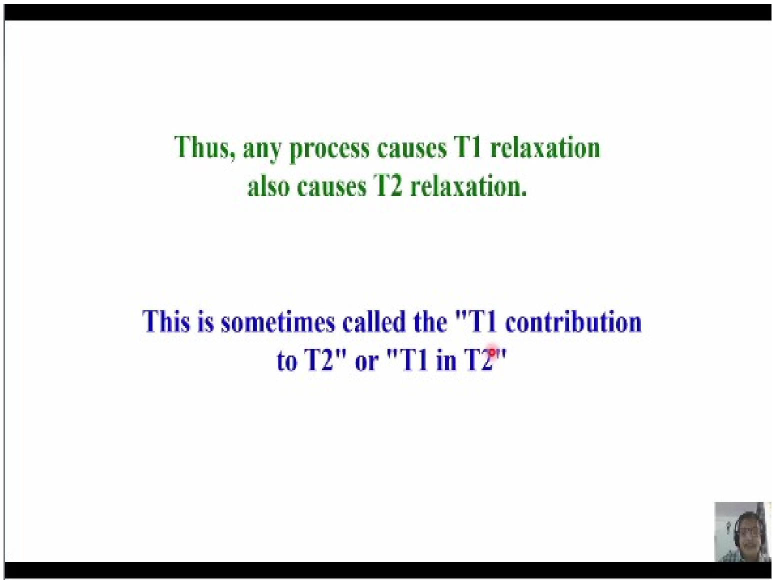

Thus, any process causes T1 relaxation
also causes T2 relaxation.

This is sometimes called the "T1 contribution
to T2" or "T1 in T2"

Is it true all the time is a next question? Of course, most of the time, any process that causes T1 relaxation also causes T2. But I will tell you later, there can be T2 relaxation without T1. This is sometimes called T1 contribution to T2 or in other words we use a technical word called T1 in T2, okay. We said T1 contribution to T2, because any process that causes T1 relaxation causes also T2 relaxation.

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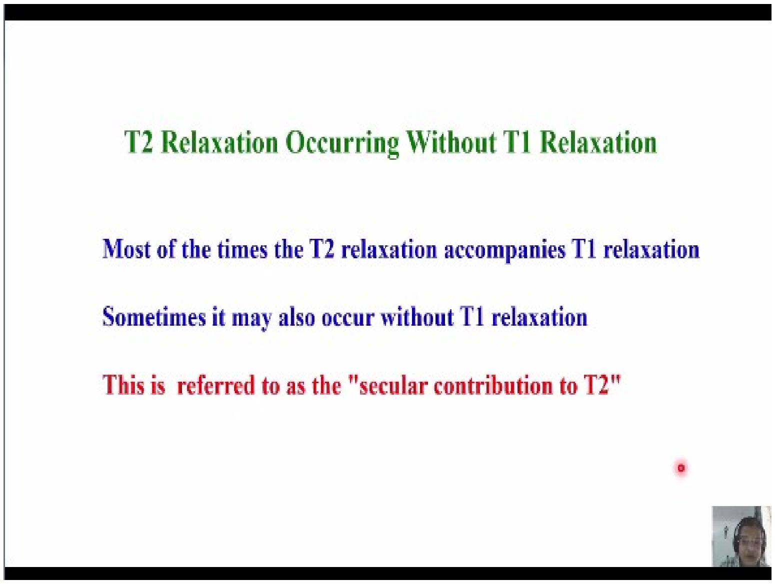

T2 Relaxation Occurring Without T1 Relaxation

Most of the times the T2 relaxation accompanies T1 relaxation

Sometimes it may also occur without T1 relaxation

This is referred to as the "secular contribution to T2"

T2 relaxation occurs without T1 also that is what I said. T1 relaxation causes T2; but T2 can happen without even T1 also. For example most of the time T2 relaxation accompanies T1, sometimes it happens without T1. This is referred to all the secular contribution to T2, it is the technical word, do not worry. Remember, when T1 contribution happens to T2, for T2 relaxation there is a T1 contribution that is called T1 in T2. The T2 happening on its own without T1, is called secular contribution to T2, okay.

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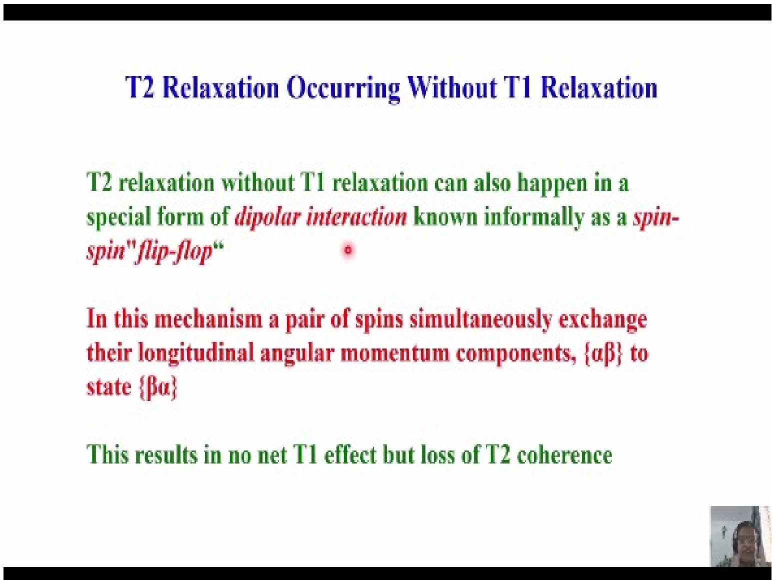

T2 Relaxation Occurring Without T1 Relaxation

T2 relaxation without T1 relaxation can also happen in a special form of *dipolar interaction* known informally as a *spin-spin"flip-flop*“

In this mechanism a pair of spins simultaneously exchange their longitudinal angular momentum components, $\{\alpha\beta\}$ to state $\{\beta\alpha\}$

This results in no net T1 effect but loss of T2 coherence

So, T2 relaxation occurs without T1 also. In some situations there is what is called dipolar interaction, where the two spins at a time undergo transitions, from alpha beta to beta alpha. It is called the flip-flop term. When a flip-flop term is there, like alpha beta going to beta alpha simultaneously, such type transitions causes what is called T2 relaxation without T1.

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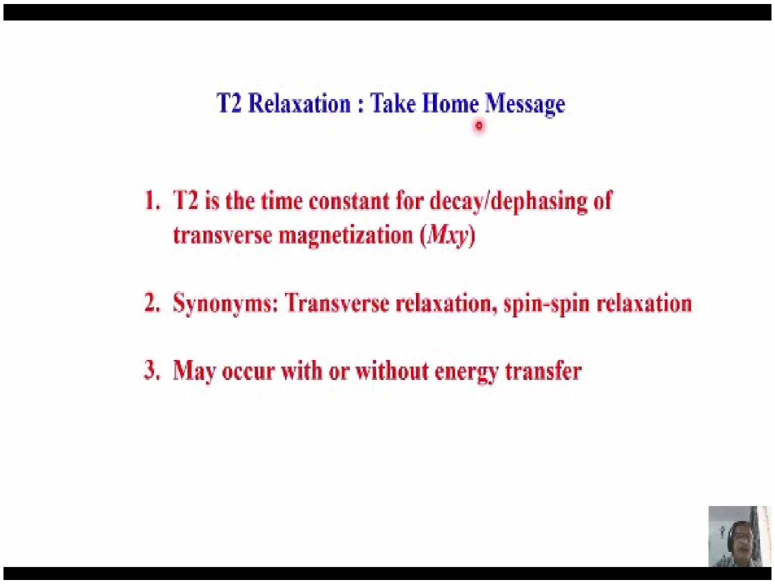

T2 Relaxation : Take Home Message

1. T2 is the time constant for decay/dephasing of transverse magnetization (*Mxy*)
2. Synonyms: Transverse relaxation, spin-spin relaxation
3. May occur with or without energy transfer

Okay, so this are more detailed, but remember the take home message is T2 is the time constant for decay or dephasing of transverse magnetization in the XY plane; that is Mxy. And synonyms for it, transverse relaxation, spin-spin relaxation, and it can occur with or without energy transfer, okay; with T1 or without T1 it can happen.

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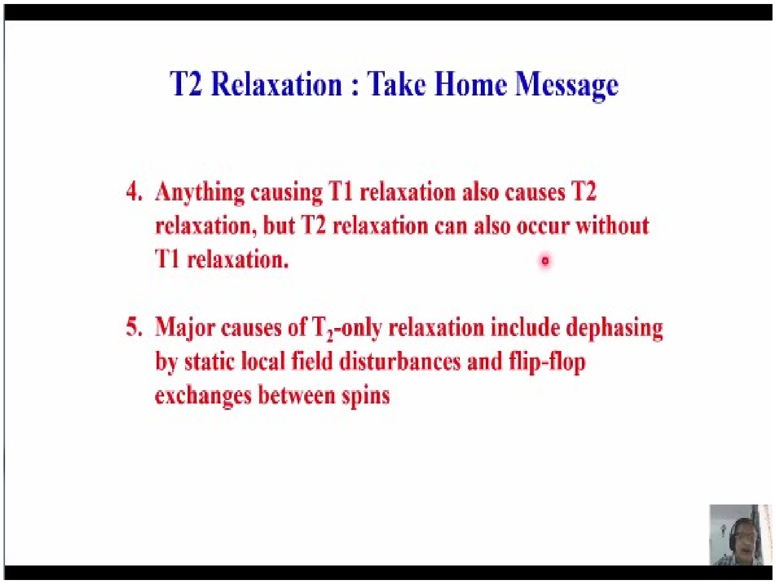

T2 Relaxation : Take Home Message

4. Anything causing T1 relaxation also causes T2 relaxation, but T2 relaxation can also occur without T1 relaxation.
5. Major causes of T_2-only relaxation include dephasing by static local field disturbances and flip-flop exchanges between spins

And anything causes T1 relaxation also causes T2, but T2 relaxation can independently also occur without T1. Please remember this point. This one is called T1 and T2; this is called secular contribution to T2. So major causes of T2, that is for the spins undergo dephasing, is a statistical local fields, that is a major cause.

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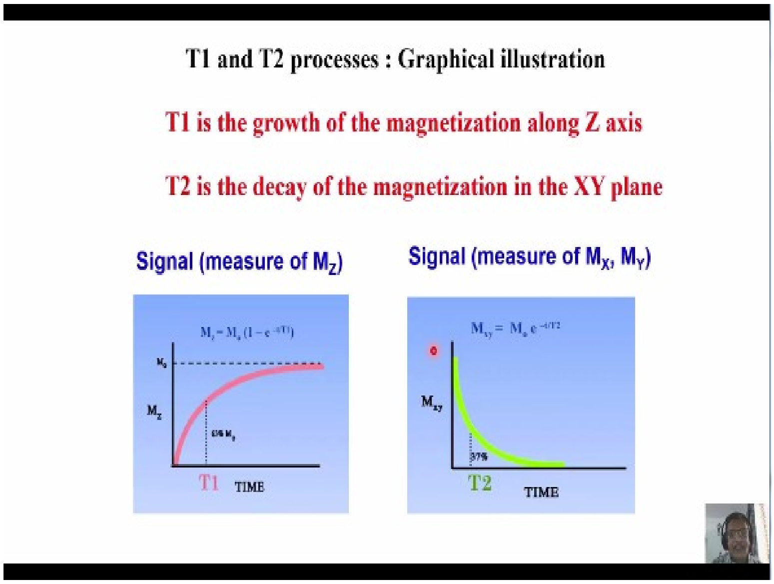

T1 and T2 processes : Graphical illustration

T1 is the growth of the magnetization along Z axis

T2 is the decay of the magnetization in the XY plane

Signal (measure of M_Z)

Signal (measure of M_X, M_Y)

Okay, this is the T1 and T2 processes. Remember these are the T1 and T2 processes; graphically I am showing you. T1 is a growth of magnetization. T2 is a decay of magnetization. Both of them follow exponential function, okay. Both of them are exponential, here is a exponential decay function, here is a exponential growth function. See $M0(1- e^{-T/T1})$, okay. So when it totally becomes 0, Mz=M0, the complete thermal equilibrium is achieved.

Here you can see, after a long time of T2, there is no magnetization at all. It keeps decaying, after long time when T2 becomes enormously long M_{XY} will become 0. And T2 because more here you can find this because smaller and smaller and becomes 0. So one is a decay function other is a growth function. Both follow exponential function. Please remember that.

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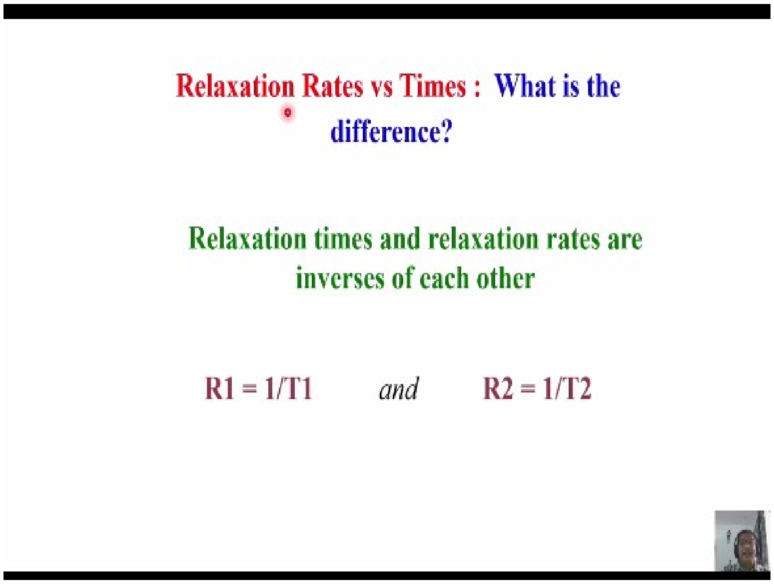

Relaxation Rates vs Times : What is the difference?

Relaxation times and relaxation rates are inverses of each other

R1 = 1/T1 *and* R2 = 1/T2

So sometimes we use terms called Relaxation Rates and Relaxation Times. What is the difference? Relaxation time is the time, which you measure T1 and T2. It is a time constant. The relaxation rates are inverse of that. Sometimes they are called R1 and R2. R1 is the inverse of T1or 1/T1. The R2 is inverse of T2. So, R2 is nothing but 1/T2. R1 is called relaxation rate and T1 is called relaxation time. So, relaxation rates and relaxation times are related like this, relaxation rate is nothing but inverse of the relaxation times, okay.

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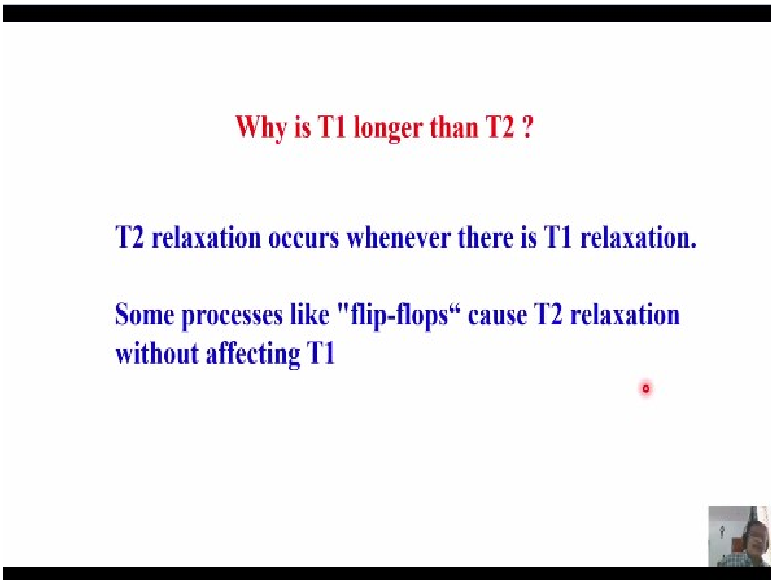

Why is T1 longer than T2 ?

T2 relaxation occurs whenever there is T1 relaxation.

Some processes like "flip-flops" cause T2 relaxation without affecting T1

So why T1 is always longer than T2 of course do not worry about that.

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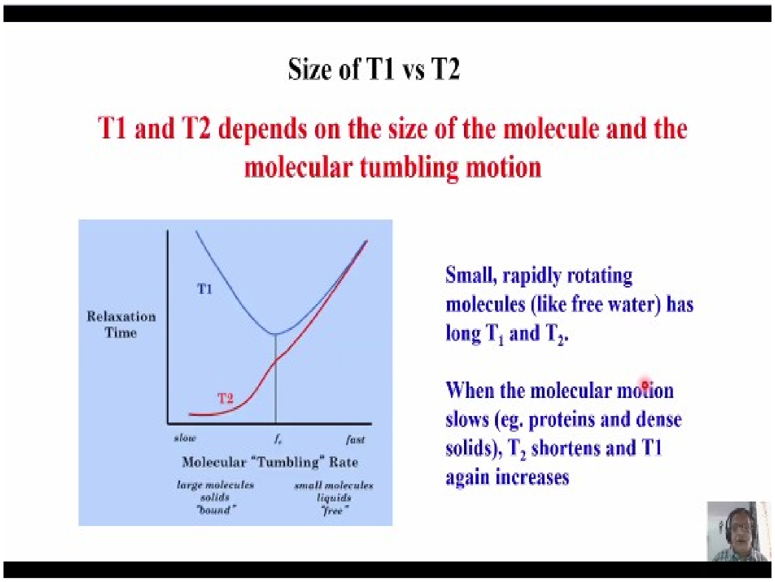

Size of T1 vs T2

T1 and T2 depends on the size of the molecule and the molecular tumbling motion

Small, rapidly rotating molecules (like free water) has long T_1 and T_2.

When the molecular motion slows (eg. proteins and dense solids), T_2 shortens and T1 again increases

Now, what is the size of the T1 and T2 if you want to see, look at this. This is a function which explains as a function of molecular tumbling, which produces fluctuating fields and enabling relaxation processes. If we look at this, this is a graph small and rapidly rotating molecules, like small molecules, free water, have a very long T1 you see. Even it is very, very long for small molecules; okay. And if we go to relaxation rate it is faster, because the longer relaxation rate means inverse of that rate, it is faster.

On the other hand, for big molecules there is slow motion; like proteins, and then in solids, molecular motions are very slow; in which case T2 get shortened, but T1 increases understand. For big molecules and solids, which undergo slow motions, T1 is very large and T2 is very short. Whereas, for small molecules, okay like this, which undergo rapid motions, rapidly rotating molecules both T1 and T2 are longer. This gives you an idea about the size of the T1 and T2 depending upon the size of the molecules, okay. T1 and T2 depends upon the size of the molecules and also the molecular motions; the tumbling motions that are going on.

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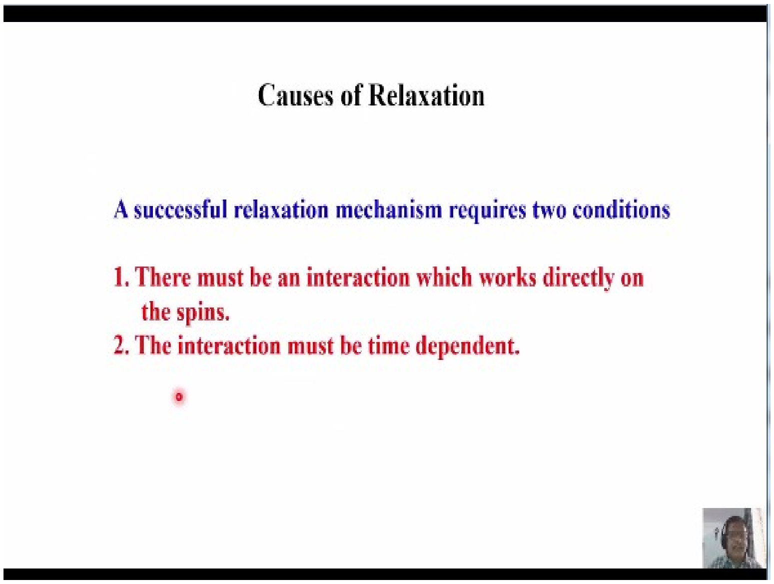

Causes of Relaxation

A successful relaxation mechanism requires two conditions

1. There must be an interaction which works directly on the spins.
2. The interaction must be time dependent.

But causes of relaxation as I said, a successful relaxation mechanism requires two conditions there must be an interaction, which works directly on the spins, the interaction must be time dependent, that is what I said for both the phenomena.

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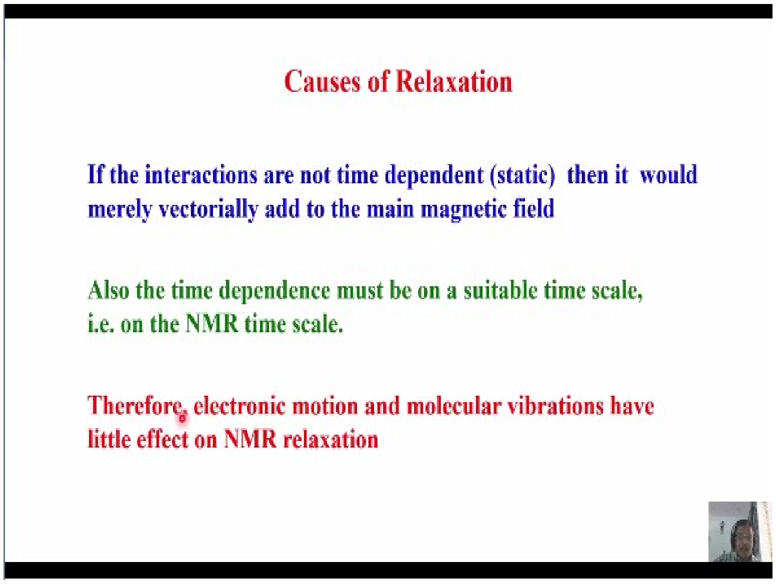

Causes of Relaxation

If the interactions are not time dependent (static) then it would merely vectorially add to the main magnetic field

Also the time dependence must be on a suitable time scale, i.e. on the NMR time scale.

Therefore, electronic motion and molecular vibrations have little effect on NMR relaxation

All right. So this we discussed already, it has to be time dependent fluctuating fields so that interaction has to take place, this cannot be static, it has to be fluctuating magnetic field and the time depends must be at suitable NMR times; at the Larmor frequency, that is what I discussed. And because it should be at the NMR timescale, and the molecular motions like vibrations, electronic motions, such type of motions will not affect NMR relaxation, only some molecular rotations and diffusions, are the very important for sources of relaxation.

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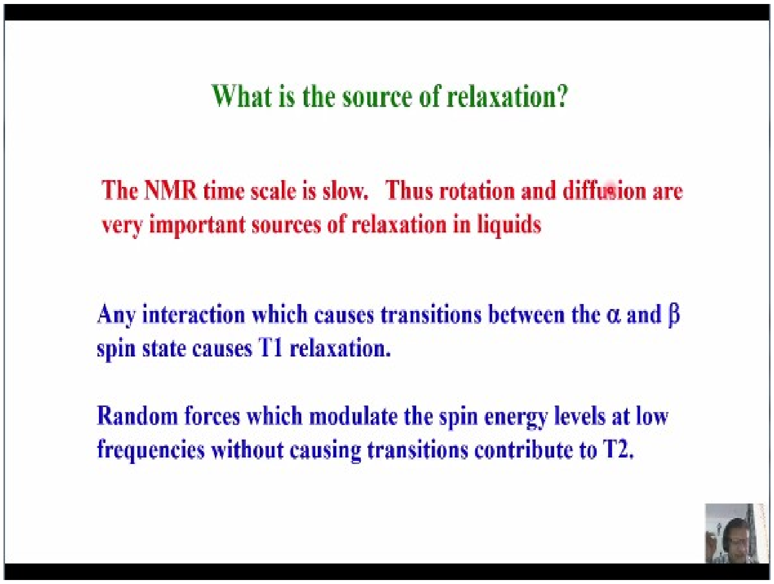

What is the source of relaxation?

The NMR time scale is slow. Thus rotation and diffusion are very important sources of relaxation in liquids

Any interaction which causes transitions between the α and β spin state causes T1 relaxation.

Random forces which modulate the spin energy levels at low frequencies without causing transitions contribute to T2.

Please remember for the relaxation process in liquids molecular rotations, molecular diffusion are important. That is the one, which helps in relaxing.

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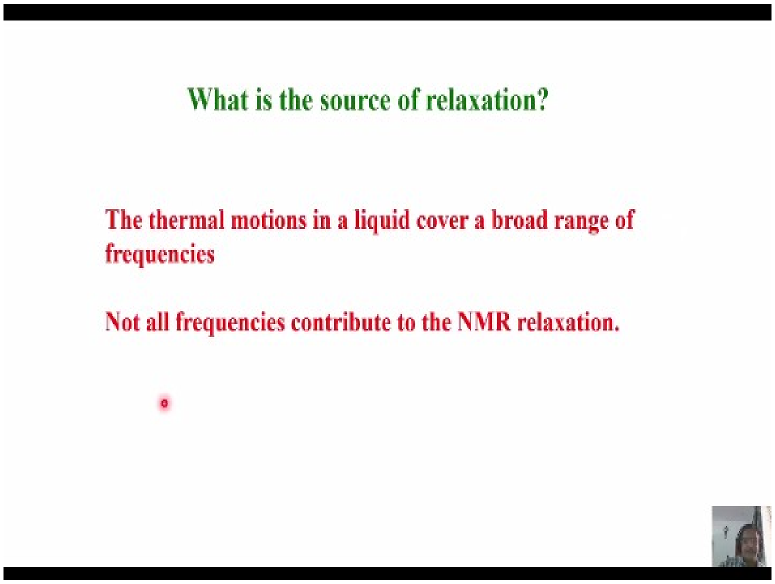

What is the source of relaxation?

The thermal motions in a liquid cover a broad range of frequencies

Not all frequencies contribute to the NMR relaxation.

Okay. Of course we have been discussing again and again. Thermal motions in liquids cover a wide range of frequencies and all of them will not contribute to this. We have to discuss about the spectral density function and everything and then molecular motion, we have to define the different correlation function, τc, etcetera, which we discussed to some extent when we discussed NOE.

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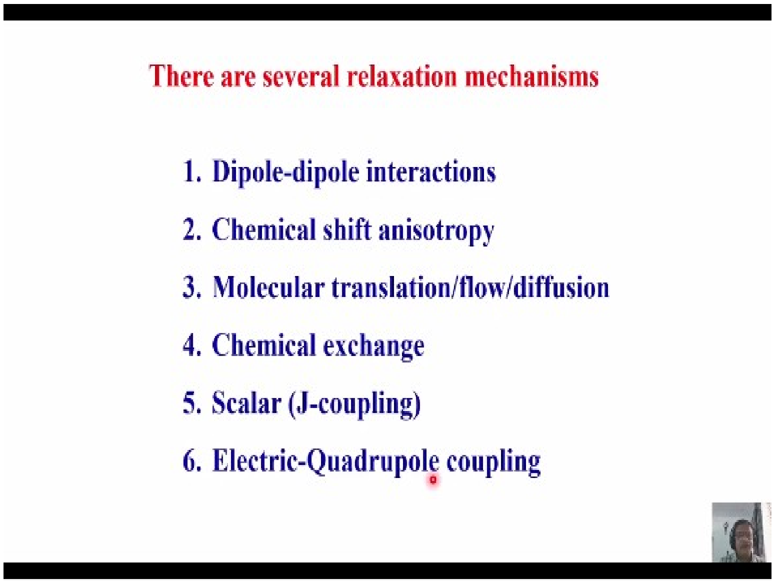

There are several relaxation mechanisms

1. Dipole-dipole interactions
2. Chemical shift anisotropy
3. Molecular translation/flow/diffusion
4. Chemical exchange
5. Scalar (J-coupling)
6. Electric-Quadrupole coupling

See this. There are several relaxation mechanisms; each and everything can be discussed for hours and hours. One is a Dipole-dipole interaction, this is the major source of relaxation, chemical shift anisotropy is a major source of relaxation. And molecule translation flow, diffusion, Chemical exchange, scalar coupling, Electrical-quadrupole coupling for spin greater than half. There are various mechanisms, all these phenomena which are happening in the molecule, in the sample, can give raise to mechanisms for relaxation. But dominant are dipole-dipole and chemical shift anisotropy interactions.

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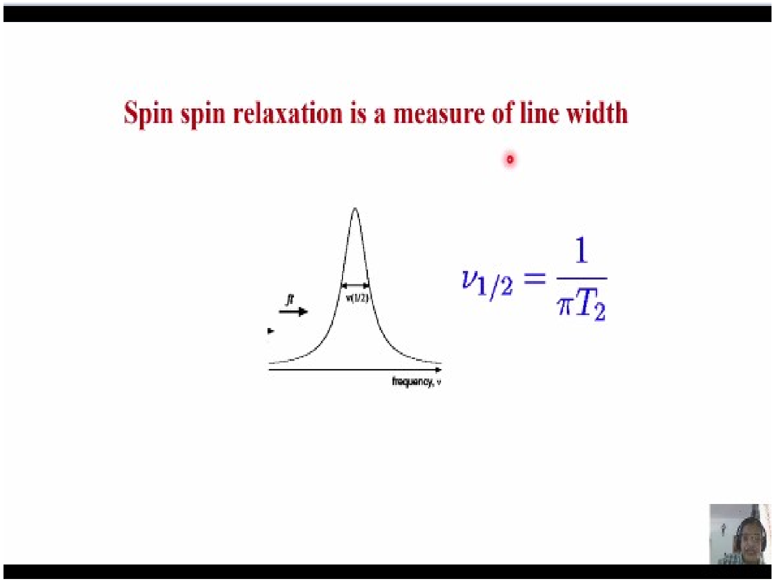

Spin spin relaxation is a measure of line width

$$\nu_{1/2} = \frac{1}{\pi T_2}$$

So, if you visualize the T1 and T2 processes together, they are not exclusive processes. I have been telling you even earlier also, while discussing NOE I said. These are all processes, which takes place simultaneously that is what I showed this earlier also. As the magnetization starts dephasing in the XY plane, simultaneously starts going along Z axis. So, it looks like it is undergoing a spiral like this.

So T1 and T2 if we visualize, simultaneously it is happening; the magnetization goes like this. It is a huge magnetization initially, full magnetization is there; there is the statistical phase coherence, maximum intensity of the signal slowly when it undergoes dephasing reduces, reduces, reduces. And afterwards keeps reducing in the XY plane, but keeps growing along Z axis like this. This is the combination of T1 and T2, if you view together it is simultaneously happening. This is the path it appears.

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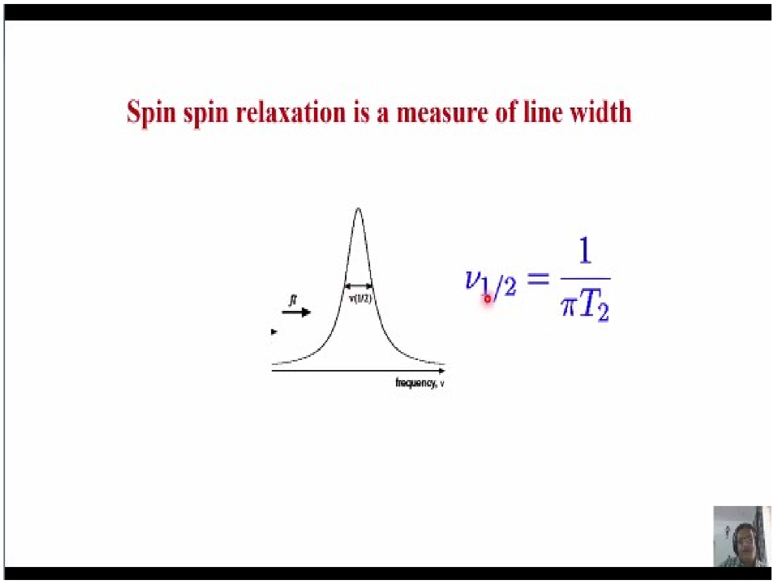

Spin spin relaxation is a measure of line width

$$\nu_{1/2} = \frac{1}{\pi T_2}$$

Of course, T2 is very easy to find out; it is inverse of half of the line width. find out the line width, that is fullwidth at half height, and take the inverse of that multiply wit π, that will give you T2. Fullwidth at half height is equal to 1/ πT2, very simple relation. So if I measure the line width, I know what is T2. Approximately I can tell you what is T2.

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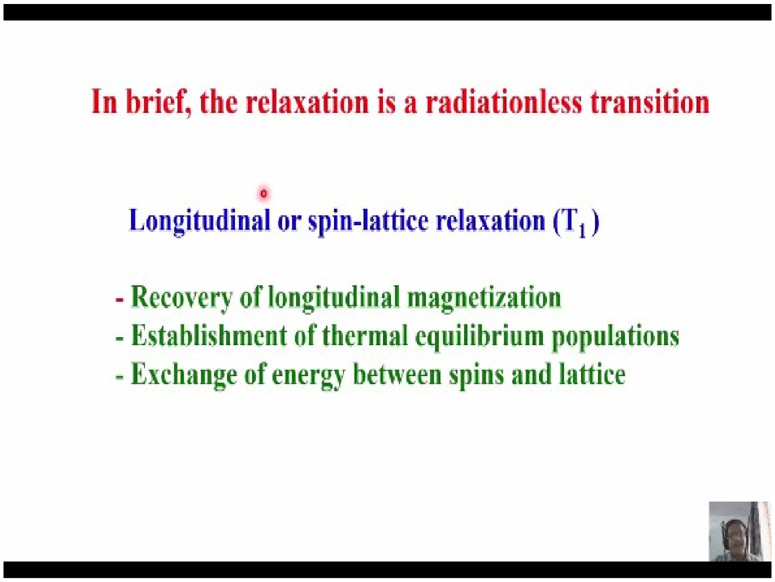

In brief, the relaxation is a radiationless transition

Longitudinal or spin-lattice relaxation (T_1)

- Recovery of longitudinal magnetization
- Establishment of thermal equilibrium populations
- Exchange of energy between spins and lattice

So, if you understand everything, remember this is a relaxation, all though it undergoes transitions between the energy states; there is exchange of energy between the spins energy state and the lattice. Relaxation is a radiationless transition, it is not a transition that you detect, the radiation is to only to aid the spins to relax, okay. It is not the transition that you are going to detect. And ofcourse, longitudinal magnetization I explained what happens, which is the recovery of magnetization and all those things; there is no need to discuss again and again.

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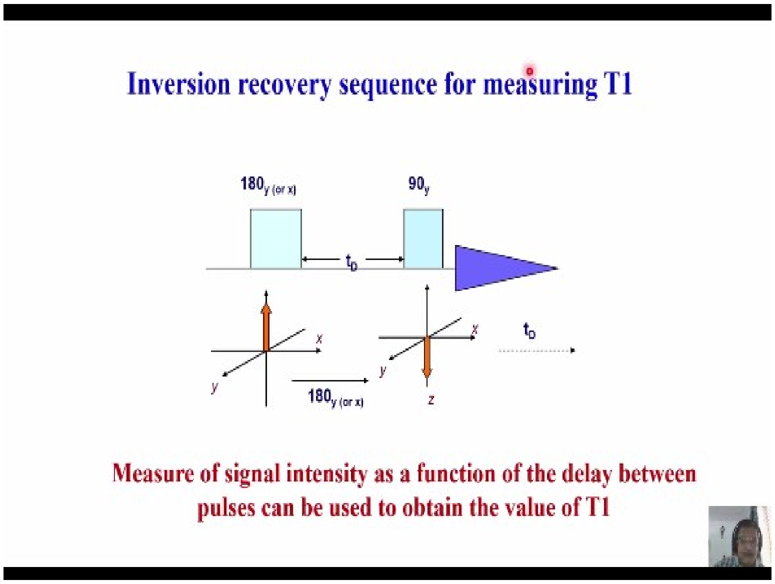

Inversion recovery sequence for measuring T1

Measure of signal intensity as a function of the delay between pulses can be used to obtain the value of T1

Now, let us see how to measure T1 and T2. These are the two important experiments, one experiment I will tell you how to measure T1. For T1, there are several experiments to measure, what is called saturated recovery; that is you can saturate the spin system first by applying radio frequency pulse and see how it recovers, how much time it takes to recover. That is one way of getting the T1. You can get T1 by the null method. There are five or six methods of measuring T1. You can see in the literature they are available. And these methods, there is no need to discuss. But the commonly used is the inversion recovery sequence. Of course, there is another one, called progressive saturation. Keep on applying the pulses one by one progressively one after other, every time you collect the signal and see when it gets saturated.

So, there is progressive saturation, saturation recovery, null method and inversion recovery. Inversion recovery is a very interesting thing. What you do is, first apply a 180 degree pulse on the magnetization. 180 will bring it to –Z axis; and okay if you have a receiver here, you are not going to see any signal here. From Z axis, you bring magnetization to –Z axis. Immediately apply a 90 pulse, you will get a negative signal.

And this one, after 180 pulse, give some delay and then magnetization would be slowly going back to the Z axis. Keep on varying this delay at every interval of delay, start collecting this signal. See how the magnetization is growing. And then this I said $M_Z=M_0(1- e^{-t/T1})$; t is the variable delay here. For different values of t you calculate this and do a curve fitting. Like this, it is a simple thing.

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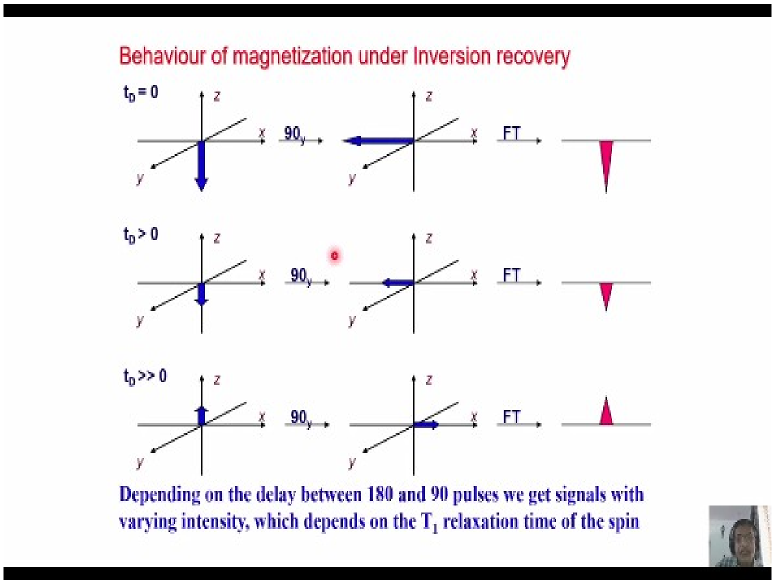

Behaviour of magnetization under Inversion recovery

Depending on the delay between 180 and 90 pulses we get signals with varying intensity, which depends on the T_1 relaxation time of the spin

First you bring the magnetization, to -Z signal is negative slowly keep reducing and then keep going along Z axis.

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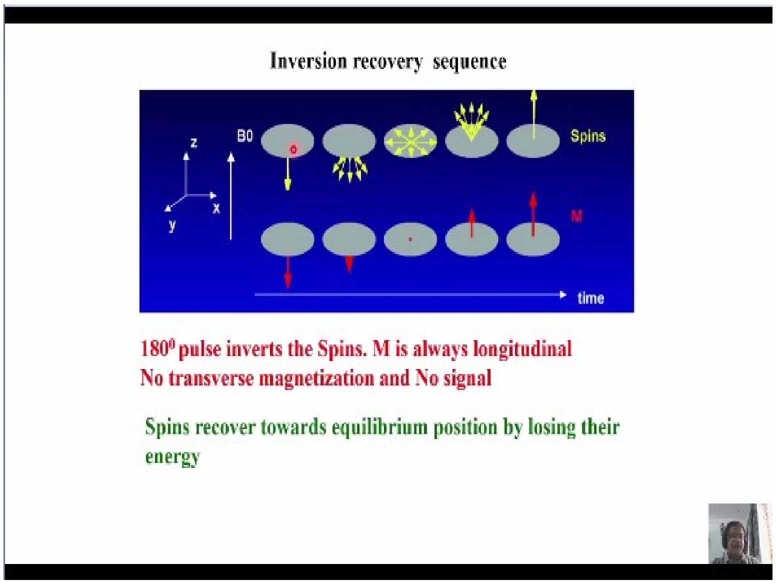

Inversion recovery sequence

180^0 pulse inverts the Spins. M is always longitudinal
No transverse magnetization and No signal

Spins recover towards equilibrium position by losing their energy

This is the inversion recovery sequence. First magnetization is brought to a negative axis, phase decoherence takes place, magnetization intensity comes down, comes down, becomes zero, this is called a null method. If you find out what is the time required for the signal to get nullified, in 180 tau 90 sequence, this tells you this is 0.693 times this t value time is the T1; because you put into that equation, okay. $M_Z=M_0(1- e^{-t/T1})$ fit into that equation. When this term goes to zero, you can find out exactly at this point if you find out, it is a logarithmic value, it turns out to be 0.693t This gives you T1 at this point. That is the null method. The signal goes further up becomes positive, positive, positive and completely comes back to thermal equilibrium. Now, each time we measure the intensity for each delay, and then do the curve fitting for the exponential function, what you are using for measuring T1; fit into the equation $M_Z=M_0(1- 2e^{-t/T1})$. In the inversion recovery it is 1- $e^{-t/T1}$, okay, that equation, why 2 comes you can see later it is simple arithmetic.

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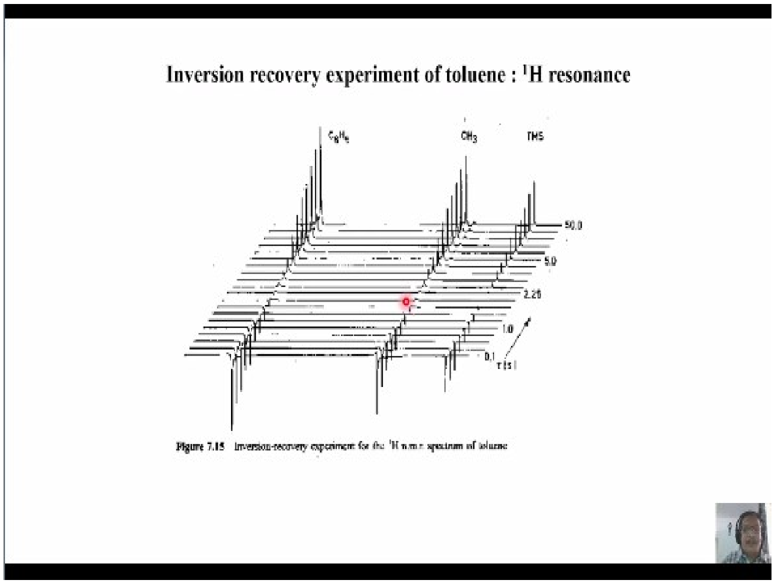

Inversion recovery experiment of toluene : ^1H resonance

Figure 7.15 Inversion-recovery experiment for the ^1H n.m.r. spectrum of toluene

This is how inversion recovery works, for example, for toluene molecule, first inverse the signal, there are three types of proton, benzene protons and CH3 and this is TMS. See the inverted here slowly start getting the signal, signal becomes positive maximum. And this one and this last one should have equal intensity. That means the thermal equilibrium magnetization was brought to –Z, slowly it goes back and go to original equilibrium situation.

See this if you fit these data points into the exponential equation, you will get the T1 value. Same way you can find out for the CH3. So, each for spin or each peak you can get the T1 individually by inversion recovery experiment. Please remember you can measure the T1 by inversion recovery experiment; this is very useful for you because you can understand dynamics of the molecule.

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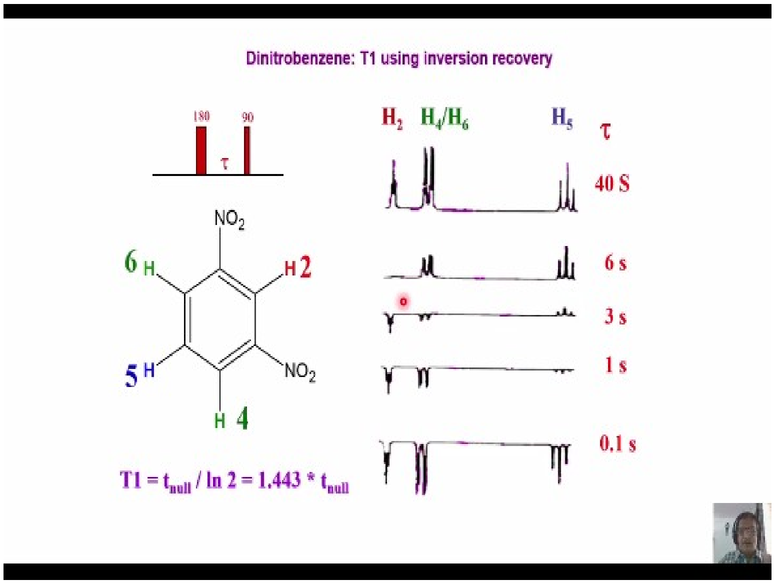

Dinitrobenzene: T1 using inversion recovery

$T1 = t_{null} / \ln 2 = 1.443 * t_{null}$

Of course, these are all some of the few examples, different spins of the same molecule can have different T1 values; okay.

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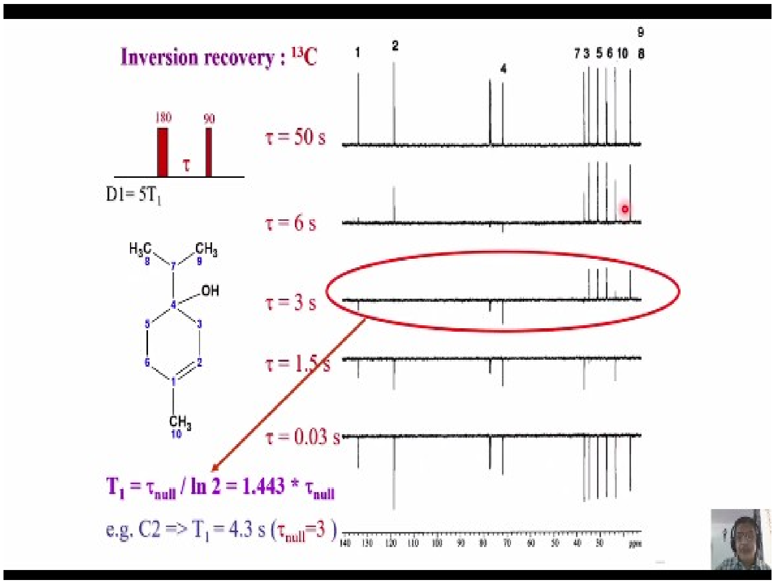

Inversion recovery : ^{13}C

$D1 = 5T_1$

$T_1 = \tau_{null} / \ln 2 = 1.443 * \tau_{null}$

e.g. C2 => $T_1 = 4.3$ s ($\tau_{null}=3$)

See in this case, see this is the null method. If you can make this null, then find out what is T1.

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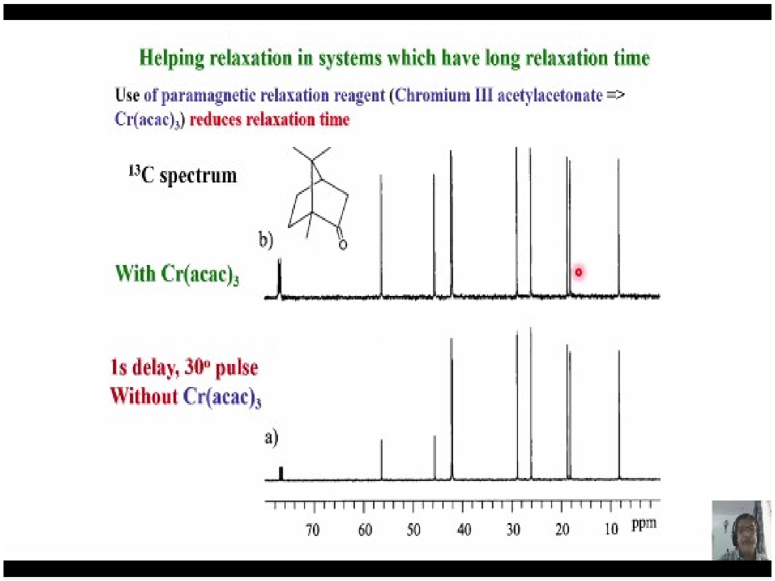

Helping relaxation in systems which have long relaxation time

Use of paramagnetic relaxation reagent (Chromium III acetylacetonate => Cr(acac)$_3$) reduces relaxation time

Okay, sometimes we adapt a trick when the system has a very, very long T1. We use material. a Lanthanide shift reagent called a paramagnetic relaxing agent. We also can use what is called chromium acetylacetate. It is not lanthanide that is different one. It is a chromium acetylacetate microgram quantity, very little you add it, it will enable these spins to relax. See this is without Cr(acac), these two peaks are weak in intensity. Now they are relaxed and we get better signal. So these are called relaxing agents Cr(acac), Chromiumacetylacetate. It is used as a paramagnetic relaxation reagent, used to reduce the relaxation time, please remember this.

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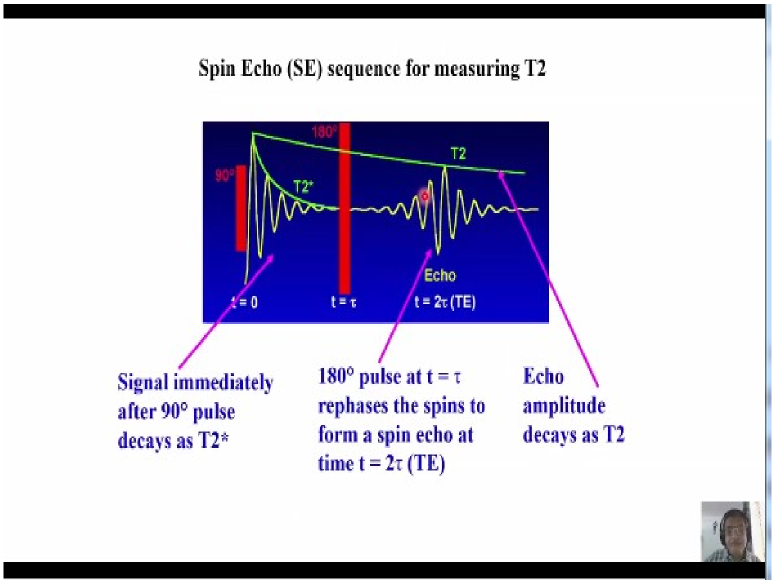

Spin Echo (SE) sequence for measuring T2

Signal immediately after 90° pulse decays as T2*

180° pulse at t = τ rephases the spins to form a spin echo at time t = 2τ (TE)

Echo amplitude decays as T2

Okay, now we can go to the similarly Spin Echo Method is what is adapted for measuring T2. Spin echo I have already discussed in depth. Vectorially also we understood. The inversion recovery method is 180 tau 90; but the spin echo is 90 T1/2 180 T1/2 or 90 tau, 180 tau and collect the signal. But here it forms a echo like this. You have to collect the signal on the top of the echo, how it is decaying, it is echo amplitude.

And this decay of the signal when you are collecting the signal as a function of an echo amplitude, can be fit to an exponential again, and you will get T2; because this echo amplitude decays as a function of T2. You understand how you can measure T2. Simply remember spin echo sequence is what is used; it is called Carr Purcell Spin Echo.

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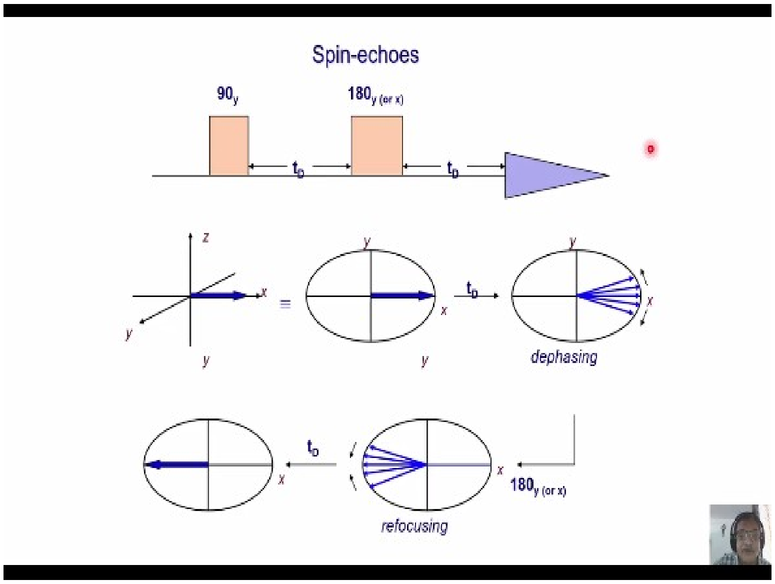

Spin-echoes

The improved version of that you can have a multiple echo's. And of course is what we discussed about spin echo, how it dephases everything earlier.

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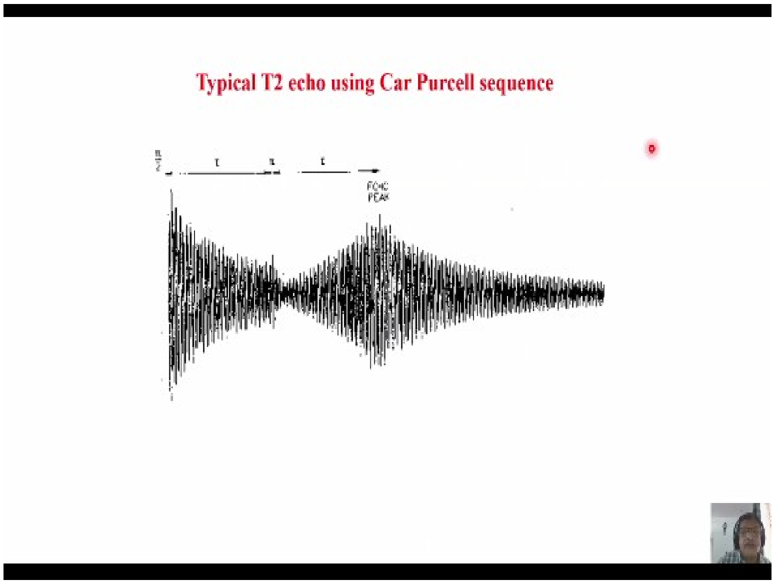

Typical T2 echo using Car Purcell sequence

So, okay this is a Car Purcell echo. In the realistic experiment, you do this. After some time apply a 180 pulse, see it goes back and forms the echo here. Fantastic, you know this is an echo peak. And how it decays as a function of echo time. There may be number of echoes like this. It is exponentially decaying; fit this echo aptitude to the decaying function, which I gave you earlier ,then you can get T2.

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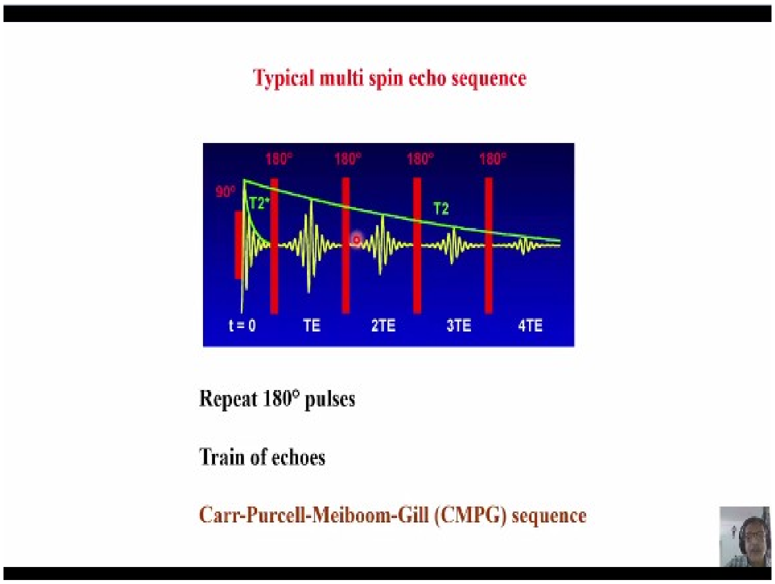

Typical multi spin echo sequence

Repeat 180° pulses

Train of echoes

Carr-Purcell-Meiboom-Gill (CMPG) sequence

And you can have multiple echoes; in the one experiment we have only 90 tau and the echo here. But to see how it is decaying, you can have multiple echoes. Keep on doing the echoes like this. See bring the magnetization from 90 to X axis. Apply 180 take it here. It will start dephasing. Apply 180 bring it here. Like that you can keep on applying n number of times; every time you can start getting the echo. And the echo amplitude, you see, reduces exponentially. Can you see it here? it is reducing exponentially. And this is what you have to fit the curve for the equation of decay function I gave you. Then you can measure the exact value of T2. Of course, this has a contribution in homogeneity, various things we have to discuss. This is not the original T2, this comes because of the contribution from magnetic field inhomogeneities also. That can also cause signal to decay; then you have to subtract that component.

So, there are several tricks adapted and anyway we will not go into all those details. But basically remember; I gave you the idea about what is T1? What is T2; conceptual understanding; What is the growth function; What is the decaying function; everything we discussed. T1 if you want to measure, you have to adapt inversion recovery method that is 180 tau 90 sequence, vary the tau value, and keep on collecting the signal as a function of tau and then intensity of the peaks you get, fit into that growth function.

For measuring T2 you adapt a spin echo sequence. YUou can have multiple echoes like Carr-Purcell-Meiboom-Gill sequence; and you get the echo amplitude that is a decaying function again; measure the echo amplitude at every echo and fit it into the decaying function. Then you get T2 value. Of course, there are lots of corrections to be applied, everything which I did not discuss, because they are not the original T2, this T2 has contributions from field homogeneities. Many things, you have to subtract and apply corrections, everything, those details I am not discussing, but I am just giving you the gist and an idea of how to measure T1 and T2.

Okay I will stop at this place at this point now, I have told you in this last class, in this class a lot about T1 and T2. Of course because of the time constraint, I have to go hurriedly because I already have exceeded number of weeks given to me to teach NMR. My number of classes are already over; still I have to teach a lot more, so I went a little faster in this class and last class, but nevertheless, I gave you the idea.

I am sure; however, fast I am speaking, I am giving you the concept. If you are attentive, I am sure you would have got the points. So, we will stop for the relaxation time and concepts and measurements for this class.