Advanced NMR Techniques in Solution and Solid-State

Prof. N. Suyaprakash
Department of NMR Research Centre
Indian Institute of Science – Bengaluru

Module-33
T1 Relaxation Mechanism
Lecture – 33

Welcome all of you. In the last class we discussed a lot about relaxation phenomenon, concepts, especially varieties of concepts we understood. We started discussing T1 relaxation phenomenon, we knew it is nothing but interaction of the spin with the lattice. We understand that spins give its energy to the lattice and the mode of giving energy is the stimulated emission. And then the fluctuating fields which is responsible for this emission should be at the Larmor frequency, that is what we said.

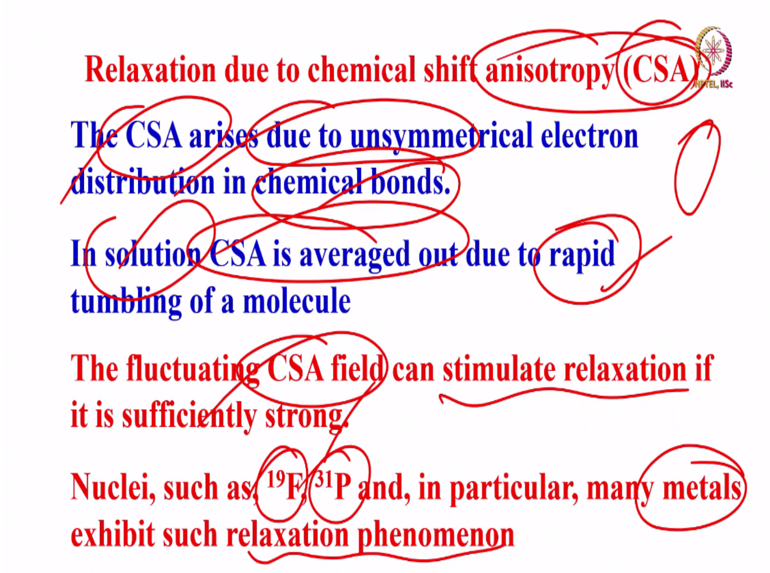
These fluctuating fields are generated because of various tumbling motions of the molecules, especially the chaotic motions. We said especially some motions like diffusion and others can contribute to this. Spontaneous emission is very less effective, especially in the RF region. So, this chaotic motion when it happens then spins can give its energy to the lattice then this energy is given in the form of a heat. It is a very small quantity compared to kinetic energy and dissipates very fast. But why it takes sometimes more time is because the Larmor frequency which is responsible for local field generated may not be in abundance. If it is not there, then spins will not relax very fast. And then what is the mechanism of relaxation? there are several ways, in the sense mechanisms for creating the local fields to aid the spins to relax. There are several mechanisms.

We understood dipole mechanism, dipole-dipole interaction where we considered two dipoles which are close in space, spatial proximity is the condition. If they are very closing space, the relative orientation or the orientation of them with respect to the external magnetic field do not change, as the molecules undergo motion. Let us consider one spin, the other spin keeps undergoing motion surrounding it, various tumbling motions. Then it keeps on changing the magnetic field, surrounding it keeps changing. The magnetism at this site of the other nuclear spin keeps changing; if it is the Larmor , it can cause relaxation. This is a dominated interaction called dipole-dipole relaxation, which is responsible for relaxation of the spins; especially in the solution state. And I said when the spins are close in space it happens that is why I said in the case of carbon 13 NMR, if we take proton attached to carbon or some other nuclei which are very close by, the spins relax very fast.

Otherwise for the non-protonated carbons I told you, like quaternary carbons take enormous amount of time to relax. Sometimes when the spins take enormous time to relax, there are external mechanisms through which spins can be allowed to relax faster; by using external agent these are called relaxing agents. I gave an example of one such is Cr (acac); Chromium acetylacetonate, it is happening and some other things are there; we can utilize that also.

So, basically we discussed about one of the important dominant relaxation mechanisms, that is dipole-dipole interaction. Among several other things, th of course few others things are very important; one is chemical shift anisotropy.

(Refer Slide Time: 03:50)



Relaxation due to chemical shift anisotropy (CSA)

The CSA arises due to unsymmetrical electron distribution in chemical bonds.

In solution CSA is averaged out due to rapid tumbling of a molecule

The fluctuating CSA field can stimulate relaxation if it is sufficiently strong.

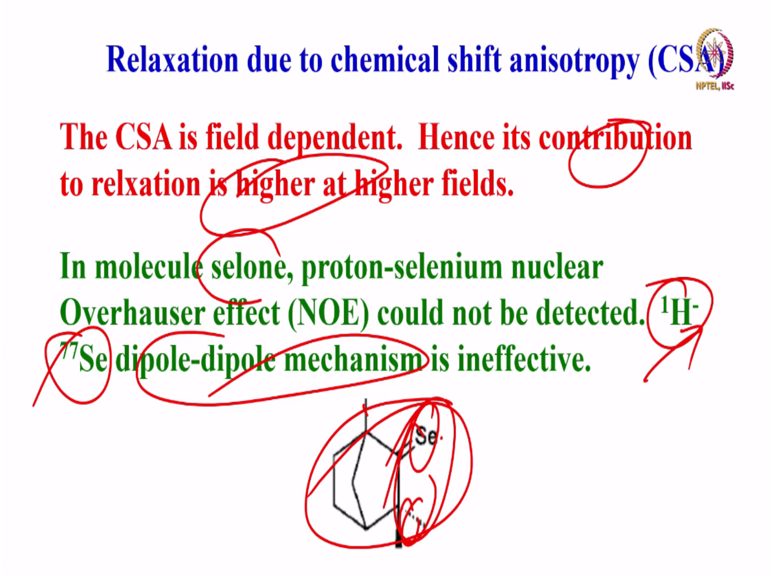
Nuclei, such as ^{19}F, ^{31}P and, in particular, many metals exhibit such relaxation phenomenon

We will today start with chemical shift anisotropy now. We will see how CSA is going to aid in relaxation. The CSA, of course, you know why it comes. It is because of unsymmetrical or asymmetrical distribution of charges surrounding the chemical bond. So, if there is a charge density which is not symmetrical; if the asymmetrical charge distribution of electrons, then the chemical shift anisotropy arises.

Chemical shift anisotropy depends upon charge distribution at the site of the nucleus. In the case of CSA, again CSA is averaged due to rapid tumbling motion of molecules, molecules undergo rapid tumbling motion. As a consequence, the CSA is averaged out. Remember I told you in the very first class among internal interactions CSA, dipolar interactions they all get averaged out in solution.

It is not possible to measure it in solution stat. But their mechanisms aid relaxation; you cannot measure CSA in solution state, but CSA which is present which creates the local field will aid in relaxation. So, CSA is another thing which gets averaged out in solution because of rapid tumbling motion, can also can also stimulate relaxation. And if the CSA is a large value it can stimulate relaxation. And when it is sufficiently strong especially in fluorine19 carbon-13, phosphorous 31, etcetera they have large CSA; especially in heavy metals they exhibit such a relaxation phenomena because of CSA. So, CSA is another dominant phenomenon of relaxation in some nuclei, like this. These are one another source of relaxation; but no source of relaxation is unique; everything could be present simultaneously; various phenomena are present.

(Refer Slide Time: 05:44)



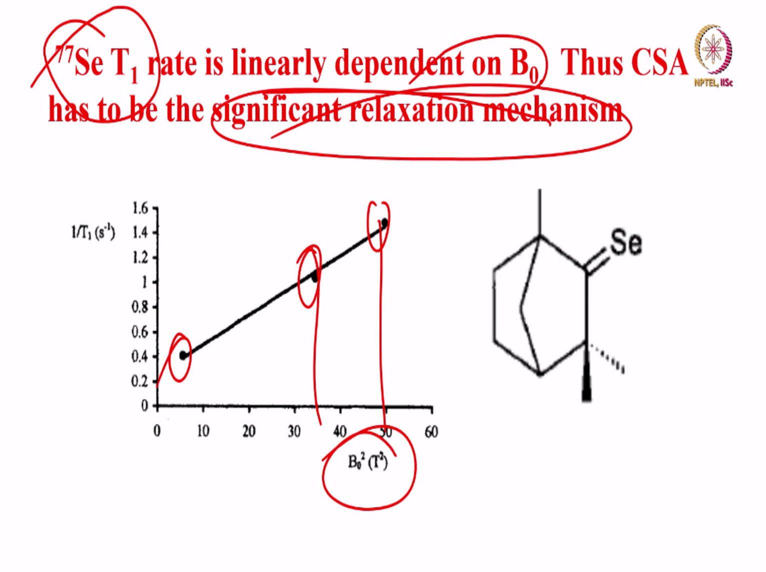
Relaxation due to chemical shift anisotropy (CSA)

The CSA is field dependent. Hence its contribution to relxation is higher at higher fields.

In molecule selone, proton-selenium nuclear Overhauser effect (NOE) could not be detected. ^{1}H-^{77}Se dipole-dipole mechanism is ineffective.

For example, if I take the CSA important point you should know is, the relaxation due to CSA is field dependent, because CSA is field dependent. So, contribution to relaxation, you know chemical shift anisotropy is field dependent, chemical shift is field dependen,t I told you it varies linearly with the magnetic field, external magnetic field. Hence, its contribution relaxation is higher at higher field; higher the magnetic field, higher the chemical shift anisotropy, larger the value. So, it relaxes faster. So, the relaxation because of CSA is field dependent say, for example, a molecule like, this is a simple molecule called selone. The proton-selenium NOE was done, like this, I will tell you what is NOE, do not worry. You can irradiate one of the protons to see the change in the intensity on the other, that can help you to find out about special proximity called NOE. In next class we will discuss all those things. And NOE from proton selenium 7,7 when they tried to do the NOE, it was not possible to detect NOE. NOE is very weak, they could not detect at all. So, the dominant relaxation phenomenon in this case was CSA. NOE comes because of dipole-dipole mechanism, we will come to that later. Main source of NOE is dipole-dipole interaction. Since they could do not see NOE, it could not be seen experimentally between selenium proton, it was assumed or it was confirmed that dominant relaxation mechanism in this case is CSA; and because this is ineffective in this molecule.

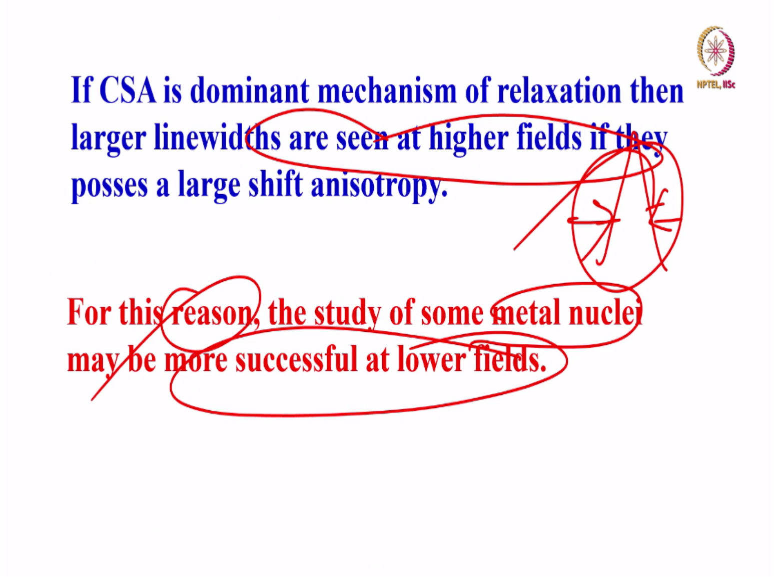
(Refer Slide Time: 07:29)



^{77}Se T_1 rate is linearly dependent on B_0 Thus CSA has to be the significant relaxation mechanism

So, look at this one selenium 77 T1 relaxation that was measured, how we measure we will see later. It was linearly dependent because CSA is linearly dependent. CSA you can see the T1 here at some magnetic field, and this at some magnetic field, it is here and here. That shows when the relaxation is field dependent like this, it is understood the significant relaxation phenomena or mechanism is CSA in this molecule. And also confirmation is, NOE phenomena could not be seen between selenium and proton which comes because of dominant dipole-dipole mechanism.

(Refer Slide Time: 08:13)



If CSA is dominant mechanism of relaxation then larger linewidths are seen at higher fields if they posses a large shift anisotropy.

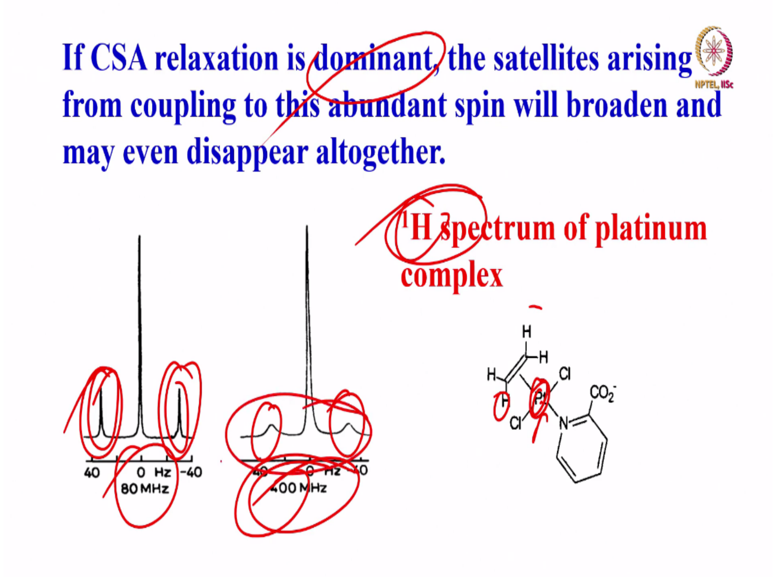
For this reason, the study of some metal nuclei may be more successful at lower fields.

So, CSA is another dominant mechanism and larger line width is seen at higher magnetic field, if there is large CSA. This is a understandable phenomena because if CSA is field dependent, as we go to higher and higher magnetic field, the CSA becomes larger and larger and then it give rise to larger line widths, especially in the solution state. We do not measure CSA in solution, but it causes relaxation phenomena.

Like I told you we can see that, if there is unpaired electron, it relaxes faster. I told you as a consequence the signals are becoming broader. Similarly, CSA as we go to higher magnetic field has larger anisotropy, means line widths becomes larger. This is one of the reasons why in some metals which have unpaired electrons, which have fast relaxation or CSA is larger, are studied only at lower magnetic fields, not at higher magnetic field.

And at higher magnetic field it is very difficult. As a consequence such nuclei are generally is preferred to study at low magnetic field.

(Refer Slide Time: 09:21)



If CSA relaxation is dominant, the satellites arising from coupling to this abundant spin will broaden and may even disappear altogether.

^{1}H spectrum of platinum complex

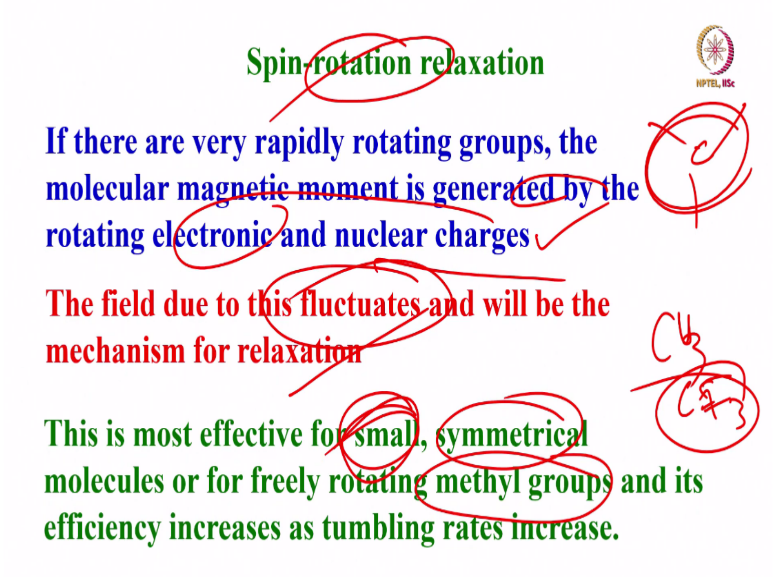
See, for example, in this molecule the CSA relaxation is dominant. Especially in this molecule there are platinum satellites. This is at 80 megahertz, and at 400 megahertz. Two spectra were obtained at two spectrometers. So, now this one is the spectrum of complex this is 1H spectrum. Now there is a platinum coupling with this. Platinum can couple to this proton so the coupling is there.

But this platinum also has little abundance, so intensity pattern is quite reasonable here. If the intensity is very, very small they are called satellites. I think we discussed this in previous course. In this course I did not talk about it, but those who are interested can see, but may be when I discuss as HSQC and others, I will tell you something, a little bit about what are satellites and everything.

The satellite intensity you see is quite sharp and intense, at 80 megahertz. The same sample and the same spectrum, proton spectrum recorded 400 megahertz, you see the satellite becomes broad. And we go to even 800 megahertz, what will happen? this will completely disappear. See these satellite are coming because of coupling of proton with platinum; that is why they are called satellites.

And these satellites become broad means, the relaxation time is because of CSA which is quite large. As you go to higher magnetic field, it is broadening the signal. If you go to very high magnetic field you may not be able to see the satellited at all; it will become completely broad.

(Refer Slide Time: 11:03)



Spin-rotation relaxation

If there are very rapidly rotating groups, the molecular magnetic moment is generated by the rotating electronic and nuclear charges

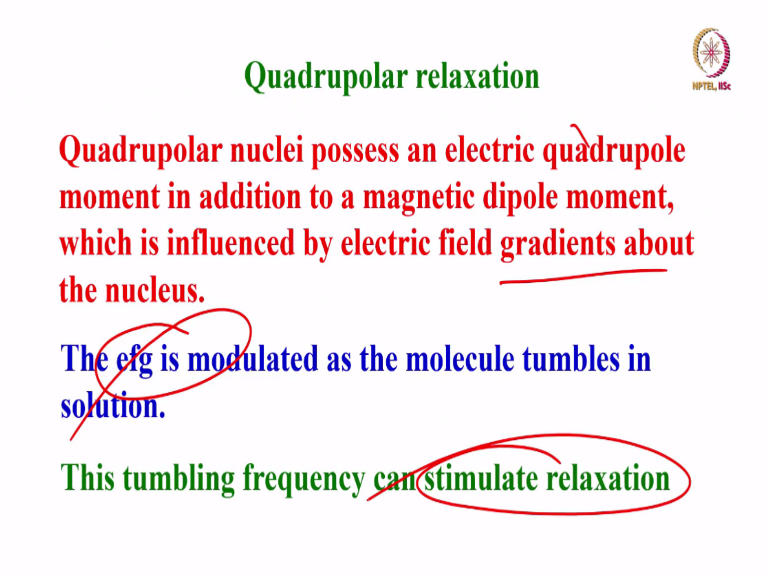
The field due to this fluctuates and will be the mechanism for relaxation

This is most effective for small, symmetrical molecules or for freely rotating methyl groups and its efficiency increases as tumbling rates increase.

So, this is why CSA is one of the important dominant relaxation phenomena; that is what we discussed. Now we will understand something called spin rotation relaxation. This is another interesting phenomena; various phenomena are there for understanding. Now let us say in your molecular rapid rotating group, what is that say for example CH3 group, or CF3 group or the molecule itself for a particular ring undergoing faster rotation, some rotation you get. Rapidly rotating group CH3, I have a proton along the CC bond this maybe undergoing very fast rotation. Then what will happen? the magnetic moment is generated by this rotating group and then because of that electronic and nuclear charges will be present; and this one produces the field because of the fluctuating charges. This field fluctuates, and aids in relaxation; it is one of the mechanism of relaxation.

Please understand, the field produced because of the fluctuation of the rotating electronic nuclear charges, you have a dominant relaxation mechanism not dominant, a relaxation mechanism. And this is very effective especially for small molecules, symmetrical molecules or freely rotating methyl groups, CH3 group CF3 group, etcetera. If they are present, they will undergo fast rotation and as a tumbling frequency of the methyl groups is faster and faster, then the relaxation increases, the relaxation efficiency increases. So this is important thing, spin rotation relaxation you can see basically in small molecules, symmetrical molecules containing fast rotating groups like methyl group and CF3 groups.

(Refer Slide Time: 12:55)



Quadrupolar relaxation

Quadrupolar nuclei possess an electric quadrupole moment in addition to a magnetic dipole moment, which is influenced by electric field gradients about the nucleus.

The efg is modulated as the molecule tumbles in solution.

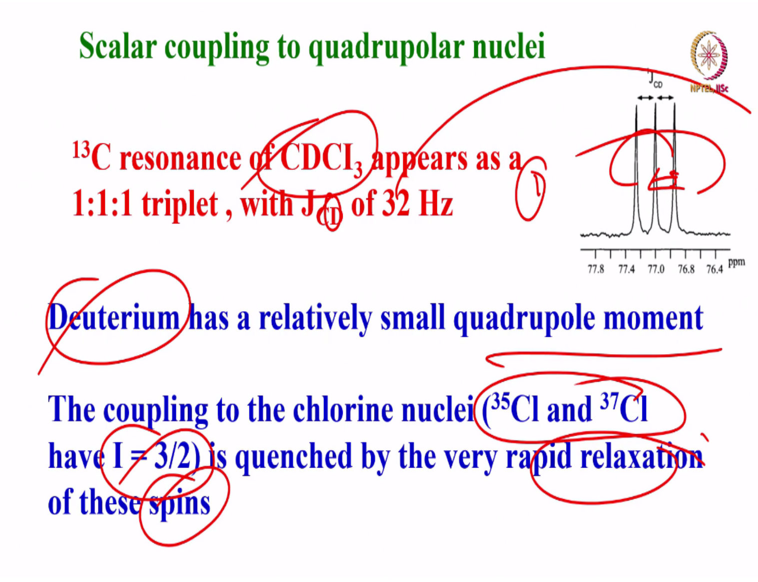
This tumbling frequency can stimulate relaxation

Now we will talk about quadrupolar relaxation. I remember I told you when we were discussing about the internal interactions, I said for the nuclei greater than spin half, there is one type of interaction which is called quadrupolar interaction. It is because of electrical interaction I told you, interaction of the electric quadrupole moment with the electric field gradient; that can give rise to some sort of a interaction, and quadrupolar coupling.

But in the solution the quadrupole coupling is not seen, it is averaged out. But though it averages out, it aids in relaxation, that is called quadrupolar relaxation. Quadrupolar nuclei posses an electric quadrupolar moment, in addition to magnetic dipolar moment and this is because we have electric field gradient at the site of the nucleus. As a consequence, it creates quadrupole moment; and then electric field gradient is modulated as the molecule tumbles in solution. That is electric field gradient which is produced at the site of the nucleus because of the electric quadrupole moment and interaction of the electric quadrupole moment with electric field gradient.

So, efg that is generated at the site of the nucleus is varying; it keep fluctuating as a molecule fluctuates. So, efg gets modulated when the molecule is undergoing tumbling motion. So, this can create relaxation. For all those things when the molecular undergoes rotation whether it is a spin rotation, whether it is a dipole-dipole interaction, or wheher it is CH3 or it is quadrupole relaxation, finally what happens, because of molecular tumbling the magnetic field, the local field generated at the site of other nuclei is changing. So, as a consequence there is a relaxation. It aids relaxation. It is a phenomenon for relaxation, and this is what happens; it stimulates relaxation; now this quadrupole relaxation.

(Refer Slide Time: 15:08)



Scalar coupling to quadrupolar nuclei

^{13}C resonance of $CDCl_3$ appears as a 1:1:1 triplet, with J_{CD} of 32 Hz

Deuterium has a relatively small quadrupole moment

The coupling to the chlorine nuclei (^{35}Cl and ^{37}Cl have $I = 3/2$) is quenched by the very rapid relaxation of these spins

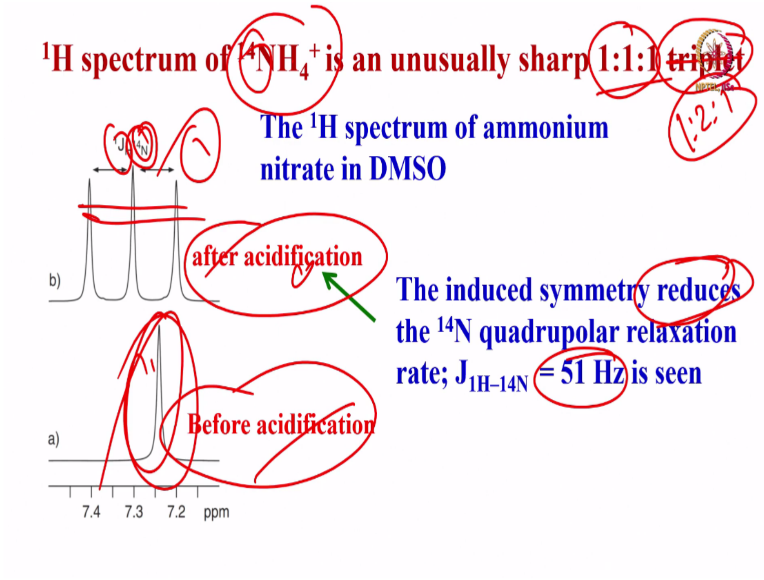
Sometimes quadrupole relaxation is so large, I do not want to go into the details of that. Remember some nuclei, exotic nuclei have a very large quadrupole moment; of the order of several megahertz 5 mega, 10 mega, 20 megahertz. Remember it is a huge number; what are the interaction strengths, Zeeman interaction strength is larger among all the external interactions. Then if you look at the internal interactions dipole-dipole interaction, then comes CSA, then comes spin rotation then comes J coupling, like that chemical shifting interaction is second after dipolar coupling then J coupling like that it goes. Whereas for the spin greater than half nuclei, the quadrupole interaction become dominant; it is really dominant. This is called quadrupole coupling.

The quadrupole interaction when it becomes dominant, generally then what happens you will not see the coupling of this quadrupole nuclei with any other nuclei. For example we take CHCl3; if you take CHCl 3 look for the proton NMR you will see coupling to carbon 13 appear as satellites; C13 NMR you will see coupling with proton and you get a doublet, but what about chlorine? Chlorine 35, chlorine 37, they have spins; they are quadrupolar nuclei, but they will not contribute to coupling because the relaxation is so fast; the quadrupole coupling is so large; it will not participate in this, and relaxes faster and you will not see the coupling. Especially if the quadrupole coupling is very large, you will not see the coupling with other nuclei , especially when the quadrupolar nuclei close by are coupled or interacting.

For example you take CDCl3 if you take the CDCl3 molecule and look for the carbon 13 NMR and very interestingly what I am going to see is a triplet like, this not triplet, three line pattern. This is three line pattern of equal intensity; and this separation gives you CD coupling, coupling between carbon and deuterium. So, this is an interesting thing we can measure here. And this is very large. It is coupled ta quadrupolar spin, spin 1. Deuterium is a quadrupolar nucleus with spin 1. But in reality when the quadrupole coupling is very, very large you will not see the three line pattern at all; in fact in some other nuclei like chlorine 35 and chlorine 37, it gets smudged and gives a broad signal. But in this case we are going to see it, that is because the deuterium has a very small quadrupole moment.

As a consequence, the coupling of carbon with the deuterium is clearly seen. In some cases for example, chlorine 35 and chlorine 37 which is are spin 3 / 2 we will not see, because of what is called quenching. We call it quenching by the rapid relaxation. This is called relaxation enabled decoupling; this is called relaxation decoupling. We will not see the coupling of chloring with carbon because of rapid relaxation; this is called quenching.

(Refer Slide Time: 18:17)



^{1}H spectrum of $^{14}NH_4^+$ is an unusually sharp 1:1:1 ~~triplet~~

1:2:1

The ^{1}H spectrum of ammonium nitrate in DMSO

after acidification

The induced symmetry reduces the ^{14}N quadrupolar relaxation rate; J_{1H-14N} = 51 Hz is seen

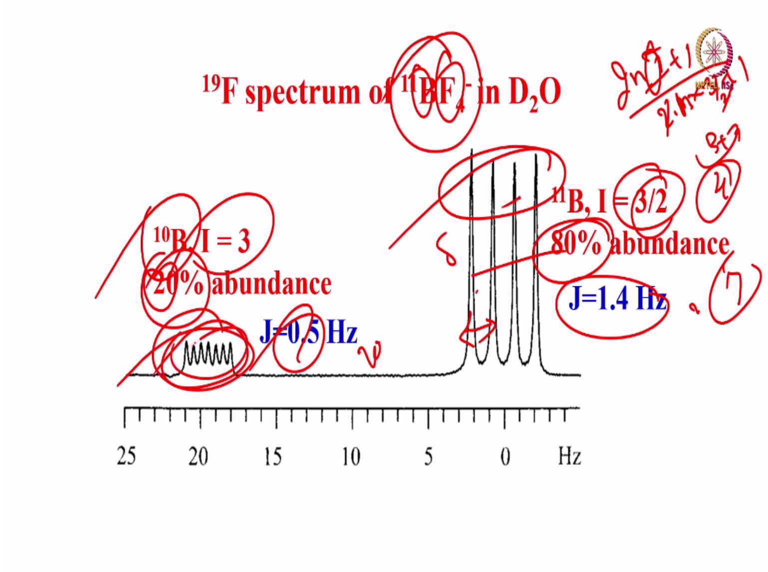
Before acidification

So, take for example proton NMR spectrum of nitrogen 14NH4 anion; if you take 1H spectrum it is 1:1:1 triplet not triplet it should be in principle called the three line sof equal intensity, loosely call triplet does not matter, but it should be called 1:1:1 three line pattern. The NH4 if you take the 1H NMR spectrum it is going to be three line pattern of equal intensity.

Why it is coming? because N14 has spin 1 like deuterium; we saw in CDCl3 with deuterium coupling. Here also we are seeing the coupling. This is without coupling and there is something which was done for this molecule. Before acidification there was no coupling seen, but here you are seeing the coupling after acidification, because the symmetry induced reduces the quadrupole coupling after some chemical modification.

The quadrupole relaxation becomes very, very fast. The quadrupole relaxation rate is very fast, it reduces quadrupole relaxation rate reduces, then coupling between N14 and proton of the order of 51 Hertz is very clearly visible. And before acidification you do not see anything no coupling seen at all; whereas after doing some chemistry you will see that proton coupled to N14 gives rise to three lines of equal intensity with a measurable coupling of 51 Hertz line width, and lines are quite sharp.

(Refer Slide Time: 19:54)



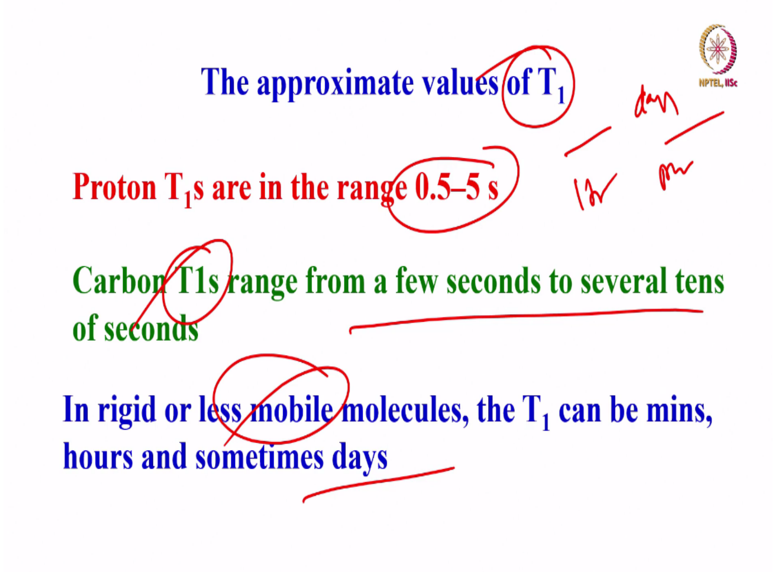
^{19}F spectrum of $^{11}BF_4^-$ in D_2O

Look at this one, this is another very interesting molecule BF4 ion, Bromine has two isotopes, we discussed this in the analysis of the heteronuclear spectra, Bromine 11 has spin 3/2 Bromine 10 has spin 3; and this has 20% abundance, this has 80% abundance. So, now we look for the fluorine NMR. When fluorine is coupled to Bromine, how many peaks you expect?

Remember 2nI+1 rule I apply, this also we discussed in earlier case. In the case of Bromine I =3/2, 2 into N there is only one Bromine; 2 into 3/2 + 1. So, what will happen 3 + 1 you will get 4 lines. So, for the Boron 11 you are going to get 4 lines of equal intensity and this separation gives Boron 11 and fluorine coupling, which is seen; 1.4 hertz J coupling we could see.

So, in spite of the coupling of fluorine with quadrupolar spin. Look at Boron 10; I = 3 put I = 3 in the same equation, 2 into 3 + 1 it will be 7 lines; you see 7 lines of equal intensity with a coupling of 0.5 Hz as you could see. In both the cases, spin 3 and 3/2, the coupling with fluorine nucleus is seen. Normally we do not see that thing, especially in some cases where there is a symmetrical charge distribution more or less at the site, somehow the quadrupole coupling reduces significantly. We are going to see this type of coupling. And why it is small intensity compared to that, because abundance is only 20%, this is 80%. So this should be four time larger intensity, and this is very small 7 line pattern you see of equal intensity. So, these are the things.

(Refer Slide Time: 21:45)



NPTEL, IISc

The approximate values of T_1

days

hr

mn

Proton T_1s are in the range 0.5–5 s

Carbon T1s range from a few seconds to several tens of seconds

In rigid or less mobile molecules, the T_1 can be mins, hours and sometimes days

So there are various other mechanisms for relaxation, like J anisotropy. I did not discuss all those things; these are all some important parameters for relaxation which I discussed. Now you may tell me, fine we are discussing about T1 mechanism, T1 what is the concept of T1 everything, but what is the value of T1? how much time it takes to relax. I said it takes some time for spins to relax to thermal equilibrium along Z axis, clear, understandable.

But what is the value of T1 if you ask I have to find out, is it in millisecond, seconds or hours, days, minutes, I must know that. So, approximately values of the T1 just to tell you, but it is not a rule as such, it can be large. It can significantly deviate from what I am telling here; I said proton T1s are in the range of 0.5 to 5 seconds; it is not a dogma it should be like that. It is an average, it can be of that order.

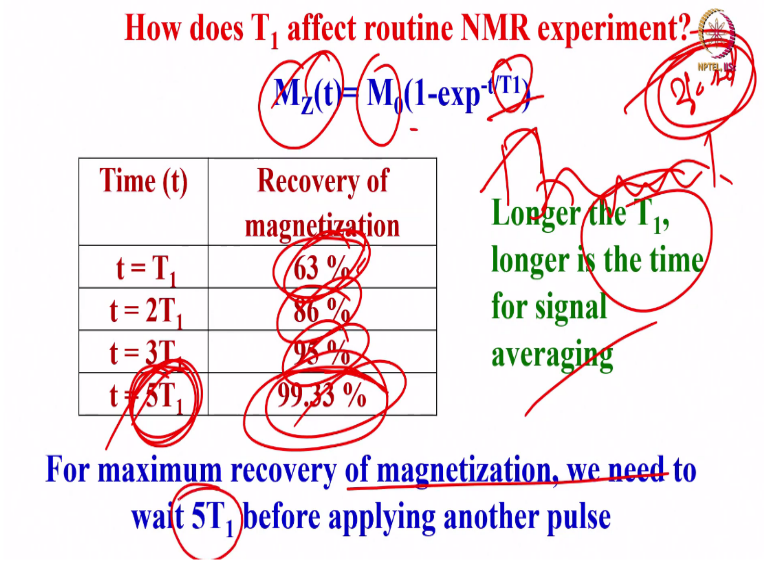
Generally proton T1 in solutions state I am talking in solution state is of this order. It can sometimes be hours, days and minutes also. It can go to several hours, it can go to minutes or it can go sometimes to days, depending upon the fluctuating field available at the site of the nucleus for the spins to undergo relaxation. Otherwise it can be fast like this, whereas carbon 13 if you look at T1; it can vary with a few seconds with a tens of seconds, that is also quite large.

Especially in rigid or less mobile molecules T1 can be minutes, hours or sometimes days simple example you take solids. It is not mobile, rigid solid you take it in the powder form or crystalline form, there is no mobility for the molecules, internally molecule may be undergoing rotational motion, but there is no transitional motion, molecules are fixed in the space in crystal or in a solid unlike in solution state, so less mobility.

T1 can be large, it can be minutes, it can be hours and days so T1 depends upon the mobility and especially that is the reason why T1 relaxation in the solids are very, very long. It can go to several hours also. So, now we can ask the question how does T1 affect? So, I know the value of T1, I know what is the approximately range of T 1 values in different situations. How does T1 affect me, why should I worry about it, when I have to do the experiment.

Of course the T1 information gives you more about the dynamics of the molecules, I told you long back when we started this relaxation phenomenon. If you just want to derive information about the dynamics of the molecule, the T1 and T2 phenomenon are very useful, fine.

(Refer Slide Time: 24:34)



How does T_1 affect routine NMR experiment?

$M_Z(t) = M_0(1-\exp^{-t/T1})$

Time (t)	Recovery of magnetization
$t = T_1$	63 %
$t = 2T_1$	86 %
$t = 3T_1$	95 %
$t = 5T_1$	99.33 %

Longer the T_1, longer is the time for signal averaging

For maximum recovery of magnetization, we need to wait $5T_1$ before applying another pulse

Why I should know the value of this? is it important for me to do the NMR experiment? Of course, yes. The reason is this is the expression we derived for the magnetization, for the spins to attain thermal equilibrium after they are disturbed. This is Mz magnetization to attain M0 when it comes to the original state, this follows exponential law, there is an exponential growth.

Now what I will do? this is exponential 1 – e to the power of t / T 1. What I am going to do is we will substitute t/ T1 different values. What we will do is, once let us say I am going to put t = T1; what will happen? e to the power of – 1 it is 1 over e, e is a 2.6752. You know that number you calculate that 1 over e what is that? then it turns out to be 1 – that e is 63 %. So, now put t = 2 times T1; it is 86; put T 2 = 3 times T1 is 95% or 5 times T1 it is almost 99%.

So, if you want the spins to come back to thermal equilibrium, maximum magnetization if it has to grow along Z axis, we have to wait 5 times to longer T1 and T1 for different spins in the molecule will be different. In the same given molecule different functional groups different nuclear spins can have a different T1. So, if we have to do the experiment, you all know what is the longest T1 of any spin in your molecule; 5 times the T1 value you have to give as the delay between the pulse, for successive data accumulation of signal.

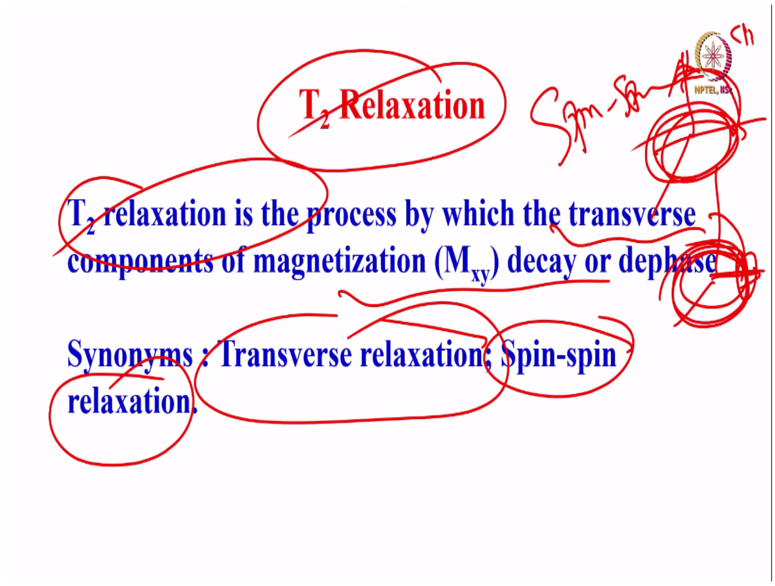
For successive data accumulation, the delay should be of the order of 5 times T1, only then you can get maximum signal, because by the time if you wait for 5 times T1 99.33% of the magnetization would have come back to Z axis. So, you apply another radio frequency pulse to collect signal you get 99% signal. So, that is the important point, you know the T1 then you can set up your experiment to get the maximum signal.

For example if your T1 is of the order of let us say several minutes some 50 minutes or 30 minutes or 40 minutes and you do not know the T1 value you start acquiring the signal with first RF pulse and start collecting the signal. Then second time immediately after collecting signal wait for one or two seconds and send another pulse you will not see the signal at all you will acquire only noise.

The reason is spins have not relaxed back to thermal equilibrium; they have not not come back to Z axis. So, as a consequence the T1 value is very important to know, so that you can set your experiment affect accordingly. The T1 affects the routine NMR experiment in this way. If you want to repeat the experiment for signal averaging after acquiring the data, if you want to send another pulse to collect signal, you must wait at least 5 times the longest T1 available in your sample in your molecule.

So, with this five the longer T1 is a time which is required for signal averaging for maximum recovery of magnetization; you need to wait for 5 T1 before apply another pulse for signal averaging.

(Refer Slide Time: 27:57)



T_2 Relaxation

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

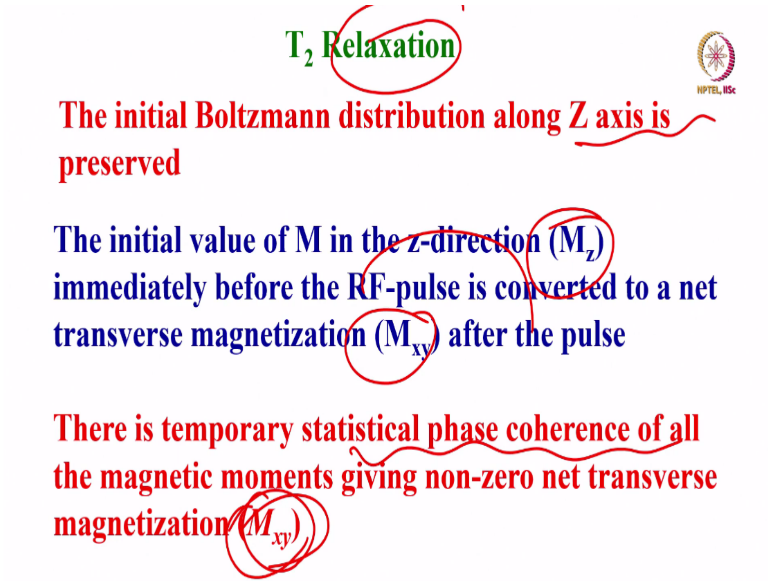
Synonyms : Transverse relaxation; Spin-spin relaxation.

So, with this T1 we have understood a lot we will talk something about T2 relaxation now. T2 is also very important relaxation phenomenon. So far we all discussed about T1, but we have not even still discuss about how do you measure T1 we will come to that after giving the conceptual ideas of T2 relaxation also. Then we will go to experimental aspects to measure T1 and T2; that is simple.

So, what is a T2 relaxation? There are two important relaxation phenomenon spin lattice and the other is called spin-spin relaxation. T2 relaxation is a process by which the transverse components of the magnetization decay in XY plane, that means if I apply the radio frequency pulse to the magnetization which is along Z axis bring it to XY plane. I told you it will go back to Z axis with time that is T1, but before that it will start dephasing in the XY plane.

Instantaneously as soon as you bring the magnetization to X axis there is a statistical phase coherence. All the spins, all the spin vectors, will be aligned along this axis; maximum signal you get. With time again because of the local fluctuating magnetic fields at the site of different nucleus, the spin vectors start dephasing, they start moving in the XY plane; then the total vector addition of all the thing if you take and look at the signal, signal intensity will come down. And if you wait for sufficiently long time, it so happens all the spin vectors here get completely decay or de-phase in the XY plane. This is called decay of magnetization in the transverse plane. This is another type of relaxation called spin-spin relaxation; also called transverse relaxation. Remember two relaxation mechanisms, spin lattice relaxation is growth along Z axis. Spin-spin relaxation is decay in the XY plane; this is called a transverse relaxation. The decay of magnetization in the XY plane is called T2 decay, Growth along Z axis is also called longitudinal axis, is called T1, also called spin lattice relaxation.

(Refer Slide Time: 30:20)



T$_2$ Relaxation

The initial Boltzmann distribution along Z axis is preserved

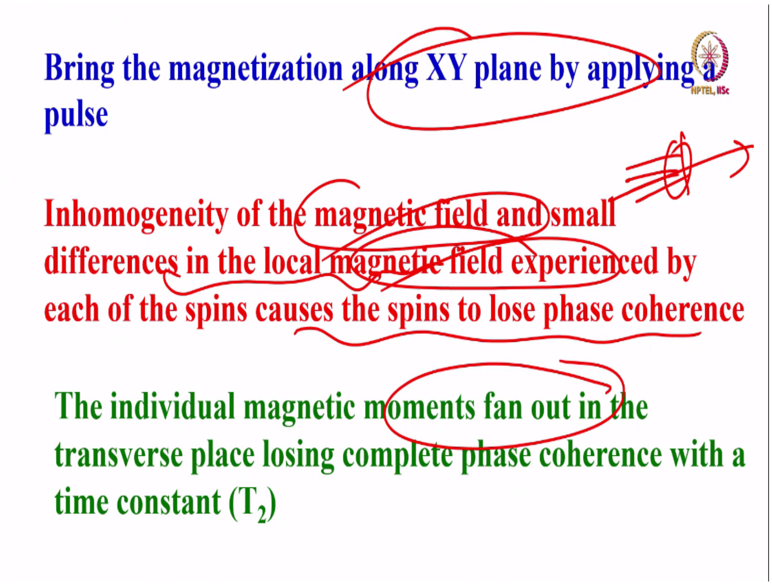
The initial value of M in the z-direction (M$_z$) immediately before the RF-pulse is converted to a net transverse magnetization (M$_{xy}$) after the pulse

There is temporary statistical phase coherence of all the magnetic moments giving non-zero net transverse magnetization (M_{xy})

And now T2 relaxation how it happens? First initially there is a Boltzmann distribution along Z axis; that has to be preserved. Initial value of M in the Z axis is Mz; immediately after the RF pulse is applied net magnetization comes to Mxy. I told you statistically there is a temporary phase coherence; all nuclear magnetic moments will be aligned in a particular axis and net magnetization is a sum of all magnetic vectors in the XY plane, or in a particular axis the maximum signal will be there.

Mxy is going to be maximum immediately after bringing the magnetization to the transverse plane.

(Refer Slide Time: 31:01)



Bring the magnetization along XY plane by applying a pulse

Inhomogeneity of the magnetic field and small differences in the local magnetic field experienced by each of the spins causes the spins to lose phase coherence

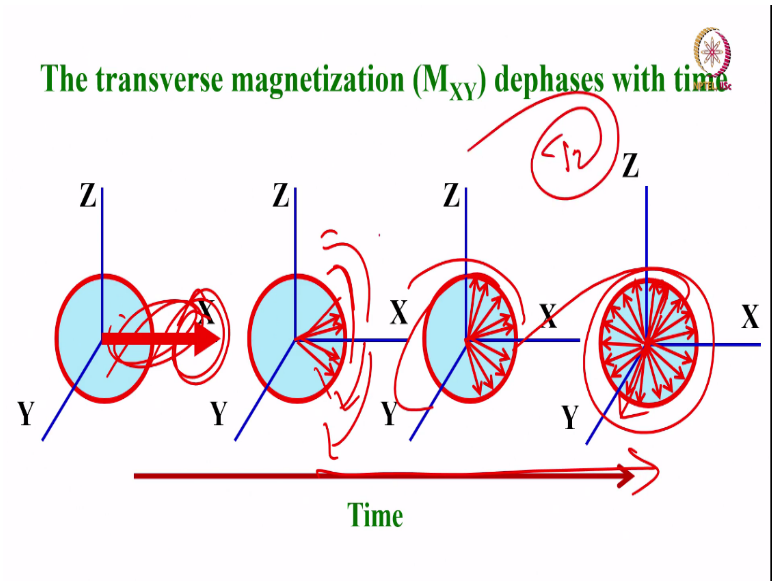
The individual magnetic moments fan out in the transverse place losing complete phase coherence with a time constant (T_2)

So, this is what happens bring the magnetization to XY plane by applying the pulse. Now inhomogeneity of the magnetic field and small differences in the local fluctuating fields experienced by the nuclear spins causes the spins to lose phase coherence. All the nuclear spin vectors will be aligned along this axis. There is a phase coherence, but this phase coherence will be lost.

That is because there is a local magnetic field experienced by the spins are different, they keep changing, they keep fluctuating. Different nuclear spins experience different magnetic fields. As a consequence, there is no phase coherence. When there is no phase coherence the magnetic moments start fanning out; they will start going out from particular axis and start moving all across the XY plane.

And then vector addition you do in the XY plane; some vectors are in this direction, some are in the opposite direction; they get nullify. Similarly, when all the nuclear magnetic moments completely get de-phase in XY plane, if you take the vector addition of all of them, there is no signal at all, it is totally zero. Magnetic moment will not be there and the total magnetization, the addition of all the individual magnetic moments if you take in the transverse plane, it is not there because they have completely de-phased. so vector addition is 0.

(Refer Slide Time: 32:28)



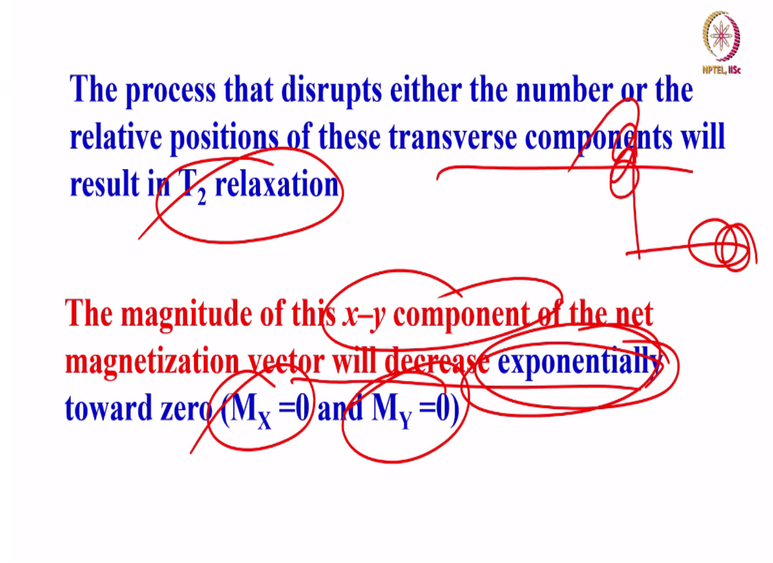
The transverse magnetization (M_{XY}) dephases with time

This is what you understand. Remember I said this in the T1 case; T1 was growth along this axis; the same thing what I showed, Immediately bring it to XY plane, there is a phase coherence now all nuclear spin vectors are in this X axis. Now some will start going like this, some will start going like this. Those which goes along this axis, which goes along this axis remember when we discussed about the evolution of magnetization we discussed, these are all called fast moving components and slow moving components.

Some moves faster like this, some moves like this as we keep waiting for some time slowly the fluctuating magnetic fields makes these spins lose phase coherence. They start de-phasing like this and after sometime there is a complete de-coherence. Now take the average of this, take the vector addition of all the magnetic moment vectors, it is 0 because at any instant of time if there is one vector like this, you can find another vector in the opposite direction.

So, vector addition of all these things becomes 0. So, this is a total de-phasing time. Now the time which is required for the magnetization which is in the transverse plane, to lose complete phase coherence is called T2; it is called spin-spin lattice relaxation time.

(Refer Slide Time: 33:59)



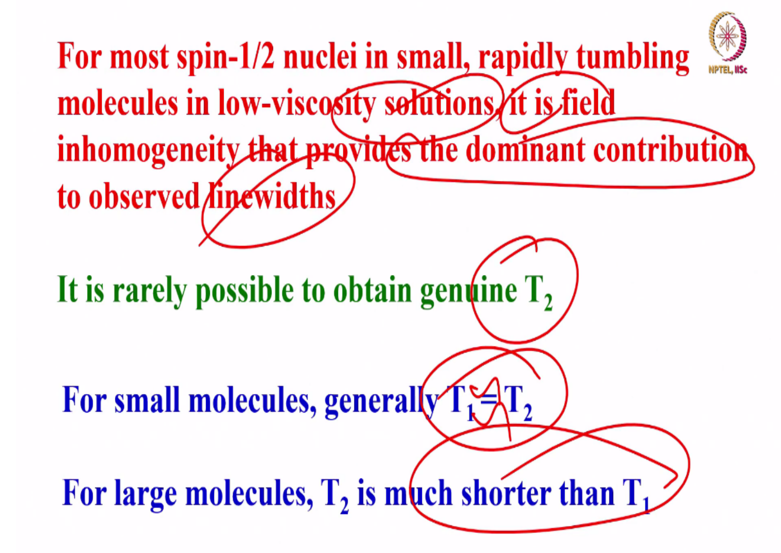
The process that disrupts either the number or the relative positions of these transverse components will result in T_2 relaxation

The magnitude of this *x–y* component of the net magnetization vector will decrease exponentially toward zero ($M_X = 0$ and $M_Y = 0$)

This is called T2 relaxation; also called spin-spin relaxation, where the transverse component will completely de-phase. So, the magnitude of the XY components of this if we take the vector addition is 0. And this is again an exponentially decaying function like exponential growth of T1 along Z axis. It is an exponentially decaying function in the transverse plane, both in X axis and Y axis.

So, that is why Mx component of the magnetization is 0, My component is 0. That is why if we have receiver here we get no signal, if we have receiver here, we get no signal. Both are zero after spins completely undergo de-phasing.

(Refer Slide Time: 34:41)



For most spin-1/2 nuclei in small, rapidly tumbling molecules in low-viscosity solutions, it is field inhomogeneity that provides the dominant contribution to observed linewidths

It is rarely possible to obtain genuine T_2

For small molecules, generally $T_1 = T_2$

For large molecules, T_2 is much shorter than T_1

And for most spin half nuclei, that are small, rapidly tumbling molecules, in low viscous solution it is a field inhomogeneity that provides the dominant contribution to observe line width. T1 is approximately equal to T2; not exactly that is a wrong statement; it should be approximately, for large molecule T2 is much shorter than T1.

More about T2 and other things we will discuss in the next class, and then we will understand something more. Since time is running short, I am stopping here. In this class we understood all about T1 mechanisms and everything; and also I introduced what is a spin spin relaxation. In the spin lattice relaxation we discussed a lot about phenomenon of relaxation, like dipolar interaction, chemical shift anisotropy interaction, quadrupole coupling, etc. All those things how they contribute and generate fluctuating fields at the site of the nucleus to ensure that they are at Larmor frequency, and they will ensure that spins give energy to the system, lattice, relax and attain thermal equilibrium, go back to Z axis. Various things we discussed. Then we also understand what is the spin spin relaxation it is nothing, but the de-phasing of the magnetization in the XY plane, we discussed that. We understood what is this thing; and it again it was fluctuating fields also and then this happens simultaneously along with the T1. We will discuss that later, especially in small molecules T1 is approximately equal to T2 and for large molecule T2 is much shorter than T1. We discuss more about these things in the next class. I will stop here. Thank you very much.