Advanced NMR Techniques in Solution and Solid-State

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Module-32
Spectral Density Function and Relaxation Mechanisms
Lecture – 32

Welcome back all of you. In the last class we discussed about the relaxation, we started discussing not completely discussed, and I introduced about the spin lattice relaxation and started understanding the various concepts involved in that, especially attaining the thermal equilibrium of magnetization after it is disturbed, this is what I called as attaining thermal equilibrium.

This is also called relaxation spin lattice relaxation or attaining thermal equilibrium or T1 various synonymous are there. We discussed also and I said that this relaxation will happen by the spins giving their energy to the lattice. Lattice, means I said, it is not a crystal lattice rigid system. It is anything other than the nuclear spins of your interest can be considered as a lattice or in other word simply for the surroundings of the spin systems, the spins will give energy.

How it gives energy? It gives energy in the form of heat. We understood that and this heat is negligible when compared to kinetic energy, it quickly gets dispersed at the body temperature, it largely gets unnoticed. And then for this to happen for the system to give the energy to the lattice it must be a stimulated emission, in the sense the spins from the upper state should come to the lower state.

Then lattice from lower state will go to the higher state; which will happen simultaneously. Only then there is a conservation of energy. Both the spins and lattice are in upper states, it cannot happen because it does not concern energy. For the spins from the excited state or upper state to come to lower state there must be stimulated emission, the spontaneous emission is not possible.

For the stimulated emission to happen there must be a fluctuating magnetic field. This fluctuating magnetic field comes because of the random fluctuations of the molecule, chaotic motion of the molecules. Electronic or vibration motions, such thing have very least effect in the emission of the energy. So, this fluctuating magnetic field is because of the motion of the molecules, molecular motions; it will be chaotic motion, diffusion and some thermal agitation and varieties of random fluctuations could be possible.

And this will generate frequency at the Larmor frequency not any frequency. So, there can be wide range of frequencies present, but all cannot stimulate emission or give energy, the spins to give energy. It must be only certain frequency to see that it will stimulate the spins to give the energy; that can happen. So, it should be at the Larmor frequency in the transverse plane.

But I also said the transverse plane it is also at Larmor frequency; the external RF is also the Larmor frequency; what is the difference then? The difference is external RF will excite or affect all the spins uniformly. Whereas the Larmor frequency or the RF that is generated due to the fluctuating magnetic field, in the transverse plan,e affect only few spins, selected spins. This is the main difference; so this is what we understood. We will go further now today and see and understand more about the relaxation phenomenon.

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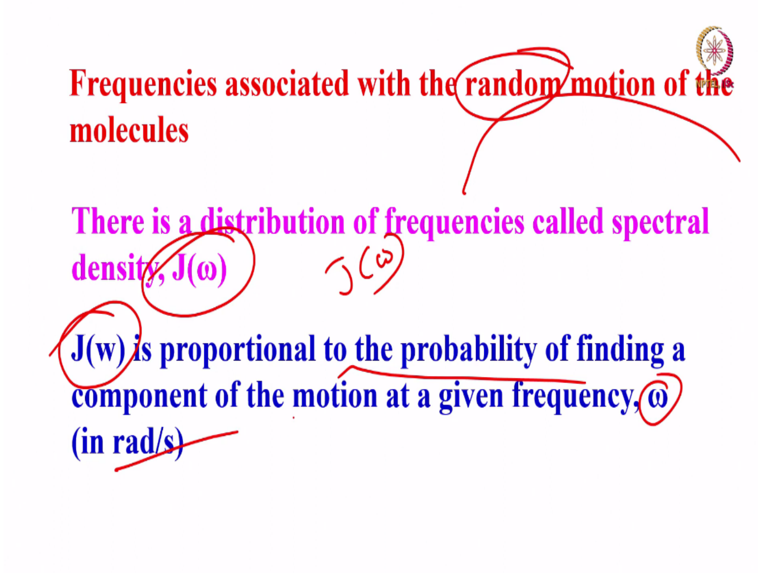

Frequencies associated with the random motion of the molecules

There is a distribution of frequencies called spectral density, J(ω)

J(ω)

J(w) is proportional to the probability of finding a component of the motion at a given frequency, ω (in rad/s)

Now frequency is associated with the random motion of the molecules. What are the frequencies? I told you it is a distribution of frequency; it is not one frequency. There is a band of frequencies and the distribution of frequencies is called a spectral density. It is given by a function called spectral density function J of omega, it is the distribution of the frequencies produced because of the fluctuating magnetic field.

And also in simple terms we can say this spectral density J omega is proportional to the probability of finding a component of the motion at a given frequency omega; it is in radians per second. This is simply the spectral density function, it is proportional to the probability of finding component of the motion at a given frequency. That is the concept you please remember that.

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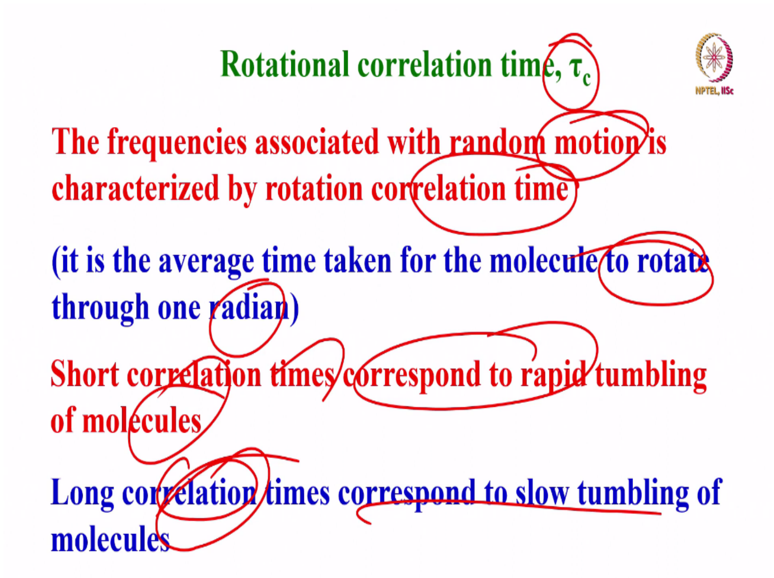

Rotational correlation time, τ_c

The frequencies associated with random motion is characterized by rotation correlation time

(it is the average time taken for the molecule to rotate through one radian)

Short correlation times correspond to rapid tumbling of molecules

Long correlation times correspond to slow tumbling of molecules

Now I will introduce another term called rotational correlation time tau c. What is the rotational correlation time? It is a frequency associated with the random motion, which is characterized by what is called as rotation correlation time. When the random motion is going on, there is a frequency associated with that. I told you not one several frequencies are present; the band of frequencies. And this is characterized by what is called the rotation correlation time.

And what is rotation correlation time? the definition of it is average time taken by the molecule rotate through one radian, that is important. See the average time taken by the molecule to rotate by one radian is called a rotational correlation time; given as tau c. This tau c and J omega they are all related, they are important. So, short correlation corresponds to rapid tumbling motion, and large correlation time corresponds to slow tumbling motion.

It is understandable, short correlation time, this tau c is very small means molecules are undergoing motion rapidly, and you can calculate what is the average time taken to rotate one radian. It undergoes very fast rotation means tau c is very, very short, correlation time. On the other hand, when there is a long correlation time then the molecules are tumbling very slowly. It can happen, because of the fast moving molecule, take in a solution which we little viscous, then the tumbling motion is very slow. In which case you will have a long correlation time. I will take simply isotropic solution like water in a bottle; their tumbling motion is much faster and a short correlation time. So, correlation time whether it is short or long, depends upon the tumbling motion of the molecules, whether it is rapid or slow this is an important point.

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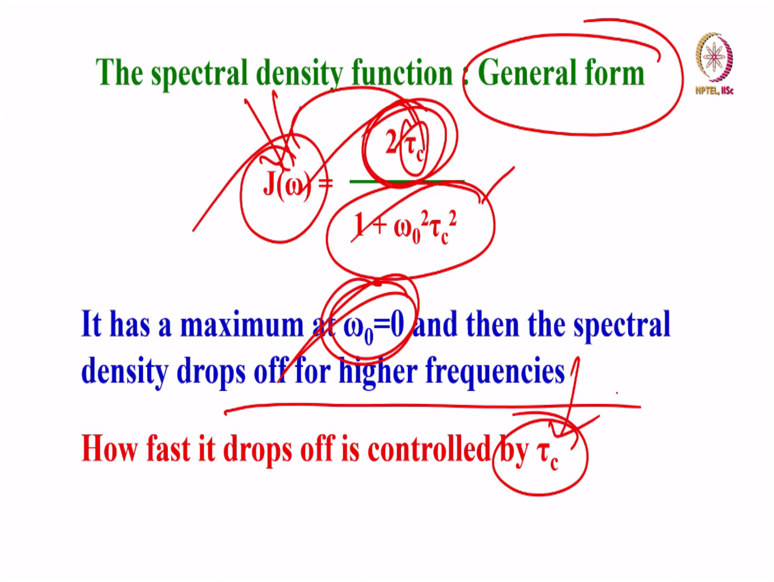

The spectral density function : General form

$$J(\omega) = \frac{2\tau_c}{1+\omega_0^2\tau_c^2}$$

It has a maximum at $\omega_0=0$ and then the spectral density drops off for higher frequencies

How fast it drops off is controlled by τ_c

So, the spectral density function now can be generally defined by a general form; a simple form general form. It is given by spectral density function J omega as 2 times tau c / 1 + omega square tau c square. So that is why I introduced the term tau c, that is a rotation correlation time. I introduced J omega that is the spectral density function and now this spectral density function can be correlated to correlation time, the motion of the molecule given by this expression.

Now you remember it is a maximum at omega = 0; and then spectral density drops off for higher and higher frequencies. How fast it drops off is controlled by tau c, the correlation time. So, this you must remember the spectral density function has a general form given like this, it depends upon tau c and the spectral density function has a maximum at omega 0 = 0 and then it drops off at higher frequencies which is controlled by correlation time tau c.

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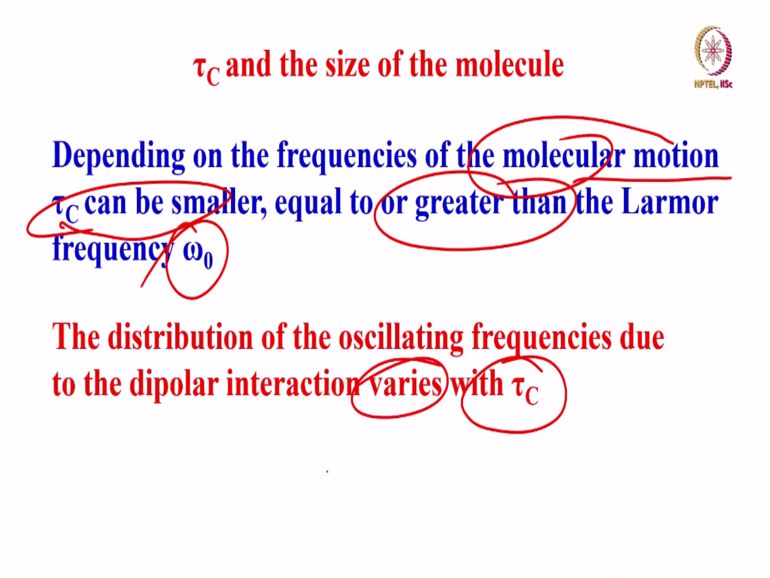

τ_C and the size of the molecule

Depending on the frequencies of the molecular motion τ_C can be smaller, equal to or greater than the Larmor frequency ω_0

The distribution of the oscillating frequencies due to the dipolar interaction varies with τ_C

And now correlation time as I told you is about the motion of the molecule. It is the average time taken for the molecule to undergo rotation by one radian. Now that means it depends upon the size of the molecule also. For example, depending upon how small or big the molecule the correlation time depends, it varies. Depending on the frequency of the molecular motion tau c can be smaller equal to greater than Larmor frequency. That is very important thing. It depends upon tau c and tau c depends on the size of the molecule.

The distribution of the oscillating frequency due to dipolar interaction varies with tau c, because it depends upon the size of the molecule.

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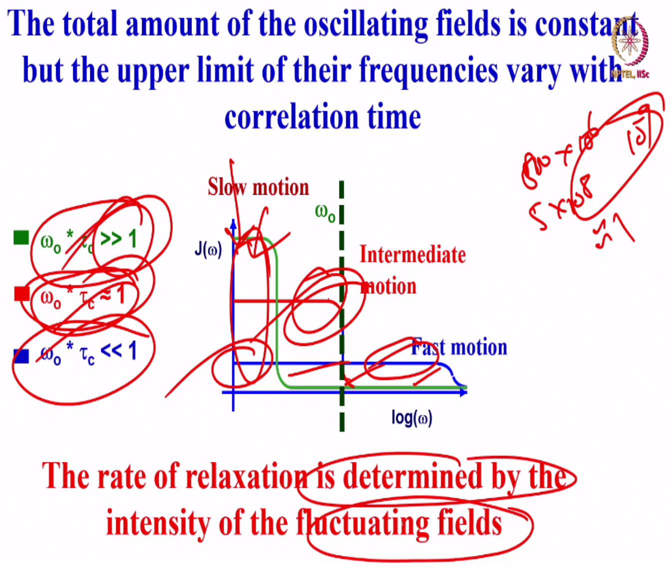

The total amount of the oscillating fields is constant but the upper limit of their frequencies vary with correlation time

The rate of relaxation is determined by the intensity of the fluctuating fields

Now the total amount of the oscillating fields is constant, but the upper limit of the frequency vary with correlation time. That means the total amount of oscillating field you have got total frequency, total amplitude is constant. But the upper limit of the frequency vary with the correlation time, very interesting thing. It can be understood by a graph like this.

See, for example, I have given three plots here one in green colour, red colour and blue colour. Green colour corresponds to slow motion; very, very slow motion that means the maximum with J omega is here and graphs are very fast in this region it is very, very small; almost J omega is practically very small close to 0. And J omega is maximum only in this region.

See as a function of omega we are plotting; if you consider this one the red, the red one is something interesting; it is in between these two, the red one is in between these two; and then it is the intermediate motion it is not slow or too fast; and the blue one is something which is very, very fast motion. See it is almost uniform all through, see the difference at slow motion, J omega is larger here, amplitude is larger, and intermediate motion it is spread over a large range J omega, but then drops off very fast.

It is fast motion regime, it is more or less it is equally all along. It drops off only very small at the end, but area of J omega as I said total amount of oscillating field is always constant except for this upper limit, which is varying here. You take this area or this area or this area, all are same. The total oscillating field remains constant, but interesting thing when does it happen you should understand.

This is a situation omega tau c is larger than 1; where omega is the Larmor frequency and tau c is a correlation time. It is always in nanoseconds. We multiply these two if it is very much larger than 1, then the J omega will be in this region. If omega and tau c, both you multiply Larmor frequency with the correlation time, which is nanosecond, the Larmor frequency is in mega Hertz like a 500 mega hertz; 500 into 10 to the power of 6 or 5 into 10 to the power of 8.

And tau c is nanosecond 10 to the power of – 9. It can so happen you multiply this, it comes close to 1, let us say. In which case it will so happen in the intermediate regime, where it is omega tau c = 1; in which case this is what the curve we are going to see. When omega tau c is very much smaller than 1, it is the fast motion, this is the region we have come across. So that means, the spectral density function, the distribution of the frequencies what I showed you now depends upon the correlation time and also the Larmor frequency.

So many things are involved, now you understand? We discussed about the molecule, we discuss about fluctuating fields, we say it is a spectral density function, that depends upon the tau c. Now omega into tau c together depends upon the J omega. So, these are the things, so please remember the J omega, omega tau c is larger than 1. The J omega is maximum here and then tapers off very fast.

The omega tau c is exactly equal to 1 is intermediate situation when omega tau c is very much smaller than 1 it is fast motion, fast motion should be having omega tau c very much smaller than 1. The rate of relaxation is determined by the intensity of the fluctuating field, that is important.

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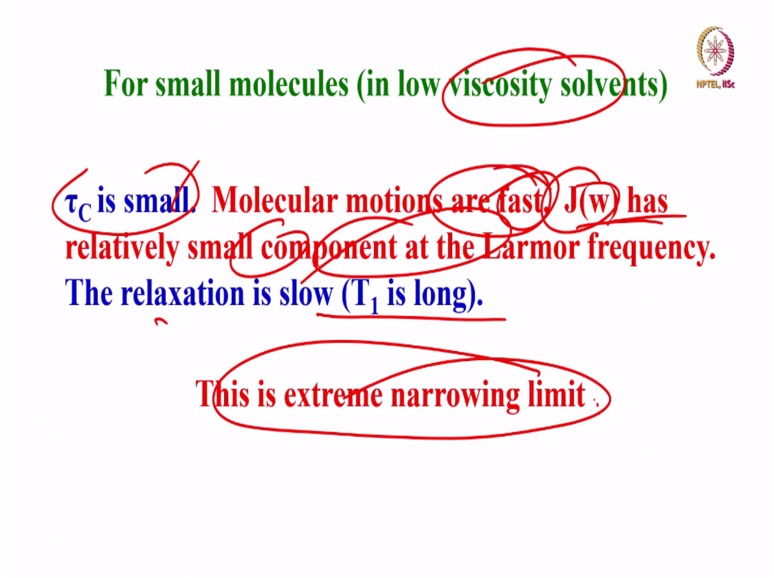

For small molecules (in low viscosity solvents)

τ_C is small. Molecular motions are fast. J(w) has relatively small component at the Larmor frequency. The relaxation is slow (T_1 is long).

This is extreme narrowing limit.

So, for small molecules and especially in the low viscosity solvents, like very low viscosity then motion is faster. When tau c is very small molecular motions are very fast; small molecules and especially in the low viscosity solvents, the molecular motions are very fast and J omega has relatively very small component at the Larmor frequency. Please understand the statement. When the molecular motions are fast, tau c is small J omega jas relatively very small comonent to the Larmor frequency.

So, the relaxation is slow, that means it takes long time for spins to relax. T1 is longer, T1 value is very long. It will be of the order of several seconds, sometimes much larger. This can happen for a small molecule especially when molecular motions are very fast, J omega has relatively small component. Now let us say this is the condition, we call it as the extreme narrowing limit. When tau c is small T1 is longer, this is called extreme narrowing limit. Then you can see here in the case of this one, slow motion and fast motion we discussed, here we are considering the molecular motions are very fast motion, we are concentrating on this condition. This is called extreme narrowing condition.

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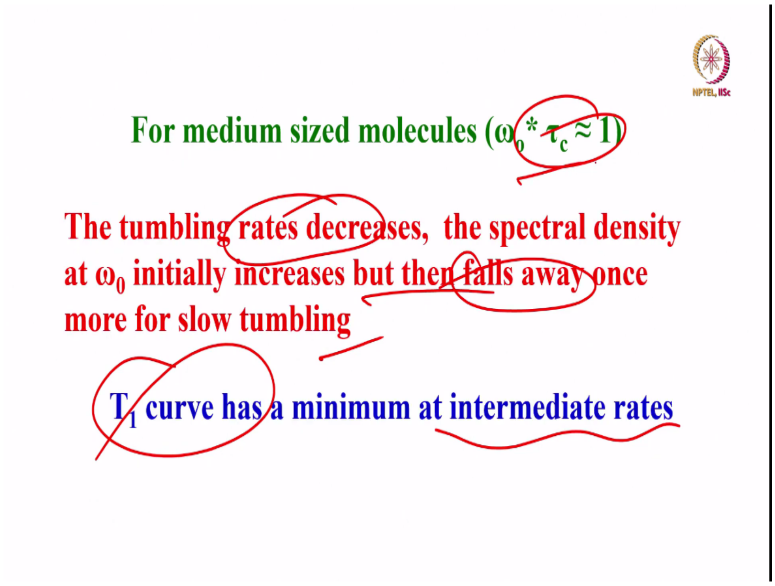

For medium sized molecules ($\omega_0 * \tau_c \approx 1$)

The tumbling rates decreases, the spectral density at ω_0 initially increases but then falls away once more for slow tumbling

T_1 curve has a minimum at intermediate rates

Now for medium sized molecules omega tau c approximately equal to 1. I told you tau c is nanosecond, omega 0 is in megahertz. Now multiply these two, if it is of the order of 1, the tumbling rate decrease, molecules do not tumble very fast like previous case. Spectral density at omega 0 initially increases and then falls. For slow tumbling motion it falls away, it is very important thing; initially it increases and then falls away after sometime.

So, this is the situation for omega tau c = 1. It is an intermediate state where T1 has a minimum in the intermediate rate. You understand in the previous case T1 was long, when J omega has very small component, so this is extreme narrowing limit, but omega tau c is to approximately equal to 1. T1 curve has a minimum and at intermediate rates.

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For small rapidly tumbling molecules, motion is faster

Under these conditions, $T_2 = T_1$

Relaxation is slower and the linewidths are narrower

Slowing

Spin-Spin

For very small and rapidly tumbling molecules, another thing rapidly undergoing motion, for faster motion under these condition T2 = T1 and relaxation is slower and the linewidhs are narrow, very, very narrow. This can happen only in solutions especially in low viscous solvents. In solutions it so happen you will come across a situation relaxation is slower and linewidths are also narrower, and that is the situation T2 = T1. What is T2? I have not discussed; it is spin-spin relaxation, another term, another relaxation phenomenon we will come to that later.

Under this condition both relaxation times are approximately equal, not exactly, well approximately. I have to put the word approximately, T2 = T1. It is a rapidly tumbling motion.

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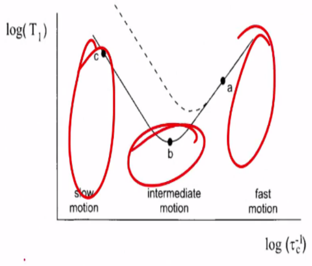
The T_1 values and the correlation time



You can look at this graph, T1 value, as a function of correlation time, see in the slow motion this is the regime, and in the fast motion regime, it goes up again, and the intermediate motion is here.

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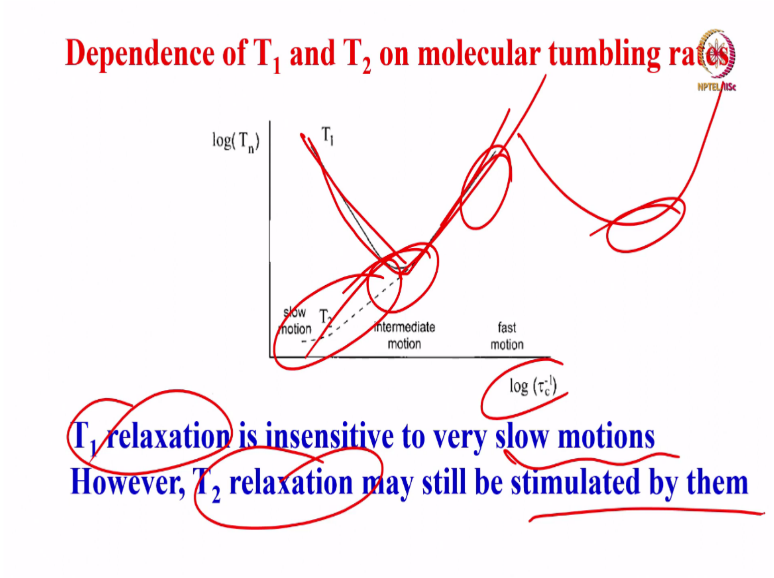

Dependence of T_1 and T_2 on molecular tumbling rates

T_1 relaxation is insensitive to very slow motions

However, T_2 relaxation may still be stimulated by them

And then let us worry about T1; T2 will come to that later. In the T1 curve comes like this decreases and then increases. It initially decreases from slow motion, as it keep on increasing the tau, as a function of tau at an intermediate motion almost reduces drastically, and then goes up again. This is the fast motion. So, it forms a curve like this, this is the intermediate case. So, both for slow motion and for fast motion T1 increases; very important thing. T1 relaxation is very sensitive to slow motions and also here and also fast.

How a T2 relaxation is still be stimulated by them; that is also possible. Slow motion can still cause T2 relaxation, we will discuss that later.

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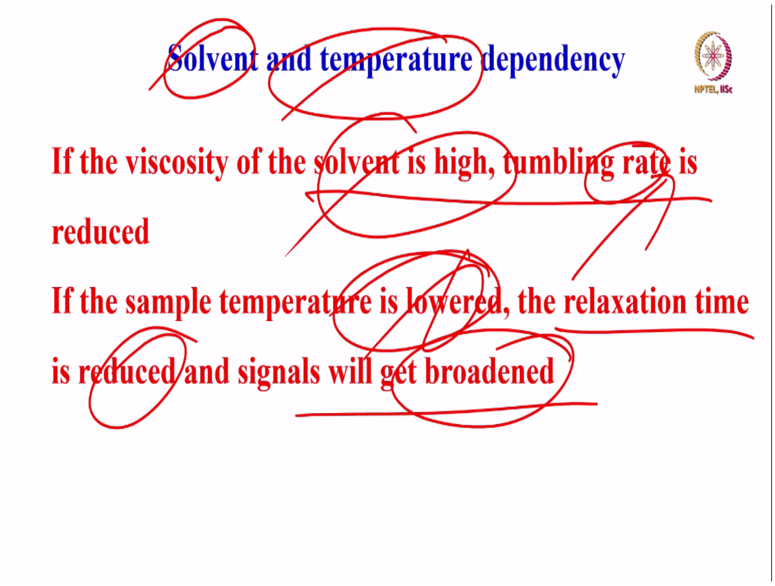

Solvent and temperature dependency

NPTEL, IISc

If the viscosity of the solvent is high, tumbling rate is reduced

If the sample temperature is lowered, the relaxation time is reduced and signals will get broadened

Now I want to introduce a term how this T1, a natural phenomenon, can we control from outside? All these things I have discussed about the motion of the molecules; and then how fast it rotates tumbling motion, correlation time, spectral density function, because the molecular motion we discussed. When can the molecules undergo tumbling motion, faster and slower? You know that; so it depends first on the size of the molecule, and depends upon the environment and the size of the molecule also.

For example in a viscous solution it cannot undergo rapid motion. Whereas if I take a less viscous solvent, just ordinary water molecules, is undergoing thermal agitation very fast and if I take highly viscous solution molecules will not undergo tumbling motion very fast and also it depends on the size of the molecules. Small molecules undergo rotations very fast and big molecule cannot rotate so rapidly. We cannot ask the elephant to rotate faster like a cricket ball, so it is not possible. So, like that it depends upon the size of the molecule.

But then externally can we control it? is there a way we can control it? Yes, we can control, it depends upon the solvent and has temperature dependency, it is like this. If the viscosity of the solvent is high, tumbling radius is reduced. That is what I said; and then if temperature is also lowered, relaxation time is reduced, then signal get broadened.

These are related to each other. So, then now you know what to do logically; when the viscosity of the solvent is very high, tumbling is reduced how do you reduce the viscosity? How is the temperature increase the temperature make sure that molecules undergo motion rapidly, that is one thing. So, when the temperature is lower it happen relaxation time is reduced and signal will get broadened.

Alternately, what you do is, you raise the temperature, so depends upon the solvent and the temperature; play with that. See that with a sharp line, lines do not get broadened. So, this is possible; signal what you get is should be narrower peaks and not get broadened because of various external parameters; you can control them with the solvent and also the temperature.

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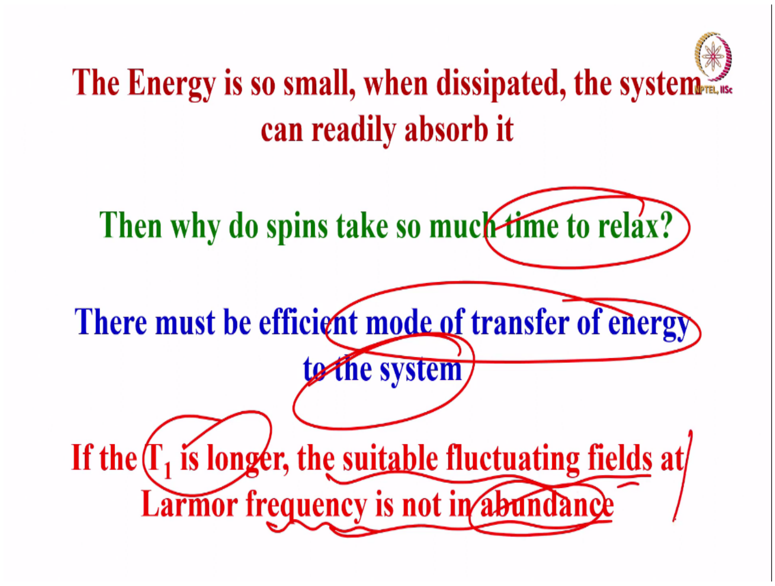

The Energy is so small, when dissipated, the system can readily absorb it

Then why do spins take so much time to relax?

There must be efficient mode of transfer of energy to the system

If the T_1 is longer, the suitable fluctuating fields at Larmor frequency is not in abundance

Now one may ask a question; so far we have been discussing various things. Now the energy is smaller than the kinetic energy and I told you it will quickly disperse from spin to lattice is very fast, and the effect is very little seen at the body temperature. I agree such a small energy. I gave the comparison of pouring hot bucket of water in to big ocean; when such a small energy is there, system readily absorbs it.

It can dissipate very fast, then the question is why do spins take so much time to relax? should it not immediately give the energy and relax faster; that is the next question we have to ask? why cannot relax faster? whysome spins takes several seconds, minutes, hour in extraordinary case as it can take days. Disturb the spin system, it will take several hour sometime days to come back to thermal equilibrium.

Why cannot all the spins quickly disperse energy and then relax faster? the problem is there must be efficient mode of transfer of energy at the system, efficient mode of transfer of energy at the system is needed then only it can happen; and if the T1 is longer the suitable fluctuating fields at the Larmor frequency is not present in abundance. Meaning the local fluctuating fields generate at the site of the field because of the rapid tumbling motion the fluctuating field is not present abundantly at the Larmor frequency.

Very little is present, as a consequence, spins are not able to relax faster. And it cannot give the energy to the lattice. So, the important thing Larmor frequency must of the fluctuating field and must be present in abundance. These are the important conceptual points which I wanted to discuss. You people are familiar with the concepts what we have been discussing about the relaxation mechanism, idea of relaxation, what are the important concepts involved.

So far I was talking about only relaxation of the spins attaining thermal equilibrium that is what is called as spin lattice relaxation. Spins lose energy to the lattice and come back to thermal equilibrium; and we understood lot of things, lot of concepts very, very important points. All these are very, very important to understand. Now we also understand some relaxation mechanism.

The relaxation one is T1 and there is another type of relaxation. But what are these mechanisms which help these relaxations in a given molecule; we have a molecule of interest which you want to study. What are the things which are in the molecule, internal interactions which can aid relaxation mechanism, to help the spins to release energy to the lattice and relax.

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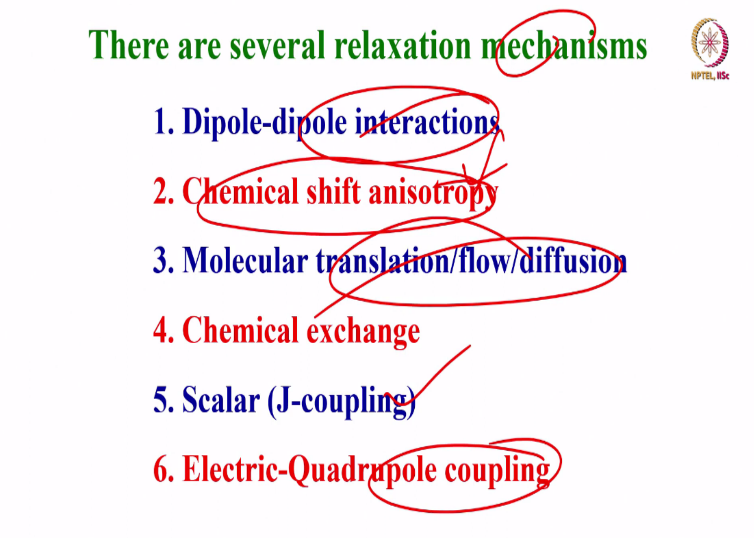

There are several relaxation mechanisms

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

There are several things here. There are several phenomena responsible for the relaxation mechanism. One is the dipole-dipole interaction; that is interaction between the two nuclear spins, chemical shift anisotropy this one when I come to solids, I will discuss what is CSA? Chemical shifts remember I told you one thing in the beginning very first class in this course and also in the previous course, all parameters in NMR at tensorial and all of them are anisotropic.

You can measure the properties in different directions, they are different. But in the solution state I told you when I discussed about the internal interaction parameters, the chemical anisotropy, dipolar coupling; J anisotropy, quadrupolar interactions they all get averaged out and especially for spin half system quadrupole coupling also would not be there. That is what I said. But these are the things present in the spin system, and they they are anisotropic in nature.

So, similarly chemical shift is also anisotropic. You may not be able to determine that in solution state, but inherently that property is there, it can aid the relaxation. CSA can aid the relaxation phenomenon; and molecular translation motion, and diffusion if it is there that can also cause relaxation; and there is scalar coupling that can cause relaxation.

Electrical quadrupole coupling, spin rotation various other phenomena are there; all of them can participate in generating the local fluctuating fields for the spins to relax and give energy to the lattice. So many mechanisms are there. I told you, the fluctuating magnetic field. The fluctuating magnetic field has to be generated at the Larmor frequency in the transverse plane for the spins to give energy to the lattice and relax.

But the sources of this fluctuating magnetic field, I said, is various molecular motions, but internally with respect to the molecule there are several mechanisms. All of them help in relaxation. So, we will understand quickly some of the relaxation mechanisms.

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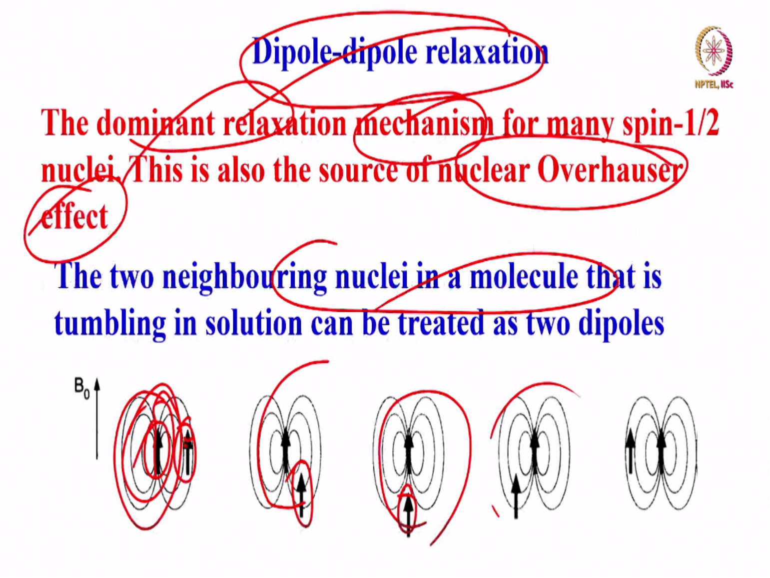

Dipole-dipole relaxation

The dominant relaxation mechanism for many spin-1/2 nuclei. This is also the source of nuclear Overhauser effect

The two neighbouring nuclei in a molecule that is tumbling in solution can be treated as two dipoles

Dipole-dipole relaxation; what is the dipole-dipole relaxation? It is a relaxation mechanism of many spin half nuclei; when they come close to each other they can interact, because these are spins are tiny magnets when they come close to each other there can be an interaction; and that cause relaxation. It is a dominant relaxation mechanism. Among all the various possible phenomenon which are responsible for relaxation, the dipole-dipole relaxation phenomenon is dominant.

When we go to the next class I will discuss about NOE, it is also source of NOE; the dipole-dipole relaxation is also source of NOE. When I discussed the chemical shift under internal interaction, I also said this dipole-dipole coupling is not present in the solution state, because of the motion averaging. True, you will not be having the dipole-dipole coupling to see; but the dipole-dipole interaction will be there to aid the relaxation.

This interaction is present; it is not going to create the magnetization for detection, we will not get dipole-dipole coupling. But it will help the spins to relax, so that will be present. So, what happens if you consider two, neighboring nuclei; they are tumbling in solution undergoing motion, and you can treat each nuclear spin this one and this one, as a dipole.

One dipole comes next to the other dipole, this influences the magnetic field at the site of it, because of this tiny magnet, there is a magnetic field surrounding it. There are lines of force here affecting these nuclear spins. So, this neighbouring nuclear spin feels the field because of the other spin, this can affect. And for this there is no need of chemical bond or anything It need not, it can happen; neighbouring nuclei neighbouring molecule they can come close by.

And what is happening is, the interesting thing is the orientation of the nuclear spins between them they will not change. It remains same; but then as it keeps on rotating its place keeps on changing the fluctuating magnetic field. You see orientation do not change, please understand.

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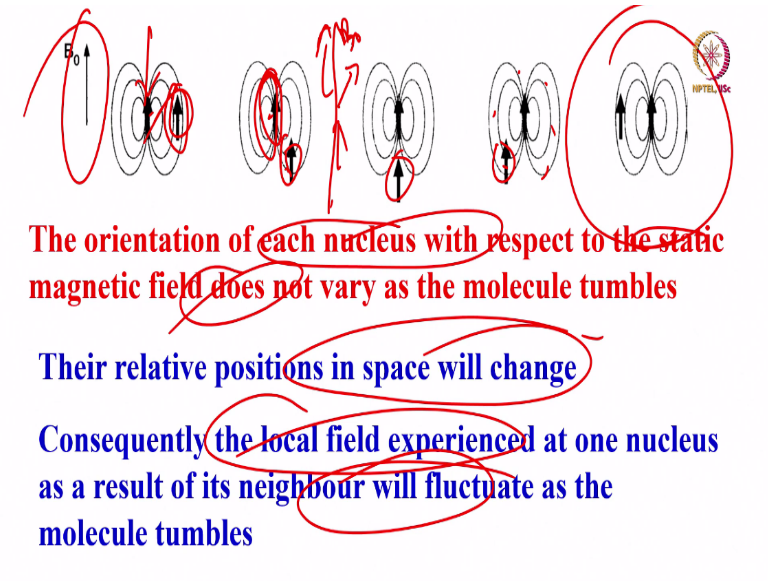

The orientation of each nucleus with respect to the static magnetic field does not vary as the molecule tumbles

Their relative positions in space will change

Consequently the local field experienced at one nucleus as a result of its neighbour will fluctuate as the molecule tumbles

The orientation of each nucleus with respect to the static magnetic field does not change. This nuclear spin and this is a magnetic field B0, I will put like this; and with respect to B0 this is oriented like this. This is oriented like this, if I have another spin oriented like this that remains same. Orientation does not change with respect to the static magnetic field, but what is happening is the relative positions in space will vary; once it is here, once is here, like here.

See let us keep this nuclear spin constant position; that position assume I have kept it constant. Once another spin is here, next it is here then comes here, here, here. So, it is undergoing rotation, changing the position with respect to this nuclear spin, another nuclear spin is changing its position, all across. What does it mean? because this is a magnetic field influencing this and the lines of force at the site of this nucleus change depending upon its position, the local field experience that one nucleus as a result of the neighbouring nuclei, will keep on fluctuating, as a function of molecular tumbling. The molecules undergo tumbling; when it undergoes tumbling, the dipole-dipole interaction it so happens, the position of two nuclear spins with respect to the magnetic field, the orientation do not change. One nuclear spin is there other nuclear spin keeps on changing its position all across retaining its orientation with respect to the magnetic field.

As a consequence the magnetic field at the side of the other spin keeps on changing. It is a fluctuating magnetic field, it keeps on changing as the molecule tumble.

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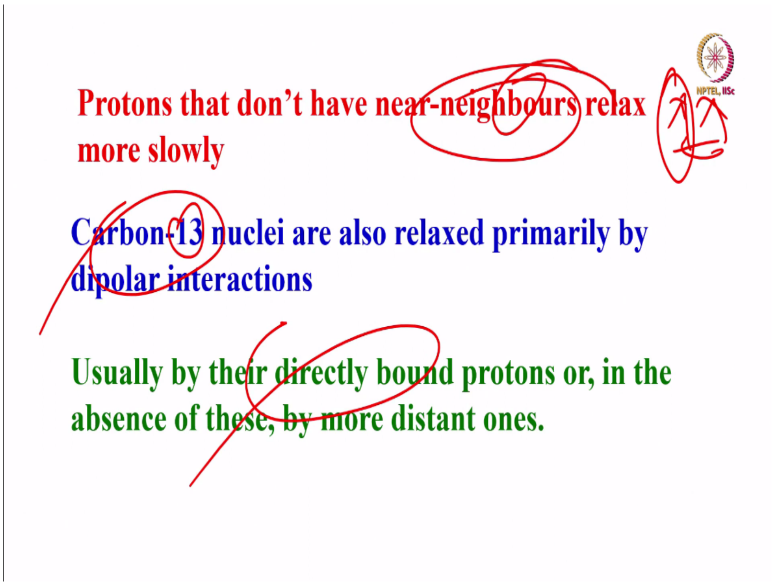

Protons that don't have near-neighbours relax more slowly

Carbon-13 nuclei are also relaxed primarily by dipolar interactions

Usually by their directly bound protons or, in the absence of these, by more distant ones.

And then this helps the protons which are neighboring to this or any spins neighboring to that to relax; and that is the reason why proton that do not have nearby protons, that is another proton which is far away, they relax more slowly. The reason is if one proton is relaxing, the other proton if they are very close by; the special proximity is very important for dipole-dipole interactions, then the field experienced at the site of this nucleus, the fluctuating field is more. So it relaxes faster, if they are far away, it relaxes slowly. This is exactly what happens when you see the carbon 13 NMR, if you try to measure the T1, the spin lattice relaxation time by some experiment in carbon 13, the carbons which are attached to protons relaxes faster. Carbons which are not attached to protons, relaxes very slowly.

This is the phenomena, you should understand. The neighbouring spins which are present the dipolar interaction will become better, the dominant interaction aid the relaxation of the nuclear spins. So, this is another thing usually directly bond protons will cause relaxation in carbon 13 spins and if they are absent relaxation will be different or if they are far away separated in the molecular structure then also the relaxation is slow.

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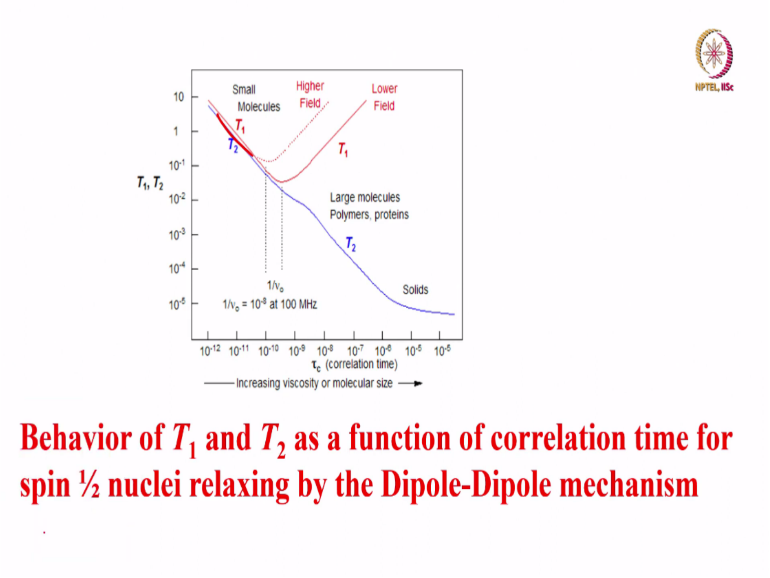

Behavior of T_1 and T_2 as a function of correlation time for spin ½ nuclei relaxing by the Dipole-Dipole mechanism

So this is a picture which shows about the dipolar interaction, way back it published, very, very long back in the very earlier stage. For the small molecule how the T1 comes here, as it keeps on increasing at higher magnetic field. T1 depends also on the magnetic field , and this is for the larger molecules here; and in the case of solids T1 becomes even longer, sorry this is T2, T 2 is very large; T1 is in red colour.

See it keep on increasing with respect to correlation time, then here it becomes larger and larger here, also T1 is larger; in between it is smaller. On the other hand the T2 keeps on changing, go to the solid state, T2 will be very small, whereas T1 will be very, very long. So, that is what is going to happen, in the case of solids. So, that is the thing which I wanted to tell you more about the relaxation phenomenon. There are several other relaxation phenomena.

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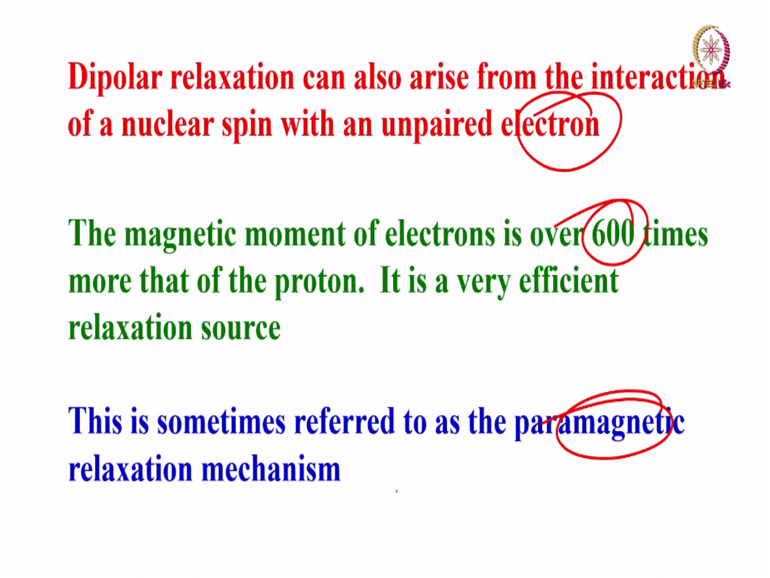

Dipolar relaxation can also arise from the interaction of a nuclear spin with an unpaired electron

The magnetic moment of electrons is over 600 times more that of the proton. It is a very efficient relaxation source

This is sometimes referred to as the paramagnetic relaxation mechanism

So, dipolar relaxation can arise with the interaction of the nuclear spins with the unpaired electron also, if there is unpaired electron. Remember electron magnetic moment is nearly 600 times more than that of the proton. So, it is an efficient source of relaxation, that is the why if there is unpaired electron, or in paramagnetic species, such nuclei relaxes very fast. So, this called as paramagnetic relaxation mechanism.

And if you have a unpaired electron in the molecule, sometimes it is very difficult to get sharp lines. The nuclear spin relaxes very fast. Its resident time in the excited state is very small the signals become very, very broad. Of course, because of uncertainty principle which we discussed this in the very first course itself.

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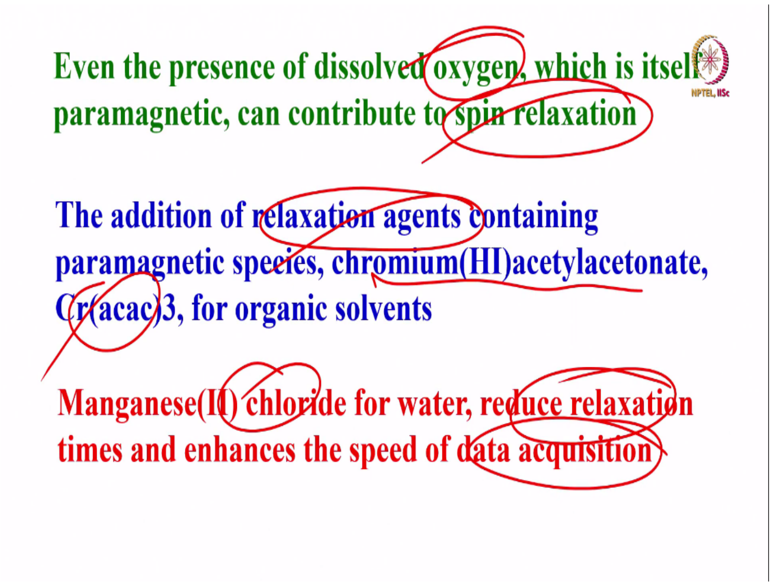

Even the presence of dissolved oxygen, which is itself paramagnetic, can contribute to spin relaxation

The addition of relaxation agents containing paramagnetic species, chromium(III)acetylacetonate, Cr(acac)3, for organic solvents

Manganese(II) chloride for water, reduce relaxation times and enhances the speed of data acquisition

So, even the presence of the dissolved oxygen, because oxygen itself is paramagnetic, that can also contribute to spin relaxation. So, there are certain things, all these things contribute for relaxation, because of the dipole-dipole interaction. Now there are some ways we reduce this. If the T1 is sufficient long, let us say, very long T1and I want to do experiment faster.

Sometimes T1 is of the order of millisecond, microsecond or hours and days. How do I do that? There are ways of reducing the T1 called relaxation agents. For example, we can use chromium acetylacetonate which is called Cracac. We can use Cracac in organic solvents addition of a micro quantity of this is sufficient, you don't have to use kilos, then you not be able to get the spectrum. Micro quantity of this will interact with your molecule of interest and then aids in relaxing the spins. The spins will relax faster. Sometimes we use magnesium chloride, various thing we can use.

And all these things are relaxing agents reduce relaxation time and helps you in speeding up the data acquisition; your experiment become faster. So, this is what is about the relaxation the dipole-dipole interaction. Next class I will discuss about various other relaxation mechanisms quickly; and then we will go about measurement of the T1 and then discuss T 2 and the measurement.

Quickly we will do that so now there are few other relaxation mechanisms, like CSA, spin rotation, quadrupole relaxation, etcetera. We will come to that later, but right now what I was trying to say is that the major dominant interaction phenomenon was dipole-dipole interaction. So, this is what we discussed today, about various phenomenon related to relaxation mechanism, concept how the energy gets dissipated, how the fluctuating fields are produced. What is the frequency of the fluctuating field; how it is different from the RF field applied, although both are at Larmor frequency, how it affects everything we understood, we correlated them with the spectral density function, with the correlation time tau c; which again due to size of the molecule and then how spectral density function affects different molecule for slow motion, intermediate motion and fast motion; all those things we discussed a lot.

And the relaxation mechanism we discussed about the dipole-dipole relaxation which is a dominant source of relaxation. I said when the two spins are there, there is a dipolar interaction,the orientation with respect to the external magnetic field B0 do not change, however, orientation getting changed because the spins keeps on changing its orientation. As the molecule is undergoing fluctuation the orientation between the fluctuating fields at the site keeps on changing; and that can induce relaxation, if it is at Larmor frequency.

So, all these things we discussed and then the relaxation can be reduced relaxation can be enhanced by using external agent called Cracac, and others and these are the dipolar relaxation mechanisms. We will come to the other relaxation mechanism in the next class starting with CSA we will discuss other things. So, I will stop here today, we will come back with other relaxation mechanism discuss in the next class. Thank you very much.