Advanced NMR Techniques in Solution and Solid State
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Module-59
Cross Polarization
Lecture – 59

Welcome all of you. Since the last couple of classes we started discussing about solid state NMR. As I was telling you the solid state NMR spectrum is slightly different from that of the liquid state NMR spectrum, because interaction parameters are different here. So, the way we have to operate and average out the anisotropic interactions so that we get sharp lines is different here. Whereas in the case of the solution state there is a natural thermal motion going on and there is a natural averaging of the anisotropic interactions. Whereas, in the case of solids it does not happen like that. So, we need to do our own way; adapt a strategy to see that the second rank tensor interactions like heteronuclear dipolar couplings, chemical shift anisotropy, all those things we need to average out.

I said one of the ways is by doing physical averaging, where we can do the spinning of a sample, keeping the material in a rotor at particular angle called magic angle which is 54.7 degree with respect to the magnetic field. And after stationing the rotor in that angle, keep on rotating at a very high speed of the order of several tens of kilohertz. Then I also mentioned to you the average orientation of all internuclear vectors will be deemed to be along the spinning axis which is making an angle of 54.7 degree with respect to the magnetic field.

And this when you look at the parameter, I said it depends upon orientation parameter called 3 cos square theta – 1 / 2. So, as a consequence what happen if you put the 54.7 degree in that equation, it goes to 0. So, that dipolar coupling can be averaged out by physically rotating the sample, keeping the rotor at magic angle; that is one way. And it of course cannot eliminate homonuclear dipolar couplings; it can eliminate only heteronuclear dipolar couplings and chemical shift anisotropy. Now also I said we can combine this heteronuclear decoupling also, that is one thing. And for homonuclear dipolar coupling the averaging can be done in spin space. Identical strategy you can adopt where you can keep on applying the radiofrequency pulses with the specified delays between them, such that the magnetization or the spins spends equal time in all the three X, Y and Z axes.

What happens at that time, when you keep on applying the RF pulses rapidly ensuring, that the magnetization spend equal to among all the X,Y and Z axes, you are basically creating a sort of a cuboid. And identically even for the magic angle spinning also; you can now imagine this should be the cuboid. And if you take the body diagonal of the cuboid, it makes an angle of 54.7 degree with respect to any of the three X, Y and Z axis.

Similarly averaging in the spin space also, you can imagine to be magnetization or the spins aligning along the body diagonal of the cuboid. So, in other words both these averaging processes can be treated as the dynamic implementation of the cubic symmetry. That is what happens. So, these things we discussed and I also said abundant spins; for example, proton and fluorine you cannot eliminate the homonuclear dipolar coupling, they are homogenous interactions, very easily by magic angle spinning. And we have to resort to the combined effect like magic angle spinning and also WAHUHA sequence, where averaging can be done in the spin space. Varieties of things are there; that is what we discussed. And I said practically most of the nuclei other than proton and fluorine can be considered as dilute spins. And that is what is normally is focused upon in the routine applications.

And high resolution for the proton and fluorine are generally not so easily you can obtain the high resolution, in spite of all the advanced techniques developed by various stalwarts in NMR. As of now the minimum line width we can get is of the order of 40 to 45 hertz. So, it is still far away from what we can think of getting high resolution NMR spectrum like in the liquid state.

So as a consequence, most of the studies are restricted to dilute spins. So, I said dilute spins like for example if you take carbon 13, in organic systems we can detect carbon. But carbon is less sensitive; gyromagnetic ratio is 4 times less than that of the proton. So, the direct detection takes enormous amount of time due to less sensitivity. So, I said there is some way we can do, we can adapt the strategy. Remember we discussed the polarization transfer technique in solution state which we adapted for INEPT sequences in HSQC etcetera, where the proton magnetization is transferred to dilute spin.

Identically we can do that in the solid state also. In the solution state, the mechanism for the transfer is anti-phase terms which are arising because of the J couplings. Now here in the case of the solids, this can be done by using what is called dipolar couplings. The same technique we can adapt; similarly we can take the magnetization of the abundant spins and transfer it to the dilute spins, it is possible.

And this is called cross polarization. So today we will discuss about the cross polarization pulse sequence, and see how we can enhance the signal intensity and also cross polarization dynamics we can discuss.

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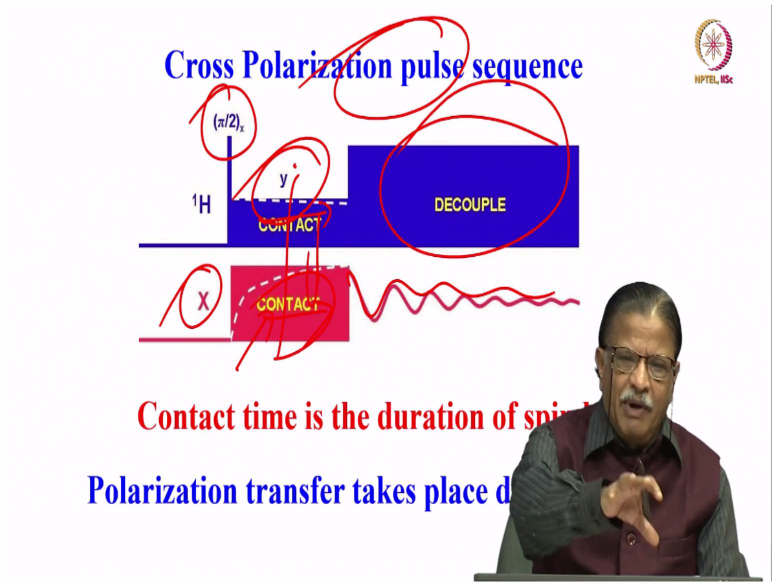

Cross Polarization pulse sequence

Contact time is the duration of spi

Polarization transfer takes place d

So, this is the cross polarization pulse sequence, very simple. Apply 90 degree pulse in the proton channel bring the magnetization to Y axes; and now we are in the rotating frame. And at the same time simultaneously apply RF pulse in the same direction on carbon 13 spin. Now the magnetization is along Y axis, apply RF pulse along Y axis. Same for the X nuclei also. Remember I earlier said it is as analogous to spin locking, when I was discussing TOCSY. I discuss this; it is the spin locking.

So, we can lock the spins. Now on both the spins independently you are applying pulses, and mixing pulses; and bringing them into contact. We are in the doubly rotating frame; and something will happen during this mixing time between the two nuclear spins, like proton and carbon. We will discuss that later. And the collecting the signal after mixing time, while simultaneously doing the decoupling of protons.

So, we are going to get the carbon 13 spectrum which is fully decoupled, broadband decoupled. But at the same time, there is a sensitivity gain because of cross polarization. And what is the duration of contact time? the duration of the spin lock; it is of the order of few milliseconds. So, during this time there is a polarization transfer that is taking place between proton and carbon.

And proton magnetization of the abundant spin will be transferred to carbon 13 magnetization. How it happens? let us try to understand the concept.

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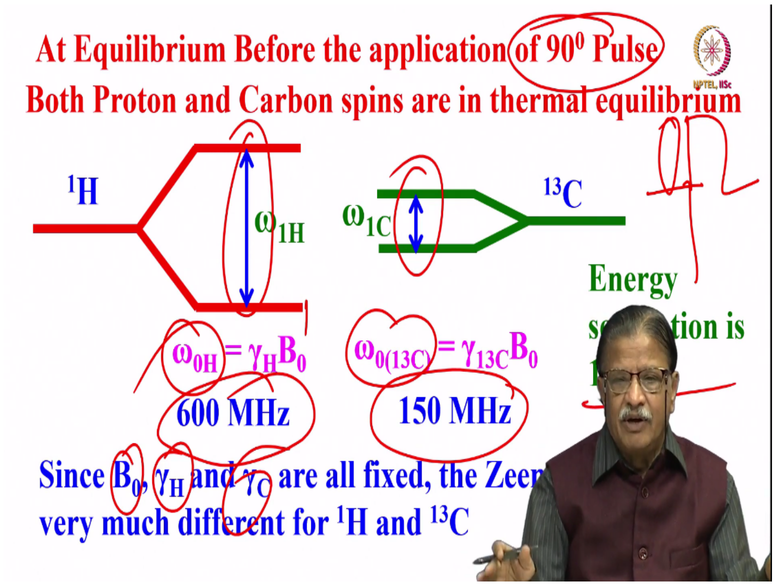

At Equilibrium Before the application of 90^0 Pulse

Both Proton and Carbon spins are in thermal equilibrium

$\omega_{0H} = \gamma_H B_0$

600 MHz

$\omega_{0(13C)} = \gamma_{13C} B_0$

150 MHz

Since B_0, γ_H and γ_C are all fixed, the Zeer

very much different for ^1H and ^{13}C

Let us see what is the magnetization at equilibrium before the application of 90 degree pulse. As you know before applying any pulse on either proton or carbon; both proton and carbon are in thermal equilibrium; that is correct; that we know. And what is the energy separation between these two? we know this is the energy separation for the proton and this is for the carbon. And carbon is 4 times less than that of protons, because of the gamma 4 times less, energy separation is also less.

So, if you go to let us say 600 megahertz magnetic field; at the resonating frequency for this magnetic field resonating frequency of proton is 600. In the same magnetic field the resonating frequency for carbon is 150 megahertz. This we all know, and energy separation also we know 1 is to 4. Now with all those things as fixed gamma B0 is fixed, gamma is fixed, now Zeeman energy separation is very much different for proton and carbon, you cannot make them equal in the thermal equilibrium, in the conventional way. If you just put the sample there is no way you can equate the energy levels between these two. But we can do it in a doubly rotating frame, in a different way.

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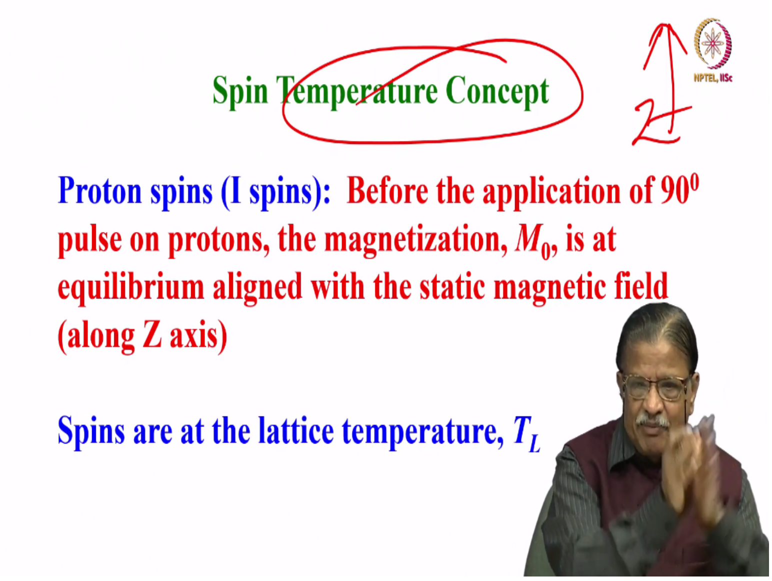

Spin Temperature Concept

Proton spins (I spins): Before the application of 90^0 pulse on protons, the magnetization, M_0, is at equilibrium aligned with the static magnetic field (along Z axis)

Spins are at the lattice temperature, T_L

Before that let us try to understand some spin temperature concept. Let us look at protons spins, I call them I spins. Before the application of 90 degree pulse on protons, what is the magnetization of proton? where is it? It is along the Z axes. In the static magnetic field the magnetization is along Z axis. And we say the spins, the proton spins are at what is called as the lattice temperature. In thermal equilibrium it is at the lattice temperature, before application RF pulse. This is what you should remember.

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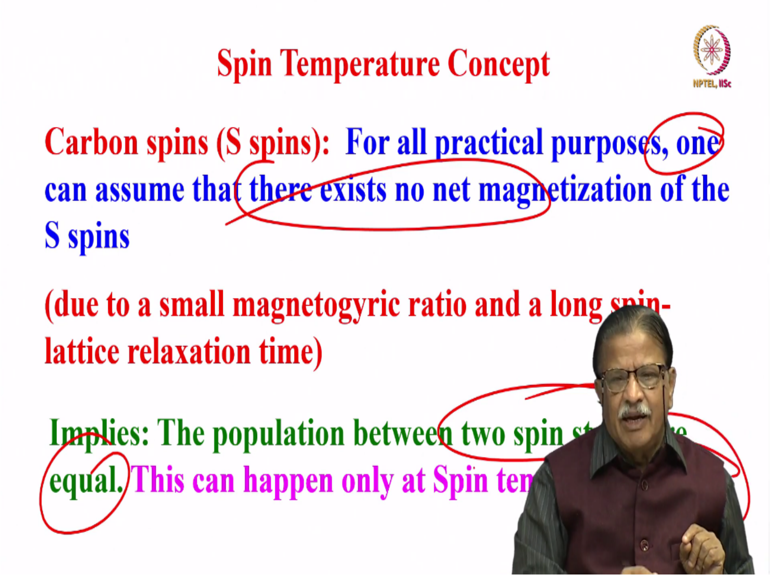

Spin Temperature Concept

Carbon spins (S spins): For all practical purposes, one can assume that there exists no net magnetization of the S spins

(due to a small magnetogyric ratio and a long spin-lattice relaxation time)

Implies: The population between two spin st

equal. This can happen only at Spin tem

Now what happen to the carbon spins? For all practical purposes we can assume there exist no net magnetization of the carbon spins. Why? because the gyromagnetic ratio of the carbon is much, much smaller than that of the proton; and because of the very long spin relaxation time practically you can assume there is no net magnetization of carbons at that time.

Now what does it imply the population between these two spin states are equal. When there is no net magnetization means it is like saturation; that is what we discussed also. When there is no population difference that means both the energy states are having equal population. It is called a saturation state. When this can happen? We discussed this spin temperature concept earlier also. I will also discuss today; if this can happen only at the temperature T which is at infinity. At infinite temperature, we can say that population between two energy states are equal.

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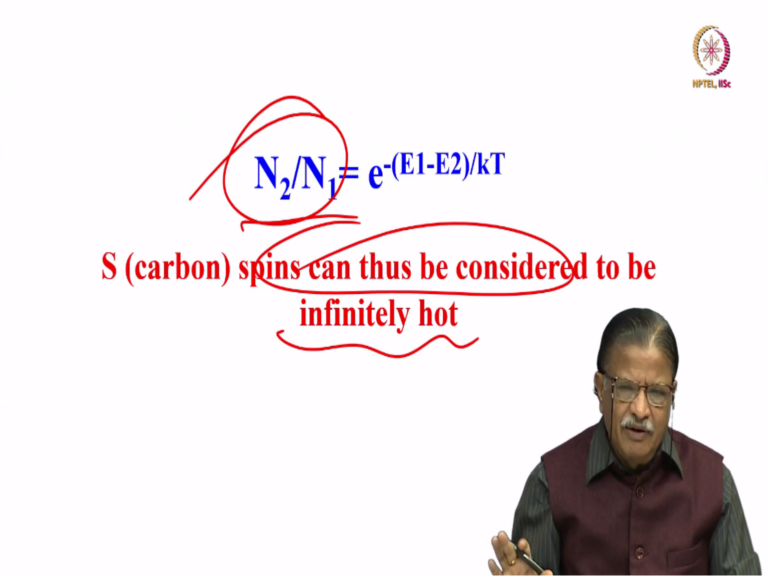

$$N_2/N_1 = e^{-(E1-E2)/kT}$$

S (carbon) spins can thus be considered to be infinitely hot

This is the Boltzmann population difference. We can see, if we look at the ratio of N2 / N1; the population difference of S carbon spins can be considered to be infinitely hot. You understand, S carbons are considered to be infinitely hot just because I am considering they are less gyromagnetic ratio and long relaxation time. So, I will assume it is like this it is infinitely hot.

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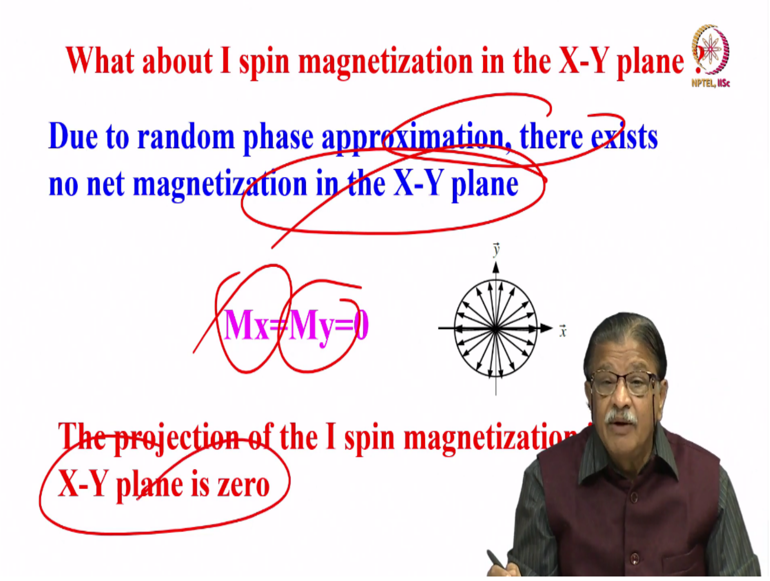
What about I spin magnetization in the X-Y plane ?

Due to random phase approximation, there exists no net magnetization in the X-Y plane

Mx=My=0

The projection of the I spin magnetizatio

X-Y plane is zero

What about I spin magnetization in the XY plane now? We come to XY plane. Before application of the 90 degree pulse, due to random approximation there exist no net magnetization in the XY plane. That also we discussed, the random phase approximation in the first or second class itself we discussed. There would not be any magnetization in the X-Y plane and in the thermal equilibrium magnetization is only along Z axes.

So Mx = 0 My = 0 only Mz is present. So the projection of I spin magnetization in the XY plane is 0. Again what does it mean?

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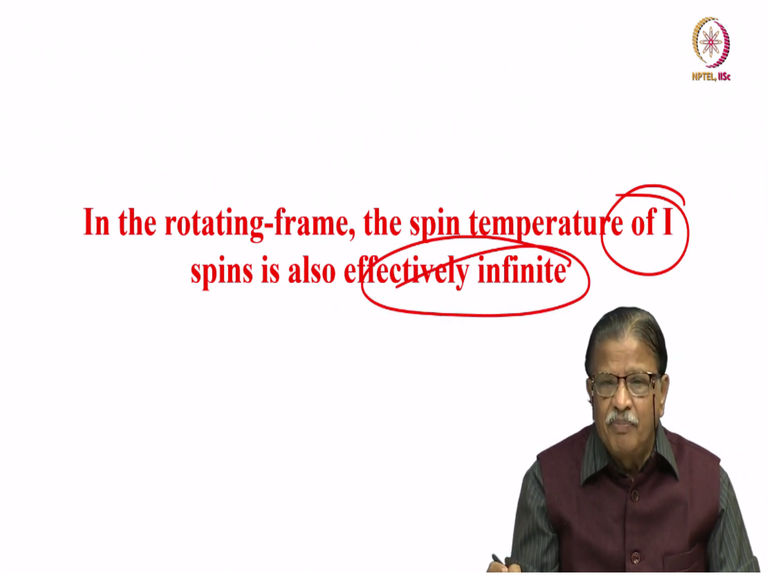
In the rotating-frame, the spin temperature of I spins is also effectively infinite

In the rotating frame or in the XY plane, if I consider the spin temperature of I spins is also effectively infinite. You understand the spin temperature of I spin, is effectively infinite.

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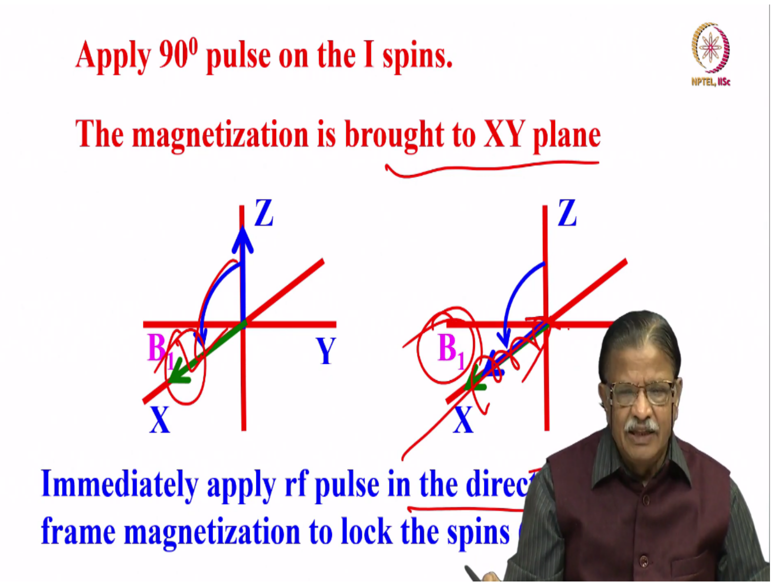

Apply 90^0 pulse on the I spins.

The magnetization is brought to XY plane

Immediately apply rf pulse in the direc
frame magnetization to lock the spins

Now apply a 90 degree pulse on the I spins. Bring the magnetization in the XY plane, like this. Apply 90 degree pulse bring the magnetization to X axis, one of the axis X or Y depending upon where you apply the pulse. Now immediately apply RF pulse in the same direction of the magnetization is brought to X axis by applying a RF pulse. In the same direction apply B1 pulse RF pulse and then magnetization gets locked; this is what we said. This is called spin locking. You can bring the magnetization to X axis apply again the RF field in the same direction, B1 field; then they get locked. This is called spin locking.

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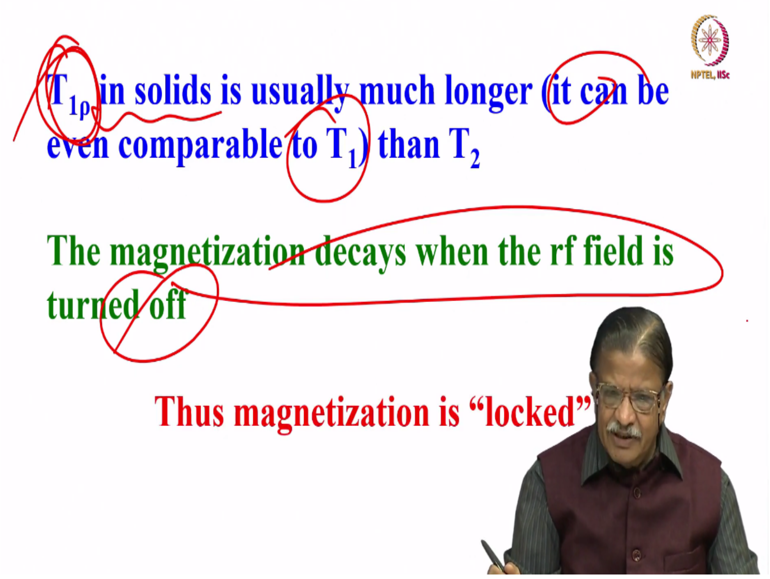

$T_{1\rho}$ in solids is usually much longer (it can be even comparable to T_1) than T_2

The magnetization decays when the rf field is turned off

Thus magnetization is "locked"

Now we are in the rotating frame and the spins can still relax in the rotating frame even though they are locked. They can relax, but on their own relaxation time; that is called T 1rho. The spins have their own relaxation time, the rate of relaxation this is T1 rho, it is called spin lattice relaxation in the rotating frame. Remember we are already in the rotating frame, because we have brought the magnetization to the XY plane. Rotating frame concept we discussed a long ago, in the previous course extensively it was discussed, those have not taken that course, please look into that.

So, what is the order of T1 rho it can be comparable to T1 of protons much. Usually in solids T1 is very long, but it is T1 rho is if we consider, T1rho is much, much smaller compared to that of the T1 or T2. The magnetization decays only when the RF field is turned off, that is the natural relaxation time. When the RF field is turned off when it is locked that relaxation is T1 rho. So, you say magnetization is locked that is one thing.

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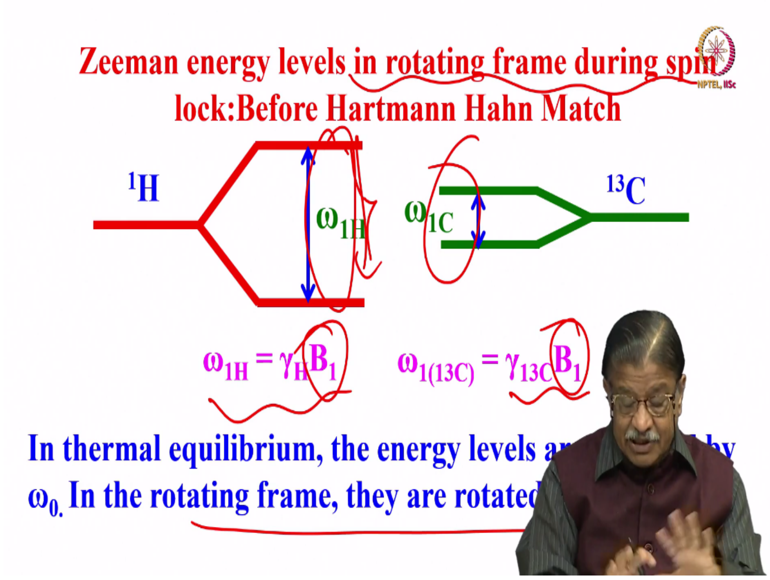

Zeeman energy levels in rotating frame during spin lock:Before Hartmann Hahn Match

$\omega_{1H} = \gamma_H B_1$ $\omega_{1(13C)} = \gamma_{13C} B_1$

In thermal equilibrium, the energy levels a… by ω_0. In the rotating frame, they are rotated

Now we will understand Zeeman energy levels in the rotating frame during spin lock. This is the Zeeman energy levels, even in the rotating frame before equating this, before some condition is attached, you have brought the magnetization of proton to let us say X or Y axes. Simultaneously apply radio frequency pulse on the carbon 13 in the rotating frame, in the X or Y axes; both simultaneously you apply pulse.

Now still the energy levels remains same, you have not changed anything. But only thing is now the separation instead of what it used to be gamma H into B0, now it is gamma H into B1, that is all. This is the RF power of the carbon 13; here RF power of the proton. Earlier in the thermal equilibrium the energy levels separation, and you have to deal with B0 magnetic field. So, in thermal equilibrium energy state and in the rotating frame they are different now that is all, but still again 1 is to 4 ratio is still there.

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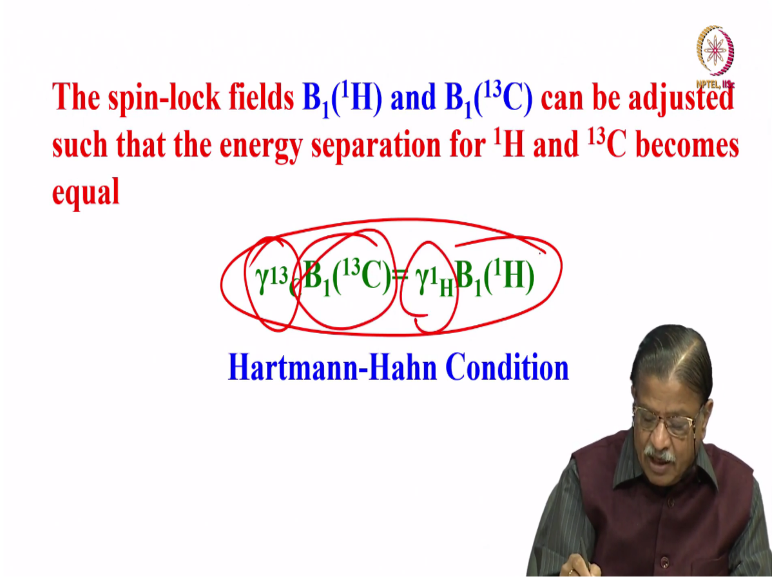

The spin-lock fields $B_1(^1H)$ and $B_1(^{13}C)$ can be adjusted such that the energy separation for ^1H and ^{13}C becomes equal

$$\gamma_{^{13}C} B_1(^{13}C) = \gamma_{^1H} B_1(^1H)$$

Hartmann-Hahn Condition

But then what you will do is, now I can adjust the spin lock power at the room temperature or when the magnetization is along Z axes in thermal equilibrium. The energy separations you cannot equate because whatever you do you, change the magnetic field simultaneously the energy states energy difference between both proton and carbon changes linearly.

Whereas in the rotating frame this is the formula so B0 I do not want to change, I cannot change; but B1 I can independently change; that is possible. So, in the rotating frame what I can do is I can change B1 of proton or B1 of carbon 13 and adjust it; how can I adjust that? I can manipulate this in such a way the energy levels become equal, it is possible; so I can do that. And this condition is called Hartmann Hahn condition. Hartmann Hahn condition is gamma of carbon 13 into RF power B1 of carbon 13 = gamma of proton into B1 of proton. This is called very famous Hartmann Hahn condition.

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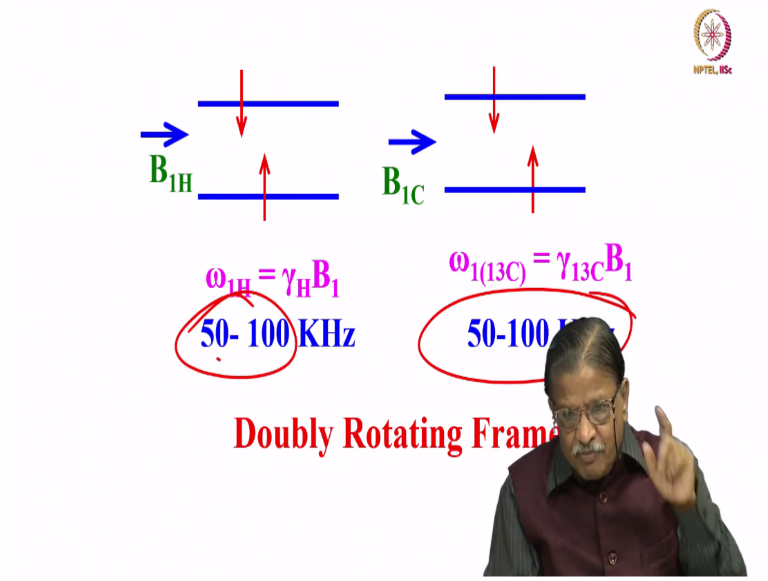

B_{1H} B_{1C}

$\omega_{1H} = \gamma_H B_1$

50- 100 KHz

$\omega_{1(13C)} = \gamma_{13C} B_1$

50-100

Doubly Rotating Fram

And now when you match this condition by adjusting the RF power of proton or carbon 13. What is going to happen? you look at this; the energy levels becomes equal; I can manipulate it. RF power I can manipulate in such a way the energy levels of both proton and carbon become equal. Now here omega1 H is of the order of 50 to 100 kilohertz; here also 50 to 100 kilohertz. I equated it. Earlier it was much larger, in the B0 field, it was of the order of megahertz. Now it is only few kilohertz; and I have equated these two and now we have entered into what is called as doubly rotating frame. In the doubly rotating frame I tune the RF power of either proton or carbon and ensure that the energy level separations between both of them are equal; then what will happen?

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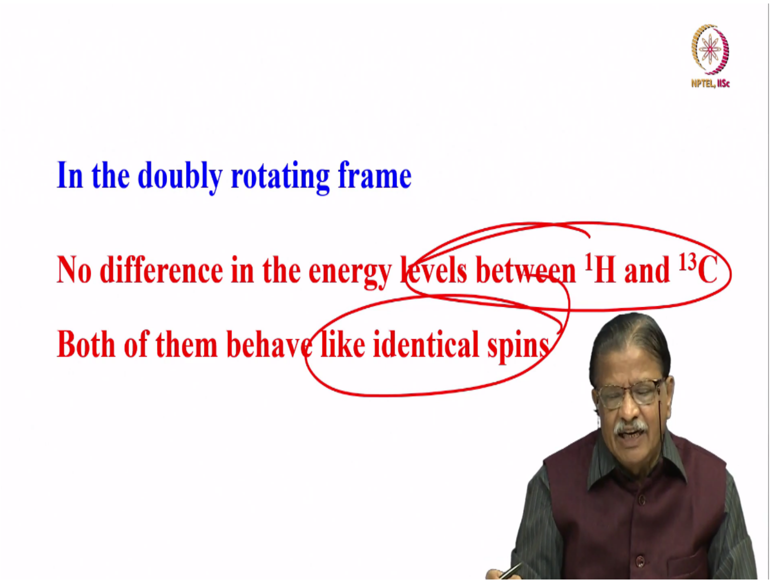

In the doubly rotating frame

No difference in the energy levels between ^1H and ^{13}C

Both of them behave like identical spins

Logically we can say when there is no difference in energy levels between proton and carbon, they behave like identical spins. They lose their identity; then you do not know there is a proton spin and a carbon spin, because energy separation between both of them are same. So that is what happens in the doubly rotating frame. Now you have created a situation the energy levels of proton and carbon are same. Both these spins behave like identical spins lose their identity; completely lose their identity.

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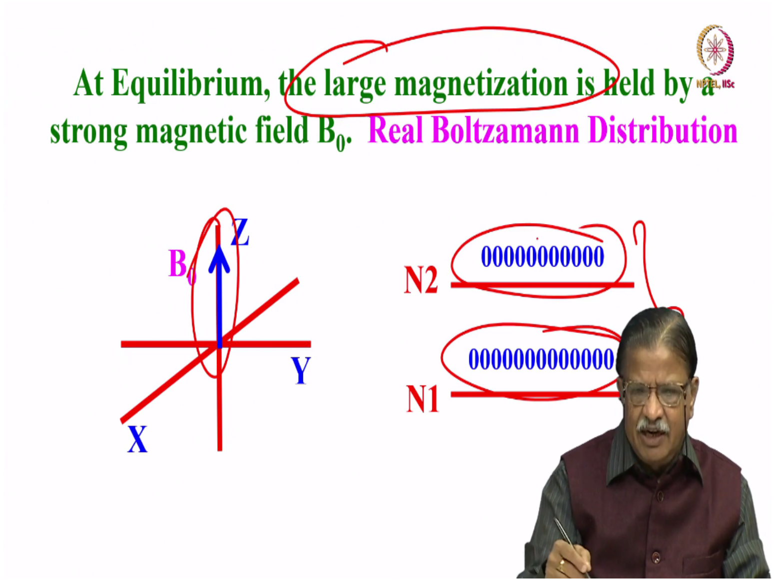

At Equilibrium, the large magnetization is held by a strong magnetic field B_0. Real Boltzamann Distribution

Now another thing let us understand. What happens when you make the energy levels equal. The energy levels of proton and carbon they are equal in the doubly rotating frame. What is going to happen? let us understand now. At equilibrium the huge magnetization was there; at equilibrium energy separation was larger because it was under B0 magnetic field. Now that was the real Boltzmann distribution which is given by Boltzmann population difference. Then when it was in thermal equilibrium this is the population difference, very small population difference, we discussed that. More spins are in this state and less spins are in the state, but the difference is negligibly small.

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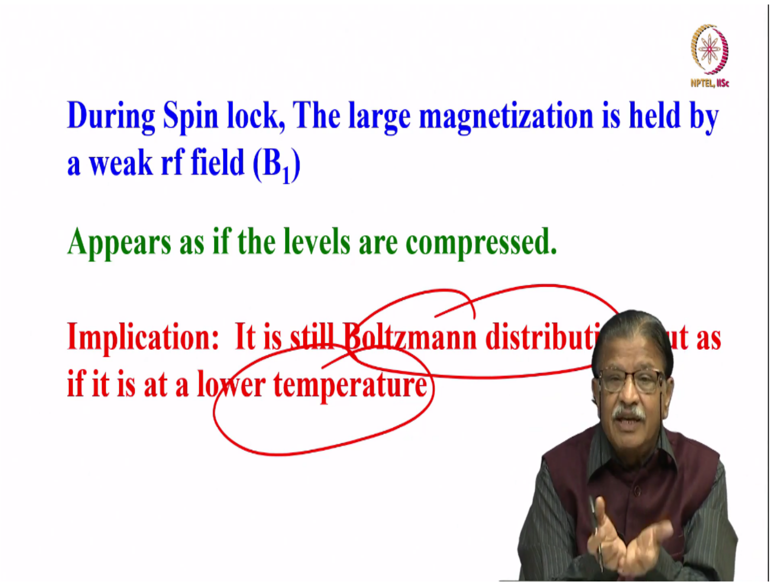

During Spin lock, The large magnetization is held by a weak rf field (B_1)

Appears as if the levels are compressed.

Implication: It is still Boltzmann distributi… ut as if it is at a lower temperature

Now during spin lock what happens? The large magnetization of the proton is held by a small field instead of B0 it is held by B1 field, RF field; which is very, very weak. Compared to megahertz it is 50 to 100 kilohertz. Where is megahertz, where is kilohertz; that is the advantage. So, now the large magnetization is held by a weak RF field. How do you understand that? I told you when the magnetic field increases the energy level separation increases, but now this population difference is same, but you have reduced the magnetic field. It appears as if they are compressed, energy levels are compressed with same population difference. So, it means the Boltzmann population distribution appears as if it is at lower temperature. You have reduced the temperature, that is what it means. So, that is the implication. Still you have a Boltzmann population difference, but it appears you have to lower the temperature enormously so that more spins are in the lower energy state.

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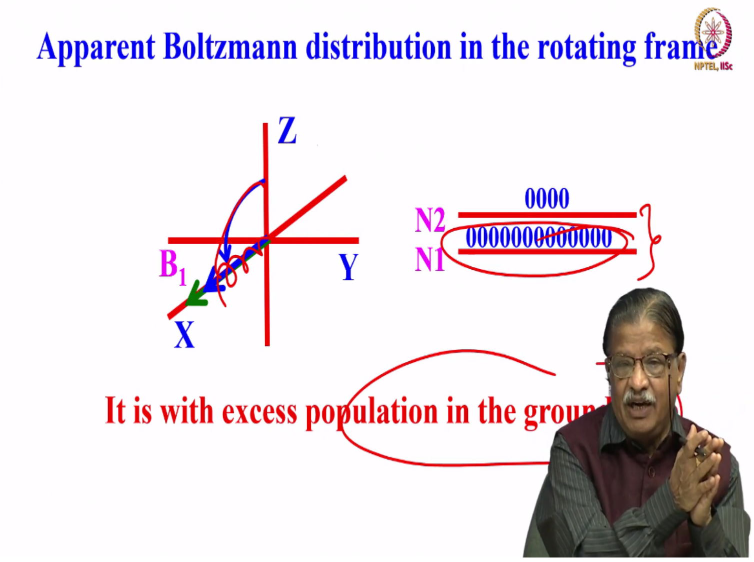

Apparent Boltzmann distribution in the rotating frame

It is with excess population in the groun…

So, then apparent Boltzmann distribution in the rotating frame is; when you bring the magnetization here and apply a radiofrequency pulse along this, during this spin lock now the energy level separation has reduced, become much smaller. It is compressed, it is now held by a weak RF field. You see more populations are there in the ground state now, in the lower energy state than in the higher energy state; much, much more; that is what happened.

So, now we can say there is a excess population in the ground state. What did you do? by going to the rotating frame by applying the spin lock pulse; there is an apparent distribution of the magnetization Boltzmann distribution. It appears as if the energy levels are compressed and large population difference which was there in the B0 magnetic field is held by a weak RF field; that is what it is.

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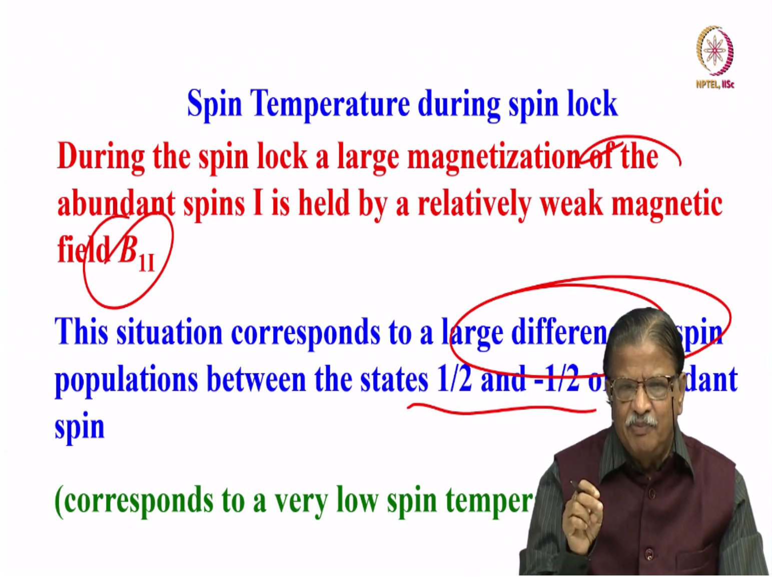

Spin Temperature during spin lock

During the spin lock a large magnetization of the abundant spins I is held by a relatively weak magnetic field B_{1I}

This situation corresponds to a large differen spin populations between the states 1/2 and -1/2 o dant spin

(corresponds to a very low spin temper

Now the spin temperature during the spin lock, what is happening is a large magnetization is held by relatively weak field for proton. This situation corresponds to large difference of spin population between plus half and minus half states of abundant spin. It means as I said, it corresponds to low temperature. It is as good as telling protons are very, very low temperature by doing spin lock, during the spin locks protons are at very, very low temperature; that is what it means.

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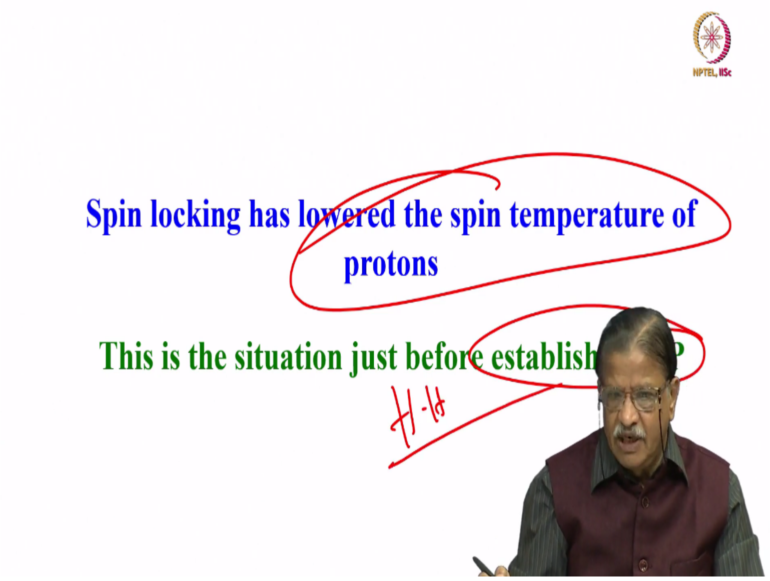

Spin locking has lowered the spin temperature of protons

This is the situation just before establish P

H-H

Spin locking has lowered the spin temperature of protons. This is the situation just before establishing cross polarization or establishing Hartmann Hahn condition; you remember that.

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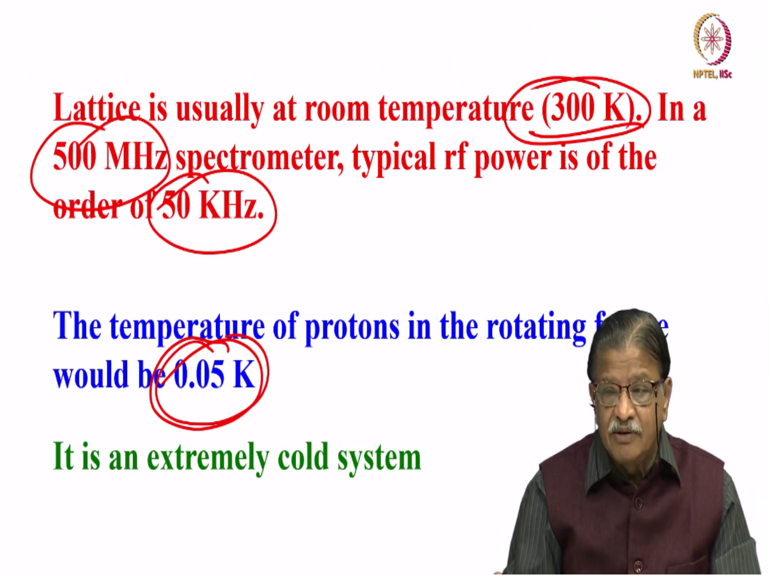

Lattice is usually at room temperature (300 K). In a 500 MHz spectrometer, typical rf power is of the order of 50 KHz.

The temperature of protons in the rotating f e would be 0.05 K

It is an extremely cold system

Now what is the temperature? how much is the lower temperature now in the spin lock. Remember at lattice temperature in thermal equilibrium, it is at 300 K. Just calculate in the 500 megahertz spectrometer the RF power we apply is 50 kilohertz. Where is 500 megahertz and where is 50 kilohertz? So, the temperature of the protons now will be around 0.05 degree Kelvin, instead of 300 K. it is drastically reduced. It is at 0.5 K that means when you are doing the spin locking you have made the spin system of the protons become extremely cold. Now the proton spin system is extremely cold spin system.

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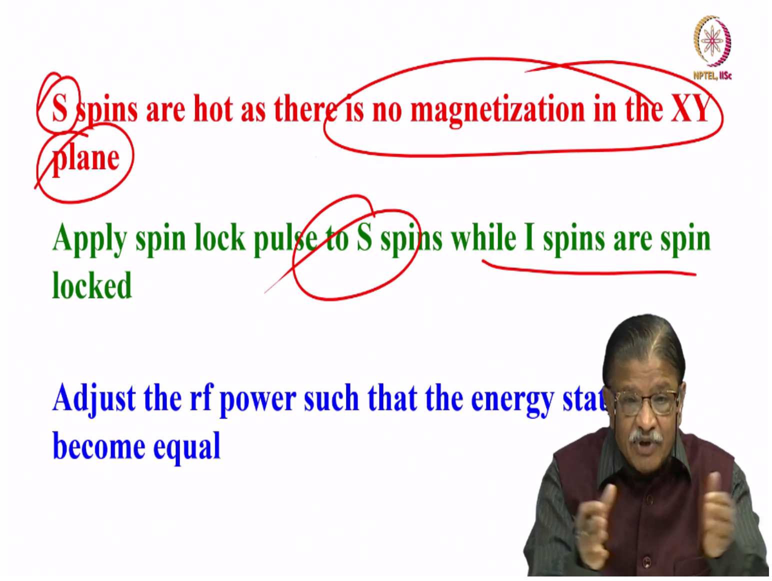

S spins are hot as there is no magnetization in the XY plane

Apply spin lock pulse to S spins while I spins are spin locked

Adjust the rf power such that the energy stat
become equal

What about the carbon spin? carbon spins or S spins they are very hot; why? because there is no net magnetization in the XY plane. There is no magnetization at all in the XY plane, I have not applied the RF pulse and brought it to this plane yet. Now apply spin lock pulse to S what will happen? when this Y spins are locked, at the same time apply RF pulse on the spins and the S spins, carbon 13. Now adjust the RF power and equate them. What is going to happen? S spins because of no net magnetization it is an infinite temperature, because you can say no population difference, there is a saturated state. But proton is at cold temperature very, very cold. Now carbon 13 is very hot. What happen if we bring them to contact? When we bring them to contact then there must be exchange of heat between two systems. Now it is two thermal bodies. One is at a very cold temperature, one is at very hot temperature; bring them to contact now. There must be exchange of heat; exchange of energy in the form of heat.

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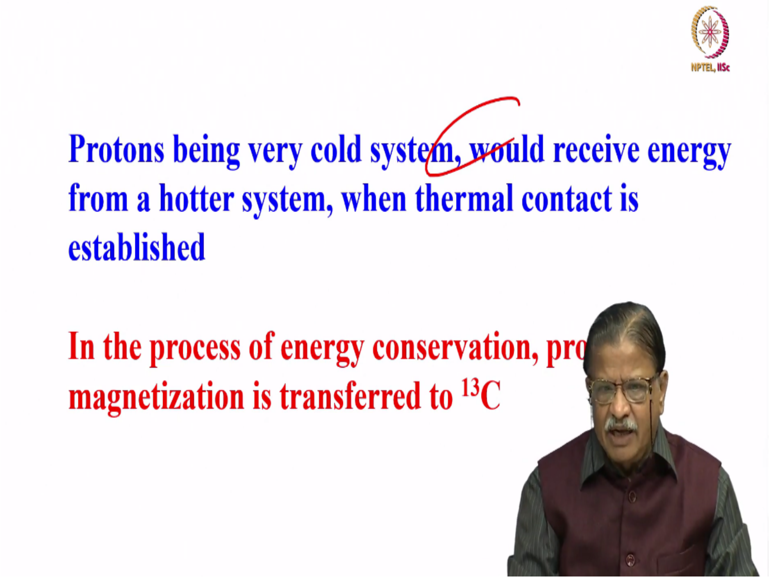

Protons being very cold system, would receive energy from a hotter system, when thermal contact is established

In the process of energy conservation, pro
magnetization is transferred to ^{13}C

Now proton being very cold system would receive the energy from the hotter system. Then while receiving what will happen? It will give its magnetization to carbon. In the process of the conservation of the energy, proton gives its magnetization to carbon 13, because it is very hot. Thermal equilibrium we are trying to establish between these two spins in the rotating frame.

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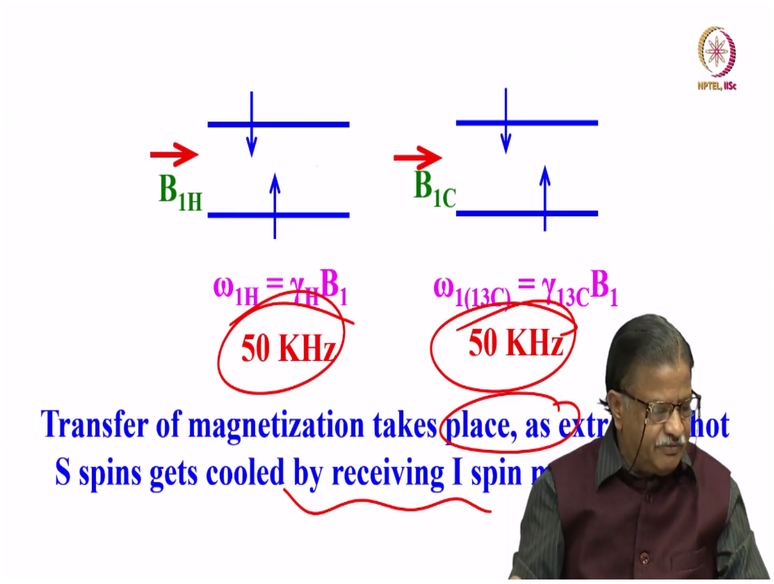

Transfer of magnetization takes place, as extr hot
S spins gets cooled by receiving I spin m

Now this is what happens. This is a 50 kilohertz, this is at 50 kilohertz. Now when we match it the transfer of magnetization takes place, as extremely hot carbon spins gets colder by receiving energy from protons. So, I spin gives energy to S spin, that is what is called cross polarization. We are transferring the polarization of protons to carbon 13. Analogous to what we discussed in the solution state where by using J coupling, using anti phase terms we transfer the magnetization between two J coupled spins.

Identically here consider the two thermal baths, one is proton and the other is carbon. Now by some mechanism we have brought them to contact and made this spin system to lose their identity. Then carbons which are very hot, proton which is very cold when we bring them to contact there is the transfer of magnetization from protons to carbons. And it will try to heat up and carbon try to cool down by itself this is what happens. This is called cross polarization.

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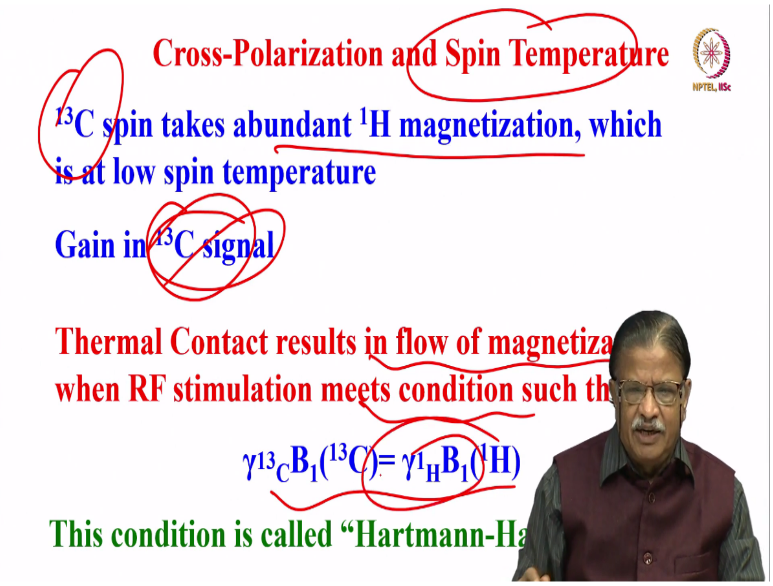

Cross-Polarization and Spin Temperature

^{13}C spin takes abundant ^{1}H magnetization, which is at low spin temperature

Gain in ^{13}C signal

Thermal Contact results in flow of magnetiza

when RF stimulation meets condition such th

$$\gamma_{^{13}C}B_1(^{13}C) = \gamma_{^{1}H}B_1(^{1}H)$$

This condition is called “Hartmann-Ha

So now if you understand what is cross polarization using spin temperature. The carbon 13 spin take abundant proton magnetization and gain in the carbon 13 signal; very large amount of gain in the signal. Now the thermal contact ensures the flow of magnetization when RF stimulates meeting this condition; the Hartmann Hahn condition when it stimulate. This condition is met by stimulating with the RF pulse; simultaneously we are applying in the XY plane, while doing spin lock.

So, the carbon 13 gain signal. Then what happens to protons? it will lose energy; huge bath of protons. You can consider like a big ocean you take just a mug of water from ocean nothing will happen; you do not lose anything, you do not feel it as a loss. Whereas the gain for carbon is enormous. That is what it is going to happen; then when you match this Hartmann Hahn condition this is happening.

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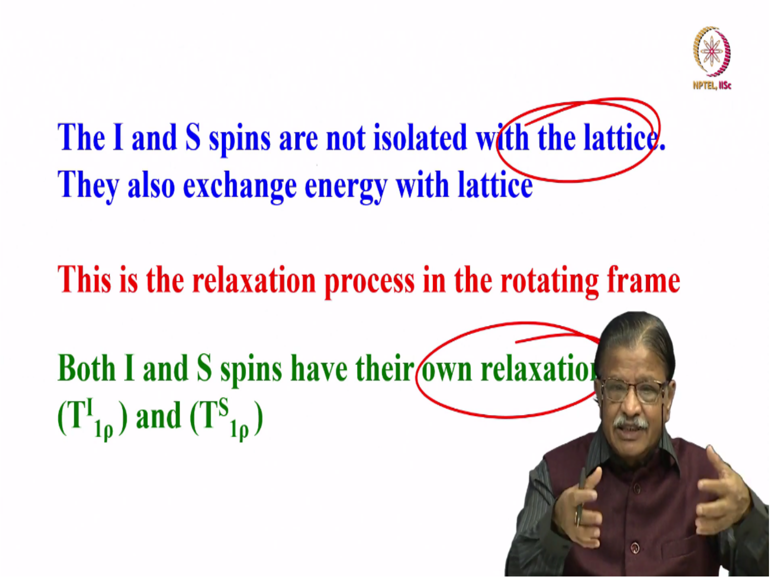

The I and S spins are not isolated with the lattice.
They also exchange energy with lattice

This is the relaxation process in the rotating frame

Both I and S spins have their own relaxatio
($T^{I}_{1\rho}$) and ($T^{S}_{1\rho}$)

But one more thing you should also understand we are establishing the contact between proton and carbon. They are not isolated systems they are also with a lattice. Simultaneously they also exchange energy with the lattice, not only between themselves. Proton can give energy to the lattice; carbon can give its energy to the lattice. This is also happening this is the relaxation process in the rotating frame T1 rho of proton is there, T1 rho of carbon 13 is also there; that is going on simultaneously. So, both have their own relaxation, they are different. T1 rho of proton is different from T1 rho of carbon 13. This process of giving its magnetization to lattice that is going on simultaneously. There is a transfer of magnetization between proton and carbon 13.

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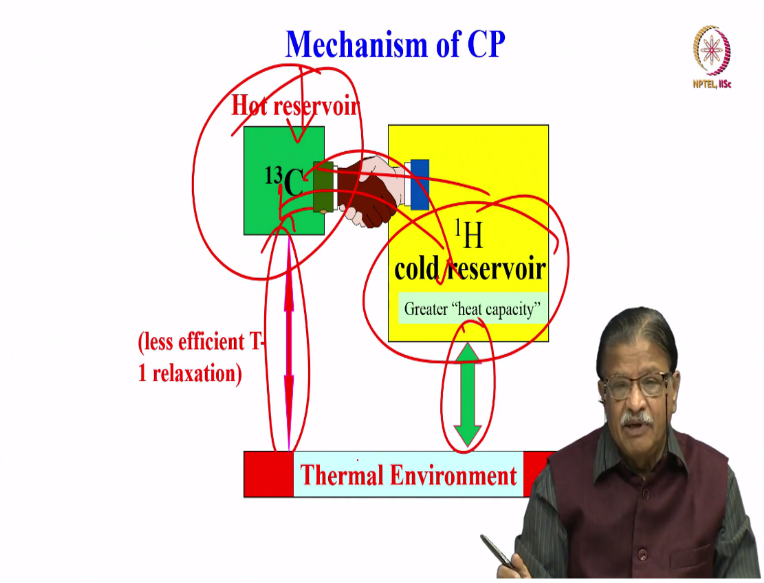

Mechanism of CP

So, what is the mechanism of CP? this is what happens. Diagrammatically we can find carbon 13 is a hot reservoir, proton is a very cold reservoir. Now you are bringing them to they are shaking their hands; bring them to contact in the rotating frame. They lose their identity; when you have to match the Hartmann Hahn condition, the magnetization transfer goes from proton to carbon, because it is hot it wants to cool down. And this will try to make sure that proton gets heated up. In other words, this will get cooled down by getting energy from proton. Simultaneously this is also going on, the relaxation; they are giving energy to the thermal environment, that is lattice.

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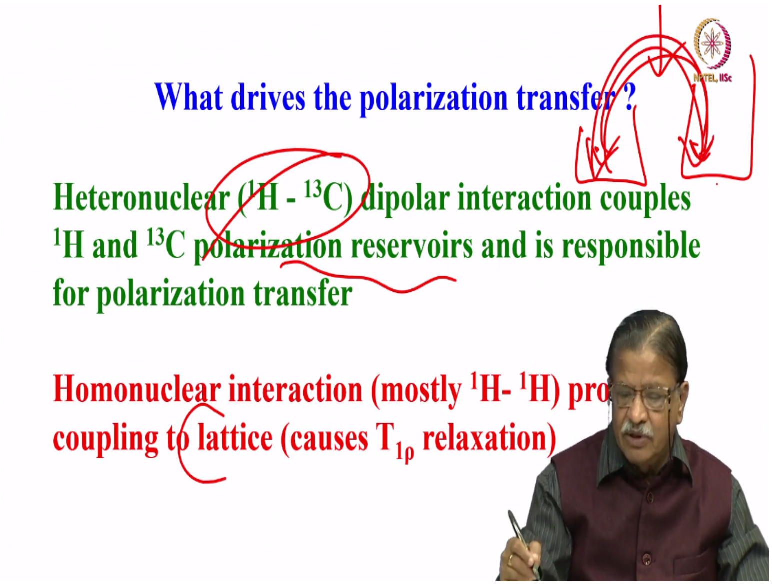

What drives the polarization transfer?

Heteronuclear (^1H - ^{13}C) dipolar interaction couples ^1H and ^{13}C polarization reservoirs and is responsible for polarization transfer

Homonuclear interaction (mostly ^1H- ^1H) pro

coupling to lattice (causes $T_{1\rho}$ relaxation)

Now you may ask me a question, fine; what is that mechanism what drives the polarization transfer? How it happens? Spin talk to each other they give energy, but how? what is the mechanism? Remember there is a heteronuclear dipolar coupling between carbon and proton. These heteronuclear dipolar interactions couple proton and carbon reservoirs. I have proton bath and a carbon bath here; and their energy transfer from proton to carbon takes place between these two baths using dipolar interaction.

Heteronuclear dipolar interaction; that is between proton and carbon dipolar interaction, this energy transfer takes place. And homonuclear dipolar coupling also is there, like proton-proton dipolar coupling. That couples with a lattice and causes what is called what is called T1 rho relaxation. I told you the spins are also interact with the lattice; and gives its energy. That is T1 rho relaxation. And this is the transfer of magnetization from proton bath to carbon 13 bath by using heteronuclear dipolar couplings. That you should remember.

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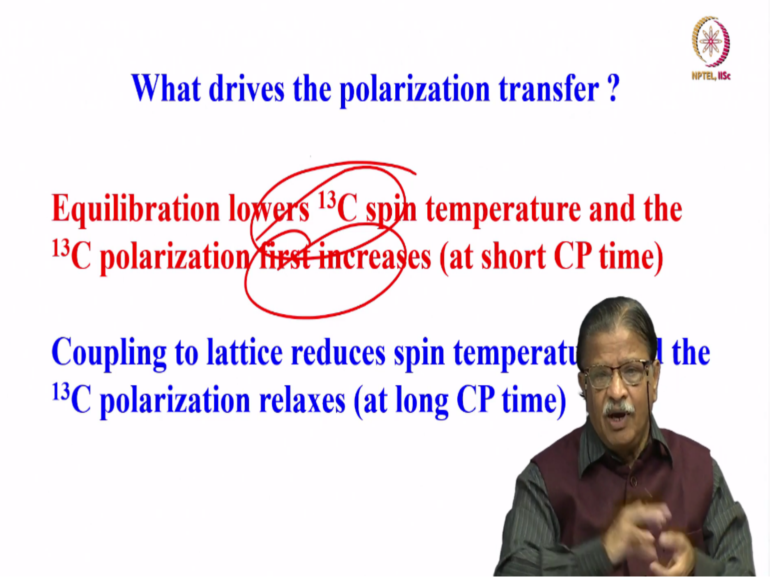

What drives the polarization transfer ?

Equilibration lowers ^{13}C spin temperature and the ^{13}C polarization first increases (at short CP time)

Coupling to lattice reduces spin temperatu the ^{13}C polarization relaxes (at long CP time)

So, what drives the polarization transfer? The equilibration lowers the spin temperature of carbon and carbon polarization starts increasing initially, as soon as we bring into contact carbon starts gaining a magnetization, becomes more and more; increases and at the same time it also gives energy to the lattice. The two simultaneous processes are going on. It is taking energy from proton, and also give it to the lattice.

This is a dynamic process and initially for a short time it takes from that from proton, but if you wait for a long time, whatever it has gained it will give to proton, also give to the lattice; that is what happens. So, T1 rho also matters, in addition to polarization transfer.

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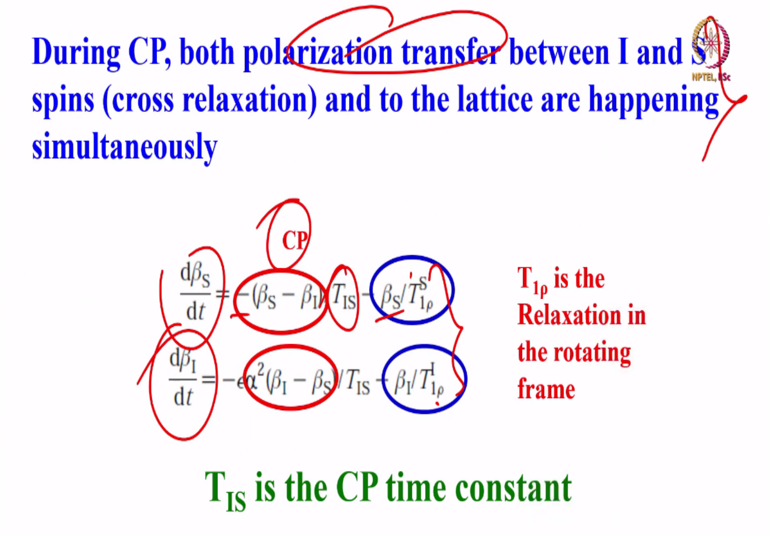

During CP, both polarization transfer between I and S spins (cross relaxation) and to the lattice are happening simultaneously

CP

$$\frac{d\beta_S}{dt} = -(\beta_S - \beta_I)/T_{IS} - \beta_S/T^{S}_{1\rho}$$

$$\frac{d\beta_I}{dt} = -\epsilon\alpha^2(\beta_I - \beta_S)/T_{IS} - \beta_I/T^{I}_{1\rho}$$

$T_{1\rho}$ is the Relaxation in the rotating frame

T_{IS} is the CP time constant

So, during CP both polarization transfer between I spin and S spins; and to lattice are happening simultaneously. Remember, simultaneously transfer of magnetization from proton to carbon and also from proton to lattice, and carbon to lattice is going on simultaneously. And they are change in the magnetization of protons and carbons is given by these equations. There is no need to derive this. It is available in the books; you can see and this is what is called as CP condition. And these T1 rho S and T1 rho I, are the relaxation times in the rotating frame. You understand simultaneously that is happening, and losing energy here. So, T1 IS the contact time during which you are going to establish cross polarization, mixing time. The cross polarization time is CP time which is T of IS.

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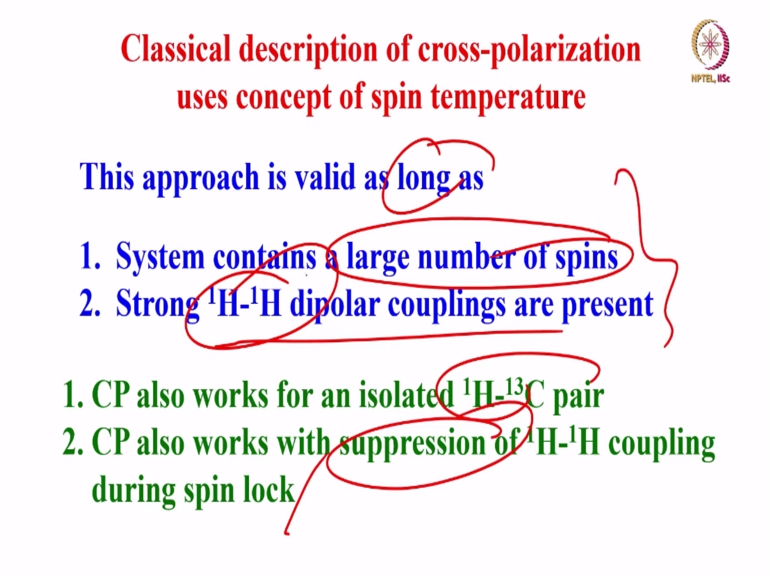

Classical description of cross-polarization uses concept of spin temperature

This approach is valid as long as

1. System contains a large number of spins
2. Strong ^{1}H-^{1}H dipolar couplings are present

1. CP also works for an isolated ^{1}H-^{13}C pair
2. CP also works with suppression of ^{1}H-^{1}H coupling during spin lock

So, classical description of cross polarization uses concept of spin temperature. That is what we have been discussing. Please understand using this concept of spin temperature to understand classically, what is cross polarization. Now is the method valid always? True there are some assumptions you have to make like in any mechanism. This approach is valid as long as the system contains large number of spins.

You cannot have an isolated spin and come to this conclusion, because we are considering the bath of spins, huge thermal bath of proton spins and carbon 13 spins. You should have a large number of spins and the strong proton-proton dipolar couplings also should be present. The CP also works on isolated spin very rarely and CP also works with suppression of proton-proton dipolar coupling during spin lock. And this assumption whatever the approach we give classically, description is valid when you have these things.

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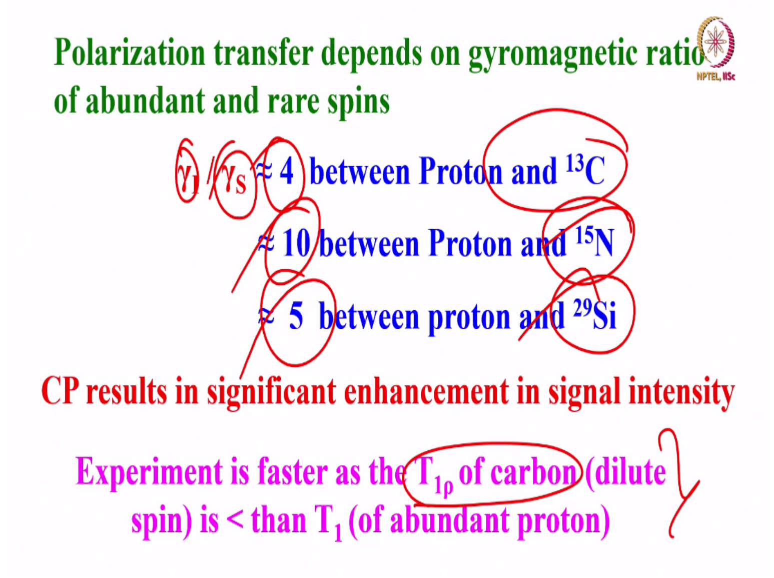

Polarization transfer depends on gyromagnetic ratio of abundant and rare spins

$\gamma_I/\gamma_S \approx 4$ between Proton and ^{13}C

≈ 10 between Proton and ^{15}N

≈ 5 between proton and ^{29}Si

CP results in significant enhancement in signal intensity

Experiment is faster as the $T_{1\rho}$ of carbon (dilute spin) is < than T_1 (of abundant proton)

Polarization transfer depends on gyromagnetic ratio of abundant spins and rare spins. For example ratio. I is abundant spin, S is rare spin. If gamma I and gamma S ratio if you take; proton and carbon 13, the enhancement ratio is 4 times. Remember 4 times you gain in the signal to noise ratio, if we establish Hartmann Hahn condition and do the cross polarization.

On the other hand if you take proton and nitrogen you get 10 times enhancement. If you go to silicon 29 you get 5 times enhancement. So, CP results in significant enhancement in the signal intensity. By using cross polarization technique we can enhance the signal of dilute spins. If you enhance the signal of dilute spins, there is a distinct advantage. You collect the signal at the faster time, then the experimental time drastically reduces. So, experiment is faster; and as the T1 rho of the carbon, of the dilute spin, or the T1 or proton are both comparable; and much, much smaller than the T1 of abundant spins, proton.

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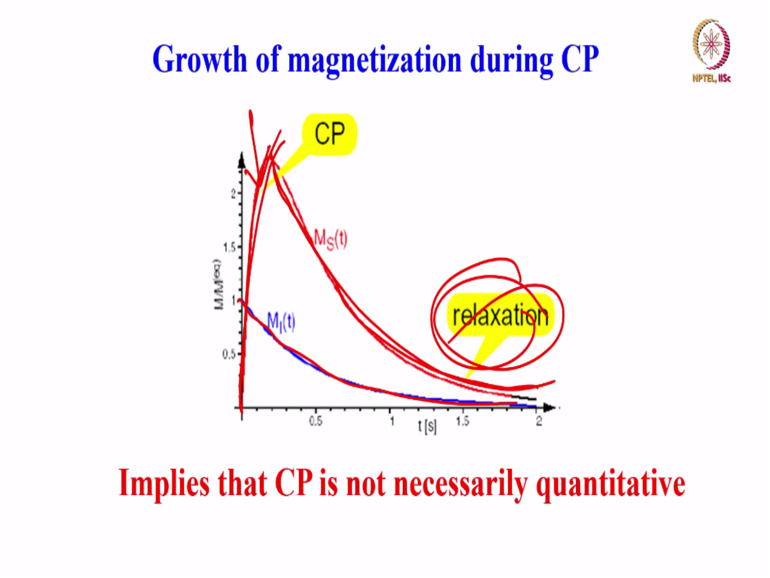

Growth of magnetization during CP

Implies that CP is not necessarily quantitative

So, this is where you have to understand the growth of magnetization during cross polarization. Initially it increases like this and after sometime it start giving its energy to the lattice. This is spin lattice relaxation, there is a gain in the signal intensity. You understand. Initially the carbon 13 signal intensity keeps on increasing; and after sometimes it gives magnetization to the lattice, and starts relaxing. This is T1 relaxation in the rotating frame.

Whereas in the case of protons straightaway start it decaying, decreasing, because it start giving its magnetization to carbon 13. So, it means CP it is very difficult to say quantitative, you can design a quantitative experiment, but it is not easy because it depends upon the mechanism of magnetization transfer between proton and carbon. So, varieties of things you have to understand, but please remember the CP is not necessarily a quantitative technique.

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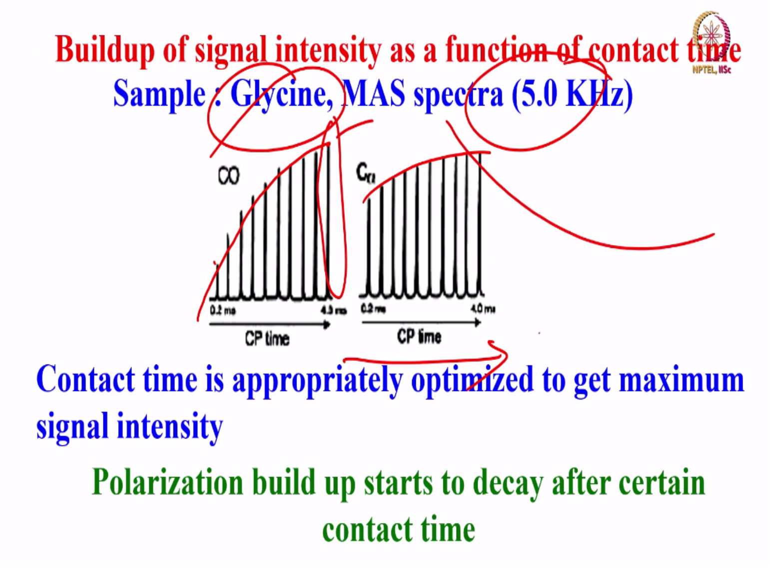

Buildup of signal intensity as a function of contact time

Sample : Glycine, MAS spectra (5.0 KHz)

Contact time is appropriately optimized to get maximum signal intensity

Polarization build up starts to decay after certain contact time

So, build up of signal intensity as a function of contact time if you look at, for example for glycine magic angle spinning spectra, if we take at 5 kilohertz; see it starts building up as the we keep on increasing the contact time in milliseconds; contact time should always in milliseconds. You cannot give larger time then you will burn the probe. So, let us say 0.2 millisecond like that keep on increasing you see the signal intensity starts growing like this. This is for C alpha carbon, grows like this. So you have to adjust the contact time appropriately and signal intensity keeps building. You have to adjust the contact time so that there is maximum gain in the signal intensity. This you have to adjust manually. So, polarization build up starts initially and after sometimes when it reaches maximum it starts decaying. This is what I said carbon 13 increases and then start decreasing.

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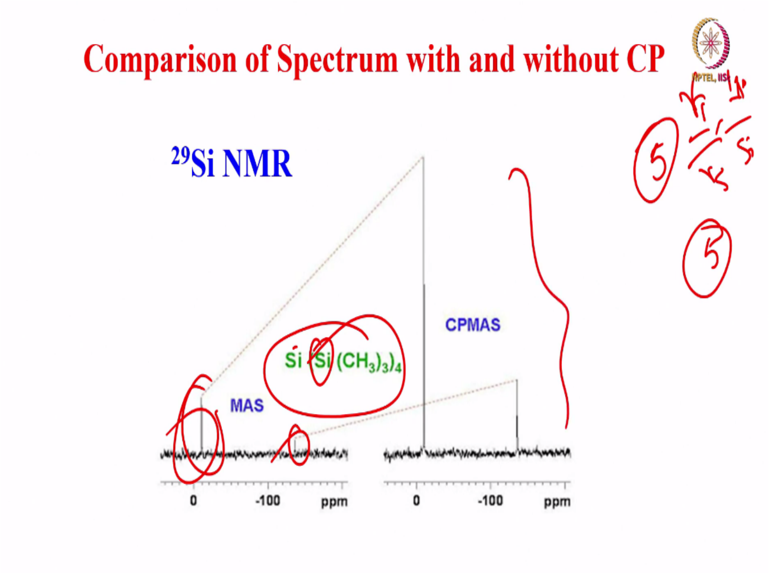

Comparison of Spectrum with and without CP

So, this is a simple comparison of spectrum with and without cross polarization. A silicon NMR of this molecule, you look at it. This is magic angle spinning; this is CH3 carbon; this is silicon attached to CH3. And this is the silicon, look at this one; this is without cross polarization just magic angle spinning. Now when you are doing the cross polarization, I told you for silicon enhancement is nearly 5 times because gamma I over gamma S, when it is proton and silicon this is proton and this is silicon; it is 5. So 5 times you see the enhancement here. Fantastic huge gain in the signal intensity.

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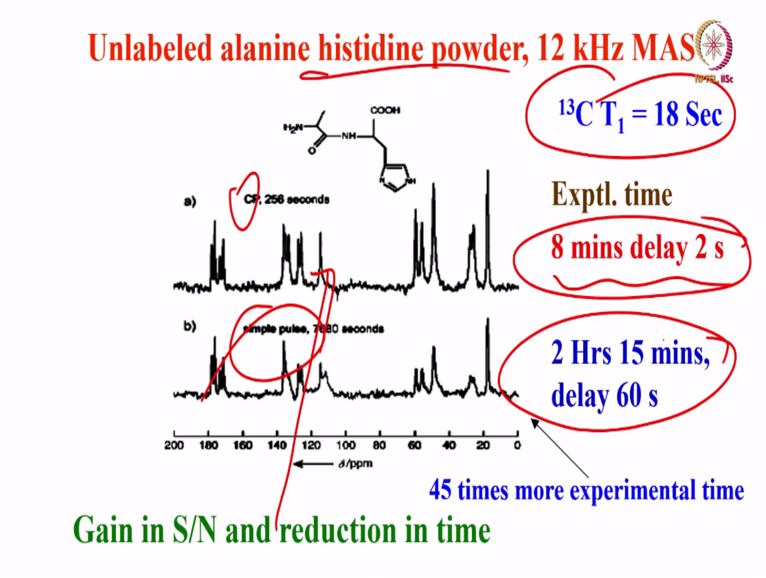
Unlabeled alanine histidine powder, 12 kHz MAS



$^{13}C\ T_1$ = 18 Sec

Exptl. time

8 mins delay 2 s

2 Hrs 15 mins, delay 60 s

45 times more experimental time

Gain in S/N and reduction in time

So, you look at this alanine histidine, some powder. This is carbon 13, T1 is of 18 seconds, this is experimental time. Normally it is for 8 minutes with the delay of 2 seconds here. And this is with 2 hours 15 minutes with a delay of 60 seconds. The advantage is, this is with cross polarization this is without cross polarization. Now enormous gain in the signal intensity is there and reduction in the experimental times; say drastically from 2 hours 15 minutes it came to 8 minutes and 2 seconds.

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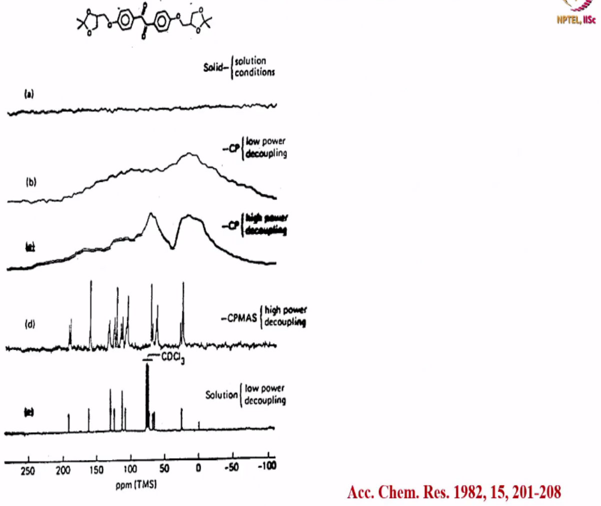
bis acetonide of 4,4'-bis (2,3-dihydroxypropyl) oxy benzyl



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So, this is where you can start comparing. okay I think this I have discussed later I need to explain more for that. So, what I am going to do is I will stop here. We will come back and continue this in next class. Today we understood this CP mechanism where the polarization transfer take place between proton and carbon, when we establish Hartman Hahn condition. The protons in the rotating frame are extremely cold.

Carbon 13 are extremely hot. Establish the thermal contact; then what will happen? the carbon 13 wants to become cooler by gaining the magnetization from the proton. Essentially its intensity goes up; and this phenomenon we understood. And simultaneously we also understood T1 rho is there, spins are also giving energy to the lattice, in addition to carbon 13 getting magnetization from proton.

So, that is one thing we understood. And the buildup curve also we saw how magnetization is going to build up during the CP. Initially it builds up and then slowly starts decaying, because of the relaxation; by the interaction with lattice. And we saw the gain is enormous, depends upon the gyromagnetic ratios. For proton to carbon it is 4 times enhancement; proton to nitrogen 10 times, proton to silicon is 5 times, depends upon the gyromagnetic ratio. And that is what we saw. And we will come back and continue further, where I will discuss much more about the CP and few examples we can look. So, thank you I will stop here.