Advanced NMR Techniques in Solution and Solid - State
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Module-22
Evolution of J coupling Polarization Transfer
Lecture – 22

Welcome back. In the last class, we discussed about evolution of the magnetization, after discussing receiver phase and transmitter phase that is the pulse phase. We discussed about the evolution of magnetization. As I said if you apply your radio frequency pulse, bring the magnetization to x axis or y axis and allowed to rotate allowed to precess for some time, or for some duration, t, then we understood how the magnetization components vary, especially, when I take the example of J split doublet or just individual chemical shift. We understood what is the difference between absorptive peak and dispersive peak and also in phase doublet in antiphase doublet; especially, when you consider the J phase doublet, how the magnetization varies with as a function of time. Then we distinguish between real absorptive positive absorptive, negative absorptive peak, real dispersive, there is positive dispersive peak, negative dispersive peak, all those things we understood.

And we know how with, when these things will ever come, when the magnetization start precessing in the xy plane, depending upon where we have the receiver, how the magnetization is moving. Then we wanted to know how the chemical shifts and coupling evolves. In on-resonance condition, when nu – nu r is 0, I told you chemical shift do not evolve, of course, the coupling if there is a multiplicity pattern, the coupled multiplets will evolve, but chemical shift do not evolve. Whereas, in off-resonance condition both chemicals shift evolve and J coupling evolve.

In the working the off-resonance condition to the example of doublets, triplet and quartet. The centre of the doublet is the chemical shift. So, hypothetically there is a peak, but hypothetically the centre the doublet is considered as a chemical shift position. You should calculate where it is and depending upon how much is the offset, decides the speed at which the spins starts precessing in the xy plane. The magnetization vectors precession also depends upon the distance of them from the center.

So, we understood that centre the doublet is a chemical shift evolution and whereas, for the triplet centre component of the triplet corresponds to the chemical shift evolution. If I take quartet, again centre of the quartet corresponds to the chemical shift evolution. We showed how they vary; for different time how, they evolve. This is the how the chemical shift evolve on-resonance condition. Now, we will discuss about evolution of couplings, how the couplings do evolve, how do they evolve both in on-resonance off-resonance condition.

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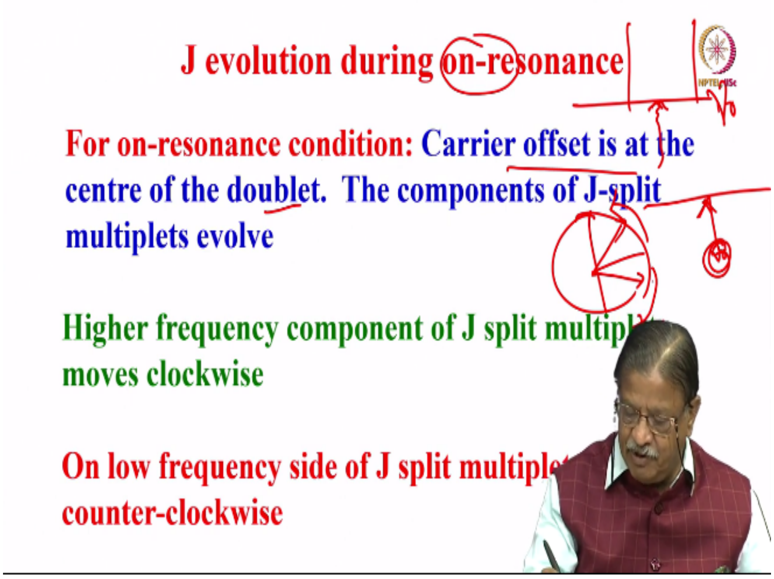

J evolution during on-resonance

For on-resonance condition: Carrier offset is at the centre of the doublet. The components of J-split multiplets evolve

Higher frequency component of J split multipl moves clockwise

On low frequency side of J split multipl counter-clockwise

So, now during the on-resonance condition what is going to happen? Carrier offset is at the centre of the doublet, that is nu naught - nu RF. The nu naught is the central frequency of the spectral width, I consider this as nu naught or nu r whatever; the nu naught I took it as the nu naught central frequency of this spectral width, the carrier offset; this is also called as carrier offset. If my carrier offset is exactly centre at the doublet; let us say I have a doublet with J split doublet. If my carrier offset is exactly at the centre, then we are in on resonance condition for this doublet. The components the J split multiplets evolve, we are on resonance the components J split of doublet also evolve, as far as chemical shift is considered, it is also on resonance. Now both are present. So, chemical shift will not evolve because we are on resonance, but J split multiplets evolve. So, the doublet components have to evolve.

Higher component, higher frequency component of J split multiplet moves clockwise and lower frequency of the J split multiplet moves counter clockwise. For example, I bring the magnetization to xy plane like this, this is one component of the doublet, this is another component the doublet. This component of the doublet starts moving like this, clockwise because it is high frequency component. The low frequency component moves anti clockwise like this. This is the important condition you remember; the high frequency component of the multiplet moves clockwise, low frequency component of the J split multiplet moves anti clockwise.

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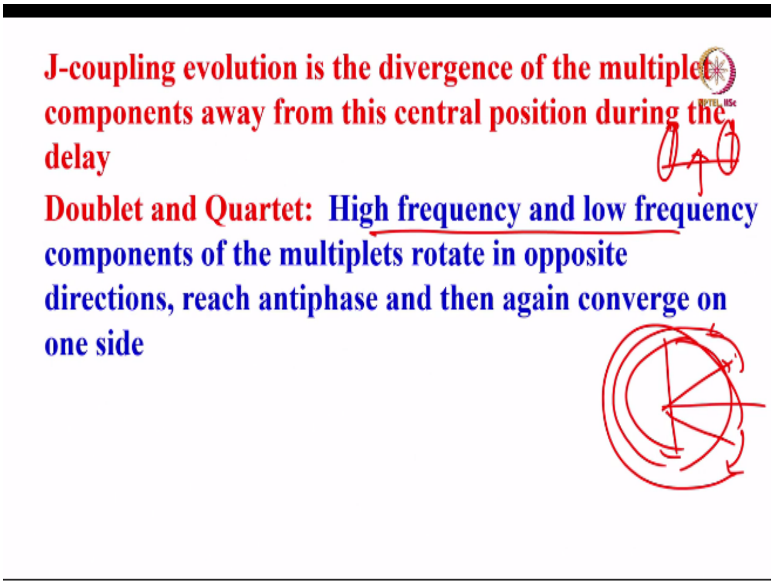

J-coupling evolution is the divergence of the multiplet components away from this central position during the delay

Doublet and Quartet: High frequency and low frequency components of the multiplets rotate in opposite directions, reach antiphase and then again converge on one side

The J coupling evolution is the divergence of the multiplet components away from the central position; that is what the J coupling evolution. Chemical shift evolution is we have understood centre the doublet, central component of the triplet, centre of the quartet. But J coupling is the movement of the multiplets; the components of the J split multiplet; it could be a doublet, the triplet or the quartet. Now, in the case of the doublet and the quartet, we have 2 frequencies because we are at the on resonance; exactly at the centre.

This peak and this peak, the high frequency component, and the other is the low frequency component, move in the opposite direction; very important thing. One moves clockwise and the other moves anti-clockwise. Now, I have the peak here; a J spilt double;t one is here, one is here, this moves like this, this moves like this.

Then what is going to happen? They continue to move in the opposite direction, for one full rotation; for J coupling one full rotation if you take, this comes like this, this comes like this both will happen. And now, what is going to happen during the process, they start moving, reach antiphase and then come back and then converge. It will go like this, keep rotating and become antiphase, come back and then again merge. So, this is what is going to happen for the doublet and quartet components; they move like this.

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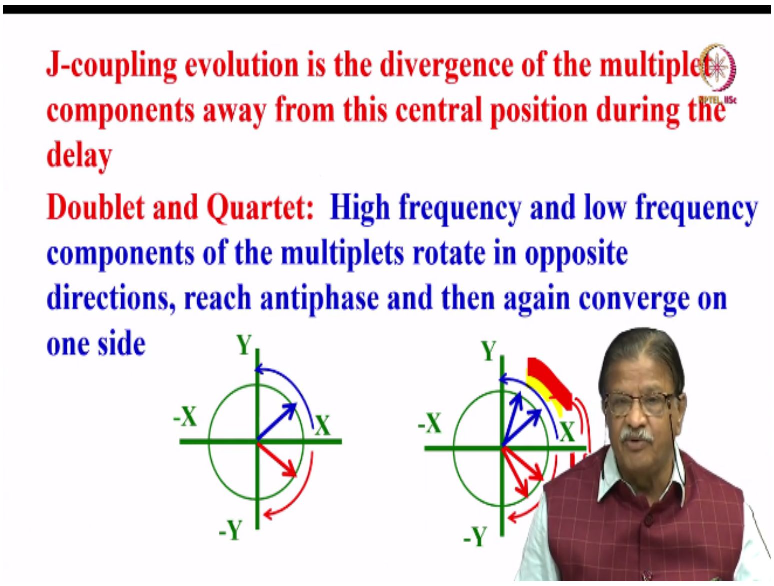

J-coupling evolution is the divergence of the multiplet components away from this central position during the delay

Doublet and Quartet: High frequency and low frequency components of the multiplets rotate in opposite directions, reach antiphase and then again converge on one side

They move in the opposite direction like this. Whereas, similarly quartet components 2 lines of the quartet that are at high frequency, they move like this, this, move like this, one move like this, other move like this. This is the quartet, 2 lines of the high frequency components, 2 lines of the low frequency components, move in the opposite direction.

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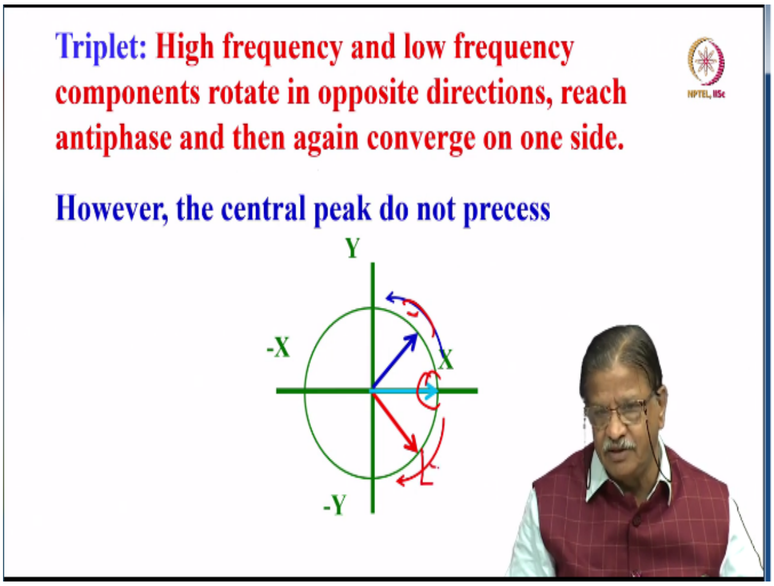

Triplet: High frequency and low frequency components rotate in opposite directions, reach antiphase and then again converge on one side.

However, the central peak do not precess

Now what happened to the triplet? Triplet interesting thing the central component will be exactly on resonance; it will not move at all. It will be remaining same; if it does not precess; whereas the other 2 components of the triplet start precessing; one in this direction, one in this direction, they are moving in the opposite direction. So, this is how the J couplings evolve.

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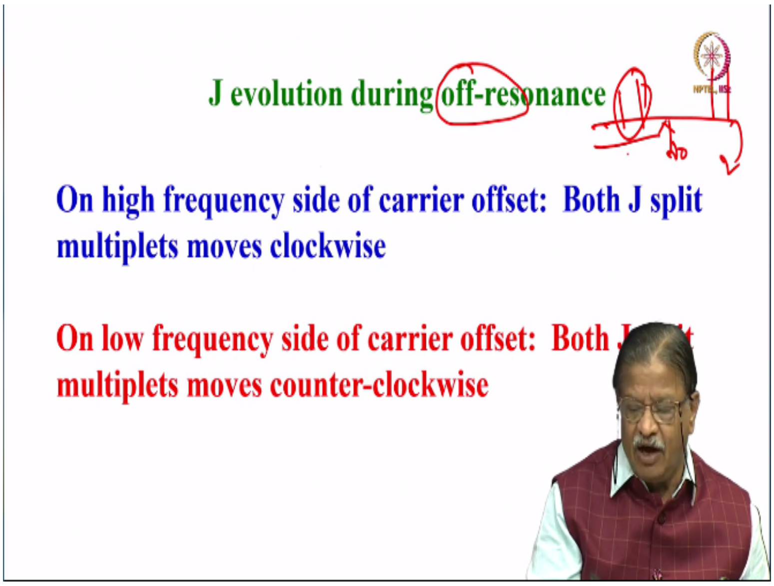

J evolution during off-resonance

On high frequency side of carrier offset: Both J split multiplets moves clockwise

On low frequency side of carrier offset: Both J
multiplets moves counter-clockwise

Now what will happen if I go to the off resonance, off resonance is means the centre is not nu 0; it is different now. How do they evolve now, what will happen is, now it depends upon where the doublet component, triplet component, quartet components are present. In the earlier case both were exactly at the centre on resonance; now nu naught is here, for the doublet both are here, that is a different question. They move in one direction; if they are high frequency, they move clockwise; if they are both low frequency like this, they move counter clockwise. Now not one component, both the components will move. We have to consider both the components; earlier when on resonance only one component is moving clockwise other component is moving anti-clockwise. That was a situation in on resonance; but in off-resonance situation all the components of the multiplets, and the doublet or all the 3 components the triplet or for that matter quartet, how they move? we should understand, if they are on the high frequency side, all the components will move clockwise. If they are on the low frequency side; all of them move counter clockwise. This is the thing we should know.

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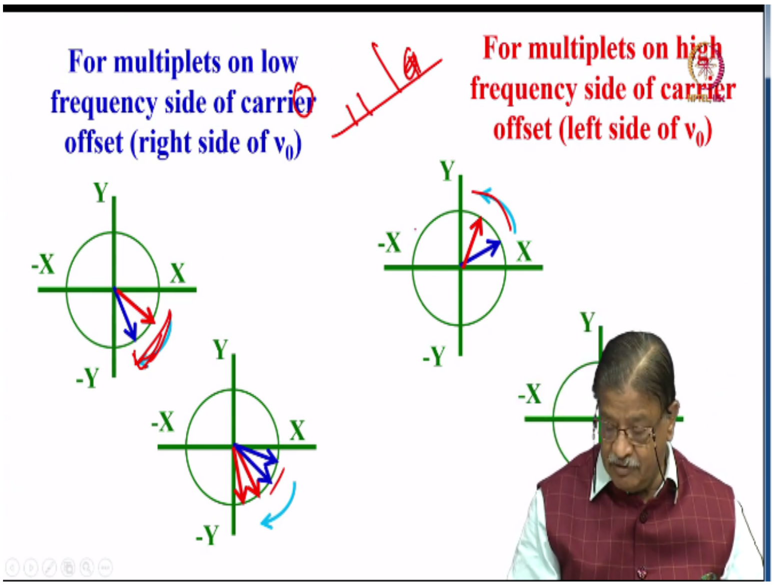

For multiplets on low frequency side of carrier offset (right side of ν_0)

For multiplets on high frequency side of carrier offset (left side of ν_0)

Now I consider a situation for multiplets and the low frequency side of the carrier; that is on the right side of the carrier nu 0; then they all start moving like this. Now on the right side of this, my nu 0; now my doublet is like this. It is not exactly at the centre, they start moving like this. Quartet, same way, I have a quartet like this, all 4 peaks of the quartet start moving like this. Now, for multiplets on high frequency side, if we consider multiplets, on high frequency side now what is going to happen; now this will start moving like this.

See this was a low frequency side, they were moving like this. Now I have taken this spectrum, instead of a doublet here, I have taken here. They start moving in the opposite direction. Similarly a quartet starts moving like this. This is the important thing.

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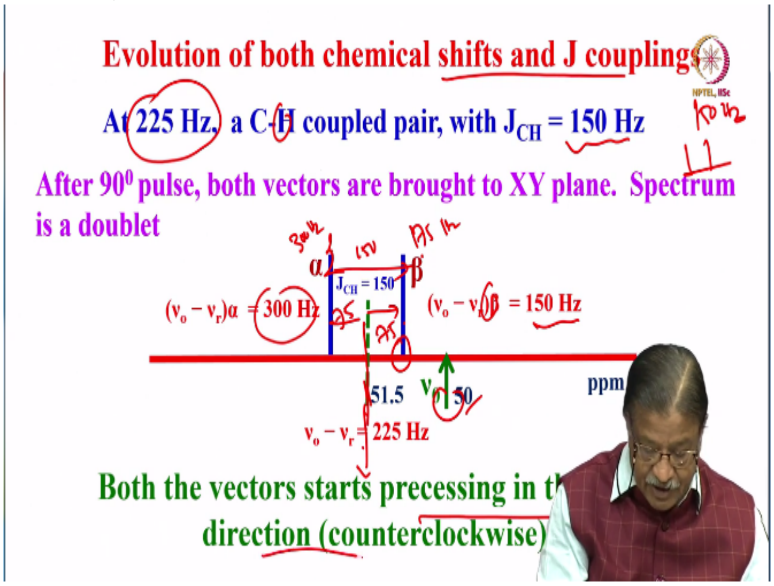

Evolution of both chemical shifts and J couplings

At 225 Hz, a C-H coupled pair, with J_{CH} = 150 Hz

After 90^0 pulse, both vectors are brought to XY plane. Spectrum is a doublet

Both the vectors starts precessing in t direction (counterclockwise)

Now what happens if you have both the chemical shifts and J coupling? How they simultaneously evolve, we are to know. Consider an example at 225 hertz, let us say a C-H doublet is there with a coupling constant of 150 hertz, it is a problem we are assuming. After a 90 degree, pulse both vectors will be brought to the XY plane. Now, this I am considering a doublet, I am considered carbon 13 spectrum, let us say, carbon 13 coupled to proton will be a doublet.

Now, what will happen this is my nu naught, some frequency for nu naught don't worry. Now, this is at 225 hertz with respect to nu naught. I have a chemical shift for this doublet. And from this place, the 2 components of the doublet; alpha and beta split like this; separation of coupling constant is 150 hertz. This is 225, this component will be 225 - 75. Now, this is 150 hertz; from here to here, from the centre this is 75 hertz and this is 75 hertz. So, from 225 from the centre, this is at 175 hertz, whereas, this one is at 300 Hertz.

So, nu naught / nu r for alpha component is at 300 hertz; nu naught / nu r for beta component is at 150 hertz; and both are one side of the carrier, that means we both are off-resonance. Now we are not both off resonance not on resonance; both are one side. Now both starts precessing in the same direction; counter clockwise, both of them start rotating counter clockwise.

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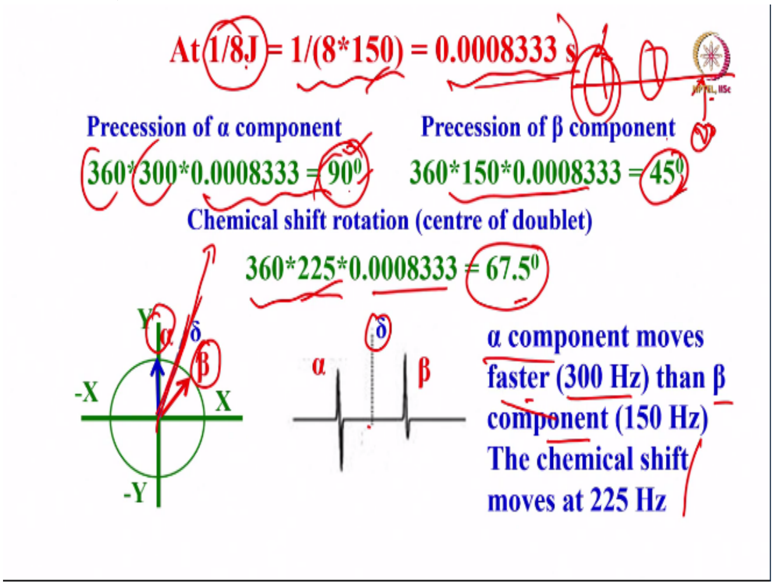

At 1/8J = 1/(8*150) = 0.0008333 s

Precession of α component

360*300*0.0008333 = 90⁰

Precession of β component

360*150*0.0008333 = 45⁰

Chemical shift rotation (centre of doublet)

360*225*0.0008333 = 67.5⁰

α component moves faster (300 Hz) than β component (150 Hz)
The chemical shift moves at 225 Hz

Now, I consider a situation what will happen to this magnetization at certain values; at some T = 1 over 8 of J, 1 over 8 multiply by 150. One component, this is the time, and now we will put this value of 150 hertz; both of them will move now, there is a separation of 150 hertz with respect to nu 0 one is at 360, and the other is at 150. Now, if we calculate that 360 to 300 and this is the value, duration we calculated for 1 over 8 of J, then it will turn out to be 90 degree. So, alpha component moves by 90 degree. Whereas, beta component if you calculate it; just plug in these values, it is going to be 45 degree. So, the precession of the beta component is 45 degree and the precession of the alpha component is 90 degree. Exactly at 1 over 8 of J, is what happens. So, the chemical shift is at the centre of the doublet; how much it has rotated, it is 360 into 225, it is this value. So, chemical shift has rotated by 67.5 degree whereas, one component of the doublet has rotated by 90 degree other component of the doublet has rotated by 45 degrees; these are the important things you can understand.

Now, I am telling with situation, a CH doublet and both of them are off resonance; away from the centre. Now, there are on the high frequency side. As a consequence one component is moving away by 90 degree forward 1 over 8 of J, J coupling is 150 hertz; you calculate this; the turns out to be a time of 0.0008333 second. In which case the alpha component moves by 90 degree, beta component moves by 45 degree; and the chemical shift at the centre moves by 67.5 degree; very interesting thing; look at this one, the alpha component is moved by 90 degree, this is move by 45 degree, but the chemical shift is here, there is no peak there, at chemical shift there is no peak. I am just telling, it is hypothetically a position here, at which if you calculate the chemical shift for this thing it will be here, it is moved by 67.5 degree. And if you record the spectrum of it alpha and beta, if you find out, this is the delta, the alpha and beta components are of mixed phase.

Alpha component moves faster, 300 Hertz, then beta component is 150 Hertz and the chemical shift is 225 Hertz. Remember, as I have been telling you, please understand, with respect to the nu naught frequency, depending upon how far they are, this component is alpha is far away from this which moves faster; this move slower. More the peak away from the reference, from the centre, faster it moves. See alpha component is far away, 300 hertz so, alpha component move faster; the beta component is 150 hertz from this, moves slowly. So, for the components of the multiplet, how they move depends upon how far they are from the centre.

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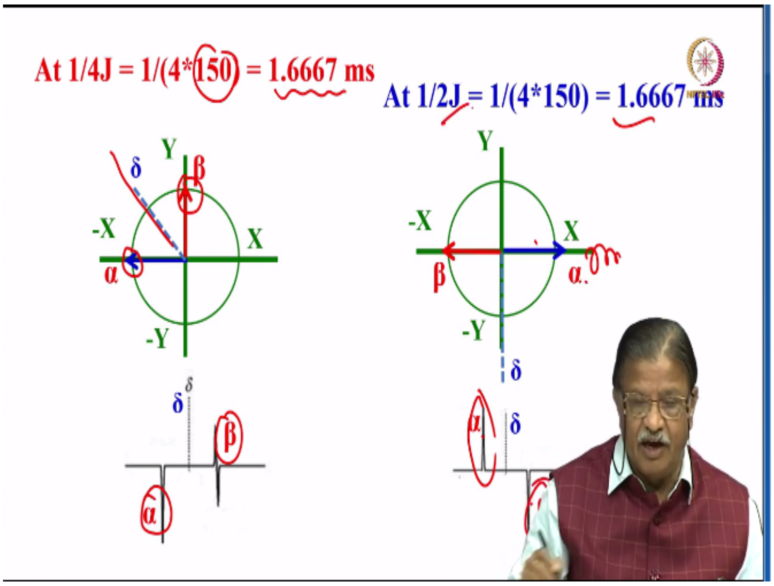

At 1/4J = 1/(4*150) = 1.6667 ms

At 1/2J = 1/(4*150) = 1.6667 ms

So, now at 1 over 4 of J what is going to happen? we can calculate. J is 150 Hz. Now if you calculate 1 over 4 times J; t is 1.667 seconds, plug in those values there; in the equation now. 360 into nu naught – nu r into t; you calculate, Now, it turns out to be that alpha component is here, beta component is here and chemical shift is here. So, it turns out to be that alpha component is negative and beta component is sort of mixed phase.

At 1 over 2J this is what you calculate. Now alpha and beta are just exactly opposite; What do you call it? we discussed this already, it is the antiphase doublet. Exactly one, alpha component is positive, beta component is negative. Why alpha component is positive, I am detecting here. So, otherwise of course, I have the receiver somewhere at a different place, I can make this as negative and this as positive; but you cannot make both of them as positive; that is what we discussed. So, alpha is positive, and beta is negative at 1 over 2J, this is the nomenclature.

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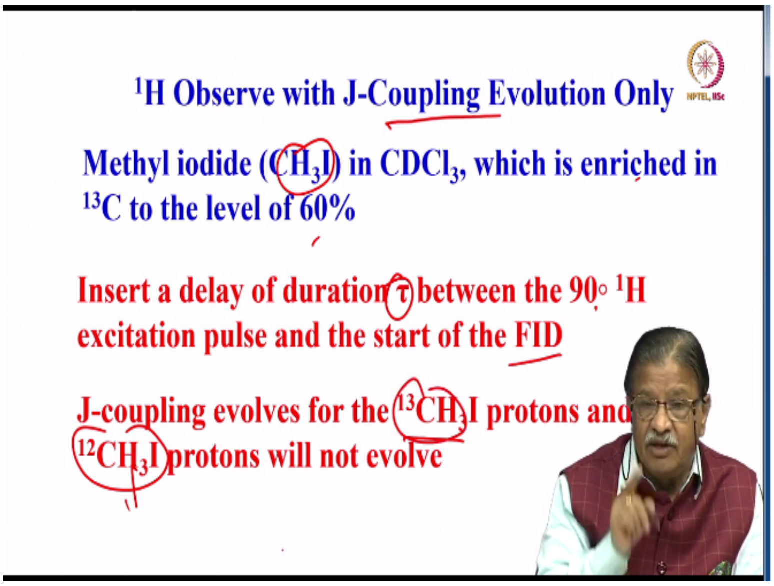

^{1}H Observe with J-Coupling Evolution Only

Methyl iodide (CH_3I) in $CDCl_3$, which is enriched in ^{13}C to the level of 60%

Insert a delay of duration τ between the 90° ^1H excitation pulse and the start of the FID

J-coupling evolves for the $^{13}CH_3I$ protons and $^{12}CH_3I$ protons will not evolve

So, if I take the 1H signal observed with J coupling evolution alone; consider the example of methyl iodide in CDCI3 with the carbon 13 enriched upto some value. Insert a delay of tau between 90 degree pulse and the 1H pulse; and start collecting this signal; and see how the J coupling has evolved. See in the J coupling of carbon 13, when I look at the proton, you get a doublet, when I look at the carbon 13, you are going to get a quartet. When I look at the C12 H proton, proton gives a single peak, when I look at carbon $^{13}CH_3$; proton is going to be a doublet, because I see that in coupling.

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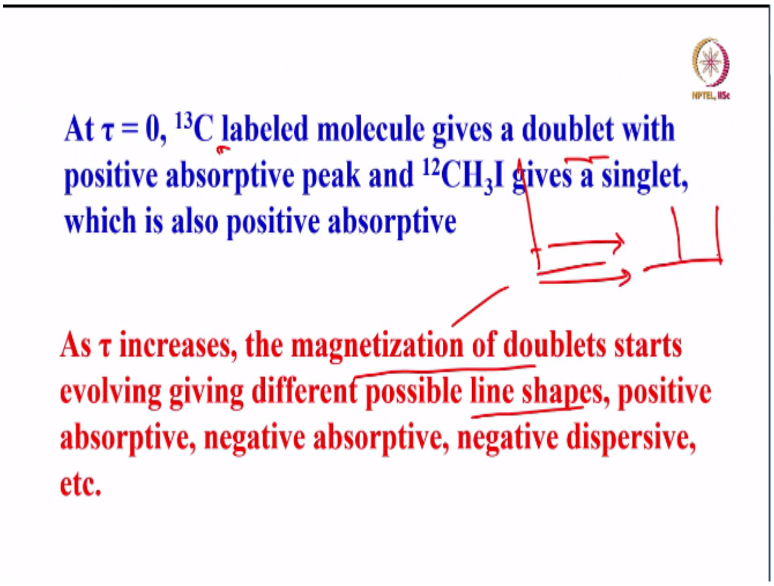

At τ = 0, ^{13}C labeled molecule gives a doublet with positive absorptive peak and $^{12}CH_3I$ gives a singlet, which is also positive absorptive

As τ increases, the magnetization of doublets starts evolving giving different possible line shapes, positive absorptive, negative absorptive, negative dispersive, etc.

So, at t = 0, 13C labelled gives a doublet. As tau, t, increases now what is going to happen? magnetization of doublets starts evolving, giving different possible line shapes, positive absorptive, negative absorptive, negative dispersive, everything you can get. At t = 0, we are going to get a doublet with positive absorptive signal. Bring the magnetization here, and this is my axis, and both of them are here; and I am going to get a signal both positive like this.

Now, I keep on giving the delay and collect the signal, allow it to precess, rotate for some time, and see the signal. You get everything possible; if you collect signal at different times you can get positive absorption immediately at t = 0; negative absorption of certain time; negative dispersion, everything you can get.

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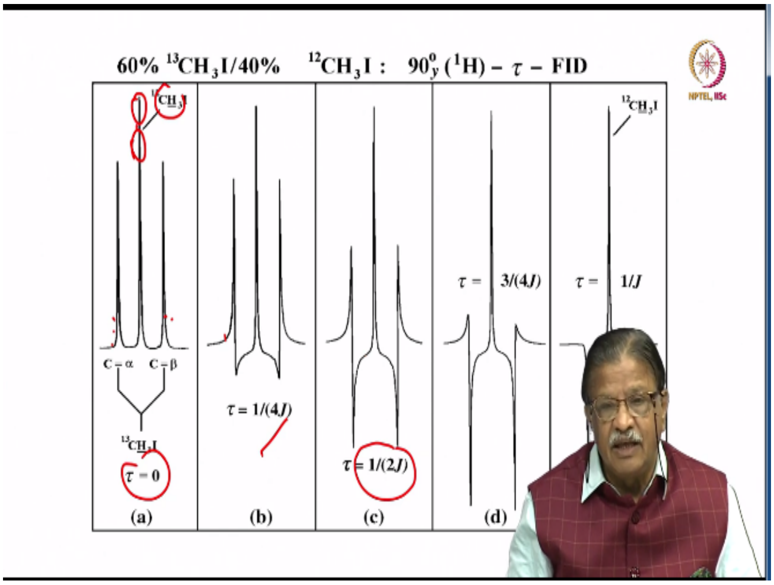

60% $^{13}CH_3I$/40% $^{12}CH_3I$: $90^0_y(^1H) - \tau -$ FID

See this is what happens. At t = 0. Immediately after this, this is central component, this is coming because of carbon 12 attached, because it is only 60% labelled, 40% carbon is C12 and that proton gives a single peak, you get a singlet and these 2 are the C carbon13 alpha and beta components, split because of the J coupling. Now at t = 0, forget about this one, we have to consider only these. we are going to get in the phase absorptive component. Inphase doublet, absorptive, positive absorptive. At time some value 1 over 4J, the phase is getting distorted; exact that 1 over 2J you see it is antiphase.

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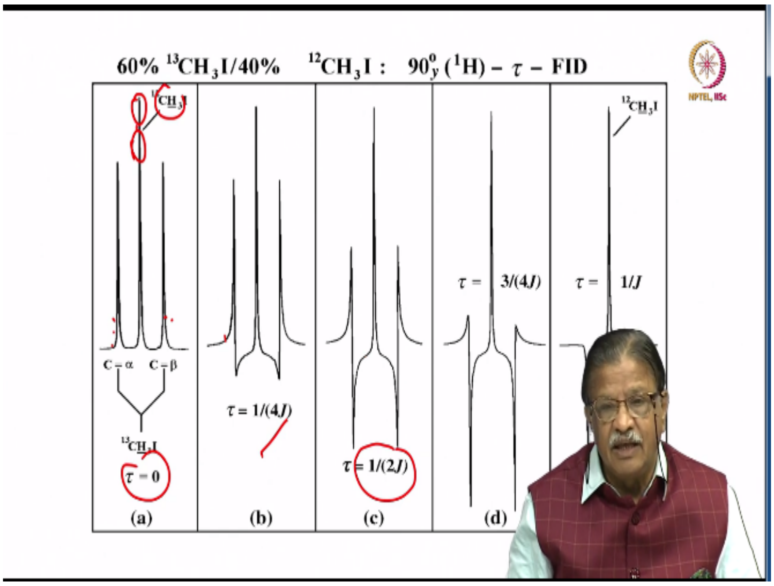

60% $^{13}CH_3I$/40% $^{12}CH_3I$: $90^0_y(^1H) - \tau -$ FID

Now, this is what we are going to get. After 3 over 4 J, you get again a little bit distorted phase; both are negative. And exact get 1 over J you get negative absorptive signal. Simple experiment you do; Collect the signal at different periods of time after sending the RF pulse at exactly t = 0 you get positive absorptive, after 1 over J, 1 full rotation if you take, 1 over J, then this carbon 13 J split doublet is exactly again negative absorptive, inphase but negative absorptive.

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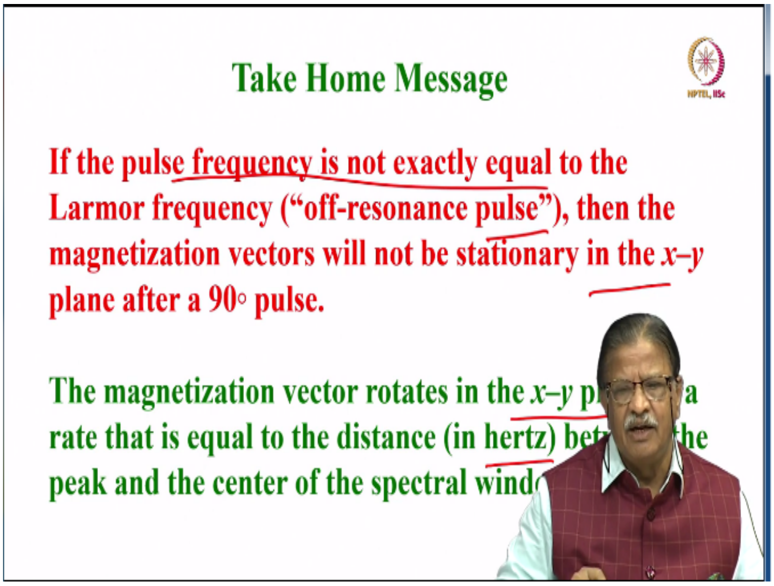

Take Home Message

If the pulse frequency is not exactly equal to the Larmor frequency ("off-resonance pulse"), then the magnetization vectors will not be stationary in the x–y plane after a 90◦ pulse.

The magnetization vector rotates in the x–y p a rate that is equal to the distance (in hertz) bet the peak and the center of the spectral wind

So, this is the take home message. What I am trying to give is if the pulse frequency is not exactly the Larmor frequency, because off resonance, then the magnetization vector is not stationary. And they will evolve in the xy plane. And the magnetization vector rotates in the xy plane and the rate of rotation depends upon how far it is from the centre of the spectral window, from the reference, from the carrier offset; how far they are from the carrier offset. Farther the peak from the carrier offset, faster it rotates.

That we took the example of C13 doublet, and both were off-resonance, on one side of the doublet; we saw how much it rotates. We saw that 300 hertz peak rotated by 90 degrees; whereas that 150 Hz higher frequency peak rotated by 45 degree, and the chemical shift was in between, this rotated by 67.5 degree.

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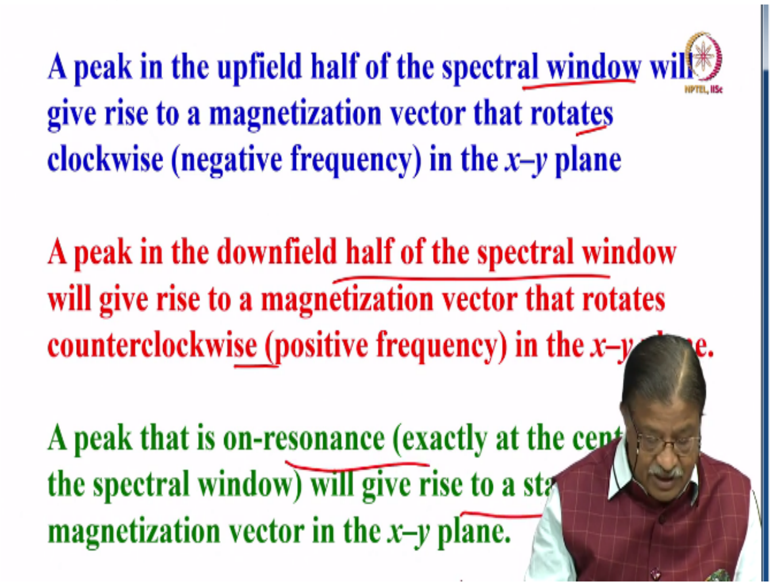

A peak in the upfield half of the spectral window will give rise to a magnetization vector that rotates clockwise (negative frequency) in the x–y plane

A peak in the downfield half of the spectral window will give rise to a magnetization vector that rotates counterclockwise (positive frequency) in the x–y e.

A peak that is on-resonance (exactly at the cent the spectral window) will give rise to a sta magnetization vector in the x–y plane.

So, this is what you should understand. Peak at this half of the spectral spectral width, gives magnetization that rotates clockwise, negative frequency and peak at the downfield of the spectral width gives magnetization vector that rotates clockwise. So, similarly the on resonance is exactly the centre, it will give rise to a stationary magnetization in the xy plane, it does not evolve at all. So, this is what I wanted to talk to you about the chemical shift and J coupling evolution.

Previously we discussed about chemical shift evolution, I discussed about the J coupling evolution now. You should understand more important thing, is about the components of the J split doublet; whether it is positive absorption, negative absorption; whether it is a dispersive, whether inphase absorption or antiphase dispersion, in phase dispersio;n all these things were observed. We understood everything.

Now with this, we will go to the next topic, I will introduce something about polarization transfer as someone time is available today; we will discuss about polarization transfer technique. Basically, how we do the polarization transfer, how we enhance the signal intensity, we will discuss. So, I will start introducing the polarization transfer techniques now.

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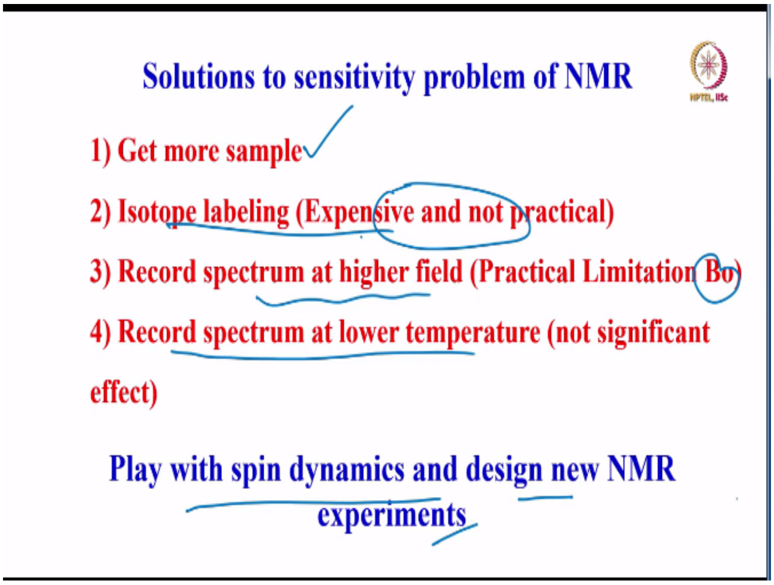

Solutions to sensitivity problem of NMR

1) Get more sample
2) Isotope labeling (Expensive and not practical)
3) Record spectrum at higher field (Practical Limitation B_0)
4) Record spectrum at lower temperature (not significant effect)

Play with spin dynamics and design new NMR experiments

Let us consider the situation I want to enhance the sensitivity of the signal; as you know NMR is basically an insensitive technique, compared to other molecule spectroscopic techniques. How to get the signal? because it takes enormous time for you to get the signal, especially for example, nuclear like carbon 13, nitrogen 15. Nitrogen 15 is the most important nuclear spin; all biology people want to detect this signal, but it is very weak and abundance is 0.37%.

Unless you label, it is very difficult to get the signal. And we have to acquire signal for a long duration. It is time consuming. So, somehow we have to enhance the signal intensity, how do you address the sensitivity challenges in NMR? First thing is you get more sample, detect, get more and more sample get higher signal. You do isotopic labelling, instead of nitrogen 15 observing at the natural abundance; enhance by labelling. But it is not practically relevant, because of course you can do but it is expensive and time consuming.

Our record spectrum of higher magnetic field. Higher and higher magnetic field enhances the signal, we saw in the very first class; what happens when you change the magnetic field. For that also practically there is a limitation for the magnetic field; you cannot take the magnetic field to infinite strength, there is a limitation for that. Another thing is record the spectrum at low temperature this also does not have significant effect, but also not feasible for all the samples. It is not possible to record the spectrum at low temperature for all the samples.

So, there are certain methods to do this, these are some common techniques people adapt depending upon their interest. Another thing what NMR spectroscopist do is to play with the spin dynamics and design new NMR experiments. When you do the design the new NMR experiment, we can design in such a way we can ensure that there is a signal enhancement; that is very interesting, let us understand how we can do that today.

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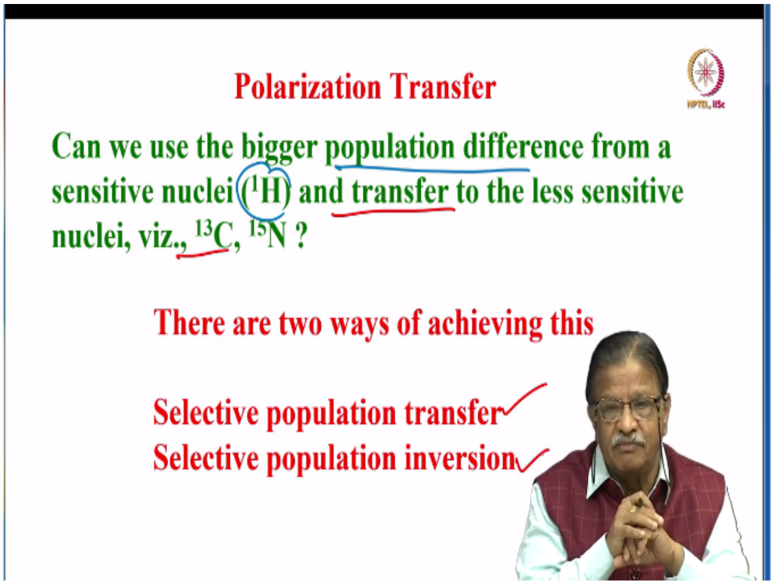

Polarization Transfer

Can we use the bigger population difference from a sensitive nuclei (^{1}H) and transfer to the less sensitive nuclei, viz., ^{13}C, ^{15}N ?

There are two ways of achieving this

Selective population transfer

Selective population inversion

This is called polarization transfer experiment, I can transfer the polarization of one spin to another spin; that is possible in NMR. So, how do we do that? We have to transfer polarization from one spin to another spin; for that you have to consider the nucleus which has a bigger population difference like proton. It is highly abundant spin and then use that and then transfer the population to less abundant spin like carbon 13 and nitrogen-15.

And also the gamma is very small here, 4 times less for 13C, for nitrogen 15 it is 10 times less, so energy separation is much smaller here; 10 times smaller, proton has the largest separation of energy levels. As a consequence, for the largest separation energy levels you are going to get bigger population difference. So, we can utilize that population difference of proton, which is larger and transfer to carbon or nitrogen. How do we achieve this? There are two ways of achieving; one is called selective population transfer SPT, other is called SPI selective population inversion; something very interesting; let us understand what it is.

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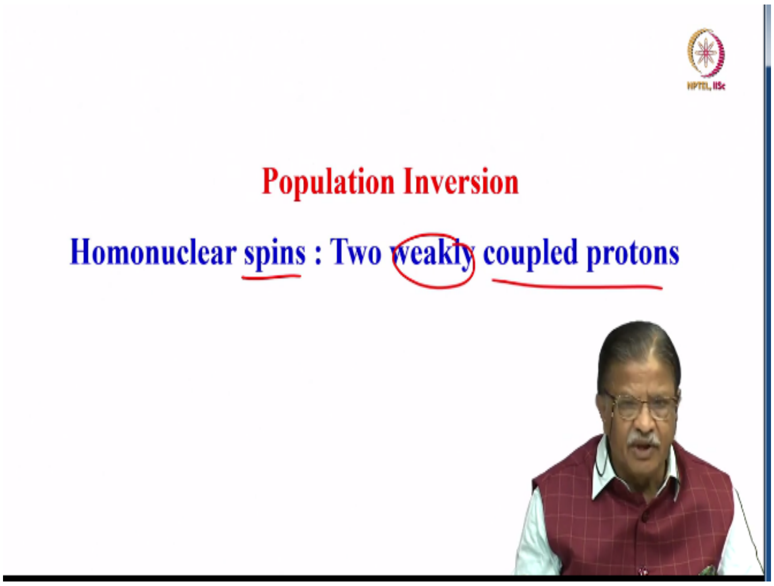

Population Inversion

Homonuclear spins : Two weakly coupled protons

Population inversion, of course you can do this for homonuclear case and heteronuclear case both. Now I consider homonuclear case of 2 spins, which are weakly coupled,\; weakly coupled already I discussed we do not have to go in detail. The 2 chemical shifts are separated far away, and then coupling constant is much more small compared to that.

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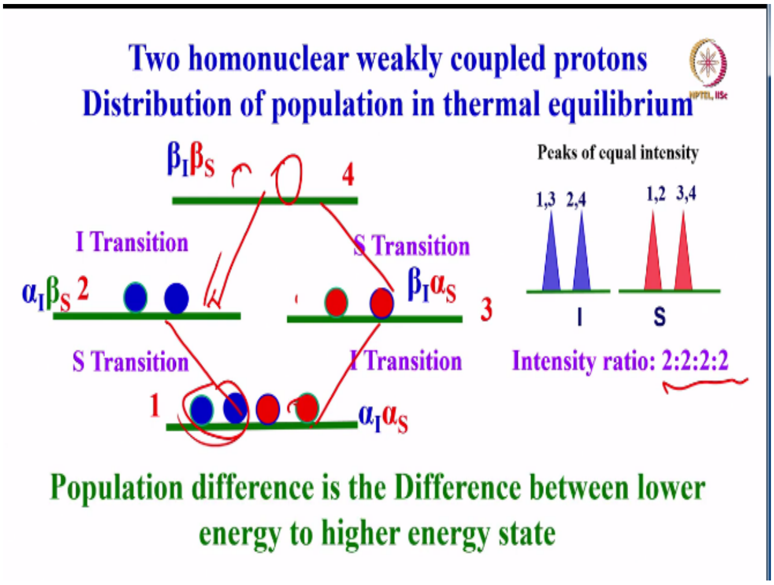

Two homonuclear weakly coupled protons

Distribution of population in thermal equilibrium

$\beta_I\beta_S$ 4

I Transition

S Transition

$\alpha_I\beta_S$ 2

$\beta_I\alpha_S$ 3

S Transition

I Transition

1 $\alpha_I\alpha_S$

Peaks of equal intensity

1,3 2,4 1,2 3,4

I S

Intensity ratio: 2:2:2:2

Population difference is the Difference between lower energy to higher energy state

Now for 2 homonuclear weakly coupled protons, the distribution of population thermal at equilibrium we understand. Of course, 2 weakly, coupled at thermal equilibrium, all the 4 lines should be of equal intensity; that is what we know. We also quantum mechanically calculated the frequency and intensity of transitions for AX coupled spin. Now I am trying to show like this, I have 4 energy states, I put 4 spins here;, 2 for I spin and 2 for S spin.

And for alpha beta and beta alpha states, I have put 2, 2 spins. 2 spins for S here, and no I spin and here 0 spin. Do not be under the impression that the beta beta state, there is no spin at all. There is enormous amount of spins distributed among all the 4 energy states. But for my calculation purpose.

I have put like this, now because I take the difference between these I transitions, I am going to get 2, for this S transition I get 2, I transition here if I take the difference I will get 2, here I get 2. The advantage is if I take the 1 3 transition, I get 2 spins. And similarly, 2 4 I am going to get 2 and for 1 2 and 3 4 transitions I get 2, 2 difference. We have intensity exactly 2 is to 2 is to 2 is to 2. This is what I wanted to show; that is why we took the populations in this range. That does not mean there is no population here.

So, this is, this population difference between the low energy state to higher energy state. Always we are going to take the difference in the population, remember, the difference between the lower to higher energy state is what is considered; not from higher to lower. This convention, the population difference between 2 states means this to this, for example, this to this population difference is 4 - 2, if I take from this to this is -2. That is what the concept. Always the population difference is from the lower energy state to higher energy state, you consider that. That is what I said, this population numbers have been chosen to make my calculation easier, do not be under the impression that there are or no spins in the beta beta state.

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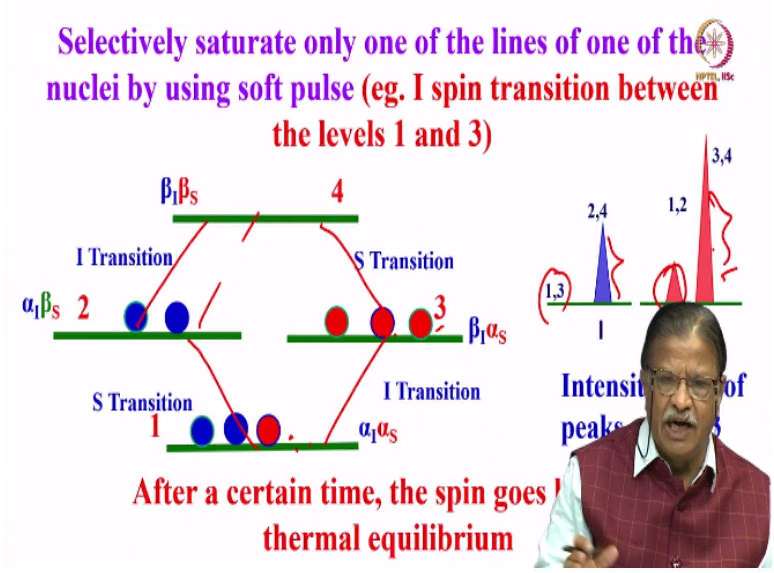

Selectively saturate only one of the lines of one of the nuclei by using soft pulse (eg. I spin transition between the levels 1 and 3)

After a certain time, the spin goes
thermal equilibrium

Now, I selectively saturate one of the lines of one of the nuclei by using the soft pulse. What do you mean by soft pulse and hard pulse? we discussed in the first course itself? Soft pulse is a pulse which can selectively excite or saturate one of the peaks among the several peaks available in the spectrum. Only one spin can be saturated. For example, what do you mean by saturation? Make the spin population between these 2 states equal; remember, we discussed this saturation at stretch, in the previous course.

So, I made this is saturate; let us say one of the states; that is the transition between 1 and 3. I saturate this, that means, this was 4 and this was 2; I made it 3 and 3. Now, when the population between these 2 is equal ;let us calculate now, what is the population difference. Now population difference between 1 and 2, one of them you consider, population between 1 and 3, is 0. There is no population difference, both are equal, saturated; the population between 2 and 4 is 2, population difference between 1 and 2, if you consider it is 1. Whereas, other one if you consider 3 and 4 the population difference is 3. So now the population difference, if you calculate it is 0, 2, 1 and 3. So, in this case population these two intensities remained same; this reduced to half, whereas this gets doubled, not double just went up by 50%. So, the population ratio of the peaks is 0 is to 2 is to 1 is to 3. What we did? We did nothing, we saturated only one of the peaks, and we measure the population difference and we found out that they change the intensity the peaks. The saturated peak 0 intensity; for other peaks one remain same, other one became reduced to half by 50%; other went up by 50%. Now, keep quiet, do not do anything. After certain time the spins go back to thermal equilibrium; they attain the same population 4, 2, 2 and then 0, it will become. So, that is after some time; they come back to thermal equilibrium.

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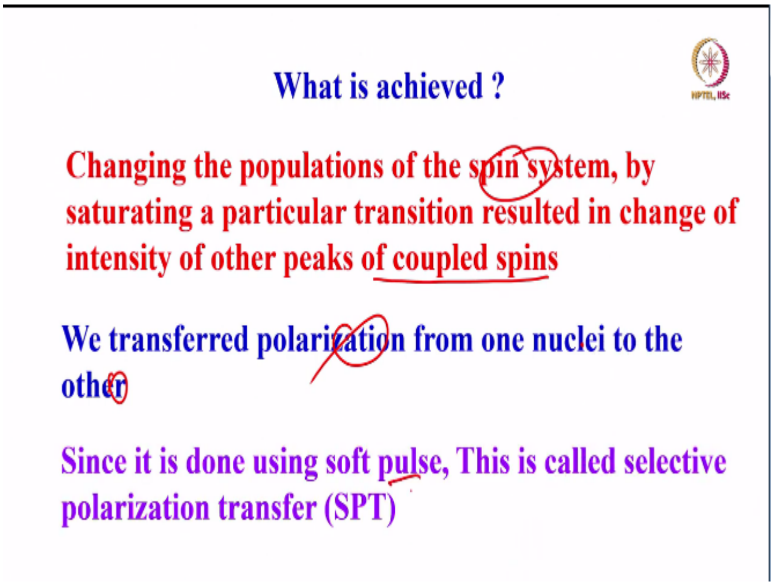

What is achieved ?

Changing the populations of the spin system, by saturating a particular transition resulted in change of intensity of other peaks of coupled spins

We transferred polarization from one nuclei to the other

Since it is done using soft pulse, This is called selective polarization transfer (SPT)

Now, what did you achieve by this? Change in the population of one of the spins of the coupled spin system, by saturating a particle transition, you have the change in the intensity of peaks of other coupled spins; very interest thing. Now we transfer the population from one nucleus to other nucleus; that is what we did. By saturating one of the peaks, we transferred the population to other coupled spin; that is thing.

So, since it is done using a soft pulse by selective population transfer to one of them it is called selective population transfer. So, this is possible, what we did by saturating one of the transition phase by a soft pulse.

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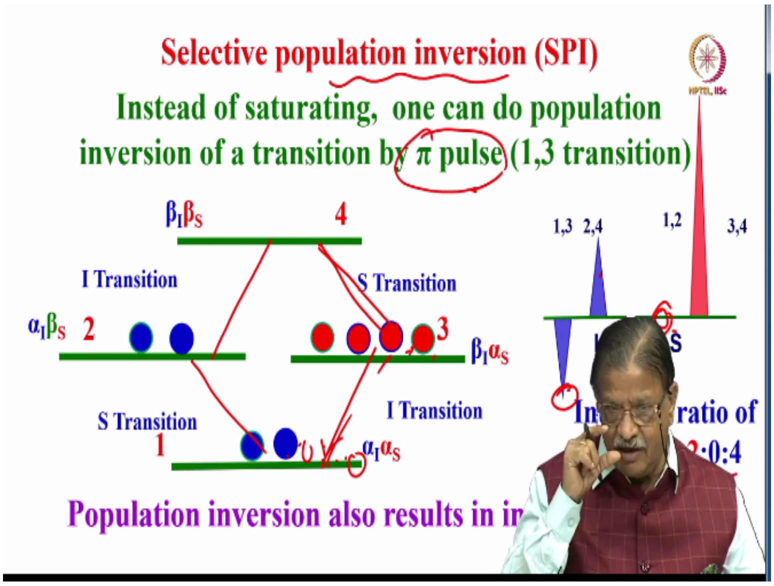

Selective population inversion (SPI)

Instead of saturating, one can do population inversion of a transition by π pulse (1,3 transition)

Population inversion also results in in

We can also do other way, can I do select the population inversion? instead of making both of them equal, you reverse the population of 2 energy states. I will take the population of this one I bring here, population this state I will take it up, I will interchange, I will completely reverse the population, is it possible to do it selectively again? We can do that; this is called selective population inversion.

Now the same thing we will do. We had 4 2 2 0; this is thermal equipment population with we took for calculation. Now, the same transition 1 and 3 I invert, this was 4 here, I took it up here, this was 2, I have bought here, that is all. This is called selective population inversion. How do you do? It is by applying pi pulse for 1 3 transition. Pi pulse inverts the magnetization; from z axis it is going to -z; that is what pi pulse does. So, we have inverted the population from this state to this state.

Now do the calculation of the population difference for all the peaks. Very interestingly now, if we calculate the population between 1 and 3, it has become negative, because always population difference is from lower energy state to higher energy state; calculate from low energy state to high energy state, now, it becomes -2; whereas, 2 and 4 if you consider we are not touching that, remains same. Whereas in this case, 1 2 if you consider 1 2 becomes 0, because 2 2.

Whereas the population difference, if you take 3 and 4, now this has become 4; it is doubled, You see, we saturated this transition, but this one has enhanced intensity and this one beccame 0; and one we can negative the other we can positive. All we did is selective population inversion. Now, the population ratios become -2: 2 :0 and 4. The population inversion also results in change in intensity, not only selective population saturation, population inversion also gives.

You can saturate the transition between 2 energy states, you can saturate them and then also it results in change in intensity, you do selective inversion then also you see change in intensity.

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Selective Polarization Transfer (SPT) on a heteronuclear system

So, this is called selective population transfer. You can do even in any heteronuclear system. So, far we took the example homonuclear case, both gammas are same, it could be protons or anything and in the coupled spin system, we saw the change in intensity. Now, that is not our interest, our interest is heteronuclear, because you have to transfer the population from abundant spin to rare spin or dilute spin. Then our intensity of the carbon 13 or nitrogen 15 will get enhanced; that is our aim.

So, we have seen the selective population transfer and selective population inversion work on the heteronuclear case, how much enhancement we are going to get we will discuss that later in the next class. So, right now, in this class we discussed quite a bit, we discussed about the evolution of the magnetization and we understood how the J coupling evolves when it is off resonance, especially if I took the example of the doublet component, how one component of the doublet becomes faster moving, evolves faster compared to the other one, which is slow moving, or with respect to the centre, the carrier offset one which is far away other is less frequency separated from the carrier. These 2 are different with respect to carrier offset, one which is far away most faster, other which is nearby moves slower. this is what we observed and we took the example and see how the phase will change.

It will become positive absorptive both and the doublets will be inphase and then it will become antiphase doublet, and also it will become completely in phase negative signal. So, these are the things we discussed. We observed the evolution of the J couplings. Of course we saw chemical shift also evolve which is the centre of the doublet. There is no peak hypothetically we can calculate what is the centre of the doublet.

We saw in one example when a J spilt doublet 150 hertz we took. The one of them was at 300 hertz other was at 150 hertz. One component of the doublet moved by 90 degree, other moved by 45 degree, but at the chemical shift at the centre, moved by 67.5 degree, this one. So, that is another thing. In the next topic we discussed about the polarization transfer, I wanted to tell you how we can enhance the signal intensity, especially when we want to transfer the magnetization from abundant spin to rare spin.

For that we took the example of a 2 coupled spin system and in the thermal equilibrium population, we understood what happens if I saturate one of the transitions. Saturation means I make the population between 2 states equal, then we recalculated the population, we found that the change in the intensity of other coupled partner. Same thing we can do with population inversion, instead of saturating, we can invert the populations between one of the transitions, then also we saw a change in intensity. We discussed with an example.

This can be done by soft pulse. Now, this is for the homonuclear case. The more interesting case for us is heteronuclear, where you can enhance the signal of the dilute spin like carbon 13 or nitrogen 15. How does it work? We will discuss this in the next class. So, I will stop here. Thank you very much. We will discuss selective polarization transfer and other things in the subsequence class. Thank you.