Advanced NMR Techniques in Solution and Solid – State

Prof. N. Suryaprakash
Professor and Chairman (Retd)
NMR Research Centre
Indian Institute of Science – Bengaluru

Module-21
Evolution of Chemical Shift
Lecture - 21

Welcome back all of you, in the last class, last 2 classes rather, we discussed more about pulse phase and the receiver phase; and we understood what happens if we apply the pulse along x axis, -x axis; and +y axis, -y axis, how the magnetization can be made to rotate in different directions whether clockwise or anti clockwise. And also we understood what happens when I tilt the magnetization from thermal equilibrium to x axis or y axis, depending upon where I keep the receiver whether I keep the receiver along plus axis. The magnetization if along x axis only then we get absorption mode signal and the imaginary part will be dispersive. So, what happens when the receiver position is changed in different axes? What type of signal we are going to get? whether we get absorptive or dispersive, is what we understood. And at the same time, what happens if there are 2 receiver channels to detect the signal, if there is an imbalance between these 2, then there is a phase error; for that I showed you, we can do different type of experiments, 4 experiments.

Each time the pulse phase and receiver phase we have to adjust in such a way, when we collect the signal, the real and imaginary parts are changed accordingly every time we change the receiver and change the pulse phase and co-add the signal; and you will see that there is a perfect balance between these real FID and imaginary FID. Then the phase error will not come into the picture, this is what we understood also. So, with that, now, what we are going to do today, we will discuss about the evolution of the magnetization.

So far we have been applying pulses and everything. How the magnetization evolves, this is very important to understand the product operators, it is very important to design your sequences. Let us see how the magnetization evolves in different pulse sequences. Now, motion of the magnetization vector in a rotating frame is called an evolution. Rotating frame we discussed long back, in the previous course, what is your rotating frame everything was discussed, we will not go to discuss in detail, but please remember one thing the evolution in the rotation of the magnetization, that is what the thing we must understand.

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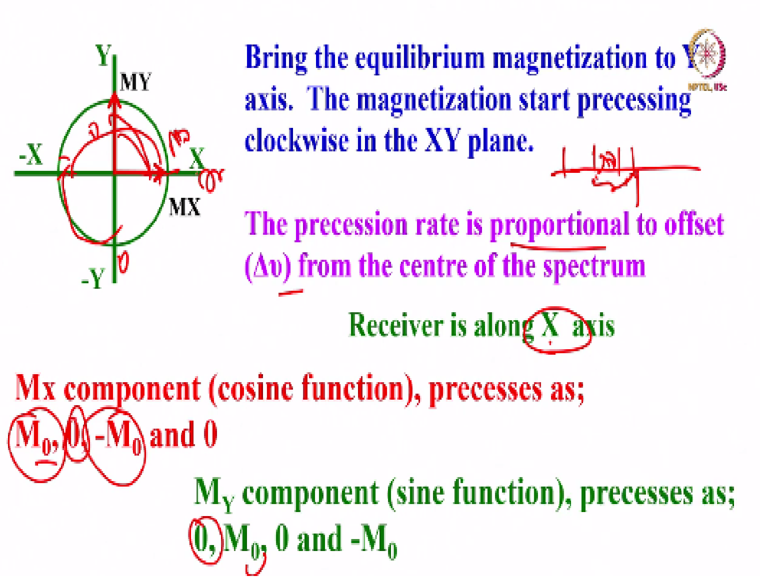

Bring the equilibrium magnetization to Y axis. The magnetization start precessing clockwise in the XY plane.

The precession rate is proportional to offset $(\Delta \upsilon)$ from the centre of the spectrum

Receiver is along X axis

Mx component (cosine function), precesses as;
M_0, 0, $-M_0$ and 0

M_Y component (sine function), precesses as;
0, M_0, 0 and $-M_0$

Now, consider the situation we have magnetization, bring the equilibrium magnetization to Y axis; what will happen to the magnetization? it starts processing in the clockwise direction in the XY plane. The precision rate is proportional to the offset from the centre of the spectrum. This is very important. In the rotating frame, let us I have a spectrum here, this is my centre, this is my offset; and if the signal is exactly here that is a different question. If the signal is somewhere here, this is what is called offset. We call it as delta nu or delta omega; this is the offset, and from the centre of the spectrum; and how far it is this will define the rate of precision. How fast the magnetization is precessing, if it is here, it is one speed of rotation; if it is here the rotation speed is different. So, the speed of magnetization rotation is understood by how far it is from the centre of the spectrum. Now we will do one thing; this is what is the important point.

Now we have brought the magnetization to Y axis and receiver is along the X axis; that is the important point. Now, what is going to happen? The MX component, first part, now I am allowing it to rotate in the XY plane. So, far we were only collecting the signal and we did not discuss about the rotation; you simply understand what happened to the signal at different phases. Now we will see how the magnetization rotates in the XY plane. The receiver is along the X axis, the MX component will precess like this;, as soon as the signal comes here MX component, it will be maximum signal. Maximum is a thermal equal magnetization M0.

Then it will go to other axis depending upon the direction of precession, it goes to Y axis you have 0 signal then it goes further, rotate like this. It comes to -X you will have -M0; the magnetization will be negative because your receiver is here. And then goes further, it will become 0. Very interesting, you see what is going to happen? Magnetization, M0 maximum 0, – M0 and it will become 0. It goes through one full rotation in the XY plane, this is what happened to the cosine part.

What happened to the sine part? it is very easily you can extrapolate this thing, sine part and cosine part are differing by 90 degrees. So, it starts with 0 then; sine part starts with 0 goes to M0 start here, when you have the receiver here the sine part is 0; then goes to M0, 0 and – M0. So, cosine starts rotating like this, sine also starts rotating like that, but there is a phase difference of 90 degrees between these 2, both the magnetization components are rotating.

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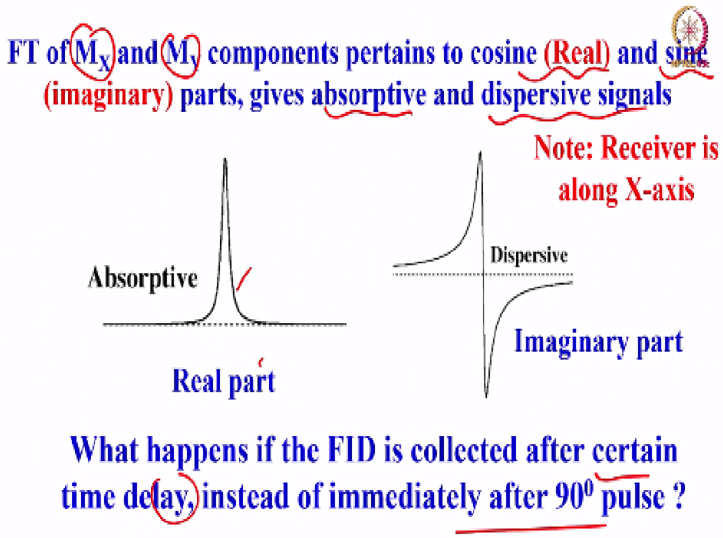

FT of M_x and M_y components pertains to cosine (Real) and sine (imaginary) parts, gives absorptive and dispersive signals

Note: Receiver is along X-axis

What happens if the FID is collected after certain time delay, instead of immediately after 90^0 pulse ?

Now, Fourier transformation of the MX and MY components we can do. What will happen if I do the Fourier transformation of MX and MY components? You will get the cosine part and the sine part; both will get. That means you will get absorptive signal and dispersive signal, I told you already we discussed in the previous class; absorptive and dispersive signal both we get.

Now, remember receiver is along the X axis. What we do? When we keep the receiver along the X axis we get absorptive signal, that is what we said.

MX is along the X axis. Immediately as soon as you apply 90 degree pulse you received it along the X axis. So, real part of the signal is absorptive and imaginary part is dispersive; that is perfect. Now what happens if the FID is collected after a certain time delay. Now I am allowing it to rotate in the XY plane; the magnetization components start moving, MX and MY. How it goes we already understood M0, 0, - M0 and 0 for a cosine, sine is 90 degree out of phase like that. So, immediately after the 90 degree pulse, instead of collecting the signal here where you get absorptive part, now I am allowing it to rotate the magnetization; starts precessing we call.

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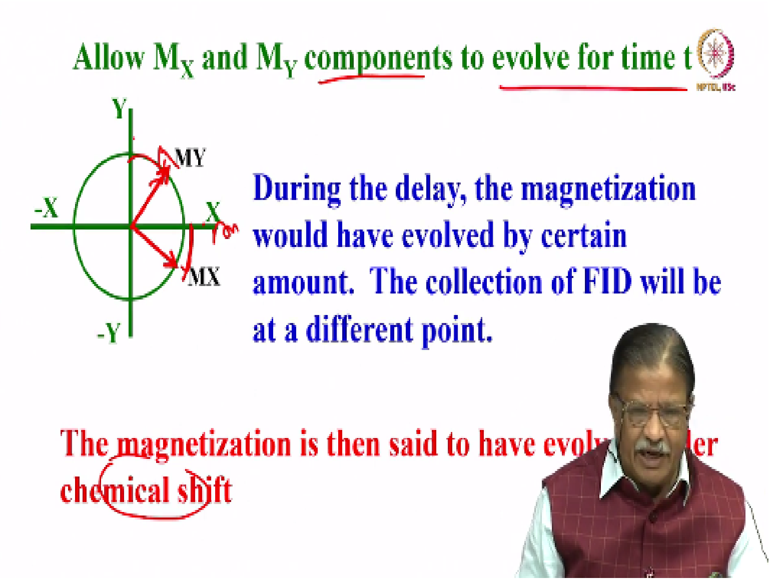

Allow M_X and M_Y components to evolve for time t

During the delay, the magnetization would have evolved by certain amount. The collection of FID will be at a different point.

The magnetization is then said to have evol ler chemical shift

Let us see what will happens if it starts precessing. And now allow the magnetization to evolve MY component for a time t; and now let us say a component MX has moved here MY has moved here. They are moved by some distance; it is not exactly a 90 degree, this has moved from here to here, this has moved from here to here. Between them they may be out of 90 degree but the receiver is here; as far as the receiver is concerned, they have moved by some distance.

So, during the delay magnetization has evolved by a certain amount; this is what is called evolution, magnetization during this delay has evolved. So, a collection of FID will be at a different point. The free induction decay is not collected the right point; it is collected at a different point. Now what do you say? the magnetization is evolved under chemical shift, because this is what is going to happen. Apply pulse bring the magnetization leave it like that; magnetization is now evolving; and this evolution is called chemical shift evolution. It evolves under the chemical shift. I am not talking about chemical shift. We are bringing coupling later.

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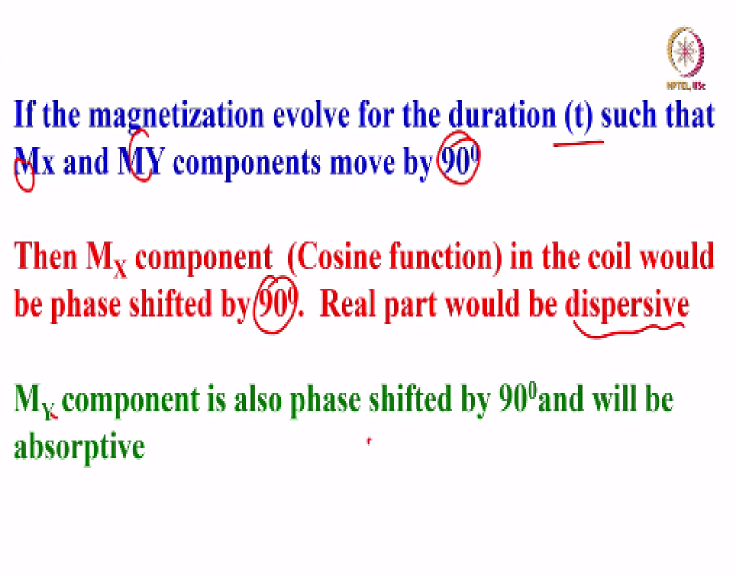

If the magnetization evolve for the duration (t) such that Mx and MY components move by 90^0

Then M_X component (Cosine function) in the coil would be phase shifted by 90^0. Real part would be dispersive

M_Y component is also phase shifted by 90^0 and will be absorptive

The magnetization evolved for the duration t such the MX and MY components move exactly by 90 degree; understand the point there are moved exactly by 90 degree. So, what will happen? MX component in the coil would be shifted by 90 degree. The real part will appear like dispersive and MY component is also phase shifted by 90 degree and will be absorptive. Now, both the components of magnetization have moved by itself. So, chemical shift evolution has taken place, this called chemical shift evolution, they are moved by 90 degrees.

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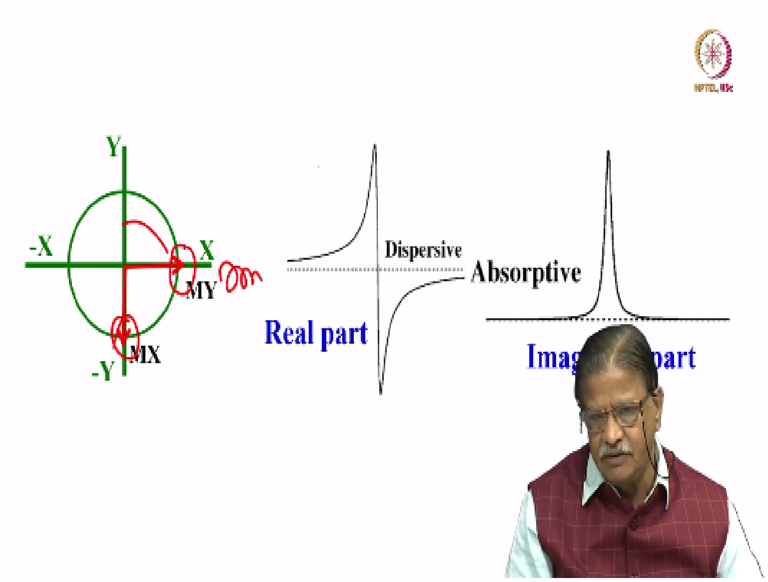

Now, MX is here MX has already moved here, MY has moved here and receiver was here. So, what is going to happen? The real part will be dispersive and imaginary part will be absorptive, this is an important point.

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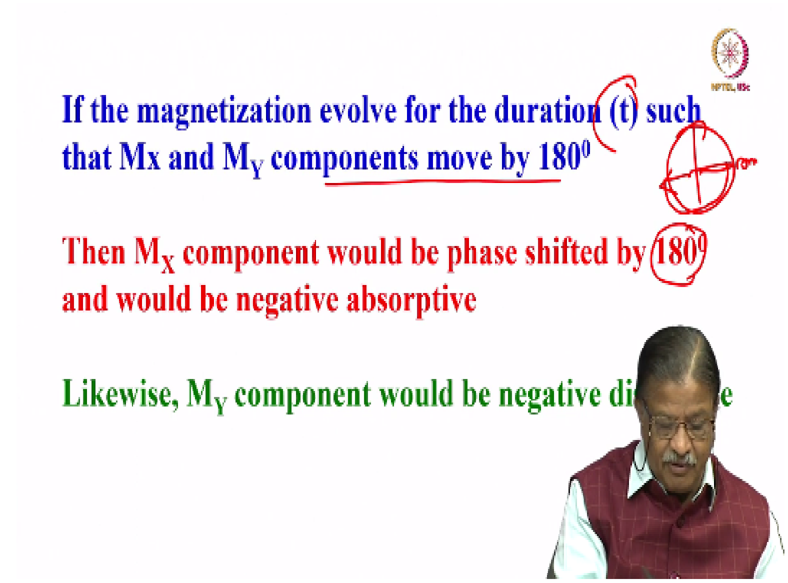

If the magnetization evolve for the duration (t) such that Mx and M_Y components move by 180^0

Then M_X component would be phase shifted by 180^0 and would be negative absorptive

Likewise, M_Y component would be negative di e

Now, the magnetization evolved for the duration t such that MX and MY components moved by 180 degree; then what will happen? MX component will be phase shifted by 180 degree, and that will become negative absorption, because from here it started moving like this. It has come to this axis, receiver is here. So, instead of +X, you are going to have the signal in the -X axis.

So, it means there is a phase shift by 180 degree, phase shift of 180 degree what will happen? The absorptive component, the positive absorptive to become negative absorptive. So that is what is going to happen. Similarly, real component becomes negative dispersive signal and the MY become negative dispersive.

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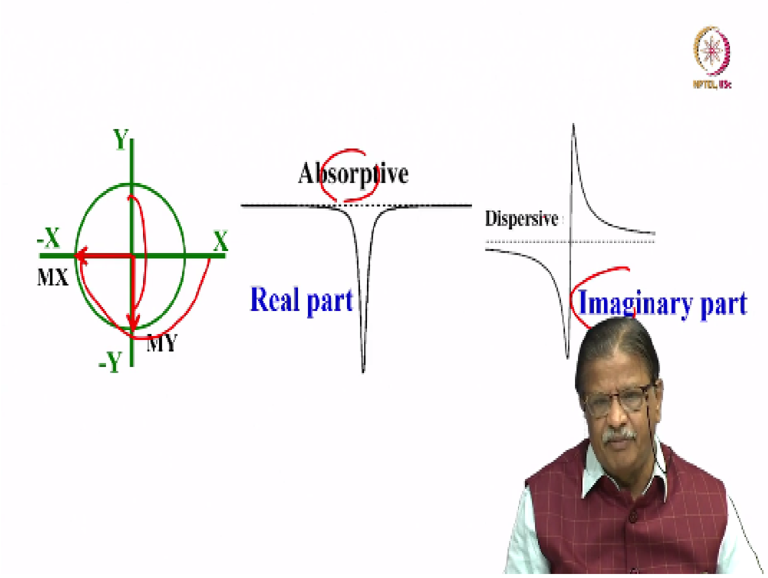

And this is what happens when moving the magnetization; MX from here it has moved to here. MY from here to has move here. So, the positive part, real part is negative absorption and imaginary part is negative dispersive. Now I am allowing to the magnetization to move, that is the component the magnetization to move in the XY plane

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Allow the magnetization to evolve for the duration such that Mx and MY components move by 270^0

Then MX component would be phase shifted by 270^0 and would be negative dispersive

M_Y component would be negative absorptive

Now I allow the magnetization to evolve for 270 degree; then what is going to happen? MX, MY will be shifted by 270, then what is going to happen? And one will have a negative dispersion other will be, you can understand what is going to happen; MX component will be negative dispersive and MY component will be negative absorptive. This is what is going to happen.

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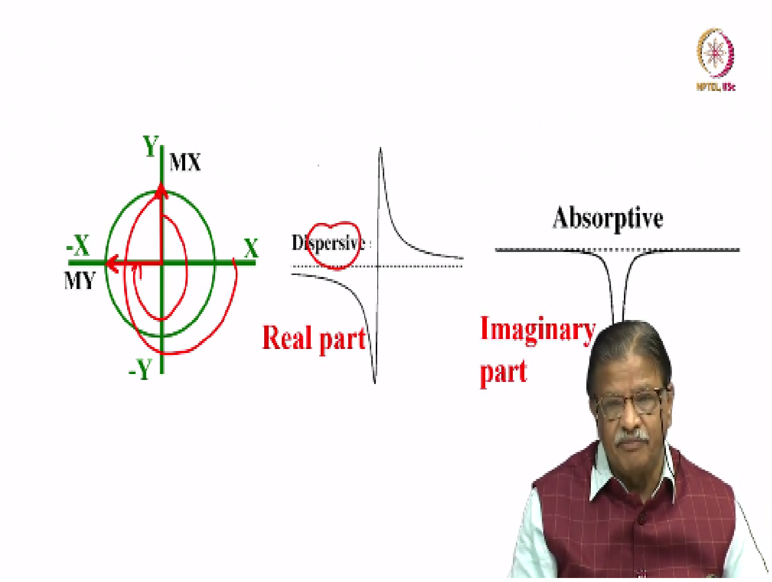

And this what it is, when you move by 270 degree MX component started here and went here and moved here. MY component is here, started here, came here. It moved like this, the real part is dispersive. And imaginary part is negative absorptive, this is what happens. And these points are very important for us to understand.

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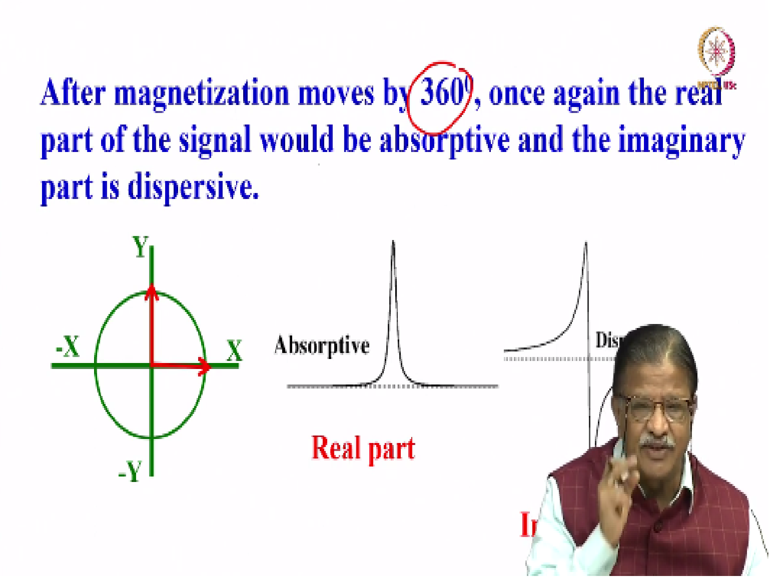

After magnetization moves by 360^0, once again the real part of the signal would be absorptive and the imaginary part is dispersive.

After 360 degrees what will happen? Both the components will undergo on full rotation. And again, it will come back and then we will have the real part as positive absorptive and imaginary part as dispersive, because one rotation has completely gone through, like this now. This is after 360 degree pulse. This is what is important. Now I just applied only one RF pulse, I am collecting the signal as a function of time; where allowing the magnetization to move with time to different axes.

It moved to different axes, when I collect the signal, you will get the signal with different phases positive absorptive, negative absorptive, dispersive, negative dispersive all you can come across.

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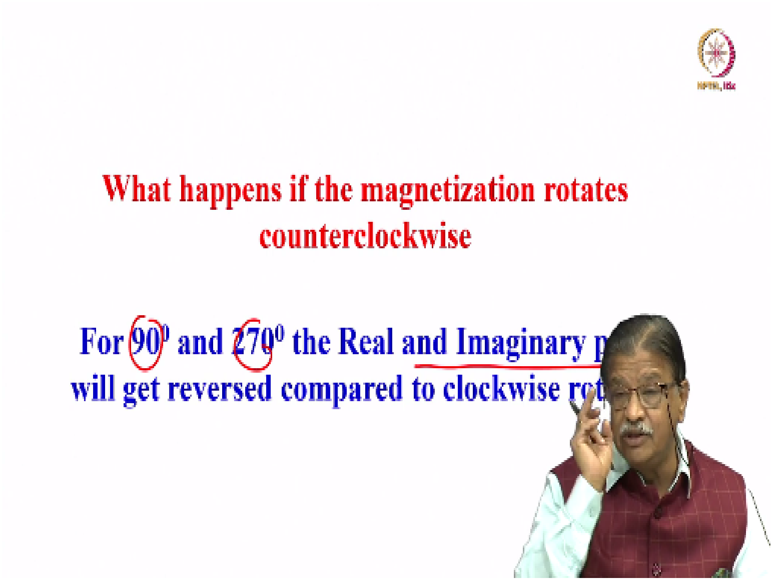

What happens if the magnetization rotates counterclockwise

For 90^0 and 270^0 the Real and Imaginary p

will get reversed compared to clockwise rot

The same thing, what happens is the negative of the magnetization is made to rotate counter clockwise. In this case, magnetization is made to move clockwise. If it is allowed to move anti clockwise what will happen, then 90 degree and 270 degree the real imaginary part will get reversed that is all. Whereas for 0 degree and 360 degree remains same; that would not affect. Whereas for 270 and 90 degrees, the real and imaginary gets interchanged, that is all. If you make it to rotate in the opposite direction, otherwise, there is no effect at all. This is what it is. So, 0 and 360 will have no effect, for 90 and 270 degrees, the real and imaginary get interchanged, if you allow the magnetization rotate in a counterclockwise direction, clear?

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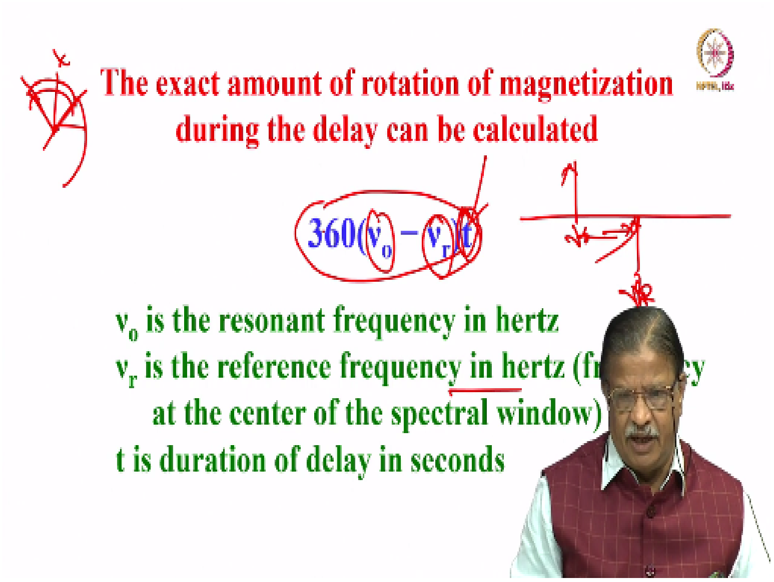

The exact amount of rotation of magnetization during the delay can be calculated

$360(\nu_0 - \nu_r)t$

ν_0 is the resonant frequency in hertz

ν_r is the reference frequency in hertz (fr cy

at the center of the spectral window)

t is duration of delay in seconds

Now, you can even calculate how much of the magnetization has been rotated during the delay that we have given. For example, I applied a 90 degree pulse, bring the magnetization components here, MX is here and then after some time MY is here; start rotating. MX and MY like this; let us say after a time t, the magnetization is moved like this; how much it has moved if I give a time t? what is the amount of magnetization that has moved? what is the degree by which has moved? We can calculate; it is not difficult at all , one can do the calculation. This is given by a simple formula called 360 into nu naught - nu r into t, nu naught is the frequency of the centre the spectrum; and nu r is the reference frequency; sorry nu naught is the resonant frequency of the signal, nu r is the reference frequency and t is the duration. This is what you have to understand. For example, this is my nu r, it is the reference frequency which is at the centre and this is the resonating frequency nu naught, then you have to calculate what is the frequency separation here.

This is nu naught - nu r and then put this into this equation 360 nu naught into nu naught - nu r into t, you will find out, if you know t how much it has moved or if you know 90 degree you can find out how much time it requires to move by 90 degree, how much delay you have to give, how much time you have to wait for the magnetization component to move by 90 degrees; or 180 degrees or 270 degree we can find out.

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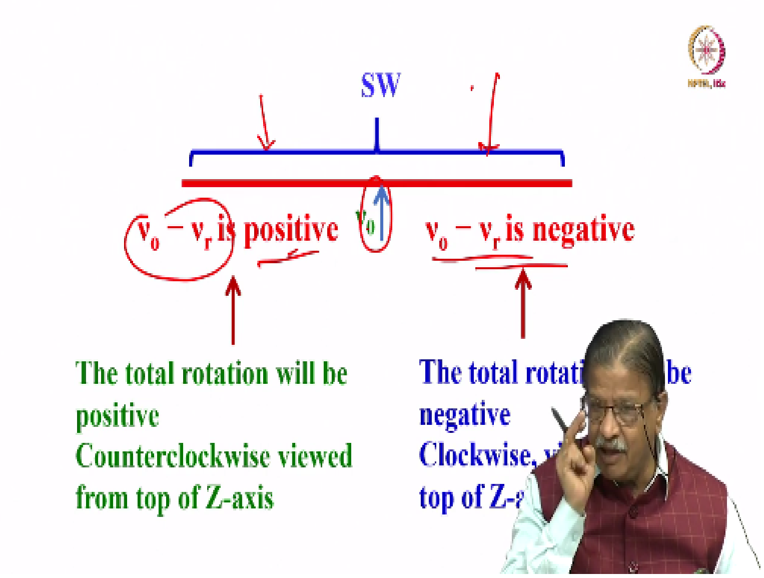

SW

$\nu_0 - \nu_r$ is positive

ν_0

$\nu_0 - \nu_r$ is negative

The total rotation will be positive
Counterclockwise viewed from top of Z-axis

The total rotati be negative
Clockwise,
top of Z-

So, let us take the example like this; this is what it is? This is the centre of the spectrum, reference nu 0. And then if I have a peak here, and I have a peak to the right side of this reference or to the left side of the reference, here nu naught – nu r is what? nu naught - nu r is positive. Here nu naught - nu r is negative. That is the convention. Remember, here when you come this side, this is going to be positive; this is going to be negative; that means the total rotation will be positive.

Counter clockwise viewed from the top. I view from the top of the Z axis, it goes in the counter clockwise; this is positive; the magnetization starts rotating counter clockwise. Whereas if there is a peak here, these negative nu naught – nu r, when you view from the top it rotates clockwise; from the top of the Z axis. This is Z axis viewed from the top, starts moving like this. If I have a peak here, it moves like that. If I have peak here, it moves like this. This is a convention; you must understand, how much it rotates for different degrees, how much for a different duration time can be calculated now. Now the direction of rotation of the magnetization will try to calculate from this.

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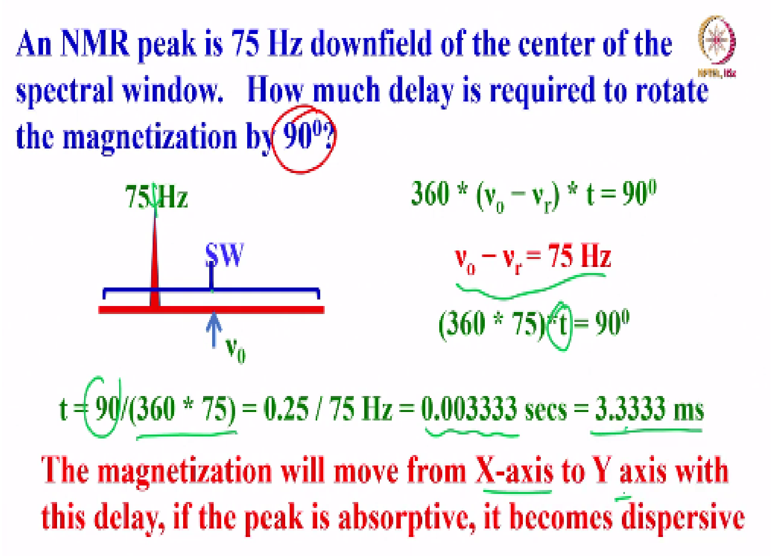

An NMR peak is 75 Hz downfield of the center of the spectral window. How much delay is required to rotate the magnetization by 90^0?

$$360 * (v_0 - v_r) * t = 90^0$$

$$v_0 - v_r = 75 \text{ Hz}$$

$$(360 * 75) * t = 90^0$$

$$t = 90/(360 * 75) = 0.25 / 75 \text{ Hz} = 0.003333 \text{ secs} = 3.3333 \text{ ms}$$

The magnetization will move from X-axis to Y axis with this delay, if the peak is absorptive, it becomes dispersive

Let us I have a peak at 75 hertz downfield of the centre of the spectral window. Understand this thing very clearly; I have a peak at 75 hertz downfield of the centre of the NMR spectral window. How much delay is required to rotate the magnetization by 90 degree? This is my question. Now, I know what is the 75 hertz from this thing, this is nu naught; and this is the nu r, called reference. This is a nu naught, this is exactly 75 hertz from the reference centre.

Now, this is what the spectrum is. My job is to find out how much is the signal has moved. You can understand by this equation. All you have to do is to plug in the values for this equation nu naught when nu r is 75, it is towards this side. Now, put it here 360 into 75 into t is 90 degree, because I have to find out how much time delay; how much t is required to see that magnetization is move from Z axis to X or Y, by 90 degrees.

So, for signal to move by 90 degree, now what I do is I calculate this by plugging into this equation all the values. It is 90 divided by this value, I would calculate this one, when the expressed in this units, it is 0.0033 seconds or 3.33 milliseconds. If I apply radiofrequency pulse, if I have a signal at 75 hertz with respect to the centre, and I wait for 3.333 millisecond, the signal exactly moves by 90 degree, with respect to the reference signal, if I take it as nu naught.

The magnetization will move from X axis to Y axis with this delay because it moved by 90 degree, the peak which is absorptive will become dispersive; fantastic! Right! I can make the magnetization to become absorptive or dispersive, just by allowing it to rotate for a period t after bringing it to the X axis or Y axis. How much time I had to wait to see that the signal moves by 90 degrees or 180 degree I can calculate by this equation.

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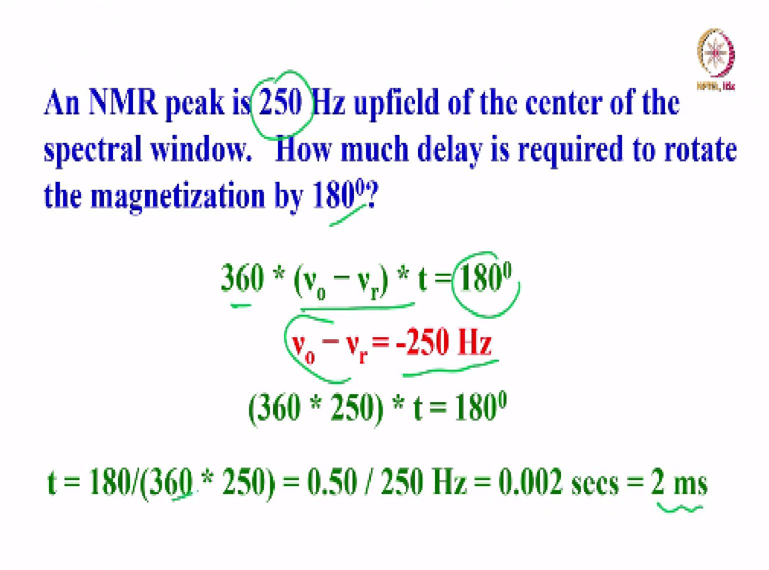

An NMR peak is 250 Hz upfield of the center of the spectral window. How much delay is required to rotate the magnetization by 180^0?

$$360 * (\nu_0 - \nu_r) * t = 180^0$$

$$\nu_0 - \nu_r = -250 \text{ Hz}$$

$$(360 * 250) * t = 180^0$$

$$t = 180/(360 * 250) = 0.50 / 250 \text{ Hz} = 0.002 \text{ secs} = 2 \text{ ms}$$

Let us consider another simple example. I have zan NMR peak is 250 hertz up field of the centre of the spectral window; up field of the spectral window. How much delay is required to rotate the magnetization but 180 degree. Now upfield means, I have to now take the difference nu naught – nu r as negative 250 hertz, now multiply with 360 into nu naught - nu r into t, now this has to be 180 degrees, this is my condition. If I want to see that magnetizations rotates by 180 degree, plug it in this equation nu r - nu is 250, that I know; it is given. And calculate t, t turns out to be 2 milliseconds, simple equation. These are the numbers I plugged in I get 2 millisecond. That means if I apply radiofrequency pulse, bring the magnetization to some axis, if I have a peak at 250 Hertz from the centre of the spectral window, wait for some time, how much time? 2 millisecond then this magnetization will move by 180 degrees. That means signal which is positive absorptive will become negative absorptive. That is what happened; you can move this signal; it has moved by itself without doing anything.

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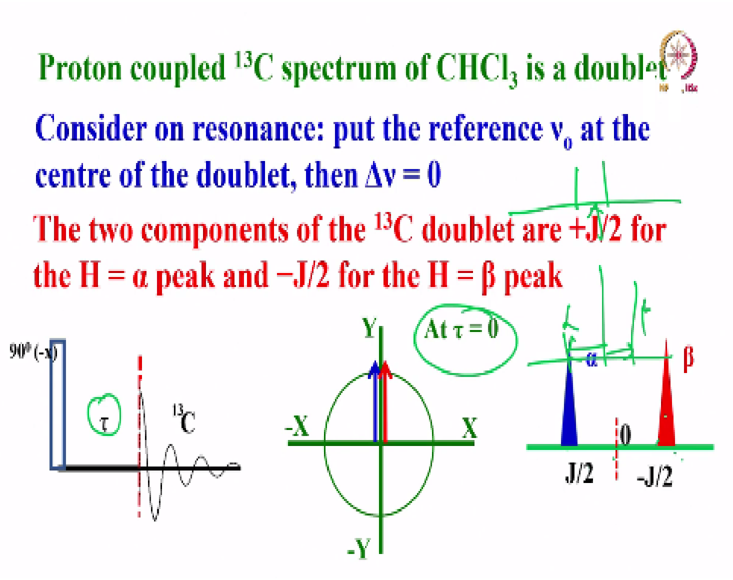

Proton coupled ^{13}C spectrum of $CHCl_3$ is a doublet

Consider on resonance: put the reference ν_0 at the centre of the doublet, then $\Delta\nu = 0$

The two components of the ^{13}C doublet are +J/2 for the H = α peak and −J/2 for the H = β peak

So, these are the things which you should understand with this idea now we will understand the evolution of magnetization under scalar coupling. This is the evolution of chemical shift because we are not doing anything we keep moving it because of the offset with nu naught - nu r; offset is also called chemical shifts. It is moving under the influence of chemical shift. Now the evolution of magnetization under scalar couplings.

I will take the example of a proton coupled CHCl3. What is the proton coupled CHCl3 carbon 13 spectrum? when it is coupled to proton it is going to be a doublet because JCH separation is about 210 Hertz. Now, consider on resonance, on resonance means at the centre of the doublet then delta nu = 0. On resonance means it is exactly at the centre frequency of the spectral width. So, now, this is the spectral width, this is exactly the centre. Now, exactly on resonance at the centre the doublet, I will take delta nu = 0. The two components doublets that we see are like this, this is +J/ 2 and this is -J / 2 from the centre; and this corresponds to alpha peak, this corresponds to beta peak, we know that. So, at t = 0, I wait for some time, that is, I apply 90 degree pulse and wait for a certain time before start collecting the signal, you will see what is going to happen now. Now the 2 components of the doublet I have taken, CH doublet means one is J / 2 from the centre, and the other is -J / 2; one is the alpha peak, another is beta peak; you know what is –J / 2 what is +J / 2. The magnetization initially will be like this; at exactly when we apply a delay and start collecting this signal, in my condition if I said t is equal to exactly 0; what is going to happen? When you start collecting the signal both the signal be in phase and from the centre they are separated by J / 2, this is called in phase doublet. Both the signals are in phase, it is a J split doublet, splitting because of the J coupling. So, this is going to be J split doublet, both are in phase.

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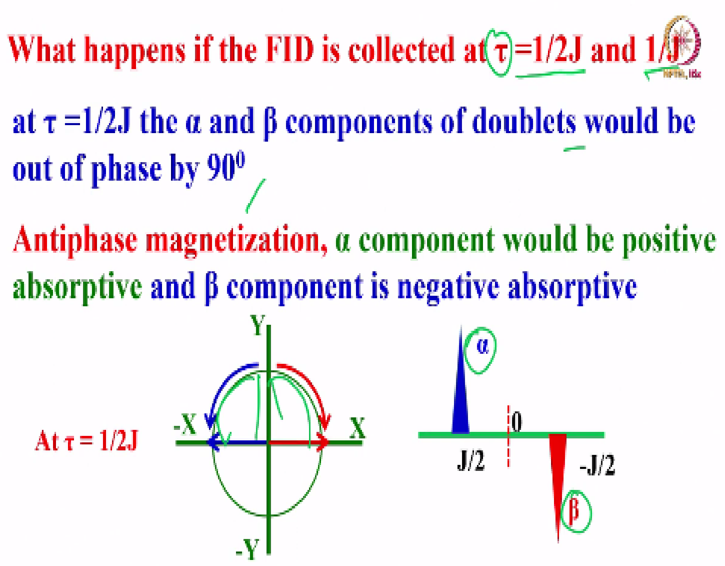

What happens if the FID is collected at τ =1/2J and 1/J

at τ =1/2J the α and β components of doublets would be out of phase by 90^0

Antiphase magnetization, α component would be positive absorptive and β component is negative absorptive

Now, I will do one thing; what happens if I collect the FID not at t = 0, at T = 1 over 2J and 1 over j and 2 collections I do. At one over 2J what happened the alpha and beta components of the doublet will be out of phase by 90 degree, they move out exactly at 1 over 2J; they will be like this, out of phase by 90 degrees. one is like this and the other is like this. This is antiphase magnetization; alpha component would be positive and beta component will be negative; see there are moving in opposite direction.

If both were like this, one move like this, one move like this. Now 1 over J / 2 now alpha component is positive and the beta component is negative. I did not do anything but I allowed the free induction decay to evolve for some time, and that time is equal to 1 over 2J, in which case we see that the doublet component, one has positive intensity, other has negative intensity, this is called antiphase doublet.

Remember, this will call antiphase doublet. In previous one we got in phase doublet both are in phase; both are positive. Here one is positive and the other is negative, this is called antiphase doublet.

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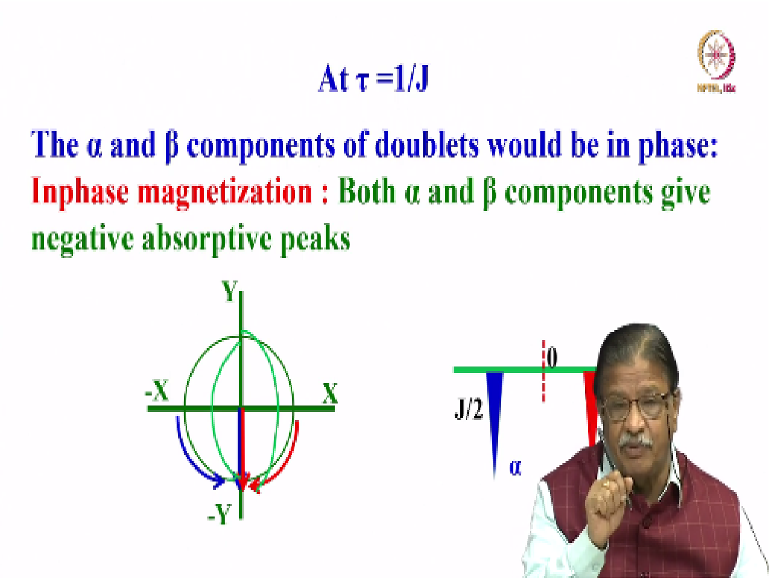

At $\tau = 1/J$

The α and β components of doublets would be in phase:

Inphase magnetization : Both α and β components give negative absorptive peaks

So, now at 1 over j what will happen? Allow the magnetization to continue further; alpha and beta components would be again come in phase. But what happens? from here this started moving like this, from here. This started moving like this, both of them are moved and they give raise to peaks here, with negative absorptive like this. This is what is called inphase negative absorptive, the doublet component in phase negative absorptive.

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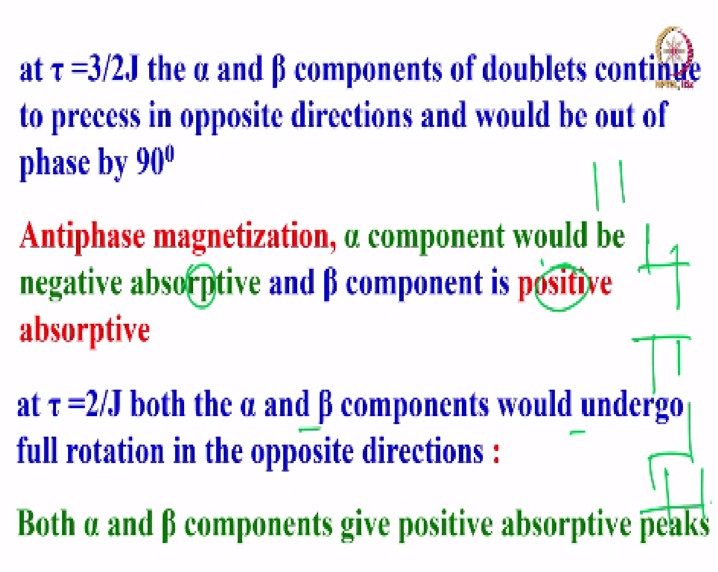

at $\tau = 3/2J$ the α and β components of doublets continue to precess in opposite directions and would be out of phase by 90^0

Antiphase magnetization, α component would be negative absorptive and β component is positive absorptive

at $\tau = 2/J$ both the α and β components would undergo full rotation in the opposite directions :

Both α and β components give positive absorptive peaks

At 3 / 2 J the alpha and beta components of doublet continues to precess in the opposite direction and it would be out of phase by 90 degree and this is antiphase magnetization. Again, alpha component would be negative absorptive and beta component will be positive absorptive. And exactly at 1 over 2J, now both alpha and beta components will undergo full rotation, and come back and give us to positive absorptive signal.

You understand now clearly; first we got the in phase, then we start moving, we will get the antiphase, then both will be in phase doublet, then what is going to happen is; this is going to be in phase negative, this is going to be positive. So, this is again antiphase. Finally, after 360 degree rotation, both will come back and we are going to get absorptive; both absorptive signals, positive absorptive signal. Start with positive absorptive, antiphase, both of antiphase components and negative absorption and then again come back.

So, this is what we are going to see as you give the delay which is equal to 1 over 2J, 1 over J, 3 / 2J and 2 / J. The entire J split doublet components will be in phase absorptive and antiphase dispersive and then again it is going to become negative absorptive, both of them inphase negatives absorptive and then completely come back after the one full rotation.

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Difference between absorptive and dispersive, and in-phase and antiphase magnetizations

So now, there is some confusion here. What is the different between absorptive and dispersive you may ask me; and we are talking about inphase and antiphase also. What is the absorptive dispersive, what is inphase and antiphase. What is the confusion we are created here?

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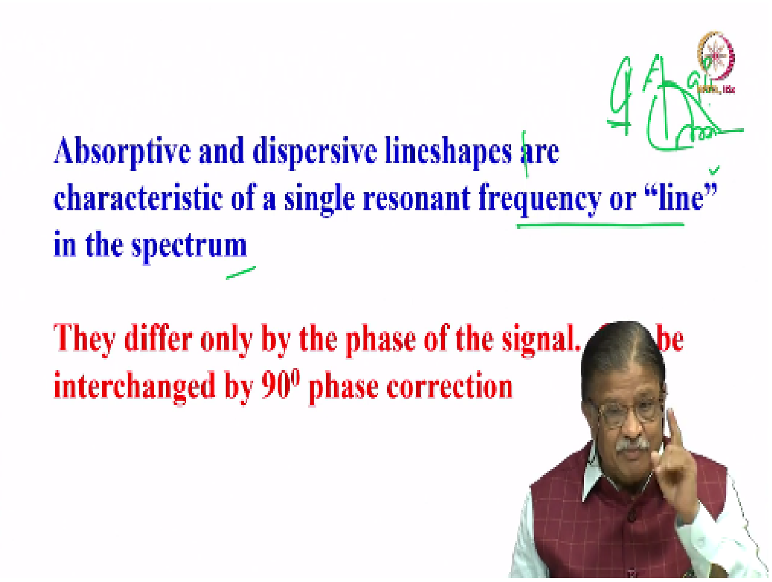

Absorptive and dispersive lineshapes are characteristic of a single resonant frequency or “line” in the spectrum

They differ only by the phase of the signal. be interchanged by 90⁰ phase correction

Look at this one; the absorptive and dispersive line shapes are characteristic of a single frequency, only one frequency line I can collect in the along X, if the receiver is here, this is absorptive and this is dispersive. That is exactly out of phase by 90 degree. It corresponds to a single peak, the differ by phase. I can make this absorptive, I can make this, this absorptive and this imaginary; dispersive either I can do. I can do the phase correction exactly I can do the phase correction, I move this here and this her;e I can make this imaginary as real, real as imaginary just by changing the phase it is possible.

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In-phase and antiphase states refer to the relative phase of the two components of a J-split doublet system

Anti phase spectrum cannot be phase correct make them appear as in phase multiplets. If one is ve absorptive, other is negative absorptive

So, in the case of absorption dispersive phase correction is possible, you can make absorption as dispersive or dispersive as absorptive. But in the case of the J split doublet, both inphase and antiphase are related to the 2 components of the J split doublet. It because of J splitting between carbon and protons, that is what we are considering CHCl3. The antiphase spectrum cannot be phase corrected to make them appear as in phase multiplets; impossible; if it is antiphase like this, you cannot make them in phase; if you tried to make this inphase these will go down.

Whereas absorptive and dispersive you can interchange them, you can make the phase correction interchange them, but here it is not possible. This is one important point you should remember. The in phase and antiphase are the multiplets of doublet; they are J split components; you cannot phase correct them to make it either positive absorptive or negative absorptive.

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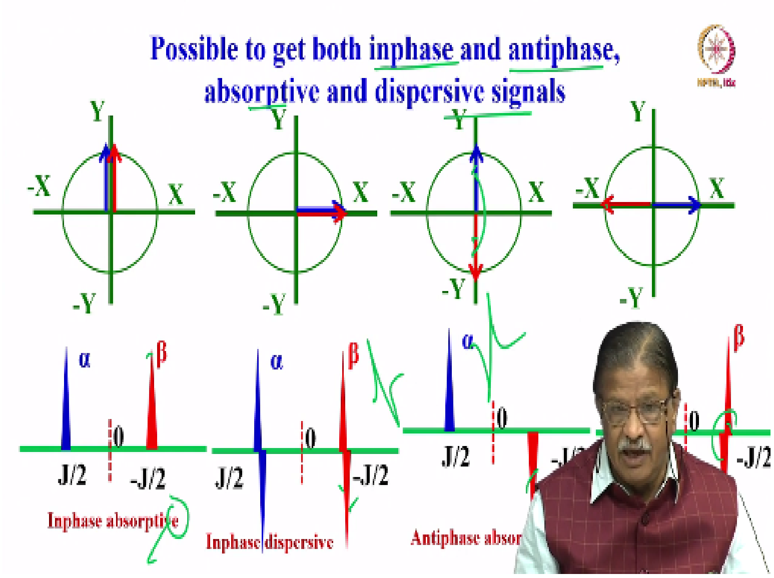

Possible to get both inphase and antiphase, absorptive and dispersive signals

So, you can also get both in phase, antiphase absorptive and dispersive. This is a combination of both is possible. Very interesting, if I take some signal, I can get in phase and antiphase signal this can be both absorptive and dispersive. Without going more into details I tell you now, the signal is like this. This is called in phase absorptive; both are in phase. And both are like this, it 90 degrees out of phase, this is dispersive and both are like this. This is antiphase absorptive; see, here both signal opposite like this. Now if they are like this, the signal is like this, this is antiphase dispersive. This is just J component, J split doublet. I am talking about both the components of the doublet are like this, the in phase absorptive, this in phase dispersive, this antiphase absorptive, this is antiphase dispersive. Antiphase dispersive and in phase dispersive you can see this goes like this; antiphase here comes goes like this, whereas antiphase dispersive it goes like this, that is the difference. So, it is possible to get a combination of both in phase, antiphase, absorptive and dispersive signal. With these now try to understand what is chemical shift evolution and J coupling evolution.

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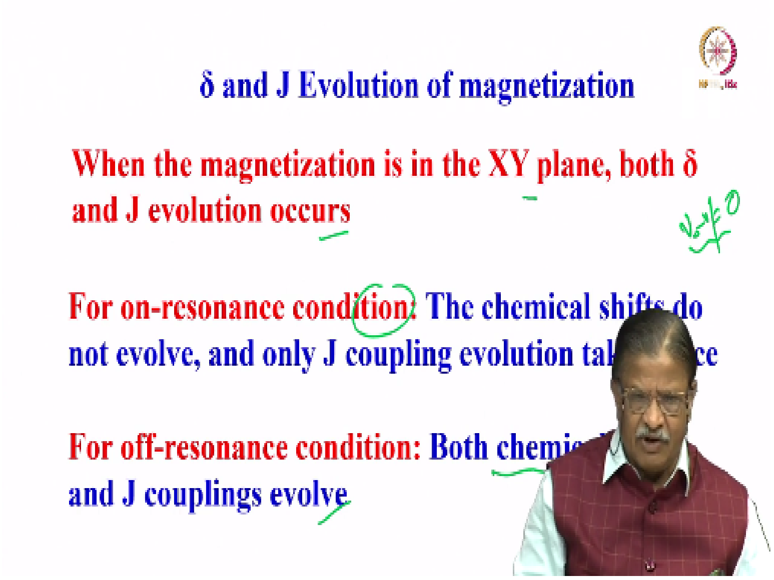

δ and J Evolution of magnetization

When the magnetization is in the XY plane, both δ and J evolution occurs

$\nu_0 - \nu_r \neq 0$

For on-resonance condition: The chemical shifts do not evolve, and only J coupling evolution tal ce

For off-resonance condition: Both chemi and J couplings evolve

Delta and J evolution is very important when the magnetization in the XY plane, both delta and J couplings will evolve, because both interactions are present, both will evolve. Now, if I consider the on resonance condition, the chemical shift do not evolve; at exactly on resonance chemical shift that means nu naught - nu r difference is 0, then chemical shift do not evolve; and only J coupling evolution takes place. For off resonance that means nu naught – nu r is not equal to 0, it is greater than 0 or less than 0 some other value.

For off resonance condition both chemical shifts and J coupling do evolve. This is the important point, please remember. The delta and J evolution takes place after the application of the pulse by bringing the magnetization to the XY plane. For on resonance condition chemicals shifts do not evolve, but only J couplings evolve. But for off resonance condition both chemical shift and J coupling do evolve. This is the point.

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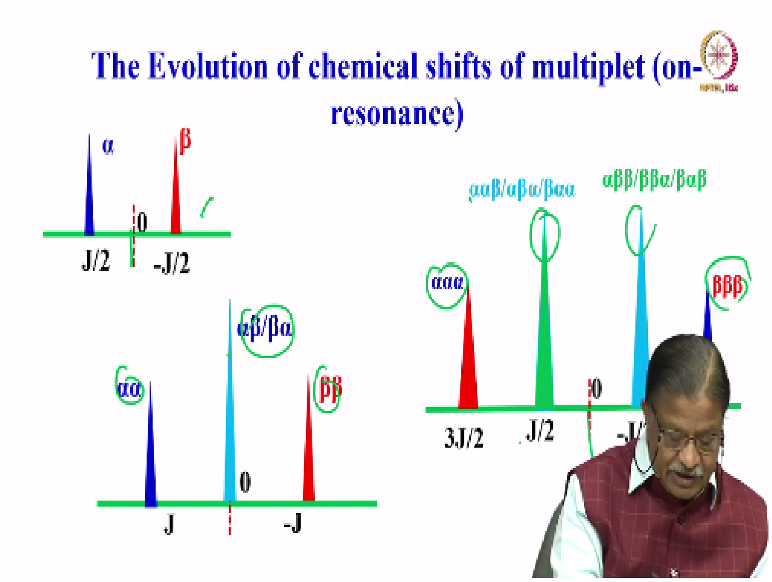

The Evolution of chemical shifts of multiplet (on-resonance)

Now, we should see the evolution of the chemical shifts and the multiplets; how they evolve. We call this as a doublet. We have alpha and beta components. We have a triplet, we have alpha alpha. beta, beta componentx; and alpha beta beta alpha component. And we have a quartet this is alpha alpha alpha, this beta beta beta; this is a combination of alpha alpha beta, these alpha beta beta there are 3 such possibilities here, 3 such possibilities. Now, how do these multiplets evolve? Always the chemical shift is at the centre for the doublet and quartet; what about the triplet? the chemical shift is the central component of the triplet.

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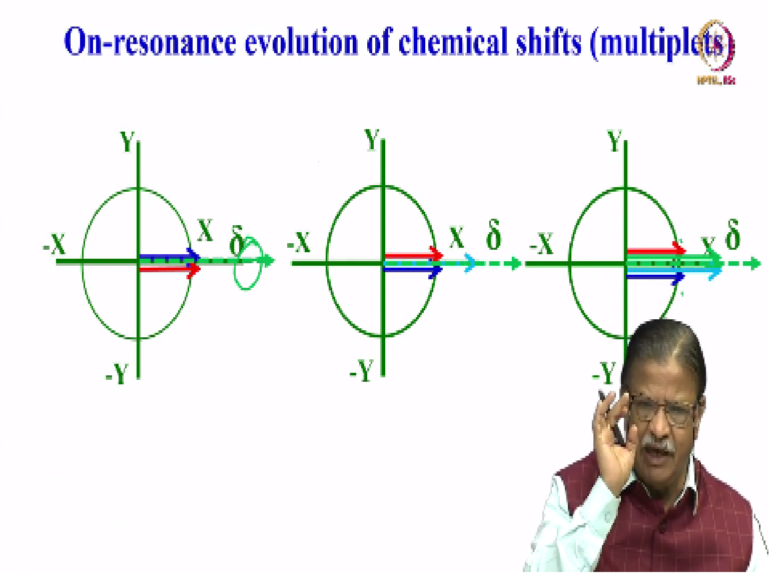

On-resonance evolution of chemical shifts (multiplets)

Now, let us see how they evolve? On resonance evolution of chemical shifts, exactly when you are on resonance, I look for the chemical shift of the multiplets; for doublet it will be exactly at the centre. Now, if I take the triplet, it is the central component of the triplet. If you take the quartet, it is exactly at the centre of the quartet. This is at on resonance, the chemicals shift do not evolve. Now of course what happen to these components, you may ask; I will show you when we go to J coupling; this J coupling do evolve even in on resonance, that is what I said; they will evolve.

But only for chemical shift to show I am telling you, when you are on resonance, it is the centre of the doublet. There is no peak there, this is what I am telling you. The centre of the doublet is the chemical shift, that is how it evolves. Similarly, this is central component of the triplet; this is centre of the quartet, how do they evolve?

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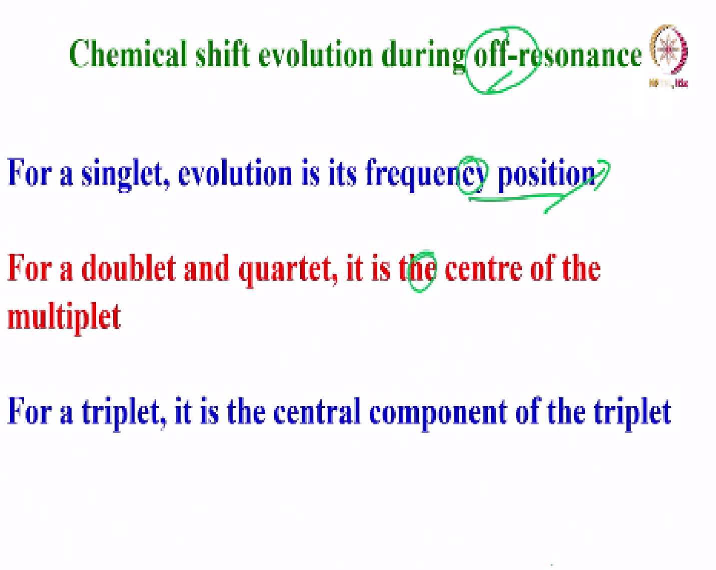

Chemical shift evolution during off-resonance

For a singlet, evolution is its frequency position

For a doublet and quartet, it is the centre of the multiplet

For a triplet, it is the central component of the triplet

So, for a singlet evolution, it is nothing but the frequency position. If I consider a singlet chemical shift during off resonance, I am considering not on resonance, how does the chemical shift evolve? It is the single frequency wherever it is, that is the chemical shift position. And for doublet and quartet, the chemical shift positions are the centre of the doublet and centre of the quartet. For a triplet, the central component of the triplet, that is important.

So, how the chemicals shift evolution take place during off resonance; singlet is nothing but the chemical shift position of the singlet; for the doublet and quartet, it is the centre of the doublet and quartet. For a triplet, it is the central component of the triplet; these are the things which evolve.

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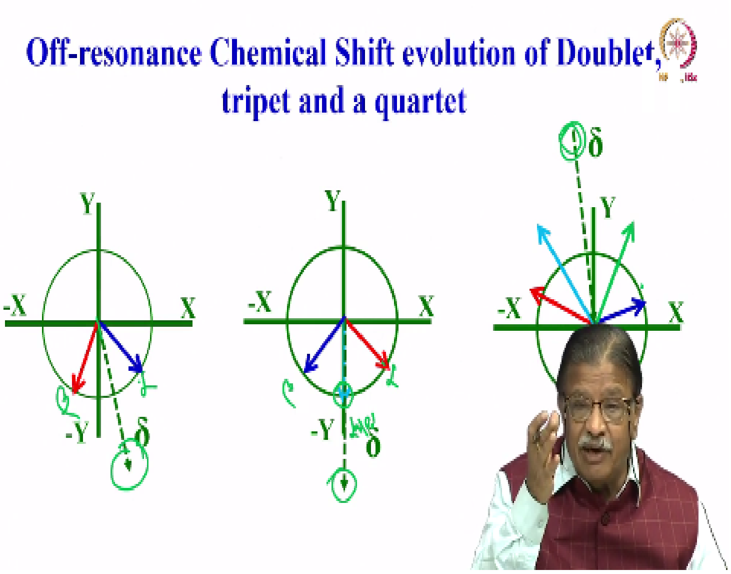

Off-resonance Chemical Shift evolution of Doublet, tripet and a quartet

Now diagrammatically we can see how it evolve; in off resonance condition, the chemical shift evolution of a doublet, triplet, quartet let us see. This is a doublet now, we are talking about off resonance, where is the chemical shift? this is one component of the doublet, let is say alpha is here beta is here; let us say alpha beta is here, it is a doublet 2 components are there, where is the chemical shift now? There is no peak, there is no magnetization vector at that place; But you should understand the chemical shift here evolves at the centre.

Similarly, now the triplet if you consider, they evolve like this alpha, this is beta; this is is alpha beta, beta alpha. Now centre is here, the chemical shift of this evolves like this. If you consider the quartet , two peaks are here, two are here, where is the chemical shift? exactly at the centre here; centre of this. So, this is the chemical shift evolution, this is the doublet centre, this is a central component of the triplet where this one again is at the centre of the quartet. This is hypothetical, there is no peak but you have to understand how the chemical shift is varying. You can even calculate the frequencies everything later.

Now we will talk about evolution of couplings. How does couplings do evolve? that also evolves in on resonance and off resonance condition; we have to consider. So, what we will do is, I think my time is up, what I will do is, I will stop here, we will come back. In the next class, I will discuss about the evolution of the couplings and then I will introduce to you more about polarization transfer. How the polarization transfer takes place between the antiphase components of the coupled spins.

And more of the other things we will discuss, product operators, various things we will discuss in NOE, MQT etcetera. But today what you understood is the evolution of the magnetization. We understood how the magnetization evolves under the influence of chemical shifts; when it is on resonance, when it is off resonance. When it is on resonance if it is a singlet, in the on resonance chemical shift do not evolve at all, but couplings will evolve. In the off resonance, chemical shift will evolve and couplings also will evolve.

Go to the under off resonance condition. If you consider a doublet, the center the doublet is the chemical shift, but there is no peak. But you can imagine the direction where it is moving. So, you can find out the axis at which evolution of the chemical shift has taken place. Whereas in the case of off resonance, the center component of the triplet tells me about the evolution of chemical shift.

Whereas, if you go to the quartet the central point of the quartet is a chemical shift. That tells me where the chemical shift is evolved. If I have to find out the center of this quartet. So in off resonance the chemical shift do evolve, in on resonance chemical shift do not evolve. In on resonance the J couplings evolve, in off resonance J coupling evolves. This is what you should understand. The evolution of J coupling and how it take place we will discuss in the next class. So, I will stop here. Thank you.