Advanced NMR Techniques in Solution and Solid-State
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Module-53
MQ and Relative Signs of Couplings
Lecture – 53

Welcome all of you. In the last 2 classes, we have been discussing an entirely different topic called multiple quantum transitions, multiple quantum NMR. And in the last class, we extensively discussed about the multiple quantum transitions detectable in 2 spins case and 3 spins case. Especially, double quantum and zero quantum in 2 spin case. And, we came to know double quantum comes at sum of the chemical shifts of the coupled spins. And, since there is no passive spin, it is only a singlet. Similarly, in the case of zero quantum also, in the case of the 2 coupled spins, there is no passive spin. Zero quantum comes at difference of the chemical shifts and the and since of course, there is no passive spin there is no J coupling. We also discussed about DQ and ZQ of 3 coupled spins, weakly coupled; went to AMX spins. There could be AM DQ and MX DQ or AX DQ.

In each case, the leftover spin is a passive spin. That can have spin states alpha and beta and split this DQ into a doublet. And DQ comes at the sum of the chemical shifts. The separation corresponds to, if there are 2 spins active, it is the sum of the coupling between active and passive spins. If it is AM double quantum, X is the passive spin, the separation corresponds to JAX + JMX coupling. Similarly, you can work out for other double quantum.

And for the zero quantum, there are 3 such possibilities. Zero quantum comes at difference of the chemical shifts and the separation corresponds to difference in the couplings, not the sum unlike DQ. That is what we understood. And, we took the example to find out the barrier to highest quantum. How many transitions that are detected when you go to 4th quantum of four spins; for example, triple quantum of 4 spins, double quantum of 4 spins; and, how many such possibilities are there. Everything you have understood. And, what is this, see in the 3 spins case, only one is a passive spin. In the 4 spins case, 2 are passive spins. That is the important thing. You should understand, each of them have, 2 possible orientations. In principle, we have alpha alpha, alpha beta, beta alpha and beta beta orientations, 4 possible orientations for passive spins.

And, it will split into doublet, in fact, four lines, doublet of doublet, it should split. In fact, what will happen, let us say we get a doublet and measure this separation. And, the separation corresponds to sum of active and passive couplings. So, we understood those things. And, we discussed a formula. Using the formula, we found out how many peaks we can get for the mth quantum of N coupled spins.

We found out by taking the examples of the 6 coupled spins, the single quantum transitions of 6 coupled spins, gives 792 transitions. On the other hand, if you come to higher and higher quantum, for example, N minus 1 quantum gives only 12 transitions. N minus 2 gives rise to only 66 transitions. That is what we observed. As a consequence, I said , as we go higher, lower the number of transitions, we get. The spectral complexity gets reduced a lot.

And I also said N minus 1 and N minus 2 multiple quantum spectra are sufficient to get the complete information about the spectrum. So, we do not need to go to analyze the complex single quantum spectrum and with redundancy in the transitions. So, this is another approach. With that we will continue further today to understand the pulse sequence of the multiple quantum detection.

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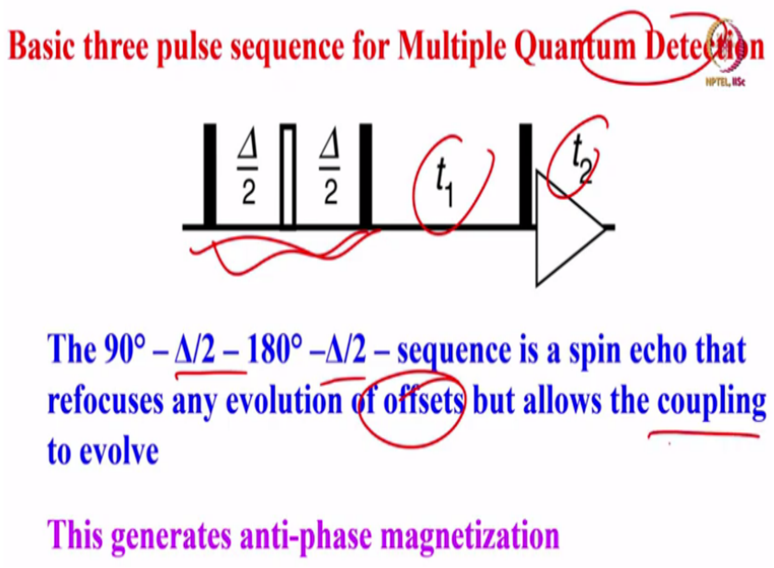

Basic three pulse sequence for Multiple Quantum Detection

The 90° – Δ/2 – 180° –Δ/2 – sequence is a spin echo that refocuses any evolution of offsets but allows the coupling to evolve

This generates anti-phase magnetization

Here is the pulse sequence for the multiple quantum detection. It is simply a echo sequence followed by a t1 and then the t2. See 90 delta by 2 180 delta by 2 is a echo sequence. It allows only couplings to evolve. Refocuses any chemical shifts, no offsets will evolve and allows only the coupling to evolve. We know that. In the homonuclear case, spin echo will only refocus chemical shifts, and coupling will evolve. So, this generates anti-phase magnetization.

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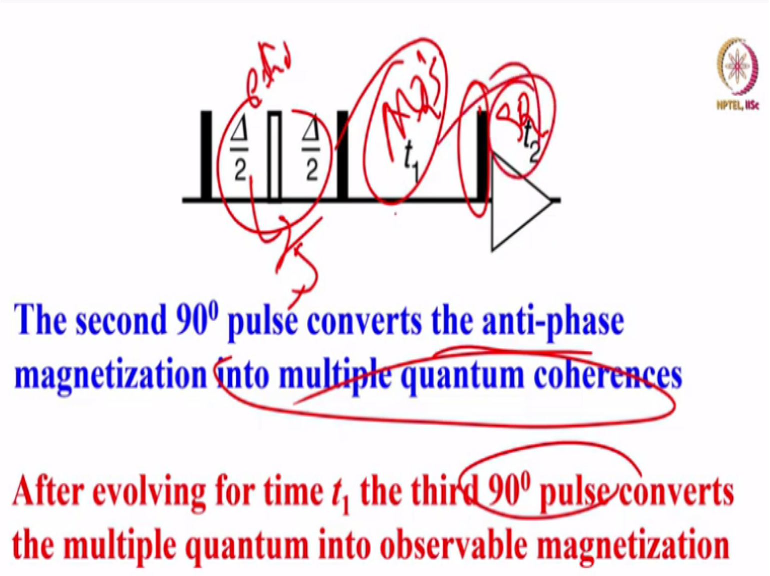

The second 90^0 pulse converts the anti-phase magnetization into multiple quantum coherences

After evolving for time t_1 the third 90^0 pulse converts the multiple quantum into observable magnetization

We have observed that and then the second 90 degree pulse converts this anti-phase magnetization into multiple quantum coherences. Here, MQs are generated. This is the t1 period. After the second pulse, MQs are generated. And, after evolving for a time t1, the third 90 degree pulse converts this MQ into observable single quantum, SQ. Here, MQ will become SQ and we are going to observe this. Here, there is a echo. This is going to prevent chemical shift evolution. Only J will evolve. Here, MQs will evolve. And here, MQ will be converted to single quantum, in the detection period. And, that is what we are going to detect.

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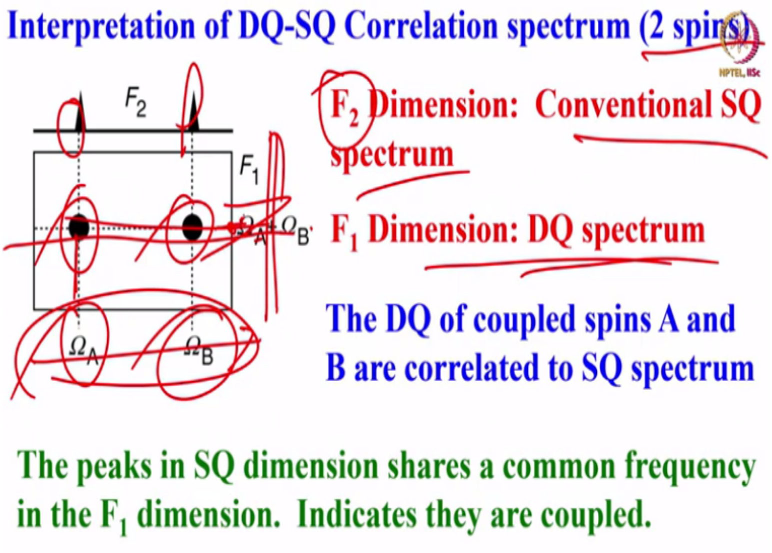

Interpretation of DQ-SQ Correlation spectrum (2 spins)

F_2 Dimension: Conventional SQ spectrum

F_1 Dimension: DQ spectrum

The DQ of coupled spins A and B are correlated to SQ spectrum

The peaks in SQ dimension shares a common frequency in the F_1 dimension. Indicates they are coupled.

So, how do you interpret the double quantum single quantum correlation spectrum? For let us say 2 spin case. This is a double quantum dimension. This is a single quantum dimension. Detection dimension is single quantum. Indirect dimension is F1, is double quantum.

Now, I have 2 spins A and B. The 2 spins are coupled. Where does it come in the double quantum? It comes at sum of the chemical shifts. That is what we have been observing. So, here it comes at sum of the chemical shifts. On the other hand, if you go to this DQ dimension, you get 2 peaks, I am sorry, single quantum dimension you get 2 peaks. One at chemical shift of A; and the other at the chemical shift of B. Only in the DQ dimension, you get sum of these 2. So, in this dimension, there is only 1 peak. In this dimension, if you go in principle, you get only 1 peak. If you take the projection here, it is only a single peak. Here, if you get the projection, in this dimension, you get 2 peaks, one at the chemical shift of A, one at the chemical shift of B. That is what is happening. So, F2 dimension gives you conventional SQ spectrum. And, F1 dimension gives you DQ spectrum. The DQ of coupled spins A and B are correlated to single quantum. This is what is called DQ SQ correlation spectrum.

Double quantum of 2 spins A and B are correlated to its single quantum spectrum. That is what you have to interpret. So, the peaks in the SQ dimension shares a common frequency in the DQ dimension. What it means is, see for example, see here for example, in this case; this is the DQ dimension. In the DQ dimension, it shares, shares common frequency; both omega A and omega B will share a common frequency in this DQ dimension, in this F1 dimension.

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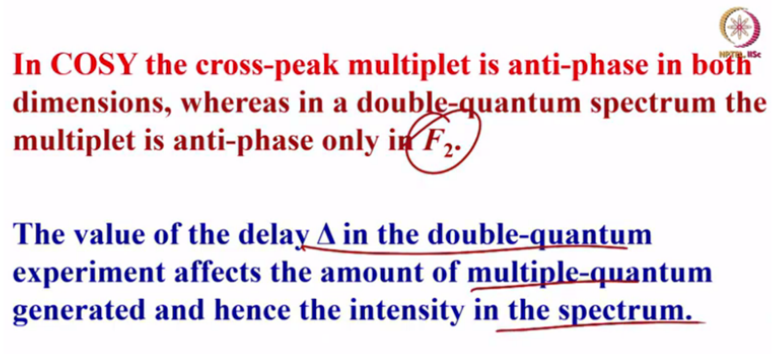

In COSY the cross-peak multiplet is anti-phase in both dimensions, whereas in a double-quantum spectrum the multiplet is anti-phase only in F_2.

The value of the delay Δ in the double-quantum experiment affects the amount of multiple-quantum generated and hence the intensity in the spectrum.

In COSY cross multiplets are anti-phase, especially the cross peaks and diagonal peaks are in phase. That is what we discussed. Whereas in the double quantum spectrum, the multiplet is anti-phase only in F2. That is important thing. The value of the delta in the double quantum experiment, in this pulse sequence, the value of the delta affects how much of the multiple quantum generated and its intensity.

That depends upon how you set your delta. That depends about the intensity of the multiple quantum and its intensity.

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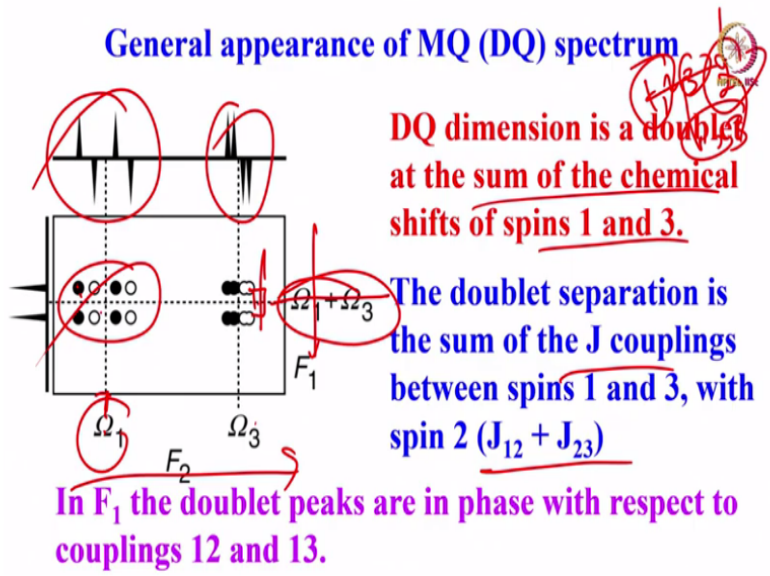

General appearance of MQ (DQ) spectrum

DQ dimension is a doublet at the sum of the chemical shifts of spins 1 and 3.

The doublet separation is the sum of the J couplings between spins 1 and 3, with spin 2 ($J_{12} + J_{23}$)

In F_1 the doublet peaks are in phase with respect to couplings 12 and 13.

So, general appearance of your MQ, especially DQ spectrum is like this. Let us say I have a 2 coupled case or 3 spin case, ABC or 1 2 3 spins. Now, I am looking at the 1 2 double quantum. So, in the double quantum dimension, you get only 1 peak exactly at the center of this, which correspond to sum of, in this case, let us say 1 and 3 is taken. So, I will take 1 and 3 again. So, this is 1 and 3 double quantum, it comes at the sum of chemical shifts of 1 and 3.

But, it is not a single peak, you look at it. In this dimension, it is a doublet. Why is the doublet coming? This doublet comes because of coupling of 1 with 2 and 3 with 2. It is a separation corresponding to J 12 + J 23. That is a doublet. So, in each case, you can see here the DQ dimension is a doublet comes at the sum of the chemical shifts of spin 1 and 3, it is a doublet. Doublet separation corresponds to J12 plus J23. That is what it is. Now, go to the conventional single quantum dimension at the center here, you take the projection; you get 4 peaks because 1 is coupled to 2 and 3. But, what is happening is, you look at it, it is doubly anti phase. You see both of them are anti-phase actually. So, in F1 doublet peaks are in phase with respect to couplings 12 and 13.

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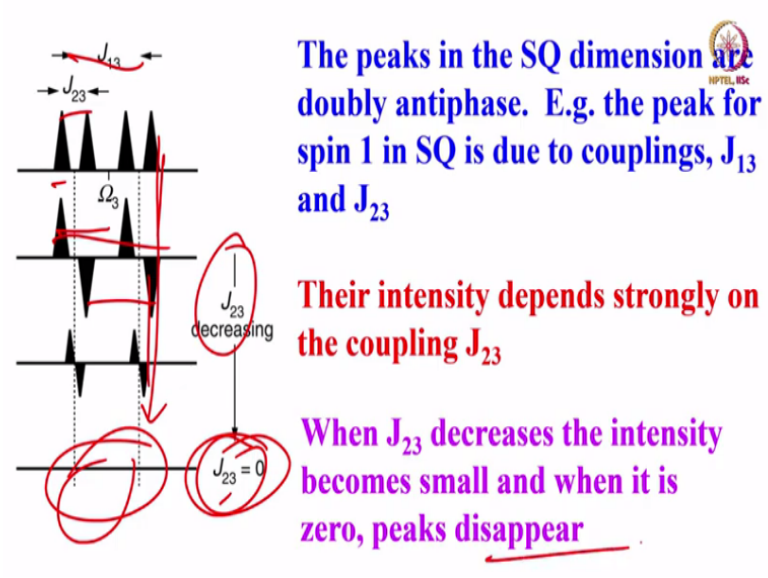

The peaks in the SQ dimension are doubly antiphase. E.g. the peak for spin 1 in SQ is due to couplings, J_{13} and J_{23}

Their intensity depends strongly on the coupling J_{23}

When J_{23} decreases the intensity becomes small and when it is zero, peaks disappear

But, in F2, they are doubly anti-phase. In this SQ dimension, they are doubly anti-phase. So, for example, peak for spin 1 in SQ dimension due to coupling 13 is seen like this. This is coupling 13. And, this is 23. And, you will see this is 13 coupling and this is also 13 coupling. So, it is going to be doubly anti-phase. So, their intensity of this peak strongly depends upon the coupling 23.

As the coupling strength keeps on decreasing, the intensity keeps on coming down. Exactly when it becomes 0, you will not see any peak at all. This can happen. If you do not see a peak in the double quantum dimension, it maybe possible that the coupling of one of them let us say 23 coupling, you are looking at 13 double quantum. One of the couplings, 23 maybe 0. You will not be able to see that. As a consequence, intensity keeps coming down. As J decreases when J becomes 0; one of them, then you will not see this peak at all. So, when J 23 becomes small, and when it is 0, peaks will completely disappear.

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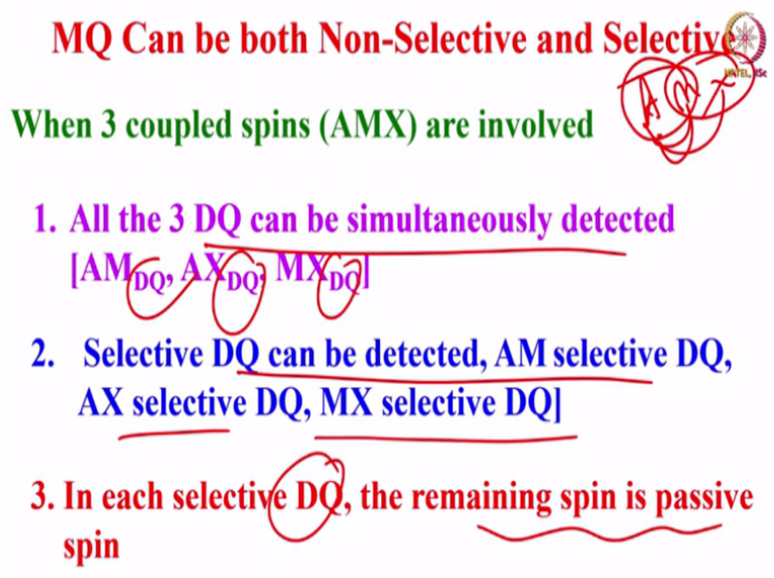

MQ Can be both Non-Selective and Selective

When 3 coupled spins (AMX) are involved

1. All the 3 DQ can be simultaneously detected [AM_{DQ}, AX_{DQ}, MX_{DQ}]
2. Selective DQ can be detected, AM selective DQ, AX selective DQ, MX selective DQ]
3. In each selective DQ, the remaining spin is passive spin

So, now, multiple quantum, can you do all double quantum of the 3 spins at a time? Can you do all zero quantum of all the 3 spins at a time? See 2 spin double quantum and zero quantum I will take. I will consider AMX coupled case. I will take 2 spin double quantum and 2 spin zero quantum. There are 3 such possibilities, for each of them. Can I do at a time? Can I do individually? Of course, it is possible. You can selectively have a AM double quantum and selectively MX double quantum, selectively have AX double quantum. Similarly, you can have selectivity AM, MX and AX zero quantum also. Also, you can have non-selective. You can do the experiment non-selective all the double quantum can be simultaneously detected. That is also possible. So, when the 3 spins are involved, the 3 DQ can be simultaneously detected AM DQ, AX DQ and MX DQ. And selectively, you can also detect AM selective DQ, AX selective and MX selective DQ, all are possible. In each selective DQ, the remaining spin is the passive spin which is responsible for giving the doublet.

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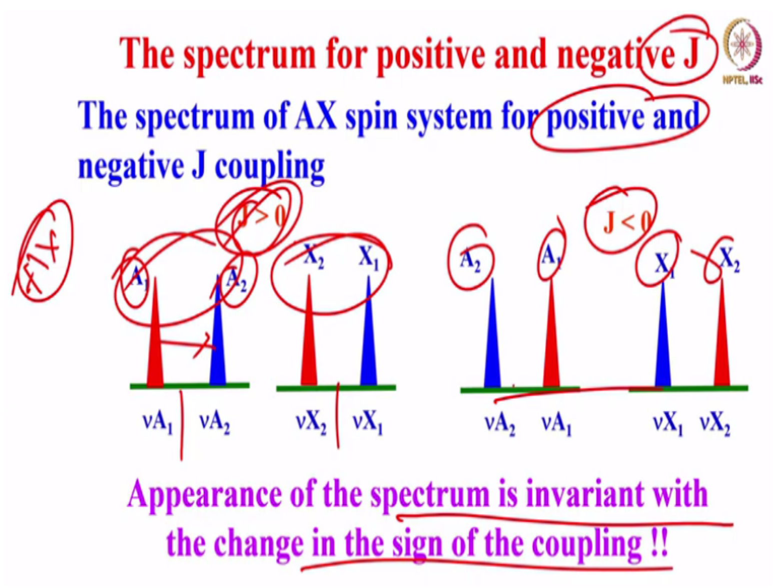

The spectrum for positive and negative J

The spectrum of AX spin system for positive and negative J coupling

Appearance of the spectrum is invariant with the change in the sign of the coupling !!

Now, very interesting application of this I am going to show you. Can we use this? Now we understood the idea that double quantum comes at sum of the chemical shifts and some of the couplings between active or passive spins, everything. That is what we discussed. For example, in the 3 spin case, DQ comes at sum of the chemical shift of 2 coupled spins. And, the separation is coupling between active spins and the passive spin. In the zero quantum it is reverse. Chemical shift comes at that difference and J also comes as the difference. Can we use this idea to find out the relative signs of the coupling? We can see that. The spectrum, how does it look if I have a positive J value and the negative J value? This we discussed extensively in the first course.

How does the spectrum look, 1D NMR spectrum when the J coupling is positive or negative? For example, this is a J is positive case. I am considering AX case. AX spin, each one will give rise to a doublet. We know that. In the AX case, AX weakly coupled spins case, A will gives you a doublet and X gives you a doublet. Fine, now, what happens if I measure this J coupling? This is a center which gives the chemical shift. Now, I do not know whether J is positive or negative. I assume this J is positive. Now, what happens to the spectrum if J is negative? Can you see the difference between this and this? Absolutely no visible difference at all; but something internally happens. Look at this. This A2 came here became A1, this A1 came here became A2. The peaks just got reversed. They interchanged. Similarly, X1 and X2 got interchanged.

So, when the sign of the coupling changes, only peak positions just get interchanged. As for the total appearance of the spectrum is concerned, it remains unaltered. The appearance of the spectrum is invariant with the change in the sign of the coupling. This is what happens. So, it means you cannot get the sign of the coupling from the conventional one-dimensional NMR spectrum.

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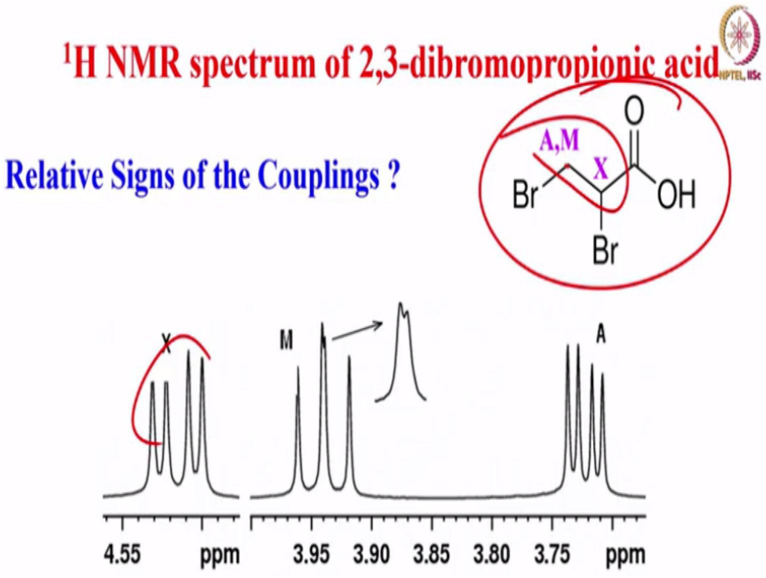

^{1}H NMR spectrum of 2,3-dibromopropionic acid

Relative Signs of the Couplings ?

Now, it is a practical example I am showing you. This is the NMR spectrum of 3 protons, this forms a weakly coupled AMX like this. We are getting 12 peaks. 4, 4, 4 for A, M and X respectively. Now, can I get the relative signs from this coupling? Of course, from the 1D spectrum, it is not possible.

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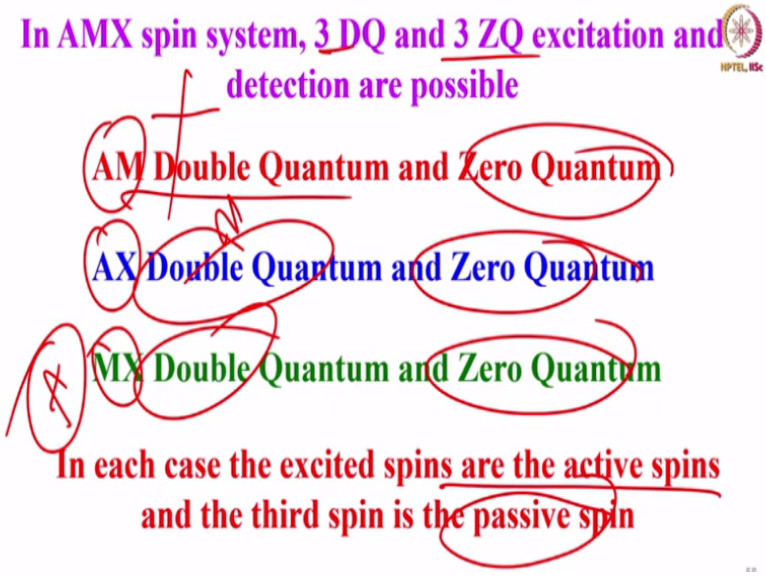

In AMX spin system, 3 DQ and 3 ZQ excitation and detection are possible

AM Double Quantum and Zero Quantum

AX Double Quantum and Zero Quantum

MX Double Quantum and Zero Quantum

In each case the excited spins are the active spins and the third spin is the passive spin

Let me use multiple quantum and see. Now, in AMX spin system, we have 3 DQ, 3 ZQ. It could be AM double quantum and zero quantum. AX double quantum and zero quantum. MX double quantum and zero quantum; all 3 are possible. In each case, the excited spins are the active spins and the third spin is the passive spin. So, in AM case, X is passive. AX case, M is passive. MX case, A is passive. So, you must get doublets for both the DQ and ZQ. DQ gives sum of the couplings, in the ZQ case, it is difference of the couplings.

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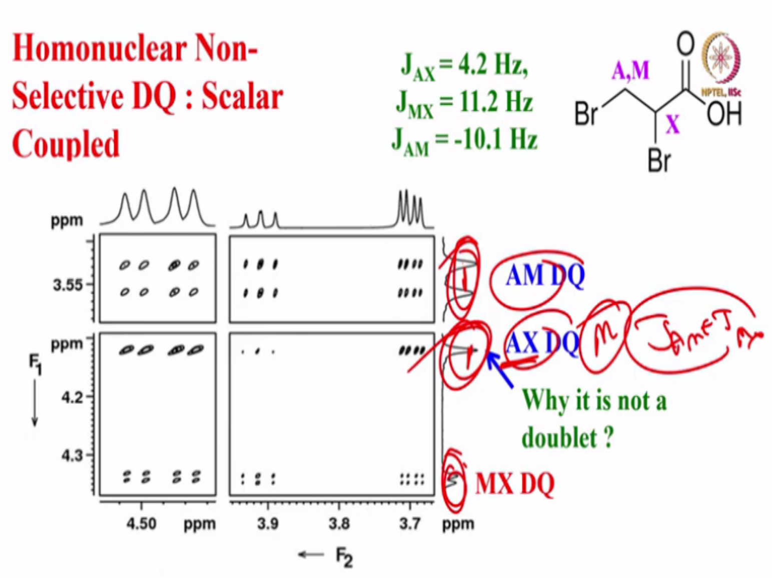

Homonuclear Non-Selective DQ : Scalar Coupled

J_{AX} = 4.2 Hz,
J_{MX} = 11.2 Hz
J_{AM} = -10.1 Hz

Why it is not a doublet ?

That is what, with that idea, an experiment was done. This was a homonuclear non-selective DQ. That means at a time all the 3 double quantum are detected. There is a J coupling. Look at this one. This is a AM double quantum. It is a doublet. This is a MX double quantum. It is a doublet. This is a AX double quantum. It is a singlet. How is it possible? I told you when there is a AX double quantum, M is a passive spin. This must be a doublet because of JAM plus JMX. That should be a doublet. But I am not seeing a doublet. I am seeing a singlet. Whereas, here and here I am seeing doublets. The coupling are different, the strengths of the couplings are different. As a consequence, the separations are different. But here, there is only a singlet. What does it mean? Why is it not a doublet? Let us try to answer it.

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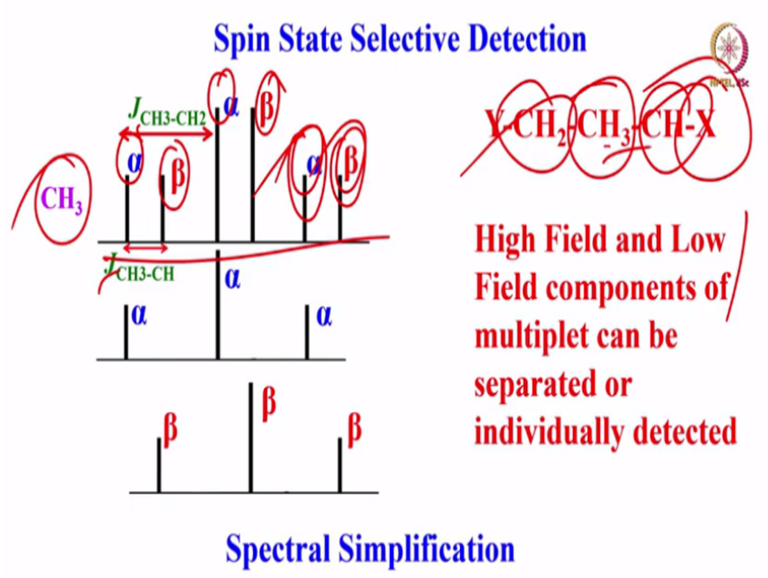

Spin State Selective Detection

High Field and Low Field components of multiplet can be separated or individually detected

Spectral Simplification

Before that, I will tell you something about spin state selective detection. What is a spin state selective detection? Look at the molecule like this. I am going to look at CH3 peak in this hypothetical molecule. How many peaks you expect? CH3 is coupled to CH2. What will happen? It will become a triplet. I am detecting CH3. Observing CH3, this will split into a triplet because of CH2. What will happen to triplet?

Each line of the triplet will split into a doublet because of a CH proton. It will split into a doublet. As a consequence, you are going to get triplet of doublets. That is what you are going to get. And, what are these components of triplets of doublet? These all correspond to alpha alpha alpha state of CH proton. These all correspond to beta beta beta states of CH proton. Now, my question is, you can measure this and get the J couplings. These are high field and low field components. These are high field components. These are low field components. Can I separate it out is my question? If I separate the high field and low field components, or instead of separation, if we can detect only beta beta beta peaks and suppress alpha alpha alpha peaks, that is also fine. Either way, I can do detect only one of the components alpha alpha alpha peaks or beta beta beta peaks. Or, I can separate them spectroscopically. Can I do that? I can get this one or I can get this one. In which case, I can drastically simplify the spectrum. This is called spin state selective detection.

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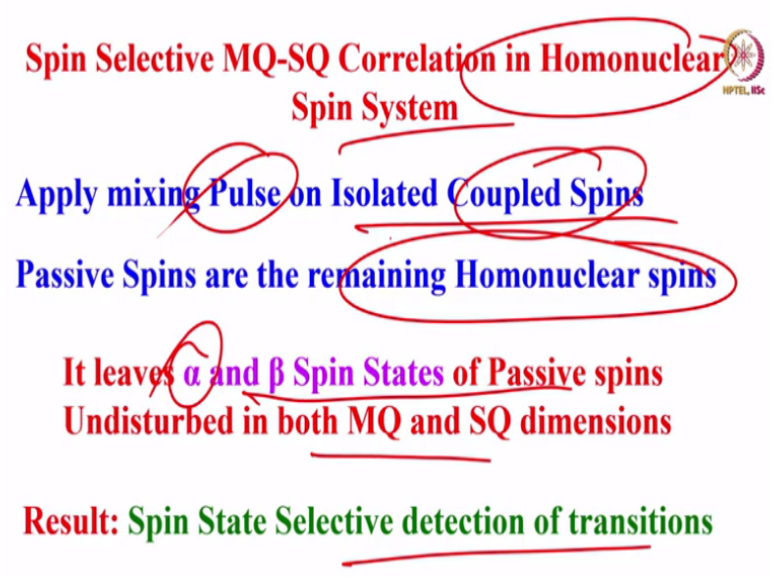

Spin Selective MQ-SQ Correlation in Homonuclear Spin System

Apply mixing Pulse on Isolated Coupled Spins

Passive Spins are the remaining Homonuclear spins

It leaves α and β Spin States of Passive spins Undisturbed in both MQ and SQ dimensions

Result: Spin State Selective detection of transitions

The spin state selective MQ SQ correlation in the homonuclear case we will understand now with the knowledge of what is a spin state selection. See, when you apply a mixing pulse, the second pulse in the pulse sequence I have given, on the isolated coupled spins, the passive spins are the remaining homonuclear spins, leaves the alpha and beta spin states of passive spins unaltered.

See, what we will do is, let us say, I am taking the AM double quantum. I selectively detect AM double quantum. I do not touch X at all. I do AM double quantum, I do not touch X at all. Then, what will happen there? Passive spin states, the passive spin X states remains unaltered in both MQ and SQ dimensions, alpha, beta remains same. Same thing is true for any double quantum you consider.

Take MX double quantum, A is a passive spin. A has alpha beta states. In MX double quantum, what will happen? in the MX double quantum, again in the both MQ dimension and SQ dimension, A spin alpha and beta states remains undisturbed. This is called spin state selection. This gives rise to what is called spin state selective detection. Please understand that. This was the homonuclear case. What happens if it is a heteronuclear case? That is a different question. I will come to that later.

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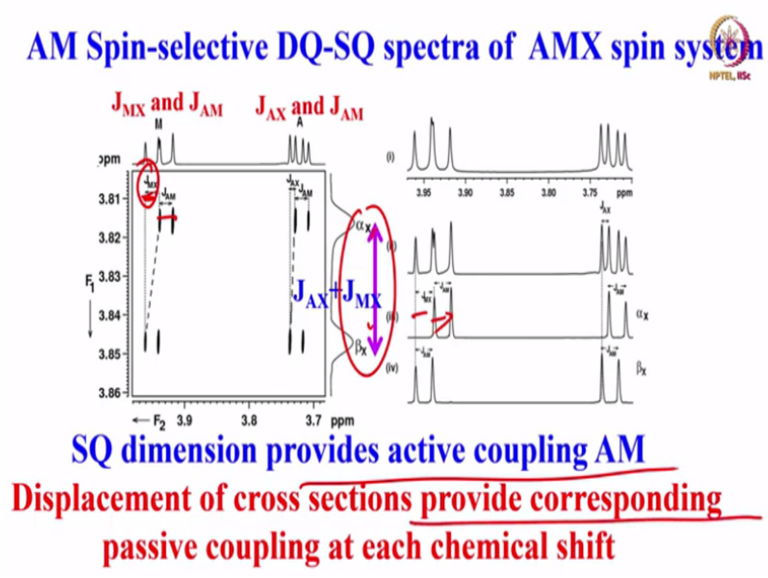

AM Spin-selective DQ-SQ spectra of AMX spin system

SQ dimension provides active coupling AM

Displacement of cross sections provide corresponding passive coupling at each chemical shift

There, it is a different way. Now, I will look at the AM spin selective DQ SQ spectrum of AMX spin system. Fantastic, it is expanded region. This is AM double quantum. So, in the single quantum dimension, I will get A and M chemical shifts. In the double quantum, what you will get? Sum of delta A and delta M; and it is a doublet because of splitting with X, because of alpha X and beta X states. Perfect, no doubt about it. Now, what is this separation gives? JAX plus JMX. That is what I am going to get it. We measure it, let us say. That is what this spectrum is. An interesting thing will happen, when there is a spin state selective detection like this, I take the cross section of each of them here and plot out separately like this. Take this cross section and plot here, take this cross section plot here. Then, there is a displacement here. That displacement gives me one coupling. And, this separation gives you me coupling here. This displacement gives me JMX coupling. This separation gives me JAM coupling. So, very easily, we can get this one. And, sum here gives you JAX + JMX. So, SQ dimension provides active coupling to AM and the displacement of cross sections provide corresponding passive couplings at each chemical shift.

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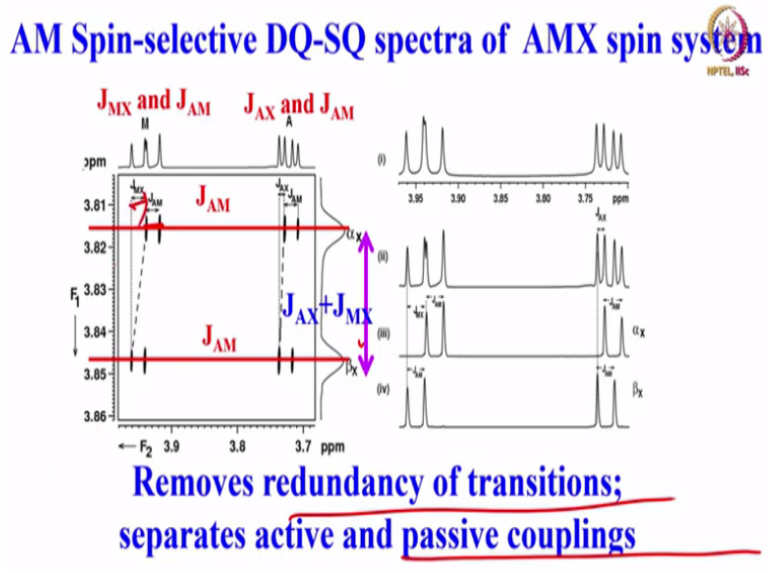

AM Spin-selective DQ-SQ spectra of AMX spin system

Removes redundancy of transitions;
separates active and passive couplings

That is what happens. Now, we have taken the cross section of each of them. And now what is happening is it has removed the redundancy. Instead of 8 peaks, I do not need to worry, I get only 4 peaks here. That is enough for me. It removed redundancy of the transitions and that also separated active and passive couplings. How did it separate out? Look at this here it separated active and passive coupling here. These are the active couplings. And, the passive coupling MX is separated out here. See, from the displacement, you can get the passive couplings.

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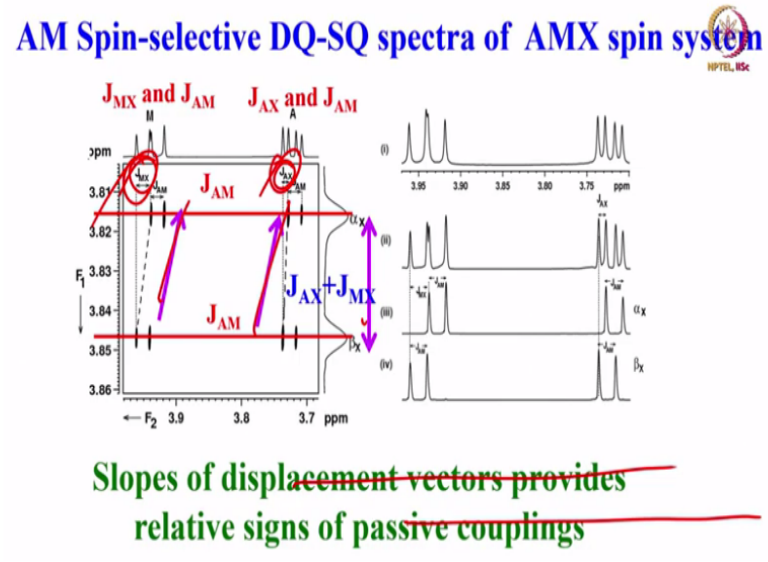

AM Spin-selective DQ-SQ spectra of AMX spin system

Slopes of displacement vectors provides
relative signs of passive couplings

And also, the direction of the displacement gives me the relative signs of the coupling. See both are tilting towards the right. So, this and this if you consider, they have tilted towards the right. Similarly, if you consider this and this, it is tilted towards the right. Both are tilted in the same direction. That means the relative signs of this coupling and this coupling is same. Here, you must understand one important thing.

Here, in this case, what you are going to get is JMX coupling here. Here, you are going to get MX coupling. You are going to get JAX coupling here. And now, both are tilted in the same direction. What does it tells me? The passive couplings JMX and JAX have the same signs; if the tilting were opposite, like this. Then, we can say they are opposite in signs. The coupling constants are opposite. But, now, they are tilted in the same direction. It tells me the coupling JMX and JAX have same signs. I do not know what is the absolute sign, I can talk about the relative signs. If this is negative, this also negative; if this is positive, this is also positive. So, it is only relatively both of them have the same signs because the direction of the tilting is identical. The absolute signs I do not know, The slope of the displacement vector gives me relative signs of the passive coupling.

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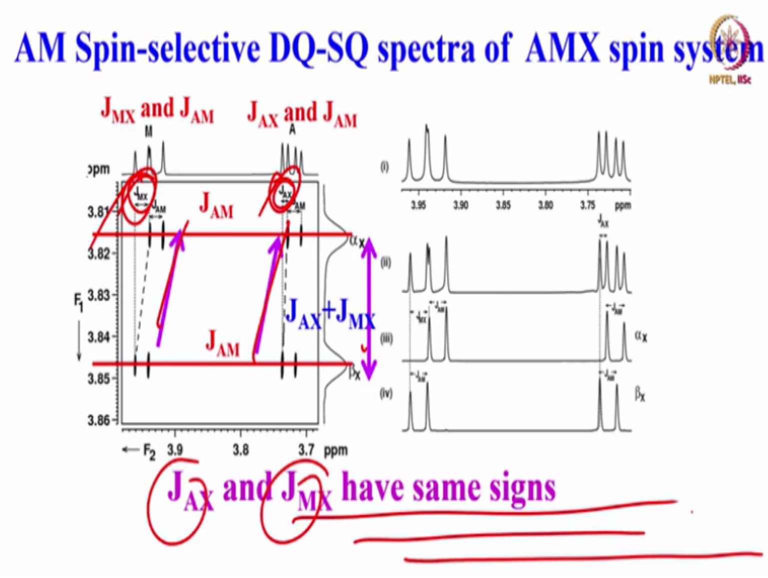

AM Spin-selective DQ-SQ spectra of AMX spin system

NPTEL, IISc

J_{AX} and J_{MX} have same signs

So, it means JAX and JMX have the same signs. Fine, we have got one knowledge.

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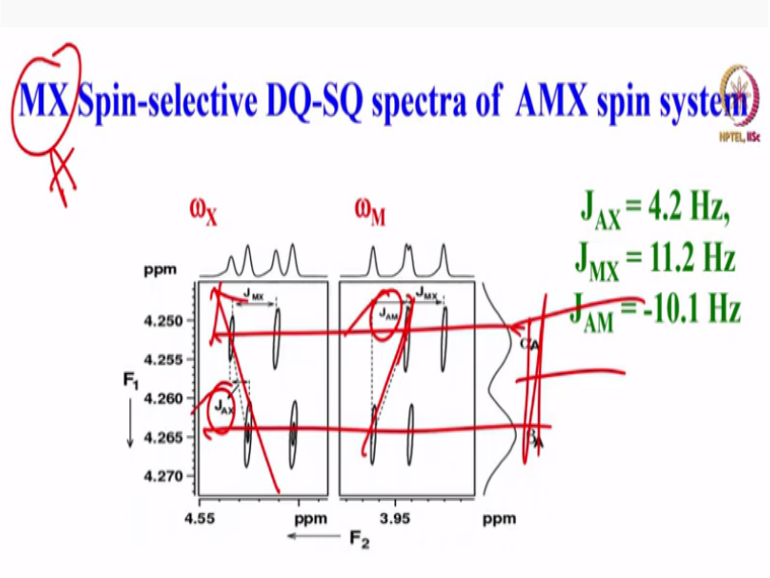

MX Spin-selective DQ-SQ spectra of AMX spin system

$J_{AX} = 4.2$ Hz,
$J_{MX} = 11.2$ Hz
$J_{AM} = -10.1$ Hz

Now, we will go to MX spin selective DQ-SQ. When I do the MX selective DQ SQ, very interesting thing happens. I am doing MX DQ. Now, what is the passive spin? It is A. So, what are the passive couplings here? JAX and JAM. This is the double quantum dimension. I have tilt of the displacement we have taken. Now, alpha and beta component gets separated out because of the spin state selection. I can get this correspond to alpha spin state. This corresponds to beta spin state. Fine, these are the 2 cross sections. But, look at the cross section. This is tilted this way. This is tilted this way. What does it mean? The passive couplings AM and AX are opposite in signs. This is what I am going to tell you. These are the passive couplings. These two passive couplings here JAM and JAX are opposite in signs.

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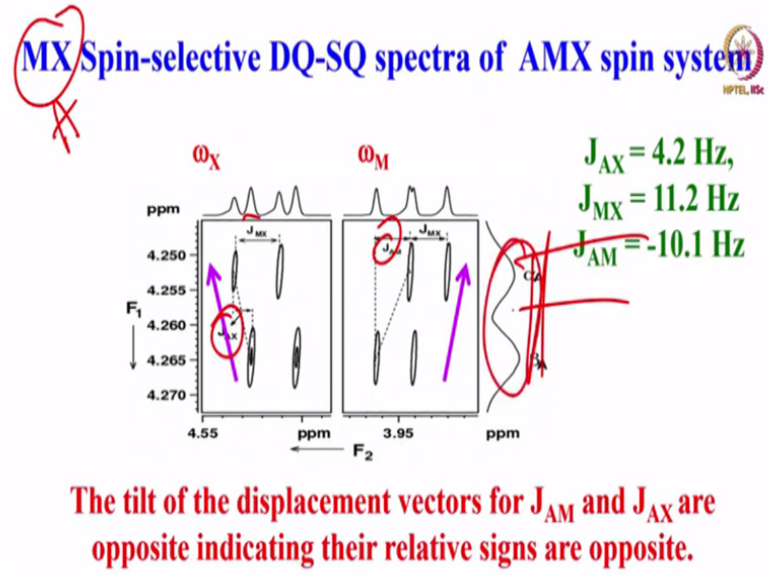

MX Spin-selective DQ-SQ spectra of AMX spin system

$J_{AX} = 4.2$ Hz,
$J_{MX} = 11.2$ Hz
$J_{AM} = -10.1$ Hz

The tilt of the displacement vectors for J_{AM} and J_{AX} are opposite indicating their relative signs are opposite.

Earlier DQ expt both couplings were with similar signs. Now, use this logic. Tilt of the displacement are different, when they are opposite.

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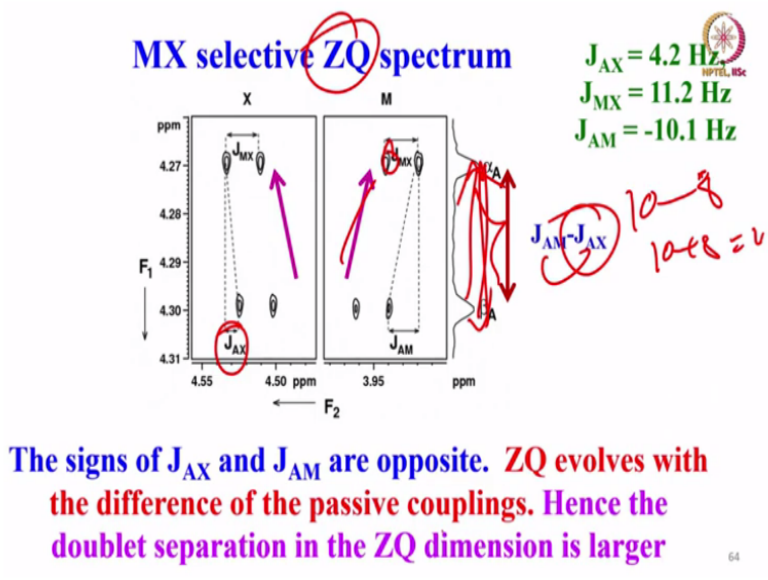

MX selective ZQ spectrum

$J_{AX} = 4.2$ Hz
$J_{MX} = 11.2$ Hz
$J_{AM} = -10.1$ Hz

The signs of J_{AX} and J_{AM} are opposite. ZQ evolves with the difference of the passive couplings. Hence the doublet separation in the ZQ dimension is larger

Now, confirm that by doing zero quantum. When you do the zero quantum, what will happen? See, look at this one. This separation is smaller. MX double quantum. On the other hand, do MX zero quantum, the separation increased. How can it happen? I have been always telling you zero quantum evolves as the difference of the couplings. But if that was a difference, then it should have reduced further. The separation should have become smaller. Instead of 10 minus 8 if I take, this should have become 2 Hz. In the double quantum, it will become 10 + 8 Hz. It will become 18 hertz. Here, it is only 2 hertz. But, on the other hand, it has become more than the double quantum. How it can happen? This can happen only when one of the couplings is negative. That is what we observed.

One of the coupling if it is negative, because of opposite signs JMX and JAX which are opposite in signs, instead of subtracting, they are adding up. This is the reason why the separation becomes larger. So, now, whatever we observed in the double quantum we have confirmed with zero quantum. And, we say these two signs, JMX and JAX are opposite in signs.

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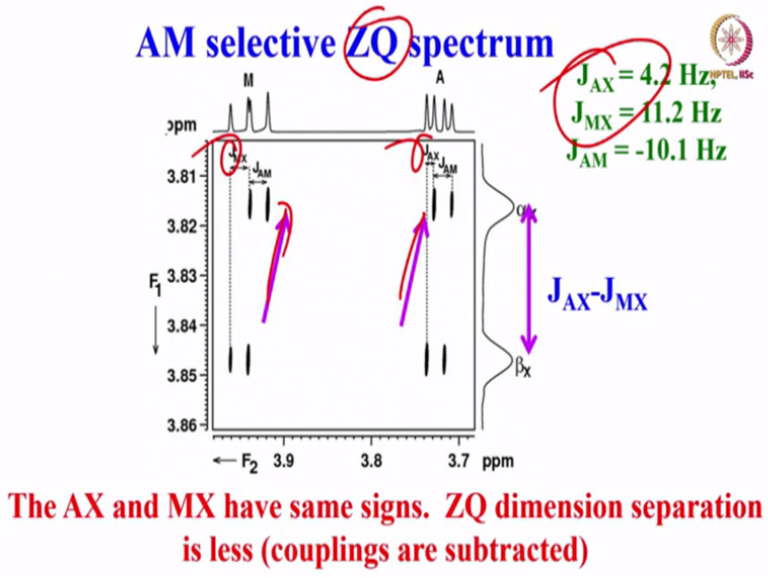

AM selective ZQ spectrum

$J_{AX} = 4.2$ Hz,
$J_{MX} = 11.2$ Hz
$J_{AM} = -10.1$ Hz

The AX and MX have same signs. ZQ dimension separation is less (couplings are subtracted)

So, we can find out AM selective ZQ-SQ I can do. Again, you can see these two are tilted in the same direction. This tells me MX and AX have the same signs.

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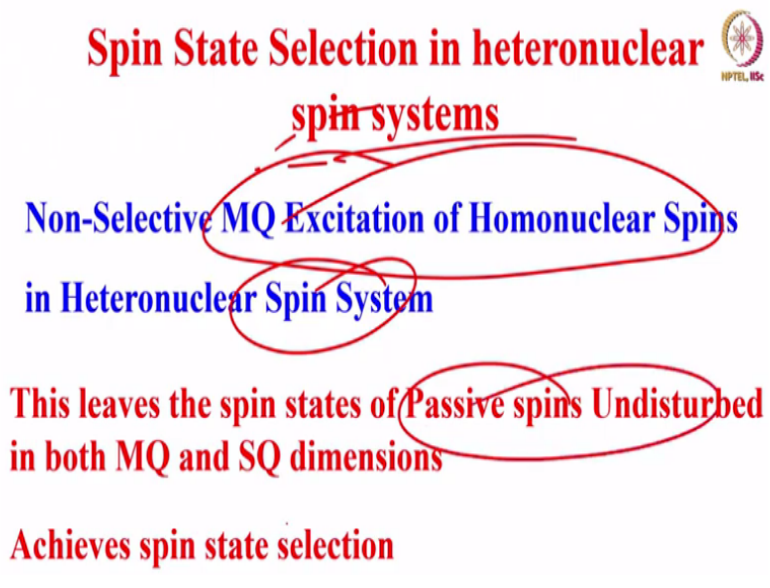

Spin State Selection in heteronuclear spin systems

Non-Selective MQ Excitation of Homonuclear Spins in Heteronuclear Spin System

This leaves the spin states of Passive spins Undisturbed in both MQ and SQ dimensions

Achieves spin state selection

So, spin state selective detection, because of this, now, what we did, we go back and then use this logic and find out more in this nonselective case. The non-selective DQ we saw this spectrum you know. Here why it is a doublet? Now, it is AX double quantum. So, JAM and JMX are the couplings. Now, they must be opposite in signs. Look at it, JAM and JMX. They are nearly of equal strength, 11.2 and minus 10. Approximately, they are coming closer. That is the reason it was nullifying. The separation reduced or almost coming close to 0. That is why it appears like a singlet, because the signs are opposite. So, we could find out the relative signs of the couplings by using selective detection of double quantum in this case.

So, now, we will go to another example of a spin state selection in a heteronuclear spin system. What happens if I see the heteronuclear case?

Heteronuclear case, you do not have to do selective excitation. Simply, nonselective excitation of homonuclear spins you do, the heteronuclear spin which is present, it will not be disturbed at all. We do not touch it at all. Then, that spin states remains unaltered both in the multiple quantum dimension and also in the single quantum dimension; that pertains to spin state selection of the heteronuclear spin. So, that is the idea. This gives rise to spin state, because the spin state of the passive heteronuclear spin remains unaltered.

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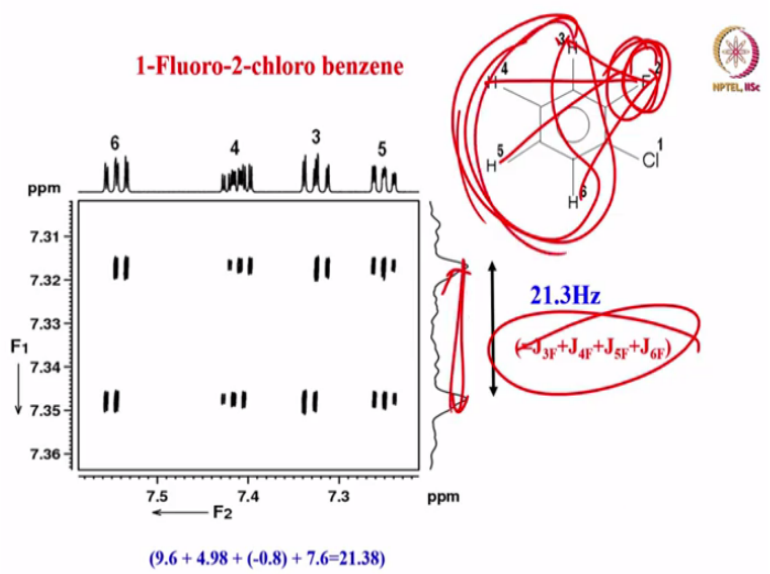

1-Fluoro-2-chloro benzene

21.3Hz

$(J_{3F}+J_{4F}+J_{5F}+J_{6F})$

(9.6 + 4.98 + (-0.8) + 7.6=21.38)

Let us look at the example of this one, this is 1-fluoro-2-chloro benzene. Now, I am looking at the 4th quantum of 4 protons here. Now, what is the passive spin here? Passive spin is fluorine. When you do the 4th quantum; now, I am numbering it as 3, 4, 5 and 6. 4th quantum will give me a single peak. All 4 protons are simultaneously flipping from alpha alpha alpha alpha to beta beta beta beta.

Now, this passive spin splits that singlet into a doublet. Fine, so, this is a doublet. What does the separation of this doublet correspond to? It is the sum of 23, 24, 25 and 26 couplings. Coupling of this fluorine with all the 4 protons together gives rise to this separation. You measure that. It turns out to be this value.

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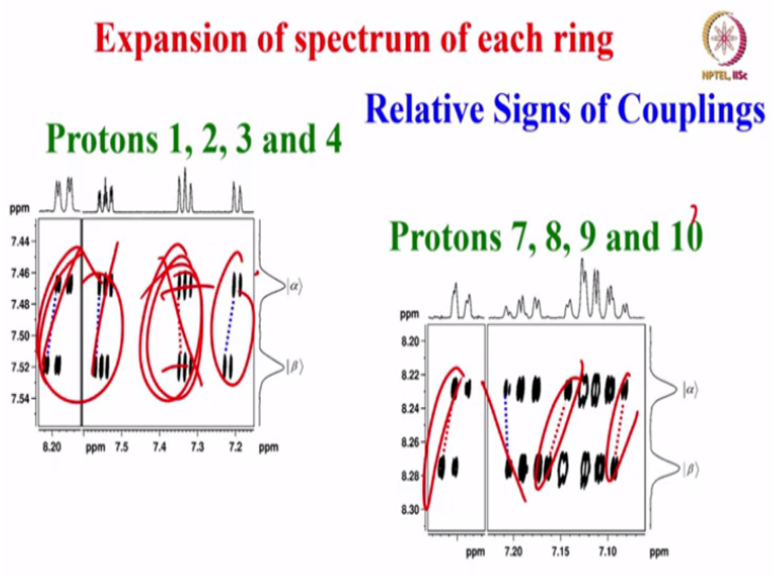

Expansion of spectrum of each ring

Relative Signs of Couplings

Protons 1, 2, 3 and 4

Protons 7, 8, 9 and 10

And then, you can find out that direction of the displacement also. Look at it. This is in this direction. This is in this direction, whereas this is in the opposite direction. So, measure the coupling from the displacement vectors and find out. If all these 3 are positive, this is negative. If all these 3 are negative, this is positive. You can get the relative signs of the couplings here. Same way in the other ring also.

In the other one, you can find out this is negative in this direction. This is like this direction whereas this is in the opposite direction. This is for a different molecule. You understand this is how we can find out the relative signs of the coupling between proton and any other heteronuclear spin.

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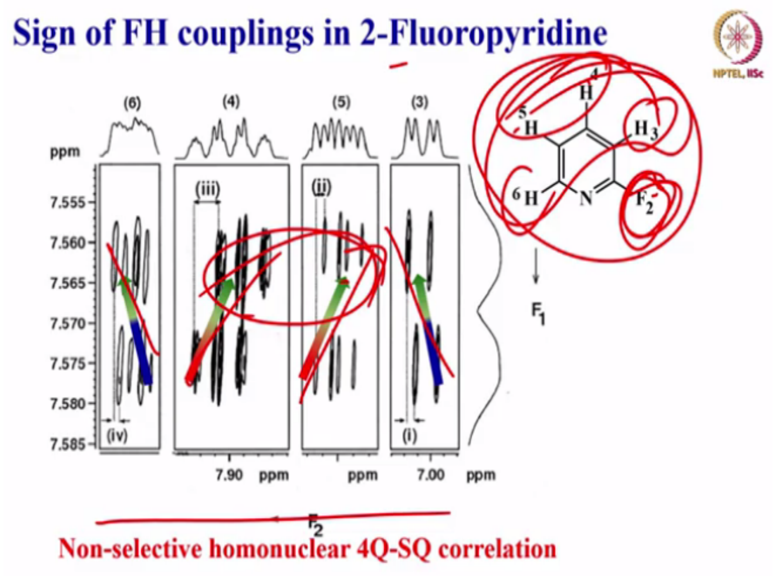

Sign of FH couplings in 2-Fluoropyridine

Non-selective homonuclear 4Q-SQ correlation

This, so, this is a simple example. If you consider now 2-fluoropyridine, fluorine is heteronuclear spin. Do the 4th quantum of pyridine here. You have got 4 protons, in the single quantum dimension. In the double quantum dimension, you can see this is tilted this way. This is tilted this way. Whereas, these 2 are tilted this way. If the signs of these two couplings heteronuclear couplings, that is sign of these protons 4 and 5 coupling with fluorine are opposite in signs compared to signs of 3 and 6 proton couplings with fluorine. This what you can get the information about relative signs of FH couplings, that is, heteronuclear couplings by doing the homonuclear non-selective excitation of the highest quantum available here.

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Spin System Filtering

So, spin system filtering, I will take in the next class. I will discuss that in the next class, the spin system filtering. And then, that will be just for 15 to 20 minutes, I do not know. I will try to cover it faster. Then, we will go to a different topic, altogether a different topic. So far, we were discussing about the solution state NMR. And, the techniques we adopt in solution state NMR and in the solid-state NMR are different slightly different. And, the interaction parameters present in solids are different than in liquids. But then, how to get a liquid like spectrum in case of solid. It is a different methodology. So, we will discuss solid state also later. In the next class, as much as possible, I will try to cover. If not, it does not matter in the remaining period, we will have enough time to discuss solid state NMR. But, what I was trying to tell you so far is the multiple quantum NMR, the varieties of things we discussed. One of the utilities we saw in this class is the determination of the relative signs of the couplings. We took the example of 3 coupled spins. You can have a non-selective excitation of all the 3 double quantum AM, AX and MX or selective excitation of DQ. Also the selective excitation of 3 zero quantum or non-selective excitation of all the 3 at a time is also possible, for both double quantum and zero quantum.

And, we observed very interestingly depending upon the splitting separations in the DQ dimension and ZQ dimension, because of the coupling between the active spins and the passive spins, we measured the separation. And we understood, what is the relative signs of the couplings. What we detected from the DQ was confirmed from the ZQ also. That is a very interesting thing we observed.

So, the relative signs of the couplings we could get by using multiple quantum NMR. So, how we do multiple quantum NMR also I showed you. It is a simple 3 pulse experiment for a homonuclear case we have a echo sequence to prevent the chemical shift to evolution and only J couplings will evolve. And then, the second pulse converts into multiple quantum. And, the last pulse converts this antiphase in to detectable coherence.

That is what we are going to detect. And, the spectrum represented as a multiple quantum to a single quantum correlation spectrum. If it is a double quantum, it is a DQ-SQ correlation. If it is a 4th quantum, it is 4Q-SQ correlation. If it is a triple quantum, it is 3Q-SQ correlation, like that. In the indirect dimension it was the highest quantum and direct dimension is the single quantum. That is what we discussed today. So, I will stop here. In the next class, I will try to discuss about the spin system filtering, one more important application. And then, we will switch over to altogether a different topic, solid state NMR. Thank you very much.