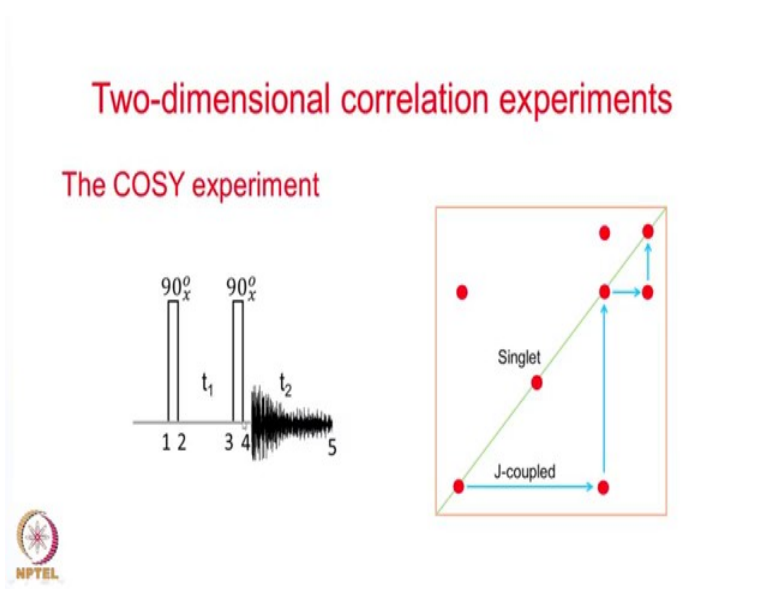


**NMR Spectroscopy for Chemists and Biologists**  
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**Lecture 46**  
**Two Dimensional Correlation Experiments-2**

We have been discussing 2-dimensional correlation experiments. This was the COSY experiment was the first experiment we developed and that is the most fundamental of all of this correlation experiments. Let us do a quick recap of what we did in the last class.

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This is the pulse sequence of the COSY experiment which is very simple, consists of 2 pulses  $90^\circ_x$  then the  $t_1$  period then  $90^\circ_x$  then the  $t_2$  period. So,  $t_1$  is one independent time variable which is systematically incremented from one experiment to another experiment and  $t_2$  is the time period which is the acquisition period where you actually collect the data. 2-dimensional Fourier transformation of such a data results in a spectrum which looks like this.

So we have these peaks along the diagonal which are called as the diagonal peaks, you have one frequency axis this is called the  $F_2$  axis or this is the  $F_1$  axis and on the diagonal  $F_1$  is equal to  $F_2$

so therefore it is called the diagonal and we have cross peaks here arising because between two spins which are J coupled. So, this is the extremely useful part of the COSY experiment. So it displays correlation between J coupled spins. So if you have a molecule which has such kind of a network that this spin is coupled to this spin then it will produce a cross peak here and this spin is coupled to this spin and this will produce a cross peak here.

And this will appear symmetrically and if there are singlets that means which they are not coupled with anybody there they lie as singlets here on the diagonal. Notice here that this period which is given as small gap here, this gap is really 0. It is not really a gap. This has been given here in this figure simply to accommodate this number 4 which is the time point we have indicated here this various time points 1, 2, 3, 4 for the purpose of evaluation of the product operators at different time points through the pulse sequence.

So, it is just for that purpose otherwise this gap is actually 0. It is just minimum required to see the effects of transmitter on the receiver directly. The transmitter is put off and the receiver is on there is to be no direct interference between the transmitter and the receiver. Only that much gap is given which is of the order of few microseconds sometimes, okay.


So therefore this is not really long time gap and starting looking at the theory of this. How these diagonal peaks arise? How the cross peaks arise? What are their structures? And that is we did part of that in the last class.

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$$\rho_4 (\text{observable}) = -[I_{kx} \cos \pi J_{kl} t_1 - 2I_{kz} I_{ly} \sin \pi J_{kl} t_1] \sin \omega_k t_1$$

The first (diagonal peak) term,

$$\begin{aligned} \rho_{5d}' &= \{ [I_{kx} \cos \pi J_{kl} t_2 + 2I_{ky} I_{lz} \sin \pi J_{kl} t_2] \cos \omega_k t_2 \\ &+ [I_{ky} \cos \pi J_{kl} t_2 - 2I_{kx} I_{lz} \sin \pi J_{kl} t_2] \sin \omega_k t_2 \} f_d(t_1) \end{aligned}$$

$$f_d(t_1) = \cos \pi J_{kl} t_1 \sin \omega_k t_1$$


So we calculated the density operator and at different time points and then we arrived at this point 4 and that density operator is called  $\rho_4$ . It had 2 parts, one was non-observable other one was an observable part. Non-observable part we have just ignored here and only the observable part is written here. Observable, non-observable arises because of what? Because the trace of  $I_{kx}$  or  $I_{ky}$  operators this has to be non-zero with the density operator.

If you measure the  $x$ -magnetization you take the  $I_{kx}$  operator. If we take the  $y$ -magnetization then take the  $I_{ky}$  operator. So whichever way, so this was the calculation which was arrived at starting from the  $k$  spin magnetization to begin with. Similar things will appear when you start from the  $l$ -magnetization also but it is enough to demonstrate taking the  $k$ -spin alone.

So therefore and we calculated the density operator at point 4 and that is  $\rho_4$ ,

$$\begin{aligned} \rho_4 (\text{observable}) &= -[I_{kx} \cos \pi J_{kl} t_1 - 2I_{kz} I_{ly} \sin \pi J_{kl} t_1] \sin \omega_k t_1 \end{aligned}$$

So this is the  $x$ -magnetization of the  $k$ -spin and you see here is the  $y$ -magnetization of the  $l$  spin which is anti-phase with respect to  $k$ . Whereas here is the in phase magnetization of the  $k$  spin and this is the anti-phase magnetization of the  $l$  spin and this is responsible for the cross peak.

Because in the evolution period the  $t_1$  period the  $k$  spin was evolving with its characteristic frequency  $\omega_k$  and that appears as  $\sin \omega_k t_1$  here and eventually this during the  $t_2$  period this will evolve with the frequency of  $l$  and this will evolve with the frequency of  $k$ . Therefore, this one will produce the diagonal peak in the end and this term will produce the cross peak in the end and we started actually calculating the evolution in  $t_2$  taking the first term which will produce the diagonal peak.

So what is the fine structure in the diagonal peak? Does it have a fine structure? So we started calculating that. So If I were to represent the part of the density operator which belongs to the diagonal peak so I call it as  $\rho_{5d}'$  and this is during the acquisition period and that one comes as a result of evolution of this part of the density operator here. So this is

$$\begin{aligned} \rho_{5d}' &= \{ [I_{kx} \cos \pi J_{kl} t_2 + 2I_{ky} I_{lz} \sin \pi J_{kl} t_2] \cos \omega_k t_2 \\ &+ [I_{ky} \cos \pi J_{kl} t_2 - 2I_{kx} I_{lz} \sin \pi J_{kl} t_2] \sin \omega_k t_2 \} f_d(t_1) \end{aligned}$$

This comes as result of evolution of the  $I_{kx}$  operator first under the influence of the chemical shift Hamiltonian that gives you the  $\cos \omega_k$  and  $\sin \omega_k$  here and then under the influence of the coupling Hamiltonian that use the terms which are in the interior brackets here. So  $I_{kx}$  term will give you these terms,  $I_{ky}$  term gives you these terms as a result of coupling evolution during the period time  $t_2$ .

And this is the one which is present here, the  $t_1$  evolution controversial  $f_d(t_1)$  is

$$f_d(t_1) = \cos \pi J_{kl} t_1 \sin \omega_k t_1$$

So now if you look at this in little bit more detail if you assume we can choose one of these to say okay we are going to get or record  $y$  magnetization or the  $x$  magnetization. So you can choose one of those if for demonstrating the principles, okay.

Now if you see either case if I take this, so I have here cosine-cosine and here I have take those and this one using cosine sine, okay in the  $t_2$  period, cosine-cosine and this is cosine sin in  $ky$   $lz$ , okay. Now out of these terms, these terms are not observable because this is anti-phase

magnetization and anti-phase magnetization is not observable. Therefore what we will be restricted to only this or this, okay.

So assuming that we record the  $y$  magnetization then we will only have this particular term  $I_{ky} \cos \pi J_{kl} t_1 \sin \omega_k t_2 \cdot f_d(t_1)$  and  $f_d(t_1) = \cos \pi J_{kl} t_1 \sin \omega_k t_1$ . So now if you expand this further as separate frequencies what this gives you?  $\omega_k$  and  $\pi J_{kl} \cos \pi J_{kl} t_2 \sin \omega_k t_2$ . This will produce you two sin terms with the frequencies at  $\omega_k + \sin \pi J_{kl}$  and another sine term with  $\omega_k - \pi J_{kl}$  in  $t_2$ .


And similarly, in the  $t_1$  period also if you take the fully transformation of this one, this will produce you two frequencies  $\omega_k + \pi J_{kl}$  along  $t_1$  and  $\omega_k - \pi J_{kl}$  along  $t_1$  which means after Fourier transformation you will get those frequencies in your spectrum along  $F_1$  axis. These ones you will get them along the  $F_2$  axis.

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This contributes to the detected FID.

Two-dimensional real Fourier transformation along the  $t_1$  and  $t_2$  dimensions leads to four peaks with dispersive line-shapes at the following frequencies (Hz).

$(F_1, F_2) = \left[ \left( \nu_k + \frac{J_{kl}}{2} \right), \left( \nu_k + \frac{J_{kl}}{2} \right) \right];$	positive, dispersive
$\left[ \left( \nu_k + \frac{J_{kl}}{2} \right), \left( \nu_k - \frac{J_{kl}}{2} \right) \right];$	positive, dispersive
$\left[ \left( \nu_k - \frac{J_{kl}}{2} \right), \left( \nu_k + \frac{J_{kl}}{2} \right) \right];$	positive, dispersive
$\left[ \left( \nu_k - \frac{J_{kl}}{2} \right), \left( \nu_k - \frac{J_{kl}}{2} \right) \right]$	positive, dispersive



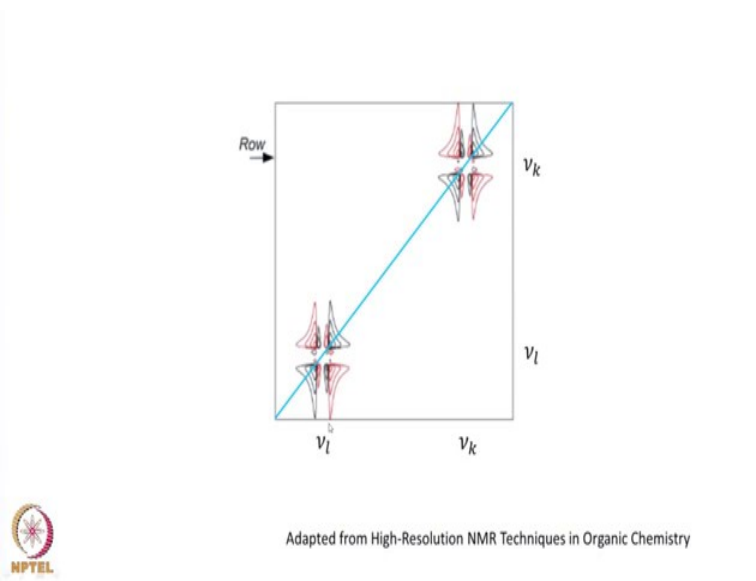
So this is represented here. So you will get a total of 4 peaks after real Fourier transformation along the  $t_1$  and the  $t_2$  dimension leads to 4 peaks with dispersive line shapes at the following frequencies. Why did we say dispersive line shapes? Because they were sin terms. The sin terms as we have seen before will give you dispersive line shapes and the frequencies that are present

are  $\left( \nu_k + \frac{J_{kl}}{2} \right)$  and now that is written in terms of hertz not in terms of the radians.

So the  $2\pi$  part has been taken out, so it is  $\omega_k + \pi J_{kl}$  is the same as  $2\pi \left( \nu_k + \frac{J_{kl}}{2} \right)$ . So the  $\nu_k$  is  $2\pi$  is taken out here. So you have here  $\left( \nu_k + \frac{J_{kl}}{2} \right)$  along the  $t_1$  and  $\left( \nu_k + \frac{J_{kl}}{2} \right)$  along the  $t_2$ . So this is a positive peak and you will have the dispersive line shape and this one is  $\left( \nu_k - \frac{J_{kl}}{2} \right)$  along the  $t_1$  and  $\left( \nu_k - \frac{J_{kl}}{2} \right)$  along the  $t_2$  and this will again be positive and dispersive line shape.

And then you will have correspondingly for the  $\left( \nu_k - \frac{J_{kl}}{2} \right)$  along the  $t_1$  and  $\left( \nu_k + \frac{J_{kl}}{2} \right)$  along the  $t_2$  positive dispersive and finally  $\left( \nu_l - \frac{J_{kl}}{2} \right)$  and  $\left( \nu_l - \frac{J_{kl}}{2} \right)$ . which is also positive and has a dispersive line shape.

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So, you get 4 peaks along the diagonal and we say this will produce peaks like this and these are the 4 peaks which are present originating from the  $k$  spin as we started calculation from the  $k$  spin. Similarly, we will also get 4 peaks from the  $l$  spin if you started calculation from the  $l$  spin

magnetization to begin with. So all of these are dispersive line shapes and all of them have the same sign, okay.

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The second (cross-peak) term in  $\rho_4$ ,


$$2I_{kz}I_{ly} \sin(\pi J_{kl}t_1) \sin \omega_k t_1$$

Here let us consider the J-evolution first. This leads to the density operator  $\rho_{5c}$ ,

$$\rho_{5c} = [2I_{kz}I_{ly} \cos \pi J_{kl}t_2 - I_{lx} \sin \pi J_{kl}t_2] f_c(t_1)$$

$$f_c(t_1) = \sin \pi J_{kl}t_1 \sin \omega_k t_1$$

Next, considering shift evolution, we get  $\rho_{5c}'$  as,

$$\rho_{5c}' = \{2I_{kz}[I_{ly} \cos \omega_l t_2 - I_{lx} \sin \omega_l t_2] \cos \pi J_{kl}t_2 - [I_{lx} \cos \omega_l t_2 + I_{ly} \sin \omega_l t_2] \sin \pi J_{kl}t_2\} f_c(t_1)$$


So now we continue with the discussion for the other term that density operator which was the second term in the  $\rho_4$  density operator and that was

$$2I_{kz}I_{ly} \sin(\pi J_{kl}t_1) \sin \omega_k t_1$$

This was the second term in your  $\rho_4$  density operator. Now, what we do here is now we have to evolve this term in the  $t_2$  time period. So in this case we shall evolve the  $J$  first under the influence of the  $J$  coupling we will evolve this operator. So I will call this as  $\rho_{5c}$  and I get here

$$\rho_{5c} = [2I_{kz}I_{ly} \cos \pi J_{kl}t_2 - I_{lx} \sin \pi J_{kl}t_2] f_c(t_1)$$

$$f_c(t_1) = \sin \pi J_{kl}t_1 \sin \omega_k t_1$$


and then after this  $J$  evolution we can see that the shift evolution, okay. So each one of these terms will evolve under the chemical shift. So, this means the  $\rho_{5c}'$  and that I write it here as

$$\begin{aligned} & \rho_{5c}' \\ &= \{2I_{kz}[I_{ly} \cos \omega_l t_2 - I_{lx} \sin \omega_l t_2] \cos \pi J_{kl} t_2 \\ & - [I_{lx} \cos \omega_l t_2 + I_{ly} \sin \omega_l t_2] \sin \pi J_{kl} t_2\} f_c(t_1) \end{aligned}$$

So this is the one inside the bracket is due to the evolution under the chemical shift.

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Assuming that we measure the y-magnetization the observable signal is given by  $\text{Tr}[\rho_{5c}' I_{ly}]$ ,

$$\begin{aligned} \text{Tr}[\rho_{5c}' I_{ly}] &= \sin \omega_l t_2 \sin \pi J_{kl} t_2 \sin \omega_k t_1 \sin \pi J_{kl} t_1 \\ &= \frac{1}{4} [\cos(\omega_k + \pi J_{kl}) t_1 - \cos(\omega_k - \pi J_{kl}) t_1] \cdot [\cos(\omega_l + \pi J_{kl}) t_2 - \cos(\omega_l - \pi J_{kl}) t_2] \\ &\quad + \cos(\omega_k + \pi J_{kl}) t_1 \cdot \cos(\omega_l + \pi J_{kl}) t_2 \\ &\quad - \cos(\omega_k + \pi J_{kl}) t_1 \cdot \cos(\omega_l - \pi J_{kl}) t_2 \\ &\quad - \cos(\omega_k - \pi J_{kl}) t_1 \cdot \cos(\omega_l + \pi J_{kl}) t_2 \\ &\quad + \cos(\omega_k - \pi J_{kl}) t_1 \cdot \cos(\omega_l - \pi J_{kl}) t_2 \end{aligned}$$


Okay, now assuming that we measure the y magnetization observable signal is given by trace of  $\rho_{5c}' I_{ly}$  okay. So, we get here because we are taking l spin magnetization in the we are looking at the cross peak, okay. So this gives me

$$\text{Tr}[\rho_{5c}' I_{ly}] = \sin \omega_l t_2 \sin \pi J_{kl} t_2 \sin \omega_k t_1 \sin \pi J_{kl} t_1$$

So if you see there are 4 terms here, this into this, this into this, this into this and this into this. So because of this minus signs here we do get combinations of positive, negative peaks here. So this into this gives me

$$= \frac{1}{4} [\cos(\omega_k + \pi J_{kl}) t_1 - \cos(\omega_k - \pi J_{kl}) t_1] \cdot [\cos(\omega_l + \pi J_{kl}) t_2 - \cos(\omega_l - \pi J_{kl}) t_2]$$

Then finally this into this gives me



$$\begin{aligned}
& +\cos(\omega_k + \pi J_{kl})t_1 \cdot \cos(\omega_l + \pi J_{kl})t_2 \\
& -\cos(\omega_k + \pi J_{kl})t_1 \cdot \cos(\omega_l - \pi J_{kl})t_2 \\
& -\cos(\omega_k - \pi J_{kl})t_1 \cdot \cos(\omega_l + \pi J_{kl})t_2 \\
& +\cos(\omega_k - \pi J_{kl})t_1 \cdot \cos(\omega_l - \pi J_{kl})t_2
\end{aligned}$$


So after 2 dimensional Fourier transformation each one of this will produce a peak. So therefore where will these peaks appear along the  $F_1$  dimension? This will be at  $\omega_k + \pi J_{kl}$  and along the  $F_2$  dimension it will be  $\omega_l + \pi J_{kl}$ , okay and this will have a plus sign and this one will produce me a peak at  $\omega_k + \pi J_{kl}$  and  $\omega_k - \pi J_{kl}$  and this will have a negative sign, okay.

And this term will again be negative in sign and this will be at  $\omega_k - \pi J_{kl}$  and  $\omega_l + \pi J_{kl}$  along the  $F_1$  and  $F_2$  dimensions. Finally this will be again positive and this will appear at  $\omega_k - \pi J_{kl}$  along  $F_1$  and  $\omega_l - \pi J_{kl}$  along  $F_2$ .

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This leads to four absorptive peaks at the following coordinates.

$(F_1, F_2) = \left[ \left( \nu_k + \frac{J_{kl}}{2} \right), \left( \nu_l + \frac{J_{kl}}{2} \right) \right];$	positive, absorptive
$\left[ \left( \nu_k + \frac{J_{kl}}{2} \right), \left( \nu_l - \frac{J_{kl}}{2} \right) \right];$	negative, absorptive
$\left[ \left( \nu_k - \frac{J_{kl}}{2} \right), \left( \nu_l + \frac{J_{kl}}{2} \right) \right]$	negative, absorptive
$\left[ \left( \nu_k - \frac{J_{kl}}{2} \right), \left( \nu_l - \frac{J_{kl}}{2} \right) \right];$	positive, absorptive



So, therefore this is what is indicated here. This leads to 4 absorptive peaks at the following coordinates. Why did we say absorptive?

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Assuming that we measure the y-magnetization the observable signal is given by  $\text{Tr} [\rho_{5c}' I_{ly}]$ ,

$$\begin{aligned} \text{Tr} [\rho_{5c}' I_{ly}] &= \sin \omega_l t_2 \sin \pi J_{kl} t_2 \sin \omega_k t_1 \sin \pi J_{kl} t_1 \\ &= \frac{1}{4} [\cos(\omega_k + \pi J_{kl}) t_1 - \cos(\omega_k - \pi J_{kl}) t_1] \cdot [\cos(\omega_l + \pi J_{kl}) t_2 - \cos(\omega_l - \pi J_{kl}) t_2] \\ &\quad + \cos(\omega_k + \pi J_{kl}) t_1 \cdot \cos(\omega_l + \pi J_{kl}) t_2 \\ &\quad - \cos(\omega_k + \pi J_{kl}) t_1 \cdot \cos(\omega_l - \pi J_{kl}) t_2 \\ &\quad - \cos(\omega_k - \pi J_{kl}) t_1 \cdot \cos(\omega_l + \pi J_{kl}) t_2 \\ &\quad + \cos(\omega_k - \pi J_{kl}) t_1 \cdot \cos(\omega_l - \pi J_{kl}) t_2 \end{aligned}$$



Because you notice here all of them are cosine terms here.

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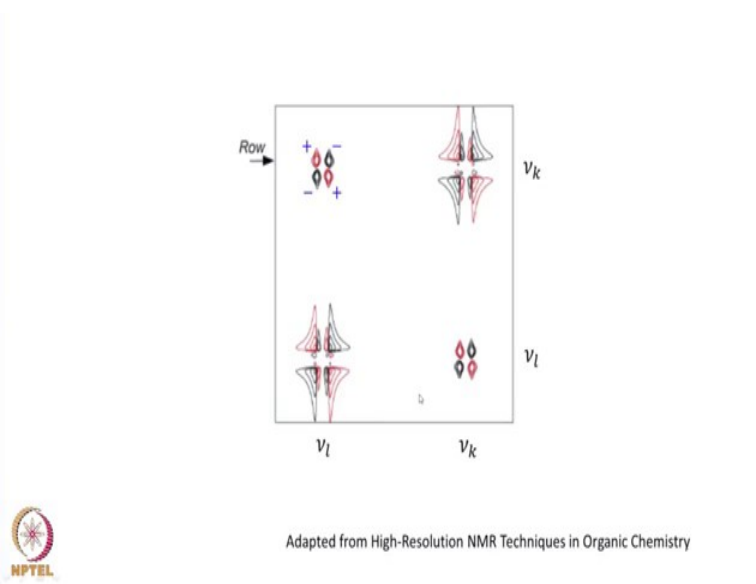
This leads to four absorptive peaks at the following coordinates.

$(F1, F2) = \left[ \left( \nu_k + \frac{J_{kl}}{2} \right), \left( \nu_l + \frac{J_{kl}}{2} \right) \right];$	positive, absorptive
$\left[ \left( \nu_k + \frac{J_{kl}}{2} \right), \left( \nu_l - \frac{J_{kl}}{2} \right) \right];$	negative, absorptive
$\left[ \left( \nu_k - \frac{J_{kl}}{2} \right), \left( \nu_l + \frac{J_{kl}}{2} \right) \right]$	negative, absorptive
$\left[ \left( \nu_k - \frac{J_{kl}}{2} \right), \left( \nu_l - \frac{J_{kl}}{2} \right) \right];$	positive, absorptive



Since, all of them are cosine terms I get absorptive peaks and then the sign are as indicated here. This is positive, this is negative, this is negative and this is positive and all of them are absorptive peaks.

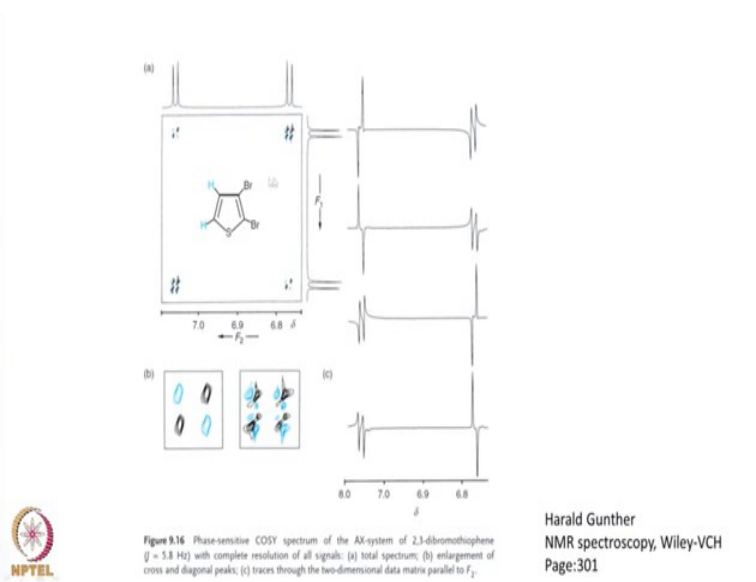
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So, that is indicated here as 4 peaks here. You can see these are the 4 peaks originating from  $k$  spin and this is so called cross peak. So the cross peak has absorptive line shapes in all the 4 components and this is indicated as minus plus, plus minus, okay. This is an important feature of COSY and you will see this is called as the differential transfer because if we look at total integral of this the total sum of this, it is 0. So therefore, there is no net transfer of magnetization, it is called as the differential transfer of magnetization.

This is a coherence transfer is differential in nature and that produces me positive and negative contributions in the cross peak. So this comes from  $k$  spin and similarly if you started from the  $l$  spin again you will get 4 peaks in the cross peak here fine structure, okay.

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Now here is an example, experimental example, you can see this is the molecule what we have. So this is taken from this book Herald Gunther NMR spectroscopy Wiley-VCH and it is directly taken from there. This one has 2 protons, this is an example, this one has 2 protons and therefore this is an ideal AX spin system okay and if you look at 1 dimensional spectrum that is indicated here. This is 2 doublets, okay along the  $F_2$  dimension also 2 doublets,  $F_1$  dimension also 2 doublets. This is one of the spins and this is the second spin.

Now we notice here this is the diagonal peak, this is the cross peak, this is the diagonal peak and this is the cross peak. And you see here all of these have same signs and their dispersive line shape and these ones are absorptive line shapes and different signs. This is indicated more explicitly by taking cross sections here. So you take the cross section at this point that is shown here. So this comes from here so you have a negative positive peak these are absorptive line shapes, okay.

Absorptive line shapes anti-phase in nature. We call this as anti-phase in nature. So you have 2 peaks, the 2 components which are anti-phase in nature you have negative and positive and the 2 peaks which are here you see these ones are dispersive in nature. They are in phase, they have the same sign. So you see this goes negative, positive this is one dispersive component, the other one is again negative positive again dispersive component. These both have the same sign and therefore they go in this manner this is the dispersive line shape.

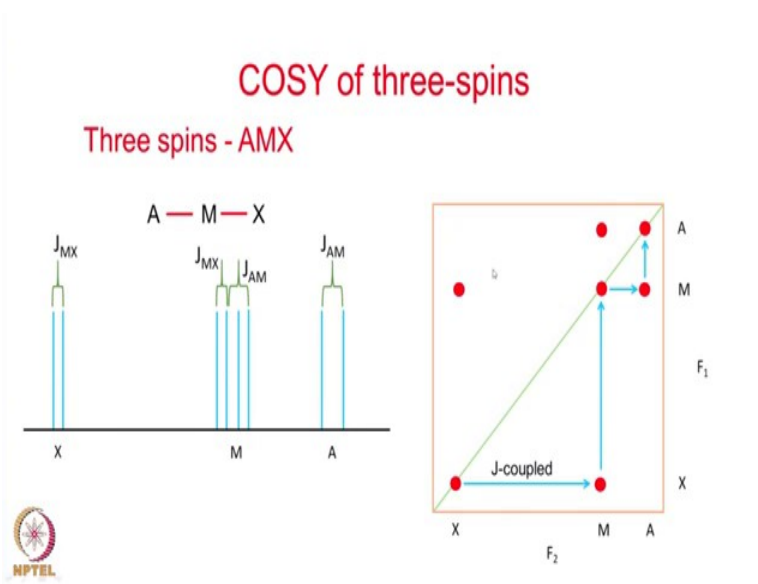
Now you take the next one here, so what was negative here becomes positive. So negative positive, this is positive negative therefore this becomes positive and this one is negative and this goes in this positive-positive fashion once more and then here you have the positive negative and positive negative both have the same sign. So now you come here, this is originating from the  $l$  spin so you have, now the dispersive components here.

So the dispersive components are here in this manner. You have this line shape this is going to dispersive components same phase in nature and the 2 peaks which are present here, they are anti-phase in nature so you have the negative positive going up here and this one is the next component which is present here and that gives you dispersive component in this manner, okay. And these are the absorptive. What was negative here now becomes positive and negative here.

This resolution is quite high, if you see here the cross peaks in all of these components, the cross peaks are very good. The intensity distribution in the 2 components whereas in the diagonal peaks that intensity distribution is not uniform simply because this dispersive peaks have big tails and this tails interfere with the other peak and therefore there is contribution of one peak to the other peak in the eventual appearance of the fine structure of the peak and that is in the contour diagram is indicated here while these are the cross sections.

Now you take the contour diagram of the 4 peaks. This is one of the cross peaks which is here so and therefore you have here this cross peak fine structure. This is the fine structure of the diagonal peak, okay.

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So that was so much for the 2 spins. We can extend of course all your molecule not only 2 spins there will be more than 2 spins and there can be 3 spins. So, what happens if there is a 3 spin? So, there are different spins of course different complexities will be there depending upon the nature of the coupling network of the spin system. So here if I take 3 spins I can call them as *AMX*, okay.

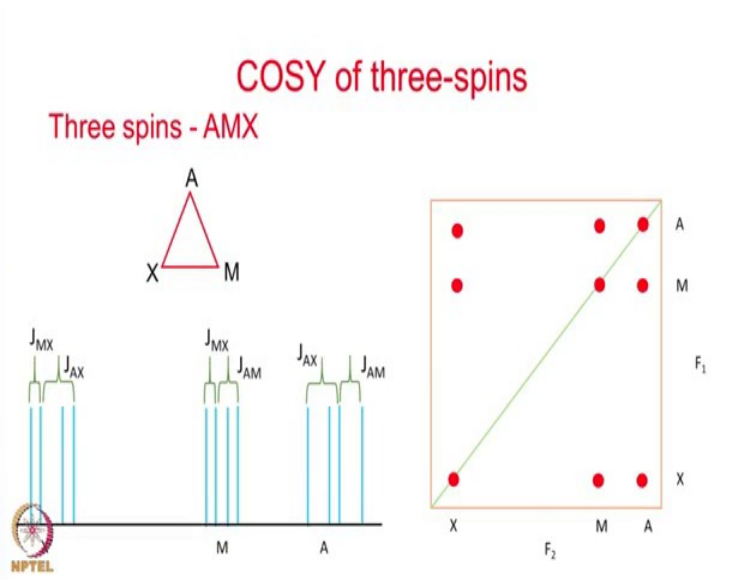
There are different ways the spins can be coupled if the geometry of this coupling is like this, that suppose this is a linear 3 spin system then you have the *A* here, *M* here and *X* here. So the *A* spin is coupled to the *M* spin, *M* spin is coupled to the *X* spin but there is no *A* to *X* coupling. So how will the 1 dimensional spectrum of this look like? We have just shown it by stick diagram so you see and with different coupling constants. They cannot have different coupling constants.

So *A* spin will be a doublet because of coupling to the *M* spin and that is indicated as a doublet here okay and the *M* spin will be a doublet of a doublet because it has 2 couplings. So it has one coupling due to the *A* spin and the other coupling due to the *X* spin that is indicated here. So, this coupling is the *MX* coupling and then from here to here is the *AM* coupling this coupling has to be the same as this. So this is the *AM* coupling, this is the *MX* coupling.

Likewise the *X* spin has the coupling due to the *M* and this coupling appears here as  $J_{MX}$  and therefore we have here a doublet of the *X* spin. So therefore this what sort of COSY spectrum you expect here in a schematic. So we will have the *AMX*, so *A* will produce a peak to the *M*

spin. So this is the  $AM$  cross peak and the  $M$  will produce a peak to the  $X$  spin cross peak and this is the  $MX$  cross peak and this symmetrically appearing here, here as well as there and all of these will have fine structures in case of the 2 spins.

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Okay, suppose we have a 3 spin which is the coupling network is like this. This is the triangle. So  $A$  coupled to  $X$ ,  $A$  is coupled to  $M$  and  $M$  is coupled to  $X$  as well. Therefore, each one of them has 2 couplings, therefore each one of them will be doublet of a doublet, okay. So there are 4 lines for each one of those and these 4 structures of individual spins is indicated here. The  $A$  spin now has a doublet of a doublet, the one spin is the  $AX$  coupling.

Here the  $AX$  coupling is assumed to be larger than  $AM$  coupling, therefore from here to here it is  $AX$  from here to here is the  $AM$  coupling and the  $M$  spin has the  $MX$  coupling and the  $AM$  coupling. Here the  $AM$  coupling is assumed to be larger than the  $MX$  coupling, therefore this one is like this and this one is like this. Ofcourse these structures can change depending upon the relative magnitudes of the coupling constants.

So, now the  $X$  spin likewise has  $MX$  coupling here. Notice this coupling has to be same what is present here okay and the  $AX$  coupling ofcourse appears here as well and appears here. Therefore this coupling has to be the same as this  $AX$  coupling here. So when we put that together so all of these things look different in their fine structures. Now in the 2 dimensional spectrum ofcourse in

the schematic you have here the correlations showing up as  $A$  to  $M$  and then you have  $A$  to  $X$  as well, okay.

And then you have from the  $M$  you have  $M$  to  $X$  and ofcourse the  $M$  to  $A$ , so therefore you have this complete plane full. You have all the couplings are displayed in the form of cross peaks. So this will enable you to identify what sort of a network of couple spins we might have, okay. So, let me just repeat this feature once more that for the case of 3 spins we will have the fine structures in the individual peaks.

This we will discuss later but at the moment it is sufficient to note that you have a network of couple spins and this network of couple spins will be displayed in the form of cross peaks appropriately depending upon the nature of the couplings we might have. And the fine structure will be present in each of these diagonal peaks as well as in the cross peaks and the features of these we can see in the next class. So, I think we can stop here.

Just to recap what we did here we looked at the fine structures of the diagonal peak and we explained how the diagonal peak has dispersive character of and in-phase character and the cross peaks have absorptive character and anti-phase character in case of the 2 spins. The similar thing will happen for the 3 spin as well that we will see in the next class and these fine structure calculations we did explicitly using the product operator formalism which is extremely useful in defining what sort of frequencies will appear? What will be the line shapes and what will be the advantages and disadvantages of this we will see in the next class. So, I think we will stop here, we will continue in the next class.