One and Two Dimensional NMR Spectroscopy for Chemist
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Lecture - 30
Analysis of Strongly coupled spin systems

Welcome back. So we will continue with our discussion on spin system nomenclature; that is what is called well known Pople nomenclature. Remember in the last class we discussed a simple two spins, which are weakly coupled; which are identified as A and X. AX spin system in the NMR jargon in the Pople nomenclature are weakly coupled, because remember I have been telling you that;

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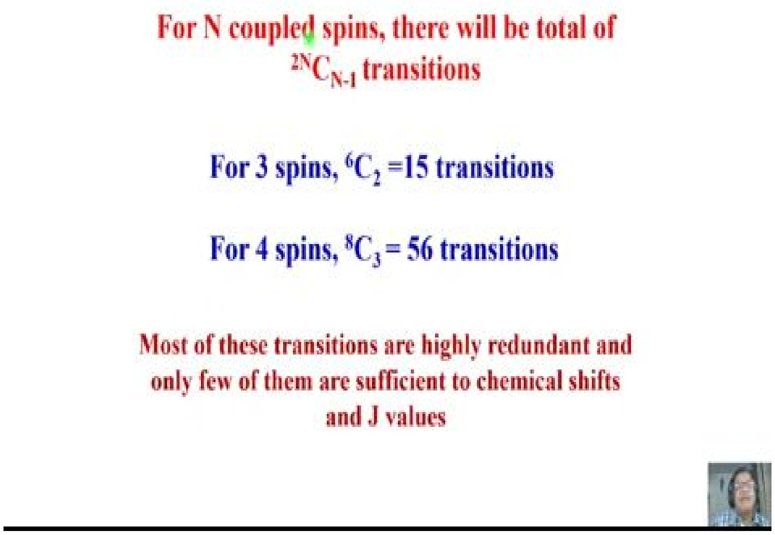

For N coupled spins, there will be total of $^{2N}C_{N-1}$ transitions

For 3 spins, $^{6}C_{2}$ =15 transitions

For 4 spins, $^{8}C_{3}$ = 56 transitions

Most of these transitions are highly redundant and only few of them are sufficient to chemical shifts and J values

A and X are far away separated in the alphabet order, that means the chemical shift separation between them is quite large, compared to the J coupling between them. As a consequence, such systems are weakly coupled. Weakly coupled are represented like this. A two spin example of AX, which is weakly coupled, we worked out and we saw that the chemical shifts are far away separated; and we know the two states, we calculated even the eigenvalues of each of the spin states, found out the frequency separations.

And we got, each spin is split into a doublet and whose frequency separations correspond to coupling between them, called JAX and the center of each doublet gives you corresponding chemical shift for the two protons. And also I said, in the weakly coupled case, the intensity ratio is 1 : 1 : 1 : 1, all the four peaks of this AX spin system are equal intensity. This is the important point which you must remember. when you want to analyze two weakly coupled spin systems.

I took the example of homonuclear spin**,** there is no reason why it should be homonuclear, you can also take heteronuclear. Heteronuclear weakly coupled is also possible, right? That is what we discussed long back. Now, I want to give you one general formula. You must remember this formula because it is always very useful in understanding and analysing the NMR spectrum. Logically, I wanted to tell you when you have two coupled spin system, we got four peaks.

When you have one spin system we got one peak, and remember when we were analyzing and calculating the number of possible transitions in three coupled spin systems, I said we are going to get twelve peaks. Remember we observed twelve peaks in the AMX spin system. In one of the classes we found out all the possible energy levels and we have got four transitions for A, 4 for M and 4 for X; and also we got a combination transitions for three, totally we got 15 transitions.

Now the logic, one spin will give one line, two spin gives four lines and three spin can give 15 lines. How many four will give, if we have five coupled spins, how many lines it can give? We can extend the logic like this, so I will give you a general formula now. Please remember, if there are N coupled spins, there will be a total of ${}^{2N}C_{N-1}$ transitions, very important to remember. If we have N coupled spins, there will be a total of ${}^{2N}C_{N-1}$ transitions.

That is, I consider the example of three spins. 3 into 2 is 6, N-1 is 2, ${}^{6}C_{2}$; it is a combination, work it out, very simple. 6 factorial, over 4 factorial x 2 factorial, then it is going to be 15. So, three coupled spin systems can give a maximum of 15 transitions. That is what we observed for AMX do you remember; 12 transitions + 3 combinations? totally 15 we observed. That is OK. Now let us go to the complicated spin system, if there are four spins coupled, that is 4 protons are coupled. How many piece I must get, remember it is the same ${}^{2N}C_{N-1}$ formula; you plug it in, N is four here, 2 into 4 is 8, N - 1; it is 4 - 1 =3, ${}^{8}C_{3}$; Which is 8 factorial over, 3 factorial into 5 factorial. So 8 into 7 into 6, divided by 6, so 8 into 7 it is 56. So 4 coupled spins will give you 56 transitions. This is amazing, you go to even higher coupled spin system, for example, if you go to simple 7 spin systems, believe me, you are going to get nearly 3000 transitions.

Six spin system can give you 792 transitions; like that if you keep on adding one spin, the number of transitions keeps on increasing drastically. But the question comes, do all these peaks are necessary to analyze this spectrum and get coupling information or chemical shift information? That is all you should get from the analysis of this spectrum. If you analyse the spectrum I get chemical shifts and coupling constants, after making peak assignments.

You go back to the simple 2 spin case, we got four peaks in the AX spin system coupled; and you got four peaks. I get chemical shift at the center of this doublet, and chemical shift at the centre of this doublet, from the separation we get J coupling. This doublet separation also will gives me J coupling. That means this information is redundant, I can get only from one of the doublets. I do not need to have another doublet, right? I do not need to analyze this one, to get the J coupling, it means remember this is for a simple two spin.

If you go to three spins, I can show you, sometimes or most of the times, the information content is highly redundant, you do not need all the transitions to analyze and get three required spectral information. Please remember, most of these transitions are highly redundant, Only a few of them would be sufficient to get chemical shifts and J couplings. Now let us go, I will give you a simple thing, what are the information which you require? A general formula. If you have N coupled spin systems, what information you will get, if all are chemically in equivalent, you get N chemical shifts; you must get N chemical shifts from the spectrum. There are N coupled spin systems, which are chemically inequivalent. Analyze each group for different chemical shifts, you must get chemical shift information. So N coupled spin system should give you N chemical shifts.

And how many couplings you get? there is a formula for it, is always given by N (N -1)/ 2. You understand? N (N -1)/ 2. Let us take the example for 3 spins case. N is 3, 3 into N minus 1, that is 3 into 2, divided by 2. If there are three coupled spin systems, maximum you can get 3 coupling information. You have to get only 3; not more than that. How? Understand? 3 spins are coupled; 1, 2 and 3, there can be coupling between 1 and 2, 1 and 3 and 2 and 3, that is all.

There is no need to worry about any other thing. Remember the formula, if you have N coupled spin system, the analysis of this spectrum will give you N chemical shifts and N (N -1)/ 2 couplings. And how many peaks will be getting in the spectrum? It is given by ${}^{2N}C_{N-1}$, these are the three important formulas, you remember.

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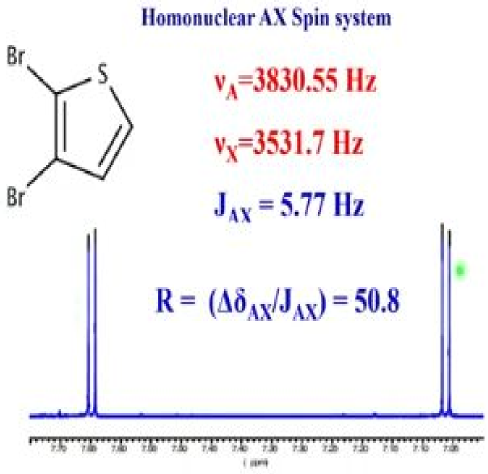

Homonuclear AX Spin system

ν_A=3830.55 Hz

ν_X=3531.7 Hz

J_{AX} = 5.77 Hz

$R = (\Delta\delta_{AX}/J_{AX}) = 50.8$

Now with this will take a simple example of a heteronuclear, sorry homonuclear AX spin system. This is a thiophene molecule, I even showed this earlier also. What is the chemical shift separation between these? The frequency is given here, already expressed in PPM, it is converted to frequency of some spectrometer, no problem. Which is A, which is X, it is my freedom, I can choose this A or this X, does not matter.

Now what is the chemical shift separation between these two? find out. It is close to approximately 300 hertz. The chemical shift separation is 300 Hz, between this and this, and the coupling is what? between these two only 5.77 Hz, now plug in this 300 as a difference value of chemical shift, divide it by J coupling. You know, what you are going to get? The ratio is 50.8. What did I say, the condition for weakly coupled? the chemical shift difference divided by J coupling should be sufficiently large, at least should be equal to or greater than 50.

So now it is of that order. And it must be a weakly coupled AX coupled spin system. A realistic molecule I am giving you. So what information you can get by analyzing this, go to the center of this doublet, it gives you a chemical shift of A, and go to the center of this doublet, it gives you the chemical shift of X. Measure this doublet separation you get J coupling, that is all, the three information you can get in just less than a minute by the analysis of the spectrum.

What did I say about the intensities of weakly coupled AX spin, all are equal intensity, like all should be 1:1:1:1 intensity.

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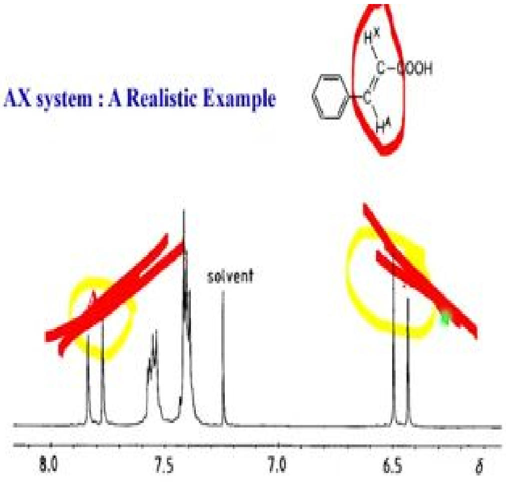

AX system : A Realistic Example

This is the realistic situation like another molecule: a molecule here, consides proton A and proton X; and this is identified as X, this is A. Does not matter how we do; it is our way of identifying. I could make this as A and this as X also, you see, this is the doublet corresponding to one of the coupled spins of AX spin system, this is another doublet. Now what information you will get, center of this will give you a chemical shift of X, center of this will give you a chemical shift of A, this separation will give you JAX.

But will notice one small thing here, what did I say about the intensity? I said the intensities have to be equal, right? Look at this intensity, are they equal? These intensities are not equal. What does it mean? I said the weakly coupled case they must be of equal intensity. There is what you call as a roof effect. It appears the peak is slanting like this and this peak is like this, it is called a roof effect. And that I will go, or when we go to be strongly coupled system, I will explain. This example tells me that these two systems, these two coupled spins, are not 100% weakly coupled. If they are 100% weakly coupled, then all the four peaks should be of equal intensity. This type of tilting in a particular direction, one tilts to the right and one tilts to the left, this roof effect will not be there. That shows it is not 100% AX coupled; there is a residual strong coupling effect, it is still there partial, you know AB character is also present here. Partially AB character, it is not 100% AX.

Now the question is, if I have to make it a 100% AX spin system with all of equal intensity, what will you do? What I have to do without doing anything? Without doing anything for the sample, I want to make it an AX spin system. I told you to remember the chemical shift separation I have to enhance it, so that the ratio of delta delta by J becomes much, much larger than 50. What do I do? Simply record the spectrum, take the sample go to a higher magnetic field.

Supposing this is done at 400 MHz, you go and then start recording the spectrum at 800 megahertz, then what will happen is, this roof effect will disappear, minute strong coupling character which is present here will disappear, you will get four peaks of equal intensity. This is what I wanted to tell you. Please remember, if there is system, which is strongly coupled and has appears weakly coupled but the minute strong coupling character is still present, simply go to a little bit higher magnetic field, and see whether this pattern disappears, and get peaks of equal intensity.

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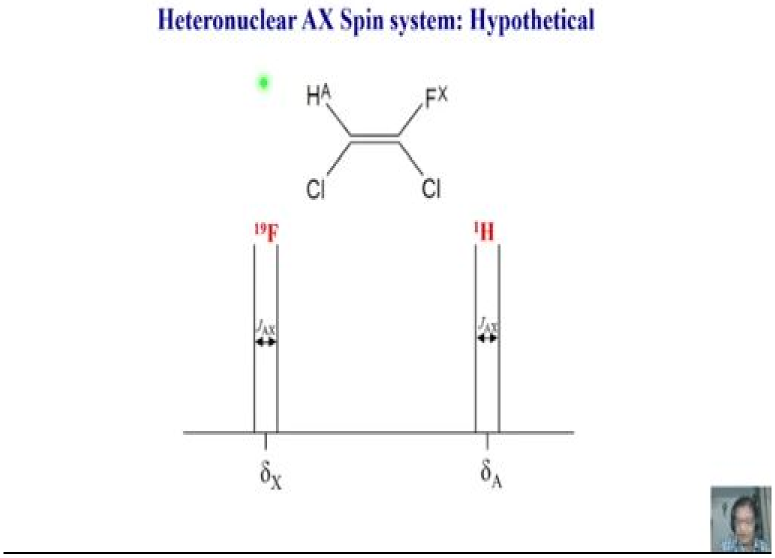

Heteronuclear AX Spin system: Hypothetical

This is a hypothetical example of AX spin system, hetero nuclear case, what happens here? A is proton and X is Fluorine. It has to be a hetero nuclear weakly coupled. Remember, I have been telling you, the hetero nuclear spins are always weakly coupled. Because this chemical shift is megahertz away, resonating frequency for this is at 500 megahertz, if it is 500 MHz, fluorine comes at 470 MHz, so about 30 megahertz away, and this coupling is very small, hetero nuclei has to be weakly coupled, look at this.

You cannot get to both the peaks in one spectrum, I will give you a break here. This is in the proton resonance, I get this proton peak, in the fluorine resonance I will get this doublet. So what you get? the center of this will give the proton chemical shift, the center of this will give the fluorine chemical shift. This separation will give me the J coupling between proton and fluorine. Same way you get this J coupling information, you can also get from proton spectrum.

Do not think that I got both fluorine and proton spectrum with one this thing, there should be a break in this. This is in the proton resonance, this is in the fluorine resonance, it is not in the same single spectrum. So if I give the break here like this, then you will understand I should clearly write, this is a proton resonance and this is a fluorine resonance. Two different spectra, it is not the single spectrum.

So with this and also you notice here because it is perfectly weakly coupled spin system intensities are exactly equal, 1:1:1:1, this is what I was telling you, we should see in the realistic example of homonuclear spins, we were not getting that. We were getting roof effect; that should not come. So now this is a real, perfect example of a weakly coupled AX spin system.

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AB Spin System

Now we will go a little bit further, I look at 2 spin strongly coupled cases. What is a strongly coupled case? This I have to represent by a letter very close in the alphabet order, earlier it was A and the X , which was far away, now I am going to take a letter next to A, that is AB, I consider JAB. So this is proton A and this is proton B.

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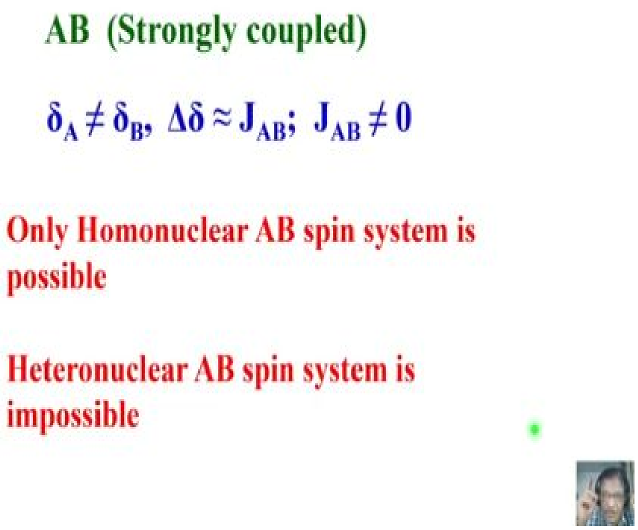

AB (Strongly coupled)

$\delta_A \neq \delta_B,\ \Delta\delta \approx J_{AB};\ J_{AB} \neq 0$

Only Homonuclear AB spin system is possible

Heteronuclear AB spin system is impossible

And what are the possibilities you can think of in this AB case, remember chemical shifts of A and B are not the same, if it is same, then it is different, they are equivalent nuclei or magnetically or chemically equivalent, no problem. But now in this case chemical shift has to be different and delta delta the chemical shift separation, unlike AX spin, is not very large, which is very small, comparable to JAB, remember this is comparable to JAB and JAB is not 0.

If JAB is 0, if you do not see any coupling that is a different case, but remember JAB is not 0. Chemical shift separation is comparable to coupling constant and the chemical shifts are not same, this is a condition for AB case, strongly coupled. And in the heteronuclear AB what happens? It is impossible I said heteronuclear coupling means they are always weakly coupled. because the chemical shifts are megahertz away compared to couplings of few hertz. So in the heteronuclear case, the strong coupling is impossible; always they are weakly coupled.

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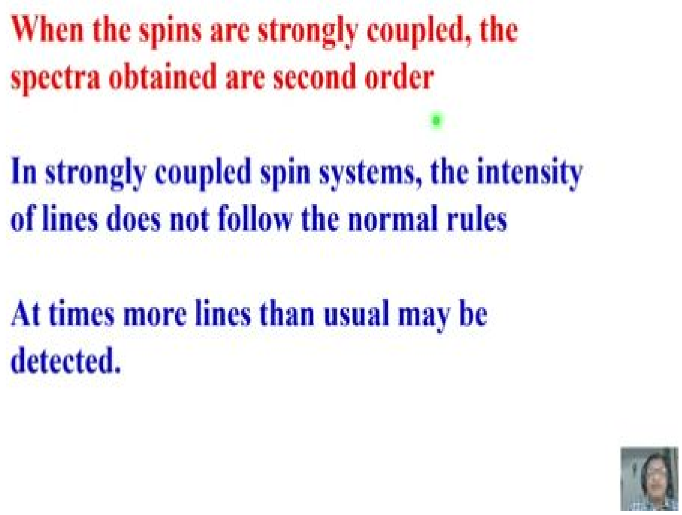

When the spins are strongly coupled, the spectra obtained are second order

In strongly coupled spin systems, the intensity of lines does not follow the normal rules

At times more lines than usual may be detected.

When the spins are strongly coupled, we say spectra are second order. And these spins are weakly coupled, the spectra are first order. What is the difference between first order spectrum and the second order spectrum? I told you several times that the first order spectrum is easily analyzable, like the AX example, get the chemical shift here and chemical shift here and measure the separation and get J coupling, that is simple first order analysis.

Straightforward analysis to get the information is a first order analysis, without getting into theoretical calculations or computation. The strongly coupled case, the intensities of the peaks and do not follow the normal rules, unlike weakly coupled case, where the intensities are equal, in a strongly coupled two spin case intensities, all are not equal. We saw that you know, in a minute AB character present in the AX case, we saw the roof effect, intensities are not same, I said there is a minute strong coupling character there, this is what happens.

Whether there is a strong coupling effect, intensities do not follow normal rules, you do not get lines of equal intensity; and it comes sometimes it may so happen instead of normally expected number of lines, you get more lines. How is it possible? You ask me a question. How can we expect more lines than what is possible? It is possible, I will give you an example when we go further. You please remember, in the AMX spin system what we do, we got 4 transitions for A, 4 for M and 4 for X. But also I showed you there are three combination transitions, where all the three spins will flip at a time, still retaining the change in the total magnetic quantum number of between two energy states, still as +1 or -1, it is that. But still three spins can change at a time, alpha to beta beta to alpha. That is called combination transitions. Such transitions are not seen in weakly coupled, but as seen in strongly coupled cases.

Understood the point? that is why in the strongly coupled spin, system sometimes you get extra peaks, more peaks than what is expected in the weakly coupled system.

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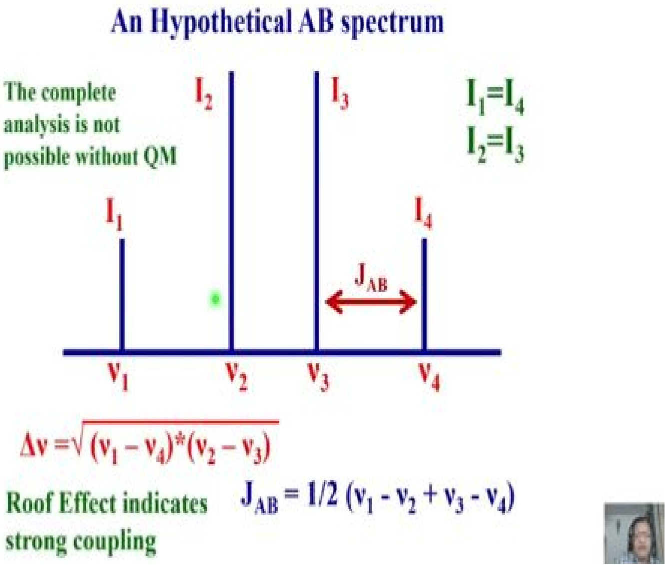

An Hypothetical AB spectrum

The complete analysis is not possible without QM

$I_1 = I_4$
$I_2 = I_3$

$$\Delta\nu = \sqrt{(\nu_1 - \nu_4)*(\nu_2 - \nu_3)}$$

Roof Effect indicates strong coupling

$$J_{AB} = 1/2\,(\nu_1 - \nu_2 + \nu_3 - \nu_4)$$

This is a spectrum of AB spin, where A and B are strongly coupled. Look at this one. Are they having equal intensity? No. This is a clear indication of AB and also there is a roof effect, look at it, this is going like this, this is going like this; this is called the roof effect. Remember in the AB coupled case the intensities of the central two lines are equal, and the intensities of the outer two lines are equal.

I2 is equal to I3 intensity of the second peak and third peak are the same, intensity of first and fourth are same. This is a pattern we expect for AB. Always remember if you observe a spectrum like this, in your molecule where the chemical shift separation is small, they are strongly coupled. In which case you do not get the chemical shift, just by taking the center of this. I cannot say, I will go and take the center and measure the chemical shift? No, it is not possible.

So, there is a different way of getting chemical shifts in that case. In strongly coupled case, you do not get individual chemical shifts. I can only give the difference of chemical shifts. You understand? In the weakly coupled case, I know the chemical shift of A, I know the chemical shift of X, very precisely. But in strongly coupled case AB, I do not know the chemical shift of A, I do not know the chemical shift of B, but I know the chemical shift difference between A and B, difference can be 10 hertz. If it is 10 Hertz, one can be 15 other can be 5, one can be 30 other can be 20 does not matter. The difference can always be said, but not the individual chemical shifts in strongly coupled spin systems. Now this is how you get the difference of the chemical shifts, simple formula, outer lines have been mentioned as frequencies ν1 and ν4 here. Central two lines are ν2 and ν3, in the same order.

Take ν1 - ν4 difference, multiply by ν2 - ν3; and take this square root of that, that gives you the difference of chemical shift. Remember this formula, it is very, very useful to analyze, do not forget that. This should be in your finger tips. In the strongly coupled AB case, the difference of the chemical shifts between 1 and 4, take the difference, multiply by the difference in the chemical shift of 2 and 3; and take the square root of it, that gives you delta delta or δν, the frequency separation of two spins.

I do not know the chemical shifts individually, but I know the difference. We understand. Now I can also get the JAB, it is very easy, you can just take the difference of these outer two lines. here or the outer two lines here, but not this one, only outer two lines of the AB pattern gives you J, alternately there is a simple formula. Take ν1 - ν2 + ν3 -ν 4 divided by 2, it amount to same; instead of taking this, you take this and this and divide by 2. Instead of that, you measure only one of them, that is enough, this gives you J coupling.

You do not have to use this formula, measure the frequency separation between any two outer lines, this line or this line that gives you J coupling. Remember this point, in the AB spectrum how to analyze. This is a complete analysis of this spectrum, though simple that it is only two coupled system, not possible without using quantum mechanics, you have to do quantum mechanical analysis.

But I am not going into detail, I am just giving the information. This is enough if you know, do not worry about how we get this, remember you take ν1- ν4, multiply by ν2 - ν3, take the square root of that, you get chemical shift difference. Just measure the outer line separations of any of these doublets you get J.

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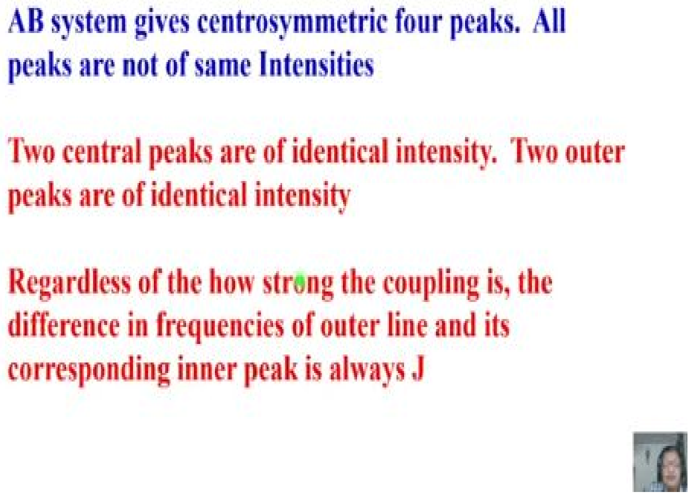

AB system gives centrosymmetric four peaks. All peaks are not of same Intensities

Two central peaks are of identical intensity. Two outer peaks are of identical intensity

Regardless of the how strong the coupling is, the difference in frequencies of outer line and its corresponding inner peak is always J

That is all the analysis of AB. AB system gives centro symmetric four lines remember, it is centro symmetric, it is symmetric with respect to the centre and all peaks are not of the same intensities. Central peaks of two identical intensity, two outer lines are of identical intensity. Whatever may be the coupling strength or regardless of whatever the coupling strength, outer lines always gives you J coupling, remember this one.

You may not know, this one you have to precisely calculate; whereas the outer lines are very simple, measure the frequency separation of the outer lines. Whatever may be the pattern you get you will get J coupling, that is very important information.

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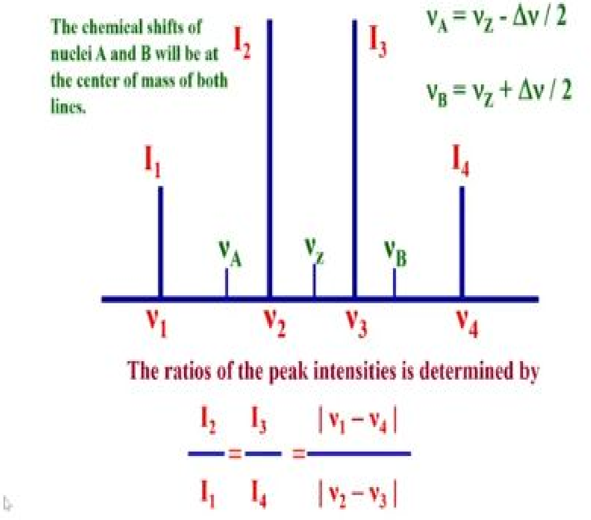

The chemical shifts of nuclei A and B will be at the center of mass of both lines.

$$\nu_A = \nu_Z - \Delta\nu / 2$$

$$\nu_B = \nu_Z + \Delta\nu / 2$$

The ratios of the peak intensities is determined by

$$\frac{I_2}{I_1} = \frac{I_3}{I_4} = \frac{|\nu_1 - \nu_4|}{|\nu_2 - \nu_3|}$$

On the sign of the coupling, again do not influence the spectral pattern, that again we knew even in weakly coupling case. So now you can also get the ratio of intensities very easily; you can find out the ratio, what is this? I know ν1, ν2 ν3 and ν4, I know what are intensities. I call it as I1, I2, I3, I4. I2 /I1 or I3 /I4, if I take, this intensity is given by (ν1 - ν4) divided by (ν2 - ν3), either of them. This is the formula we have to use, take the separation of this and take this separation of this. Divide this separation by this separation that will give you intensity.

Now this separation becomes larger and larger what will happen? Consider an example now, ν1 - ν4 becomes larger, this one peak comes here, one peak comes here. This becomes larger, then what happens? This numerator becomes larger, denominator becomes smaller and smaller, the intensity ratio becomes larger and larger, that means this is more intense, this becomes less intense.

You understand the point, it is simple arithmetic I am showing you, in a strongly coupled case, you will get a spectrum like this: take the ratio of the outer separation, ratio of the internal two peaks separation and then take this ratio. Chemical frequency separation here and between these two and take the ratio, that will give you intensities of the peaks. When this separation becomes larger and larger, then what happens?

The intensity ratio becomes larger and larger means outer lines, I am sorry, internal lines become more and more intense, and these internal lines become more and more intense, outer lines become lesser and lesser intense, this is what happens. So what does it tells you, depending on the spectrum or depending on the chemical shifts or depending on the separation, or J coupling, your spectral intensity pattern drastically changes. Do not forget this.

Depending upon the pattern, depending upon the spectral information like J coupling strength and chemical shift separation, your spectral pattern changes, intensity pattern changes drastically, that is a very, very important thing.

Now, I will consider a situation, J coupling is very, very small, what does it mean? I said in this strongly couple case outer line separation gives J, it means this becomes very small. Let us say this peak here and this peak comes here because J is small, then what should be the intensity pattern?

Look at this, ν1 - ν4 remains, ν2 - ν3 becomes very small, this intensity ratio because very large, so I2 will have a large intensity compared to I1 then what will happen? You get a spectrum like this. If I keep on increasing, let us say J coupling becomes much, much smaller, then it will become like this, too close and high intense and outside lines like this. So what happens? As a coupling strength decreases, outer lines become smaller and smaller intensity and internal lines become larger and larger intensity.

Another interesting thing happens, these separation keeps on coming down that also happens. The separation between the internal peaks keeps coming down. And this separation between internal peaks and outer peaks keeps on increasing. Very interesting phenomena. So do not have to worry too much, simply look at this equation. Do some rough calculation, keep on varying the frequency separation between this and this, and see what is going to happen.

ν2 - ν3, if I find out, you keep on reducing this value and keep on increasing this value. Play around and see how the intensity changes here, a very interesting phenomena, you are going to observe, and this pattern completely will be different when you change the chemical shift separation, we have to see that now.

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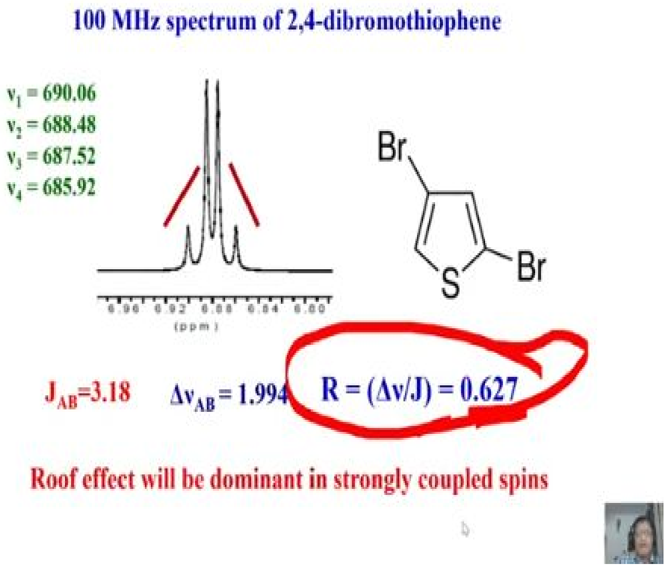

100 MHz spectrum of 2,4-dibromothiophene

$\nu_1 = 690.06$
$\nu_2 = 688.48$
$\nu_3 = 687.52$
$\nu_4 = 685.92$

$J_{AB}=3.18$ $\Delta\nu_{AB} = 1.994$ $R = (\Delta\nu/J) = 0.627$

Roof effect will be dominant in strongly coupled spins

This is a classic example of 2 4-dibromothiophene, it is a strongly coupled AB spin system. Look at this pattern, what is happening? Here is the roof effect, that clearly indicates it is a strongly coupled spin system. So now I am giving you the frequencies here. When I give you the frequencies, you know, what are J coupling? What is J coupling? It is the frequency between any two outer lines. Now take this as separation of these two, 7.52 forget about the first two digits, 7.52 or 5.9 take it as 6, close to 1.6 Hz for J coupling.

I think it is something wrong written here, Anyway it is the outer lines has to be J, some calculation mistake is there, do not worry. Now chemical shift separation you find out, what is JAB, this is frequency of the first line to fourth line divided by, you know that one, I have already discussed. How to get the chemical shift? This separation multiplied by this separation, and take the square root of that, it gives you chemical shift separation.

So now you find out what is the ratio of chemical shift separation by J coupling. It is much, much smaller, which tells you it is a strongly coupled system.

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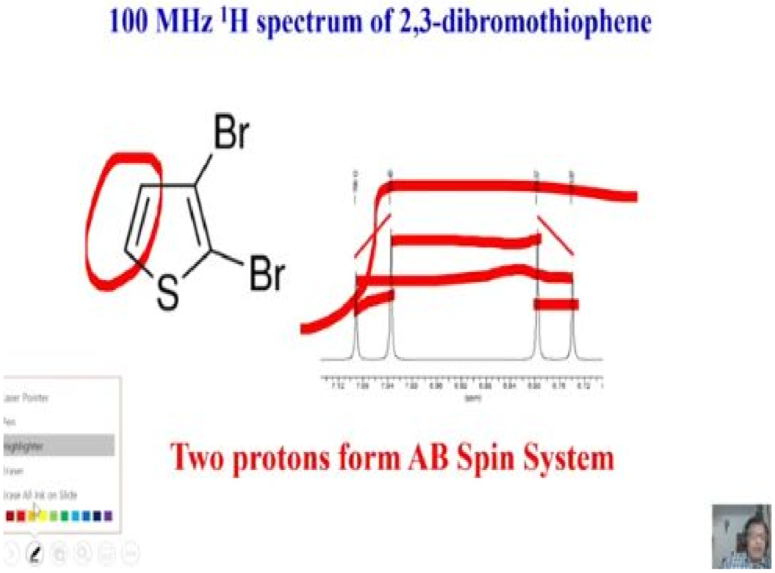

100 MHz ¹H spectrum of 2,3-dibromothiophene

Two protons form AB Spin System

Now this one, again 100 megahertz spectrm. What happens? Look at this one, this is a different thing, it is, let us say this is 1, 2, 3, 4, this is 3 and 5 dibromo. In this case it is 4 and 5 dibromo, this also AB spin system. Look at this roof pattern, you can see, it is a perfect AB spin system. Now you can measure the separation, this separation gives J, get this separation and get this separation multiply, take the square root of this, we are going to get δAB.

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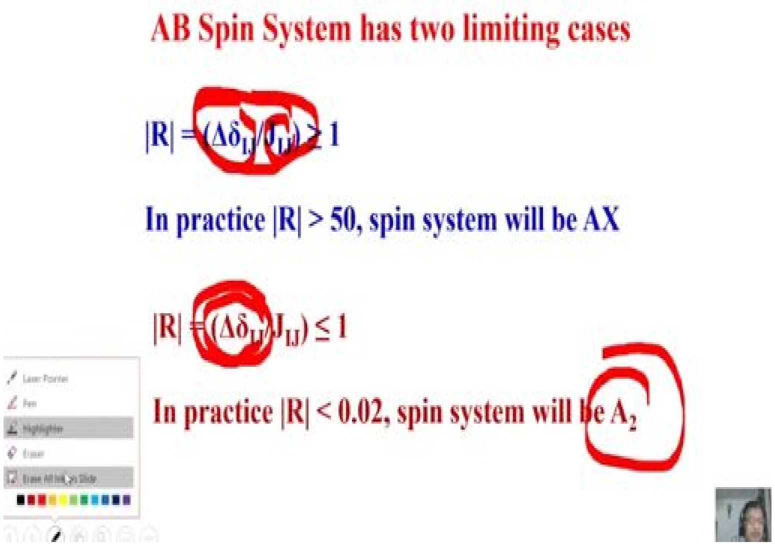

AB Spin System has two limiting cases

$|R| = (\Delta\delta_{IJ}/J_{IJ}) \geq 1$

In practice $|R| > 50$, spin system will be AX

$|R| = (\Delta\delta_{IJ}/J_{IJ}) \leq 1$

In practice $|R| < 0.02$, spin system will be A_2

AB spin system has two limiting cases. When this becomes larger and larger the chemical shift separation, compared to J coupling you can take this to AX, that is what you can do. I told you I have a strongly coupled spin system, increase the magnetic field quite a bit, then this becomes larger so you can make it AX, that is one limiting case. Alternately you can keep on reducing such that, so small and after some time, make sure that delta IJ is 0. There is no chemical shift difference at all, they are equivalent spins, they overlap, it is A2 spin system, like CH2 group both are equivalent protons. There is no coupling between them is seen, then that is a situation where you are going to get A2 spin system. So AB can be taken, by increasing the magnetic field enormously, to AX spin system, or it may so happen if the chemical shift separation, if it is made to be 0 and the coupling between them is not reflecting in the spectrum, it can become A2. So these are the limiting conditions of AB.

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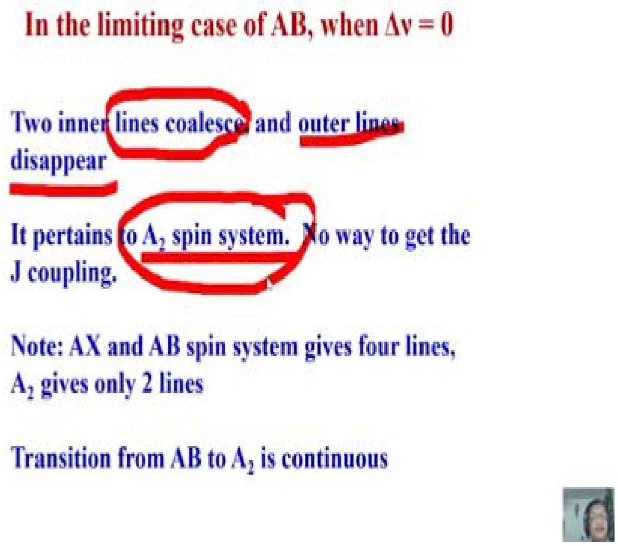

In the limiting case of AB, when $\Delta v = 0$

Two inner lines coalesce and outer lines disappear

It pertains to A_2 spin system. No way to get the J coupling.

Note: AX and AB spin system gives four lines, A_2 gives only 2 lines

Transition from AB to A_2 is continuous

So in the limiting conditions of AB, when chemical shift become zero, two internal lines overlap or coalesce, two internal lines will completely overlap and you get a single peak; and the outer lines will completely disappear. That is a very, very important point, remember outer lines will completely disappear. This is standard example for an A2, For A2 how many lines you get? Simple example I gave, a hydrogen molecule.

There are two protons, they are chemically equivalent, no J coupling is seen, how many lines we expect? Only one peak. Classic example of A2 is hydrogen molecule. So how do one line come? In principle when two protons are coupled you must get four lines. I said easily you can calculate ${}^{2N}C_{N-1}$, how many lines you get, for two spins, you can write down the formula ${}^{2N}C_{N-1}$. So what is 2N, for two spins it is ${}^{4}C_{1}$.

You must get only four lines, but how I got one line. In the formula I did not say the strongly coupled or weakly coupled, general formula when two spins are coupled you must get ${}^{2N}C_{N-1}$ transitions, that turns out to be four lines, but why I got only one line in the A2. Remember still we have to happen so as in the A2 case, two central lines will coalesce, will give a single peak, and two outer lines will disappear.

How does it happen, what does it mean, why you are not getting four peaks? That is because in the A2 case what happens is when we go ahead further I will show you, it so happens, there will be three symmetric energy levels and, one is anti-symmetric energy level. The symmetric to antisymmetric transitions are forbidden. As a consequence, you will not see four peaks, you will see only two peaks of equal intensity in the case of A2. So that is why A2 system always gives single peak.

And single peak is nothing but two peaks overlapped and outer peaks are not visible at all; and you can smoothly go from AX to AB and A2. Start with AB, you can keep on increasing the field take it to AX, start with AB take it to AX. Start with AB keep on reducing the chemical shift separation, make them equivalent you can bring it to A2. It is a continuous transition, transition from AB to AX and AB to A2 is also continuous, so this is what you, please remember.