One and Two Dimensional NMR Spectroscopy for Chemists

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Lecture - 32

Analysis of Three spin coupled systems

Welcome back, today we will continue with this spin system nomenclature, analysis of weakly and strongly coupled spin system again. Again a huge topic, but I will give one or two simple example of three spins and stop for the day.

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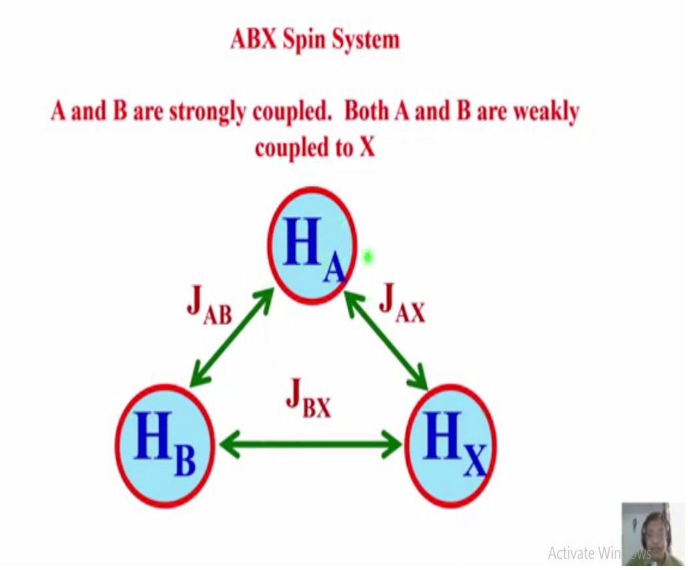

ABX Spin System

A and B are strongly coupled. Both A and B are weakly coupled to X

We will see this, already we saw AMX, three weakly coupled spin systems, I showed you we get 12 lines and we have 3 combination transitions which do not coupling J information but combination of all of them together gives you chemical shift information. Now, I come across a situation after the AMX, let us say two of them are strongly coupled, and both of them together weakly coupled to X. This is called ABX spin system.

Remember A and B are strongly coupled, we already know how to analyze the AB, two strongly coupled spin system, you got four lines two central lines of higher intensity and outer lines of weaker intensity. We have already analyzed how to get J coupling, chemical shift difference everything. Now exactly similar situation will come for AB here; but together individually both of them are coupled to X. It is a JAB coupling here, and JAX coupling and JBX coupling; all are present.

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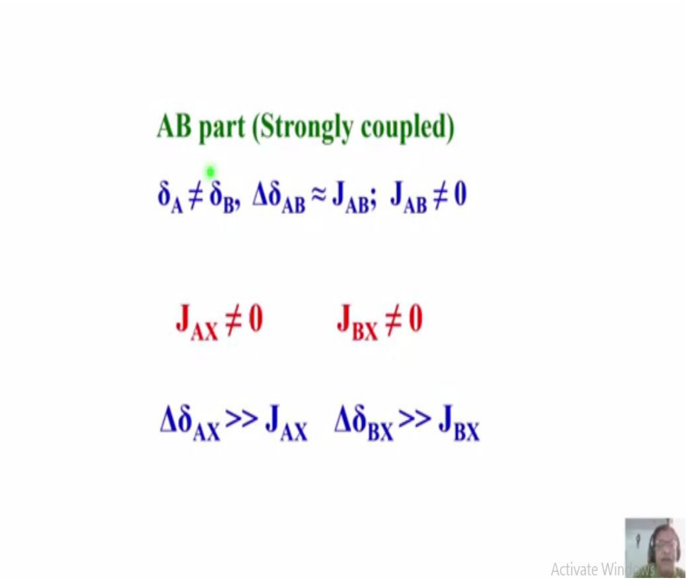

AB part (Strongly coupled)

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

$J_{AX} \neq 0$ $J_{BX} \neq 0$

$\Delta\delta_{AX} >> J_{AX}$ $\Delta\delta_{BX} >> J_{BX}$

Now this is situation AB part is strongly coupled where chemical shifts A and B are not equal, but delta AB is almost close to JAB. Of course, this is a condition for AB I told you; and JAB is non zero, it is visible in the spectrum. So JAB is non-zero, it has some value, but the chemical shift separation is comparable to JAB and chemical shifts A and B are not identical, they are non-equivalent spins. Now AB is coupled to another third spin called X.

Now JAX is non zero. Similar JBX is nonzero, They are weakly coupled. Interesting part is, the difference in the chemical shift of A and X, delta AX, is larger than JAX. Similarly chemical shift of B and X if you consider delta delta BX is larger than JBX. So together AB becomes strongly coupled, and with this condition when they couple to third spin with this condition it is a weakly coupled spin system. So there is a combination of two strongly coupled and two of them weakly coupled to the third spin together. This is a 3 spin case ABX;

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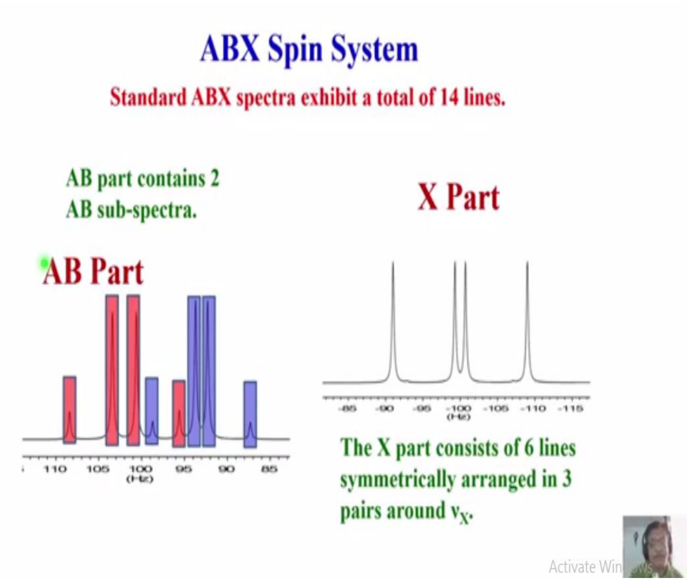

ABX Spin System

Standard ABX spectra exhibit a total of 14 lines.

AB part contains 2 AB sub-spectra.

X Part

AB Part

The X part consists of 6 lines symmetrically arranged in 3 pairs around v_X.

And it is very easy to analyze, AB part we know how to analyze, this is an AB part. Remember ABX case, AB part contains two AB sub-spectra and an X part. X part in principle should have 6 lines, but you are getting most of the times only 4 lines. It is symmetric with respect to center. If you carefully see, you can see a peak here with minute intensity. Can you see it? You can still see 6 peaks.

But these two generally most of the time not seen. The 2 lines of weak intensity is not seen, only 4 peaks are seen, that is fine. But AB part is something, we get 2 AB sub-spectra. Here can we identify 2 AB? of course. I colored it, here one AB part, here is another AP part. So now how to analyze AB part is easy, we know that. This is called sub-spectral analysis, you can do that and get the information. Of course, something more is there.

ABX spin system gives conjugated solutions, you cannot just like analyze without taking into account the intensity pattern, we will not go more into the details. I am just giving you information, in the ABX case you get an AB apart and an X part. X part has 6 lines symmetrical with respect to the center and two weak transitions are generally not seen. So you get only 4 peaks for the X part and on the other hand AB part contains 2 AB sub-spectra which can be analyzed.

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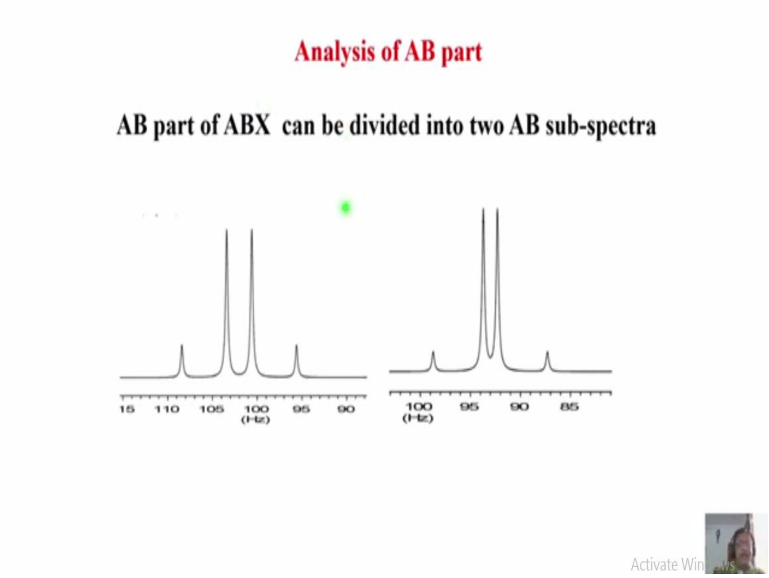

Analysis of AB part

AB part of ABX can be divided into two AB sub-spectra

And this if you expand that, AB part can be divided into two AB like this and this.

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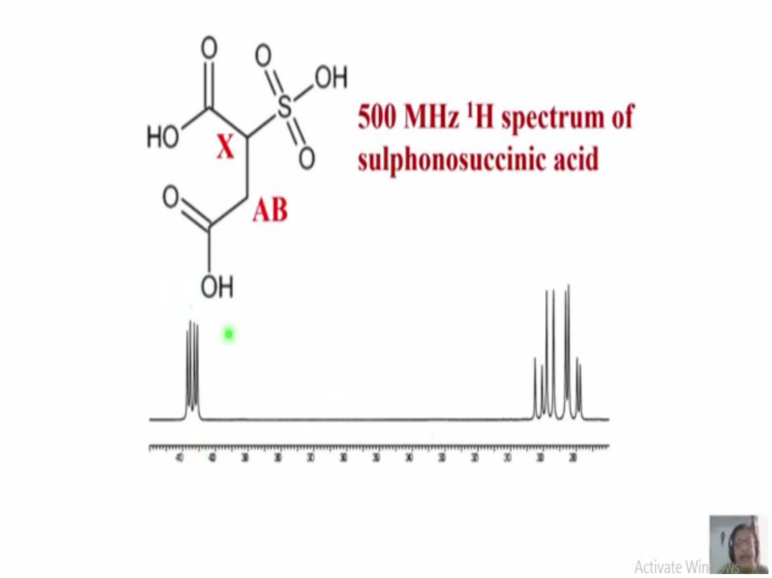

500 MHz ^1H spectrum of sulphonosuccinic acid

And this is a classic example of ABX. It is 500 megahertz proton spectrum of sulphonosuccinic acid. These two protons are chemically non equivalent; form an AB spin system, a strongly coupled. But together with this proton they are weakly coupled, these two are strongly coupled, each of them with this is weakly coupled. So it is a classic example of ABX spin system. As I told you AB part has two AB sub-spectra and the X part has 6 lines, 2 are not visible. So you get 4 lines. It is an example of an ABX.

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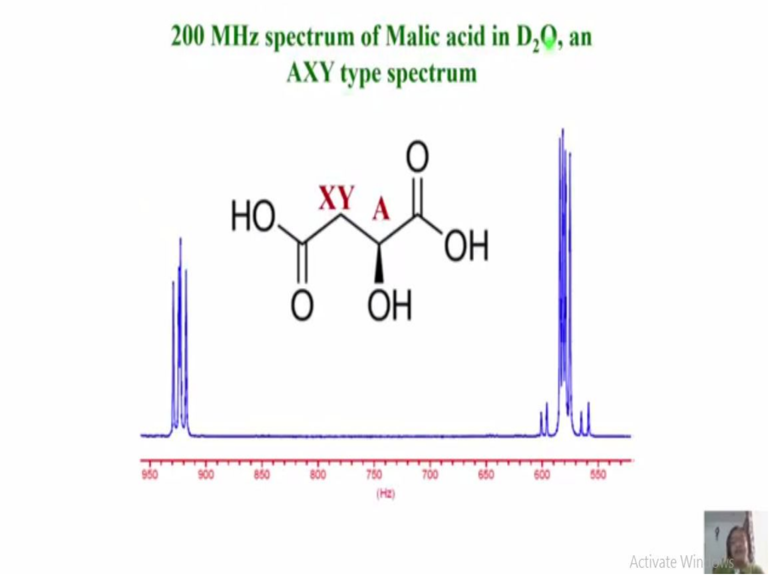

200 MHz spectrum of Malic acid in D_2O, an AXY type spectrum

How do we analyze? We can see that, of course, you can call it ABX or AXY also, some people call it AXY does not matter. This is strongly coupled and this is weakly coupled. It is analogous to ABX, depending upon how we look at it? Please look at this one, this is the AB part or XY part, this strongly coupled X part, okay? This is spectrum of Malic acid in D2O; AXY type.

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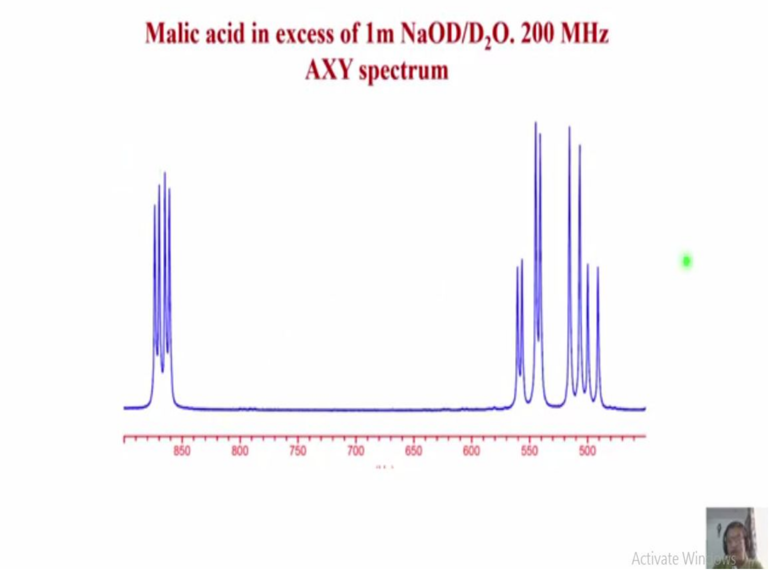

Malic acid in excess of 1m NaOD/D_2O. 200 MHz AXY spectrum

This is spectrum of Malic acid, again 200 megahertz. You see the change in this AB pattern. AB pattern gets crowded here, but we can use some tricks in NMR spectrum to see the chemical shift dispersion becomes better, and that is what is done here. By adding a small little bit of excess of this thing, NaOD and D2O, you will get better resolution here. So what is this? Very easily you can identify which are the two AB part, which is the X part. You can identify which are the two AB sub-spectra, and then analyze these to get coupling information.

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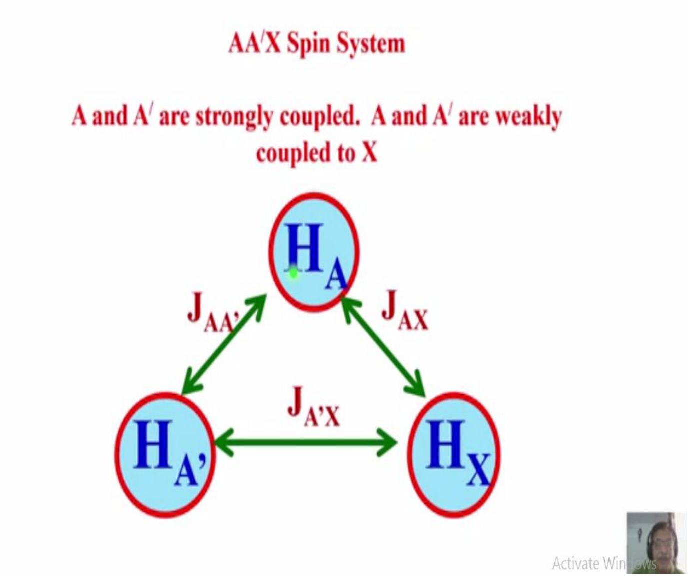

AA$^{/}$X Spin System

A and A$^{/}$ are strongly coupled. A and A$^{/}$ are weakly coupled to X

I do not want to go to the details of analysis, I just wanted to show you this spectrum. When you get such a sub-spectrum, for analysis you have to be careful. This is the AA'X spin system. I am giving you deliberate example of this because it is very useful for you. This is a classic example where AA prime is a situation A and A prime are chemically equivalent, the chemical shifts are same, and there exists a coupling between them which is visible in the spectrum, you got the point? If the chemical shifts are same and couplings are not visible in this spectrum, it is strongly coupled A2. But this is a case chemical shifts are equivalent but couplings are visible. This is what I said you know, prime notations while using Pople notation, this is AA' spin system. Similarly, this is A'X and JAX, this one. So AA prime must be strongly coupled, together they are weakly coupled with X spin.

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AA' part (Strongly coupled)

$\delta_A = \delta_{A'}$ $\Delta\delta_{AA'} \approx J_{AA'}$; $J_{AA'} \neq 0$

$J_{AX} \neq 0$ $J_{A'X} \neq 0$

$\Delta\delta_{AX} >> J_{AX}$ $\Delta\delta_{A'X} >> J_{A'X}$

And this spectrum is very easy to analyze. It is an AA' part; delta A is equal to delta A prime, and they are different. delta-delta AA' is close to JAA'. As a consequence, they are strongly coupled and it is non-zero. Of course, it must be non-zero. If the coupling is zero or not reflected in the spectrum, it will be A2. Now between AA' and X you see, JAX is non zero, JA'X is also non zero and this is the condition where chemical separation should be larger between AA' and X; so that AA' weakly couples to X.

These are the conditions for AA' X. I hope you are with me, I am repeating again the AA' case chemical shifts are same and coupling constants is comparable to the difference in the chemical shifts and coupling constant is non-zero because it is visible in this spectrum. But together these two are coupled to a third proton and their couplings; A coupling with X, A' coupling with X are non zero; and also the chemical shift separation, AA' and X is larger than this coupling. So it is a classic example of AA'X spin system, we can see this type of molecules

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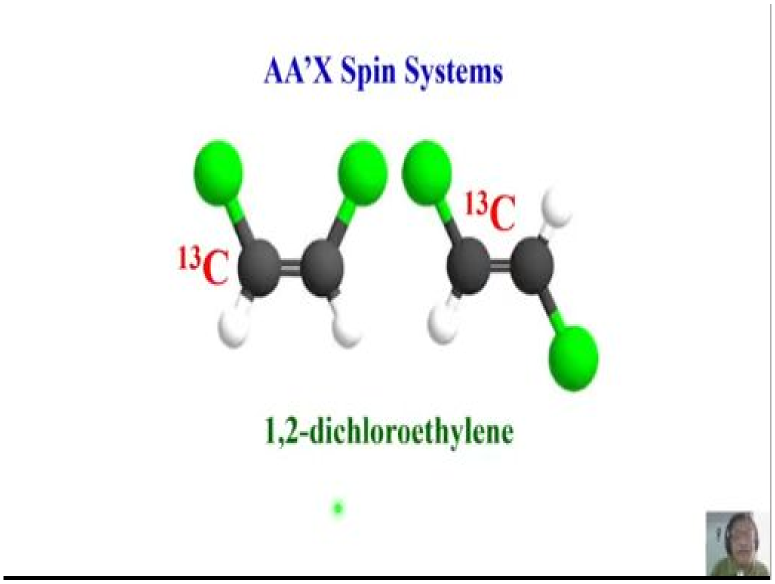

AA'X Spin Systems

1,2-dichloroethylene

It is a 1,2-dichloroethylene. We have a cis configuration and also trans configuration. But look at it, we have carbon 13 also present in the natural abundance here. Why I took this example because you can use it in your analysis later. Now I will ask you a question, look at this molecule, there is a symmetry, these two protons are equivalent. Similarly, if you go along this axis symmetric axis, these two protons are equivalent, chemically equivalent. But, you will not see the coupling, there exist a coupling, but you will not see the coupling. You understand? this is analogous to A2 spin system, here also coupling is there, okay? But you will not be able to see this in the proton spectrum, but you can get it in a different way. So in this case, this is cis and this is trans configuration, 1,2 dichloroethylene, if I take.

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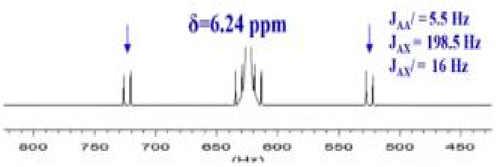
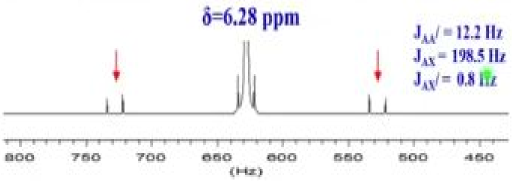
^{1}H NMR spectrum : cis dichloroethylene, AA' part of AA'X



^{1}H NMR spectrum : trans- dichloroethylene, AA' part of AA'X



If you look at the spectrum of proton, see this is proton part, is AA' part. See this is the proton part. What is the type of spectrum we are going to get here? Only one line. Here we get one line because of symmetry. Can I break this symmetry of this molecule? Of course, I can break this symmetry of molecule without doing anything. What I will do is now I will consider carbon 13 also, which is present in natural abundance.

If I take this carbon-13, let us any given instant of time, you will see one carbon, not both are not possible to consider here. I will explain to you when I come to carbon-13 NMR. See I consider this carbon in natural abundance. Now the equivalence is broken. It is not AA', because of coupling for this and this are different. So what is going to happen? You are bringing in X coupling, X also, AA' X spin system.

Now the coupling between AA' can be seen in the X part. Also, you can see the coupling in the X part easily. Now look at this one, this is the proton spectrum of cis dichloroethylene. Single peak is there, which is enhanced in intensity quite a bit. The drastic enhancement in the intensity is there. But if you carefully see this thing, there are two doublets here and two doublets here. What are these doublets?

I have not explained to you so far, these are called satellites in NMR. I wanted to explain to you later, but I just took the example, so I had to explain now. These are called satellites in NMR.

What does it mean? Take an example of CHCl3. Single proton, you should get one peak, 99% is carbon 12 attached. So you will get no other coupling, you will get a single peak. But there 1% of the molecule attached to the carbon 13; that will couple to proton.

In this proton spectrum I must see the coupling of proton with carbon. Where do these lines will come? because it splits proton peak into doublet of very small intensity, 1% intensity compared to main peak; on either side you will see that. Because it is very small intensity, nearly 1% of the main peak, they are called satellites. Satellites are coming because of the more very low natural abundance of the coupled spin.

You can extract coupling information from that also. So we will go more into this satellite analysis when we come to different types of spectra. But here I just wanted to tell you, these two are called satellites, because of coupling with carbon. This proton now, I am taking in natural abundance here, this can couple to this proton, this can couple to this proton also. So I can get all the three couplings here. JAA' I can get, JAX I can get, JAX' also I can get.

Very easily I can measure it, how? Look at this one, this is coupling between carbon and proton. Understand? What is this coupling? AX coupling, and here A'X coupling both are same. This is AA'X coupling, it is around198 Hz or 200 Hz, this is the coupling with carbon-13. You understood the point? This is coupling with carbon. I can take this as A'X or AX, does not matter, one of the protons I will consider.

This if I measure from the center of this to center this. I will get carbon proton coupling. Which carbon, which proton? This carbon and this proton coupling, I am getting. But what about this carbon this proton coupling? Are they same? No, this is one bond coupling, this is two bond coupling. So A to X coupling is measured here. Remember you see two more peaks here. What are they? That is coupling of this carbon 13 to this proton, A' to X.

If this larger coupling is AX, this is AX'. You understand? So this coupling will give me coupling of this carbon to this proton. Now when the symmetry is broken, what about proton - proton coupling, AA coupling? That is also visible. This separation tells me what is AA coupling? Please understand, now the analysis of this you have to understand slightly in a different way. First separation from this to this, this center to this center, gives you carbon proton coupling, carbon which is directly bonded to proton, you will get CH coupling.

Center of this to center of this gives you three bond, sorry two bond carbon proton coupling, this one. That is on either side you see but each of the satellite peaks are split into doublet. Why is it so? That is because there is a proton-proton coupling also, which is reflected. This separation gives me proton-proton coupling, AA' coupling, which was invisible in the proton spectrum, moment I break this symmetry by taking carbon 13 into account, now you are seeing HH coupling.

This is a classic example I wanted to tell you, when you have an equivalent spin system, how do you measure the coupling? This was the question I asked you sometime back. For example, I took ethylene, I said all the four protons are identical, you get a single peak. But still we know there are three different couplings in ethylene molecule. One proton coupled to three different protons with three different peak coupling strengths.

Then how did we measure that? This is an example. One of the ways is to break the symmetry by taking natural abundance carbon 13 or if possible label one of the carbon, then you have broken the symmetry. Then you are going to get all the couplings by analysis of the proton spectrum with carbon couplings. That is one way, okay? Very easy or go to the carbon 13 spectrum where all these couplings, because your symmetry is broken can be seen, you understand.

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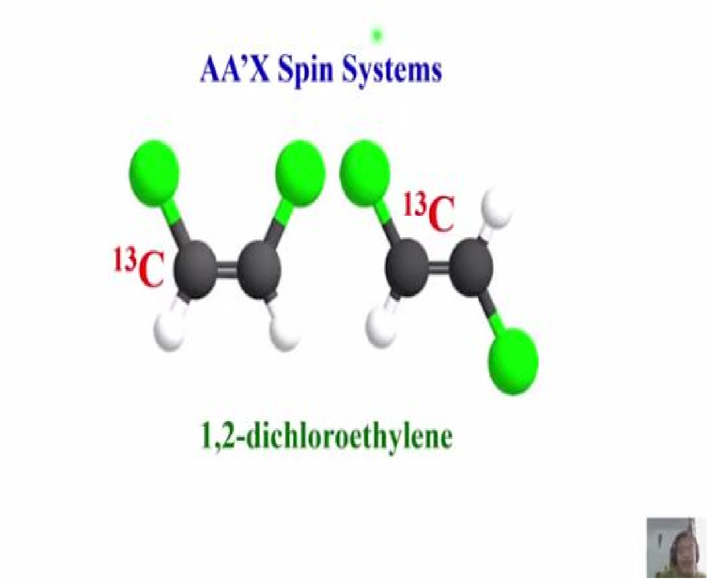

AA'X Spin Systems

1,2-dichloroethylene

For example, I go to the carbon 13 spectrum here, then I get a large doublet because of this and each of the doublet is split into another doublet because of this. It is a very simple weakly coupled. So carbon 13 will give four lines, so you can measure this separate couplings from carbon 13 or from the proton spectrum you get this coupling also, very easily you can measure all these couplings. Of course in carbon 13 you also get, you will not get AA' spin coupling, you know, why?

When I observing this, it is an active spin, these 2 are passive spins. You always get coupling betweeen active and passive spins. But between passive spins you will not see. So in the carbon 13 spectrum, we do not get proton-proton coupling, an important point you remember okay? So now in the protons spectrum you get CH coupling and proton-proton coupling, everything is observed here. This is an example for cis dichloroethylene.

What happens if I get trans-dichloroethylene? Remember cis and trans if I take configuration, trans coupling is always larger than cis coupling. Very clearly obvious here, see this separation this J-coupling is 5.5 hertz. Look at this separation, if you measure AA' coupling, it is 12.2 hertz. This clearly tells me if you give me cis dichloroethylene, trans-dichloroethylene, I take a proton spectrum, I will get a single peak and if you still ask me how do you identify which is which?

I will do a simple analysis of carbon 13 satellites, looking at the proton-proton coupling which is reflected in the satellite spectrum. I know which is trans and which is cis. You got the point now, how to identify cis-trans isomerism by looking into carbon 13 satellites. This is where the spin system analysis that comes into a picture. So now it is AA' X spin system, if you know how to analyze that, you can get all the three couplings which are expected. If you do not see the protons spectrum, you will see in the 13C satellies.

All I have to do, but you do not do anything, simply in the normal case you do not see satellites, in other case simply enhance the satellites**,** here are the satellites, analyzing these things, you will get everything. Remember, the spectrum of carbon of 12 attached and carbon 13, all overlapped but only thing is in normal course you would not see it. But if you want to analyze, enhance the intensity to enhance the vertical intensity so that these small peaks are seen. Now you analyze the satellites and you get all the information.

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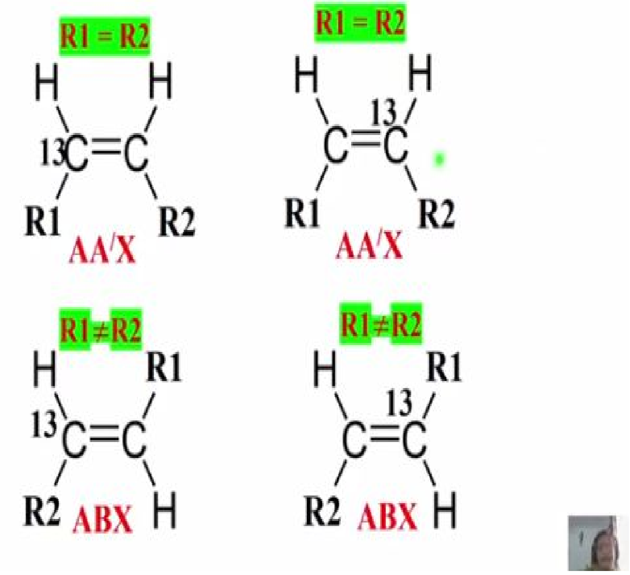

Here is one example. There are a number of such examples. You can see, this can be AA' X, if I take this molecule R1 is equal to R2 in this molecule. In this molecule, let us assume R1 is equal to R2, again if I take this carbon 13 instead of this, it is AA' X. Consider this molecule, I can make it if R1 not equal to R2, symmetry already broken here, it is not AA' X, it is ABX. If you consider R1 and R2 to not equal in this case and I take this carbon also into account, this is again ABX. See in the substitute of ethylenes cis and trans, depending upon whether the substitutes are same R1 equal to R2 or R1 not equal to R2, depending upon which carbon you are taking into account, you can identify the spin system as AA' X or ABX.

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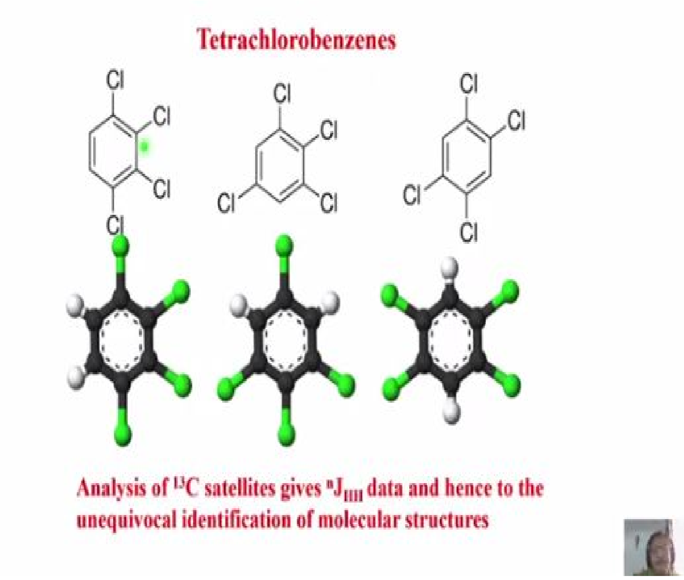

Tetrachlorobenzenes

Analysis of ^{13}C satellites gives $^{n}J_{HH}$ data and hence to the unequivocal identification of molecular structures

So this is a tetrachlorobenzene, if you take it, you are going to see carbon 13 satellites. Analyse, we get the coupling between these two. Look at this one, if I have this in the A2X or in this case, here it is a case AA'; in this case again A2. So coupling is there which is not seen here, in this case also coupling is there, it is not seen, they are chemically equivalent. So if you analyze the 13C satellites of all these molecules, you will get proton-proton coupling and proton-carbon couplings, everything you are going to see.

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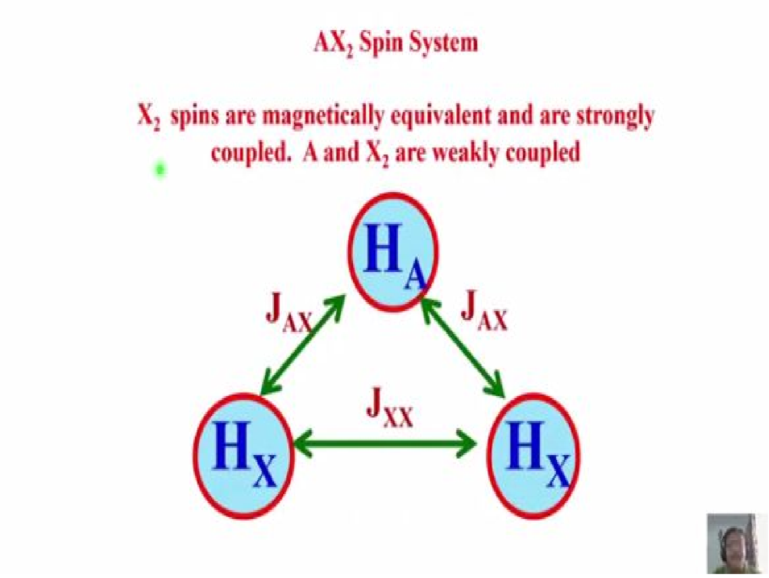

AX$_2$ Spin System

X$_2$ spins are magnetically equivalent and are strongly coupled. A and X$_2$ are weakly coupled

Now, I will give another simple example for the AX2 spin system: a very easy analysis. AX2 is that proton, A is there and X2 is there. X2 is chemically equivalent because their chemical shifts are same and couplings are not visible in this spectrum. Whereas A is coupled to X and another X equally, that is the AX2 spin system.

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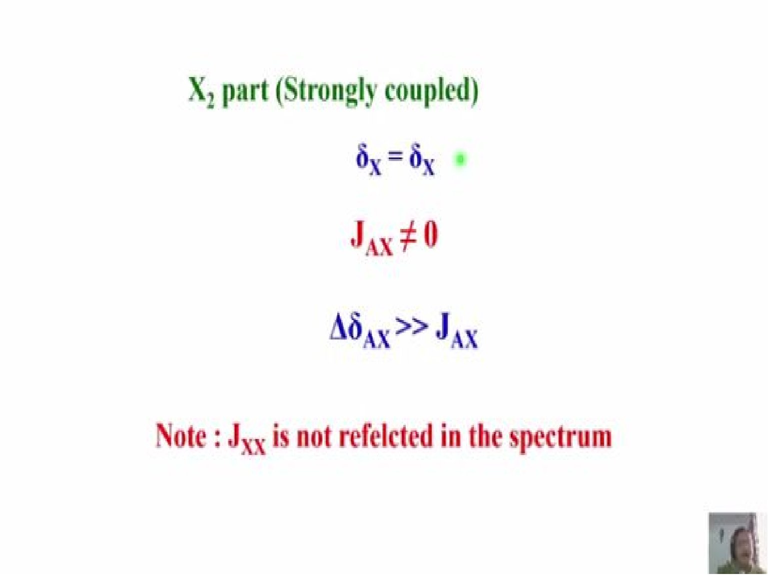

X$_2$ part (Strongly coupled)

$\delta_X = \delta_X$

$J_{AX} \neq 0$

$\Delta\delta_{AX} >> J_{AX}$

Note : J_{XX} is not refelcted in the spectrum

Delta X equal to delta X and which is far away from delta A and JAX is not equal to 0 and this is the condition that the chemical shift separation for AX is sufficiently large compared to JAX, which is called AX2 spin system. This is X2 and in this case X-X coupling is not seen in this spectrum, please remember.

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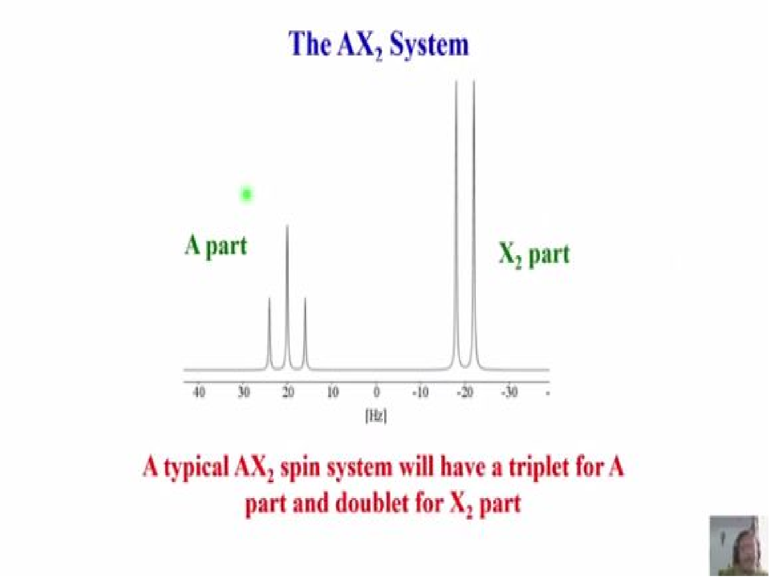
The AX_2 System

A typical AX_2 spin system will have a triplet for A part and doublet for X_2 part

The same classic example of the AX2 spin spectrum, X2 part and A part. What is A part? A part is 1 proton; a single proton, but this A is coupled to 2 equivalent protons, apply your 2NI +1 rule, it has to be a triplet, exactly it is a triplet. What about the X part? The X part is coupled to only a single proton; it has to be doublet. So when you get the spectrum like this, this is A part split into a triplet because of X2 and this is X2 part split into a doublet because of A.

AX2 spin system is very easy to analyze, this gives you a chemical shift of X, the center of this gives you a chemical shift of A, this separation gives you AX coupling. Only one coupling is visible, coupling between X2 is not visible, so you will get only one coupling from this spectrum.

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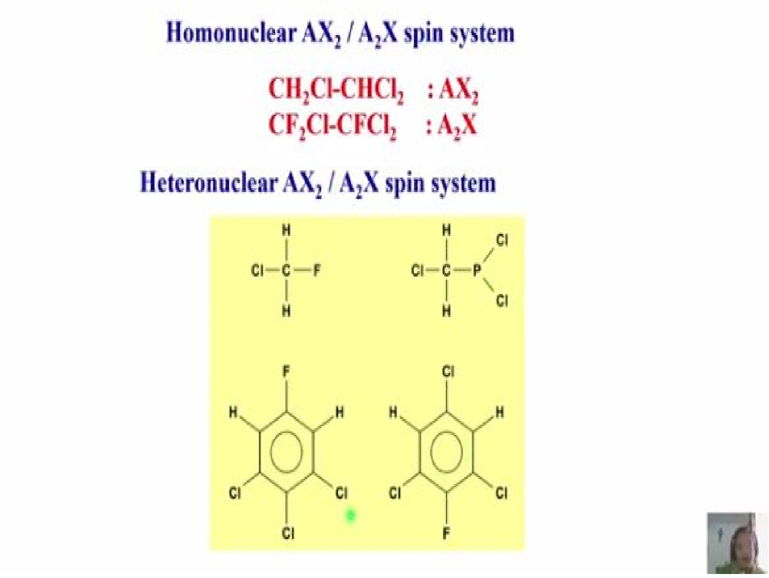

Homonuclear AX$_2$ / A$_2$X spin system

$CH_2Cl\text{-}CHCl_2$: AX$_2$

$CF_2Cl\text{-}CFCl_2$: A$_2$X

Heteronuclear AX$_2$ / A$_2$X spin system

Very easy, so these are examples for the AX2 spin systems, if we look at this, it can be and heteronuclear AX2 or homonuclear AX2. In this molecule if you consider, this is AX2, this is equivalent spin, this is A and this is X2; this is a heteronuclear AX2. Here again, this is fluorine, this is X2, this is also heteronuclear AX2. Here fluorine is in the ortho position of both the protons, it is in para position, they are different molecules, but the spin system is the same. You call it AX2 or A2X, it does not matter, it depends upon how you look at it.

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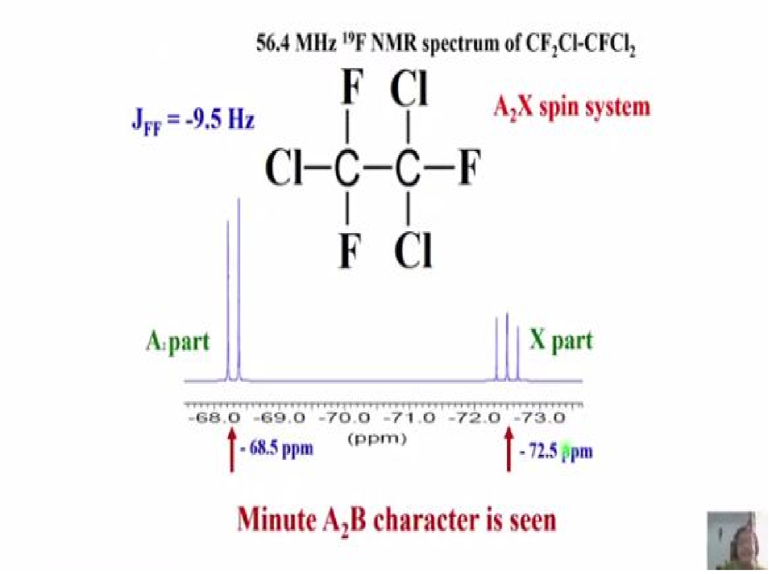

56.4 MHz ^{19}F NMR spectrum of $CF_2Cl\text{-}CFCl_2$

J_{FF} = -9.5 Hz

A$_2$X spin system

Minute A$_2$B character is seen

And this is the ^{19}F spectrum of this molecule. In the fluorine case, this is A part and this is X2 part, they are equivalent here, they is a symmetry axis here, look at it. As a consequence, these two are equivalent. You see the X2 part and look at this X2 part, you are going to see 4 lines and A2 part ,you get 2 lines. But if you carefully observing, it is not just A2, see this central line is split into small doublets, it is not exactly overlapping.

In principle, in A2 they are perfectly equal, this should be a triplet, it is not a triplet, there are 2 doublets. The central peaks are not overlapped, the couplings are not exactly equal, so there is a minute A2B character also seen, it is not A2X. Nevertheless first order analysis can be still feasible here.

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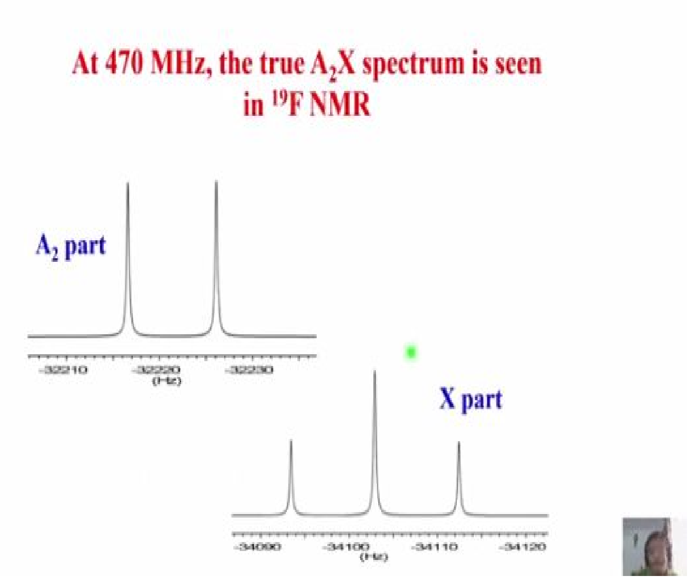

At 470 MHz, the true A_2X spectrum is seen in ^{19}F NMR

And this is the A2 part and the X2 part, very clearly see, if you go to higher frequency, this is at with 56.4 megahertz, that is about 80 megahertz or so. Now go to 500 megahertz, at 500 megahertz fluorine comes at 470 megahertz, now it is is a beautiful X part and beautiful A2 part, everything is clearly seen.

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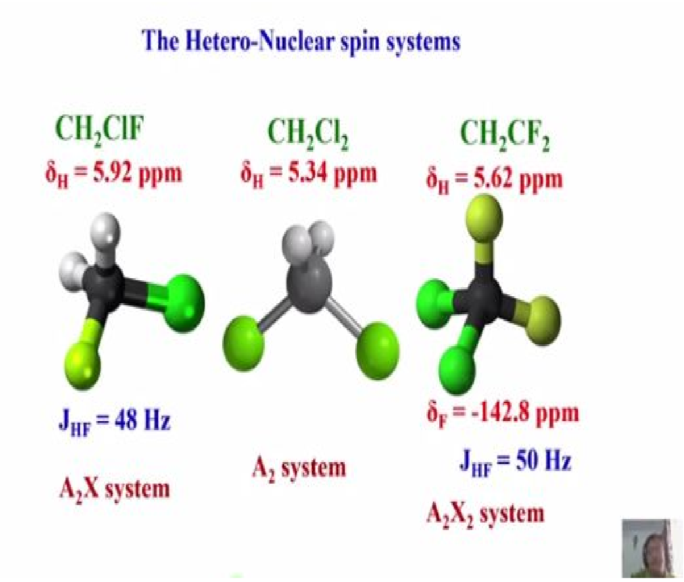

The Hetero-Nuclear spin systems

CH_2ClF
$\delta_H = 5.92$ ppm
$J_{HF} = 48$ Hz
A_2X system

CH_2Cl_2
$\delta_H = 5.34$ ppm
A_2 system

CH_2CF_2
$\delta_H = 5.62$ ppm
$\delta_F = -142.8$ ppm
$J_{HF} = 50$ Hz
A_2X_2 system

Now in heteronuclear spin systems if you consider a molecule like this, CH2ClF. Now this can be considered as A2X spin system. In this simple example there is no fluorine, it is A2 spin system; this is CH2CF2 it is A2X2 spin system. Because these are equivalent and these are equivalent, this is A2 part, this is X2 part. Here only protons are there, coupling with chlorine and carbon are not there, so it is an A2 spin system. In this case you see A2 part, fluorine is far away; it is heteronuclear, it is A2X spin system.

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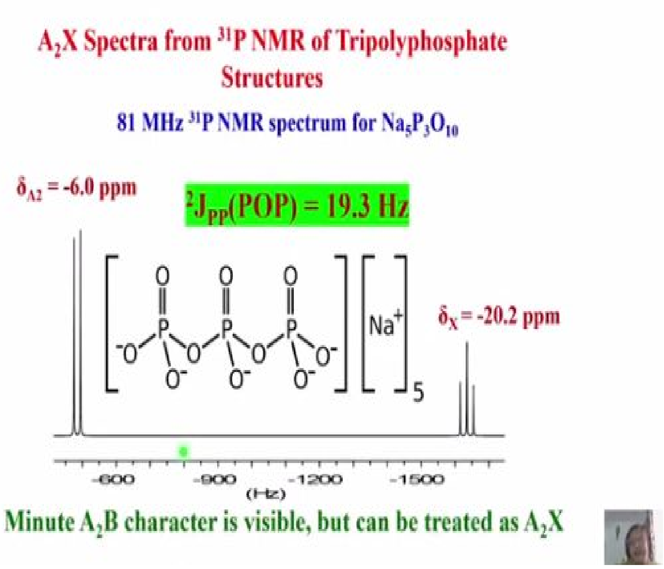

A_2X Spectra from ^{31}P NMR of Tripolyphosphate Structures

81 MHz ^{31}P NMR spectrum for $Na_5P_3O_{10}$

$\delta_{A2} = -6.0$ ppm

$^2J_{PP}(POP) = 19.3$ Hz

$\delta_X = -20.2$ ppm

Minute A_2B character is visible, but can be treated as A_2X

So this is the way you have to identify the spin systems.

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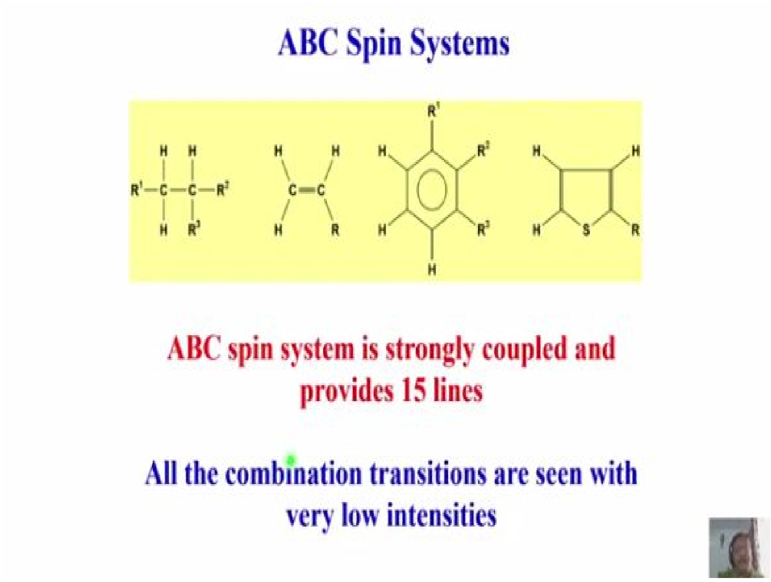

ABC Spin Systems

ABC spin system is strongly coupled and provides 15 lines

All the combination transitions are seen with very low intensities

And in some examples the couplings are very, very small compared to chemical shift separation, these are called ABC, not AMX. All are strongly coupled; but all the chemical shifts cannot be individually determined, but all couplings are present in the spectrum. This is a very strongly coupled case where you get 15 lines.

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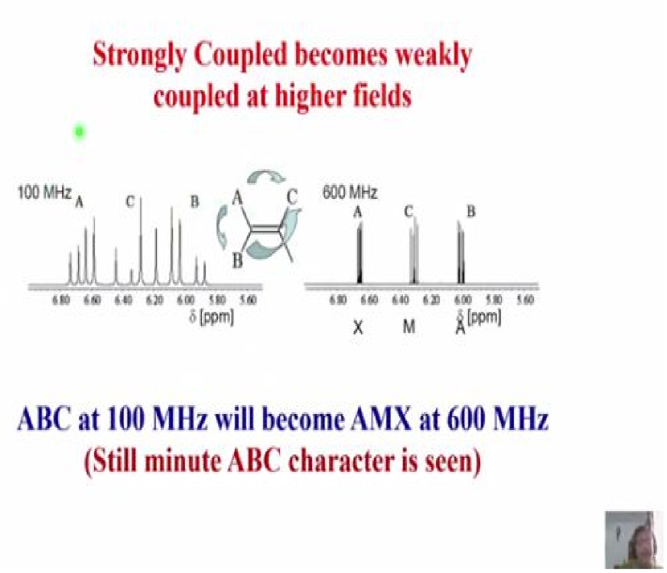

Strongly Coupled becomes weakly coupled at higher fields

ABC at 100 MHz will become AMX at 600 MHz

(Still minute ABC character is seen)

This is an example of ABC. In this case, in this molecule these three protons are strongly coupled and this is the type of spectrum we get at 100 megahertz. The same thing you take at 600 megahertz, it becomes AMX, this is the advantage. So strongly coupled will become weakly coupled at 600 megahertz. Even at 600 megahertz if you carefully see, it is not perfectly weakly coupled, you see, the intensities are not equal, still there is some anomaly. The minute ABC character is there, but by and large first order analysis for measuring couplings and other things is working. But the intensities are different, but coupling constants, more or less we get precisely; we can get precisely.

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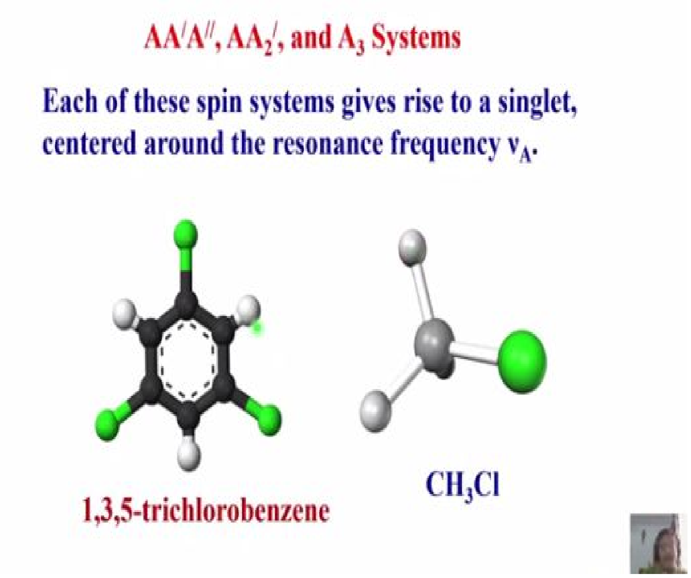

$AA^{/}A^{//}$, $AA_2^{/}$, and A_3 Systems

Each of these spin systems gives rise to a singlet, centered around the resonance frequency v_A.

1,3,5-trichlorobenzene

CH_3Cl

So similarly you can get AA'A'' case, where all the three protons in 1,3,5-trichlorobenzene, this proton, this three proton and this proton have the same chemical shifts, but you have couplings present in that. So it is a classic example of AA'A''

This is A3 spin system.

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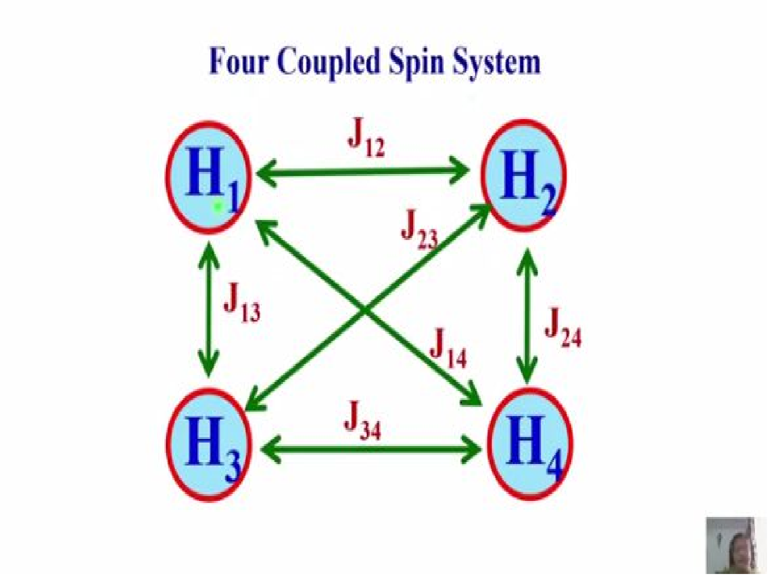

Four Coupled Spin System

And in the four coupled spin system, look at this, one, two, three and four all the four protons are present, you can think of varieties of possible combinations and one of them is weakly coupled case, where all the four are weakly coupled; and this we call it as AMPX spin system.

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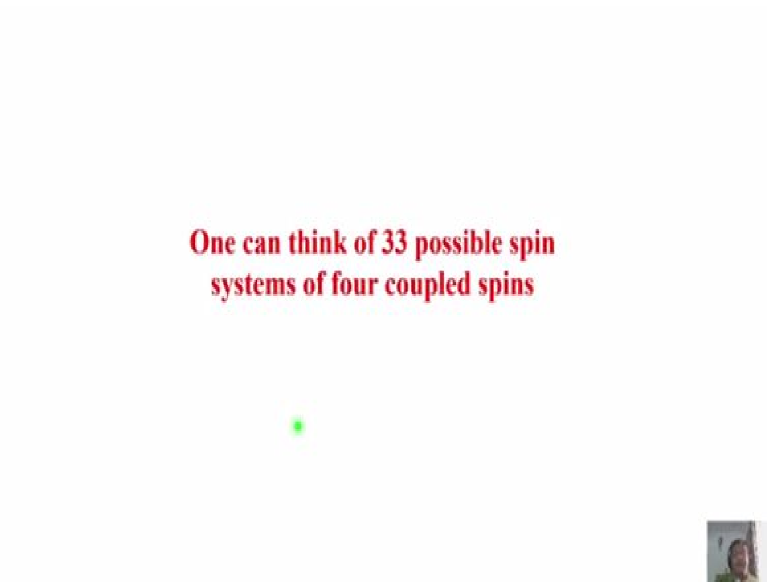

One can think of 33 possible spin systems of four coupled spins

Look at this one.

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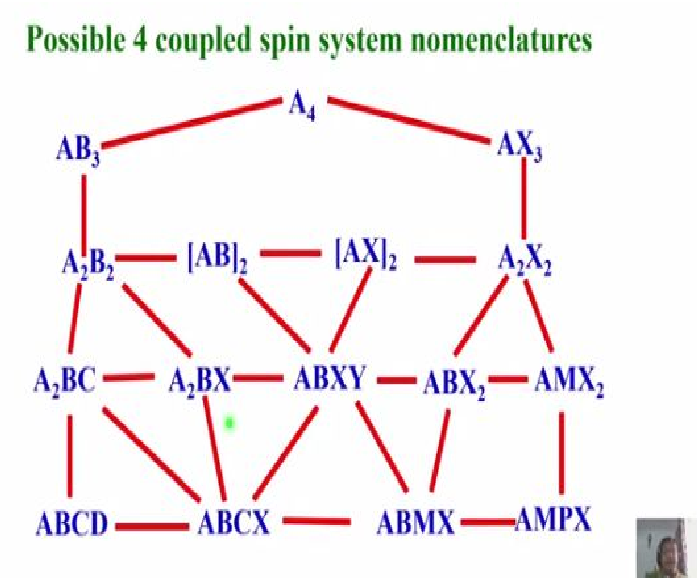

Possible 4 coupled spin system nomenclatures

A_4

AB_3 AX_3

A_2B_2 $[AB]_2$ $[AX]_2$ A_2X_2

A_2BC A_2BX ABXY ABX_2 AMX_2

ABCD ABCX ABMX AMPX

Look at here, You can think of 33 possible combinations here. All four coupled protons, it could be A4, AB3, AX3, any varieties of combinations you can think of and, you will get a simple spectrum. First order analysis of four spins is possible in some cases. A4; first order analysis is simple, only chemical shift, no coupling.

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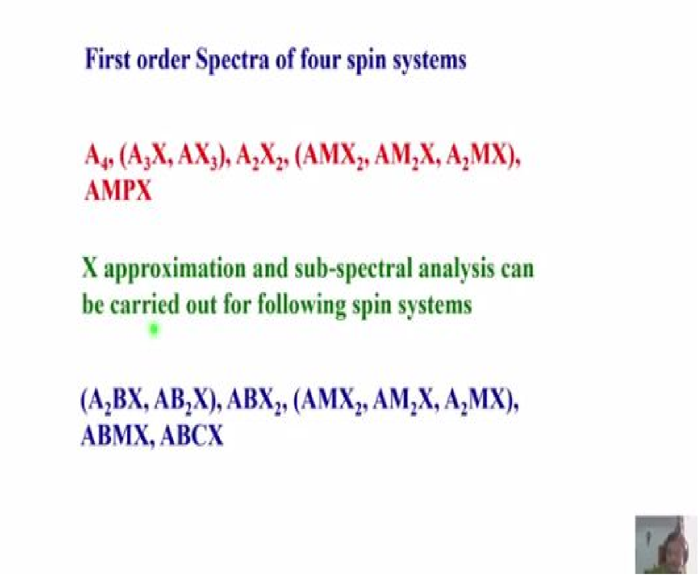

First order Spectra of four spin systems

A_4, (A_3X, AX_3), A_2X_2, (AMX_2, AM_2X, A_2MX), AMPX

X approximation and sub-spectral analysis can be carried out for following spin systems

(A_2BX, AB_2X), ABX_2, (AMX_2, AM_2X, A_2MX), ABMX, ABCX

A3X; still possible, this should be a quartet, this will be a doublet. Similarly AX3 is fine, A2X2; this will be a triplet and this will be a triplet, easily analyzable, AMX2 also. So all these are weakly coupled spin systems, they are analyzable in the first order manner, first order analysis is feasible.

But the same thing when you slightly reduce this magnetic field or go to a lower frequency, they will become A2BX, AB2X, ABX2; like this. These are not analyzable by first order.

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Weakly Coupled AMPX System

$\delta_A \neq \delta_M \neq \delta_P \neq \delta_X$

Six Independent Couplings

J_{AM} J_{AP} J_{AX} J_{MP} J_{MX} J_{PX}

First Order Analysis is feasible

So I will take a simple example of AMPX before stopping, if all are weakly coupled, it is a weakly coupled spin system, chemical shifts of none of them are also equal, they are all different, there are six couplings present, all are different.

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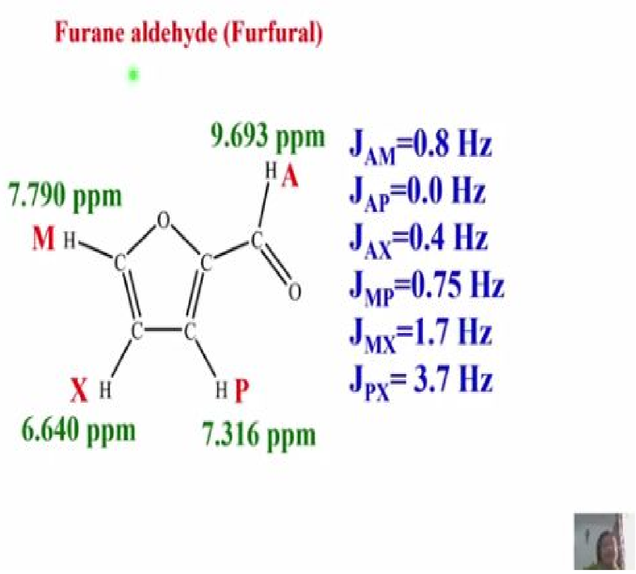

Furane aldehyde (Furfural)

J_{AM}=0.8 Hz
J_{AP}=0.0 Hz
J_{AX}=0.4 Hz
J_{MP}=0.75 Hz
J_{MX}=1.7 Hz
J_{PX}= 3.7 Hz

First order analysis you can do, take a simple example of furane aldehyde, this molecule I call it AMPX because the chemical shift you see is 9.69 ppm, 7.79, 6.64, and 7.316; all are well separated compared to J-couplings. In J-coupling maximum you get is 3.7 hertz. Look at the chemical shift separation here, so let us say 7.8 to 9.7; close to 2 ppm, two ppm if you take 500 megahertz, it is 1000 hertz, whereas AM coupling is 0.8 hertz, see these are all perfectly weakly coupled spin systems.

Similarly if you look at AP, chemical shift separation is 2.3 ppm, what is the JAP coupling? It is zero; a fantastic case or particular case, not zero, it means it is we are unable to measure it because of the line width.

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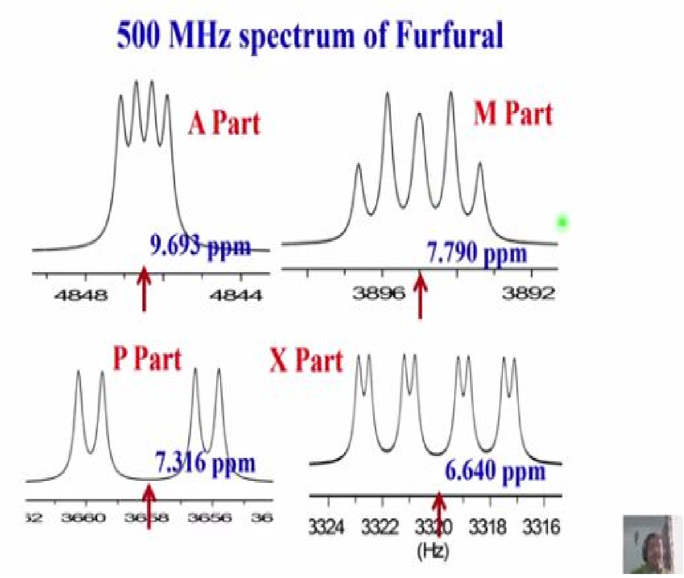

500 MHz spectrum of Furfural

So this is the case, in this case or if you take this molecule, this is A part, this is M part, P part and X part. Very easily you can analyze these things.

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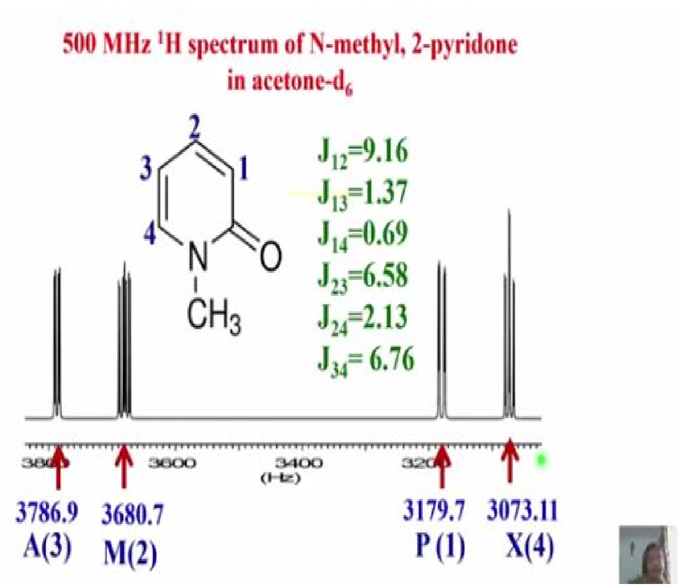

500 MHz ^1H spectrum of N-methyl, 2-pyridone in acetone-d_6

$J_{12}=9.16$
$J_{13}=1.37$
$J_{14}=0.69$
$J_{23}=6.58$
$J_{24}=2.13$
$J_{34}= 6.76$

And this is the example of N-methyl, 2-pyridone in acetone d6, this is A part, M part, P part, X part, they are very clearly separated, intensity anomaly slightly is there, but easily first order analysis is possible.

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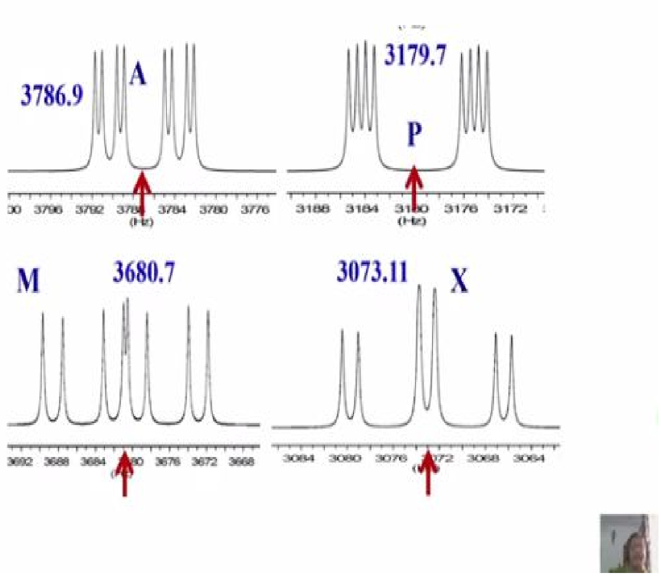

This is the AMPX case, you see more or less equal intensity is here all of them and I know the chemical shifts of all of them, I can easily measure the coupling constants.

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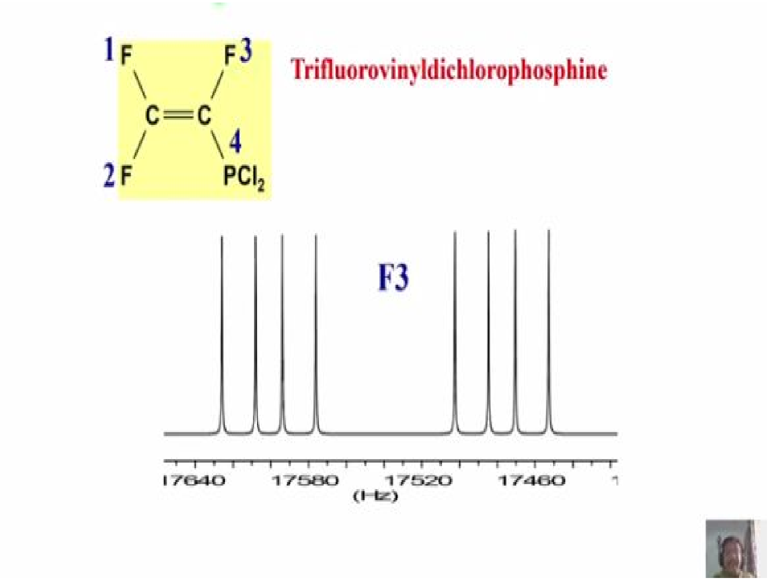
Trifluorovinyldichlorophosphine

So this is the example of a case where all the three fluorines are present and phosphorus is also there. It is a heteronuclear AMPX, phosphorus is coupled to 3 fluorines, all of them are not equivalent now this is the F3 part of the spectrum of fluorine three, fluorine one, fluorine two. So phosphorus spectrum I have to record in phosphorus resonance. I have not got this spectrum.

But essentially what it tells you is, all this thing heteronuclear spins systems; are also perfectly weakly coupled AMPX spin system. Very easily you can analyze. Take the centre of this, you get the chemical shift of this fluorine; and by separations you can get couplings. These three F3, couplings you can extract easily taking this also into account.

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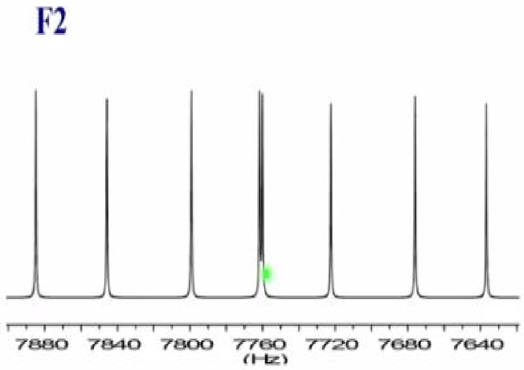

So like this number of examples can be given, I do not want to drag further. In last one or two classes as I was explaining about the spin system nomenclature and the analysis of the protons spectrum. Please remember these are all very important, especially when you want to analyze small molecules, if you want to get the precise coupling information, precise chemical shift information, you should have the knowledge of analysis of the spin systems.

So with this I will stop today and what we are going to do is I will continue further from tomorrow onwards. Please come prepared with the analysis of proton spectra of different spin systems, not like this, real spectrum recorded I take and will interact together and try to analyze.