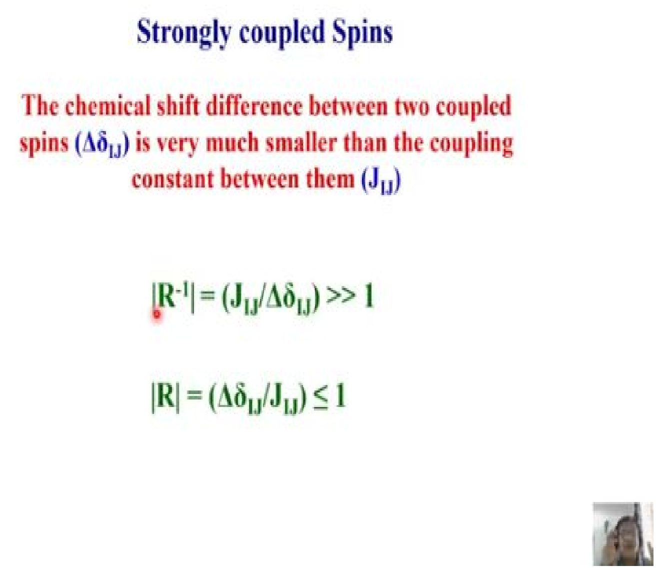
One and Two Dimensional NMR Spectroscopy for Chemist
Prof. N Suryaprakash
NMR Research Centre
Indian Institute of Science Bangalore

Lecture - 28
Spin system Nomenclature

Welcome back, in the last class we started discussing about strong and weak coupling spins, we discussed more about weakly coupled spin system in the homonuclear and the heteronuclear case and also in the labelled system, even in the molecule with natural abundant molecule 1% of carbon or 0.37% of abundant of nitrogen you can label them and bring in the hetero nuclear coupling or homonuclear coupling in molecule like CC coupling are CN coupling and measure the couplings; because they are heteroneuclei, that is what going to happen is their chemical shift separation is of the order of megahertz. As consequence they are all weakly coupled spin systems. So, few examples I gave you, and one of the most important condition I said is the chemical shift separation should be sufficiently than larger than J coupling. I even showed you the delta, delta by J coupling should be greater than 50. If take the reverse order; J over delta delta must be much, much smaller, less than 0.01, 0.001, like that. Then these coupled spin systems are called weakly coupled spin systems. Why I am telling all those things? You may ask question, so what? if it is strongly or weakly coupled, how does it matter?. Please remember I will go ahead and show you, the weakly coupled spin systems are easily amenable to first order analysis. What I mean is directly you can assign and get the chemical shift and J couplings.

But in strongly coupled spin system you cannot do that, it is not possible. So we should know what is weakly coupled and what is strongly coupled spin system for analysis.

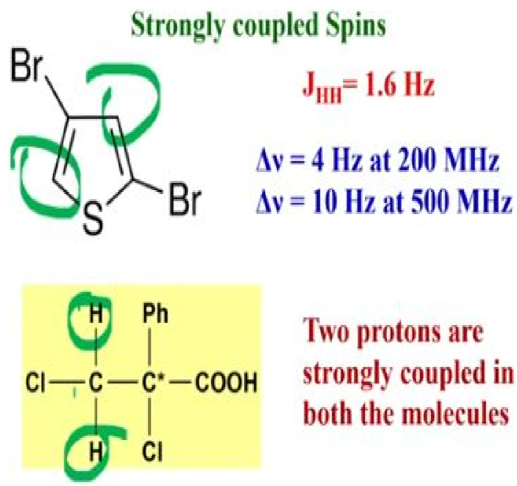
(Refer Slide Time: 02:16)



Now, I will introduce today what are strongly coupled spins. What strongly coupled spins? it is it is exactly opposite of weakly coupled. What you have understood for weakly coupled, make a reverse of it, it is strongly coupled. There chemical shift separation was much, much larger than J coupling, now in this case we say, this is almost comparable to the coupling; Or it can be 0 no problem. Then it is even more strongly coupled spin system. I will show you later when you go ahead. So, this is a strongly coupled spin system. One of the important condition is the chemical shift difference between two coupled spins must be much, much smaller and it is comparable to that of J coupling. Remember, J by delta delta in the previous case of less than 1, 001.01. But here it is more, much much larger than 1.

In the other case delta delta J was approximately 50 or even more than 50, I said. But it is less than 1 here. So these are the cases, when you come across such a situation, it is called strongly coupled spin system. These are all spin systems of strongly coupled.

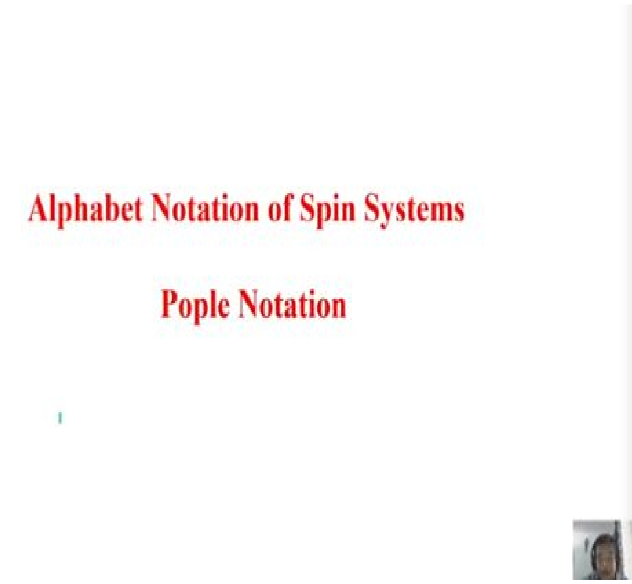
(Refer Slide Time: 03:34)



Let me give an example of a strongly coupled spin, look at this proton. This is a thiophen system, substituted by 2 bromines. JHH between this proton and this proton, is of the order of 1.6Hz. See; this is 1.6 Hz. What is the chemical shift separation? It is only 4 Hz at 200 MHz, does not matter you go to even 500 MHz, even then it is 10 Hz. At 500 MHz, if you go to even 1 gigahertz it can become only 20 hertz. Now take the ratio between J over delta; or Delta delta by J, and it does not fit in to your weakly coupled spin system equation.

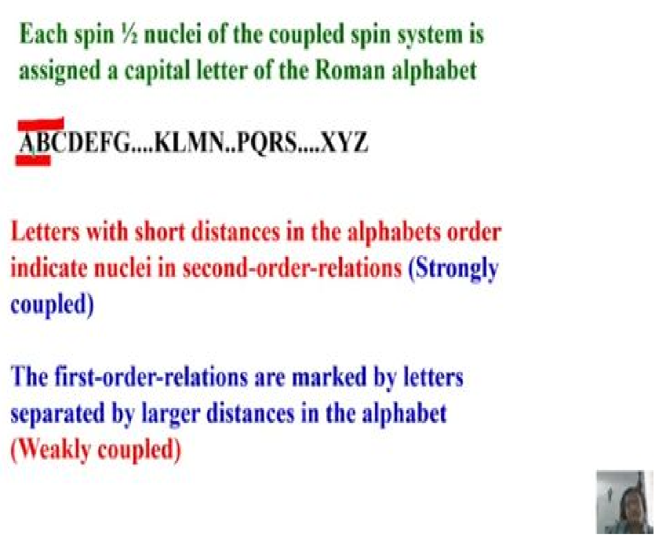
Now this chemical shift separation is almost of the order J coupling. What does it mean? It means these two spins are strongly coupled; this proton and this proton are strongly coupled. Let us take the example of two protons, here and here. They are also very strongly coupled

(Refer Slide Time: 04:56)



These are all simple examples to show the definition of strong coupling and weak coupling. But in NMR jargon, there is a notation to define this strong and weak coupling. This is called Pople notation, remember this word, it is called Pople notation.

(Refer Slide Time: 05:16)

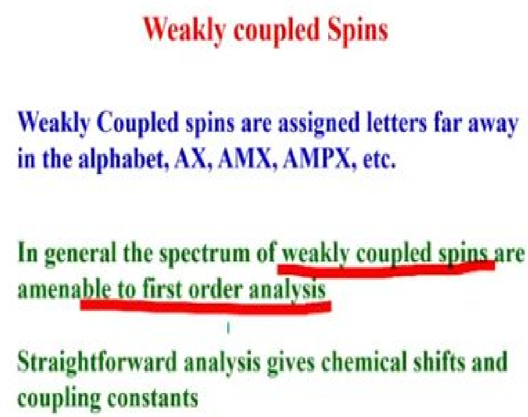


What we do in the Pople notation is a very simple logic. Please understand this very carefully. Each spin of nuclei in a coupled spin system, you know, what is a coupled spin system, I have already discussed, long ago. In a coupled spin system, each spin of nucleus is assigned to a capital letter of the Roman alphabet. What is the meaning of that? The meaning of that is I am going to say we take only ABCD letters, alphabets. ABCD up to Z you can go, no problem.

Each spin of nucleus is assigned a letter. So what, how do you assign it? Next question, Letters with short distances in the alphabets indicate strongly coupled spin system. Letters which are far away in the alphabets indicates weak coupling. Very good definition, right? Now, let us say I have two protons, here one proton and another proton here, they are coupled. If I call this as A and if I call this as X, by nomenclature using Pople, it means this chemical shift separation of this and this are far way separated, compared to J coupling between these two; compared to J coupling. So what does it mean? It means these two protons are weakly coupled, very, very weakly coupled and the other hand I have proton here, I have proton here. And I will write it as A and I write it as B, what does it mean? The chemical shift separation between this and this is almost comparable to coupling between A and B, it is a strongly coupled spin system

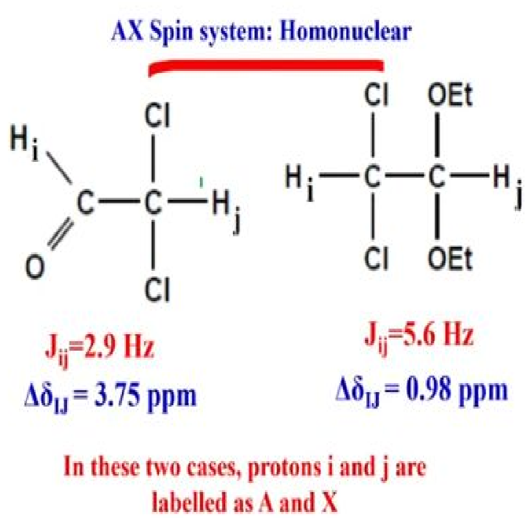
Please remember, if the letter if you are representing the interacting spin, of coupled spin system by a roman alphabet. If the letters are written far away in the alphabet order, in which case they are weakly coupled. If you take next to each other it is strongly coupled, for example A, M, X spin system, remember I analyzed 3 spin system spectrum AMX, we have showed 4 peaks for A, 4 peaks for M, 4 for X. We also understood and wrote down the energy level diagram and looked at the transitions, everything. I also said it is weakly coupled at that time, I remember that. That means the letters A to M is far away compared to other letters, M and X are far away in between there are many letters. That shows if the three spins are weakly coupled, I can write as A, M and X. When only two are coupled A and X, if four are coupled, I will say A,K,P,X that is a 4 spin weakly coupled. Now on the other hand, if I say I have two spin which are strongly coupled I write AB. I write 3 spins, strongly coupled I write A,B,C. This is the nomenclature for strongly coupled you have to write alphabets next to each other, this is a simple thing.

(Refer Slide Time: 08:41)



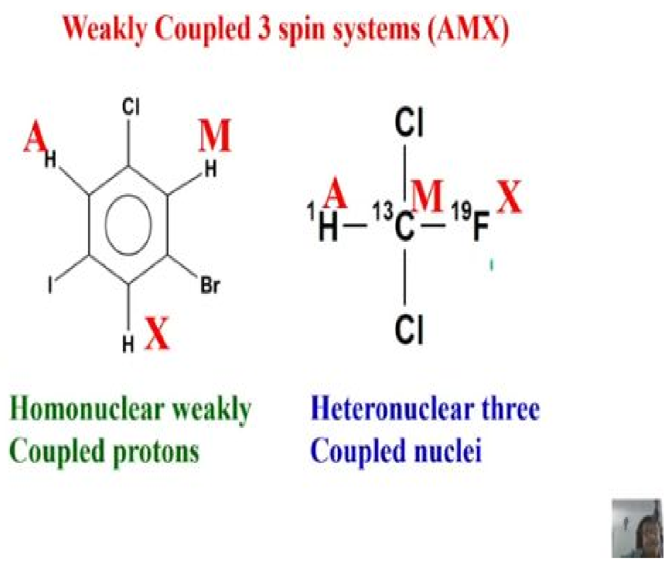
Now of course we will go more into that, there are lot more to understand. Now we will see here weakly coupled are assigned letters like this AX, AMX, AMPX etc. In general, the spectrum of weakly coupled spins are amenable to first order analysis. This is my definition I told you. It means if I give you a spectrum simply looking at this spectrum you can assign and get chemical shift values and coupling values straightforward, without doing much of any mathematical operation, computation, etc. This is first order analysis. Second order analysis is little difficult, so this case is first order analysis.

(Refer Slide Time: 09:25)



AX spin system if I take homonuclear. I told you this is AX, already I have given example of this.

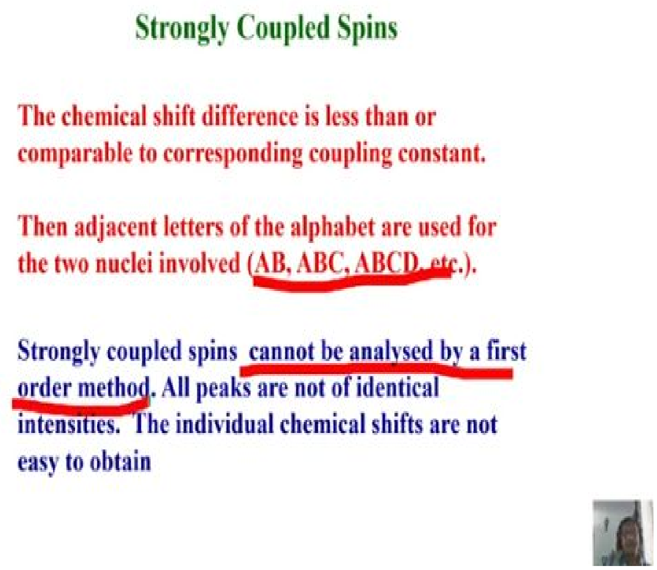
(Refer Slide Time: 09:33)



And weakly coupled AMX is like this. I took the hypothetical example. I took chlorine bromine Iodine in symmetrically substituted benzene. Then there are 3 protons here. This proton and this proton and this proton have their chemical shifts far away separated. It is the weakly coupled spin system. So what I am going to say, I am going to write it as weakly coupled homo nuclear AMX spin.

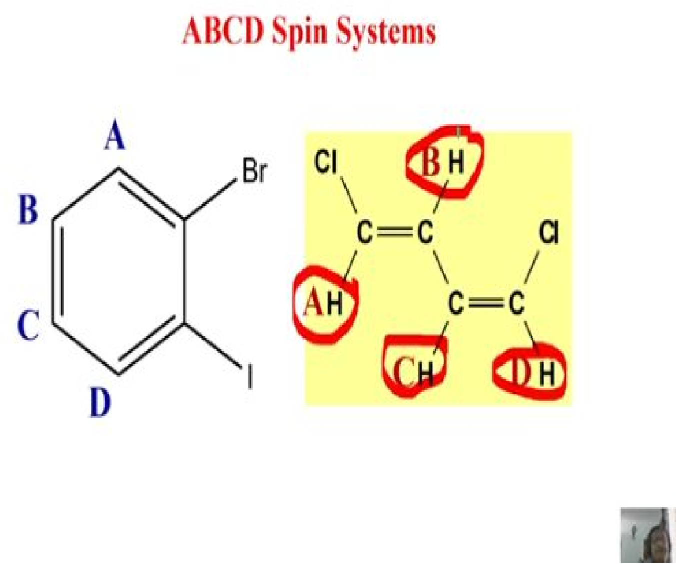
Heteronuclear AMX, look at this molecule I have proton here carbon 13 labeled and fluorine. What is fluorin,e it is a 100% abundant nuclei, this is a 100% abundant nuclei, carbon I label it let us say, that is also 100%. I have 100% carbon 13, some chemistry we do, I label it. Now what happens? remember I told you heteronuclear spin systems are all weakly coupled, because chemicals shift separations are so large, because their resonating frequencies are far apart. As a consequence, in this case these 3 nuclei are weakly coupled heteronuclear AMX.

(Refer Slide Time: 10:52)



Strongly coupled, now let us see how we describe, I told you they are represented by the letters that are close in the alphabet. And you cannot analyze by a first order method. straightforward analysis is difficult, in strongly coupled cases, please remember this point.

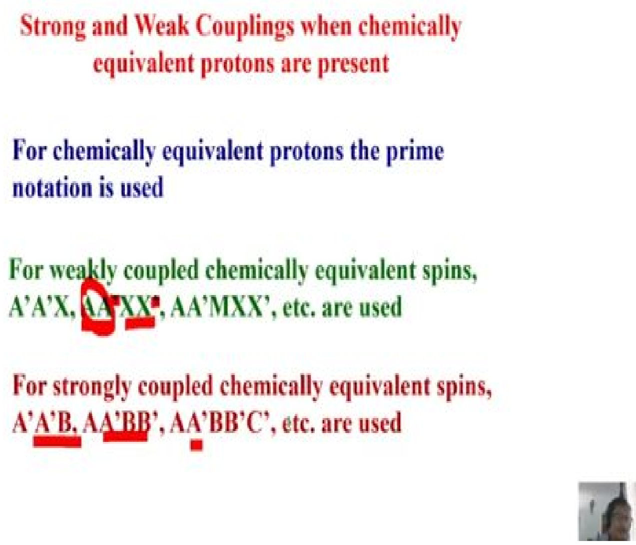
(Refer Slide Time: 11:10)



Now I will give you an example of strongly coupled, take a molecule like this A, B and C D. I will record this spectrum at 200 MHz, you know what happens this chemical shift, this chemical shift separation is much smaller this is still smaller and this is still smaller and this is this to and these to this is smaller. So, chemical shift separation of the protons among themselves is much, much smaller or comparable to the coupling constant.

For example, coupling constant between this and this 8Hz, this and this 8Hz, this is 8Hz between this and this is 1.5 Hz. So if the chemical shift separation is comparable to coupling constant, then I represent research strongly coupled, ABCD spin system. Look at this molecule, this is a classic example this proton, this proton, this proton and this proton, all have nearly similar chemical shifts, close by, the chemicals shift separation is not much larger compared to their coupling constants. Then this a very strongly coupled ABCD spin system.

(Refer Slide Time: 12:30)



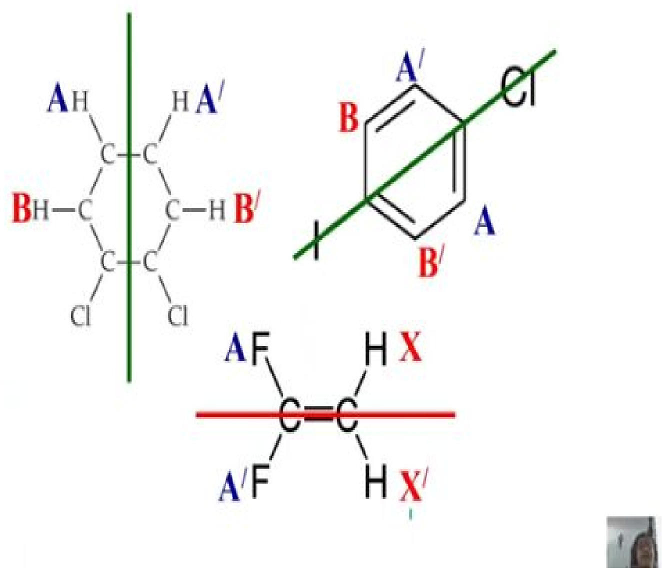
Now I was so far taking spins which are standing alone like see one proton, one carbon one nitrogen like that. But in reality your molecule it is so happens there can be chemically equivalent present, there can CH3, there can be CH2, then how do you represent by alphabets? How do you use Pople notation for that? In which case remember but for chemically equivalent protons or chemically equivalent protons, chemically equivalent we will talk forget about magnetic equivalent protons.

For the chemically equivalent protons a prime notation is used. First thing, forget about magnetically equivalent we will come to that later, and equivalent groups of spins. Take an example for weakly coupled case, we use a prime, AA prime, AA prime, XX prime, AA prime, MXX prime, etc. what is this XX prime, AA prime? Do not get confused, I give you an example;

similarly strongly coupled use AA prime, AA prime, BB prime like this, what do you mean by AA prime here?

It means, AA prime means, we will take this one AA prime, means there are 2 protons are 2 spins having the same chemical shift. Chemical shift is same, because they are chemically equivalent, remember they are chemical equivalent 2 protons. But there is a coupling between them, coupling is not 0. Only chemically equivalent, in such cases when chemically equivalent has same chemical shifts, use a prime notation, similarly X and X. What does it mean? There are two protons which are far away from this A. Far Away from A there are two protons having the same chemical shift again, they are chemically equivalent. Then you have to use prime notation if you call those two spins X and X prime. Same way you can write for strongly coupled A prime, AA prime, BB prime, ABC, AB prime, AB all the things you can write.

(Refer Slide Time: 14:55)



I give you an example, you will get more clarity by taking an example. Consider a molecule like this 1-2 dichlorobenzene, this is symmetry axis. What is the meaning of that? This proton and this proton are chemically equivalent, this proton and this proton are chemically equivalent. Now how many types of protons are there in this molecule? There are only two types, because this and this are same, this and this are same , chemical equivalent give one peak. This will give one chemical shift, this will give you one chemical shift. That is all. But the coupling is not 0, there is no coupling between this is not absent. Coupling between this and this is not absent, it means they are chemically equivalent, but not magnetically equivalent. We will now worry about those parameters later, but remember now this and this are chemical equivalent, this and this are chemically equivalent.

Now, how do I represent this using Pople notation? Simple if I call this as A, I call this as A prime, because there exists a coupling between these two. If this I call B, I call this as B prime. Simple, I use a notation because chemical equivalence is there, I can use notation. And between these two, what do you say? This is A this B means, these two protons are strongly coupled. These two are also strongly coupled, but the chemically equivalent. These two are also strongly coupled B and B prime means, strongly coupled, but they are chemically equivalent. Remember these two are strongly coupled chemically equivalent, these two strongly coupled chemically equivalent. So you write the notation like A A prime, here B, B prime; but these two are strongly coupled but not chemically equivalent, write different letters A and B.

Understand how to write Pople notation for strongly coupled, chemically equivalent spins. I suppose you are catching my point, consider this example now metachloroiodo benzene. Hypothetically I have written the molecule, this is a symmetry axis. Now what is going to happen? this proton and this proton are having the same chemical shifts, chemically equivalent, this and this are chemically equivalent. So I call this A and A prime and I call the other one B and B prime. Provided a chemical shift separation between these two are comparable to this coupling. If by some reason these two protons, let us say, are far away, what do I do then? Then I call it as AA prime and XX prime, between these two they are strongly coupled, between these two they are strongly coupled and between them weakly coupled.

So in the given system you can come across one or two protons can be very strongly coupled and between them, between that coupled proton strongly coupled and with other one there may be weakly coupled. Fantastic, many things can happen, so in this example here also, this and this are strongly coupled, this and this are strongly coupled, this and this are also strongly coupled. By some reason this and this become weakly coupled, this proton this proton, AA prime becomes weakly coupled to BB prime. Then I call it XX prime, understand? For equivalent system always use prime notation, but the nomenclature of weak and strong coupling remains same, if it is strongly coupled use the nearest neighboring alphabet or, if it is a weakly coupled use the alphabet which is far away in the list of alphabets, that is important, you must understand.

Now let us take this example, what do you call this spin system? It is very simple molecule. Now this fluorine and this fluorine are chemically equivalent, there is a symmetry along this axis. And this proton and this proton are chemically equivalent. What is the resonating frequency of fluorine compared to proton? Several megahertz away. I told you a heteronuclear spin systems are always weakly coupled, it can never be strongly coupled. So what do you call this spin system? AA prime, XX prime. why call it AA prime? because there existing coupling between these two if there is no coupling it is a different nomenclature, I will come to that later. Because there is coupling between these two, and they are chemically equivalent, I use the notation AA prime, similarly for this I used XX prime. Are you all with me on how to use the notation?

(Refer Slide Time: 20:44)

When proton (s) are coupled to groups of chemically equivalent protons, e.g. in CH_2, CH_3 groups, etc.

Each letter is given the subscript to identify the number of protons in that group.

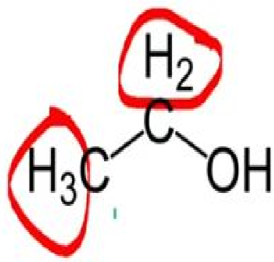
For strongly coupled spins, AB_2, A_2B_2, AB_3 ....

For Weakly coupled spins, AX_2, A_2X_2, $A_2M_2X_2$, etc...

Now when I have a group of chemically equivalent protons like this, earlier I took only individual chemically equivalent protons, now if I take a group like this CH2, CH3 etc. then how do you represent using alphabet? Very simple, in which case for strongly coupled you write AB2 where, in B2, the two represent a number of protons in that group. If you say AB3 it will tell you the number of protons in that group, for example, this is a H3 group, and it is something else.

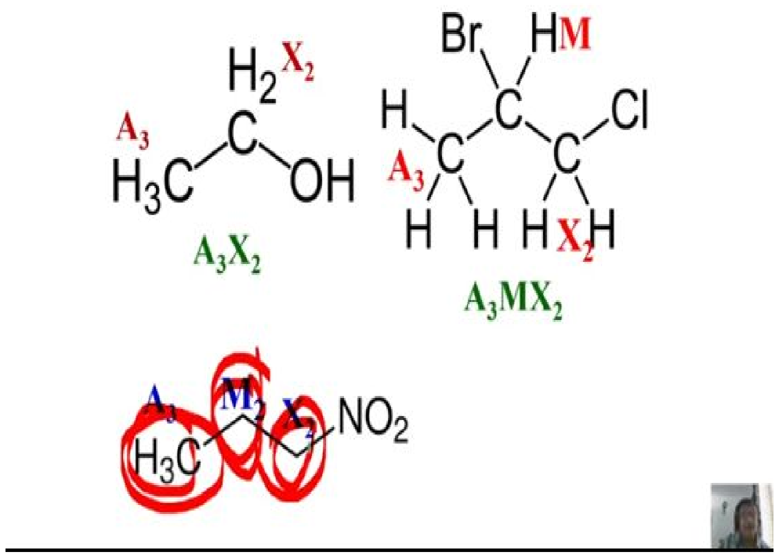
Take this as CH3 group or CH2 group here like that, for the weakly coupled, again you write it as AX2, A2X2, A2M2X2 like that. So there is no prime notation here, it is equivalent spins in a group here. Here also, of course equivalent case can come, CH2 here and CH2 here can be equivalent, then you have to call it as A2A2 prime, A2X2 prime, that is also possible. Give prime notation even in weakly coupled case here also. Are you all listening? I hope I am carrying all of you with me.

(Refer Slide Time: 22:03)



Now let us analyze this molecule. I want you to tell me what is the Pople nomenclature for this molecule? Remember there are two protons for this CH2; there are three protons for this CH3, I am not worried about carbon, worried about only protons, and these two are well separated carbon CH2 comes here CH3 comes here let us say separated by some 3 or 4 ppm or 2 or 3 ppm and coupling between these two is very small. I would say it is a weakly coupled spin system.

(Refer Slide Time: 22:44)



In this case, what is the notation we have to use? Think carefully ,now what is the notation you have to use it is A2 or A3X2 or A2X3 whatever it is. This is I call it A3 because I have 3 protons, I call it X2 here because there are two protons. Here it is called A3X2 spin system. There is notation subscript count correspond to or subscript refers to the number of equivalent protons present in the group, understand? This is A3X2 spin system.

What about this one? very interesting thing; there are 3 protons here all equivalent. I call it A3 no problem there are two protons here, both are equivalent I call it let us say X2, is only one is left. So equivalent I wrote the subscript by number. Now what is the type of spin system it is? Simple logic it must be A3MX2 and they are very well separated. Chemical shift of this is far away here is CH3 then CH2 then CH very far away separated. As a consequence, it is A3MX2 spin system. Let us ask you a question. What happens if their chemical shifts are not large, they are not well separated; then what you would have called this spin system? You would have called it as A3BC2, or A3BD2, like that. Because we are writing A3MX2 they are weakly coupled, because we know chemical shifts are far away separated, if they are not separated you have to bring the alphabet next to each other.

This is A3MX, what about this one? Very easy to analyze we have CH3 protons. It is A3 this is CH2 and CH2. What do you call this spin system, very simple A3M2X2, the reason is nitrogen pulls this one far away, this is X2 and this Che is high field, and this CH2 comes somewhere in between. So I call this as A3M2X2 spin system.

(Refer Slide Time: 25:24)

Analysis of NMR Spectra of Different Spin Systems

Very interesting, so far I was telling you about the Pople notation. Now we analyze this spectrum of different spin systems. All A3, A2, AX, AMX we analyze now that gives you an idea, more about NMR spectrum.

(Refer Slide Time: 25:44)

Number of Coupled spins	Possible Spin Systems Nomenclature
1	1
2	3
3	10
4	33

We will consider number of spins and possible spins system nomenclature. What is possible spin system? I will come to that, do not worry we will go ahead. Let us say I have only one proton in the molecule. Then what is the possible spin system, only one, because it can be $CHCl_3$, only one proton, this is either A, X whatever it is, only one spin.

Let us say I have two coupled spin system, two protons are coupled. What is the possible nomenclatures you can think o,f both can be very well separated away. Then the weakly coupled they come close by, strongly coupled chemical separation much smaller. It becomes AB, it can so happen the chemical shift can be same, overlapped, then if there is a J coupling it is AA prime. If they are magnetically equivalent, it is called A_2. Understand AX can become AB and if J coupling is not seen, then it becomes A_2. A_2 means it is equivalent the coupling between them is not seen.

You are not seeing the coupling in this spectrum there is coupling but you do not see it in this spectrum, then it becomes A_2. So there are 3 possible spin systems, when two spins are coupled. The three possible spins systems are, AX, AB and A_2.

Now what happens if the I take three spin system here. Believe me, there are 10 such possibilities you can think of, it can be, let us start with all 3 equivalent chemical shift be the same, you will not see coupling in this spectrum. What is it possible nomenclature for it? A_3.

If there is a coupling between them which is seen in the spectrum, but chemical shift is same. Then what you call it A, A prime, A double prime. You have to use prime notation for equivalence, Chemical equivalent. What happens if they are very well separated, far away from the chemical shifts weakly coupled. AMX.

If the 2 or strongly coupled one is weakly coupled it can be ABX.

All the three are strongly coupled, it can be ABC.

If two are equivalent with the same chemical shift, no coupling is seen in this spectrum, another is weakly coupled is A_2X.

This 2 are very strongly coupled same chemical shift no coupling is seen in this spectrum, but this is also strongly coupled another proton it is A2B. So like that you can start thinking of all possible spin nomenclatures.

You do not have to worry about it I have already done it, there are 10 spin nomenclatures. Each of them can be analysed in a different way. Remember they are not same, analysis will be different for each of them, we do not want to do that. If I start doing that, that will be one semester course itself on the Pople nomenclature. We will not do that, I will simply give another example, and go to other things.

So now if you go to the 4 protons coupled, You know believe me or not, there are 33 possible nomenclatures, you can think of. I will just show you possible nomenclature, yes, we do not analyze all of them. For the sake of giving an idea of coupled spin system, how to analyze, we will take only 2 spins and one or two simple example of 3 spins and stop it. Otherwise there is no end for it this itself you can speak for hours and hours, weeks and weeks. I will not do that because I have lot more things to cover later. We have to analyse hetero nuclear, carbon13 NMR, hetero nuclear NMR, I have to tell you decoupling, relaxation, DEPT, INEPT experiments, polarization transfer, NOESY, 2D, Relaxation and lot of things, I have to teach in the remaining classes, we do not go into the details. So we will just take example of one spin, and 2 spin, 3 spin, one or 2 examples of this quickly and finish it. With that we really take the spectrum of the molecule in the spectrometer and start analyzing; or the spectrum is recorded and available to us will analyze it, let us see.

(Refer Slide Time: 30:30)

Single Spin System

Single Spin, No detectable couplings with any other spin

Now a single spin system, no other coupled spin, no detectable coupling with any other spin, only one spin how many peaks you expect. Simple I told you, you will get only one peak.

(Refer Slide Time: 30:49)

Examples of Single Spin Systems

Molecule	Detected Spin
$CHCl_3$	^1H
C_2HCl_3	^1H
C_6HCl_5	^1H
$CFCl_3$	^{19}F
C_6FCl_{11}	^{19}F
PCl_3	^{31}P
$Pt[Cl_6]^-$	^{195}Pt

Now, what are the examples of the nuclei which can give single peak? Look at it CHCl3 can give one peak. C2HCl3 can give only one peak. Why? Because carbon 13, I assume to be natural abundant and intensity is very weak you will see only satellites. When I have a go to satellite analysis, I will tell you. Chlorine do not couple, quadrupolar spin. It generally do not get coupled to proton.

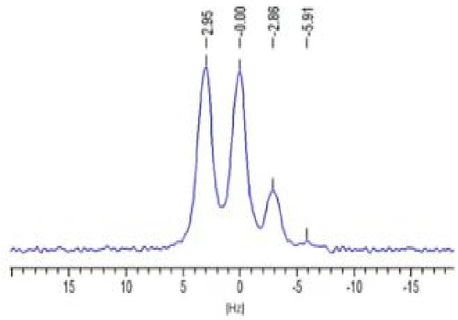
Similarly C6H5Cl2, CFCl3, fluorine, you must get fluorine NMR; if I do I get 1 peak. C6CFL3 fluorine NMR you get one peak, PCl3 phosphorus NMR you will get only one peak. Platinum195 NMR, we get only one. These are all single spin systems, examples of only one spin system without coupling to other spins.

(Refer Slide Time: 31:48)

Single spin system, can also give multiple peaks, this is a very, very interesting thing. To understand, it appears as single but sometimes I will give you interesting example, you will really flabbergasted to see how NMR is so beautiful. It appears very simple molecule, but gives 4 peaks CHCl3. To me it appears like it should give single peak, but in reality it gives 4 peaks. Where do we get these 4 peaks from? But they are real peaks, we have to analyse.

(Refer Slide Time: 32:25)

470 MHz ^{19}F spectrum of $CFCl_3$



I will give an example like this, take the example of CFCl3, 470 Megahertz Spectrum. 4 peaks all are real. Intensity of this one is 100, this one is 95, this one 30 and this one is 3 intensity. It is very interesting, no doubt at all, it is a real spectrum. How do you analyze? And I can assure you there is no coupling between carbon and fluorine detectable here, they are all satellites. I am not worried about it, there can be very minute peaks like this, called satellites when coupled to carbon.

I am not seeing that. This chlorine is not coupled to fluorine, all information I am giving you, but still how I got 4 peaks, something strange. How can you expect 4 peaks for CFCl3 when this is not coupled this are 1% natural carbon 13 coupling, we do not see. We are not bothered to see this chlorine, it will not couple to this. We have only one fluorine in reality I must get only one peak. But literally I got 4 peaks, how do you analyze this?

All are realistic peaks, I give an intensity 100%, 95%, 30%, 3%, very interesting example. What we will do is will come back in the next class and try to analyse these things. That will give you an idea how beautiful NMR can be utilized in solving many small, small chemical problems. It is the simple chemistry problem, but you can solve it easily. So we will stop for the day, today I have already a lot of information about scalar coupling, coupling strengths and how it can be used using karplus equations and also I brought in People nomenclature.

How do you represent Pople nomenclature, in weakly coupled or strongly coupled cases, what happens when the chemically equivalent spins are present? What happens when there are groups of equivalent spins are there, like CH2 proton, CH3 groups are there, how do you represent all those things and we took the examples of spin systems for each, we saw what are weakly coupled, what are strongly coupled conditions and what happen when there are homonuclear weakly coupled. What happens if I take heteronuclear coupled, whether it is strong or weakly coupled, the lot of things you understood. Now using Pople nomenclature also we wanted to know what are these spin system analysis? Very interesting thing we will continue next class.