Advanced NMR Techniques in Solution and Solid-State
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Module 7
Multiplicity Patterns of Coupled Spins and Analysis of 1H NMR Spectrum
Lecture - 07

In the last class, I introduced a new interaction parameter, that is the internal interaction parameter in a given molecule called scalar coupling. We discussed a lot about various salient features of coupling constant; we discussed, we came to know that it is a small number compared to Zeeman interaction, but nevertheless for the n number of chemical inequivalent protons which are present in the given molecule, there can be a lot of interactions, one spin can interact with other spins through covalent bond, it is a covalent bond mediated coupling. The spin polarization transfer takes place between 2 interacting spins mediated through covalent bond. And as the number of bonds intervening between interacting spins, increases the coupling strength keeps on decreasing; that is what we understood. At the same time, we also understood 1 proton or 1 spin can experience coupling with n number of other spins simultaneously. It could be both homonuclear or heteronuclear and the coupling strength can be different; they can be of varied strengths; they need not be same; they can be of different coupling strengths. And there can be coupling between homonuclear spins and coupling between heteronuclear spins; both are possible and at the same time. I took simple example to show why the multiplicity comes; how the multiplicity comes?

We took simple example of 2 protons coupled between themselves. 1 proton splits into doublet because of the other proton, because of 2 possible spin orientations. As a consequence, this proton sees 2 possible orientations, so the effect is each proton will become a doublet because of 2 orientations. So if there are 2 protons coupled between themselves, the total number of lines you are going to get is 2 to the power of 4.

And at the same time for each proton the number of transitions what we are going to see is 2 to the power of n – 1. In this case it is 2 to the power 2 - 1, 2. That is why when 2 protons are coupled, at the chemical shifts of site of each of the protons, you get 2 lines. If you have 3 protons, I showed at the site of each of the protons we get 4, 4 lines. Similarly, if you go to more number of spins we generated the formula for the number of transitions.

And we know the number of peaks that you are going to see when a weakly coupled spin system for any chemically inequivalent spin, the number of transitions that you are going to see at the site of each spin is given by 2 to the power of n - 1. And the total number of peaks you are going to see in a spectrum is given by n into 2 to the power of n - 1. That is what we discussed and the mechanism of splitting also we understood, taking the example.

Now in continuing further today what we will do is, how the multiplicity comes. We will discuss, of course we already discussed for 2 spins, and it depends also on the chemical equivalence. And I will introduced another term called magnetically equivalence today. I remember I introduced chemical equivalence where I said the 2 protons can be interchanged due to symmetry operations.

And then I said they are chemically equivalent, gives rise to the same resonating frequency or the same chemical shift. But what happens if there is a coupling between them or what happenes to the coupling between different protons? I introduce a new term called magnetically equivalence and how the spectrum gets affected. Based on their chemical equivalent or magnetic equivalent nuclei present how this splitting pattern comes?

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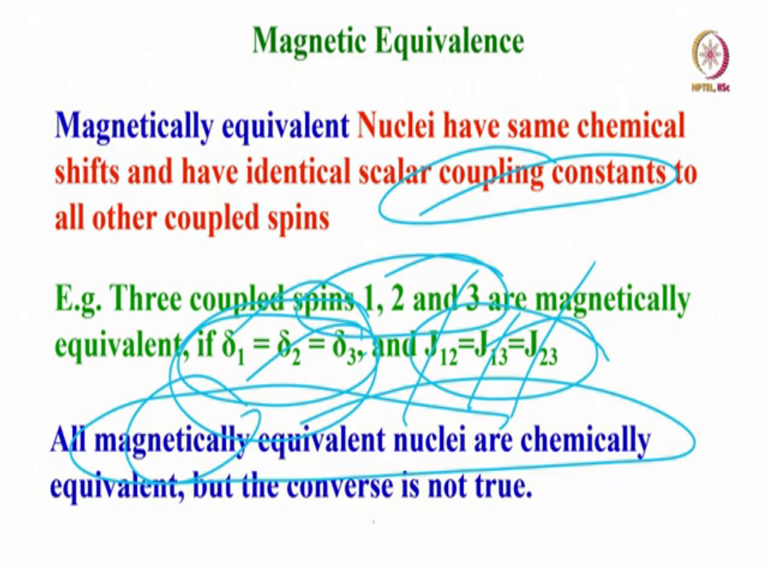

Magnetic Equivalence

Magnetically equivalent Nuclei have same chemical shifts and have identical scalar coupling constants to all other coupled spins

E.g. Three coupled spins 1, 2 and 3 are magnetically equivalent, if $\delta_1 = \delta_2 = \delta_3$, and $J_{12}=J_{13}=J_{23}$

All magnetically equivalent nuclei are chemically equivalent, but the converse is not true.

What is a magnetically equivalence? Magnetically equivalent nuclei have the same chemical shifts and have identical coupling constants also; very important thing, identical coupling to all other coupled protons. For example, if there are 3 protons 1, 2 and 3, all are coupled. What is the main condition to call it magnetically equivalence? For calling it as chemical equivalence this is correct only chemical shift are same, they are chemically equivalent.

At that time, we did not discuss J coupling. Now I bring the J coupling also into account condition for magnetically equivalence in such a situation is, not only chemical shifts are equivalent, the coupling J12, J13 and J23 also should be identical. They should be same, then such nuclei are called magnetically equivalent spins, or magnetically equivalent nuclei. So remember this is the most important thing; all magnetically equivalent nuclei are chemically equivalent. But the converse is not true, all chemically equivalent nuclei need not be magnetically equivalent, because they may have same chemical shifts but couplings could be different. Whereas magnetically equivalence spin is a special case where not only chemical shifts are same, but couplings are also same.

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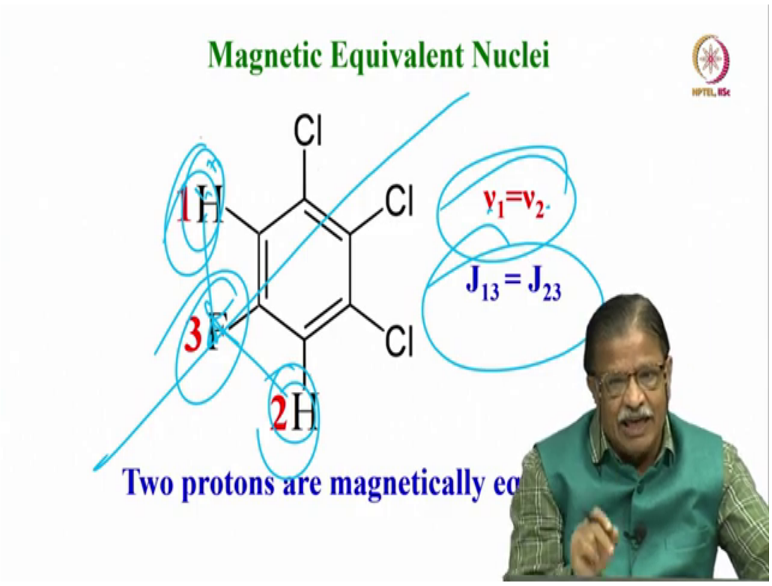

Magnetic Equivalent Nuclei

$\nu_1 = \nu_2$

$J_{13} = J_{23}$

Two protons are magnetically eq

So take an example for a molecule like this I take 3 protons 1, 2 and 3. I am sorry, 2 protons and fluorine; there is a symmetry axis here. Now because of that chemical shift of proton 1 and 2 are same, ν1 = ν2. At the same time this proton can couple to fluorine; this proton can also couple to fluorine. So 13 and 23 couplings are present. If 13 is also equal to 23, in addition to ν1= ν2; it means, these 2 protons are magnetically equivalent. That is the condition, remember these 2 protons are called magnetically equivalent in this situation.

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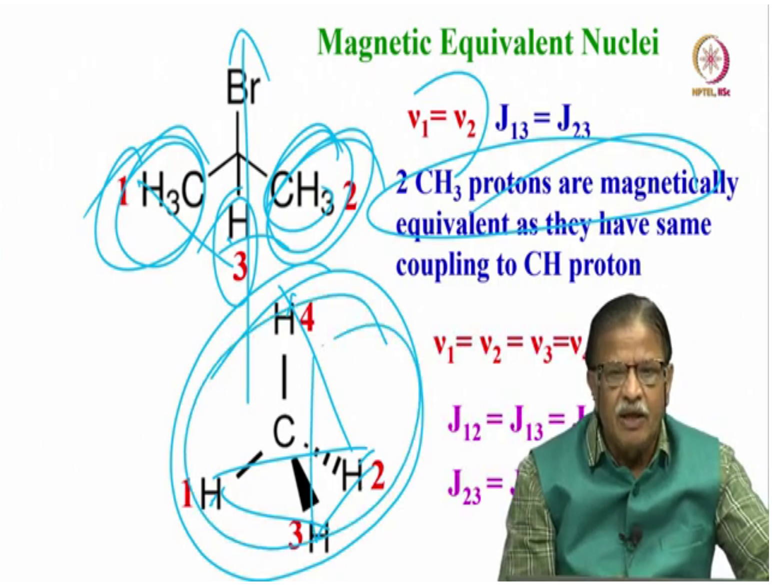

Magnetic Equivalent Nuclei

$\nu_1 = \nu_2$ $J_{13} = J_{23}$

2 CH_3 protons are magnetically equivalent as they have same coupling to CH proton

$\nu_1 = \nu_2 = \nu_3 = \nu$

$J_{12} = J_{13} =$

$J_{23} =$

Now take another example like this. Is there a symmetry axis for this? Yes, along this axis. Now ν1 = ν2. All the 3 chemical shifts with these 3 methyl protons and these 3 methyl protons chemical shift are same; identical. So ν1 = ν2 but the coupling between these methyl protons and the CH proton; and this methyl proton and the CH proton are same. J13 = J23. So two CH3 protons are magnetically equivalent, as they have same coupling to CH proton; not only chemical shift is same, but couplings are also same.

I take another simple example; this is methane, has 4 protons, all are chemically equivalent. The coupling of 1 proton with any other protons, if you consider, exactly they are same. 14, 12 and 13 coupling 23, 24 coupling 34 coupling everything you consider, they are same. So this is a magnetically equivalent spin system.

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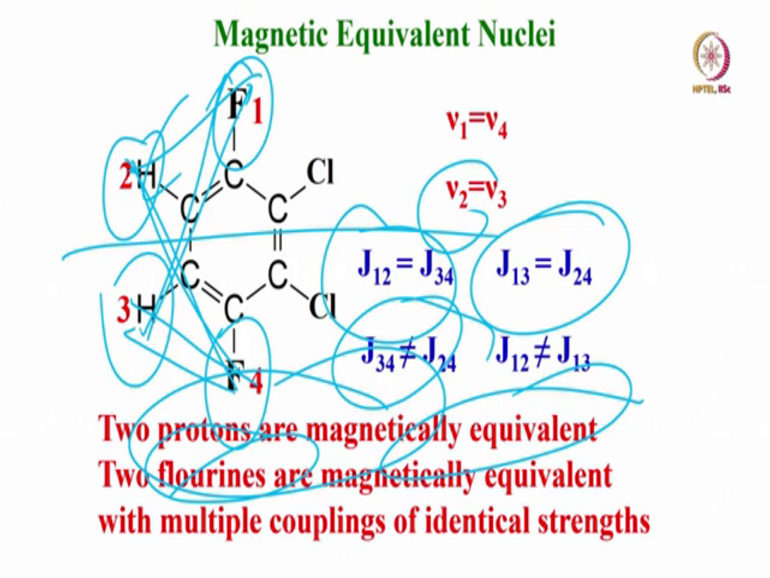

Magnetic Equivalent Nuclei

$\nu_1 = \nu_4$

$\nu_2 = \nu_3$

$J_{12} = J_{34}$ $J_{13} = J_{24}$

$J_{34} \neq J_{24}$ $J_{12} \neq J_{13}$

Two protons are magnetically equivalent
Two flourines are magnetically equivalent
with multiple couplings of identical strengths

Now we go to magnetically equivalent nuclei like this. The heteronuclei are present here, for example ν1 = ν4, there is a symmetry along this axis. So ν2 is also equal to ν3. Consequently, but remember, 12 coupling and 13 couplings are not same. This is 13 coupling and this is 14 coupling. Similarly, 34 coupling and 24 coupling are not same; they are different. But nevertheless 12 = 34; and 13 = 24 both are same, but 34 is not equal to 24 that is another thing. You should remember, similarly 12 is not equal to 13. So the 2 protons are magnetically equivalent, and 2 fluorines are magnetically equivalent. How do you say magnetically equal and the couplings are different? Just now we said coupling should be same. But remember both the protons experience 2 different couplings, but the 2 different couplings are also same. So this is a special example where both the fluorines are magnetically equivalent, both protons are magnetically equivalent with multiple couplings of identical strengths.

There are 2 types of couplings; both the types of coupling of fluorine and proton are identical. As a consequence they are magnetically equivalent with different coupling strengths.

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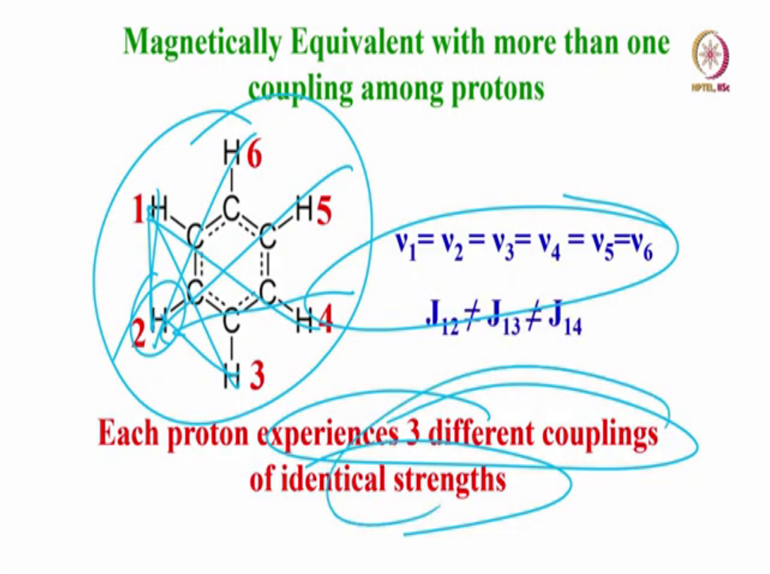

Magnetically Equivalent with more than one coupling among protons

$\nu_1 = \nu_2 = \nu_3 = \nu_4 = \nu_5 = \nu_6$

$J_{12} \neq J_{13} \neq J_{14}$

Each proton experiences 3 different couplings of identical strengths

Take for example this benzene now, come back to this benzene. What do you mean by this? all 6 protons of benzene are chemically equivalent nu 1 = nu 2 = nu 3 = nu 4 = nu 5 = nu 6. Now each proton experiences 3 different couplings of identical strengths; proton if 1 if you take, you have an ortho coupling, meta coupling and a para coupling. Take this proton 2, again it has ortho coupling, meta coupling and para coupling, all are same. That means each proton experiences 3 different types of couplings of identical strengths. So, this is also magnetically equivalent with 3 different coupling strengths.

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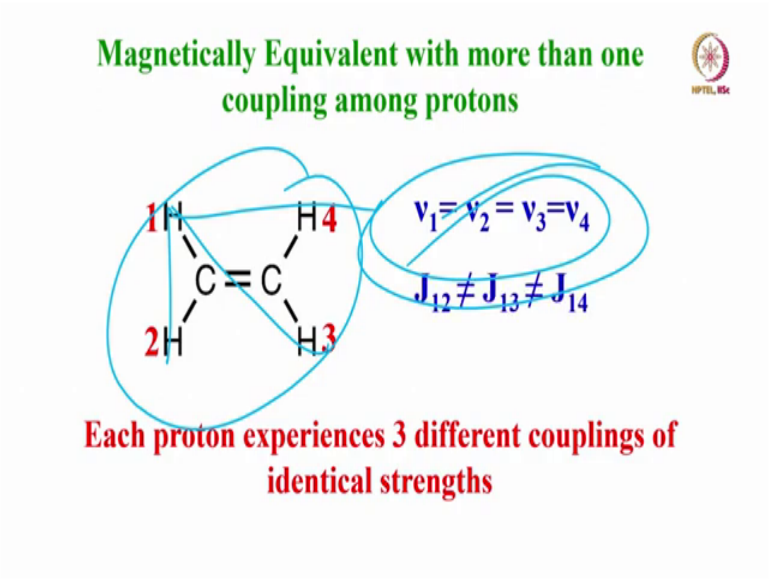

Magnetically Equivalent with more than one coupling among protons

$\nu_1 = \nu_2 = \nu_3 = \nu_4$

$J_{12} \neq J_{13} \neq J_{14}$

Each proton experiences 3 different couplings of identical strengths

So this is simply another example to show nu 1 = nu 2 = nu 3 = nu 4. if you consider this, molecule ethylene, all 4 protons are chemically equivalent. But this coupling, this coupling and this coupling all are different. Thus each proton experiences 3 different couplings of identical strengths. And again, this is the magnetically equivalent spin with 3 different couplings.

Now we will understand coupling between chemically equivalent spins. Last time by understanding with the family tree approach, we know 1 become 2, becomes 4, becomes 8. They are all for chemical inequivalent spins we were discussing. But now we are talking about chemically equivalents spins. Now we understood magnetically equivalence. Let us see what happens when there is 1 spin experiencing coupling with chemically equivalent spins, different spins have different strengths also, we will see that.

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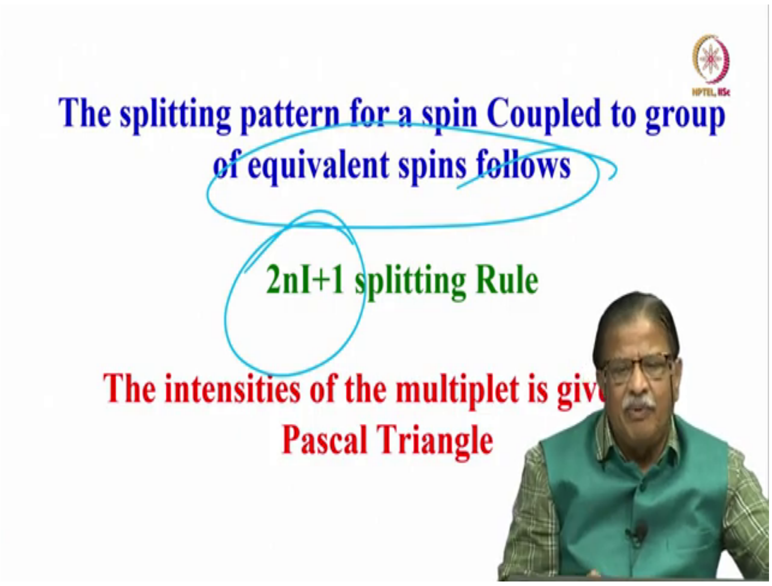

The splitting pattern for a spin Coupled to group of equivalent spins follows

2nI+1 splitting Rule

The intensities of the multiplet is giv
Pascal Triangle

And simple formula when 1 spin is coupled to chemically equivalent spins, it is given by the splitting pattern, and is given by a formula called 2nI+1. 2nI+1 means is a simple formula you must remember; and the intensity of each of the multiplicity is given by what is called a Pascal triangle. What is the Pascal triangle? They are nothing but the coefficients of the binomial expansion. That is all you should understand. For those people who are scared of mathematics, it is simply a Pascal triangle which I showed you, how it comes.

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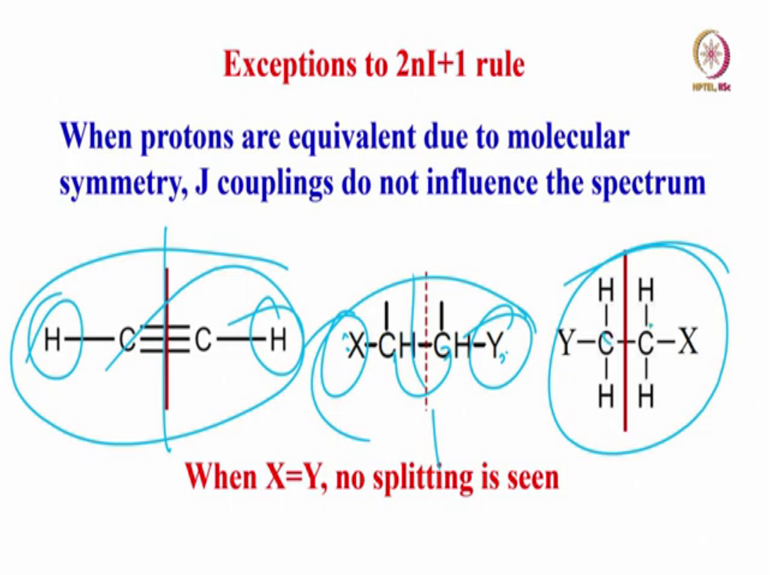

Exceptions to 2nI+1 rule

When protons are equivalent due to molecular symmetry, J couplings do not influence the spectrum

When X=Y, no splitting is seen

But there are also exceptions for 2nI+1 rule. Consider a molecule like this, acetylene, there is symmetry axis along this. When there is symmetry this and this proton coupling is there, but you will not see in the spectrum. Remember coupling is not 0; coupling is still present but they are not getting reflected in the spectrum. Similarly, if X and Y are different here, in this molecule, the CH can couple to this CH, these 2 protons will couple and give rise to multiplicity.

On the other hand, if X becomes X = Y both have same substitution; then no coupling is going to be seen, because then symmetry will be maintained in a molecule. which has symmetry like this, the coupling among the equivalent groups is not reflected in the spectrum. Same example here, when X = Y there is no coupling between these 2 groups this an exception for 2nI+1 rule, please remember.

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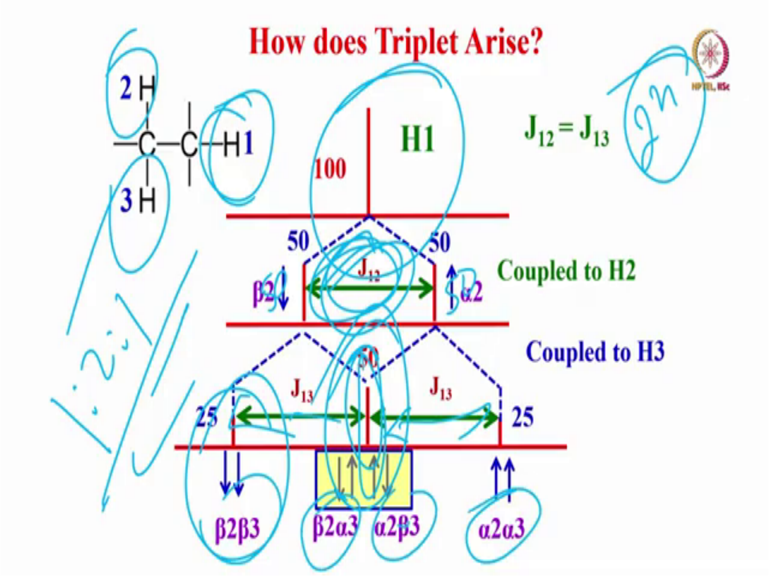

How does Triplet Arise?

Now how does this triplet arise? We will understand, I will give you an example. When 1 proton is coupled to 2 equivalent protons you will get a triplet. That is a coupling pattern for equivalent protons, 2nI+1. 1 is coupled 2 equivalent protons; 2 into 2 is 4. Spin is half for proton, which is 2 + 1 = 3 lines. So when 1 proton is coupled to equivalent protons, you get a triplet. 3 lines; the pattern, the intensity ratio is coefficients of binomial expansion is 1 is to 2 is to 1. How does a triplet come? We will understand this now.

I consider 1 proton, an hypothetical molecule. Proton 1 is coupled to proton 2, and 3. Now J12 = J13; that is my assumption because they are magnetically equivalent. 2 and 3 are chemically equivalent and is coupled to proton 1 equally; they are magnetically equivalent. Now without coupling, initially for the time being I ignore the coupling; I will say for proton 1 I get only 1 line. Now intensity is 100, like I call it 100%.

Now this will couple to this proton 2. what will happen? It will become 2 lines of equal intensity. Now the intensity is 50 : 50. This is what we understood. Same thing now also; what is the separation? it gives J12. Now we bring in coupling with proton 3; then what will happen? Each line will split into 2, 2 lines of equal intensity. Now what will happen this coupling and this coupling are same exactly equal; to 4 lines will be there again, but the 2 lines here are overlapped.

See the 100 becomes 50-50 intensity; now there are 4 lines of equal intensity 25, 25, 25, 25 but because the couplings are identical, 2 lines of the center overlap. So as a consequence, you get triplet but the intensity ratio is 1 is to 2 is to 1. But remember there are 4 lines; like 2 to the power of n lines we should expect; you know according to that formula. It is true you get that many lines but because of symmetry, and because of magnetic inequivalence some lines overlap and the spectrum appears simple; it is not 4 lines; you see triplet 3 lines; this we say in NMR jargon, this is because of possible orientations beta 2, beta 3, this is beta 2, alpha 3; like this. And then this will be both in alpha position, both in beta position both beta alpha, alpha beta both are equally possible; and you get 2 lines overlapped with equal intensities.

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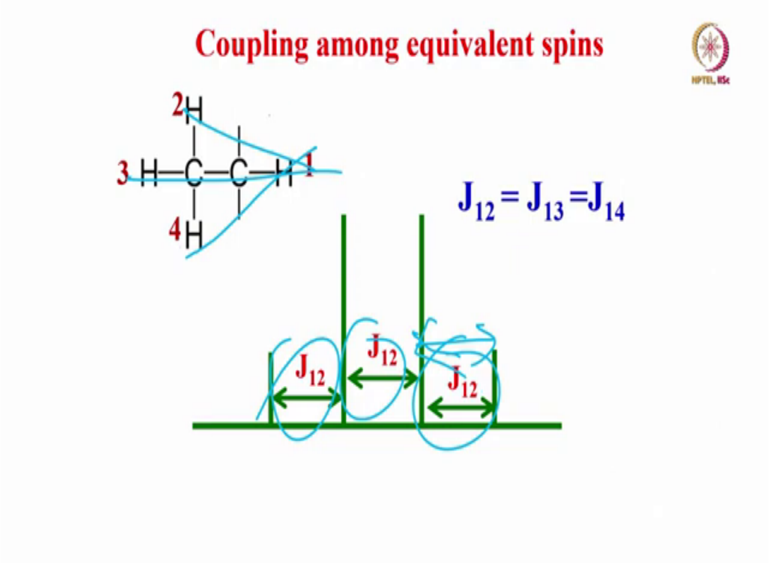

Coupling among equivalent spins

$J_{12} = J_{13} = J_{14}$

Now among 3 spins if I consider simple logic. Coupling between 12, 13 and 24 are all same I have assumed, that they are same. Again they are magnetically equivalent in which case I will expect a quartet, interesting. How do we get the quartet? We will see that later. But you see, separation of each of these lines gives rise to take adjacent separation of any of these multiplicity pattern, you get coupling constant between 12, 13 and 14; they are same.

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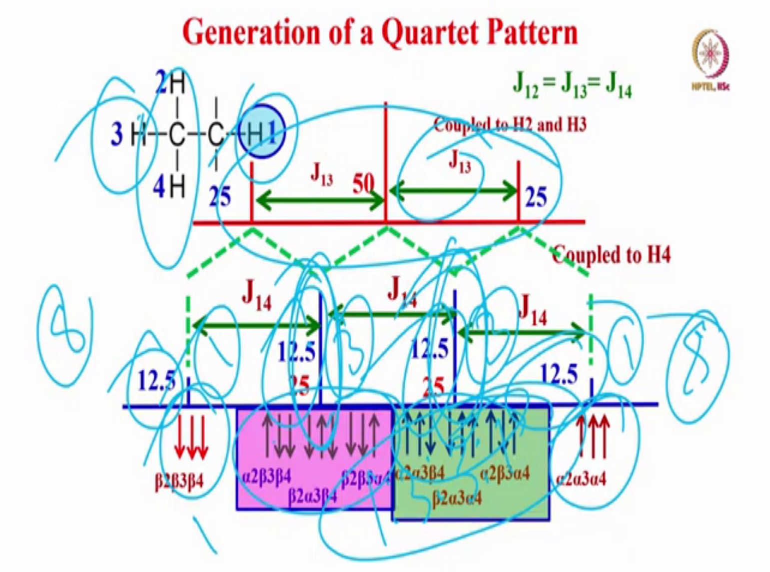
Generation of a Quartet Pattern



Now how does this quartet appear? We will generate this now. Take 1 up to 2 protons we know it is a triplet, I do not have to go through that carefully we already got triplet, because 1 is coupled to 2, in the previous example, we saw when the 2 equivalent protons are coupled this became a triplet. Now I am bringing third proton, then what will happen? Same coupling strength, intensity was 1 is to 2 is to 1; that is 25, 50, 25.

Now each will split into a doublet it will become 2 lines, it will become 2 lines it will become 2 lines, because the couplings are same 12, 13, 14 couplings are same these 2 lines will overlap. Now here 2 lines, here 2 lines overlap so it will become 3 lines here, 3 lines here, 1 line here and 1 line here. In principle we should get 8 lines. We are getting 1, 3, 3, 1, quarter. But because of the overlap of the transitions what we are seeing is these 3 lines overlap these 3 lines overlap.

We are getting a multiplicity pattern of the intensity ratio 1:3:3:1. It is called a quartet in NMR; remember in NMR triplet is intensity 1 is to 2 is to 1. The quartet is an intensity of ratio 1:3:3:1; now the intensity is further divided 12.5; this is a 37.5, is 37.5, 12.5 intensity 1, 3, 3, 1. And this comes because 3 spins are all in beta, beta. If we talk more in NMR jargon all the 3 are in alpha, alpha alpha, here there are 3 possibilities 2 alpha 1 beta or 2 beta 1 alpha here is 2 alpha 1 beta. There are 3 such possibilities as a consequence intensity is 1, 3, 3, 1 here. This is how we talk about quartet pattern.

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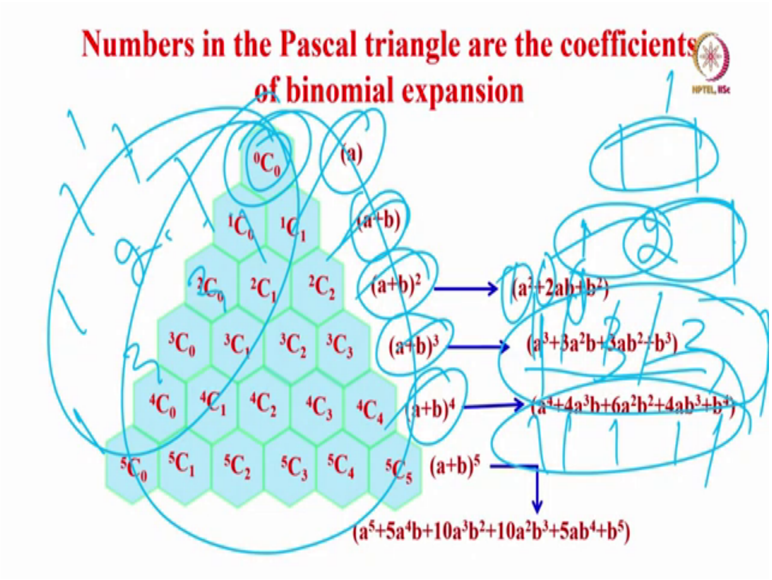

Numbers in the Pascal triangle are the coefficients of binomial expansion

(a)

$(a+b)$

$(a+b)^2 \rightarrow (a^2+2ab+b^2)$

$(a+b)^3 \rightarrow (a^3+3a^2b+3ab^2+b^3)$

$(a+b)^4 \rightarrow (a^4+4a^3b+6a^2b^2+4ab^3+b^4)$

$(a+b)^5 \rightarrow (a^5+5a^4b+10a^3b^2+10a^2b^3+5ab^4+b^5)$

And simply the intensity is given by the coefficients of binomial expansion. First no coupling single line, and just doublet 2 lines of equal intensity and now 2 equivalent protons coupled, a + b whole square; the coefficient is 1, 2, 1; the coefficient of the binomial expansion, if it is coupled to 3 this is the expansion coefficient 1, 3, 3, 1; if it is coupled to 4, then the coefficients are 1, 4, 6, 4, 1; like that. So it is nothing but the coefficient of binomial expansion but we call it as a Pascal triangle here.

What it means is take this one and this one. It is nothing but the sum of the two, if this is 1, then put 1, 1 next one take the sum of these t20; 1, 2, 1; then for the next one if it is coupled to the third proton take some of these two, 1, 3, 3, 1; like this you keep writing. So generation of the Pascal triangle is very easy here; write first one, the 2 lines of equal intensity for that another spin, for the third spin write the intensity first here and add intensity of these 2. And then 1 for this third spin write 1 here add intensity between these 2, 3. Add intensity between these 2, 3 and 1 extra we add. So 1, 3, 3, 1; like that you can generate. This is a Pascal triangle or in other words that is nothing but the coefficients of binomial expansion; please remember this.

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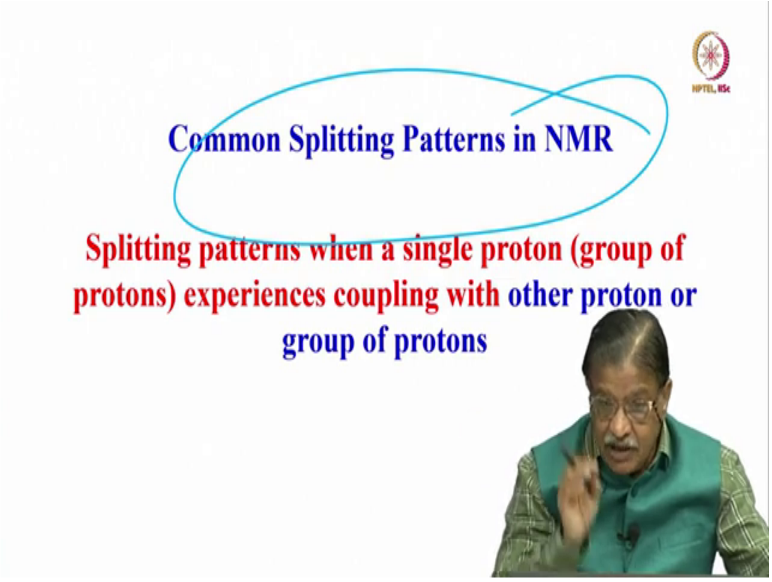

Common Splitting Patterns in NMR

Splitting patterns when a single proton (group of protons) experiences coupling with other proton or group of protons

The common splitting patterns in NMR we will discuss; the splitting patterns when a single proton experiences coupling with other protons or a group of protons. I told you n number of spins can couple simultaneously with different strengths and different chemically equivalent or nonequivalent groups also. Let us see how this splitting pattern comes.

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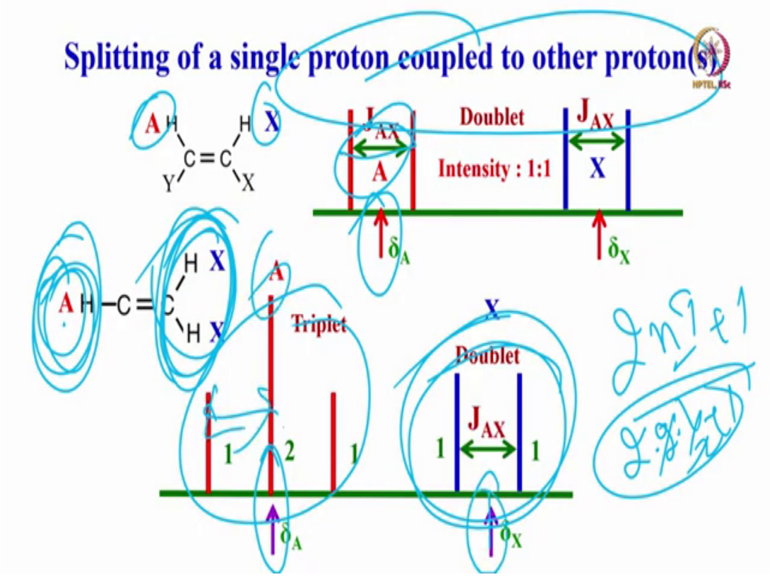

Splitting of a single proton coupled to other proton(s)

Splitting of a single proton coupled to other protons. For example, if X is coupled to A it will be a doublet. That is what we saw when the 2 protons are coupled they will be doublet of equal intensity. Now 1 is coupled to chemically equivalent, then it will be a triplet for A because of 2 spins coupled here will be a triplet. Now, the question I asked what happens if I see A? That is a triplet, but if I see X, X is this proton, only 1 proton. So it has to be a doublet. Please understand carefully when I see A, A is coupled to 2 equivalent protons; 2nI+1 rule you apply. Then 2 into 2 into half; the spin of proton plus 1 then you get 3 lines, intensity Pascal triangle. Whereas if I see this one it will see only 1 proton, there are only 2 possible spin states, that is alpha and beta; as a consequence it is a doublet. So when different groups are coupled the pattern will be different like this. So now let us see what is going to happen. And always remember center of the multiplicity gives the chemical shift of that particular spin, and the separation gives the J coupling here the center of this gives the chemical shift of A, center this doublet gives the chemical shift of X, and the separation gives you J coupling.

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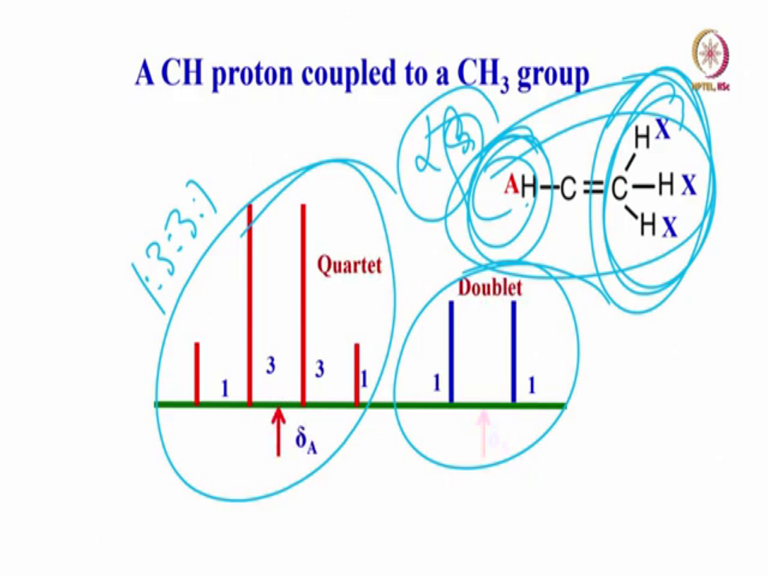

A CH proton coupled to a CH_3 group

Now I consider the example of CH proton coupled to CH3, a simple example, very easy to understand. Already I explained 1 proton when it is coupled to 3 chemical equivalent protons we generated the quartet pattern. So A will become a quartet. What is the intensity? 1, 3, 3, 1 because of Pascal triangle. But what happens if I see X? X is seeing only 1 single proton A, which has states alpha and beta; as a consequence X3 group will become a doublet. CH3 group will become a doublet, whereas CH protons become quartet. This is how you will have to understand the multiplicity patterns.

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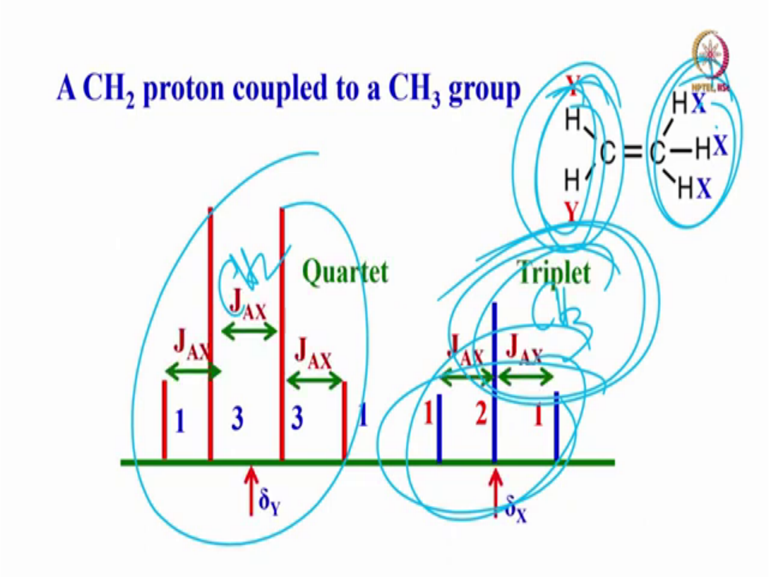

A CH$_2$ proton coupled to a CH$_3$ group

Now I will consider a situation where CH2 is coupled to CH3. Consider another special example then see what will happen? This CH3, because of coupling with CH2 will be a triplet. There are 2 equivalent protons we understood it gives rise to a triplet, so CH3 because of coupling with CH2 will be a triplet. Now CH2 because of coupling with CH3 will be a quartet. So immediately without thinking you must say this must be CH2 group, and this must be CH3 group.

This is how using multiplicity pattern, you can start the assignment of the peaks. To enable you to make the assignment of the peaks you have to use the multiplicity pattern, this how it is; triplet and quartet, etc.

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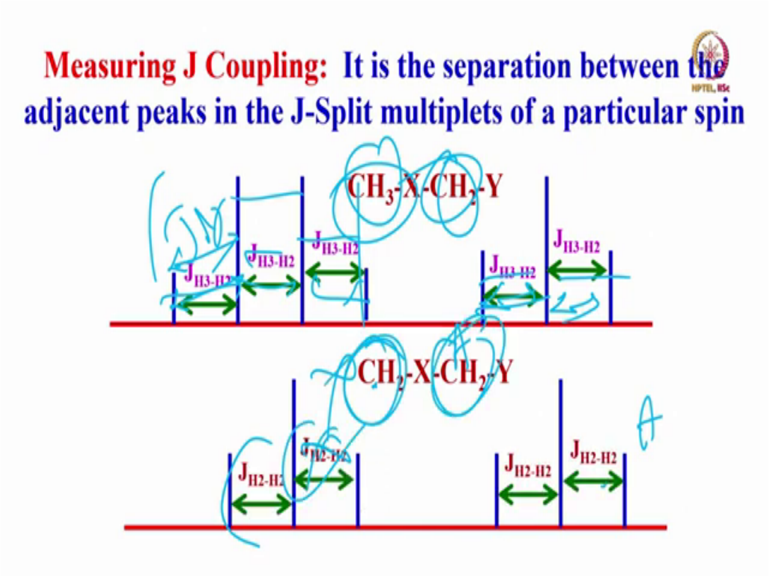

Measuring J Coupling: It is the separation between the adjacent peaks in the J-Split multiplets of a particular spin

Now how do you measure the J coupling? it is very simple CH2 is coupled to CH3. Let us see the CH2; this triplet separation is a J coupling. This is also same because there are only 2 groups are coupled; whether you measure this or this both are same. But you have to measure adjacent peaks; you cannot measure separation between this and this no, that is not right. You have to measure the separation between this and this. The frequency separation; this is J coupling between CH3 and CH2 protons. Similarly this is same; here also same.

So you can measure the J coupling between this; measuring this, measuring this, this or this. There are 5 ways; 5 possibilities to measure the J coupling here. What happened if I take CH2 coupled to CH 2? Remember CH2 coupled to CH2 will be a triplet; and let us say this is A and this is X, A is a triplet, X is a triplet because A will see CH2 and become a triplet; X will see A the CH2 and become a triplet. Now the separation directly you can use to measure the coupling.

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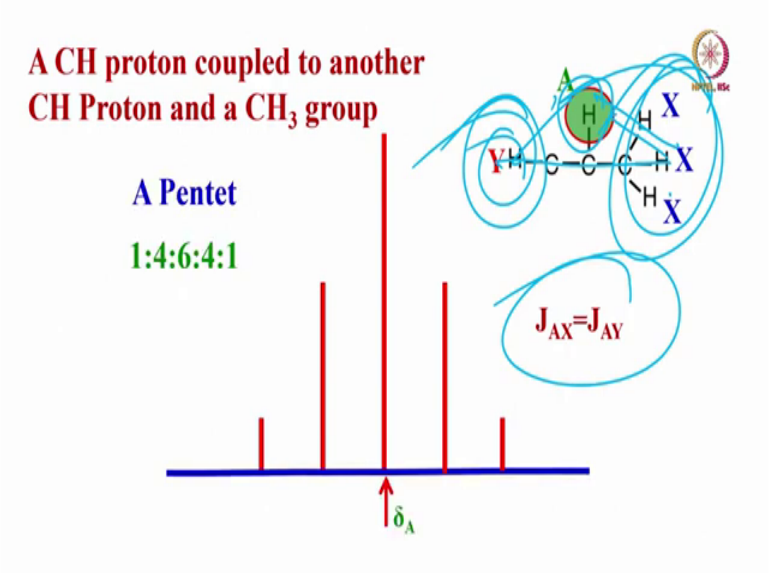

A CH proton coupled to another CH Proton and a CH_3 group

A Pentet

1:4:6:4:1

$J_{AX}=J_{AY}$

So consider an example of a CH group proton coupled to another CH and another CH 3. Now I am making more complications; 2 groups are coupled to 1 proton which is highlighted in green here. Now what is going to happen? I can assume a situation JAX = JAY. Somehow I assume that this coupling and this coupling are same; everything is same; no difference at all.

Then how does the pattern come? It will give rise to what is called a pentet; very interesting. This proton coupled to CH3 and also to CH will be pentet. How does their pentet come? First it will become a quartet because of this and each line of a quartet become a doublet because of CH proton; because the couplings are same they are equivalent couplings. So you get a pentet of intensity 1, 4, 6, 4, 1.

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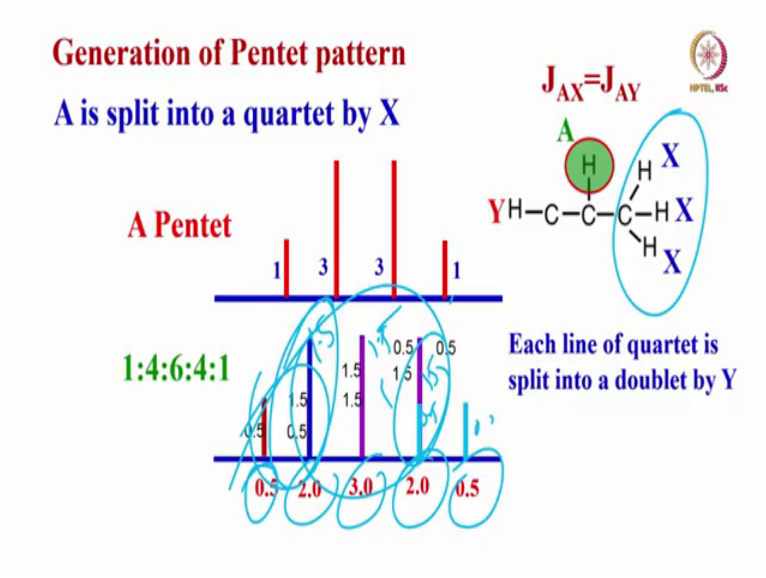

Generation of Pentet pattern

A is split into a quartet by X

A Pentet

1:4:6:4:1

$J_{AX}=J_{AY}$

Each line of quartet is split into a doublet by Y

How you get the pentet you can work out very easily. I will just show you an example like this. A is split by X into quartet that is correct; the intensity of ratio 1:3:3:1. Now each line will be a doublet. This is a doublet with intensity half-half; this will be a doublet with intensity 1.5 and 1.5. Now these 2 gets added up; now this is again a doublet, 1.5, 1.5 this is again doublet 0.5, 0.5; here they get added up. So what are you going to get here?

You add up everything this will be combined and gives intensity 0.5, 2.0, 3.0, 2.0, 0.5 is 1, 4, 6, 4, 1 intensity, because the couplings are the same; some of the lines here are overlapping. You understand, as a consequence you got a pentet. Youu see this is a pattern; invariably you get in your molecule when the couplings are same; 1 proton is coupled to CH3, coupled CH group you get pentet when the couplings are same.

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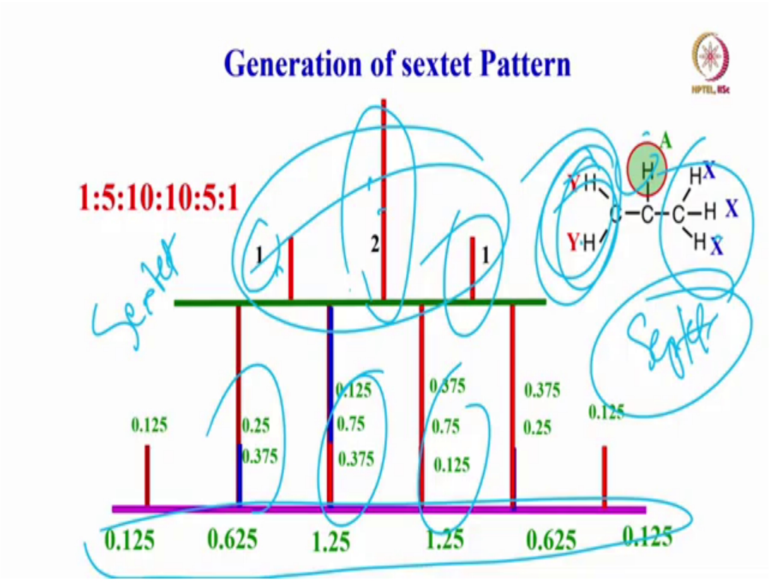

Generation of sextet Pattern

What happens if it is coupled to CH2 instead of CH? same group now CH, I made it CH2; very interesting. Now instead of pentet we get a sextet; very easy to understand. First consider A, it will split because of this into a triplet; and each line then is split into a quartet; this will become a quartet, this will become a quartet, this will became a quartet and this will become quartet. The intensity ratio is, 1 is to 3 is to 3 is to 1 when you add up thye distribute among these lines, and add up all the intensities here first 1, 2, 1. And then divide into 4 lines 1 will be divided into 1, 3, 3, 1 intensity. This will be divided into 1, 3, 3, 1; this will be divided into 1, 3, 3, 1 intensity. And they overlap here. Add up all the intensities, then finally you get the this intensity pattern; you are going to get 0.125, 0.25, 1.25 like this. And this intensity pattern if I could calculate the ratio is 1 is to 5 is to10 is to10 is to 5 is to 1. This is called a sextet. See in pentet 1 proton coupled to another CH and CH3. But sextet 1 CH is coupled to CH2 and CH3. Extend the logic, pentet, sextet, next is septet. When do you get septet? very simple logic, instead of CH2 make it CH3. Of course, now here you can ask me a question, why did I take CH2 first? why not CH3 coupling with A and then work out the triplet? First, I took triplet and made each line into your quartet. Instead if I take this coupling first, make each line into a quartet and then make each line of the quartet into a triplet what will happen?

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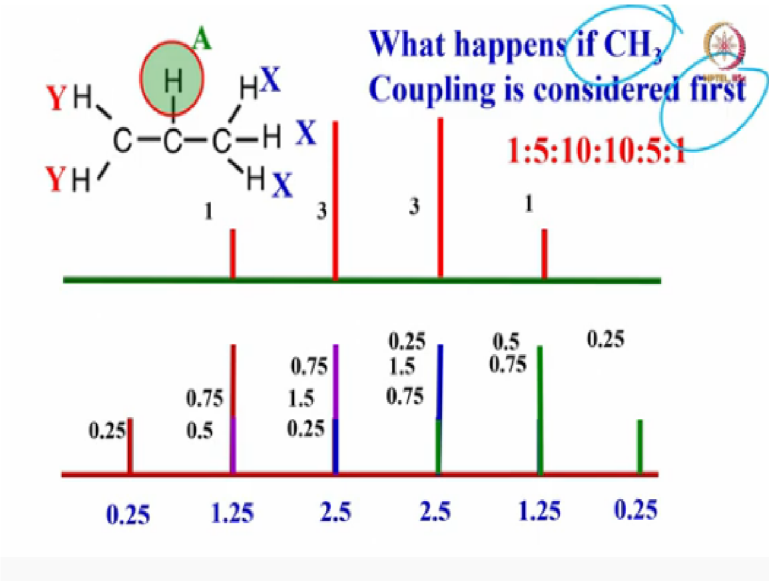

What happens if CH_3 Coupling is considered first

1:5:10:10:5:1

That is the question one can ask; whether you take CH3 first, CH2 first, does not matter. The is the order in which you take the coupling for understanding the splitting is immaterial; either way you take, quartet first and make the splitting; or take triplet first and workout the splitting finally get only sextet.

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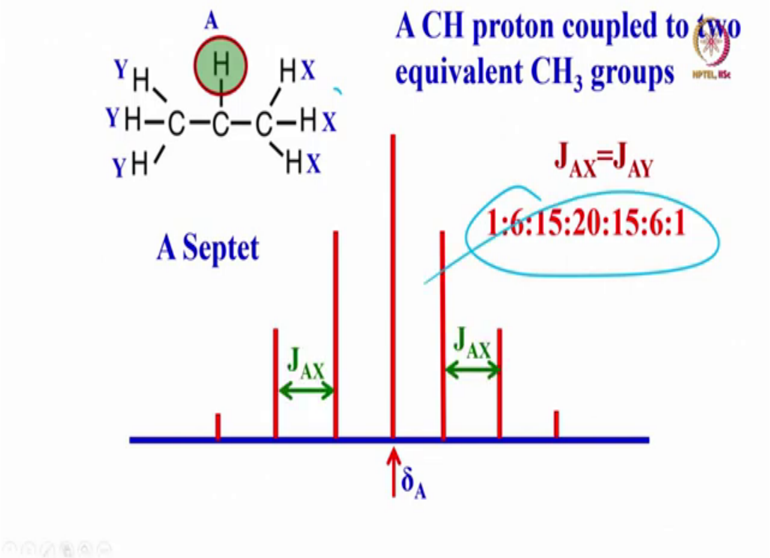

A CH proton coupled to two equivalent CH_3 groups

$J_{AX}=J_{AY}$

1:6:15:20:15:6:1

A Septet

So now, we will have this group. As I told you extending the logic this has to be a septet; very simple. I do not go into the details; you can work out. This proton will become a quartet because of this; 1 is to 3 is to 3 is to 1 intensity, and each line of the quartet becomes further quartet 1, 3, 3, 1. And because of the couplings being same, they will overlap. And as a consequence, you are going to get a septet with the intensity ratio 1 is to 6 is to 15 is to 20 is to 15 is to 6 is to 1. That is what you are going to see the septet pattern here, you understand. So how you are going to get the multiplicity pattern here very easily you can understand. So when 1 proton CH group is coupled to 2 CH3 groups of equivalent coupling, you are going to get a septet with intensity ratio of 1 is to 6 is to 15 is to 20 is to 15 is to 6 is to 1.

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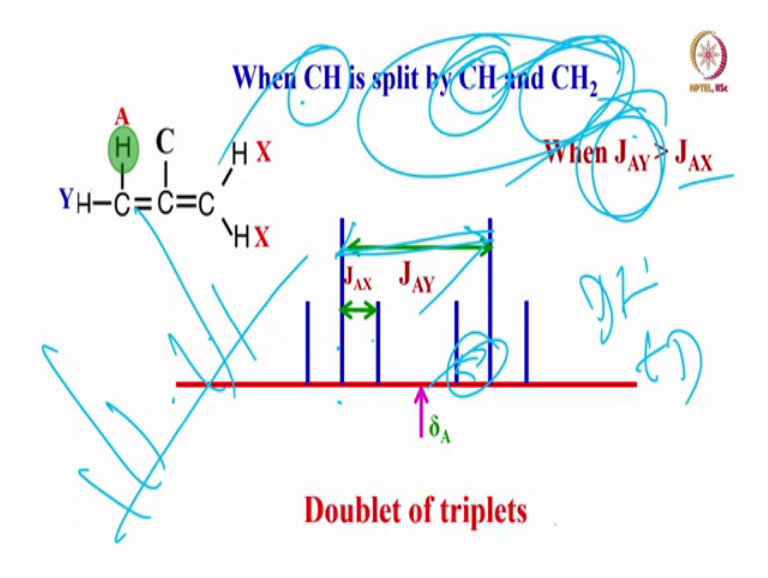

Doublet of triplets

And now we can have a different types of couplings. When 1 CH is split by CH and CH2 what will happen? A CH will split into a doublet; this CH splits this CH into a doublet. Now I am putting a condition JAY is larger than JAX; not equal. Earlier equivalent spins equivalent couplings I was taking. Now deliberately making this coupling larger than this one. What will happen when CH is coupled to this one. This coupling is larger, it will become a doublet, correct? one CH splits due to another CH into a doublet.

Now each line of a doublet will be split by CH2. What will happen? Each line will become a triplet. This is a pattern you are going to get. What do you call this pattern in NMR? Is it triplet of doublets or doublet of triplets. There are 2 possibilities you can think of; triplet of doublets, the 2 triplets, which is a doublet or it could be doublet of triplets. Always you are to take the larger coupling first, larger coupling is doublet. And smaller coupling is triplet. This larger coupling is from the center of this to center this, it gives rise to doublet and this adjacent splitting here gives rise to coupling between this and this. So this is larger coupling, is a doublet, and the smaller coupling is triplet. So this is called doublet of triplets. This is a pattern in NMR; when you get this type of pattern you have to call it as doublet of triplets.

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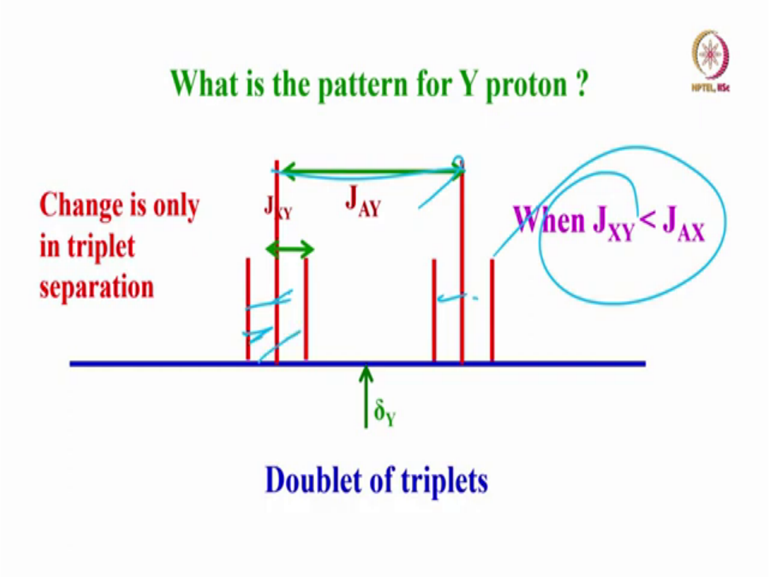

What is the pattern for Y proton ?

Change is only in triplet separation

When $J_{XY} < J_{AX}$

Doublet of triplets

On the other hand, what is the pattern if I see Y? instead of A if I see Y what will happen? See here, I was looking for this proton and got doublet of triplets. Now, I look at Y what is going to happen? I assume the condition JXY is less than JAX; in which case exactly you will get the same pattern. But the only thing is; these couplings strengths are different. The change is only in the triplet separation pattern. This coupling is smaller, this coupling is larger that remains same, but this coupling is small. So, the triplets separation becomes smaller. Again it is called doublet of triplets, if we look at Y.

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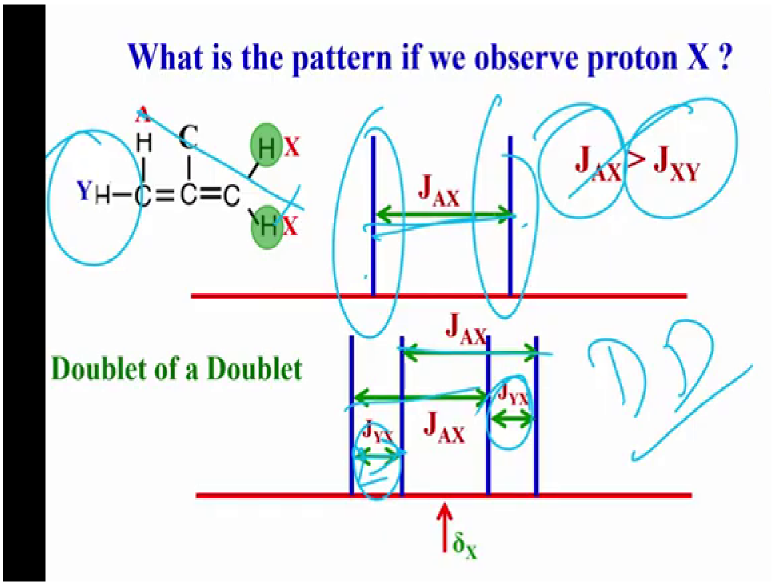

What is the pattern if we observe proton X ?

$J_{AX} > J_{XY}$

Doublet of a Doublet

Now, I will ask you what happens if I see X? if I see CH2 you can think of it easily; again we assume the condition JAX is greater than JXY. So first it will become a doublet because of the coupling with X. it is a larger coupling and each line of this doublet will become what? Again a doublet; so it will become doublet of doublet of equal intensity. This is called doublet of doublets. And how do you measure the coupling? very easy, and this separation gives the coupling between A and X.

And further it splits into two. This separation gives you this YX coupling. Uou can measure various ways; you can measure here or here; AX couplings you can measure here, here. Either way you can measure from the doublet of doublets, you understand. So like this we can talk about lot and lot about the splitting patterns. Now what I am going to do is there are some more 1 or 2 examples which I can take it and then I will give a little example of this thing.

And then again after taking a few more examples, where in the nonequivalent case and equivalent cases we generate the multiplicity pattern, then afterwards, we straight away go to the analysis the NMR spectrum. For analysis of the NMR spectrum what you require is a knowledge of the chemical shifts and knowledge of the coupling constants; or in other words, at least the knowledge of the multiplicity pattern is required.

That is why I was spending more time on these multiplicity patterns. So you will understand how do you get multiplicity, when one proton is coupled to other type of protons which are sitting next to each other; and we can start making analysis of that. So in this class what we understood is more about the splitting pattern, we understand what is the doublet? What is the triplet? How a triplet comes? How the intensity of the quartet comes? How the intensity of the triplet comes? What is the magnetically equivalent spin?

And what happens if one proton is coupled to two different groups of equal strengths or unequal strengths? What happens if there are three protons, groups of protons are coupled, if I observe A, how the pattern comes? If I observe M how the pattern comes? If I observe X how the pattern comes? All these things we understood, and we started generating the multiplicity pattern, we also understood if one proton is coupled to different groups, we generated the multiplicity pattern. Does not matter whether you take this coupling first or this coupling first; both are same. The coupling pattern remains invariant with the order of the coupling you choose to generate the multiplicity pattern. So these are the things we understood so I am going to stop here. And in the next class, I will continue this maybe for about 5 or 10 minutes; and show you another 1 or 2 multiplicity patterns in the couplings and then we straight away jump into analysis of the proton spectra and also spectra of other hetero nuclei. Some interesting spectra I will take and try to analyze them, so I will stop here. Thank you very much.