One and Two Dimensional NMR Spectroscopy for Chemist
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Lecture - 26
Coupling among non-equivalent spins

Welcome back. So we have been discussing about scalar couplings, since more than two or three classes. Today will continue with the multiplicity pattern.

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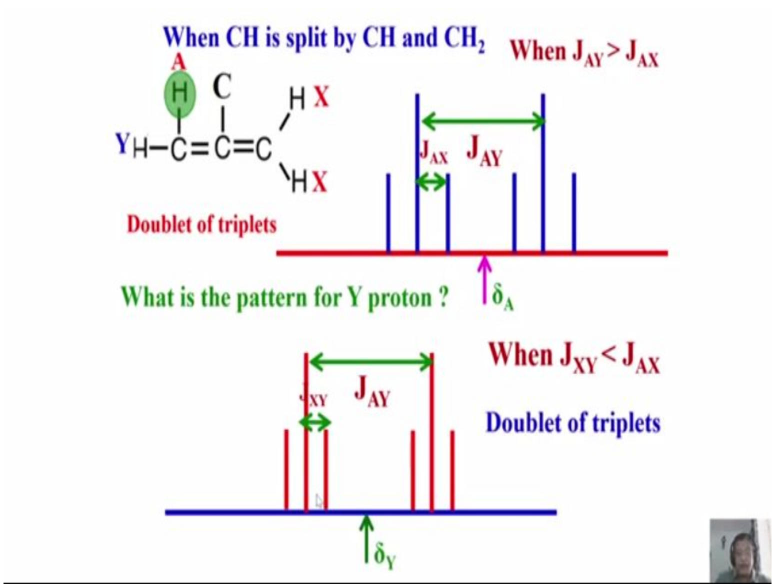

Yesterday I showed you what happened to the multiplicity pattern when a hypothetical molecule like this I took. I looked at proton A, when it is coupled to Y and CH2 proton. A single proton and this is 2 equivalent protons. I assumed the condition AY is larger than AX, that means this coupling is larger than this one. Then first largest splitting is doublet, then each of them is further split into small couplings with triplets, and this easily we could analyze and this is called doublet of triplets. I told you, please remember it is called doublet of triplets. Always larger couplings should come first, then smaller couplings. It is not triplet of doublets, it is doublet of triplets.

So what is the pattern for Y? Remember in this case AY is a larger than YX. It should not be AX, it should be YX. So now in this case I told you this is larger coupling AY and this is XY. So when this XY coupling if you see, 1, 2, 3, 4 bonds away, are much smaller.

Pattern is similar to this. It is also doublet of triplets. Only thing is in this case this coupling was slightly larger than this coupling. So this triplet separation becomes much smaller, that is all. But the pattern is doublet of triplets even for this.

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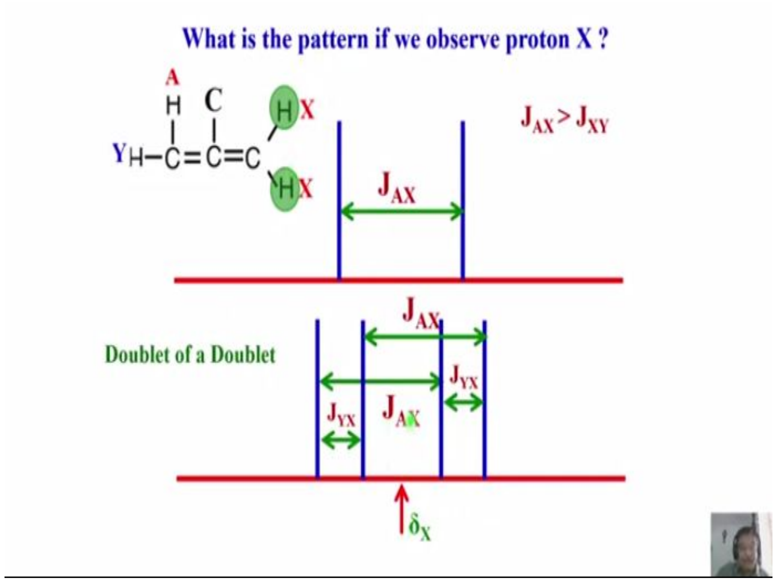

Now we will go further. What happens is we observe proton X? This is another thing. See we are now looking at proton X. Proton X is coupling with proton A and proton Y. Now we assume the condition this coupling is larger, A and X coupling, than XY. Look at the multiplicity pattern. First A splits the CH2 protons, this group, into a doublet. This splits into a doublet, because this is a larger coupling AX, then comes XY. XY is also a doublet. But this coupling strength is smaller. So first it is going to split into large doublet because of this proton A, and each line of the doublet is split into further doublets, because of coupling with proton Y. This gives you J_{AX} or JAX or JYX. Alternatively, you can take the center of this doublet and measure you get JAX. Otherwise take separation from one peak to another similar peak of the other doublet. Let us say this is left peak of the doublet. Take the left peak of this doublet, measure this separation that is also same. That is also use AX coupling.

But the smaller separation gives you YX coupling. This point is clear. Now what will you call this pattern. Previous was the doublets of triplets. Now it is doublet of a doublet. One doublet splitting into other one. See when the same molecule, when I see proton, this one, remember when I was seeing this proton, this was doublet of a triplet. When I saw this proton also this was doublet of a triplet with a smaller separation for the triplet.

Now I am looking at this. This is a large doublet because of this and a smaller doublet because of this, it is a doublet of doublets. And separation is very easily you can measure. This is J coupling AX and further splitting gives you JYX and the center of this multiplicity pattern gives you chemical shift**.** You remember all these, a particular proton is giving a multiplicity pattern; always center of that multiplicity pattern is the chemical shift; the corresponding chemical shift is always at the center.

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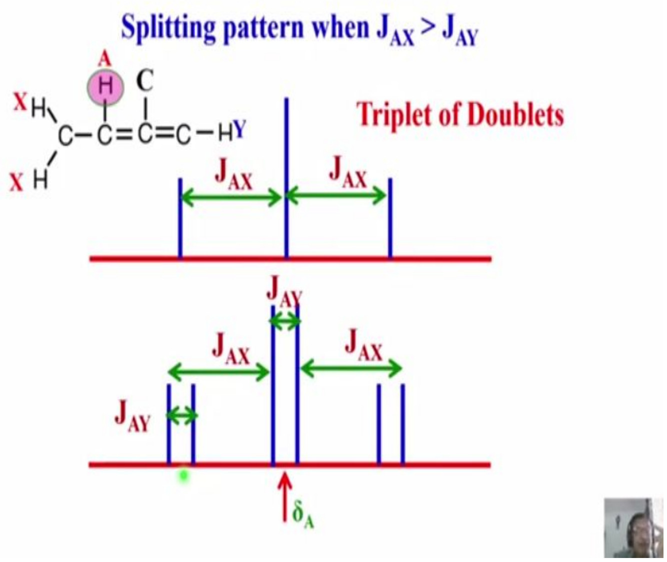

Now what happens to the situation in this case, I took AX is greater than XY. Now what happens if I take AX is greater than AY; now this is larger than this one. I am looking at A. AX is larger means, this is going to be a triplet, larger coupling and then this is split by Y, this proton. What is this proton, it is a single proton. What it should do? It should split each line of this triplet into doublet. So it will become like this, first it is a large splitting because of AX this gives you JAX, now coupling to proton Y each line of this triplet is going to be a doublet, it is going to give a small doublet like this. What this separation giving me? JAX, this one? JAY. What do you call this pattern? Remember what I said we should always consider the largest value, largest splitting value. Largest splitting pattern is triplet here. This splitting strength is larger than this doublet separation. That means, this pattern is called triplet of doublets. Remember, earlier it was doublet of triplets, but now it is triplet of doublets.

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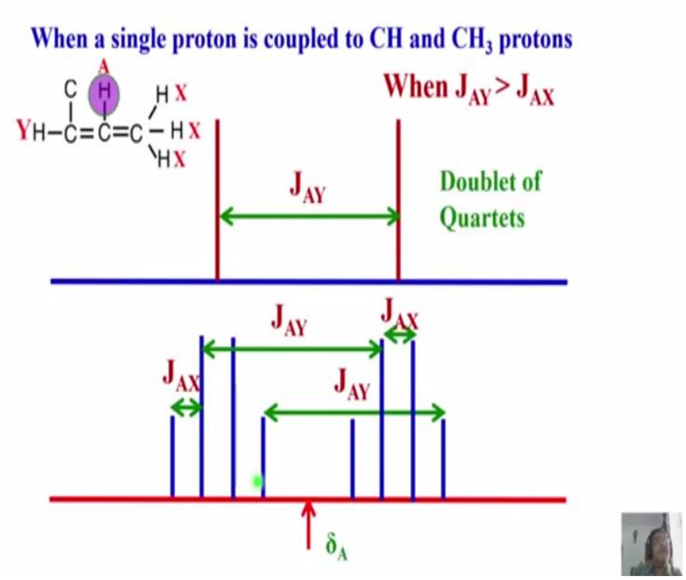

Now when a single proton is coupled to CH and CH3, what will happen? same. Now we have to consider this proton. Consider a situation AX is larger than AY. I am sorry, AY is larger than AX. When AY larger this, what will happen? This proton splits this into a doublet. This is single proton. This is single proton. This one will split into a doublet, large doublet; this coupling larger. Now this also experiences coupling with CH3 protons. Now, it is equivalent protons. Apply 2nI+1 rule. What are you going to see? This will be 2nI+1, You see this, it will split this line, each of this doublet into a quartet, because of this. You have already understood 2nI+1; how methyl group splits; we have already discussed several times. Now each line of this is going to split into a quartet. What is this quartet separation? This separation gives me AX coupling; and the centre of this quartet to this quartet gives me JAY. This is what it is, or from center to center of particular separation from this line to this, this to this, this to this, this to this, it does not matter, identical line of each of the quartet if you take and measure the separation, that also gives you JAY. So this is JAX, that is JAY, very easily understood. Now what you call this pattern? Largest splitting is doublet, the smallest splitting is quartet, which should be called doublet of quartets.

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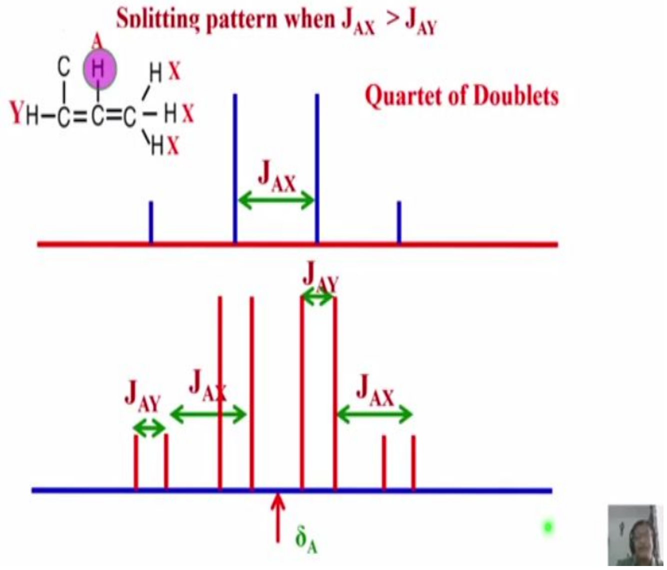

Now consider a situation AX is greater than AY. That means this coupling is larger. The quartet coupling is larger. This adjacent lines of the quartet, what does it give? JAX. Remember, I am concentrating on this proton. This proton peak is split into quartet because of CH3 protons. As a consequence, you got a quartet. Now each line of this quartet is split into a doublet because of this proton.

So this can experience coupling to this and coupling to this. This will give you a quartet. This will give you each line of the quartet as a doublet, and so you are going to get a pattern like this. This is JAX, this is JAY. What do you call this pattern? What is the largest coupling? Largest coupling is a quartet and the smallest coupling is called a doublet. It is called quartet of doublets. Remember it is called quartet of doublets.

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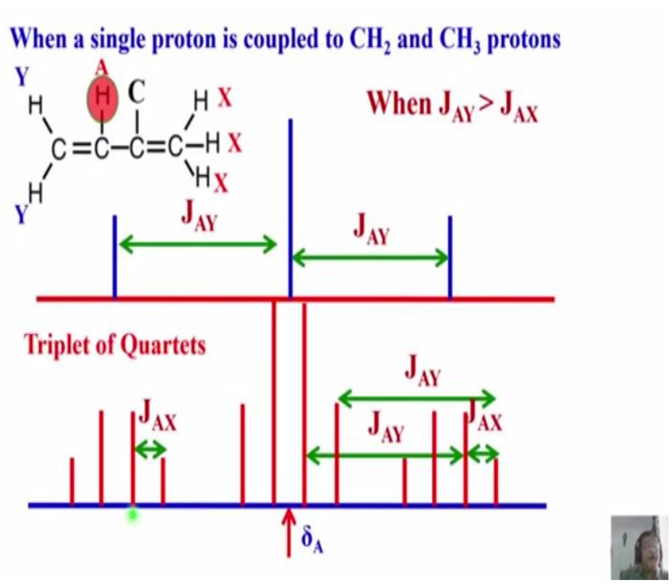

So, you can keep on extending the logic, some one or two coupling patterns which we routinely use we will tell you. Now I have removed this single proton I put a CH2. What do you call this now? Look at this one. I consider situation AY is larger than AX. This is the condition I am taking. Then what will happen to this proton, when it is split by CH2 protons, this is equivalent protons. Apply 2nI + 1 rule. There are two protons, and this will become a triplet with an intensity 1 : 2 : 1. Now this also experiences coupling with methyl group. So these 3 protons, equivalent protons, split each line of triplet into quartet again. The first one is a larger coupling, this is JAY, this is JAY quartet; this is a smaller coupling; this gives you AX coupling. What you call this one? pattern. What is larger coupling? Triplet, smaller coupling is a quartet. So it is called triplet of a quartets, so is called triplet of quartets.

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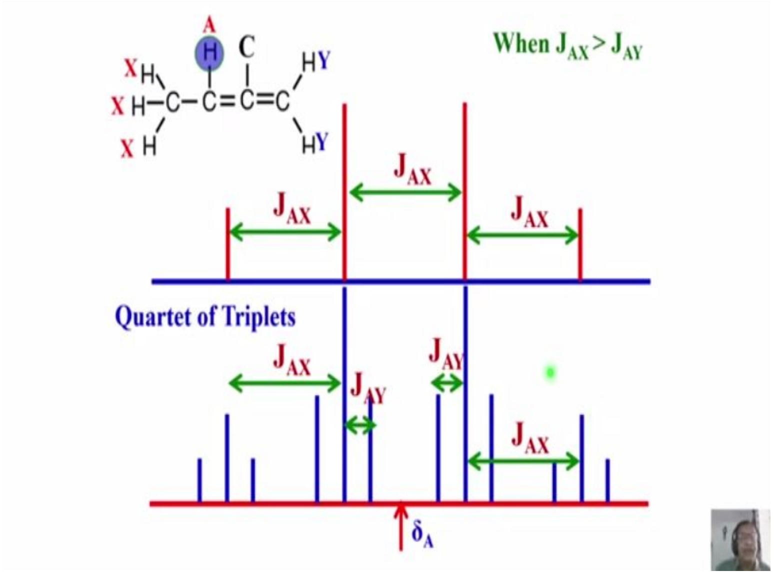

On the other hand, I will reverse the situation. Now, this coupling is larger, let us say AX coupling is larger than AY, what happens? This proton is split into this one, largest coupling by CH3 into a quartet. This is equivalent protons; 2nI+1 rule, this will become a quartet. Now each line of this quartet will split into triplet because of this. What will become now? This separation is larger separation gives you JAX, each separation will be a triplet and this will give AX; and the smaller separation gives you AY coupling; what you call this pattern? Larger coupling gives quartet, smaller suppression gives a triplet; it is called quartet of triplets. Remember it is called quartet of triplets and as always I tell you the center of the multiplicity pattern gives you chemical shift for the particular proton. Now I am seeing this proton and I am going to get the chemical shift of A.

Let us go into a situation like this. For the same molecule, I will actually ask you a simple question. I look at this one, what I am going to get. I will not drawn the stick plot, let us try to understand. I will pose a question to all of you. If I look for this one what is going to happen? Remember this coupling is larger. Now, of course, I have to worry about this coupling. This coupling is larger than this coupling. AY is larger than XY. In this situation what happens? This will first become a doublet because of this large doublet and each line of the doublet will split into quartets. Remember, It is called doublet of quartets.

On the other hand, I will look for this methyl group**.** What will happen? Larger coupling let us say AX than XY, this should become a doublet because of this, and each line of this doublet is a triplet because of this. You get doublet of triplet. See the pattern, if you look at this one, it is quartet of triplet. If you look at this one, it is doublet of quartets. If you look at this one it is doublet of triplet.

You see in the same molecule depending upon the proton you are looking at, and depending upon the number of equivalent protons it is coupled to, and the coupling strength you can arrive at the pattern, what type of pattern it is ,and give a name for it. And name for this is called the quartet, triplet, etc. accordingly.

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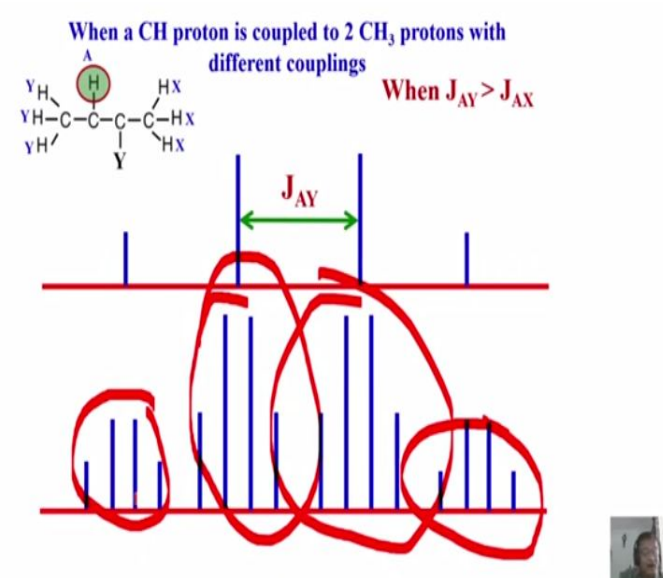

Next another simple example. I am taking an example of a molecule where CH proton is coupled to two CH3 protons of different strengths. When they were equal we saw, what happens, we saw, sextet, septet, etc everything we observed. Now they are different couplings. First, AY is larger. Because AY is larger, it is a quartet. AY is larger. So what this separation will give you JAY. Now each line of this quartet is split into further quartets because of this coupling.

What will happen now? You see remember when I see that, So now this is one quartet, this is another quartet, another quartet and another quartet. So how many quartets you got? 4 quartets.

So what do you call this pattern? Large coupling is quartet, small coupling is also quartet, so it is called quartet of quartets.

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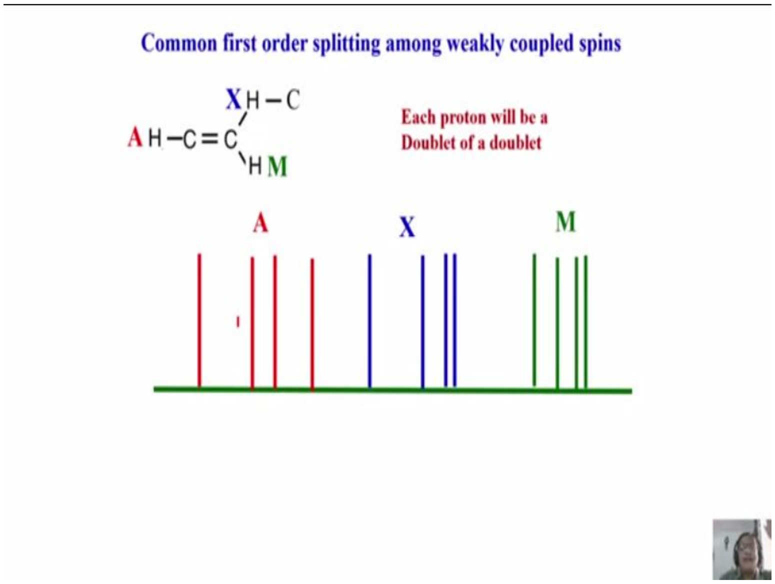

So now common first order splitting among all the weakly coupled spins, many of them you have understood. Now, I consider situation like this, they are not equivalent groups. They are different protons, A, M and X. What will you get? A will split by X and M, we observed this A,M,X pattern; it is doublet of a doublet, each proton will be doublet of a doublet. This is doublet of a doublet, this is doublet of doublet this is doublet of doublet.

But remember intensities are same here. Unlike equivalent spins, where you get triplets, quartets etcetera and when all are single protons, they will be of equal intensity and then you will get a pattern like this. Then you simply start calling doublet of a doublet, doublet of a doublet, doublet of doublet of doublet, like this we can keep on talking.

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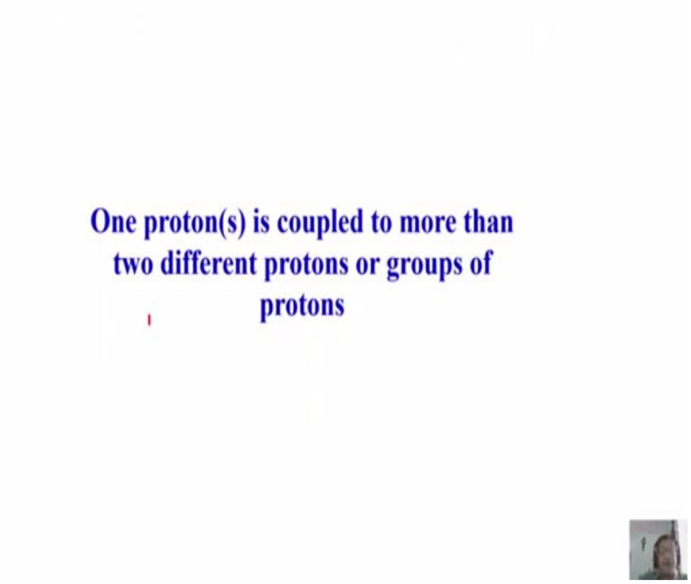

Now one proton is coupled to more than two different protons or groups of protons.

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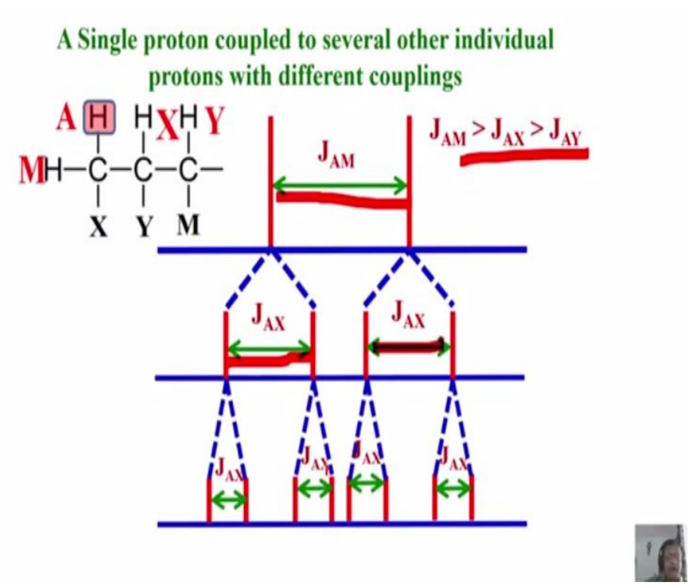

Let us take the example now, this is the situation one proton is coupled, a hypothetical molecule, to X, Y and M, I am looking at proton A which is highlighted. So what are you going to see if I see this one? I am going to see I put a condition AM is larger than AX, is larger than AY. Just a condition. Now look at this spectrum first A will become a doublet because of JAM and then each line of this becomes a doublet because of AX.

And now we get the doublet of doublet of doublet of equal intensity because of AY coupling. This we observed. We discussed last time, one or two classes before. So now will call this pattern; as a DDD; doublet of a doublet of a doublet.

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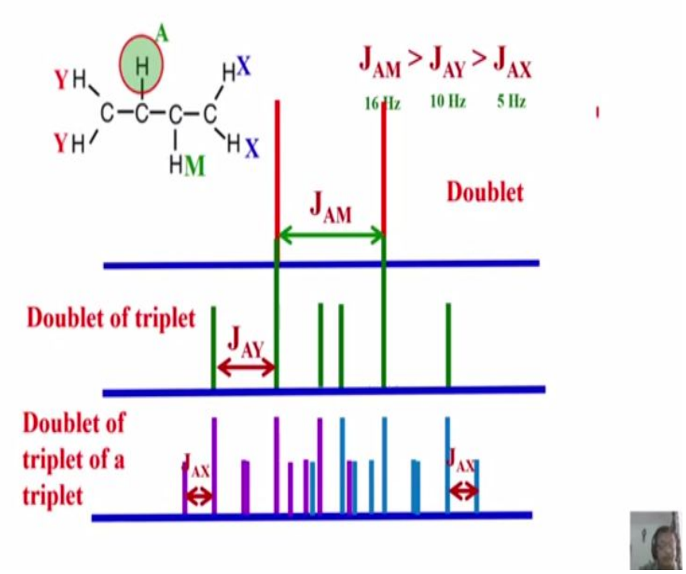

So similarly we can workout varieties of nomenclatures, you can come out and this is a situation another example I took. I am giving you more examples because for you in the chemistry class, they are very important to analyze complex molecules. Without doing this it is very tough for you. That is why. So now taking this molecule proton A coupled to this CH2 and now AM is larger, this one, it is doublet, then comes AY; each line of a doublet is a triplet, then comes AX each line of triplets will become another triplet.

Each line will become another triplet. It is a doublet and each line of a doublet is a triplet and first doublet gives you AM coupling, second doublet gives you AY coupling, second triplet. Now each line is a triplet like this. It will overlap you know, very difficult to identify sometimes and what you call this one? the larger coupling is doublet then triplet and then triplet is called the doublet of a triplets of a triplets. It is called DTT, doublet of triplets of triplets.

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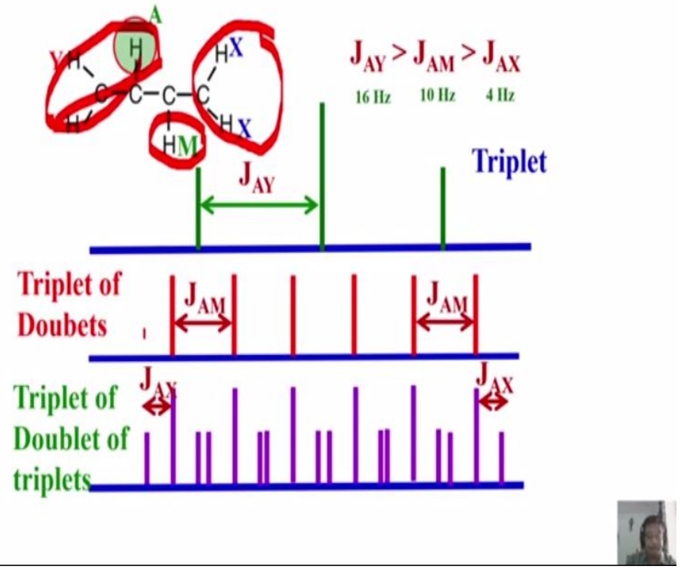

Now in this situation, consider the situation, AY is larger than AM, which is larger than AX. Now this is a triplet because, this is larger coupling I am taking first, this is going to be a triplet with this coupling and then that is further split by proton M. So it is a doublet each line will be a doublet because of a single proton. So each line of triplet will become doublets of equal intensity A**.** Now what happens each of them is further split into triplet because of CH2. Triplet, triplet, triplet, tripet, tripet. So the first it become triplet, then triplet of doublets, now it is triplet of doublets of triplets. TDT. In the nomenclature when you write your papers you write as TDT, triplets of doublets of triplets.

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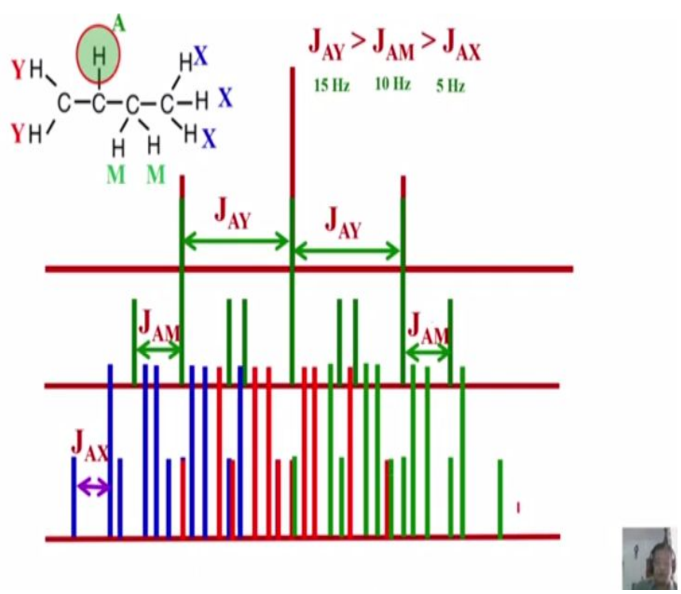

So this example is another last example, possibly I will give. Look at this on,e AY is larger than AM larger than AX. AY is larger, this is a triplet, then each line of this triplet is another triplet and then it will become a quartet. So, first triplet gives you AY coupling. Second triplet gives AM coupling. Now each of them splits into a quartet, 1 quartet, 2 quartet, 3 quartet, 4 quartet. So it is overlapped multiplicity pattern; and this gives you AX coupling.

What do you call this pattern? very complex it looks, when you want to analyze the spectrum you see it is very complex, but you have to give a nomenclature for this splitting. What do you call this one? Larger is triplet, smaller is doublet then even smaller. NO, sorry, larger is triplet, then triplet and quartet. So it is called triplet of triplets of a quartet; remember, triplet of triplets of a quartet is called it is called TTQ.

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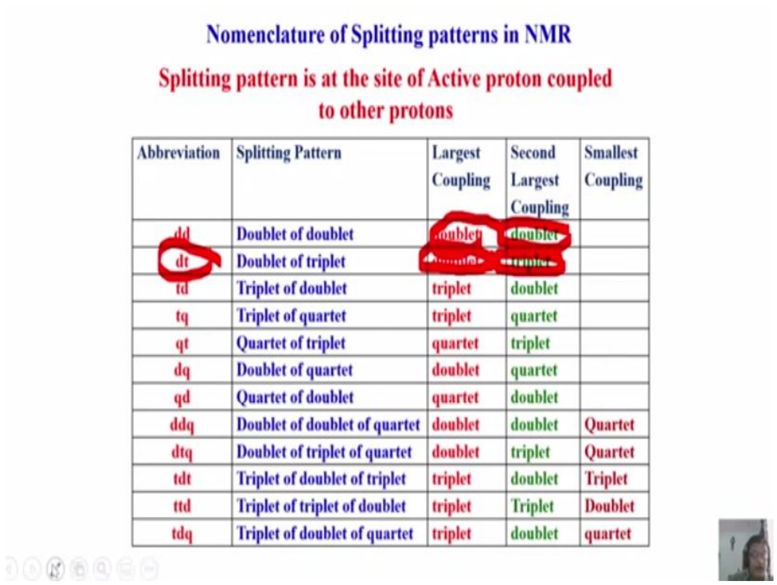

Nomenclature of Splitting patterns in NMR

Splitting pattern is at the site of Active proton coupled to other protons

Abbreviation	Splitting Pattern	Largest Coupling	Second Largest Coupling	Smallest Coupling
dd	Doublet of doublet	doublet	doublet	
dt	Doublet of triplet	[illegible]	triplet	
td	Triplet of doublet	triplet	doublet	
tq	Triplet of quartet	triplet	quartet	
qt	Quartet of triplet	quartet	triplet	
dq	Doublet of quartet	doublet	quartet	
qd	Quartet of doublet	quartet	doublet	
ddq	Doublet of doublet of quartet	doublet	doublet	Quartet
dtq	Doublet of triplet of quartet	doublet	triplet	Quartet
tdt	Triplet of doublet of triplet	triplet	doublet	Triplet
ttd	Triplet of triplet of doublet	triplet	Triplet	Doublet
tdq	Triplet of doublet of quartet	triplet	doublet	quartet

So with this I will give you some table of nomenclature of splitting patterns in NMR. This splitting pattern is at the site of an active proton, coupled to other protons. Remember I took several examples; do not get confused; in a given molecule there are many functional groups. When you look at the chemical shift of particular proto, when it is coupled to all other protons, this is the pattern you get. It can be doublets of doublets, larger coupling is doublet, then smaller coupling is also doublet, it is doublets of a doublet.

Doublet of a triplet is called DT; that means larger coupling is doublet and smaller coupling is triplet, you understand. So that is what happens. Like this it is a triplet of a quartet larger is triplet smaller is quartet, like that you can keep writing. When there are three spins are coupled**,** first one could be a larger, it is called DDQ, doublet of a doublet of a quartet, first coupling larger is doublet then second is the doublet, third is quartet.

If I say TTD, triplet of triplet of doublet, first coupling larger is triplet, second largest coupling is triplet, third is doublet. So depending upon first largest coupling second largest coupling and like that it goes in decreasing order; and depending on that you name your multiplicity, like TD, TQT, TDQ, triplet of doublet of quartet like that. So this table tells you how we have to do the nomenclature of varieties of multiplicity pattern.

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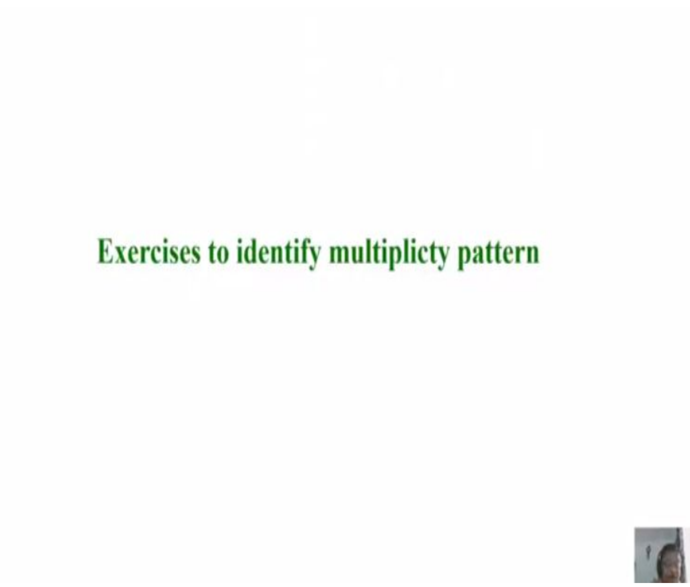

Now with this I will take couple of exercises to identify. I hope I have given you sufficient ideas about how to get the multiplicity pattern everything. Lots of examples I have given you. You must be able to follow with this. Mind you it is a big exercise to understand and do these things. Please try yourself. A number of such spectra are available in books or in literature. Take an NMR spectrum, look at the pattern, start analyzing. You will get to know what is this pattern.

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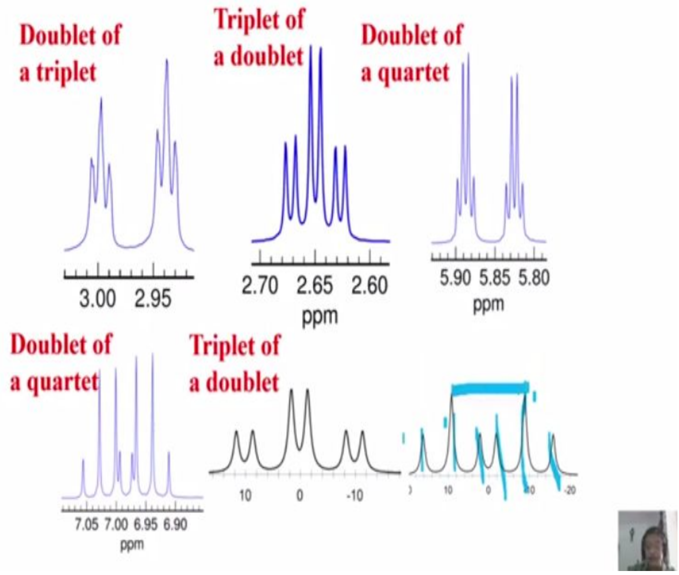

So now we will take a simple example for this. If I give a spectrum like this, and I will ask you what is this pattern? What do you say? Look at the large coupling, large coupling is this one. It is a doublet. Each line of a doublet is a triplet. So what do you call it? It is doublet of triplets.

What is this one? Large coupling is triplet and each line of the triplet is split into doublets, it is called triplet of the doublets.

What about this one? large coupling is a doublet and each line of the doublet is a quartet. It is called the doublet of quartet.

What about this one? Looks complex, Do not worry. Now 1, 3, 3, 1, this is one quartet, if you look at this one, I will put a highlighter here. See this one, this one, this one, and this one. It forms one quartet. Now, I will take a different color. I will take this one, for example this one, this one, this one and this one. These four lines 1, 3, 3, 1 is another quartet. Now what do you understand by that. Largest splitting is doublet and each line of the doublet is split into quartets. What do you call this? doublet of quartets.

Now this one, largest splitting is triplet. Each line of the triplet is split into a doublet, if you see the center of this, it is a triplet coupling and each of line of triplet is split into doublet. What do you call this? it is called triplet of doublets.

What about this one? look at this one, this one, this one and this one; is one triplet. This one, this one, and this one is another triplet; and center of this triplet is a doublet. This is the larger splitting, this is the smaller splitting. What do you call these? Doublets of triplets.

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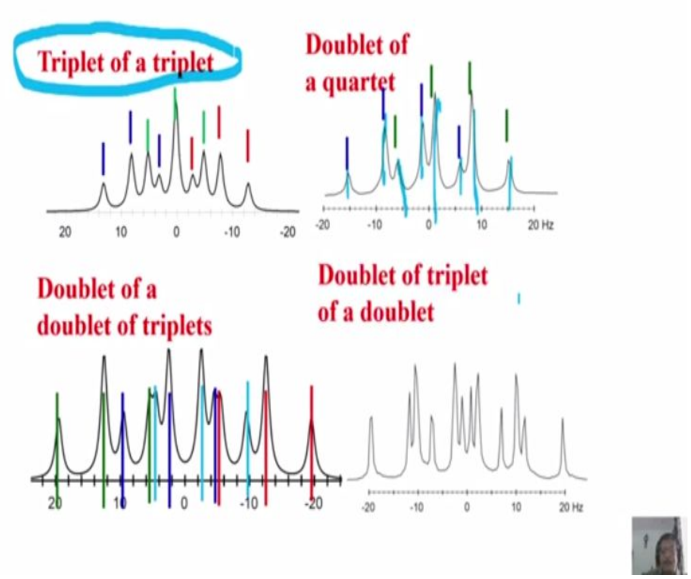

This is little complex, let us see how to go ahead. Looks simple, it is not that complex, but we have to start thinking how this pattern will come. This is perfectly symmetric right? with respect to this. Now there is a way to understand. It is called triplets of a triplet, you know why. This is one triplet, this is another triplet; this is another triplets. There are 3 triplets overlapped and largest value is this, this or this any of them you can take this. Center of this to center of this one; and center this one, gives you one coupling. Other coupling has smaller value, so it is called triplets of a triplet.

What about this one. Do not get confused, look at this peak, 1, 3, 3, 1 what is this? This is the quartet. Now 1, 3, 3 and 1. What is this? It is another quartet. So it is two quartets, it is a doublet each line of the doublet is split into two quartets, it is called doublet of quartets.

What about this one? bit complex, you must try to understand these things, because for this exercise, I have deliberately taken lot of examples for you to understand. This is doublet of triplets. How? One triplet, one triplet, one triplet and one triplet. It is doublet of doublet of triplets. Two doublets will be there, and then each line of doublets will be triplets.

This one is little complex; but doublet of triplet of a doublet. I did not write down, how it comes doublet of triplets of doublet, but you can take this one. Go out take assignment, start working yourself, what is this pattern, you should tell me what is this pattern. So this is what it is. Now I will discuss lot about these things; we will go further.

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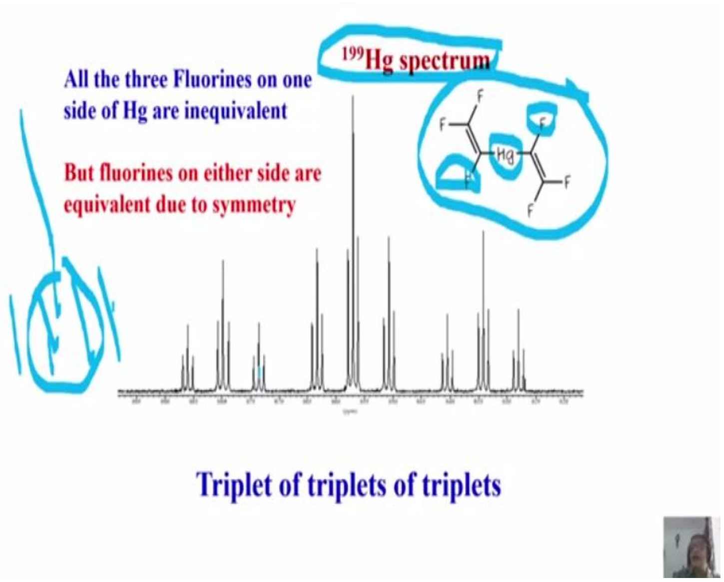

Take a simple example of a spectrum like this. This is a mercury spectrum. The hetronuclear NMR I have not discussed, I will come to it later. But it does not matter. Now this is mercury spectrum, this is the molecule I am taking; and looking at mercury; and this is the pattern I got. Fantastic, how do I get it? Remember this and this proton are chemically equivalent but it is coupled to this. There is no coupling between this and this, that is a different question because of chemical equivalence, whereas this mercury is coupled with these two, equivalent coupling. So when the couplings are equivalent, what pattern we get? Initially this will split by fluorine into doublet. This fluorine also splits this into doublet. But two doublets are of equal coupling constant, so what do you get there? Central line of the triplet two lines overlap, so what you get? a triplet. Remember, you get two lines, two doublets. When the couplings are equal these two lines overlap; and become double intensity, so it is 1, 2, 1 triplet. So what is that one first one this is a largest coupling close by. Then the second is this is two bonds away, this is three bonds away, this is also three bonds away. First you consider one. This is; I did not write down. the first is the biggest coupling triplet.

Then each of the triplets is split into by two Fluorines into a triplet and each of these triplet is split by these two Fluorines to triplet. So this pattern is called triplet of triplets of triplets. TTT. It is called triplets of triplets of triplets. So this is the pattern it is written here.

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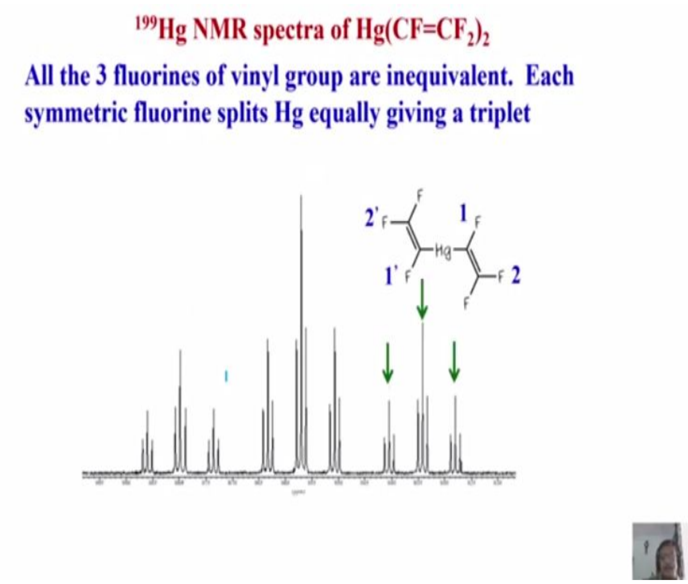

Now this is one triplet, and this is another two triplet and each line of these triplets is split into triplets, Fantastic you know.

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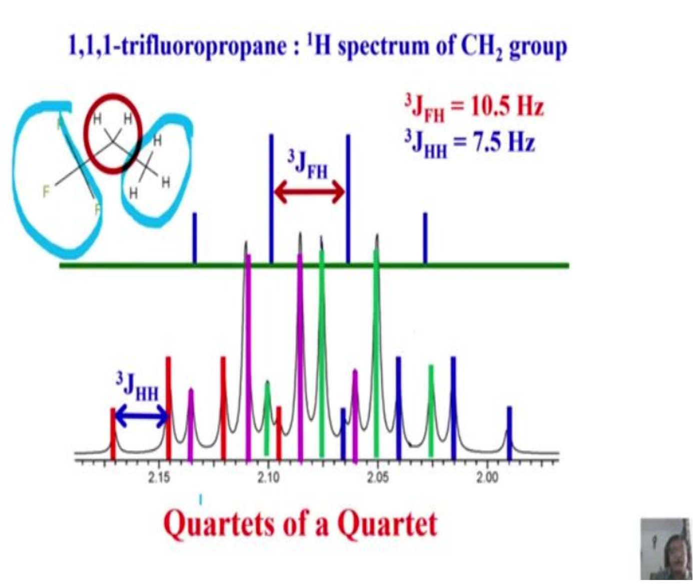

So now we will look at the trifluoropropane 1H spectrum of CH2 group. Now very interestingly. I tell you this 3JFH coupling is larger than the 3JHH coupling. These are the two couplings. I am looking at this one. So what is the pattern we are getting for CH2? Look at this one. First it splits into a quartet and each line of the quartet splits into another quartet because of HH coupling. So FH coupling makes it a quartet and this CH3 splits each line of the quartet into another quartet.

Now look at this one, dont not get confused. Now this is CH3, these are chemically equivalent groups CH3 apply 2nI+1 rule. This will become a quartet, again apply 2nI+1 rule for this. It will become quartets of quartets. How they are coming? one quartet and then each split into another quartet like this, another quartet and another quartet. All lines can be asinged. This is called quartets of a quartets, marvelous, right?

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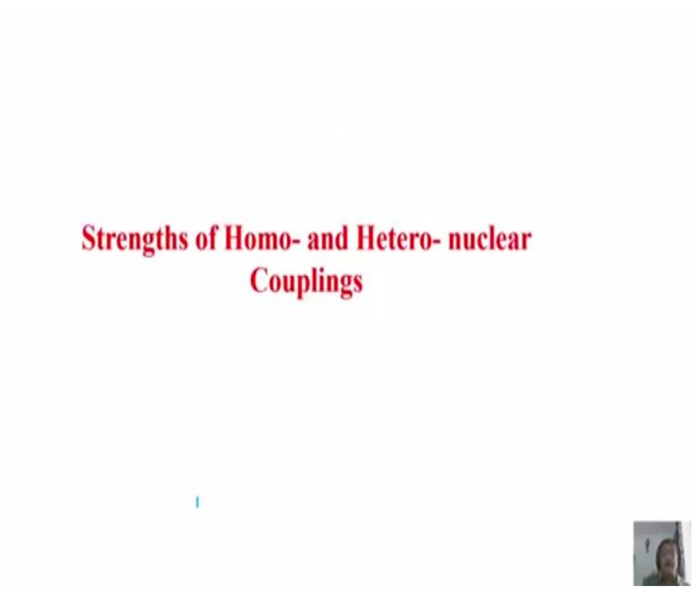

So now with this I will give you some idea about strength of homo and hetero nuclear coupling. Lot of examples, I gave about how this splitting pattern comes, how to analyze, everything. Now, let us understand strengths of homo and hetero nuclear couplings. WE will continue with this for sometime. We will see.

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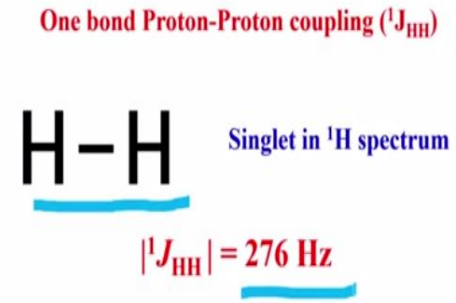

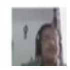

What is the largest coupling? remember when I was giving salient points about the scalar couplings, I made one statement; the strength of the coupling decreases with the increase in number of sequential bonds. I told you 1 bond coupling is larger than 2 bond coupling, two bond is larger than 3 bond, three bond is larger than 4 bond, like that. I gave examples. But this is general trend**.** Do not worry there are little deviations in many cases. But this is a general trend.

Now I consider proton, which is the 1 bond coupling between protons I can think of? which molecule is having only 1 bond coupling. This is nothing but a hydrogen atom. Sorry, hydrogen molecule. In hydrogen molecule these 2 protons are equivalent. This and this are equivalent. When they are equivalent, it does not show the splitting at all. In NMR spectrum, the equivalence spins will not show the splitting pattern, that is what I have been telling you.

So it will give rise to a single peak. Equivalent spins, splitting is not reflected in the spectrum; I have been telling you, please remember. These 2 are equivalent, it will give a single line. Like I said in benzene all are protons equivalent we get single line. I took methane, all are equivalent we get single line. I took ethylene all are equivalent we get a single line. Similarly, you get single line. But there is a coupling between these two, it is not 0.

Similarly in benzene there are ortho meta para couplings, they are different, I told you. Similarly in ethylene; one proton is coupled to 3 remaining protons; all the coupling different. It is there but still gives a single peak, because in the equivalence system, I have been telling you again and again, the couplings are not reflected in the spectrum. Nevertheless, we know how to measure the coupling for such spin systems.

In the next class I will discuss more about it. But then, if I measure tha,t this one bond coupling of this HH, it is nearly 276 Hertz, quite large. I am writing only the magnitude. I do not write the sign. So magnitude of 1JHH is so large, the proton-proton coupling in the hydrogen molecule is 276 hertz.

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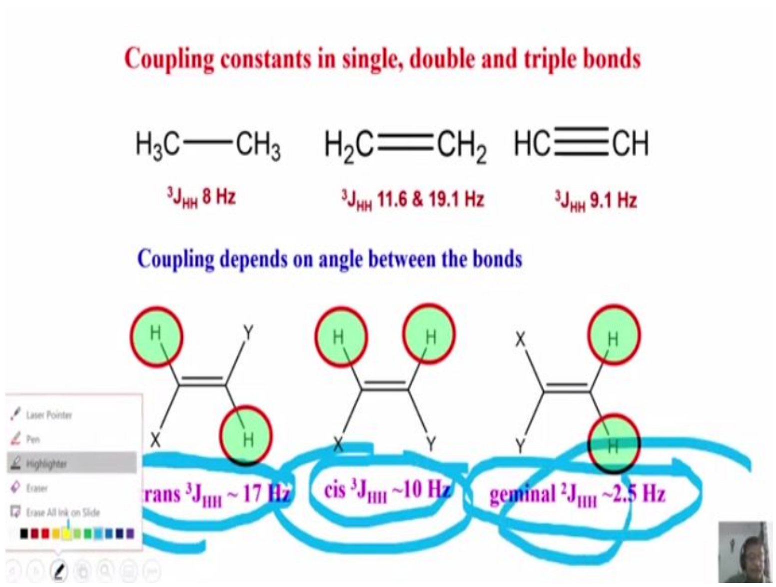

Now let us look at the couplings constants in single, double and triple bonds. Take a molecule like this. What you call ethane. This molecule will give rise to coupling between the protons, 3J coupling and 8 of Hertz, if you take a double bond C2H4, it is ethylene. So now 3J coupling is quite large. In this case, the cis coupling and trans coupling are different. One is cis, other is trans; depending upon how you write, see C-C here, H here and here H. And here you write H.

Now, what happened? this is trans coupling. This is cis coupling. Both are vicinal couplings. The trans coupling in NMR is always larger than cis coupling. Remember this point. In ethylenic molecules like this, if you write down, the trans couplings are always larger than cis couplings. So there are two types of couplings here; one is 19; another one is 11. See compared to this, the double bond coupling is larger.

Coming to triple bonds here, it is special case where we get 3J coupling of 9.1 Hertz. Do not go by the logic; 1 bond is 8, 2 bond is 18 or 12, 3 bond must be 30. No, it does not go by that logic. Do not apply, it is sequential, linearly I can write the coupling constant, it is not possible.

So this is another example, which I wanted to tell you what happens is; the coupling depends on the angle between the bonds. In this case, it is a trans coupling. Trans coupling is quite large, you see it is 17 hertz. Three bond coupling. One, two, and 3 bond coupling. This is called vicinal coupling. And this is also 3 bond, vicinal coupling, but this is cis. cis coupling is smaller than trans. And this is 2 bond coupling, it is called Geminal, that is very small. Geminal Couplings are generally much smaller. This point you must remember.

It is very useful in analyzing many spectra. When you are analysing the spectrum you will understand trans coupling is larger than cis, cis is larger than Geminal. That is the general trend which we have come across.

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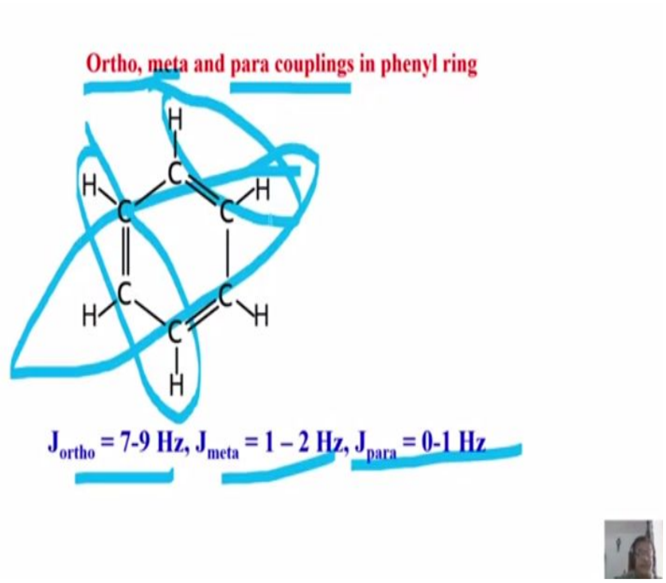

Now, the benzene, phenyl ring if I take, we have ortho coupling, meta coupling and para couplings. See ortho coupling between where two protons in benzene is between 7 to 9 hertz. If you consider meta coupling here. This is 1-2 hertz. If I consider para coupling here, this is 0 to 1 hertz. So these 3 different couplings are present in the benzene ring, although it gives a single peak, we know how to measure this. I will tell you later.

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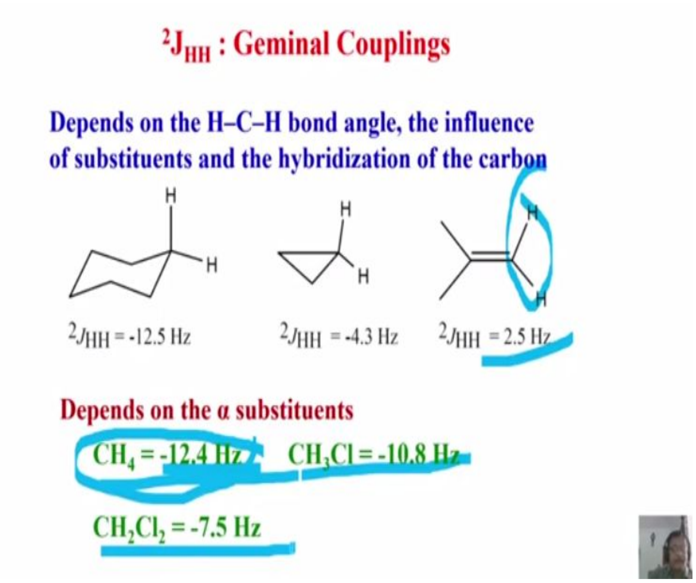

So Geminal Coupling if you come, Geminal Coupling 2J, generally Geminal Couplings can be negative. Look at this one, how do you get this sign of coupling? I will tell later. This 2J coupling is quite large, depends upon H-C-H bond angle in this case, and also depends on what type of substituents we have here. And the in this case it is 4 hertz negative; and in this case Geminal Coupling between this and this, is 2.5 hertz.

Like that depending upon the substitutions we can have the different couplings. Take methane, you will get a single peak, but still I said I will measure the coupling in the equivalent spin system. I get -12.4 here. If we go to CH3Cl it is -10 hertz, CH2Cl2 is -7.5. So depending upon the alpha of the substituents, we have different couplings here. These are all strength of the Geminal Couplings.

Well we can talk more about this couplings and everything. What I am going to do is, I will stop this today and most likely in the next class I will finish all about couplings and then maybe I can to finish in about 10 minutes today, but normally we should not take more than 30 to 35 minutes. That is how we have to stop, otherwise you will be losing interest in learning new things for continuous lecturing beyond 30 or 40 minutes.

It is a psychological study, people cannot understand beyond that. We will stop here, come back in the next class tomorrow where I will finish all about this type of coupling information homo and hetero nuclear, and then will really get into complex spectrum and analyze together.