One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture No: 35
Analyses of ^{1}H NMR Spectra

Welcome back, in the last class we analyzed couple of proton NMR spectra. Couple of proton NMR spectra; and we learned how to interpret the spectrum, based on the chemical shifts, based on the intensity pattern, based on a multiplicity pattern, coupling information; varieties of information you can consider and taking all this information into account you are able to analyze the spectra of many, many molecules, right from small molecules, reasonably big molecules to make you more comfortable.

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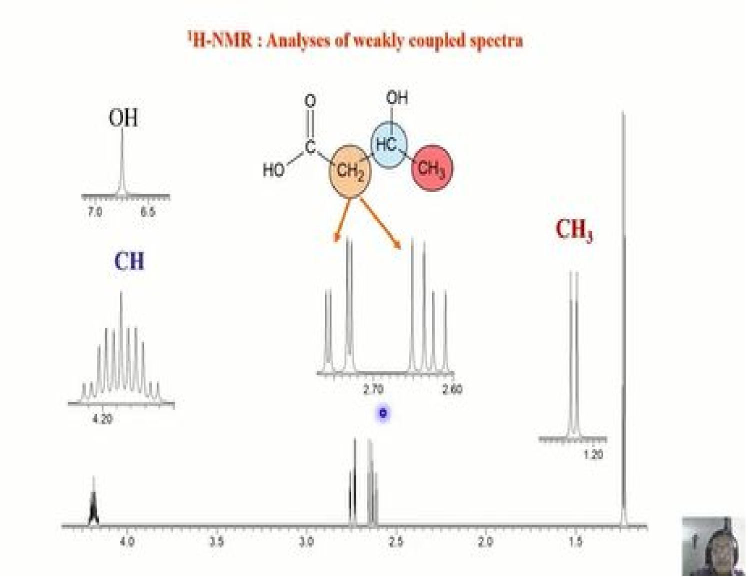

Let us continue with this for some time today, because we will come across with some tricky situations, which I am going to tell you. Now, you look at this spectrum of this molecule, it is a proton spectrum. Now if you look at it how many groups are there here? There is CH3; there is CH, OH, CH2 and OH. So 1, 2, 3, 4, 5 different groups are there; there are 5 different groups of protons are available here, in this spectrum.

Let us just look at this one, there is one group here, this is one here, one here, one here, what is happening to the other one? We will see where are other things are later. Now, you see one more proton peak is coming here which is at 7.6; this is comfortably assigned as OH peak. Now, we will have to make the assignment of other peaks. How do you make the assignment of other peaks? Start with CH3; this is a well known thing which we have been doing for quite some time.

Now what do you expect the pattern for the CH3? Look at this, it is attached to CH proton that means CH3 has to be a doublet, true; see there is one peak and further you all know CH3 comes at a very high field in the NMR spectrum. So, there is in the high field you see a clear doublet. So comfortably we can this is CH3 and it is a doublet because of it is coupled to CH proton; that assignment is done, fine.

I will say that is CH3, and this same thing is expanded here the same doublet to make it clear for you so it is a doublet. that what is clear here, you saw that. Next we will go to other one, this CH proton is written here; this is peak, this is bunch of peaks correspond to this proton CH proton. Why does it come? If you carefully see this CH experiences coupling with CH3 protons and it has to be a quartet; apply 2NI +1 rule, this CH because of CH3 will be quartet of intensity 1:3:3:1.

Now in addition to that this experiences coupling with this CH2; another interesting thing because of that this is going to be a complex pattern. I remember, I am telling you each line of the quartet is; I am not telling you it is going to become a triplet, remember my statement? I did not say I said because of CH3 it can be a quartet, it is a quartet, not it can be, it will be quartet. But further with our understanding if it is coupled to CH2 group each line of a quartet must be a triplet; but I am not stressing that yet, there is a different reason for it.

Right now, I simply say that CH is a multiplicity pattern coming like this. Of course, one of them should be a quartet because of this; remaining will see why it is coming later. You can count the number of peaks here 2, 5 by 10 + 2 there are 12 peaks here. Twelve peaks are coming for this; then you understand why it is 12 peaks coming later. Now coming back to this CH2, this CH2 peak if it is coupled to CH what is the pattern I expect? I expect this to be doublet.

That is what we have been discussing all along. But now why it is not a doublet? What is this funny pattern you are getting? It is a different pattern you are getting, we are not getting to doublet at all; what could be the reason? We will go further and of course, what happened to this OH proton, it is somewhere there. We will see one of them is not seen only one of them is written, otherwise somewhere broadened out and it is far away from the spectrum.

That is not of much interest for us at the moment. Our interest lies in this CH2 peak and CH peak. Now CH, I have identified as multiplicity with 12 lines and CH2 instead of getting a doublet I am getting 8 lines pattern, what is this 8 lines pattern? We have to understand, where do we begin? First conclusion you have to draw; if it what to be equal is your magnetically equivalent or chemically equivalent protons; this should have split each line of the quartet into a triplet pattern.

But I did not insist on that; I did not say that. So what you conclude from my statement? It means I am telling these two protons are not equivalent. It is not CH2 group; they are non-equivalent protons, Oh, something interesting, fine. If they are non-equivalent protons now, can we explain this pattern, how it comes? Let us try how to do that? Let us see. If there is equivalence; you are going to apply 2NI+1 rule with this and this will be a doublet.

Since, it is non-equivalent now, we have 3 protons coupled these 2 non-equivalent. 2 protons and this one; there are 3 protons coupled. What is the pattern you are expecting? And remember, they are far away separated one group here, one group here, and one group here. What is the pattern you expect for this? This is 3 coupled spin system, we can take it as an AMX pattern.

Now, we remember we analyzed the AMX; when there are 3 weakly coupled protons. What is the pattern we are going to be expect? We said each line of the AMX spin system or each proton of AMX will give rise to 4 peaks; that is what I said. Each of them should give rise to 4 peaks. Now, let us try to see what are those 4 peaks, why they are coming? Now, interestingly if I write like this, I can write this structure of this like this.

See for this one, I will let C here, one proton here and write another proton here, C and one proton here. This is the structure I am going to write for this group; for this CH2 group. And this CH, now I call this as A proton; I call this as M, I call this is X; and X is coming here, which is experiencing coupling with these two protons; in addition to CH3; very interesting, right? So now it is a quartet, and each line of the quartet is split into the doublet, because of this; and further it is split because of this proton. As a consequence you are getting multiplicity like this; otherwise you should get only quartet of triplets. Now, we counted we have got, 12 peaks, we are expecting; are we getting really 12 peaks; or more? In fact we should get 16 peaks here, how? Because this is a quartet; and each line of the quartet will be doublet because of one coupling. So it will be 8 line pattern; and the 8 lines will further split into a doublet, because other proton. It should be 16. 16 lines could be present but we are not seeing all 16 because, some of them are overlapping, do not worry. So, as a consequence you are observing only 12 peaks, 4 of them are hidden or overlapping, with one of these things. This pattern is understood, coming back to this; these 2 are non-equivalent.

What do you mean by that non-equivalent? Know, how? What is the coupling we are expecting? What is the pattern we should expect? When this proton is like this? This proton is coupled to this proton, look at this one; see here, see here and this proton and we have this proton and this proton. Now, we have to worry about these 2 protons; one of this proton when it is coupled to this, let us say, this configuration if I take, it is a trans configuration, it is a large coupling, I agree it is a trans configuration, a large coupling.

In addition to that, it experiences a geminal coupling you understand? So this proton experiences the trans coupling of large value, plus it will split into a doublet because of this proton with the geminal coupling which is smaller in strength, where is that group look at it. This is a large separation here this corresponds to this trans coupling; quite large value and each line of this one is further split into a doublet, because of this geminal coupling.

Of course, there is some intensity anomaly we worry about it when time comes later, we will discuss that later, But at the moment you saw this one. Now, what about this proton? Now we analyze this one. This proton experiences one vicinal coupling of one plus geminal coupling you understand?

And now you have to see, in this case I have to write one of the protons, let me write like this only; it is easy to understand instead of getting confused. I wanted you to write a better way let us see, does not matter. So one of the proton experiences of the two protons vicinal coupling and geminal coupling and one of them experiences trans coupling and cis coupling. So, each of these two protons is split by this one, and this one into 4 line pattern, because these 2 protons are non-equivalent. Remember in the weakly coupled spin system what we are seeing, this is a special example, this is clear, this is clear, whereas if you want to understand this one you have to make sure these two protons are non-equivalent, that is the condition you have to take otherwise you will not be able to analyze this.

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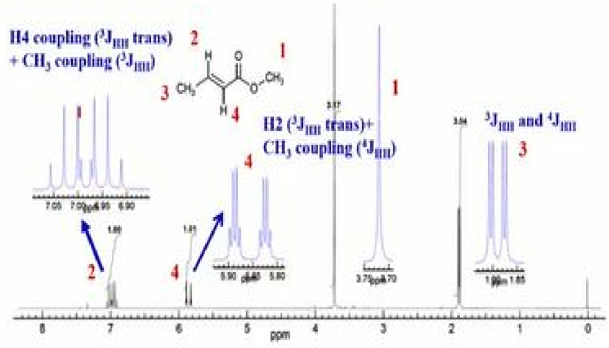
250 MHz ^{1}H NMR spectrum in the solvent $CDCl_3$



We will see that much better now, there are some intensity anomalies, everything which we have to understand why everything later. Also clearly to say which is cis and which is trans? I do not know the frequency differences here, I do not know, and one of the experiences say trans coupling like this other is cis coupling like this, we have to see which is which and everything, when I get the frequencies I may come back to you. But at the moment now we will come to this molecule, a similar molecule now.

Look at this one, this molecule has one group of proton, 2, 3 and 4 now there are only 4 types. How many peaks are present here? One here, one here, one here, and one here. Analysis is simpler, first, you can analyze very easily one of the peaks what is that? OCH3 it is not coupled to any of the protons; it gives a singlet and also we know methoxy protons comes close to 4 ppm in the chemical shift range.

See, there is real peak at 4 ppm; a strong peak is there with intensity 3. That means this has to be OCH3 that assignment can be done, there is no doubt about it. Next, we have to see this CH3 this H and this H. How we are going to assign the CH3 group. In the normal examples which we took earlier, what was the pattern used to see? we always took CH3 coupled CH2, CH3 is triplet or it is singlet or when it is coupled to CH is a doublet, they are very easy to analyze.

But, now look at this, this high frequency region I am sorry, in high field region you are seeing a spectrum with 4 lines of equal intensity. Why this is coming? what is the peak corresponding to? You simply look at this molecule you will understand. If this peak is doublet of a doublet. Now, we are after analyzing this, we are left with only these 3, it cannot be this, because if there is a long range coupling with this one, it will be a quartet; it cannot be this; because of coupling with this, this will be a quartet.

So, there is no quartet pattern see here, but we are seeing doublet patterns and 2 doublets of doublets, to be precise. Why is it? Then obviously it must be CH3, this one; because this CH3 will have one coupling with this, it gives a doublet and that doublet is split into another doublet because of this proton, so this is one coupling. This splits into a doublet; the doublet of this one further split into doublet because of this. As a consequence, see here, 4 lines of equal intensity; so this must be CH3. You agree with me, this must be a CH3 and this assignment can be done easily. Now, let us go to the next one, this is assigned, and this is also assigned in this case, if I remove the highlighter you will understand more. Now, this is proton 3, correct, because this experiences 3JHH, 1, 2 and 3; 3JHH between 2, and 3 and 4 JHH between 1, 2, 3 and 4; 3 and 4 coupling, so this is 3, 4 coupling; this is 2, 3 coupling.

So, as a consequence, what is larger coupling here? This larger coupling has to be 2, 3 coupling and this further started coupling with this, it is 3,1 coupling; understand, so this doublet of a doublet for methyl can be understood. So we can safely assign this group, this one for methyl group, methyl proton. Now, we are left with only these two; what are these two? Now, carefully look at it; this proton experiences the trans coupling with this, that is usually larger and also it experiences the 3 bond coupling with this CH3, you understand?

This experiences trans coupling, further coupling with CH3. What about the other proton? This proton. This also experiences trans-coupling with this + 4 bond coupling with this. Now you have to use the idea of 3 bond, 4 bond coupling with CH3 to make the assignment; because both this protons experience trans coupling. If one is cis and one is trans, we could distinguish by the couplin;g but now both have the same coupling strength both are trans.

This also has a trans coupling with this, this also has a trans coupling with this; but this pattern will be different because of coupling with CH3. This is a 3 bond coupling; it is a 4 bond coupling with CH3. Now, our assumption is we assume 3 bond coupling between CH3 proton and this is much larger than this one. Now, how do you assign this? You take this one, what is this one? This, I would say the proton H2.

Why? It has a 3 J trans coupling and CH3 coupling 4 J, this is sorry for this proton 4, not 2 sorry, this is proton 4. When is I say, this is proton 4, this is a trans coupling which is quite large, centre of this two centre of this is a trans coupling, and it has a 4J coupling with this CH3. So, first it is going to be doublet because of this which is quite large coupling and each line of the doublet is a quartet, understand? Each line of the doublet becomes a quartet; as a consequence it is going to be doublet of a quartet, you understand? This is going to be doublet of quartets. Now look at this proton, this proton also has a large coupling; trans coupling + it is a 3J coupling, 3J coupling between methyl and proton. Now, as a consequence there is a large coupling here between this and this. That is exactly equal to this, there is a trans coupling; but further this is a 3J coupling, which is quite large.

So, 1,3,3, 1, this is one peak, one peak, one peak, and one peak, these 4 are the quartets and another peak of the doublet will be another quartet like this. So, you got doublet of quartets again. But the quartet separation is much better here than this because it 3 bond coupling, it is a 4 bond coupling; which is much smaller. As a consequence, we could safely say this is proton 2, this is proton 4, this is proton 3, it is a proton 1. Now it is very clear how we analyze taking it account the multiplicity pattern and trans coupling you could easily analyze.

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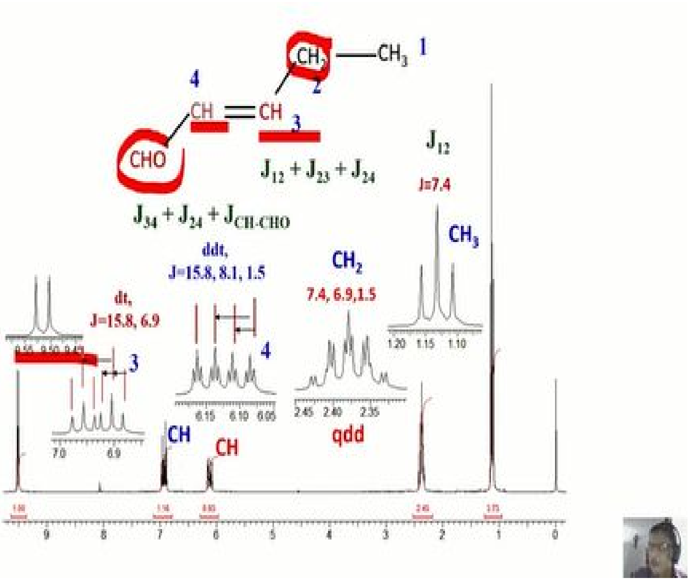

Now, coming back to this one; let us see how do you assign this spectrum? How many chemically in-equivalent groups are there, 1 CHO, 2, 3, 4, and 5. First before starting analysis, we should find out how many chemically in-equivalent protons are there in the molecule. Now, we will start with one by one, it is a simple logic; this is CH3 all along we have been talking; what should we be this pattern? It is coupled to this CH2, so it has to be triplet, see this is the triplet; it has to be a triplet it expanded here.

So, we know this is CH3. What other thing you can comfortably assign? and this CH2 has to be a quartet because of this; and each line of quartet has to be a doublet, where can you get that? see 4 triplets are there. It is a different question; whereas we look at this one, this pattern; it is little bit complex pattern, but I safely say initially before confirming, let me say, this must be this CH2 because it gives quartet pattern and each line of the quartet is a doublet and some lines overlap and as you see you can see doublet at the far end of this spectrum , far end of this group. Let us assume that, you go further that is done and this is true, but not only that; interestingly this proton experiences coupling with this also. As a consequence long-range coupling is there it is going to be quartet, which proton? This proton CH2 is going to be a quartet, because of this and a doublet because of this and further doublet because of a long range coupling with this.

So, as a consequence this becomes quartet of doublets of a doublet, first it is a quartet because of this and a doublet because of this, this is the long range coupling with this proton. As a consequence doublet of quartets are further split into another doublet, each line of that, so it is going to be quartet of doublets of doublets, very clearly we could make assignment and also is clear from the complex pattern here; that is done.

What is the next one? Next one you have to see this proton. This proton has a long range coupling, large coupling with this one; it is a doublet, very clear it has to be doublet like this, this proton because of this. But remember if you look at this CHO proton which comes down field CHO is a doublet. How can this CHO is a doublet? Because, it is coupled to this CH, this CHO is coupled to this CH; that means you also expect coupling of this CH with this one here also.

So, first is going to a doublet like this; and each line of this doublet is further split doublet like this, 4 line pattern. But it is not just 4 line pattern you have triplets for each line, where does it come from it is a long range coupling with this CH2; this one has a long range coupling with this CH. As a consequence each line of this doublet of doublet is going to be a triplet like this, this is what you see, so this is proton 4.

So, now it is clear for you each proton is experiencing multiple coupling; this is experiencing coupling with this, this and this; because of these two couplings a single proton, it gives doublets of doublet and each line of this doublet of doublet is going to be a triplet because of this and this is the pattern we get for proton. So, that is very clear for you to understand now. So, we understood this, we understood this, we understood this; and we understood this also.

So what is left over this? only this. Of course this can experience coupling with this is a doublet and it is going to be a triplet because of this, this one first it is going to be doublet; and then each line of the doublet is going to be triplet because of this proton. Now this CH proton, does it have a long range coupling? 1, 2, 3, 4 bond coupling with CH3; may be it is not seen here so that is the reason why the CH has to be only doublet of triplet, so this is proton 3.

So, now everything is assigned, I hope you are all with me I did, I hope you are not confused very simple I am going to summarize this. This is a CH3; triplet because of this; and this CH2 is a quartet because of this; and also each line is a quartet of a doublet because of this, it has a long range coupling to this. As a consequence it is going to be quartet of doublets of doublets. Now, if you come to this; 4 proton, this is going to be doublet because of this; doublet of doublet because of this, this has long-range coupling with this.

So, it is going to be this; doublet of doublet of triplet; and if you come to this proton, if you come to this proton, this is doublet because of this, and each line of the double is a triplet because of this and long range coupling is not seen here, in this case. So, now CHO is a doublet all the peaks and the pattern is assigned. It is clear for you now?

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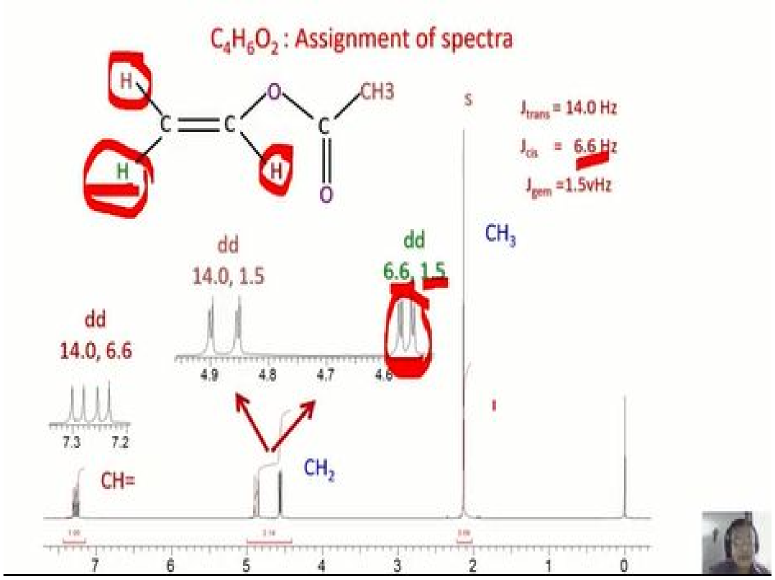

$C_4H_6O_2$: Assignment of spectra

J_{trans} = 14.0 Hz

J_{cis} = 6.6 Hz

J_{gem} =1.5vHz

Now, this is a simple example, which we were discussing earlier. Look at this molecule; this is C4H6O2; three different types of protons are here; and one CH3 there are 4 protons; OCH3, I mean C double bond OCH3, it isv ery easy to assign; it is a single peak, we get it here, an intensity is three and is singlet, no doubt about it that; you can assign. Now, you are assignment should be for these three protons; how do you do it? Remember, each proton is chemically independent.

Let us consider one of the protons, let us say consider this proton, this proton experiences a trans coupling with this; trans coupling is quite large, 14 Hz and also experiences geminal coupling with this, geminal coupling is very small. So, it must be a large doublet and each line of the doublet that should be split into another small doublets, that has to be this. This large doublet is trans coupling and small doublets is because of vicinal coupling. I would say this is this proton, this is this proton. I can assign it.

Now, I come to this proton this proton has a trans coupling of 14 hertz and cis coupling 6 Hz, so this is a large separation of trans coupling is there and each of them is further split by cis coupling of 6.6 hertz, where it is going to be very clear well the resolved doublets of doublets. So, this I can assign for this proton, you are clearly understanding this, so this proton is assigned to these and this is assigned to this.

Now, what is left? Only this, so what type of coupling this proton will experience it can experience? It can experience a vicinal coupling with this proton of 6.6 hertz and a geminal of 1.5 hertz. It is doublet of 6.6 and further doublet of the doublet because of geminal coupling; and this type of pattern can be assigned to this proton. Do you understand? How to do that? So, now what I showed you is a simple molecule utilizing the idea that trans coupling is larger than cis coupling, which is larger than geminal coupling. Looking at the pattern of the spectrum; all the three protons are in-equivalent; and I could make the assignments really easily. This is why I was telling you when I was discussing about couplings, trans coupling is always larger than cis, you remember, Many number of times I told you with varieties of examples. This is a reason those ideas will come into practice for you, when you want to analyze this spectra; you can use those ideas.

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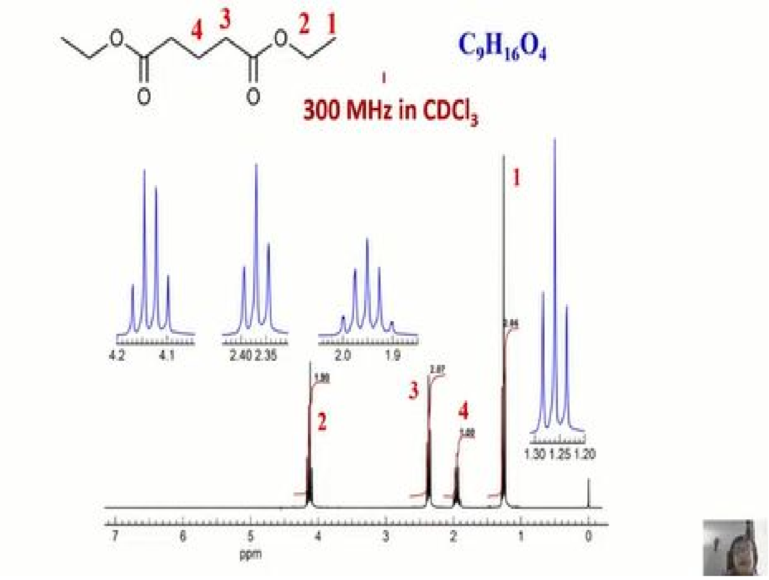

So, this is the next simple example, the perfect symmetry is there in this molecule, so as a consequence 1, 2, 3, and there are only 4 types of protons are present. This is nothing great, you can easily analyze, very easily can analyze. This is CH3 a triplet very clear, this is CH2 is a quartet, where do you see that quartet this one. Now, our problem is to assign these 2. What is 3? 3 is split by CH2 in to a triplet. I understand, what about 4? 4, experiences coupling with this and alsothis this.

Remember, in the chemically magnetically equivalent case I was telling there is a N+1 rule exception these 2 do not couple, but does not mean it should not couple to this. It is coupled to this. As a consequence, it is going to be triplet of a triplet, a funny pattern, if you expand you get 121 triplet, 121 triplet, 121 triplet. They overlap and you get a pattern like this. So, very clearly simple molecule we can start analyzing this by just looking at the pattern.

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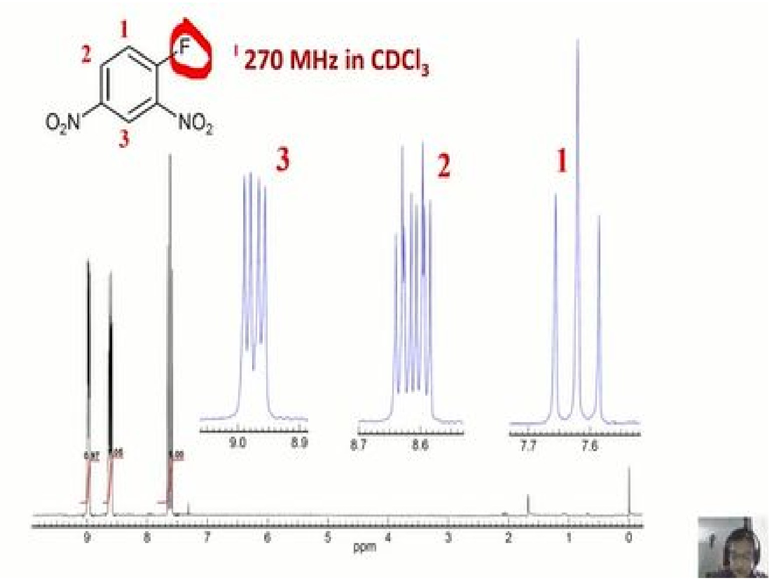

Now, we will take another example where in the proton spectrum, the coupling to a different nuclei come into the picture; get my point coupling to a different nuclei will come into the picture; that is heteronuclear coupling. But remember this resonance is not seen here, it is seen only in the fluorine resonance. But you are getting a proton spectrum, you have to focus only and this proton and this proton and this proton. So, there are 3 groups of peaks, 1, 2, and 3, that is all.

And, this is a passive spin, but coupling at each of the chemical shift position, which are active spins, the coupling to passive spin, fluorine is present, remember. And I am seeing here proton 1, we have 1, 2 coupling 1, 3 coupling 1, 4 coupling; all are passive couplings. when I see proton 2 this is active spin, I will get 1,2 coupling 2,3 coupling and 2 and fluorine coupling. Similarly, when I see 3, I get 3 and F Coupling, 3, 2 coupling and 3, 1 coupling; all are seen.

So coupling to the fluorine is visible in this spectrum do not forget that point. With that now we have to analyze. Let us look at the assignment; first one, I will say this is 3, I made this assignment very simple for you. Look at it; Why? I said it is 3? Remember, let us say this is fluorine, one of the coupling, this is fluorine; this is proton. This fluorine will have 3 bond, I am sorry, meta coupling to this proton.

Similarly, this proton has meta coupling into this proton; but the coupling strengths need not be same; the coupling strengths could be different. As a consequence what happens is, first this splits this into a doublet, further this splits into a doublet. So, you are going to get doublet of doublets because of different coupling strengths. Then, you may ask me what happened to this proton? A 5 bond coupling, para coupling could be there.

But remember, I told you the para couplings are very small of the order of 0.5 hertz, that is why sometimes you see sometimes you do not see; that is the reason why you are not seeing them. Now, what is the next one? Next one, I will say this is 2, why this is 2? You must understand why this is 2, it is a very simple case; look at this one; This proton experiences the coupling with this one; ortho coupling with the large coupling of 8 hertz.

Then it experiences the meta coupling with this fluorine and meta coupling with this proton. So each line of the doublet become doublet of doublets. First it is a doublet because of this, two lines; and each line is going to be doublet of doublets, because of this. You are understanding my point very clearly? please remember this proton is going to be doublet because of this ortho coupling to this proton, so we write one doublet.

Now, what is going to happen? This is going to be split into doublet because of this, it also is going to be split into doublet, each line of this because of this; 8 lines, see you are getting 8 lines here, count it you can get 8 lines. So, you can measure which is which, and analyze and you get 8 lines for this; that is proton 2. Now, what is left for you? This, proton 1, and the assignment is easy; why it is a triplet? Look at it carefully this can experience coupling with this proton and also with this fluorine.

And, the couplings are nearly same it appears as if it is a triplet, but it is doublet of the doublet as they are not equivalent, so it is not triplet; it is doublet of doublet but 2 lines of this central peak overlap because of nearly equal coupling. As a consequence, this appears as a triplet like pattern, it is not triplet, doublet of doublet with 2 lines, central lines overlapping. Then what about this coupling? long range coupling? I do not see, I told you; you know in this case we did not see this 1, 3 coupling.

Consequently, when you observed 3 you do not see 3, 1 coupling. So that is what happens so assignment became very clear for you now with this. I hope you are all with me, I took several examples, simple molecules, analyzed based on the multiplicity pattern, I also took hetero nuclear coupling, so that you will know the hetero nuclei being present, the couplings will always be there, but what happens If I see fluorine resonance?

It is only one peak, one chemical shift only one fluorine is there; but there is a splitting because of this and this, very easy then to analyze. This is the doublet because of this, doublet of doublets because of this, and doublet of doublets of doublets because of this. So if you see the fluorine resonance similar to this we will get 8 peaks; and you can analyze that and get all the 3 coupling with this.

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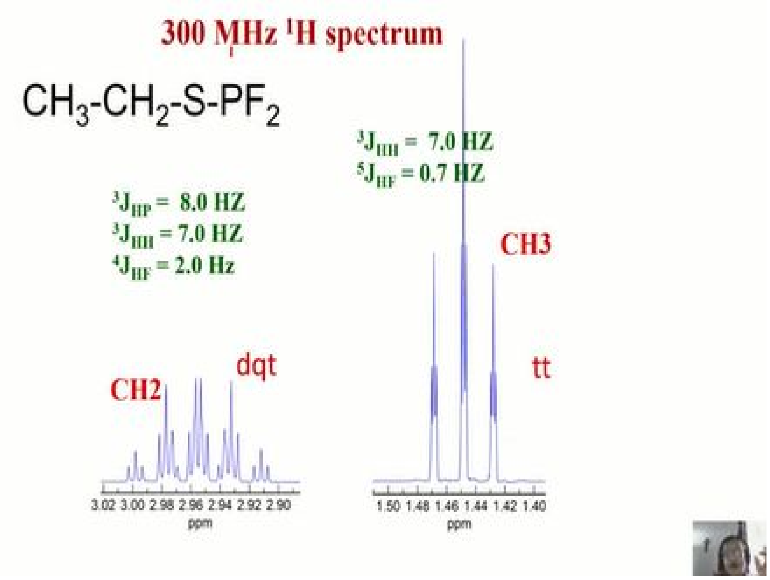

So, what I am going to do is; I will analyze another simple example to the hetronuclear coupling No, I will not do this, will come to the later.

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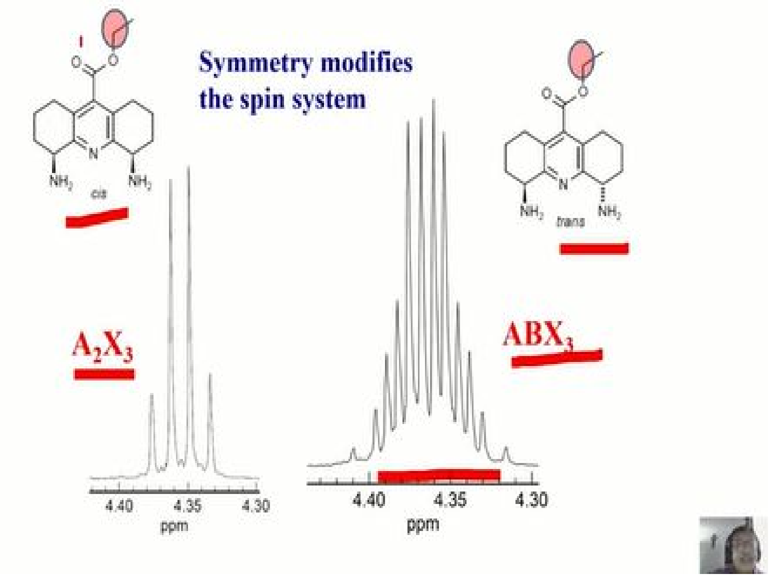

Symmetry modifies the spin system

I will show you a trick with an example, how sometimes spin system gets simplified because of symmetry. Look at this molecule and this molecule. Now, the possibility is in this case, it could be this conformation or this conformation; we do not know, cis and trans, what they call as cis or trans here. If it is cis, you get one type of spectrum; if it is trans you get another type of spectrum; but how do you identify that?

If it is cis, it is the A2X3 spin system, it is trans it is going to be these two will be non-equivalent, the ABX3 spin system. So the conformation of the molecule, if you look at it; you can by looking at the spectrum can also say, whether it is equivalent or non- equivalent, whether this is trans or trans. In this the ABX3 case, this ABX3 pattern we are going to get four quartets very easily you can see that.

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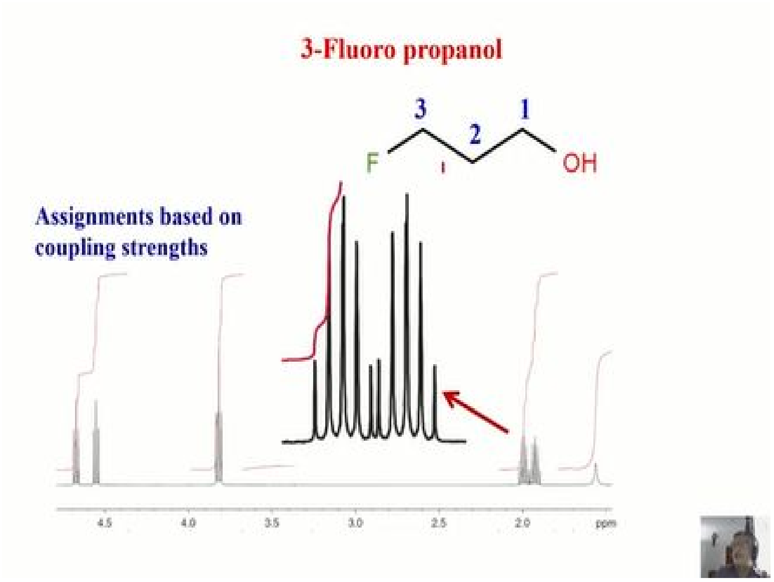

3-Fluoro propanol

Assignments based on coupling strengths

I will give you another simple example in a molecule like this, the 3-Fluoro propanol. If I start analyzing that spectrum it is going to take more time. What I will do is I will stop today at this place. I have given you some gist of various examples; and in the next class I will take you to heteronuclear analysis, like how carbon 13 spectra, heteronuclear spectra, heteronuclear coupling constants, etc. I am going to introduce.

So, next class I will give you one simple example of a proton spectrum with the different heteronuclear couplings, and then straight away go to analysis of the heteronuclear spectra and other ideas.