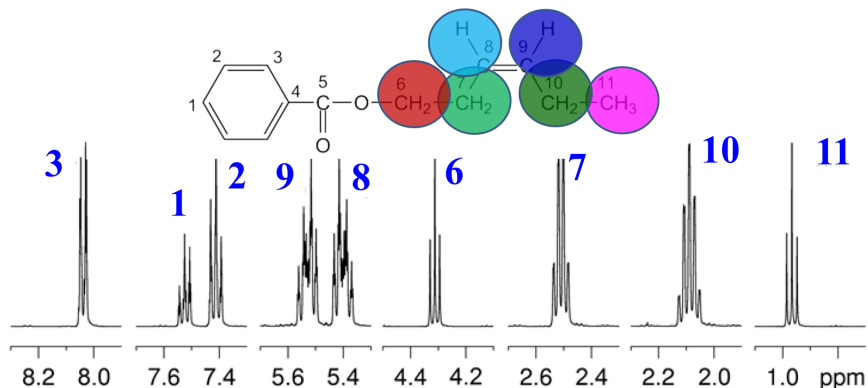


**One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis**  
**Prof. N. Suryaprakash**

**CSIR Emeritus Scientist, Solid State and Structural Chemistry Unit**  
**Indian Institute of Science – Bengaluru**

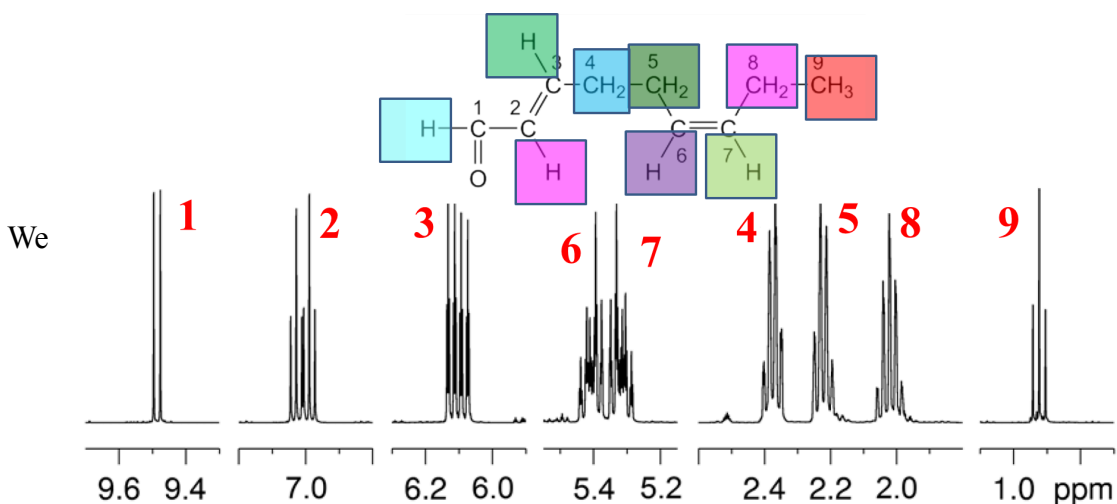
**Lecture 20: Analysis of  $^1\text{H}$  NMR spectra-II**

Welcome all of you. In the last class we started analyzing the NMR spectrum. We took a simple example of a hypothetical molecule, I showed you how we can generate a spectrum using the family tree approach. And then we took a molecule  $\text{CH}_2\text{D}_2$ , we simulated the spectrum for different nuclei, I just showed you how in a simple molecule spectrum of different nuclei can be different, appears different. And how do you extract the coupling information everything is a different thing. There I had the idea of the coupling using that idea I simulated the spectral pattern, because I know what are the functional groups present there, carbon coupled  $\text{H}_2$ , Deuterium, etcetera. And then we simulated the deuterium spectrum carbon, proton everything. We took realistic examples, and showed in few examples how we can analyze the proton spectrum, fairly simple molecules, just by using the knowledge of chemical shift, intensity of the peaks, and a little bit of using the idea of chemistry where it should come, like the idea of shielding and deshielding, etcetera. And of course, using the multiplicity pattern and using chemical shift, these simple molecules can be straightaway analyzed. They are called first order spectra, which are analyzable in the first order way, they are called weakly coupled. Most of the time, unless you are very much interested in getting the intensities, you have to go into the quantum mechanical analysis for strongly coupled. Generally, for characterization purposes which most of the chemists use, this way of analysis will suffice. We will continue further and see how we can analyze few more spectra of several molecules; how we go ahead and analyze. I will take a lot more examples today, not only just proton spectrum. Now, so far I have analyzed only proton spectrum, there can be heteronuclear coupling, there can be symmetry, the variety of possibilities we can think of. In each of these cases one or two examples I will take, and show you how we can analyze this. We go to the next molecule, this is the next molecule which I am showing here. Here, how we can go ahead and analyze it?



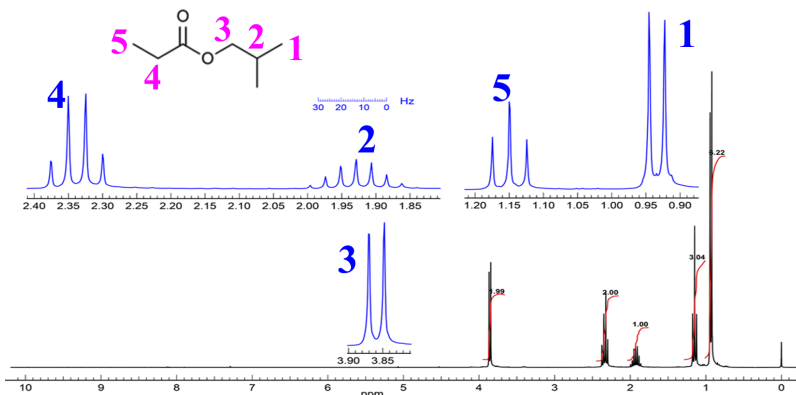
Of course, this phenyl group is a different, that always comes at 7 to 8 ppm. How to analyze the spectrum of a phenyl group in a molecule that contains a benzene ring or a phenyl group, I will tell you that later. But right now, you understood what I have written. This is proton 1, proton 2 and proton 3. Why I wrote this as proton 3, why I wrote this proton 1? First of all from the intensity pattern and then, multiplicity pattern. How the multiplicity pattern is arrived? How I arrived at for this phenyl ring? just in this class itself, may be after couple of slides you will understand. So, do not worry about the phenyl part, I have written 1, 3 and 2, I have made the analysis already. We will assign the other part. Of course, other part is fairly simple. First one is CH<sub>3</sub>, always start with the right side, the right most CH<sub>3</sub> or the left most phenyl group or OH or NH something would be there, and very easily you can assign this. What is the next one? This CH<sub>3</sub> can couple to CH<sub>2</sub>; and then, this CH<sub>2</sub> will become a quartet. But that is not the end of it. It may be having the geminal coupling with this or coupling with this or it can have a coupling with this, we do not know. The pattern would be entirely different, very complex. And if you come to this one, I can fairly interpret it in a simpler possible way. Because CH<sub>2</sub> is attached to oxygen, it comes down field and that is the only proton which can appear like a triplet apart from CH<sub>3</sub>. Look at it, this is coupled only to this and there is a breakage here, because this is this phenyl protons, and are not coupled to this which is far away. So, obviously, there must be one more triplet. This is proton 6 because there is only one triplet. Then, the problem comes. These four different types of protons 1, 2, 3, 4 are here and they have a funny pattern. How do you interpret that? So, this is what we have to understand and then, these are all assumptions I am going to make to analyze. If you want to really assign this one, we have to resort to two dimensional techniques. And I would say this is a proton 10. Why? Just my assumption is this is the high field because attached to CH<sub>3</sub>, it comes here, becomes a quartet and then, each line of the quartet is split because of these two protons, and the multiplicity pattern is there. I call it a quintet or a pentet whatever you are getting it, And I will call this as proton 7. Why proton 7? This is going to be a triplet. This because of this and each line of the triplet is becoming a doublet because of geminal and trans coupling with this. So, it will be doublet of triplet which overlaps, I showed you earlier could be a quartet. This could be my assumption. This I would safely say is the proton 7. Of course, still there is a difficulty we will understand later. This is proton 6, I will say. I already told you this is the only proton which can become a triplet because of this, nothing else. And then, this one, this is proton 8. Proton 8 is very fairly complex because it has a geminal coupling with CH<sub>2</sub>, and is a triplet. It has a trans coupling with CH<sub>3</sub> is a quartet and it is going to be a having a cis coupling with this proton. It is going to be a veryvery complex pattern and this complex pattern is not only for this, it is also true for this proton, other proton also. See this complexity pattern you can get for both 8 and 9; similar pattern, because both of them have a similar environment, almost except CH<sub>3</sub>, for this CH<sub>2</sub>. This proton

experiences CH3 and two CH2. This also experience 2 CH2 couplings like this. So, pattern is almost similar. So, there are only 2 such groups like that 8 and 9; that has to be 8 and 9. We can assign that. We make a rough guess, which is 9 and which is 8, I still do not know. It is only a guess I am making. I will show that when you go to 2D experiment 2 dimensional COSY, I show you how we can clearly pinpoint and see this is proton 8 and this is proton 9. Right now only on the basis of spectral complexity and the coupling because of the neighboring groups I made this assignment. By and large it is OK, except there is confusion between these two, most of these things I know I am correct, there cannot be anything wrong.



will go further. This is the molecule, very interesting molecule. There is no phenyl group here. When there is no phenyl group and only aliphatic groups like this complexity is much better, very difficult to analyze and extract the information. But easy to make the assignment of protons, but if you want to analyze and get the J couplings, it is not easy for it takes lot of time; more involvement is required. One thing you can again say this is CH3; no doubt about it. And then this is coupled to CH3 becomes a quartet, and then each of them will become a doublet of quartet because of this. And these 2 protons as always I said in the previous slide is very complex. This can have a trans coupling with trans coupling with this is, geminal coupling with this, coupling with this. Same here coupling with this geminal and trans coupling with CH2. So, these 2 protons 6 and 7 are fairly complex. So, this has to be here, that I can say. Of course, very easily you can go ahead and analyzing most of the things. If you consider this CHO proton this CHO proton can have only maximum coupling with this one, nothing else. What else there? where

else it can be there is no way it can to any other So, obviously, doublet I



coupled? other coupled proton. this would

say it is a CHO. if you consider this proton coupled to this, it is going to be a trans coupling; doublet plus it is also coupled to the CHO, it is also possible. So, it is fairly a complex pattern. So, it will be starts you know becoming bit and bit messier and messier how do you understand this thing is a fairly a difficult thing we have to resort to little bit of advanced technology advanced technique called 2 dimensional number for this, but right now I will make a rough guess of the analysis and we will confirm it later based only on the multiplicity pattern I will start making as element this is proton 9 this is proton 8 true because it is a complex pattern and this I would say proton 5 why I would say this is a proton 5 this can coupled to this become a triplet and each line of the triplet is further split because of the trans coupling with this and then general coupling with this similarly this is a proton 4 this proton 4 can only become a triplet because as you said the doublet because of this each line of the triplet will be a doublet. So, I would say that and this is proton 6 obviously, I told you it is complex. Similarly this is 7, even that is also complex then what is left with you? then what is left is this proton, this CH proton this CH proton is proton 3 can experience coupling with this, can experience coupling with this, and experience coupling with this that is very interesting when it is experience coupling with trans coupling with this it will be a doublet and even it is also having coupling with this. It is going to be doublet of doublet and each line of the doublet of doublet becomes a triplet, because of that you get that pattern. It is here, doublet of doublet, and each line of that is a triplet. Obviously, that is proton 3. Now next is this one proton 2, this proton 2, is very easy to understand. First of all it is going to be a doublet, trans coupling with that and doublet of doublet because of long range coupling with this. Let us see that is proton 2 and this CHO has a coupling only with one of them. So, it is a doublet that is how we can make the assignment. That is a very simple assignment.

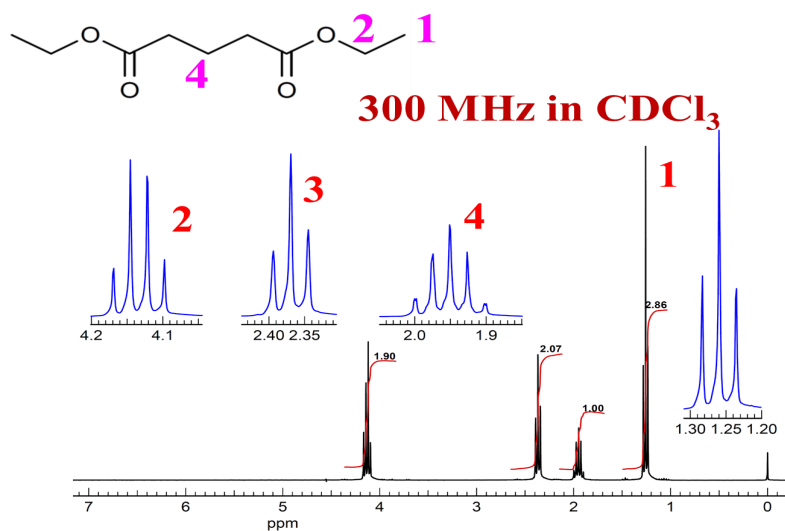
We will go to the next molecule, this is a simple molecule isobutyl propionate in chloroform. Here you have to see there are two groups of protons here one this is one coupled spin system this is another coupled spin systems, and in between there is a C=O-O. As a consequence there is no interaction between this group and this group, they

are separated, very well separated. Now we have proton 1 2 and 3. These are all these two are methyl groups; this methyl group is coming to the high field. But you look at it carefully, this is expanded here. This is a doublet why it is a doublet? you should understand. These two are equivalent protons, methyls both are equivalent, coming at the same chemical shift and because of splitting with this one it becomes a doublet. This methyl is a doublet because of coupling with this. Then what is the next one? this proton 2 has coupling with these six protons like this and coupling with this one, very complex pattern. So very easily you can understand that. What about proton 3? a very simple thing.

CH, this single H is CH<sub>2</sub>. going to because with CH is a is proton have very

this is a is a because

coupling with six methyl protons, and then it is also coupled with the CH proton. This will be a doublet this will be a more complex pattern. And coming to this four and five; five is a methyl group which is a this, and has to be a triplet because of CH<sub>2</sub> and this CH<sub>2</sub> has to be a quartet because of this CH<sub>3</sub>. Where do you see that? one CH triplet and quartet, this is a triplet and this is a quartet. Obviously this is a terminal CH<sub>3</sub>, this has to be CH<sub>2</sub>. So, very easily we could assign this, there is no difficulty at all.



This is only a is C only whereas this So, this is be a doublet, of coupling proton. This doublet. this 3. So, we clearly understood doublet. This quintet is you know

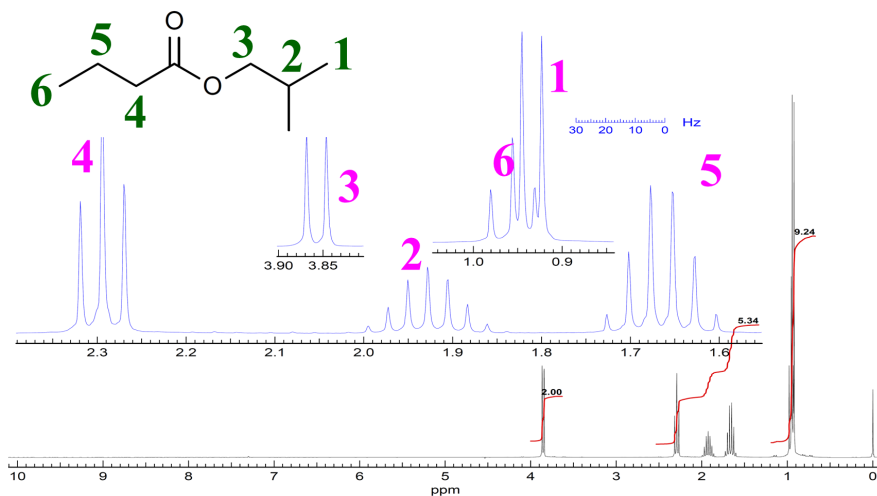
This is a simple molecule, the similar molecule extended further. But here the interesting thing you should observe. In a molecule like this look for the chemically inequivalent groups. There are only four chemically inequivalent groups, because there is symmetry for

along there

So, one CH<sub>2</sub> This

and 2

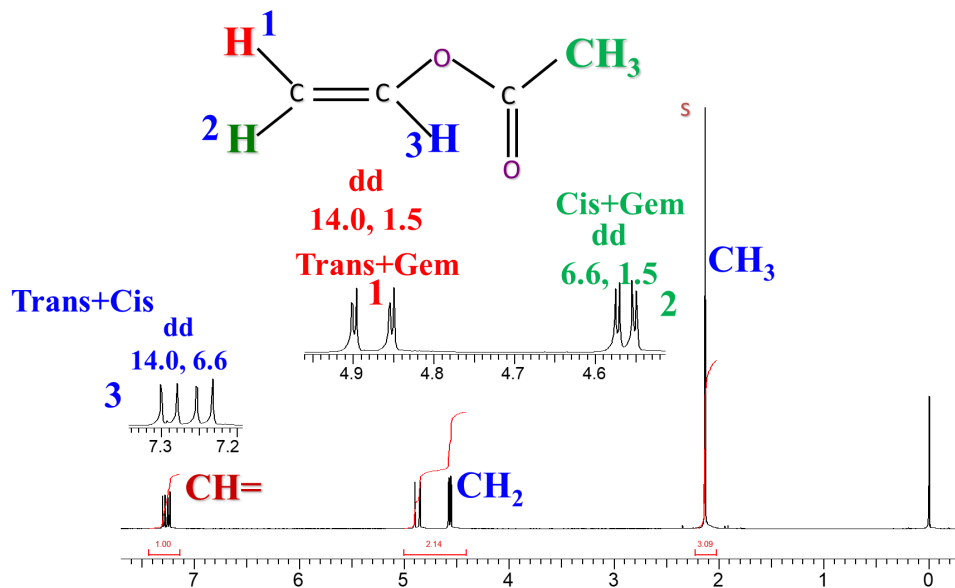
a



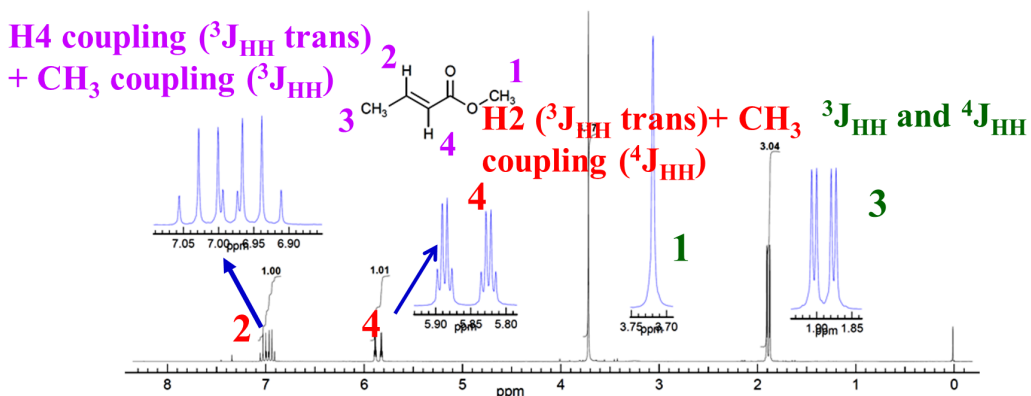
the molecule this axis, is a mirror symmetry. we have CH<sub>3</sub>, CH<sub>2</sub> and CH<sub>2</sub>. is easy protons 1 because quartet and triplet,

very easily you can assign this one. What about this one? that is also easy. What is a triplet that also can be assigned. The problem comes only for this proton. What pattern we expect for this proton, for this proton what is the pattern we expect? for this proton 4. Remember this proton 4 experiences coupling with this CH<sub>2</sub> and this CH<sub>2</sub>. As a consequence it will be triplet of triplet. But you can see that, one complexity is here; this is a next complex group. Obviously this is proton 4. See there is a symmetry up to this, it is fine, but this one, although there is a symmetry this can experience coupling between this and this, It can experience coupling with 3 and also with this group. That is the pattern you are going to get for this. And we make the assignment. This is proton 1, 4. 2 and 3. simple molecule.

We will go to a isobutyl butyrate another different molecule earlier up to this is clearly known. We already understood that. This is going to be a doublet, CH<sub>3</sub> because of coupling with this CH proton is very complex because of coupling with this one and this CH<sub>2</sub> and this is going to be a doublet. This CH<sub>2</sub> that is also known. Here this up to this we knew in the previous molecule. Here now we have to understand. Here we have only extended this one. Of course, this was this is CH<sub>3</sub> group terminal group has to be a triplet because of this; and this has to be quartet because of this. And each line of the quartet split because of this into a triplet. It is a very complex quintet or sextet, you know the exact pattern, whereas, this one is only a triplet. So, with this idea now you can make the assignment. First this is a very easy, you can start assigning this proton 1, understandable, it is a doublet because of coupling with proton two. Proton 2, this is coupled with three methyls and this one, then it has to be more complex pattern. Proton 3 it is coupled to this one, only a doublet. Two CH<sub>3</sub>s are far away. There is no coupling, fine and this is proton 4, it has to be triplet because of this. And proton 5 is a more complex pattern because of two CH<sub>2</sub>s like this. And it could be a sextet. And what about the other one? it is proton 5, very easily you know that one. The proton 6 is known, it is a triplet, proton 5 is known; proton 4. Now all the peaks have been assigned, simple molecule. But why I am taking this example is to show is, when we have to see one proton sitting between two other protons how do you assign the peak? that is what you should look at the multiplicity pattern and then start assigning.

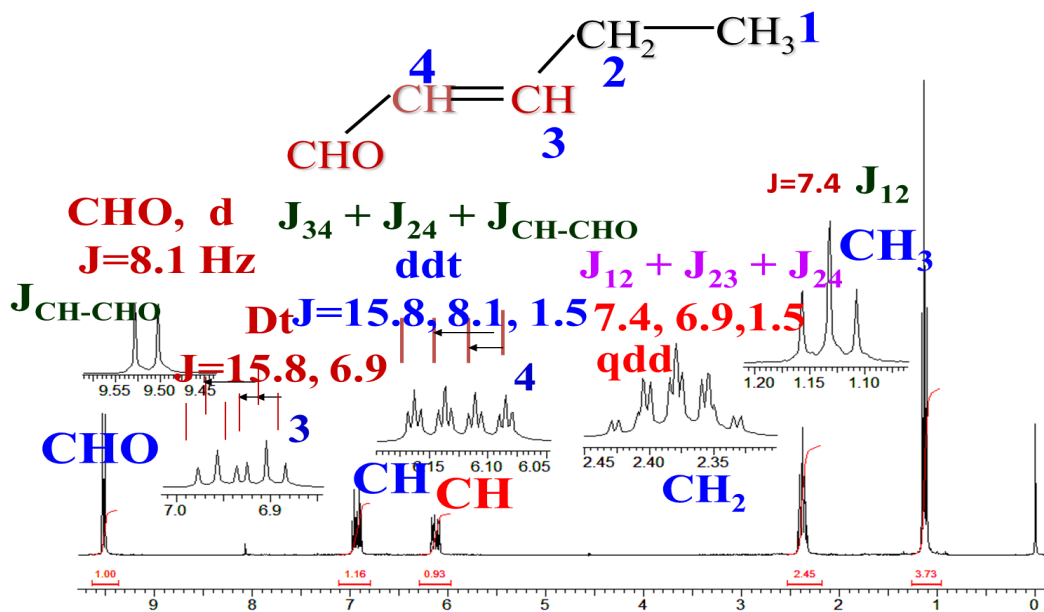


This is fairly a easy molecule, but let us see how you can assign this one. First of all if you look at this molecule there is one terminal group CH<sub>3</sub>; this has no coupling with any other proton, because the other protons are far away. Obviously it has to be a singlet with intensity more, where do you see that singlet? This is here, I can safely say this is a CH<sub>3</sub> group. Next is three different protons; all are different here. You have to use your idea of cis and trans couplings. Remember when I was explaining the Karplus curve, I did explain and I did say trans coupling in such type of molecules are larger than cis coupling and cis coupling is larger than geminal coupling. This is the order I explained to you. First geminal coupling is weak more than that is cis, more than that is trans. Now look at this, if you want to analyze this you have to consider this one. This proton experiences of one trans coupling, the large coupling and one cis coupling, that is fine. Look at this proton, this experiences one cis coupling three bond, vicinal coupling and one geminal coupling. Whereas this proton experiences one trans coupling, and one geminal coupling. They are all of different strengths. So looking at the multiplicity pattern, looking at the separation of the peaks. you can assign which is which here, Very simple, okay. What we will do is this. I would say this is a CH<sub>2</sub> group; this has been expanded here. This is CH, okay, this this H<sub>3</sub> experiences, this proton 3, a trans coupling which is larger which is of the order 14 Hz, and then a cis coupling. That is why it is two doublets, well separated. Next one is this proton. One is a large coupling, trans well separated, and then each of them is split into a small coupling because of geminal which is only 1.5 Hertz. Continue further this has to be a proton 2, because this has a vicinal coupling smaller than trans coupling of the order of only 6.6 Hz, and each of them is split into a doublet because of geminal coupling of 1.5 Hertz. Very easily you can interpret. Here we use the idea of cis trans coupling strengths. Okay. Remember in such type of molecules when you have ethylenic like molecules you have to use the knowledge of trans coupling which is larger than cis coupling and cis coupling is larger than geminal coupling. Based on that splitting pattern we can start interpreting okay.

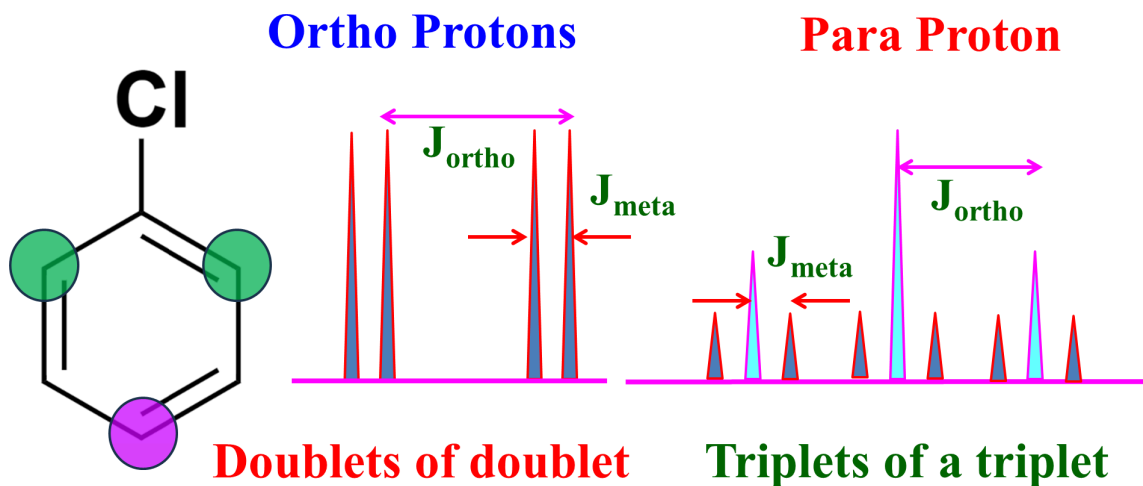




We will go for this molecule similar molecule but instead of proton here I have replaced this with the methyl group. This will be identical explanation. This CH<sub>3</sub> proton is already known this is CH<sub>3</sub>. This is proton 1, notice no splitting nothing. Very well resolved. You know strong singlet is there. Easily I can do that. Then what is remaining exactly like the previous example. You have to consider all the three couplings. You have to consider the trans coupling, cis coupling and geminal coupling for each of them. 1 is done. Now 2 3 4 we will assign. I would say this is proton 3. Why did I say proton 3? logic is simple. This proton can couple to this proton and become a doublet and this can also couple to this, vicinal coupling, become doublet of doublet. So this large separation is vicinal coupling and each of the doublet is a doublet because of geminal coupling. And it cannot have any other pattern. Whereas other two groups you see, there is a quartet like pattern. That means it is coupled to CH<sub>3</sub>, when we are looking at CH<sub>3</sub>, it is coupled only to show single protons. Obviously very authentically I can say this is proton 3. There is no doubt about it, okay. Now go further I would say this is proton 4, why I would say proton 4? it has a trans coupling very very large, and then each line of this doublet is split into a quartet because of this. See vicinal coupling, cis coupling is there. And go to this one, this proton 2, this is a trans coupling and also geminal coupling here, okay. Very easily looking at each of them will be a doublet and further each line of the doublet is split into quartet because of coupling with CH<sub>3</sub>, okay. This how we can analyze. We will go further, more complexity as you go go higher and higher, we see complexity keeps increasing.



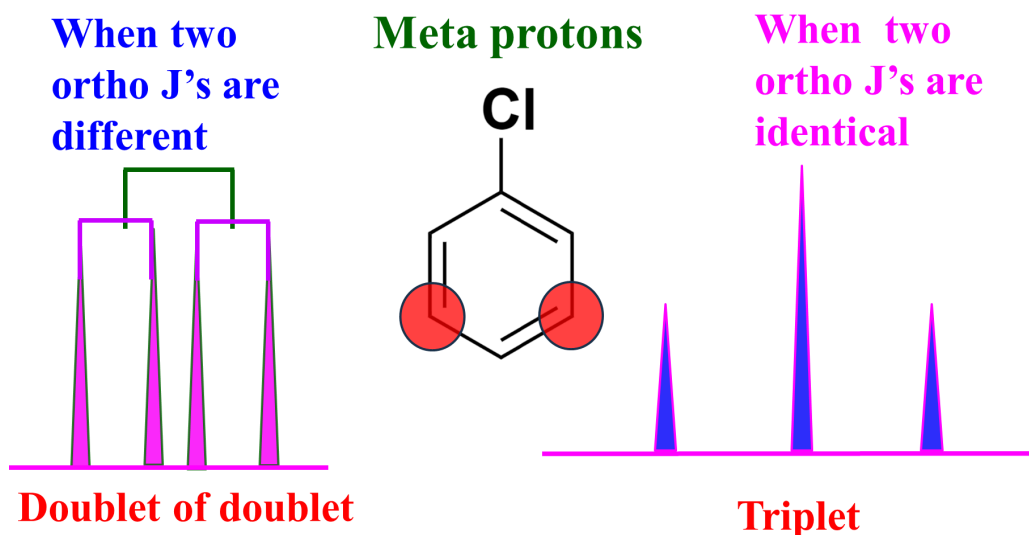
A molecule like this very easily you can do that. This is CH<sub>3</sub>, that is a first assumption there cannot be anything wrong; Proton 1, it will be a triplet. Go to next one CHO, it comes to downfield because it is attached to oxygen and that will be split into the doublet because of CH. You can see it, This CHO is a doublet, okay. see this is CH<sub>3</sub>, this is CHO is doublet of the order of 8.1 hertz coupling between this and this CH and CHO and go to proton 3, this I will say proton 3. Why proton 3 is a doublet of triplet, very easy because it is doublet because of this, and each of the doublet line is a triplet because of



this. So that is proton 3. What about this one? this is a complex pattern. This can experience coupling with this, with this, and also there is a long range coupling with this. So that must be proton 4, we can interpret that one, and go for this. So like this more or less all of them have been interpreted, all the peaks have been assigned. So I will go back again and you can see carefully I will removed all the marking this is CH<sub>3</sub> a triplet; this is CHO is a doublet because of CH coupling, and this is proton 3. This is proton 3, has a is expanded here, it is doublet of triplet; and this is proton 2. This is having quartet of doublet of doublet, because it is a quartet because of this, doublet because of long range coupling with this, and this proton 4 is doublet of doublet of triplets, because it is a doublet because of this, doublet because of this and also long range coupling to this. And that is how we understood this one. This is all. So far we were discussing about the analysis of the proton spectra of molecule containing only aliphatic protons, so far we did not bring in the phenyl group; only one example was there but I said I will explain it later. How do you analyze the spectrum of molecules containing phenyl groups? that is what we should understand today. Before going further please always remember if I have aromatic protons especially benzene rings this is the order of coupling we should remember. Ortho coupling in benzene is between 7.5 to 8.5 Hertz, it could be anywhere around that, meta coupling is 1 to 2 Hertz, and the para coupling can go from 0.3 to 1 Hz, even sometimes 1.5 Hz. That is approximately you can say are less than 1 Hertz. We can say 5 bond coupling para, 4 bond meta, 3 bond ortho coupling. This information is

needed for us if you want to analyze the proton spectrum of aromatic systems. How do we get this splitting pattern in different phenyl groups? the phenyl groups can have substitution it can be monosubstituted, symmetrically disubstituted asymmetrically disubstituted, symmetrically trisubstituted, asymmetrically trisubstituted. In each of these cases the spectrum would be different. The way you see the spectrum will be different. Then we can use this knowledge to analyze this spectrum of such molecules.

We will start with a monosubstituted benzene. This simple molecule, there is a symmetry along this axis, this and this are identical, these two are ortho protons are same. These two ortho protons when I look at it in this molecule this is going to be doublet of a doublet. Why it is a doublet of a doublet? because these two are identical, single proton but each of them is split by ortho coupling into a doublet see it will be split into a doublet

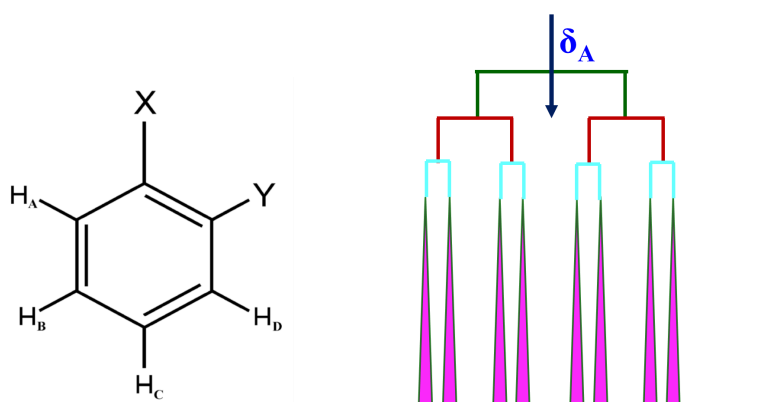


like this and each line of this doublet is split by a para coupling of the order of 0.5 Hz. That is why it is a doublet of doublet larger separation correspond to ortho coupling, and the smaller separation correspond to meta coupling, If I have a monosubstituted benzene if you get a pattern like this large doublet; and each line of this doublet is a doublet, fairly you can assume this is ortho to the substituent. Next we will go further this is the ortho proton, what is the next one we can think of? this is meta dit is called doublet of doublet. We have to para proton what is the pattern we expect for a para proton? very simple both this this thing will split this into a triplet. Before that of course, there are two ortho couplings, large couplings, these ortho coupling will split this into a triplet, and each line of the triplet is further split into another triplet because of two equivalent meta protons. And this how the pattern you get. And here it has to be ortho couplings and they have to be identical, because it is a mono substituted benzene. There is a symmetry axis. As a consequence this coupling and this coupling are identical. When the couplings are

identical we also discussed we will get a triplet, 1:2:1, because two lines of the center overlap. And you get a triplet and each line of the triplet has a meta coupling like this, become triplet of triplets. And if you have a para proton in a mono substituted benzene you get a pattern like this triplet of triplets, so easily you can identify that and make the assignment. It called triplets of triplet.

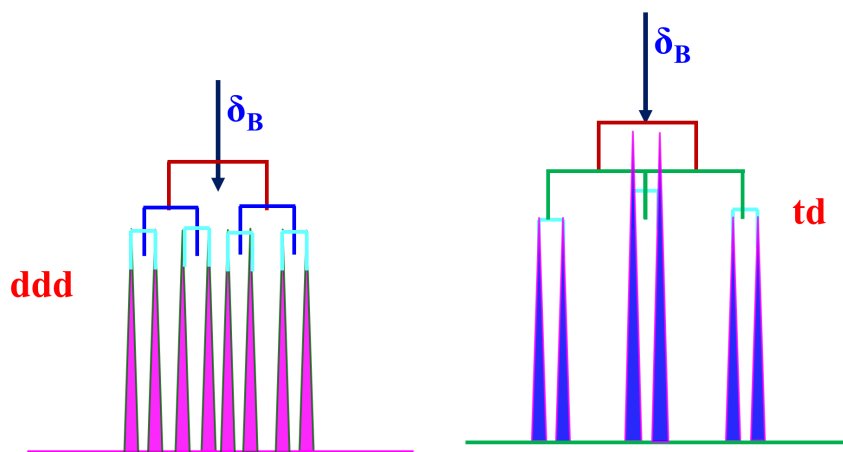
What about the other one? now meta protons, this is fairly difficult. Here we can think of when the two ortho couplings are identical, okay, and the two ortho couplings could be different or identical. But we have to say in this case because of the symmetry they are not different. Of course only for this one; be same because of the symmetry, in which case if they are different normally they would be this will be doublet of a doublet, because large coupling is one ortho coupling and other one is other ortho coupling, usually because there is a symmetry they are same in which case you are if both are identical, again this para proton is going to be a doublet. This possibility is very low, you will not see, unless there is a distortion in the molecule, Normally there is no distortion because of substitution there is a symmetry along this axis. As a consequence this proton will have ortho coupling with this and meta coupling with this. So, it is it has to be only triplet okay. And meta coupling if it is there, has one coupling with this and one coupling with this, is a triplet.

We look at



asymmetrically ortho disubstituted benzene it is a mono substituted. Now let us take the example of asymmetrically ortho disubstituted, what will happen? asymmetrically means these two substituents are different; X and Y. Then what is the pattern we expect. Is there any symmetry for this molecule? no symmetry at all; or all these four protons are chemically inequivalent, A is different, B is different, C is different and D is different, Let

us see what do you get at the proton chemical sheet of proton A What is the multiplicity pattern you get. p)Proton A can experience ortho coupling with this, can experience meta coupling with thi,s and also experience para coupling. So, what is the pattern we expect? you expect first ortho coupling and each of the doublet is going to be doublet of doublet because of meta coupling gives doublet, and each of them is going to be doublet of doublet because of para coupling and this is the pattern you are going to get. You see the point; this is what you are going to get if you have asymmetrically disubstituted benzene. If I look at one of these protons you are going to get eight line pattern. And from the pattern you can understand from the centre is a chemical shift, this is one ortho coupling, this is meta coupling, and this is para coupling, all are different.



Same way if you look at the proton B what will happen? In this molecule at proton B, proton B experiences one ortho coupling, one ortho coupling and one meta coupling. When two ortho couplings are identical again, it gives you triplet of doublets. If the couplings are different, it give rise to again eight line pattern, because of two ortho coupling and one meta coupling, assuming that ortho couplings are different. If two ortho couplings are different you get like this, and you will have a pattern like this ddd. If two ortho couplings are identical, you look at the proton B here, if you look at the proton B here it can have two ortho couplings and meta coupling. if two ortho couplings are identical again it is ortho, then you will get triplet of doublets; two ortho couplings gives triplet when identical, and every tripletline is going to be a doublet because of meta coupling. So, two ortho couplings are identical with this is the pattern triplet and then because of meta coupling, it will be triplets of doublets.

What about the proton C? again same here I have written correctly, if J ortho are equal it is going to be triplets of doublet, if the J ortho are different, are not identical, then it is going to be ddd, similar to proton B, Here also if you see this one, it can have this and

this ortho coupling, if they are identical it will be a triplet and because of the meta coupling it is going to be a doublet of triplets. If they are all different it is going to be ddd, 8 lines pattern. Go to this last one proton, last one is proton D. This one is exactly as the pattern similar to A, because it has one ortho coupling, one meta coupling and para coupling; it will be 8 lines pattern. This is how you will get the spectrum if you have asymmetrically ortho-disubstituted benzene. So, simply remember if you have asymmetrically ortho substituted, the protons which are close to the ortho to the substituents can have ddd, 8 length pattern protons, which are meta to the substituents can be a doublet of triplets or 8 lines pattern, depending upon whether the ortho couplings are identical or different.

So, this is how you have to start analyzing the proton spectra of phenyl ring. Lot more examples are there about what happens if you have meta substitution, symmetrically or asymmetrically, how does the pattern come? we will explain that, and then take the real example of this thing and we will start discussing that in the next class. So, today I took the example of analysis of the proton spectra, example of many molecules. We analyze the protons spectra, simple they are all weakly coupled, first order analysis was possible. We are looking at the neighboring group looking at the multiplicity pattern, looking at the chemical shift, looking at the intensity pattern we were able to assign lot of peaks. Very easily we can do that for olefins. Or you know like ethylene molecules with a double bond we understood depending upon the trans coupling, cis coupling and geminal coupling strength you could easily assign which is which; that was not difficult at all. So, we took the example of many such molecules; one molecule can have two couplings, coupled with two protons, three protons, or groups of protons. The multiplicity patterns become very complex. Looking at the complexity of the multiplicity pattern we could make rough assignment of all the things, by and large they are correct. But how do you authentically say that, we have to go to the higher advanced NMR techniques. Further we went to the phenyl groups, we also said in the phenyl group mono substituted how do we get, if it is ortho asymmetrically or ortho symmetrically substituted, how we get and we understood the spectrum. So, we can go further and see what will happen to different substituents from the next class and then we analyze more complex spectrum with heteronuclear couplings, satellite spectra, varieties of things subspectral analysis we can do we will continue that further. So, I will stop here. Thank you very much.