

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

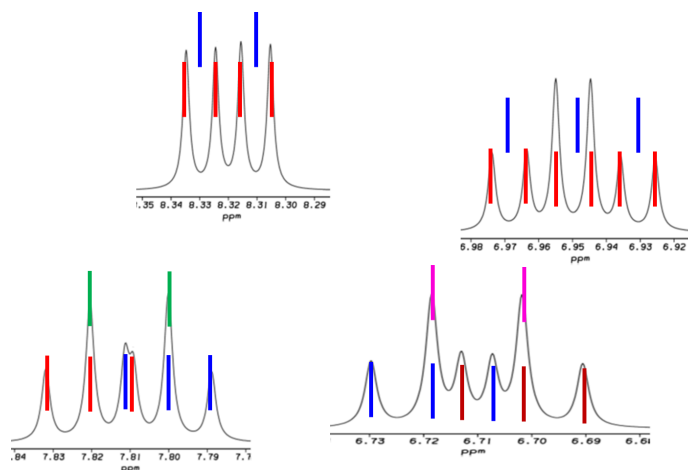
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**Lecture 15 Analysis of multiplicity patterns**

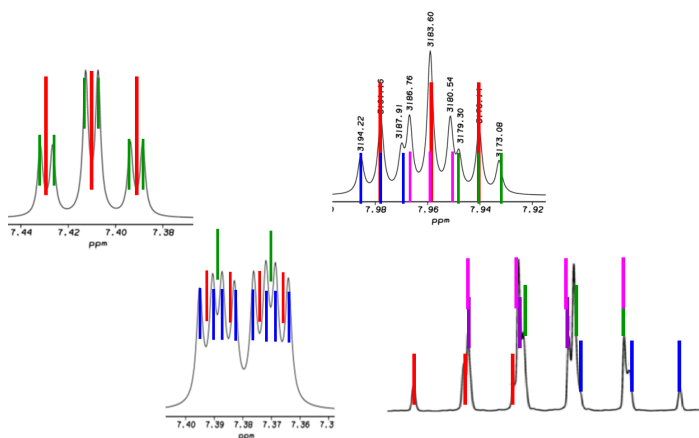
Welcome all of you, we have been discussing about scalar coupling and especially in the last one class and two classes, we have discussed extensively about the multiplicity pattern, because that is very very important especially when you are working with a complex molecule. The pattern what you are going to get is very important. If you know what is a pattern, then you know how to extract the coupling information. See if your aim is just to characterize the compound and say I have got a CH<sub>3</sub> peak, I have a CH<sub>2</sub> peak, just for the assignment purpose without getting into the pattern, the coupling information, just for identifying whether the molecule what you have synthesized has particular peaks, that is a different question. But if you want to get the coupling information etcetera, to get more information about the structure of the molecule, geometry of the molecule or conformation of the molecule, then these patterns are very very important to understand. Only then you will know how to interpret the spectrum. And for that purpose we took a several examples and understood about the multiplicity patterns. Hypothetical molecules I took, one proton coupled another single proton or CH<sub>2</sub> proton, CH<sub>3</sub> proton, and then when it is coupled to two groups of protons single or multiple, like chemically equivalent groups like CH<sub>2</sub> or CH<sub>3</sub>. And I showed that when one proton is coupled to CH and CH<sub>2</sub> it is going to be doublet of triplets, depending upon which coupling is larger. If the CH<sub>2</sub> coupled to CH proton is larger it is going to become triplet, then other one will be a doublet. So, it will be doublet of triplets or triplets of doublet depending upon which coupling strength is larger, exactly the pattern gets reversed. Similarly you can have CH<sub>2</sub> proton coupled to CH<sub>2</sub>, or CH<sub>3</sub> or another two 3 CH<sub>2</sub>, two 3 CH<sub>3</sub>; or one variety of combinations we can think of. And I showed for many examples I took. I showed you the examples with the stick plots, how we get the multiplicity pattern. But always remember when you have a multiplicity pattern for any particular group of protons or a particular proton the center of the multiplicity correspond to your chemical shift.

If it is triplet, then center of the triplet line; if it is a quartet then center of the quartet; if it is a doublet center of the doublet, like that. And then further multiplicity gives rise to splitting because of various couplings. But how do you measure the couplings? Also I explained to you which coupling is larger, which coupling is smaller. See this needs some

some sort of an expertise. You can start working with that for couple of examples. If you do it you will know by looking at the pattern how do you get the couplings. With this today we will take some examples and do some exercise ourselves to understand and identify the splitting patterns.



What I showed you was a stick plot. What is the real complicated spectrum? the realistic example, how do you get that? We will go ahead and do that. For example, this is a spectrum which we have got what do we call that pattern? 2 lines 4 lines of equal intensity. Obviously, this could be one doublet this could be one doublet or from the center of this this could be one doublet this could be another doublet, does not matter. We call this as doublets of doublet.

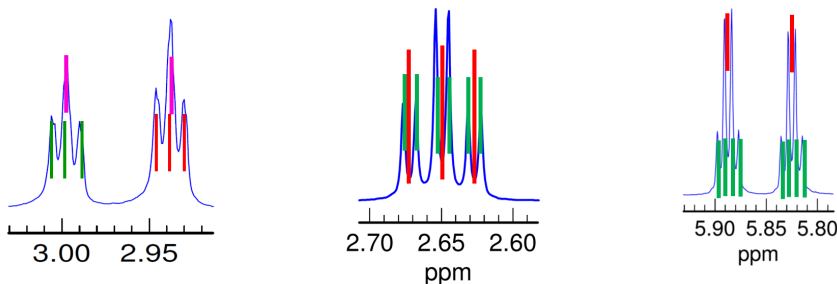


What about this pattern? Very easily looking at the pattern we already got one stick plot, we saw that. See this will be one triplet, this this and this will become other triplets, and

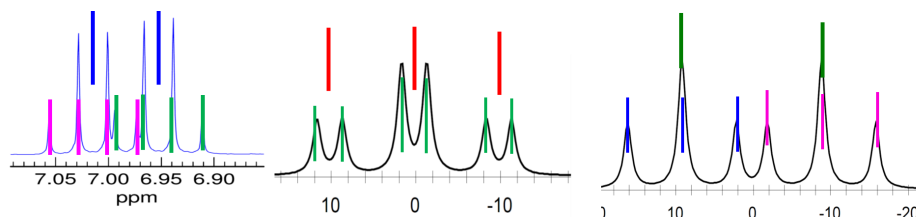
this will be a doublet. So what do you call that? each line of the triplet is going to be triplet; and each line of the triplet is split into a doublet like this. And that is how you are going to get triplet of doublets.

What about this one? the larger separation is a doublet and each line of the doublet is split into triplet like 1 2 1; 1 2 1 intensity. So, that is a triplet. Similarly here also 1 2 1 intensity was there and it became doublet; here 1 2 1 triplet and each line of the triplet is going to be for doublet. And each line of the doublet is going to be a triplet that is fine. What about this one again identical to this. This is also doublets of triplet. What about this pattern? see very interesting real spectrum of a molecule larger separation you can see here is a triplet 1 2 1 so the first separation of the splitting pattern is a triplet and each line of the triplet is split into a doublet. And separation from this line to this line, or from this line to this line, or this to this, or this to this, gives rise to larger coupling triplet coupling whereas, separation between these adjacent lines of this doublet gives you doublet strength. So, this pattern is called triplets of doublet.

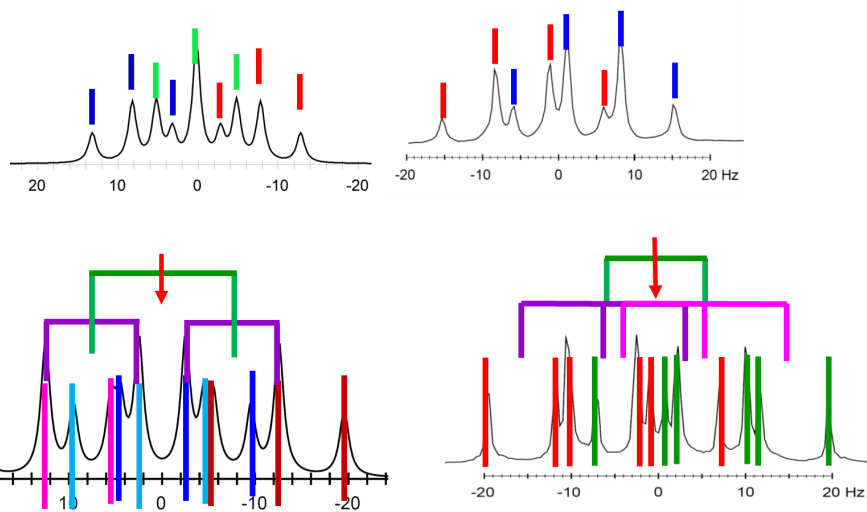
What about this pattern? this looks more complex. What I told you, this is how we have to get the analysis done. It looks like a pentate, or a sextate. But of course, it is because of overlap of the couplings. Fortunately here there is not much of an overlap very easily you can identify. If you carefully look at this pattern, you will see there is going to be one triplet here larger triplet and then each line of the triplet is split into another triplet like this what do you call this it is triplets of triplets, a realistic example. What about this one the doublets of doublets of a doublet. We saw that, one example I gave you a AMPX example, and I said each line is split into doublet of doublet of doublet, and we got 8 lines, which is coupled to 3 other protons. Exactly here one proton is coupled to 3 other protons. As a consequence it is going to be doublets of doublets of doublet. Look at this one this is a very interesting pattern if you carefully see initially it looks more confusing, but if you carefully see this line this line this line and this line one more here it looks like a quartet, and each line of the quartet is split into a triplet. First it is quartet and each line of the quartet is split into a triplet. It is called quartet of triplets. The larger separation is quartet and then each line of the quartet is split into triplets.



What about this one? of course, this is a doublet the separation is larger, and each line of the doublet is split into a triplet, it is called doublet of triplets. What about this one? Triplet of doublets, because this larger separation is a triplet and each line of the triplet is split into a doublet. This one very easily you can identify, first this large separation is a doublet and each line of the doublet is split into a quartets. So, it is called doublet of a quartets.

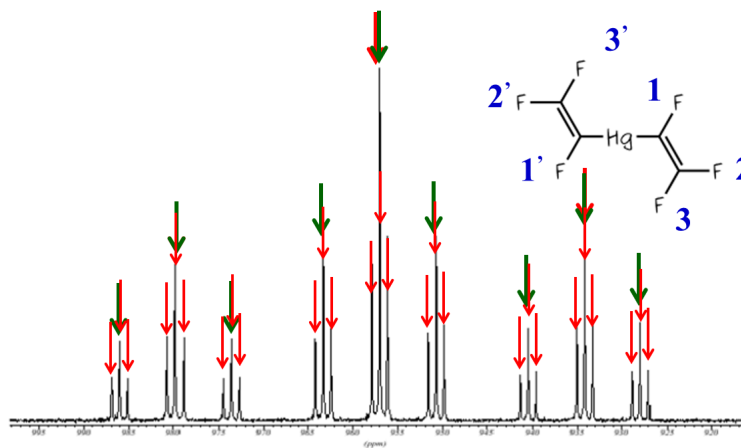


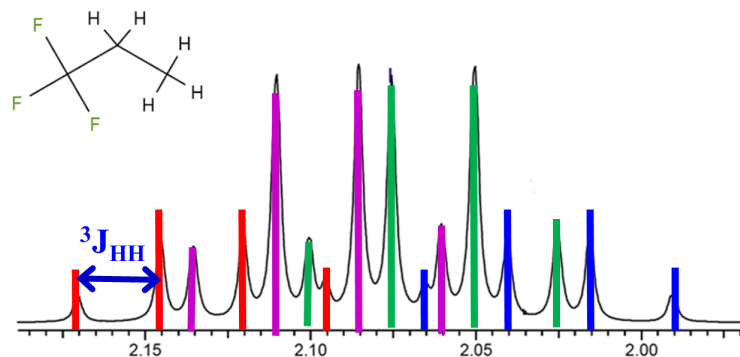
This one; Again this line centre to this centre, is a doublet. And then each line of this doublet is split into quartets like this. So, it is called doublets of quartets. What about this one? Very easily you can identify, it is similar to what we saw here. Only thing the spread is larger. It is also triplet of doublets, here the larger separation is triplet. This is another thing. Here this is triplet of doublet, but here it is doublet of triplet, because this is a large separation and each line is split into a triplet. Larger strength here is a doublet, and the smaller coupling is a triplet. It is called doublet of triplets.



What about this one? if you carefully see as you go now complexity will become more. More and more complex and you need to have some idea as how to analyze. This is called triplets of a triplet. So, this one, the center of this and this one for example, is a triplet. First it is a triplet and each line of the triplet is split into another triplets like this. So, central line is a of this triplet remains an altered, it remains at the same frequency.

But then each line of this triplet, center line remains same, is split further into triplets, 1:2:1 triplet. It is called triplets of a triplet. This is another interesting thing. If you carefully look at it; you can identify very easily. it is one quartet, another quartet and then center of this quartet to center of this quartet is a doublet. So, what we call this pattern? doublets of a quartets. This is more complex. Now, we have to understand why we are going to get this type of pattern. If you carefully see, first of all you have to know how to discern this multiplicity pattern. It is very very important. If you look at this pattern, I would first, the center of this is a chemical shift, that is always I told you, is the centre of the multiplicity. From the center, first it is going to be a doublet; and each line of the doublet is further split into two lines, doublet of doublet. And then each line of the doublet of doublet become triplet. One triplet, another triplet, another triplet. You see all lines can be very clearly assigned. And this is what is called doublet of doublet of triplets. See understanding the pattern is very important. Always starts from the center of the multiplicity pattern. You should carefully think what could be the pattern, based on that you can start arriving at the pattern. Look at this one even more complex, of course, start from the center here, this is the chemical shift; and it is a doublet and each line of the doublet is a triplet and each line of the triplet is again split into a doublet. So, it is called doublets of triplets of doublets. Here it is doublet of doublet of triplets. Here it is doublet of triplets of doublet. So, you look at the patterns, they completely different. If you carefully see here, the pattern is completely different. This pattern and this pattern see are completely different. So, doublet of doublet of triplet and doublet of triplet of doublets makes lot of difference especially in the appearance spectrum.



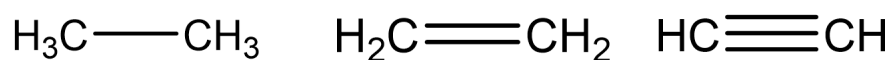


Now, we will go to a realistic example of a molecule like this. Mercury 199 spectrum of this. We will discuss more about these things when we come to heteronuclear NMR spectrum analysis. Now, this is a particular molecule these fluorines split this into a triplet because of equal strength similarly this and this this and this split the mercury with equal strengths. All the three fluorines of this vinyl group are equivalent, but each of them is symmetric with respect to mercury this is with symmetric with respect to this this is symmetric with respect to this. This is symmetric with respect to this. As a consequence what you are going to see is a spectrum; very very easy to understand. So, first this mercury split into a triplet because of this. This will split this into a triplet. This will further split each line of the triplet will split into a triplet; because of symmetry central line will overlap. As I have been telling you, it is a triplet. Now, these two fluorines will further split each line of the triplet into one triplet, s?another triplet, another triplet. What happen to other remaining fluorines? These two fluorines again are equivalent. They will split each line of the triplet into another triplet like this. So, it is a triplet of triplet of triplets. This is a pattern you are going to see for this realistic molecule.

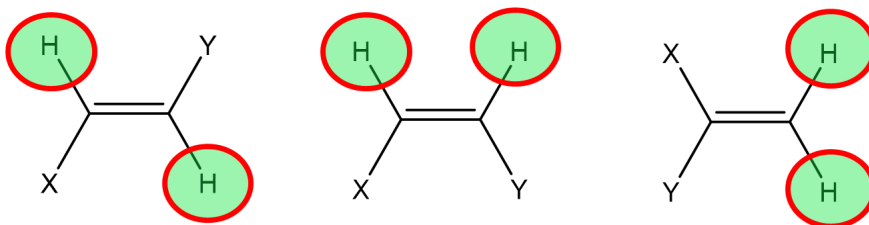
Look at this molecule. This is 1,1,1-trifluoropropane. I am looking at the CH<sub>2</sub> proton. There are three fluorines here, three protons here. Equivalent CF<sub>3</sub> group and CH<sub>3</sub> groups. Now, what is happening? I know the coupling FH coupling, I have written to you. This fluorine with this fluorine coupling; this proton to this proton coupling, the strengths are known. Then what is the pattern you are going to get? because of this three equivalent fluorines? This is going to be a quartet. Again each line of the quartet is split into another quartet because of protons. So, fluorine will split proton into a quartet. This CF<sub>3</sub> splits this CH<sub>2</sub> into a quartet and each line of the quartet is further split because of this. So, this is one quartet; and each quartet line of this will be further split into another

quartet like this. I see four different quartets. I put four different colors to make you understand. And this is called quartet of quartets. This is what you are going to get.

With all this thing now we understood the multiplicity patterns and everything. But we should know what is the strength of the coupling. We have been discussing lot about multiplicity patterns, but if I measure the coupling strength or even if I do not measure, I should have some idea. What is the proton-proton coupling strength? It could be one bond coupling, two bond coupling, three bond coupling. I told you coupling can extend up to two bond three bonds. And of course, as the number of bonds keeps increasing consecutively, the coupling strength keeps coming down, does not matter. But we should know the strength. Now which is the one bond coupling among the protons? first thing you can think of is the hydrogen molecule. But how do you get the coupling here? it is a symmetric molecule, you are going to get a single peak. With single peak how do you measure the coupling? at least you must have a doublet to measure the coupling, and it is a singlet. It is a different question, I will tell you later how do you measure coupling among the equivalent spins. But remember one bond coupling of proton is around 276 Hertz in the hydrogen molecule.

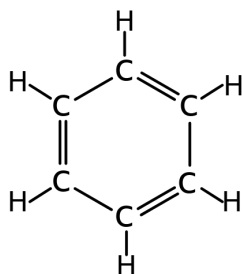


Look at this type of molecule we have CH<sub>3</sub> and CH<sub>3</sub>. Again you may ask a question there is a symmetry and there may not be coupling. I told you these are all exceptions for 2NI+1 rule. But somehow we can adapt tricks and try to measure the coupling. Do not worry how you do. Do not come to a conclusion that there is no coupling here. There exist coupling, but the couplings are not reflected in the spectrum. But we can somehow adapt some tricks to measure the coupling. Those things we discuss in the next class. But in a molecule like this single bond, the three bond coupling with this proton 1, 2 and three bond coupling is about 8 Hertz. And again there is a double bond in this molecule, it is about 12 to 20 Hertz. When there is a triple bond like this, it can be of the order of 9 Hertz, in acetylene molecule.

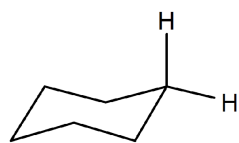


And also the coupling depends upon angle between the bonds. depends upon what is angle in which these two protons are making. Look at this one, in a molecule like this.

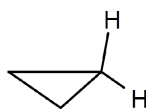
These two protons are trans to each other. The trans coupling is about 17 hertz approximately, it can be way different it can be 12 to 14, 15, 17, 18 Hertz also.\, does not matter. You should remember trans coupling is always larger than the cis coupling. This is the proton, there is a trans coupling, 3J coupling; and this is geminal coupling. The geminal coupling is generally is very very small. The geminal coupling is very small , then comes cis coupling, then comes trans coupling. The trans coupling is the largest of all in these types of molecules.



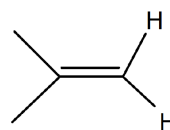
Go to phenyl rings. If you go to the phenyl ring, as I told you benzene gives a single peak. When I was discussing the magnetic equivalence I told you each proton can have a ortho coupling meta coupling and a para coupling. If you consider this can have a ortho coupling, meta coupling and para coupling. Like each proton will have three couplings and the strength of the coupling is about 7 to 8 hertz for ortho, for meta it is 1 to 2 hertz and for para it is from 0 to 1 Hertz less than 1 Hertz. Then how did you measure this? all are chemically equivalent in benzene. I told you it will give a single peak if you take benzene NMR proton NMR. Then how did we measure the J coupling? That is that is what I am going to tell later.



$${}^2J_{HH} = -12.5 \text{ Hz}$$

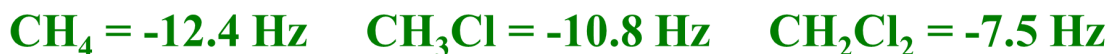


$${}^2J_{HH} = -4.3 \text{ Hz}$$



$${}^2J_{HH} = 2.5 \text{ Hz}$$

And if you come to the two bond geminal couplings, I already told you geminal couplings are very small, but in fact it depends again on HCH bond angles, in molecules like this. And also depending upon the substituents, hybridization of the carbon, all those things matters. What I am trying to tell give you is only a gist. A sort of a bird's eye

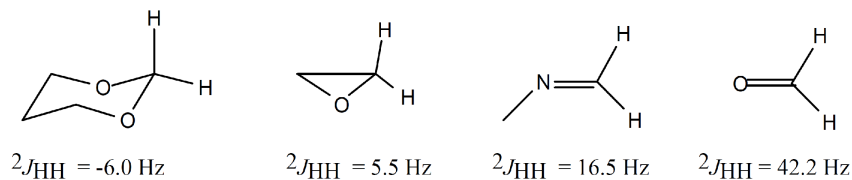


view. You should know, not that all sort of this type of molecule have the similar couplings. It can be different. But I am just trying it to tel you that this geminal coupling

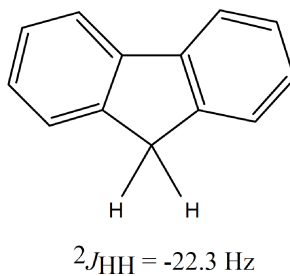


depends upon HCH bond angle and the hybridization of the carbon and type of substitution. For example, in this type of molecule two bond J coupling is 12.5 Hertz and also with a negative sign. And in this type of molecule it is 4 hertz; and for this, I already showed in the previous example geminal coupling is much smaller than cis coupling and then even that is smaller than the trans coupling.

So, this is what I said and it depends also on the substitution at the position for example, if I take CH<sub>4</sub> it is going to be -12.4 Hertz; instead if one proton you knock off and make it CH<sub>3</sub>Cl, the coupling become -10.8. knock off another proton make it CH<sub>2</sub>Cl<sub>2</sub> it becomes -7.5 Hz. Here it also depends upon the substituents not only HCH bond angle, but depends upon the hybridization; depends upon the substituents. All those things matters.



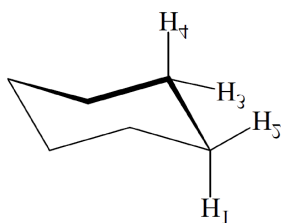
Extend further in a molecule like this 2 bond can be 6 Hertz; here it is 5.5 hertz and if there is a nitrogen here instead of C carbon 2 bond, the coupling can be very large. See 2 bond geminal coupling is ethylenic molecule I showed you about 2 to 3 hertz, but you see when instead of C is double bond C you have N double bond C then it is going to be even larger 16 hertz. So, all those things you cannot remember and mug up everything because it is available in the books, but you should know the coupling matters a lot. It depends upon the varieties of factors, such as, substitution and varieties of parameters like HCH bond angle etcetera. Take an example of a CH<sub>2</sub>=CHX. Very easily you can write a structure like this H and X. Now, depending upon the substitution of the X, 2 bond coupling can be different. If X is a lithium 7.1 Hertz, if X is a proton geminal coupling is 2.5 something else. Let us say chlorine OCH<sub>3</sub>, fluorine, couplings are different; that depends upon the substituents.



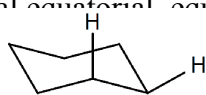
In a molecule like this geminal coupling can be -22 hertz. Remember this coupling is 22 hertz, it is geminal coupling, but in other example I showed you it is 2.5 Hertz. in some

examples I showed you it is about 6 hertz. So, it depends on the type of molecules. There is no general hard and fast rule, but it depends on the molecule. But by and large the guideline is such that trans coupling is larger than the cis coupling; this is larger than the geminal coupling in ethylene type of molecules. But you have to carefully see about the substituents while arriving at this type of information.

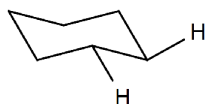
If you go to alkanes like this, it depends upon what is the bond angle it makes; what is the dihedral angle. See for example, in this case you are going to get  $\phi$  equal to 60; in this case  $\phi$  is equal to 180; in this case angle dihedral angle is 60. And in such a situation here 3 bond coupling is 2 hertz; here 3 bond coupling is 10 to 16 hertz. It depends upon how this in the C triple bond C, n alkenes, what is the dihedral angle between these protons, in these groups. So, on an average if you take 3 bond HH coupling is of the order of 7 hertz, because we have Gauche and trans coupling has to be taken; and then take the average of that, It is 7 hertz it is an average conformation. If you get a 7 hertz coupling between these things when you measure, then if the 3 bond coupling is 7 hertz means it is the average confirmation.



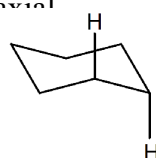
Cyclohexane especially if you consider the chair conformation remember when we analyze the spectrum of some of the cyclohexanes, sugars etcetera I will discuss, it depends upon what is the conformation, whether chair or boat. If you consider a chair conformation, the axial axial coupling is always larger than axial equatorial coupling, and these are always larger than equatorial equatorial coupling. Remember axial axial coupling is larger than axial equatorial, which is larger than equatorial equatorial coupling. For example, in a molecule like this 12 coupling is larger, about 14 Hertz, then 13 then 14 coupling is larger, see this 2 3 coupling. This is just a general guideline. Of course, in this type of cyclohexane when you have a chair conformation, by and large this order is maintained; by and large axial axial coupling between 2 protons which are axial to each other coupling is larger than axial and equatorial, which is larger than equatorial and equatorial protons. Go to cycloalkane derivative, the couplings can be like this; the axial equatorial, equatorial equatorial and axial axial



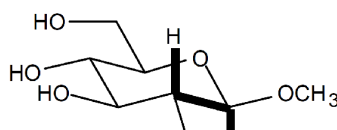
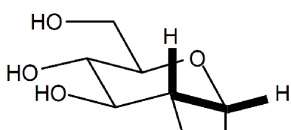
$${}^3J_{ae} = 2-4.5 \text{ Hz}$$



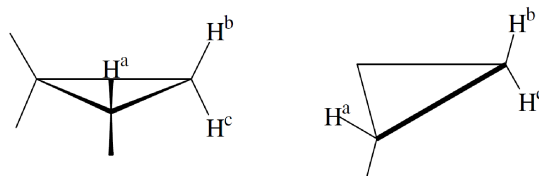
$${}^3J_{ee} = 2-4.5 \text{ Hz}$$



$${}^3J_{aa} = 8-11 \text{ Hz}$$

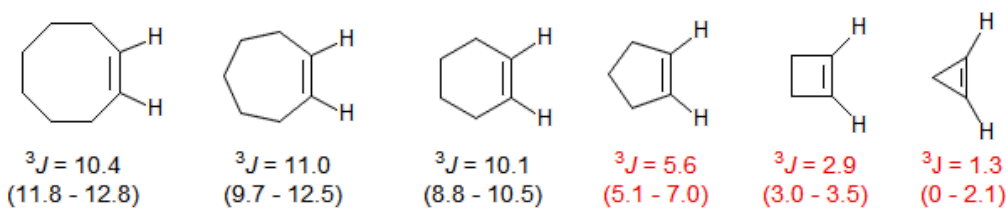


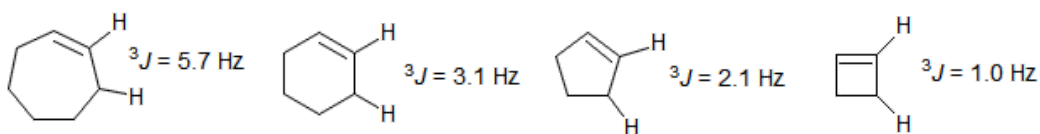
Again remember axial axial is larger than axial equatorial, and then it comes to this. But in this case both are going to be similar. But of course, as I told you these are all the guidelines. In this case  $^3J_{HH}$  is 4 Hz, and here  $^3J_{HH}$  is 9 hertz. Usually 3 bond coupling is quite small. We say 1 bond coupling is larger than 2 bond, than 3 bond. But the coupling strength also depends upon whether the molecule is linear or has the zigzag pattern, all those things matters.



If you go to cyclopropane if you consider this proton depending upon whether the conformation is trans, what is the angle, trans or cis, then in this case cis coupling is larger than trans. But remember in the case of ethylene group I told you C double bond C with substitution trans is larger than the cis, but in the case of cyclopropane cis is larger than the trans. These are all some of the things which you should know.

The magnitude of the coupling in substituted aromatics. Consider a molecule like this, in an aromatic like this. As I told you already ortho coupling is quite large then meta coupling then comes para coupling. For meta coupling in fact 1.5 is highest you get, generally less than 1.5 hertz or something. This is 1 to 1.5 hertz for meta coupling. But depends upon the substitution, where you are substituting whether you are substituting in the ortho position, meta position, para position. Whether symmetrically substituted, disubstituted or monosubstituted. See whether it is symmetrically disubstituted or asymmetrically disubstituted, everything matters. But always remember ortho coupling is generally larger in phenyl groups,] than meta coupling, than para coupling. That order is more or less maintained. And also depends upon the bond strain. You know as the angle keeps on decreasing, look at this is a 7 membered ring then 6 membered ring and 5 membered and 4 membered and 3 membered ring.





Here the coupling is quite large., it is of the order of 5.7 hertz, here it is 3.1, 3.1 and 1.2. You see as you decrease the bond angle, the HCH bond angle, the coupling strength comes down. Coupling constant decreases with the bond order. Look at this one this is 11.6 in this case 7.6 in this case 8.6. And heterocycles if you consider generally they will have a smaller coupling constant compared to hydrocarbon. Heterocycles have a smaller coupling look at this one; this is heterocycle, here ortho coupling is 6.9 Hz, in this case ortho coupling is 4 to 6 hertz. Otherwise in benzene I said it is about 7 to 8 hertz, sometimes 8.5 or 9 Hertz like that. Look at this, it is 1.9 Hz. If you consider furan this coupling is smaller, where this is even smaller though it is ortho coupling. So, like this coupling depends upon varieties of information.

I will give you something about what is called a Karplus curve. We can use a 3 bond coupling to get some information about the dihedral angle. This is a famous equation, why it happens? because the magnitude of the J coupling depends upon the bond angle, overlap of the orbitals. So, that that means J value depends upon the dihedral angle there is a conclusion.

So, J<sub>HH</sub> is maximum when 2 CH bonds in a molecule like this H is C H if you consider unit when 2 C H bonds are parallel. Parallel means it is 0 degree or 180 degree dihedral angle, then J coupling is maximum. J coupling is minimum in this type of molecules if the H CC H if this bond angle dihedral angle is 90 degree. That is important you remember. So, for example, if it is eclipsed if it is 90 degree if it is trans or anti you can find out. If it is eclipsed 0 degree, coupling is this much. If it is 90 degree orientation  $^3J$  coupling is 2 Hertz, and if it is anti 180 degree it is 13 Hertz. So, I said  $^3J$  coupling is very important that throws light on the conformation of this molecules, very important. And how do we get this dihedral angle this is given by a famous equation called Karplus equation. Remember it is,  $a + b \cos^2 \phi + c \cos \phi$ , It is a famous Karplus equation. It is a quadratic equation in  $\cos \phi$  It can have infinite solutions for different  $\phi$  value. If  $\phi$  value is fixed it has 4 solutions because quadratic equation has 2 solutions and  $\cos \phi$  and  $\cos \text{minus } \phi$  are same. So, it will have 4 solution. So, that is one thing is if  $\phi$  value can vary you can have infinite solution. This is a famous Karplus equation and A, B and C are the constants, which are arrived at empirically to fit the curve. The

curve is also different, which I did not show that it is going to be enormous discussion, but basically you get the idea 3 bond cis coupling or this trans coupling, whatever we get 3 bond coupling  $^3J_{HH}$  we can use to get the dihedral angle. And this is the idea. In the olefinic systems trans coupling is always larger than cis, in the 1 2 disubstituted ethanes, which we saw  $J_{Gauche}$  is less than trans. And using Karplus equation we can obtain the dihedral angle and we can estimate it by measured  $^3J_{HH}$ . If you take saturated hydrocarbon if the J coupling is less than 2 Hertz, I showed you here J coupling is less than 2 hertz here approximately, that means dihedral angle is 90 degree, that is the idea.

So, here also you can get the information, if J coupling is of the order of 2 hertz then probably there the dihedral angle is 90 degree between them. And in acyclic system if you consider  $^3J$  coupling is usually associated anti relationship, small J coupling correspond to Gauche relationship. And vicinal coupling is of order 7 hertz is nothing but time averaged, average conformation, that is the guideline for you to understand. So, simply understand axial axial coupling is 180 degree for 11.8 hertz; axial equatorial is 3.9; equatorial equatorial 60 degree.

So, in the chain conformation of cyclohexane the coupling between two axial protons is always larger than equatorial. I have been telling you please remember if you have a chain conformation in a cyclohexane, axial axial coupling is larger than axial equatorial and then that is larger than equatorial equatorial. So, equatorial equatorial coupling is smaller always compared to axial axial coupling. And this is the idea you can use to analyze one or two sugars, the spectrum of the D glucose we will understand. Go to sugars  $^3J_{HH}$  coupling is used to distinguish between alpha D glucose and beta D glucose. Take D glucose we have alpha glucose and beta glucose structures are like this. For example, in the alpha glucose axial equatorial coupling is 3 hertz, but in the beta glucose the structure is different, as a consequence axial axial orientation is there in beta has axial axial orientation, between these two protons coupling is larger. In this case it is axial equatorial orientation coupling is smaller.

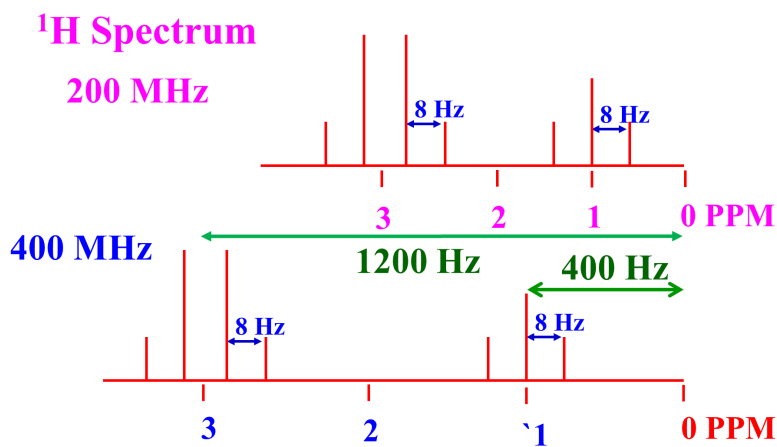


So, if you have a sugar molecule measure this coupling there you know whether the coupling is smaller or larger based on that you can say whether it is alpha glucose or beta glucose, very easily you can get it. So, cis trans isomers in the olefins  $^3J_{HH}$ ; trans is always

larger here than cis. This is the basically an idea you should know to get the conformation.

Long range couplings. You know generally after 3 bonds coupling will drastically come down, after 4 bonds most of the time it is 0 you will not see. But there are classic example like this. This 4 bond coupling can be of the order of 9 hertz; 5 bond coupling can be of the order of 3 hertz and depending upon whether it is a linear chain like this or a zigzag fashion like this, this type of molecules can have 5 bond coupling 4 bond coupling etcetera. And in the classic example 5 bond coupling is of the order of 3 hertz and I will go to a bigger molecule, we can get 5 bond coupling of even 5 hertz. And in such type of molecules linear chain you can get 6 bond coupling, 5 bond coupling. Very regularly you can see 3 to 6 hertz this is rare. I tell you it is not easy because after 2 or 3 bonds drastically the coupling strength comes down, but these are all classic examples where you can get the coupling even up to 5 bonds 6 bonds. Also in an example like this if you look at the coupling between this proton and this proton separated by 9 bonds you can see of the order of 0.4 hertz. So, in principle we say as the number of consecutive bonds increases the strength of interaction comes down, it is true. But there are examples in a linear molecule like this and a molecule which have zigzag pattern significant coupling strengths, very large coupling strengths of 4 bond, 5 bond, 6 bond, sometimes 9 bond have been observed. This is what I wanted to tell you.

And last I want to tell you remember when we were discussing the chemical shift I said chemical shift is dependent linearly on the magnetic field. As the magnetic field increases the chemical shift dispersion changes I showed several examples; 200 megahertz; 400 megahertz; 600 megahertz in the ppm scale it remains same. But in the frequency scale I showed you how the spreading becomes better and better, the same thing.



Now,

what will happen to the

j coupling when we change the magnetic field? We will understand this one. Let us take an example of a proton spectrum at 200 megahertz, I have a triplet and a quartet and at 0 ppm is the chemical shift of tetra methylsilane, somewhere here. This is the chemical shift of 1 ppm for proton 3; this is CH<sub>3</sub>. This is CH<sub>2</sub>. The CH<sub>2</sub> is a quartet because of CH<sub>3</sub>. CH<sub>3</sub> is a triplet because of CH<sub>2</sub> and this is at 1 ppm this is at 3 ppm. And what do you get this is a in frequency? this 200 Hertz and 600 hertz we know. This adjacent line separation gives you coupling constant, fine. Now, I am going to double the magnetic field, I go to higher frequency spectrometer; 400 megahertz. The 1 ppm remains same, 1 ppm 400 hertz and 3 ppm remains same in ppm scale, but in frequency it is 1200 hertz. There is lot of dispersion I told you. The chemical shift changes linearly with the magnetic field. you have dispersion. What about this? The j coupling, the adjacent line separation if you measure j coupling, it is 8 hertz 8 hertz; here also 8 hertz. What does it mean? it means the J coupling whether you go from 200 to 400 megahertz or go to 800 megahertz does not matter, j coupling is always invariant with the magnetic field. The J coupling does not change with the magnetic field. It remains same, only chemical shifts varies linearly with the magnetic field, ok.

So, with this more or less I have covered a lot about the scalar coupling. Lot of information I gave you today. In fact, we discussed a lot about varieties of multiplicity patterns and took number of examples, realistic examples; and looking at the complex multiplicity pattern how do you put a nomenclature for each of these multiplicity, what is the doublet, triplet, doublet of triplet of triplet, all possible examples we took. And afterwards I showed the strength of the j coupling; one bond coupling in the hydrogen molecule is large 276 hertz; as you go to other different type of molecule like ethylene molecules I showed trans coupling can go from 12 to 14 or 18 hertz, whereas cis can go upto 6 to 10 hertz; geminal is very small to 1 to 2 hertz or 3 hertz depending upon the substitution and depending upon what is the type of bond, whether it is C-C bond or C-N bond. Again I took the example of phenyl group I showed you ortho coupling is about 7 to 9 hertz meta is 1 to 2 3 hertz whereas para coupling is less than 1 to 1.5 hertz. But all these are chemically equivalent, but still we got a single line, but there is a way we can get the j coupling. That information how we get it is different, we will work it out. So, number of such example I took and I said 3 bond coupling can be utilized  $^3J_{HH}$  and fit it in the Karplus equation, the quadratic equation of cosine of phi; you can get the diagonal angle. The bond coupling can be used to obtain the conformation and obtain the diagonal angle in many such molecules like, cyclohexanes the chair conformation of cyclohexanes. We can use the 3 bond coupling to distinguish between the alpha glucose and beta glucose. That is what I said. And further finally, I also showed you j coupling if you measure in a given molecule at any particular frequency, double the frequency go to any other spectrometer frequency it remains same. So, J coupling does not depend upon

the magnetic field. It is invariant with the magnetic field; it is a very important parameter. If you remember chemical shift changes linearly with the magnetic field whereas the J coupling is invariant with the magnetic field, it remains same. This is what I wanted to tell you. With this I have covered extensive scalar couplings. In the next class we will start interpreting the NMR spectrum, how do you analyze the spectrum right from spin system nomenclature, Pople nomenclature and then realistic example of the analysis we will start. So, I am going to stop here. Thank you very much.