One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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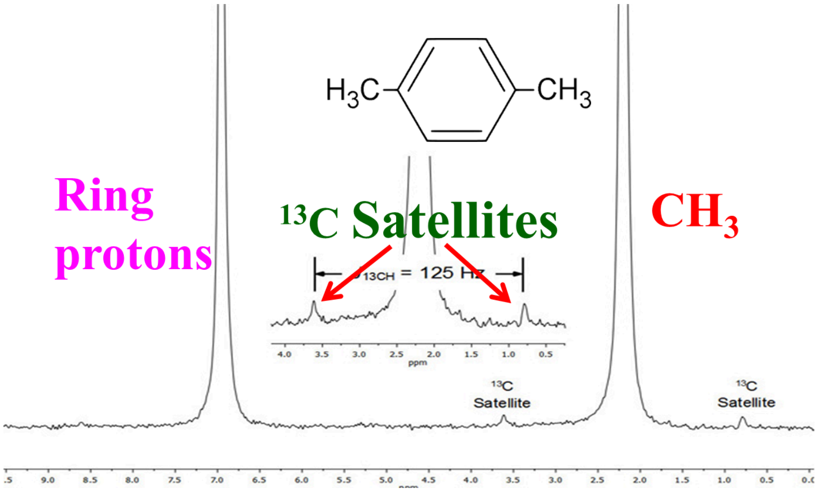
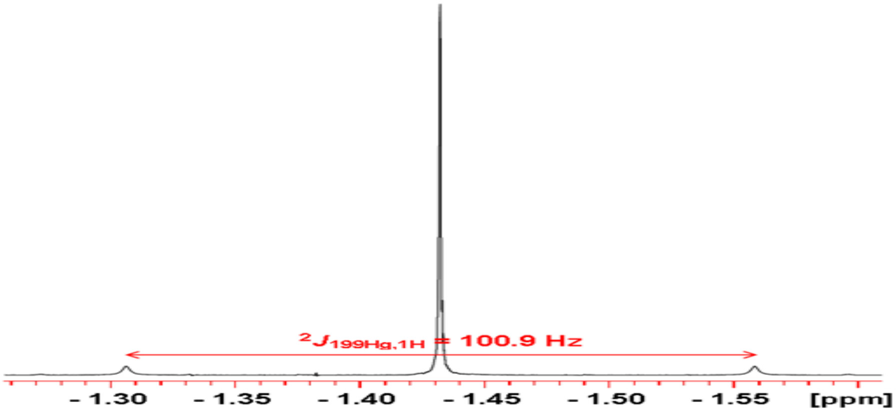
Lecture 23: Coupling of 1H with other nuclei-II

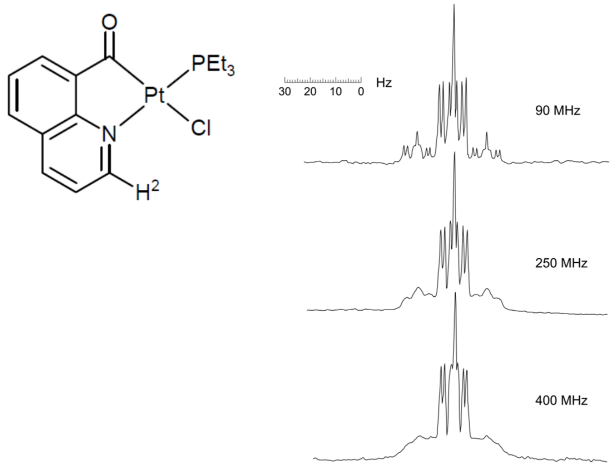
In the last class, we started embarking on the analysis of the proton spectra consisting of hetero nuclear spins, both abundant spins and dilute spins. Especially, when we have abundant spin like phosphorus and fluorine, spectrum becomes bit complex because splitting is directly reflected on the spectrum, multiplicity pattern would be there and you have to analyze this to extract the coupling information. And I took several examples and showed how we can get hetero nuclear couplings when a single hetero nucleus is present or two extra nuclei are present, or more than that. And also, what will happen is sometimes the hetero nuclear need not be 100 percent abundant, there could be dilute spins, less abundant spins. For example, carbon 13, nitrogen 15, silicon, etcetera. Their abundance is very small and interestingly such type of isotropomers are NMR active, they can give rest coupling with the abundant spin to which it is coupled to. And I took the example of tetramethyl silane where coupling of silicon with proton we saw and I showed how we can measure that. At the same time, it has also got carbon. Carbon 13 and silicon both will couple to proton and give rise to satellite peaks on either side. Similarly, $CHCl_3$, there is only one carbon, but single proton comes because of 99 percent of the molecule containing carbon-12, which does not split, it gives a single peak, strong, huge, intense peak. Then carbon-13 is 1 percent of the molecule which couples with proton, splits into a doublet because of the 1 percent abundance, the intensity is 1 percent. Further due to splitting, it becomes 0.5 percent; and they are called satellites. So, in one molecule, there can be satellite corresponding to one lesser abundant spin. You can also get peaks corresponding to two or three less abundant spins for which I took the example of tetra methyl silane. We also took the example of SIHCl3 where the proton spectrum Si coupling of nearly 340 or 350 hertz we could easily see; and they are very weak in intensity. Intensity of the satellites depend upon the abundance of the dilute spin. It can be for example, carbon-13 1 percent, nitrogen 0.37 percent, silicon may be 4 percent, selenium may be 4 or 7 percent, like that, it can vary. So, with this, we will now go further and take few more examples and I would like to finish the analysis of the proton spectrum today, so that we can go to heteronuclear tomorrow at least. Another example of this thing, this we discussed, selenium satellites. I want to show this proton spectrum of paraxylene. It is a very simple molecule and all four protons of aromatic protons are equivalent, and two CH3 groups are equivalent. CH3 group is going to give a strong peak, but on either side of it, you see two small peaks, they are satellites. Of course, here also you can see, if you carefully see, there are peaks which is not shown, but here they are very clearly visible.You can see that and measure the separation, you can get SiH coupling.



This is from the ring proton, this is from CH3 proton and carbon 13 satellites are there. So, carbon 13 satellites we saw, silicon satellites we saw, selenium satellites we saw.

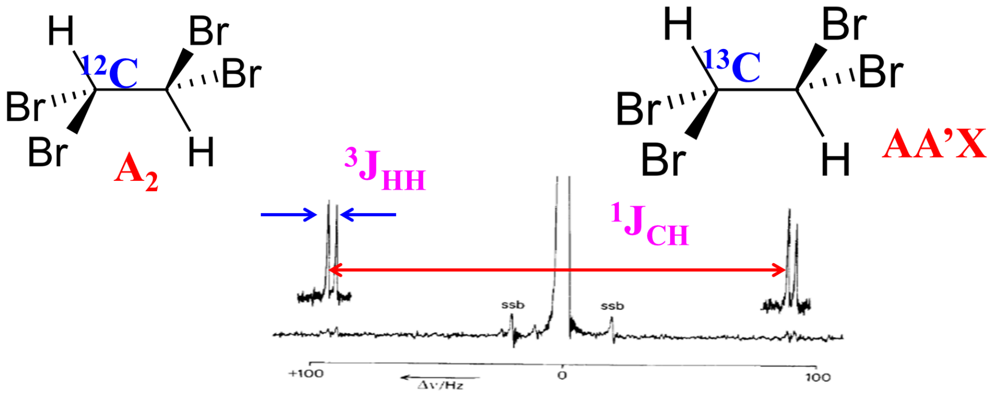


Look at the mercury. Mercury is another thing, very low abundant and if I look at the mercury spectrum of dimethyl mercury, mercury 199, if we will look, mercury 201 is there, but mercury199 is the one which is usually practiced. And look at it, these mercury satellites, mercury coupling appear as satellites and it is a huge coupling of the order of 100 Hz. See, in the heteronuclear couplings, can be very large values. Homonuclear coupling we saw, of the order of proton-proton coupling, maximum was 284 for proton, two hydrogens, hydrogen atom and two protons are one bond separated. Whereas, in the heteronuclear, the coupling can be enormous, sometimes can be of the order of several thousand hertz. Simple example I am showing you here, in the case of mercury is also 100 hertz. These are mercury 199 satellites.

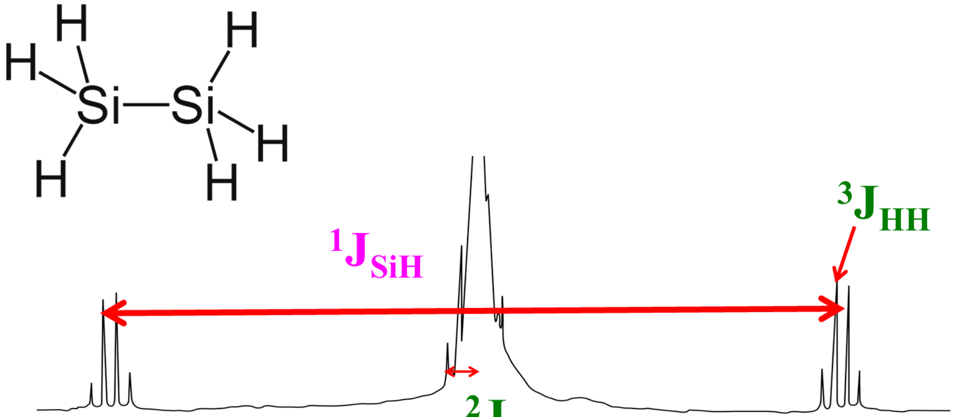


This platinum coupling, you look at the ^{1}H NMR spectrum of platinum, a small complex. We are looking at the proton, but especially I am concentrating on this proton H2 of the ring. Of course, we are not worried about it. Since, we are worried about only the satellite in this part, I am not looking at the other part of the spectrum correspond to other protons. We will worry only about this, and see how we can get the coupling.

This proton, of course, in the phenyl group I told you, it can experience coupling with ortho-proton with this one, which is quite large and then with this one, but when there is a hetero atom, I told you ortho coupling will be very small, $^{3}J_{HH}$ coupling about 6 hertz, $^{4}J_{HH}$ coupling is there about 2 Hz and this can also couple to phosphorus here. This is separated by 1, 2, 3, 4 bonds. It can couple to phosphorus that is very large, 4 bond phosphorus coupling; and it can also couple to platinum 1, 2, 3 bonds away and that is quite large. So, this one proton can simultaneously experience coupling with abundant spin and also dilute spin. Abundant spin is phosphorus and the dilute spin is platinum, and in addition to that, it has coupling with other two protons. So, it is a very complex pattern and interestingly, this proton spectrum has been recorded at three different resonating frequencies. You can see at 90 MHz, at low frequency, you can see these are the peaks which are coming here. What are these peaks? As you go ahead, you see at higher frequency, these peaks are getting broadened out. You are not seeing. And these things, one proton, you know, can experience coupling with 2, 3 and 4. It will be very complex; 2^{4}, it should be 16 lines could be present here. The multiplicity pattern is because all the couplings that are different, doublet of doublet of doublet doublets, it should be dddd will be there, 4 d's. So, it should be 16 peaks, and are there. And if you carefully see identical pattern is there in either side, that is because 8 peaks are here, the remaining should be with the platinum, they come as a satellite and that is seen here, platinum proton coupling for this one. And other couplings are seen here, they are abundant, platinum coupling is appearing as a satellites here. Identical pattern you see, exactly like the pattern of the main peak, that is what you see. And on increasing the resonating frequency, interesting thing happens, this will reduce. This is to do with what is called chemical shift anisotropy, relaxation due to chemical shift anisotropy, this becomes more and more at higher and higher frequency. So, we will worry about it when we come to relaxation part, when I discuss relaxation. But right now you remember, we have coupling of this proton to all the 3 abundant spin plus 1 less abundant spin which come as satellites. This is called platinum satellites, platinum coupling.

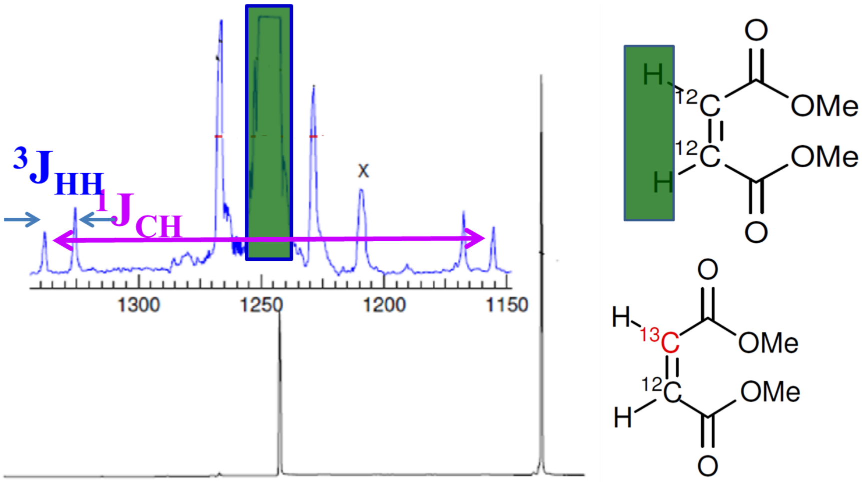


So far, we understood one thing. From the satellite analysis, we got the less abundant and high abundant spins coupling, like proton carbon-proton; nitrogen-proton, and selenium-proton couplings. Can we get the proton-proton coupling from the satellite spectrum? Is it possible to get it? why not, we will see that example. Take the example of 1,1,2,2- tetrabromoethane, it is a simple molecule. These 2 protons, if you carefully see, they are chemically equivalent. How many peaks it will give? it will give only a single peak. When there is a single peak, how do you get the HH coupling? You cannot get. At least there must be a doublet to measure the separation and to get the J coupling. So, in chemically equivalent spins, couplings are not reflected, even the in spectrum splitting pattern is not seen and coupling, though present, are not reflected in the spectrum. Not that coupling is absent, though it gives a single peak, there exists a coupling, trans coupling between these 2 protons. But unfortunately, that coupling is not reflected in the spectrum. As a consequence we get a single peak. But I tell you, there exists a coupling, how do you measure it. This is what we do. We break the symmetry of the molecule. Remember, when I was explaining to you about Pople nomenclature, these 2 are chemically equivalent, we call it as A2 spin system. But this A2 spin system, what I will do is break its symmetry. This is A2 when I look for only carbon 12 attached protons. But I am going to a situation like this, in the

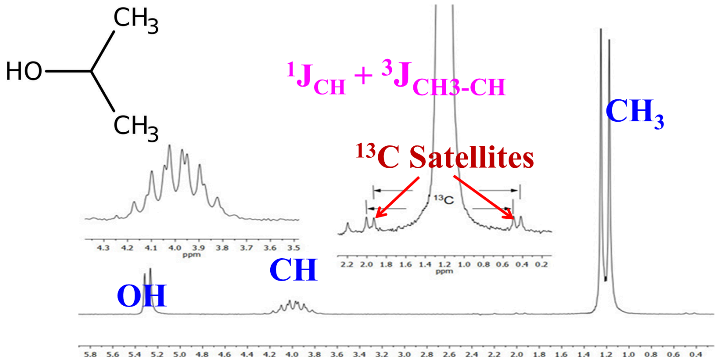


sense, instead of carbon 12, I look for carbon 13, 1% of the molecule. Then what will happen, if I say, instead of carbon 12, here is a carbon 13 here, carbon 13, this is a 1 bond coupling, this is a 2 bond coupling, they are different. That means, symmetry is broken. You have broken the symmetry of the molecule. That means, the A2 spin system, which is a nomenclature for this molecule, Pople nomenclature, now we call it as AA'X. What do you mean by AA'X? I told you, when I explained in Pople nomenclature, these 2 are chemically equivalent, but there exists a coupling between them, which is not reflected. Now, you can see the coupling. In the A2, you will not see the coupling, even though it is present. But in AA', you can even extract the coupling information. And for that, you broke the symmetry by bringing in carbon 13 in its natural abundance. Of course, you can label it if you want, but we took only natural abundance. In which case what happens? since it is AA'X, I am going to enhance the intensity here, I see the satellites here. So, this satellite will give one bond coupling, it is the 1 bond coupling $^1J_{CH}$. But remember, this satellite is not a singlet here, each of them is a doublet. Why the doublet is coming? If I consider this proton, this is a 1 bond coupling, plus because symmetry is broken, is also coupled to this, that is getting reflected in satellite spectrum. So, this doublet separation correspond to JHH, this correspond to 1JCH. So, you can get the homonuclear coupling, which is not possible to get from the proton spectrum because of chemical equivalence. You can get from the satellite analysis, because you are breaking the symmetry of the molecule by bringing in less abundance spin. You are not doing anything for the molecule, just you look at the molecule with isotope carbon 13 present, that is all. Then you are breaking the symmetry and coupling of proton, proton is seen here. This is what it is.

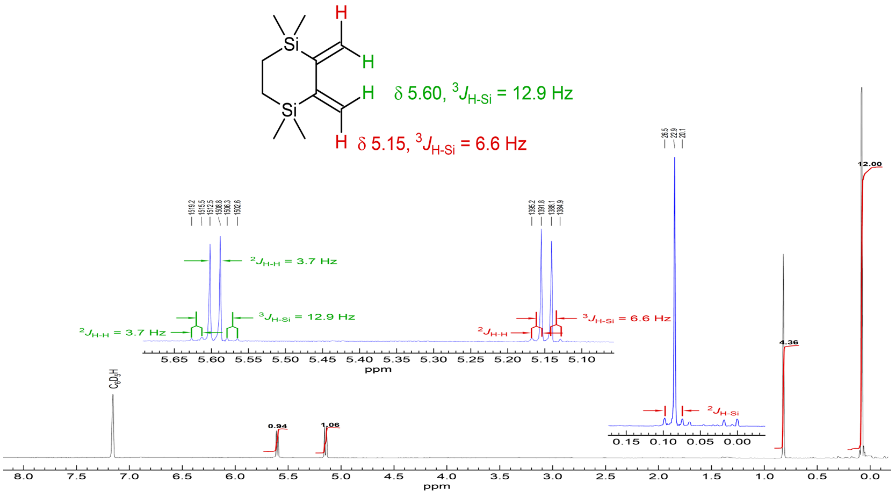
Same thing you can do here. This is Si2H6 molecule. Now, we have silicon which is 4.7% abundance, plus we also have 1 bond and 2 bond couplings. This silicon has 1 bond coupling here and also has 2 bond coupling here. There are 2 types of couplings you can think of. If you take the proton NMR of it, this correspond to one of the isotopes. Silicon has several isotopes, but we are considering only Si29, which is coupled. All other things other than 29Si will be here, which gives a single peak. When the Si29 is present, symmetry is broken, then you will get coupling of this with this, coupling of this with this. That is also possible. So, now we are going to get the coupling like this. This is 1 bond SiH coupling. 1 bond SiH coupling, but at the same time, you are going to get here 3 bond HH coupling. Each of this proton, because symmetry is broken, will become a quartet. You see, this is a $^{3}J_{HH}$ coupling you are going to see. This is 1 bond the SiH coupling. But carefully if you see, this can also have a 2 bond SiH coupling, which is not seen here because they are hidden within the strong peak. Under the strong peak, they are hidden. As a consequence, you are not seeing it. So, you can see the satellite spectrum. From the satellite, you can also get the proton-proton couplings.



This is classic example of another molecule, where again these two are chemically equivalent. You get a single peak here. This corresponds to the situation where both the carbons are carbon-13. And of course, these are all some of the satellites and sidebands and you do not worry about it. What is happening is, I am considering a situation like this, where one of the carbon is instead of carbon-13, I consider it as carbon 13. Again, you have broken the symmetry. Since you have broken the symmetry, now you are getting a strong peak here. On either side of the strong peak, you have satellite peaks here due to 1 bond proton-carbon coupling. And each one of the satellites is a doublet because of proton-proton coupling. So, from the satellite analysis of this molecule also, you can get the HH coupling. These are all some of the examples, where you can get it like this. You can continue like this with large number of examples.

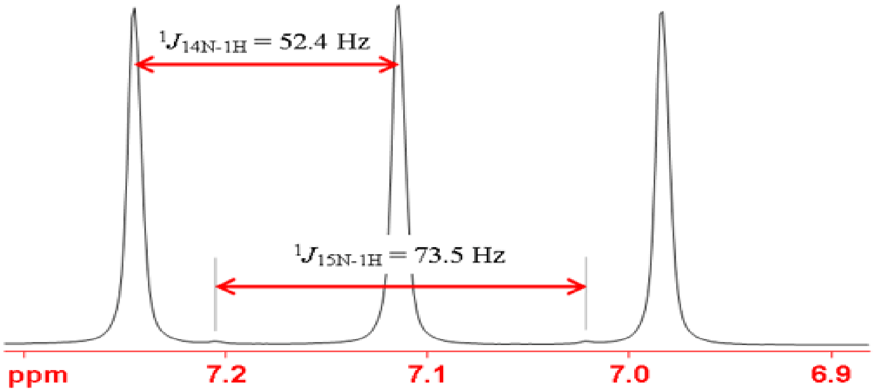


In this case, this is a spectrum of 2-protonol, where 2-CH3s are present here. They are all split because of CH proton here and it is a doublet. If you expand it and see, each of them is going to be doublet. It is a satellite pattern. Each line of the satellite is a doublet and this separation from this to this gives you CH coupling, whereas this separation gives you HH coupling. So, like that you can get lot of these things. And of course, there is no point in going further. You can have large number of such examples.

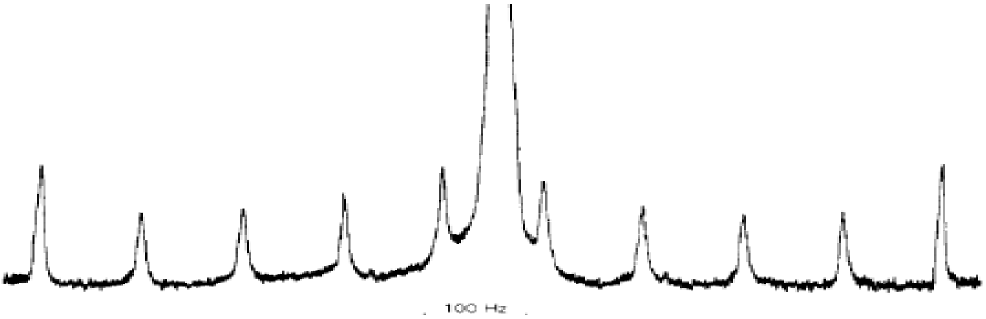


But I want to show you one example like this, where a molecule like this, if the symmetry is not broken, both are identical, these protons are identical. Whereas, when I take the NMR spectrum of it, you see this one proton, one proton, etc, easily. But I have expanded two peaks here. These two peaks correspond to these protons. Okay, One is this proton, other is this proton, because there is a symmetry. If you carefully see, each of them is a doublet. Why each of them is a doublet? There is HH coupling, geminal coupling is there. At the same time, each of these protons can experience coupling with the silicon. It can have silicon, this proton coupling, silicon to this proton coupling. Both are present, both are 3 bond couplings. This is what it is, one proton and one proton, both are here. This proton is coming here and this proton is coming here. You can find out from this. This proton is because of this and this proton is because of this. But on either side of this thing, you get satellite peaks because of selenium coupling and each of the satellites is a doublet which gives you HH coupling. Not only you can get here, you can also get from the satellites here.

So far, we discussed a lot about varieties of things. But remember, what did we discuss? We discussed coupling between proton, selenium, silicon, phosphorus, fluorine, etc. Most of them are or all of them I would say are spin half nuclei. Proton is spin half. Carbon is spin-off nuclei. Of course, I took the example of boron 10 and boron-11. Apart from that, most of them I took have interaction with spin half nuclei. But there can be coupling between spin half and spin-one nuclei or more than that. We will see now.



Take the example of proton spectrum of NH4Cl. NH4Cl, interestingly, nitrogen 14 is highly abundant; almost 99.6 and 0.37 is the abundance of nitrogen 15 and N14 is spin-one, N15 is spin-half. So, N14 when it is coupled to proton, it will give three lines of equal intensity, 1:1:1 because there are three possible spin states, plus 1, minus 1, 0 and plus 1, three possible spin states. So, it gives three line pattern. Whereas, nitrogen 15 is spin-half, it has only two possible spin states alpha and beta. As a consequence, it will give two lines, only doublet. But look at the intensity, this is 0.37 abundance of nitrogen 15. Further,it is split into two very, very weak intensity peaks, we will not see that. So, nitrogen 15 gives a weak doublet, which are satellites. Whereas proton coupled to N14, an abundant spin, which gives three lines of equal intensity. Whereas, you can get this example, look for CDCl3. When I come to carbon NMR, I will show you. Carbon coupled to deuterium, deuterium is spin-one, carbon is spin-half, we get three lines of equal intensity there also. So, when the spin-half nuclei is coupled to spin-one nuclei, each line is going to be split into three lines of equal intensity. Whereas, spin-half nuclei

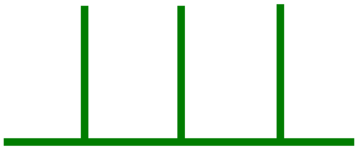


give a doublet like this. This is an example of nuclei spin greater than half.

This is a germanium 73, spin is 9/2, abundance is about 7.7 percent and I am looking at the proton NMR. How many peaks I expect for this? Of course, this is germanium 73; will give rise to coupling like this. The one which is high intense is corresponding to other isotopomer, which does not couple to proton. So, how many peaks it will give? Put it into this equation, you are going to get 10 peaks. What is the intensity? Almost 7.76, close to 8 percent compared to the strong peak. You count there will be 10 peaks 1, 2, 3, 4, 5, 6, 7, 8, 9, 10; and this intensity ratio is almost 7 or 8 percent with respect to the strong peak. This is a coupling of germanium with proton whose spin is 9/2.

H–H **Singlet in ^{1}H spectrum**

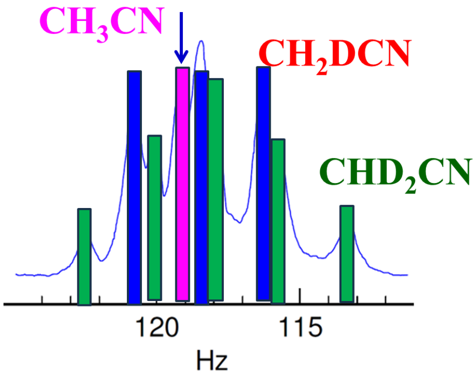
H–D



$$|{}^1J_{DH}| = 42.54\ \mathrm{Hz} \qquad {}^1J_{HH} / {}^1J_{DH} = \gamma_H / \gamma_D = 6.488$$

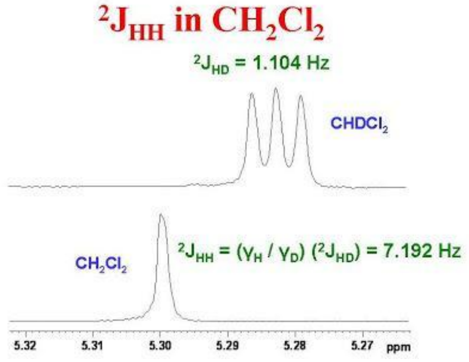
$$|{}^1J_{HH}| = 276\ \mathrm{Hz}$$

With this, I am going to introduce another term called coupling between magnetically equivalent protons. That is something interesting. What is that? Consider the proton-proton coupling in hydrogen molecule. How many peaks it will give? There is a symmetry, it will give only one peak. Take the proton NMR spectrum of hydrogen molecule, you will get only one peak. But remember, I told you JHH in hydrogen molecule is about 284 Hz. In one of the classes I said it is 284 Hz. Huge coupling is there, one bond coupling between two protons. How did we get this? How did I know there is a coupling between them? Because proton NMR gives a single peak. Then what is the way I can measure the coupling? How did I know that? There is a way. What you have to do is, in such cases, you do what is called isotopic substitution. In the sense, molecule should remain same. You cannot have another substitution. Then molecule will be entirely different. I want to retain the same molecule, character should be remaining same, but I must extract the coupling. Easiest thing is simply remove one of the protons by deuterium with isotopic labeling. Now, what is happening? Symmetry is not there. You have broken the symmetry. Like we said, when carbon 13 is there in CHCl3, some of the molecules I showed you, when I took carbon 13, symmetry was broken, A2 became AA'X spin system. Like that, here symmetry is broken, then this deuterium can couple to proton. You should now be able to understand what is the pattern we are going to get for this molecule. If I look at deuterium, which couples to protons spin half, it will be a doublet. If I look for proton, it is coupled with deuterium which is spin 1. So, it will be three lines of equal intensity. I told you NH4, an example, nitrogen 14 spin is 1. It gives three lines of equal intensity. Similarly, deuterium is going to give three lines of equal intensity here, because of HD coupling. So, okay, I get a spectrum like this. Then what are you going to do here? If I measure the separation, what do you get? You measure this, you get JHD. Fine, I got JHD, but I still have not got JHH. My idea is to get JHH. JHH is the one which is not getting reflected in the spectrum. JHD if I get, what is the use? But remember, the fantastic, very good formula. If I know J coupling between proton and deuterium, I can get the coupling JHH by using the ratio of the gyromagnetic ratios. For example, proton-deuterium gyromagnetic ratio is 6.488, 6.5 times you take, approximately. So, if I know this ratio, and this is the equation which relates the coupling between HD and HH. If I know J between proton and deuterium, I can calculate this by taking the ratio of this. Remember, JHH or JDH is going to gamma H or gamma D. And this ratio is known, 6.488. And I know this one, then how do you get it? So, JHH is going to be 6.488 into JDH. 6.488 JDH, I can measure from the separation, which is 45.54 hertz. So, multiply this by 6.488, you got this, 276. This is what the HH coupling. In a hydrogen molecule, where there is a perfect symmetry, you will not get the HH coupling. But by isotopic substitution, you get JHD. When I know JHD, I know the ratio of the gammas between proton and deuterium, simply multiply JHD by the ratio of proton gamma over deuterium gamma, you get HH coupling. Very simple. This is how we can get the J coupling between magnetically equivalent spins. Take for example, benzene, all all 6 protons are equivalent. It gives a single peak. Then how did I say, there is ortho coupling of 8 Hz, meta coupling is of 1.5 Hz and para of 0.5 Hz. How did I say that? One way is you can do isotopic substitution. Otherwise, break the symmetry by looking at carbon 13, which you already did that earlier. So, when you break the symmetry, looking at carbon 13 present at one of the sites, then it is going to be AA'BB'CDX, some particular spin system. Then analyze that carbon 13 satellite spectrum, you get or carbon 13 spectrum directly, you get JH carbon and CH coupling and HH coupling, everything you will get. Of course, carbon if you analyze, you do not get HH coupling, but you analyze proton spectrum with satellites, you get HH couplings also. That is how we get couplings smomg the magnetically equivalent spins.



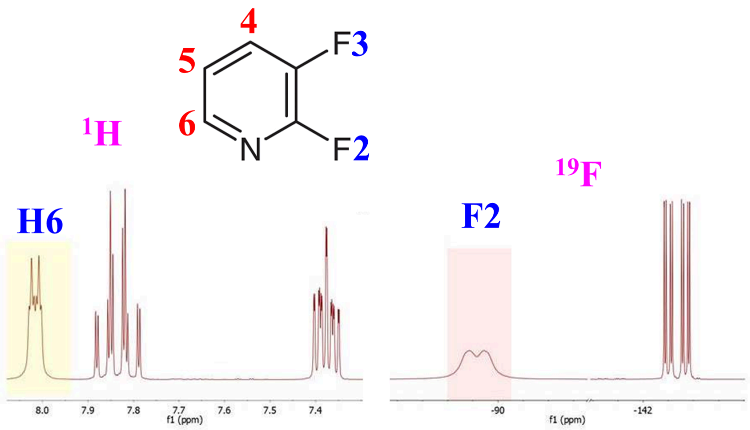
Take for example, CH3CN. how do I determine the J coupling? CH3CN is astonitrile, all the three protons are magnetically equivalent, you get a single peak like this. This corresponds to a single peak of CH3CN. But what do I do? Just now I told you, we can do isotopic substitution. I knock off one of the proton and put a deuterium. Then I look for CH2 proton because of deuterium, it is going to be three lines of equal intensity, deuterium is spin one. Now measure the separation, it gives you JHD. Use the JHD, use the ratio of the gammas, gamma of proton or gamma of deuterium 6.48, whatever I gave you, multiply by this, you get the HH coupling. Alternately, you can also do other one. Instead of one proton, you can replace two protons by deuterium, then it will become CHD2CN. Then you get a five line pattern because two deuteriums are there which are coupled, you are going to get five lines. Remember, when I explained CH2D2 molecule, I showed you, we get five lines of intensity 1, 2, 3, 2, 1, if you remember that for the two deuterium coupled to proton. Similarly, here we get five lines for the proton CHD2CN and you measure the separation of this exactly or this molecule, you will directly get the JHH. From JHD, you can calculate JHH. You may ask me a question, I replace all the protons by deuterium, then you cannot do it, because there is no proton. Then of course, you can do it by going to carbon 13, but you get carbon deuterium coupling, carbon proton coupling, but HH coupling you do not get. So, that means, you cannot have all the protons replaced by deuterium. You understand? So, we remove one of the protons by deuterium, replace by deuterium or two of them and get the multiplicity pattern, analyze it and you get the HD coupling and calculate HH coupling. So, in this case, for example, JHD 2.58 was the value after multiplying with JHH, we will get 16.8. So, acetonitrile though gives a single peak in NMR, in reality, coupling among any of the two protons in CH3 group is 16.8 hertz. There is a way we could measure the coupling.

Look at the CH2Cl2 molecule, how many peaks it gives? CH2 molecule, CHCl2 proton NMR gives a singlet. What I do is, I make it CHDCl2, replace one of the protons by deuterium. I am giving another example just to make you more comfortable. So, this is third example I am giving on how to get the coupling among the magnetically equivalent spins. Now, proton couples with deuterium and gives three lines of equal intensity. We got it, measure it. Use my formula JHH over JHD which is equal to gamma H over gamma D, whose value is 6.488, whatever it is I told you already, calculate it. you get the coupling.

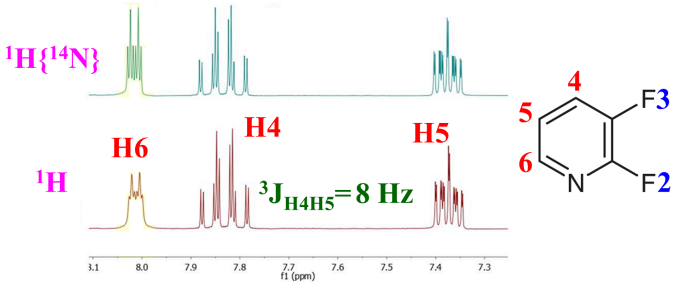


So, this is the real spectrum of CH2Cl2. 1H NMR spectrum of CHDCl2. This is CH2Cl2 spectrum which is singlet. This is by replacing one of the protons by deuterium. You got three lines of equal intensity, realistic spectrum and JHD was measured to be 1.104 here and then using this ratio, we calculate it JHH as 7.192. This is what it is. So, in the magnetically equivalent spins, we know how to calculate, how to determine the coupling even though the coupling is not reflected in the spectrum. All you have to do is isotopic substitution. Whereas in molecule like benzene and others, you have to break the symmetry by taking into account carbon 13, then you will get HH coupling. That is how we could get all the information and with this, I want to tell you one more small thing very quickly. Wherever there is an opportunity, if the spectrum is complex, we can remove the complexity by doing what is called decoupling.

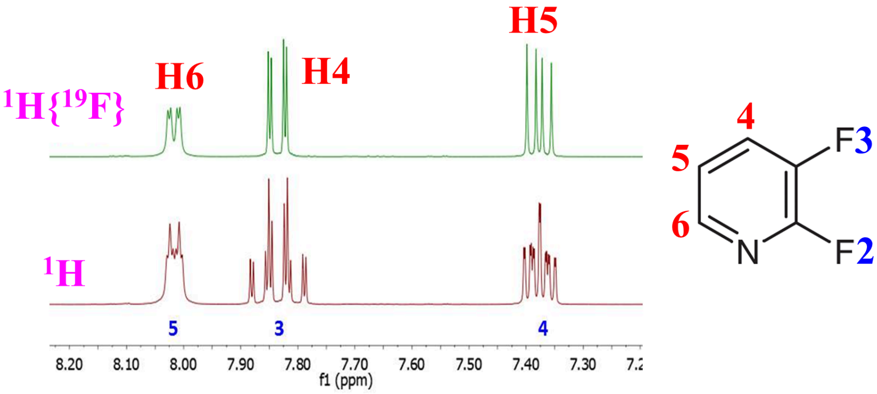
I will tell you more about decoupling later. Quickly I will show you one or two examples. In this molecule, look at this proton 6. Look at this fluorine.



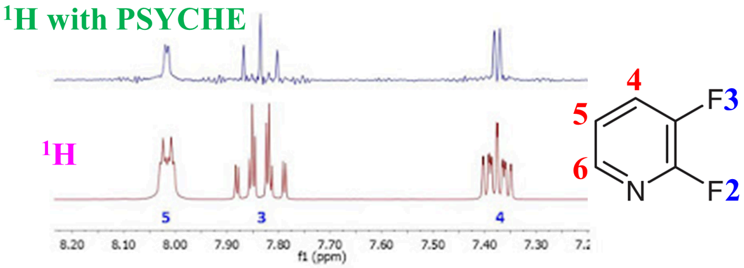
They are very broad here. Proton 6, look at it, very broad. Do not worry about the analysis part. What I am going to do is I will do nitrogen 14 decoupling. What do you mean by nitrogen 14 decoupling? I will break the coupling of nitrogen 14 with proton. How I do, I will tell you when I explain to you the decoupling. So, simply we have to saturate that nitrogen 14, so that this proton does not see nitrogen 14 in any of the three spin states, minus 1, 0 or plus 1. Then you see the broadening disappears and we have sharp peaks. Very easy.



Or you can do one thing. I want to get the spectrum of proton by decoupling fluorine. That is also possible. Then you have to break the proton fluorine coupling and get only HH couplings. There is no FH coupling. This is a real spectrum whereHH, FH coupling, both are present. But here FH coupling is removed. From this spectrum you get only HH couplings. Understand? If you analyze the spectrum, you have to get HH couplings and HF couplings both. But here you get only HH coupling.



Then you may ask me a question, can I remove HH coupling and get only FF coupling? That is also possible. There is a way of removing proton-proton coupling. It is not easy. When we have to discuss about the pure shift, I will have to tell you that. There are several experiments called pure shift experiment where broadband decoupling can remove all the protons coupled among themselves.



Here no protons are coupled. All we can remove by using a technique called psyche. Then HH are removed. What is that left here then? Only FH coupling. See when the spectrum is complex, there are ways of simplifying it. When it is too broad, we made it sharp by decoupling N14. When the spectrum is too complex, in the previous example like this, we made it simple by here, by removing fluorine coupling. And here even simpler by removing proton-proton coupling, we get FH coupling. Like that we can get complete information about all the couplings, This is the example where it is too complex for a molecule with phosphorus. This is a CH3 group with a CH2 group.

See it is very complex. This is coupled to phosphorus and CH3 group is a doublet because a long range coupling. Whereas, I do decoupling, this disappeared. This is also fairly simplified. So, what I am trying to say is there are number of ways you can analyze the proton NMR spectrum. In summary, we took lot of examples where homonuclear coupling, heteronuclear coupling of abundant spins, heteronuclear coupling of many abundant spins present in the molecule, heteronuclear coupling of less abundant spins, less abundant many spins present in the molecule. And when it is too complex, how we can simplify it by breaking the coupling between proton to other abundant spins or even you can do coupling by breaking the coupling with less abundant spin like carbon 13. Lot of things are there. When the spectrum is too broad at times because of the nitrogen 14 or oxygen, we can do even that decoupling also. Nitrogen 14 decoupling to sharpen the peaks. So, all these things we can adapt and I gave a number of examples to see how we can analyze the spectrum and get the information, make the assignment of chemical shifts and extract the coupling information which helps in getting the structure of the molecule, conformation of the molecule. We have extensively discussed about proton for a long time. In the next class, I will go for carbon 13 and lot of things we have to discuss about carbon 13 and also about other heteronuclei. Then subsequently, we move to 2D NMR where too many things we discuss also. So, I will stop here and we will continue with the carbon 13 NMR in the next class. Thank you very much.