One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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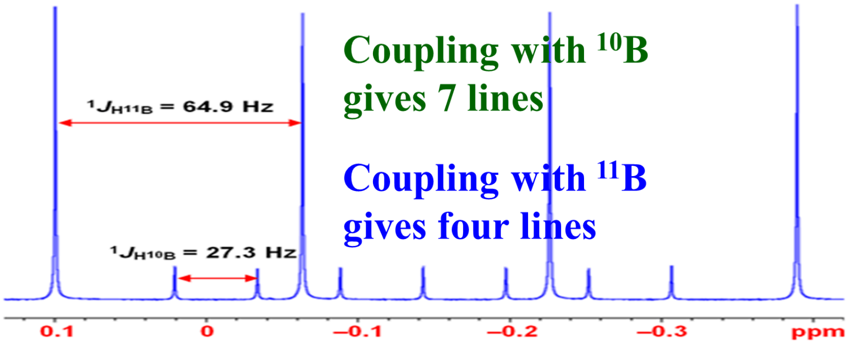
Lecture: 22 Coupling of 1H with other nuclei-I

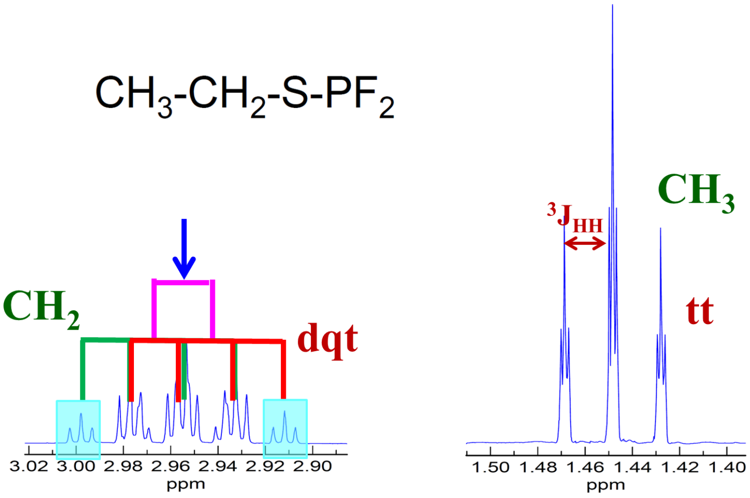
Welcome all of you, we will continue with our discussion on the analysis of the proton NMR spectrum. In the last class, I discussed about the multiplicity pattern for the protons of the phenyl group which is present in the molecule. And I told you depending upon the substitution, whether it is a mono substitution or symmetrical/asymmetrical disubstituted ortho meta or para benzene, and for each of the protons, we arrived at the multiplicity patterns, depending upon where the substituent is there. For example, I am looking for one proton and it has a substitution which is asymmetrical disubstituted in meta position; for that, then I can look at it and say what are the couplings it experiences whether it is ortho, meta or para; whether it is experience one ortho coupling or two ortho couplings or one meta coupling or two meta couplings. Then I can arrive at the multiplicity pattern. If both the ortho couplings and meta coupling which is experienced by the proton are identical, then we may get a multiplicity pattern like triplet. And another proton which can interact with this can give rise to what is called triplet of doublets. If all the couplings are different, there is no way they are overlapping. Then each proton can experience coupling with the remaining three protons, I am talking about disubstituted benzene groups, in which case you are going to get 8 line pattern; doublet of doublet of doublet.

So, we arrived at that and I took one or two examples in the molecule to show how to analyze the multiplicity pattern. And also depending upon the substituent present in the molecule in the benzene group at which position of a proton you are looking at whether it is ortho position, meta or para position and type of substitution which is there. There is a table of values which can be which says what is the contribution of this substituent for that chemical shift position of a particular proton. For example, I take a proton A that could be ortho substitution to the nitrogen, meta to be meta or para can also be nitro group or some other group. Pick up the value for that from the table, take the base value as 7.28 as the benzene to the addition of that it is always it could be positive contribution or negative contribution does not matter. Whatever the sign is there in the table you take it simply do co addition of all of them and get the value that is a predicted value of the chemical shift for protons of the phenyl group. And I showed you with two or three examples; by and large the predicted values agrees with the experimental values, agrees to a reasonable extent. As I said the nothing can beat the experiment the prediction is prediction, experiment is experiment. So, experimental values are the real values, but you can say it is very close to predicted values. Use that as a starting parameter for the assignment. Based on that after the assignment go back and look at the multiplicity pattern. What is the multiplicity pattern we are going to see, for each proton like what I have already discussed, whether it agrees or not. And that is one easiest way to make the assignment of the protons of the phenyl group. Any type of phenyl group, depending upon whatever the substitution you have, in what are the position, we can make the assignment. With that you have fairly understood. Lot of analysis we have done, and we can go further.

So, far we are looking only at the proton spectrum where you are looking at the proton-proton couplings. The J coupling is what we saw are only among protons. Can there be a heteronuclear coupling with protons? Can heteronuclei couple to protons? Why not? it should couple. Then what will happen to the spectrum? How it will get reflected? How do you extract the heteronuclear coupling? We look at it now. Take for example, a molecule like BH4 an ion. I am looking at the proton there is a boron attached to it.

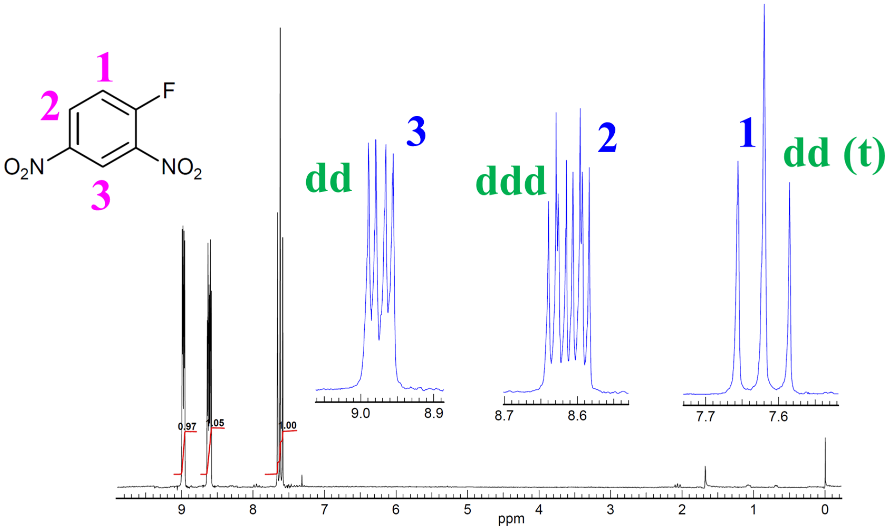


Remember boron has 2 isotopes; boron spin 3 and spin 3/2. Boron 10 has spin 3; boron 11 has spin 3/2. And each of them has a different abundance and the ratio is 1:4; the abundance ratio 1 is to 4. And boron will split this proton. I am looking at proton, but it is coupled to boron and what is a multiplicity pattern you get? Simply let us put 2NI+1 rule. Even for this though there is no chemical equivalence I am talking about only 1 boron, put n is equal to 1, I take an example of boron 10, spin is 3 plus 1. So, it should give 7 lines for boron 10; should give 7 lines. Put for boron 11, then what will happen? 2 into 3 by 2 into 1 plus 1. So, it would give 4 lines. So, boron 11 should give 4 lines and boron 10 should give you 7 lines. But intensity ratio is 20:80. See boron 10 intensity is small it should give 7 lines of intensity, at least one fourth of the bigger line. So, both the isotopes of boron 10 and boron 11, individually they are coupled to proton. So, that means you if you take 100 molecules of BH4, 20 molecules are with spin B10, $^{10}BH_4$ and 80 molecules are $^{11}BH_4$. Both the molecules present, both isotopomers are present; you understand both isotopomers are present. As a consequence you get the spectrum of in this proton spectrum with couplings of both boron 10 and boron 11 present. It is an overall of a spectra of both molecules. So, one spectrum for boron 11 spin 3/2 peaks are there of equal intensity. That is what we calculated that is a boron 11 BH4 molecule. And there is another 20 percent of molecule will have boron 10 with spin 3. That gives us to 8 lines and intensity ratio you see 1:4. And this separation gives me 11 boron proton coupling; thisseparation gives me 10 boron and proton coupling, you understand. When there are 2 different isotopomers, because of 2 different isotopes then both of them can couple to the proton and the spectrum is a overlap of both isotopomers. This is a classical example of BH4. I am looking at the proton NMR where B10 and B11 both are coupled; in the sense they are not in the same molecule. Please always remember they are 2 different types of molecules boron 10 BH4 is one molecule, boron 11 BH4 is another molecule. Their abundance ratio is different and is 20 is to 80 and coupling is different because spins are 3 and 3/2. As a consequence the pattern is different. And measuring this separation gives you ^{11}BH coupling; this separation gives me ^{10}BH coupling; that is what it is, we got everything. So, we can easily understand all those things.

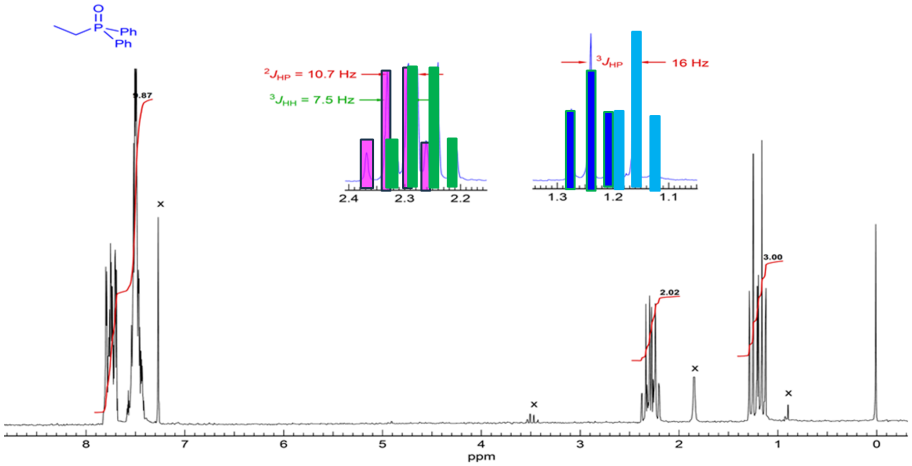


We will go to the next molecule. There need not be one heteronucleus. Remember when I was explaining the spin spin interactions, scalar coupling salient features I said 1 spin can experience coupling with N number of other protons, other NMR active nuclei simultaneously with different coupling strengths. So, if I consider CH3 proton it can experience coupling with this CH2 proton with proton spin half. Of course, if I label, it can couple with carbon also, since it is in natural abundance we will not worry about it, will be satellites. sulfur will not couple, phosphorus will couple, spin half. Fluorine will couple, spin half and extent of coupling depends upon how many bonds they are separated. As a consequence if I look at a simple molecule I can find out multiplicity pattern depending upon the interactions. Znd of course, I am looking at the proton NMR. Then if I look at the proton NMR; there are only 2 groups. It gives the proton signal for this is CH3. I can clearly say high field region is CH3; and low field region is CH2, no doubt about it. And why CH3 is a triplet? because it is coupled to CH2 that is fine. But now look at this molecule. This also can couple with phosphorous and fluorine. If you carefully see, this molecule you will see each line of the triplet, this triplet separation is HH coupling, and each line of this triplet is further split into triplet because of fluorine. See this separation if I take ,this triplet here, this separation if you measure it will give me JHF coupling for CH3 proton. And this separation gives me HH coupling. Then you may ask what will happen to phosphorous? phosphorous is experiencing, 1 2 3 4 bond coupling, which may be very small. The 4 bond proton phosphorous coupling may be very small. So, you are not seeing; whereas, this 5 bond coupling may be visible. You are seeing that. So, as a consequence in this case of this molecule what you are looking at is a CH3 proton, this CH3 proton is a triplet of a triplet. And the first triplet is coming because of CH3 coupled to CH2; and each line of the triplet is split into another triplet because of F2 and phosphorous is not coupled to this. That is it. I can measure the separation. I know HH coupling between this and this is 7 hertz; I know 5 bond coupling is 0.7 hertz. You got triplet of triplet, phosphorous is not coupled to that here.

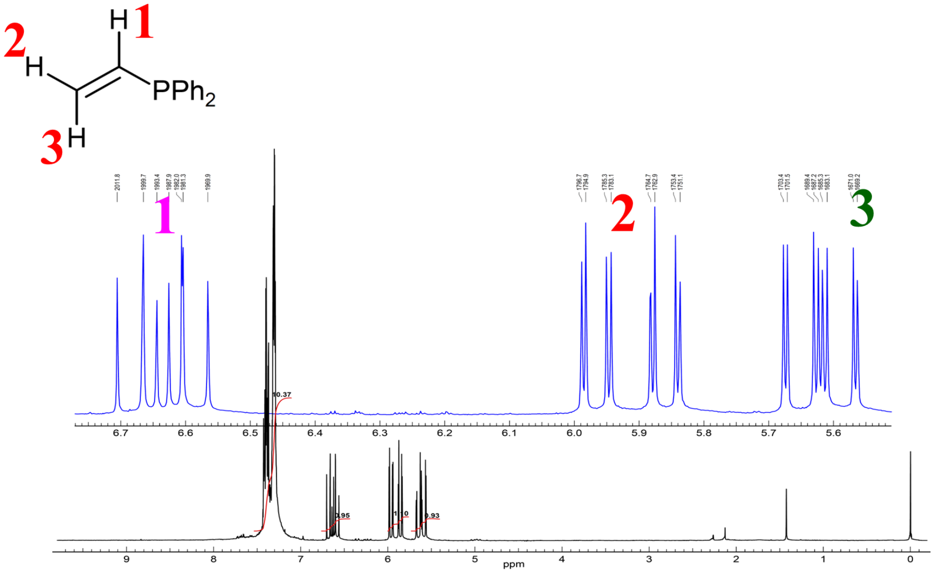
What about this one? obviously you can say this is a CH2 group. And CH2 group will couple to this one. What is the pattern we expect? we expect that pattern to be a quartet. Further what will happen? This CH2 is not far away, from phosphorous and fluorine. It couples to both of them. Then depending upon the strength of the coupling, let us say this coupling is larger then each line of the quartet is going to be a triplet, because of fluorine. And then it is going to be quartet of triplets. Further what will happen? it also splits each line that into a doublet because of phosphorous. Depending upon which is larger, which strength is larger, whether it is triplet, or triplet of doublet or quartet of doublet of triplet or triplet of doublet of quartet we do not know. That depends upon the strength of the coupling. That you can measure. Ee will start like this. For this molecule let us say this is the chemical shift. It is always at the center of the multiplicity I told you. That is CH2 proton, that initially splits into a doublet because of phosphorous coupling because that coupling is larger. That is how I worked out the multiplicity pattern here. Then it also has a coupling to this; this is second largest coupling. The first largest coupling I took to be HP; that is very large, and each line of the doublet is becoming a quartet, because of coupling with CH3 protons. This is one quartet, another quartet. I deliberately put two different colors. Now what will happen? it is also coupled to fluorine. Here fluorine is far away. So in the other case phosphorous was far away and was not coupled; but here phosphorous is also coupled, and fluorine is also coupled. We have equivalent 2 fluorines. So it will make each line of this quartets of doublet into a triplet, because of two fluorines, equivalent fluorine. You get like this, it is doublet of quartets of a triplet. This is a pattern you are going to get; simple molecule. Okay. I am looking at the proton NMR but still I am able to get the couplings. I am able to measure coupling of hetero nuclei. So the hetero nuclear couplings are reflected in the proton spectrum. Now I will ask you one question. and this molecule what anout PF coupling? why we are not seeing here and here. You must remember, I told you this is a passive coupling. You are looking at proton, it can give rise to coupling with phosphorous and fluorine; whereas, phosphorous and fluorine are passive spins. The passive spin coupling is not reflected at the site of the active spin. Now both the protons you are looking are active spins, and P and F are passive spins, their couplings are not seen here. You understand this; that is the PF coupling is there, but not seen here. Okay.



Go to the next molecule. This is a simple molecule where one fluorine is present and there are three protons. I can start making the assignment very easily. There are three groups of protons here, fairly easy to analyze. If you look at it, this is a broad triplet with a separation quite large. Here there is a triplet, what this could be? I would say this proton has two ortho couplings with proton and fluorine. By the by, mind you, ortho coupling in the benzene between proton and fluorine is similar to the values that of the proton proton ortho coupling. If it is in benzene 8 hertz, with fluorine also around it is 7-8 Hertz; generally of similar strength. So this coupling and this coupling are identical, and I would say this triplet corresponds to proton 1. That is my assumption. Then what about the next one? the next one is proton two what are the possible couplings we can think of for the proton 2. If this is proton 2, you can have one ortho coupling and two meta couplings. And if both the meta couplings are different, then it is going to be 8-line pattern. Large separation is because of this ortho, and is split into eight lines like this. It is going to be doublet of doublets of doublets. So this could be proton 2; my assumption. Then what is the last one? This is proton 3. The proton 3 has two meta couplings, and they are different 2-3 coupling and fluorine-proton; this fluorine-proton couplings are different. So it is doublet of doublet. Very easily you can start interpreting all those things. So this is 3. What I said is correct. This is 2, this is 1, perfect. Very easily we can interpret these things. So this is doublet of doublet; this is doublets of doublets of doublet. This is also doublet of doublet. In principle it is triplet, two lines are overlapped. So very easily we can get the HF coupling here. In the earlier case PF coupling and HF coupling both were there. Here HF couplings are there.

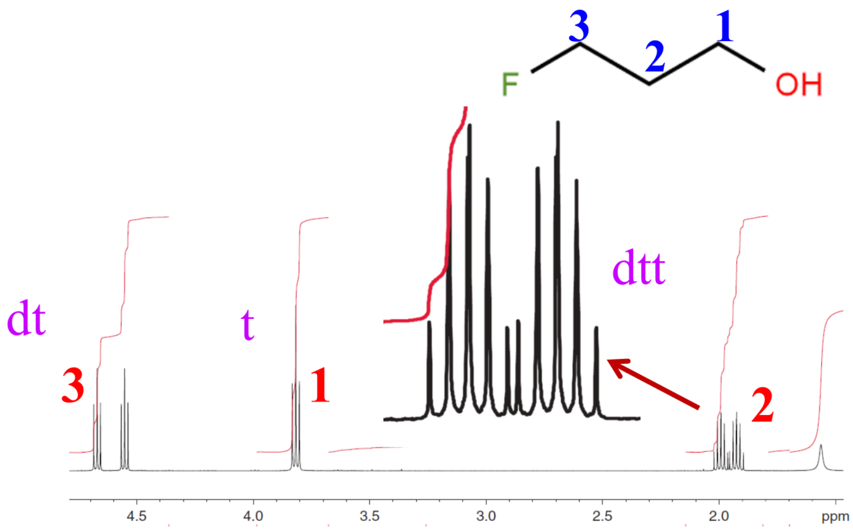


Now take an example of a molecule like this. Very simple molecule. Now we can expect two bond and three bond proton and phosphorus couplings here. It can couple with CH2. It can also couple with CH3 and there are phenyl groups. Forget about it; they are

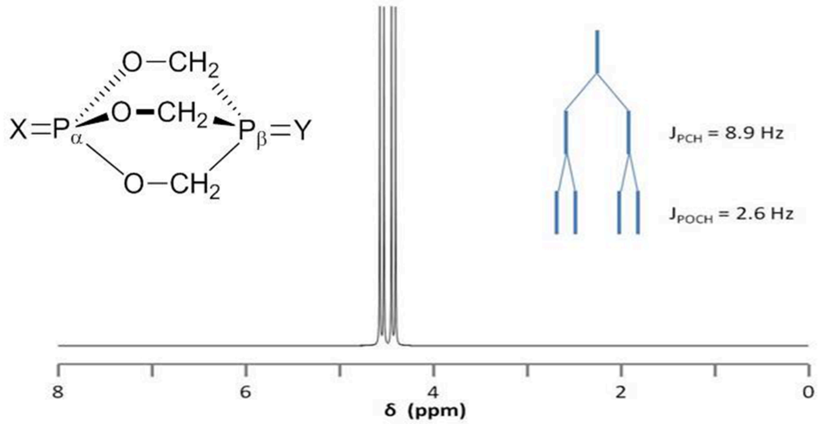


overlapped here. Of course there also proton might have two bond three bond couplings very difficult fairly difficult to extract. I am not analyzing that region. We are analyzing only this region. That means coupling of phosphorus to CH2 protons and CH3 protons are the only two things we can think of. Now if I think of that, I know this is CH3. I know this is CH2. This CH3 is going to be a triplet because of CH2; that is well-known HH coupling. And each line of the triplet is further split into doublets because of coupling with this phosphorus. Look at it. This is what it is. Okay, this is CH3. We will come to that, okay. We will also analyze CHw. The CH2 is going to be a quartet because of this, fine. And each line of the quartet is a doublet because of phosphorus coupling. Sodepending upon which coupling is larger, it is doublet of quartet. Similarly it is doublet of triplets. Look at this one. This is one quartet, another quartet; and this separation here gives me HP coupling. The coupling between phosphorus and proton. And this separation is going to give you HH coupling, it is a quartet; there are two quartets, very easily you can identify. Similarly, here this one triplet because of coupling of CH3 with CH2. Another triplet and this separation of each of this identical lines, you can consider leftmost to leftmost, right to right, or center to center, measure the separation that will give you HH coupling. Exactly what you got here. Hee also you will get HH coupling. And interesting thing what you notice here is, see here, very interesting thing. I want to tell you the three bond proton coupling is 16 Hertz. Whereas, two bond proton coupling is about 10 Hz; proton phosphorus coupling is 10 Hertz. Usually what we say, as the number of bonds keep increasing, consecutive bonds, the coupling decreases. But you see you can also see strange things here. The three-bond phosphorus proton coupling is larger than two bond phosphorous proton coupling. Strange things do happen in NMR. Please remember. This what it is. We could make the analysis of this thing very easily.

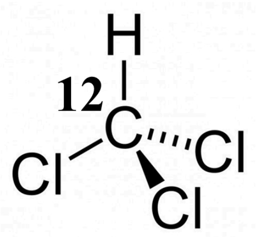
We will go further now. Another molecule I am going to take. This is a very interesting molecule I am not worried about the phenyl group. I am concentrating only on these three protons coupled to phosphorus. I am looking only at the proton NMR and these three regions are there corresponding to three protons, 1, 2 and 3. And you can easily understand. If I consider this proton it can have a geminal coupling with phosphorus, trans with this and cis with this. Similarly consider this one, this can have a geminal with this, trans with this, and cis with this. Consider this proton, this can have geminal with this, cis with this, and trans with this. Each of these protons experiences three different types of coupling including one of them is a phosphorus. So very easily you can interpret depending upon the strength of the trans coupling. Of course, we know that the trans coupling is larger than cis, than geminal. Same this thing follows here also. I would say this is proton 3, for the reason I would say trans coupling of proton is larger than cis coupling of phosphorus, and proton, which is about 14 Hertz. And then geminal coupling of proton is very small. This is geminal coupling is usually 1 to 2 Hertz, I told you or maybe 3 Hertz. So very easily you can see, this is going to be a first doublet and each line of this doublet is further split into doublet and then they will further split because of geminal coupling. It is 8-line pattern, ddd correct. What is the next one? the next one I would say is proton 2. Why did I say that? Remember the trans coupling is larger and further the trans coupling of phosphorus with proton is huge; of the order of 32 Hertz; quite large. So there is a large separation here, into a doublet and each line of the doublet is split because of the cis coupling into two doublets; and further each line split into doublet because of geminal coupling. It is a 8-line pattern. Go to the next one. Obviously this is proton 1. The proton 1 has one trans coupling, cis coupling and also geminal with proton. See the geminal with this phosphorus is 12 Hertz, trans is 18 Hz, and this is 11.4 Hz. We know that. You start writing down. This is the pattern you are going to get. Large coupling of trans with proton, then geminal with phosphorus, and then cis with proton. So it is going to be 8 line pattern. There are 8 lines. If you carefully see some are overlapped here, so this is a ddd pattern. So very easily you can understand.



We will go further and we see the coupling with fluorine. This is a simple molecule called 3 fluoropropanol. We should get proton fluorine couplings here. Why I am taking proton, phosphorus etc. they there all abundant spins. If they are less abundant spin you do not get like this. You get like satellites. I will come to that later. In this molecule if you expand this, it is going to be doublet of triplet of triplet. If you expand this, it is a triplet. This is again doublet of triplet. Why it is like that? I can say this is triplet. Where is the triplet coming from? This one, this proton is a triplet. Why it is a triplet because it is coupled to CH2. And what about this one? This is going to be a triplet because, of this, triplet of a triplet because of this and this. Also has a coupling with fluorine. This one is a triplet because of this, and also doublet because of this, very easily we will start explaining the multiplicity pattern based on the coupling strengths. Look at this. This I will say is proton 3. The proton 3 is a triplet because of this large coupling and then there is a one bond coupling with fluorine FH coupling. That is quite large, that is doublet 45 Hz. And then it is going to be a first doublet, each line of the doublet is split into triplet like this. That is why I would fairly say, this is proton 3. Then I will say proton 2, the proton 2 again is a pentet. You know like I told you already, where we have two CH2 groups are coupled to one CH2 group, or one CH we get a quintet like pattern, like this, 5 line pattern 1 4 6 4 1. And that is split into a doublet because of coupling fluorine, which is about 24 Hz. That is why it appears as doublet of, actually it is a quintet, it appears like triplet of triplet because two triplets are overlapped. This is experiencing triplet because of this, and triplet because of this. If triplet of a triplet is overlapped, unresolved it looks like a quintet. So, it is doublet of triplet of triplet, that is also correct. Then obviously, left over is proton 1. What is it proton 1? this proton 1 does not experience a fluorine coupling. It experiences only coupling with this CH2, and is a triplet, very easily you can interpret this one, and get the proton fluorine coupling in this molecule.

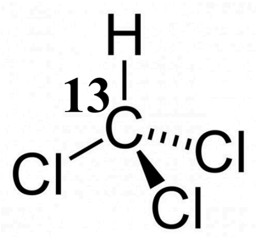


Look at this one, is a very simple molecule with a phosphorus coupling. And we have only one group of CH2 here, but there are two types of phosphorus here; one has a small coupling and the other has a large coupling. So, if any these three protons, all the there are chemically equivalent, you take it you will get one line, and it will splits into a doublet because of this phosphorus, and splits into another doublet because of other phosphorus. And you get 4 line pattern of equal intensity. It is a fantastic example of weakly coupled spin spins, all the lines are of equal intensity, because they are heteronuclei. I always said earlier. remember this heteronuclear spin systems are always weakly coupled. With this you have got some idea about how do we extract, the coupling heteronuclear coupling from the proton spectrum. So, far I was considering only abundant spins. What happens when you have a less abundant spins like carbon 13 nitrogen 15, silicon, selenium, like that. How do we get the spectrum? We look at it now.



99 molecules

NMR Inactive

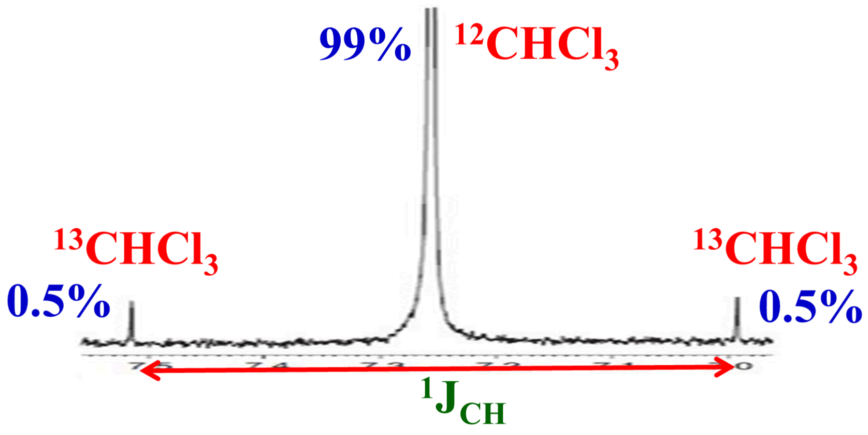


1 molecule

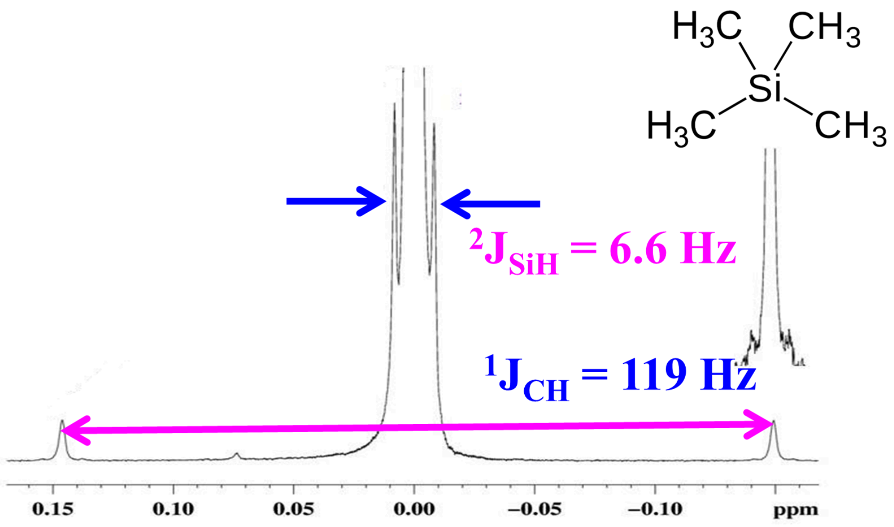
NMR Active

Before that I go into the isotopomers, which you already most of you know, I will tell you again.

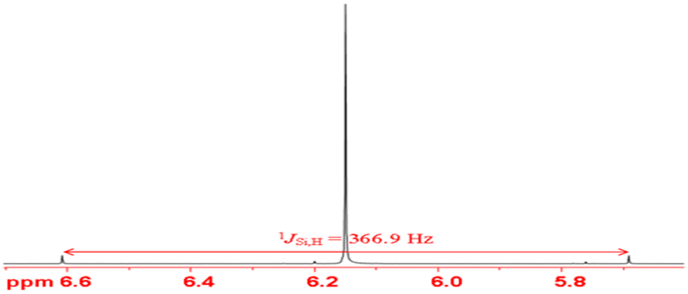
Consider CHCl3, 100 molecules. There is one carbon, one proton and three chlorines. We will not worry about chlorine isotopes. We will consider only carbon. Carbon has two isotopes, forget about carbon 14. This is 99% abundant, this is 1.1%, take it as 1%. So, if you have 100 molecules, 99 molecules are carbon 12 and one molecule is carbon 13. That means this carbon 12 will not give the signal at all, only proton will give carbon 12 will not give the signal. Whereas here the proton will give signal but it also comprises of this carbon. You know there is 1% abundance. It is spin half nuclei. The carbon 12 is spin 0; carbon 13 is spin half. It can couple to that and give rise to splitting. And this one molecule has NMR active. The 99 molecules here are NMR inactive, as far as carbon is concerned; not for proton. So, the intensity of the 13C, now when it is coupled to proton. If I have 1% molecule if I consider I say proton signal is 99%; the 99% signal comes from carbon 12 attached proton; because that carbon 12 will not couple, you get a single peak. But 1% of the molecule is there, that will couple to proton and splits into a doublet. And this intensity is only 1% and 1% intensity on either side further split into two it will become 0.5 here and 0.5 here. These are all very small compared to these big peaks, that is why they are called satellites. Satellite peaks are seen when an abundant spin is coupled to low abundant spin like nitrogen 15, silicon mercury, etc. You will see the example of that. I hope you understood. When you have abundant spin coupled to rare spin, rare spin splitting is seen as small weak peaks on either side of the coupled main peak, and they are called satellites.



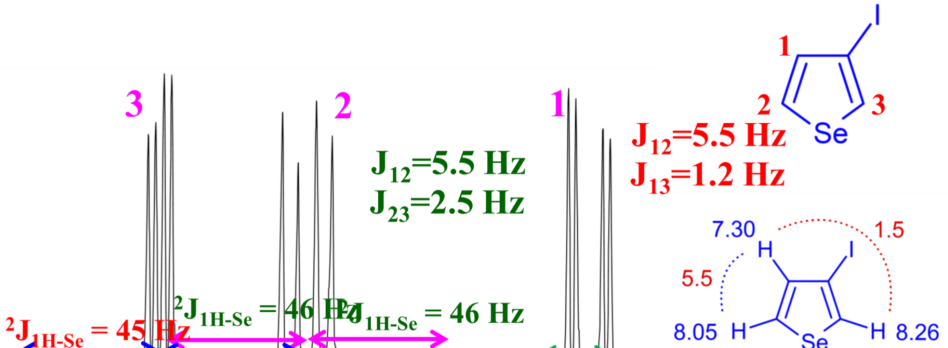
If you analyze the satellite spectrum you will get the coupling between proton and the coupled spin, which gives signal as satellites. Take for example CHCl3; that is what I explained to you, 99% of molecules are present as C12, and the main signal of proton comes because of this C12 attached, which will not split this proton it gives only single peak. The intensity is very high; but 1% of the molecule will split because of carbon 13. So the proton will become a doublet; and this doublet separation what does it give you then? It will give you J_{CH}, the coupling between carbon and proton. Already 1% abundant, further split into two so it will become 0.5% intensity; 0.5% here, compared to the main peak. And very small peaks, sometimes you will not see it unless you enhance the signal very high. Vertically you have to enhance the signal; then only you will see. That is why these are called satellite peaks, satellites. And this separation gives me one bond carbon proton coupling. You understood; less abundant spin can also couple to abundant spin and you get the coupling from the satellite pattern.



Let us look at the TMS. TMS if I look at the proton spectrum, the major signal comes because of this proton. And there is also silicon. Silicon has an abundance of about 4.7% and that gives rise to, of course, coupling here. And that is because of coupled to carbon 1%. And is also having silicon 4% and coupled; here you can see two peaks; here these two peaks are because of silicon proton coupling. See this is because of carbon proton coupling. This is because of silicon proton coupling. There are two lesser abundant spins here, silicon and carbon. Both of them can couple to proton. it is a one bond carbon proton coupling, it is a two bond silicon proton coupling. So, one bond carbon proton coupling is as nearly 119 Hz. Whereas, this is two bond, 6.6 Hz. You got everything; very easily you can measure coupling between lesser abundant spin and abundant spin from the satellite spectrum.



We will look for another molecule $SiHCl_3$. It is a simple molecule. Look at the proton NMR. It is huge and it is coupled to silicon. There is no carbon here. Then this separation gives me one bond silicon proton coupling. It is huge and is of the order 366 Hz. You can see one bond silicon proton coupling; you could get from the satellite spectrum of this molecule.



Let us look at this molecule, it is a fairly simple molecule, but the spectrum is very interesting. If you look at the 100 MHz spectrum of this molecule, there are three groups of protons, this is iodine, this is selenium. Selenium is also less abundant; even it couples to these three protons. This also gives rise to satellites. First you have to make the assignment for the proton peaks. First I make the assignment for the proton peak like this 1, 2 and 3, by using idea of my splitting pattern which I already discussed several times. I will say this is proton 1, which has a large ortho coupling then meta coupling, so, it is like this. Then 2 is this, both of them are nearly equal coupling; you get like this. And 3 is very small; both very weak couplings. As a consequence I would, based on the splitting separation of the multiplicity pattern of the coupled spins, and the peaks separation I would say this is proton 3; this is proton 2 and proton 1. That is fine, that assignment is good, but carefully if you see something interesting you are going to see. What are these lines coming? They are exactly matching with this these lines; matching with this separation. They are the satellites. This silicon can couple to this proton; two bond coupling is there, and this is the coupling strength. I have written this is two bond proton selenium coupling. This is another side. So, this three protons can couple to selenium; and each of these lines is split into two peaks on either side you get. They are satellites and measuring of the center of this to the center of this peak will give you proton selenium coupling, you understand. That is what I said, this gives you proton selenium coupling; and this also gives satellites. You already saw in the previous example, they come on either side. Similarly if you go to this proton, this also has 46 Hz coupling. This is proton 2; from center you have some peaks which are overlapped; and from this one you see four peaks here separation exactly like this. So, satellites are there for this group also. One is here, the other is overlapped. For this one satellite is here, others are here, you see hidden. Go to this proton 1. This also has a long range coupling 1, 2 and 3. The 3 bond selenium proton coupling and you can see that is separated and is about 8 Hz. This is one coupling, see one satellite for this one and for this also you have two peaks on either side; exactly similar pattern of the main peak you see on the higher side as chota chota peaks like this, small small peaks. They are called satellites. So, from this satellite I can get the selenium proton couplings also in this molecule. Very easily we can understand this.

So, I gave an example today about how we can analyze the proton spectrum, in this class, about a heteronuclear coupling. So, far we analyze the heteronuclear spectrum, now I showed you how we can get heteronuclear coupling. Proton can couple to abundant spins like phosphorus, fluorine and I showed many examples how we can extract phosphorus coupling; fluorine coupling. Simultaneously proton and fluorine both can be present; you can have simultaneous coupling of both heteronuclei, both can be extracted. We took the example of a molecule where proton is experiencing coupling with phosphorus and also with fluorine. In the other example, proton is experiencing coupling only with phosphorus and only with fluorine. All examples we saw. They are abundance spins. There are examples it can couple to less abundance, means like carbon, nitrogen, tin etcetera. Selenium, silicon we saw some examples. They are all less abundance, means they give rise to satellites because the major abundance portion is different, and they will not have spin and they will not generally coupled to this. And then other one, like for example carbon 13 carbon 12 spin is 0, that will not couple. Whereas, carbon 13 will couple, gives rise to satellites on either side, The small small peaks like this we can get. From the satellite spectrum measure the separation which will be at equidistance from the center you get the coupling between the protons and the dilute spin. Like this we can analyze the spectrum and get the heteronuclear coupling between abundance spin and the rare spin or dilute spin. So, I will stop here we will continue further in the next class. Thank you.