

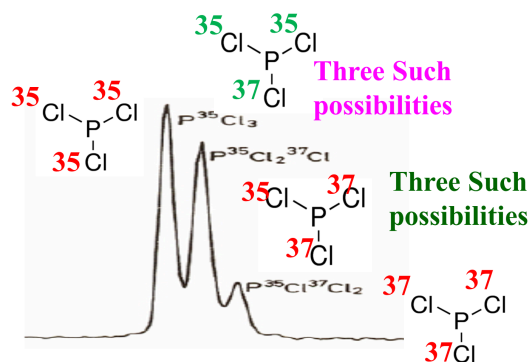
One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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Lecture 30: Analysis of spectra of Heteronuclei

Good morning, welcome all of you again. In the last class, we started discussing about analysis of the spectra of various nuclei. We started with fluorine NMR, I said fluorine is spin half nucleus, 100 percent abundant and it is very friendly nuclei and we took several examples analyze the spectra of fluorine where you can extract fluorine fluorine coupling hetero nuclei coupling between fluorine and abundant spins like phosphorus and also we could get coupling with rare spins, like dilute spins. At the same time, I also said about what is called effect of isotopic substitution on the fluorine chemical shifts. We took several examples I showed what happens when I take the molecule like CHFBr_2 , where we saw that in the fluorine because of 4 different types of isotopomers present because of 2 different isotopes of bromine, we got 4 peaks; 2 are overlapped and appear like a triplet. And we took another example like that and several examples of fluorine where isotopic effect is dominant and then we went into phosphorus NMR, analyzed several spectra and I came to one molecule where we could show that what phosphorus can experience couplings with proton, fluorine, nitrogen etcetera 3 or 4 different hetero nuclear couplings, which gave a very complex spectrum. And I had no time and I could rush up. I will repeat with that and then continue further with the analysis of the spectra of other nuclei today including phosphorus and some other nuclei. Let us come back and this is the molecule which we started. We wanted to see the phosphorus ^{31}P NMR of this molecule. There is only single phosphorus obviously we have only single chemical shift and its chemical shift is written as -83.4 ppm with respect to 85 percent H_3PO_4 reference, that we use for phosphorus. The spectrum looks fairly complex for a single phosphorus being present, and it is understandable. First of all you should see there is a large coupling; one bond coupling which is of the order of nearly 836 Hz; huge coupling is there. It is going to be a doublet like this; and then further the phosphorus experiences couplings with two fluorines which are chemically equivalent, it is a PF_2 group. So, what is what going to happen is, see 1JPF is there which is going to be a triplet. One line of the doublet is split into a triplet because of two equivalent fluorines. Another line of the doublet which is here also split into a triplet because of two fluorines. And it is 1:2:1 triplet here. Similarly this is 1:2:1 triplet. There are two triplets here. One doublet was there initially because of HP coupling and that doublet became two triplets each line of the doublet became a triplet, that is because of coupling with PF_2 . Further what is happening is this also experiences coupling with two nitrogens. See this is a very

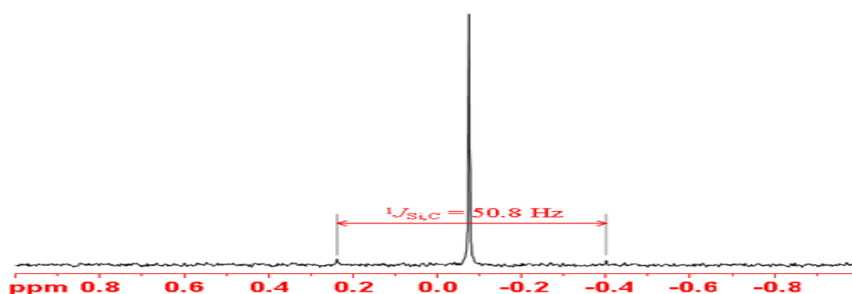
interesting aspect we should see two nitrogens are present. So, what does it mean each line of this triplet there are two triplets now each line of this triplet is further split into triplet because of two nitrogens, which have equal coupling with phosphorus. As a consequence you are going to get three triplets like this; three lines 1:2:1 triplet that is coming because of coupling between phosphorus and nitrogen. See there is lot of coupling one by HP coupling is huge; then PF2 coupling is huge; now phosphorus nitrogen coupling is also there; that is also quite large about 54 Hz. So, each line of the triplet became another triplet and that is what is expanded here. Each one of them see there are six lines, that one of them I have put here to show there is a one bond PN coupling two PN couplings making it a triplet. Further this phosphorus also experiences coupling with two protons, two equivalent protons, like NH2 groups which are there four protons. So, there are four protons it is going to split into a quintet pattern like this, or a septet; whatever it is, you are going to get pattern like that. Each one of the triplet is further split into a quintet like this. That is how it comes. So, this single phosphorus is experiencing one bond coupling, one bond coupling, one bond coupling, and two bond couplings; so many couplings are there. The overall pattern is a doublet of triplets of triplets of quintets. The total number of lines we expect is 90. That is 2 into 3 into 3 into 5. See this one single phosphorus gives 90 peaks. Fortunately, many of them are you know easily analyzable, by a first order way. Most of them are weakly coupled because only one chemical shift is there and all couplings, and the peaks are quite well dispersed. So, we are going to get the information very easily, that is it.



So, next another simple example I want to take for phosphorus 31 we took the example of PCl₃. Okay in this case very surprisingly we got 4 peaks. There is only single phosphorus remember CFC13 peak we discussed in the fluorine NMR. So, CFC13 gave rise to 4 peaks because of chlorine has 2 isotopes chlorine 35 and chlorine 37 chlorine, each of them has different percentage of abundance which is 0.76 and the other is 0.24. As a consequence we could calculate the distribution of populations of different isotopomers of CFC13 and we arrived at 4 different peaks with intensities and then 95, 90, 30 and 3 that we could easily interpret. Exactly analogous to that in phosphorus also you can think of know varieties of isotopomers. First of all there are 2 chlorine isotopes, chlorine 35 and

chlorine 37. I can say there are several isotopomers. First one all chlorine could be 35. There is one possibility, 76 percent abundance. The second all chlorine can be 35 that is 24 percent abundance that is also fine. Then we have other possibilities; 2 other possibilities where 2 chlorine could be 35, one is 37 there are 3 such possibilities. There could be 2 chlorine 37 one is 35, again 3 such possibilities. So, the population distribution, analogous to CFCl_3 analysis what we did, you can also do it. And then each peak population can be worked out. First of all we took this one, 76 percent abundant and this is a strong peak; scale it as 100. With respect to that other intensities can be calculated. Next one is this possibility, there are 3 such possibilities. And then intensity if you multiply by 3 scale it with respect to this. This how it is. The next possibilities again 2 chlorine 37, and chlorine 35. These are possibilities and the last one is all are 37. Somewhere here weak intensity, we are not seeing it. You understand 4 such different isotopomers are there; and the intensity of the each peak can be worked out based on the distribution of populations, statistical distribution of populations. So, that is it. So, we discussed a lot about the phosphorus NMR, fluorine NMR.

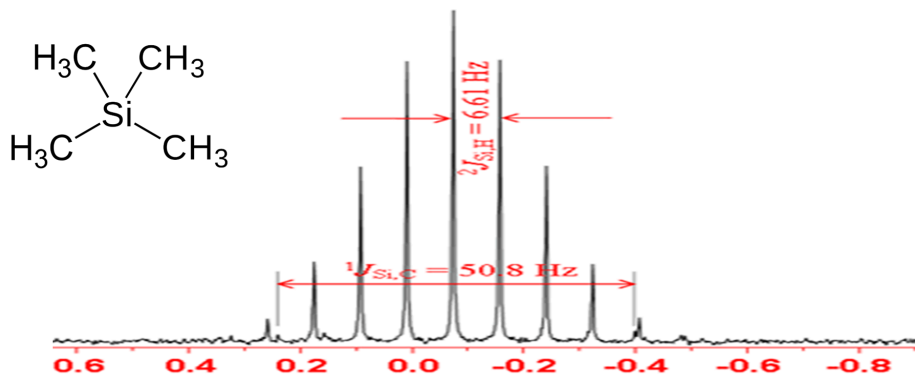
We switch over to another important isotope silicon. Silicon NMR is also very often done especially when the people are working with glasses and then zeolites etcetera. The silicon and aluminum are routinely done. So, however we do not take the material or example of that. We will look at the examples of simple one or two organic molecules. Again silicon is a friendly nucleus, spin half nucleus. Its abundance is 4.67 percent and chemical shifts are usually much smaller than ^{13}C chemical shift in common organic solvents. This chemical shift of silicon is much smaller than carbon 13. It is just for information.



Let us look at the silicon NMR of tetramethylsilane. How many peaks we expect? it depends upon two types of experiments. you can do. You can do silicon NMR with all protons completely decoupled, in which case we get a singlet. There is possibility all 12 equivalent protons are coupled to silicon, you can get proton coupled spectrum also. How does the spectrum appear when it is decoupled and coupled, we look at it and this is the silicon spectrum with proton decoupling, fantastic. There are no more couplings of

protons with silicon then why we have a doublet here? two satellites, weak peaks. I have already written here, you see it is carbon 13 coupling to silicon. One bond direct coupling; and four such carbons are there; they are all equivalent. So, you are going to get a doublet with carbon coupling to silicon. And it appears as a satellite we are going to get measure. If you measure the separation you get one bond silicon carbon coupling. As I

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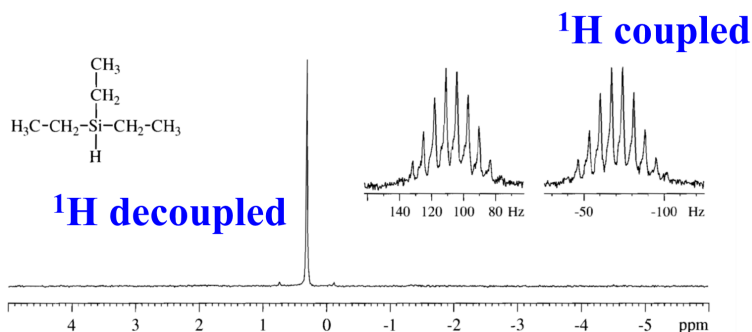
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spin like silicon itself then you do not worry about the abundance of that, you treat it as a abundance spin itself, and then other dilutes spin coupled to that gives rise to satellites. Like if I look for protons silicon is a satellite, but I am looking at silicon itself that I can treat it as abundant spin then carbon coupled to that will be a atellite. So, we have got satellite peaks, and because of silicon one bond silicon carbon coupling, these are 13C satellites.

Another thing is proton coupled silicon in the same tetra methyl silicon. I do not do the decoupling how many peaks we expect? Very important, if you remember 2 ni plus 1 rule here and now there are 12 protons which are equivalent put it 2 into 12 into half plus 1, then you are going to get 13 peaks. It is called tridecouplet spectrum; 13 peaks are there. You can start counting from that see here there are peaks. And of course, you also see carbon 13 satellites whose separation we already measured in the other case. There

are 13 peaks and separation of each of them gives you silicon proton coupling; 2 bond silicon proton coupling you are going to get; and this is how it is. So, you should get 13 peaks. How do you get the intensity of all those peaks? how do you arrive at it? Of course you have to go to Pascal triangle. When there are that 12 protons coupled what is the intensity pattern? like we have for 2 protons coupled equivalent 1 2 1 when 3 are coupled 1 3 3 1, that we know. Go to the Pascal triangle and find out how many peaks we expect what is the intensity pattern. Easily you can work out and this how it is, all 13 peaks are there. And the highest intensity peak is 924. Compared to that other peak is only 1% intensity that is why we are not seeing that. This is a proton coupled TMS spectrum.

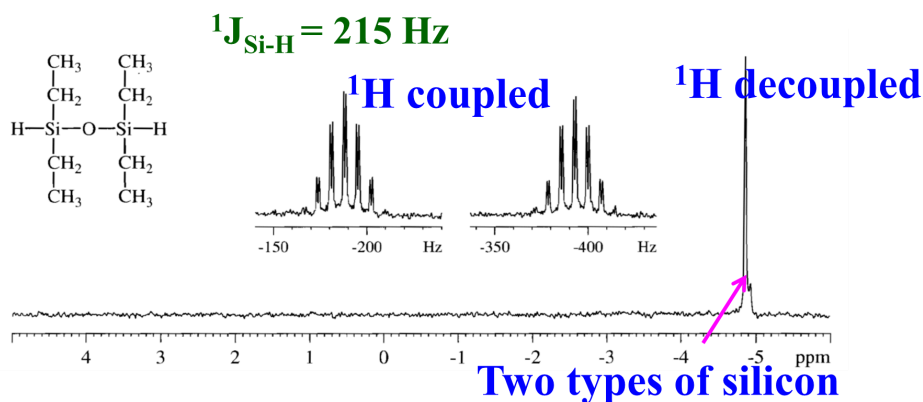
Now, we can go to another molecule; a simple molecule. Look at this molecule, an organic molecule.



We are looking at silicon, but here we have we have 2 types of experiment done. Again proton decoupled and proton coupled. When there are proton decoupled what are you going to see is a single peak. That is what only one silicon is there we got a singlet. Of course we got 2 satellites. What are these satellite coming from? because of coupling of silicon with carbon. So, this is going to be separation, if I measure I am going to get silicon carbon one bond coupling, that is because of carbon that in satellites. This is decoupled spectrum. There is also coupled spectrum it is plotted in 2 bunches, 2 expansions separately. There is a break breakage in the plot here you can see. And why it is coming? first of all remember there is one bond proton silicon coupling. Here 1 bond silicon proton coupling it is huge, quite large. What is that going to do? It will split silicon peak into 2 peaks; a doublet of the order of 175 Hertz see we can separate out here. Starting with that somewhere around 75 this is about 125 you can see the separation. If you accurately calculate silicon separation one bond silicon proton coupling is 175 Hz. It is a doublet, but what is going to happen now? We also have 2 bond silicon coupling with proton; 3 bond silicon coupling with proton. This one can coupled to this, this. and this. There are 3 such CH_2 s. What is going to happen now? Each line of this doublet is going to be triplet of triplet of triplets 9 lines. Further it also experiences

coupling with CH₃s. What will happen? Each of these 9 line will become a quartet, 36 times will be there in each of them. Each bunch should contain 36 peaks if all the couplings are resolved. So, it has 2 bond zinc 3 bond couplings. It is very very complex spectrum, but all of them are not resolved. As a consequence only few bunches are seen here. At least you can get one bond coupling and with difficulty you can even expand and try to get 2 bond silicon proton coupling, with CH₂, with the expansion of this.

Similar molecule now you can also see again there is a symmetry along this axis. There is one bond silicon proton coupling. It splits into a doublet. Of course this is a proton



decoupled, you get a single peak, but if you carefully see there is another peak here which possibly gives an indication there could be 2 different types of silicons here, other is not resolved very well, but an indication there may be 2 types of silicon. Let us not worry about that chemistry part.

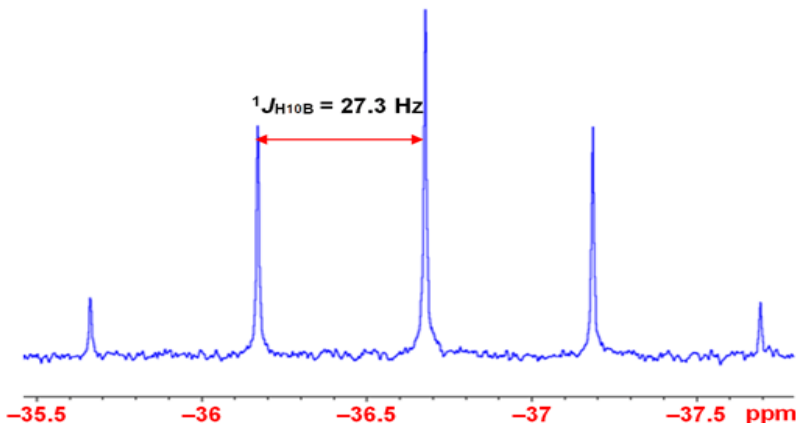
As far as the structure is concerned that will worry later, but right now a proton decoupled silicon spectrum gives a singlet because there is only 1 silicon, another one also. But both are chemically equivalent because of symmetry and this large separation is a one bond silicon coupling 215 Hz and further each of this peak is split by 2 CH₂. What is the pattern you are going to get? triplet of triplets. And many of them will overlap. And

you get a spectrum like this pattern. Remember we worked out lots about what will happen when we get triplet of triplet like that. Further each line of this is experiencing coupling with 2 CH₃s. As a consequence it is going to be a very very complex pattern. This is the type of spectrum you are going to get. That is one of the examples about silicon NMR. You understood silicon NMR, especially if you go to organic molecule there will be hardly couple of silicons. I am sorry maybe one or two silicons very easily 2 chemical shifts will be there and if you carefully see decoupled coupled spectrum you can get all the information, provided you are able to resolve everything. Analyzing the molecule like this which is very complex, all are not resolved would be difficult. But you can do a special experiment and get every information.

We will go to next molecule, next nucleus called boron. Boron NMR. Boron has two isotopes boron 11 and boron 10. We also discussed this when we discussed proton analysis, when we were looking for proton coupling to boron. So again I am repeating boron spin is 3/2 abundance is 80% and boron 10 spin is 3 abundance is it should be 19.9. I made it 80 so consider as 80:20; 1:4 is the abundance approximately. And I am not worried about precise value, boron 10 spin is 3. So if any spin half nuclei like proton or carbon is coupled to boron, how many peaks you expect? you expect $n + 1$ peaks; n is 3 here and n is 1 but spin is 3 so we are going to get 7 peaks. When it is coupled to boron 11 you get 4 peaks because $2 + 1$, so it will get only 4 peaks. And these boron 11 coupling will give strong peaks, 4 peaks of equal intensity. Boron 10 coupling will give 7 peaks which is 20% weaker compared to this, intensity wise. But of equal intensity 7 peaks. This is a simple example. But one thing I want to tell you if you want to do boron NMR you must use quartz NMR tubes. Do not use normal tube because that could be made up of borosilicate glass and then you are going to get the signal from the NMR tube. So it is a caution when you are trying to do boron NMR, you always use quartz NMR tubes.

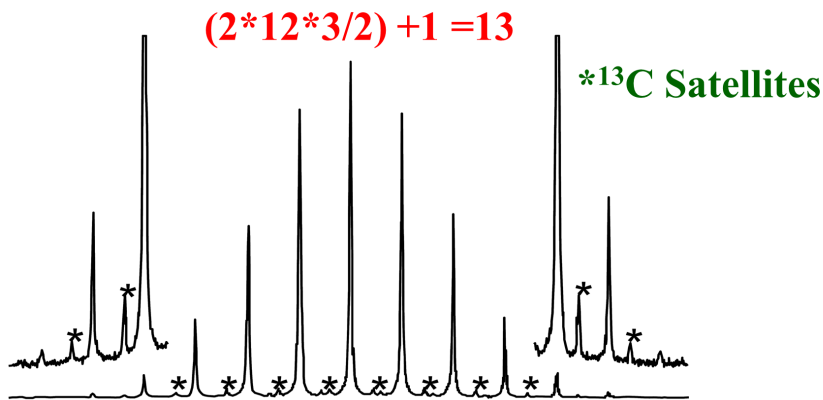
And this is simple molecule BF₃ OEt₂ coupling to proton is not usually observed. Only in exceptional cases like BH₄ molecule you can see boron proton coupling; otherwise coupling to boron is usually not observed. Generally you will get only a single peak for boron; no coupling. But on the other hand as I said if you go for boron BH₄ ion when dissolved in water, the proton coupled spectrum if you take, I am looking at boron 10. Boron 10 should give how many peaks? I told you, it should give 7 peaks. There must be another peak somewhere here and here so there should be 7 peaks that is what you are going to see. But I am sorry we are not we are not looking at proton we are looking at boron. Boron coupled to proton. We are not interpreting proton spectrum you should see it is a boron 10 spectrum, not proton spectrum. So our interpretation should be in a

different way. For boron 10 coupled to proton 4 protons are equivalent, 2 Ni plus 1, 2 into 4 into half plus 1, you are going to get 5 peaks. And the separation of any two adjacent peak gives you boron 10 and proton coupling.



Go to the boron 11 carefully if you see boron 11 peaks are quite sharper and more sensitive compared to boron 10. Here also you are looking at the boron 11 NMR coupled to proton. How many peaks you should expect? like in previous example 4 chemically equivalent protons are coupled to boron, it is going to give 2 Ni plus 1 so it will be 5 peaks of equal intensity. I mean intensity ratio like this, and this separation gives you 1 bond

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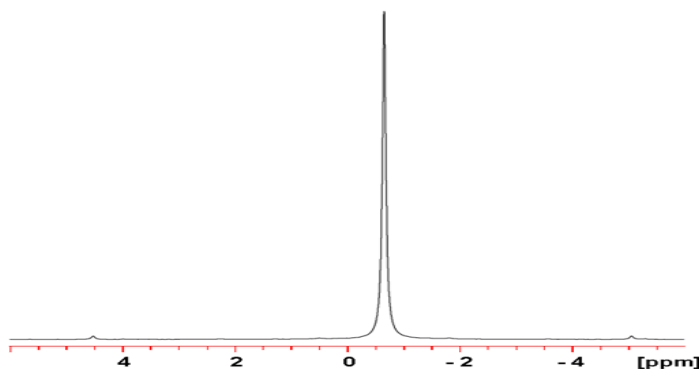
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So if

you take the boron NMR of this molecule you get two different spectra one couples with boron 10 other is coupled with boron 11. In a special example like this type of molecule you can even get boron proton couplings also.

Take another example of this molecule $K[B(CF_3)_4]$. How many peaks we expect? if I look for boron 11 now I am looking for boron looking for coupling with fluorine. Incidentally as I said this is also spin half nucleus. There are 3 into 4 12 equivalent fluorines. We use the $2nI + 1$ rule, 2 into 12 into $3/2$; so you are going to get 13 peaks. If you carefully see you must get 13 peaks here. Remember I am looking at boron 11 coupling to fluorine, so I must get 13 peaks. And these are all expanded here you see 1 2 3 here 4 5 6 7 8 9 10 11 12 13 you should expect somewhere here 13 peaks are there. So 13 peaks are there and what are the peaks which are marked star here? they are coupling with carbon. The carbon is also spin half nucleus, they are carbon 13 satellites. Each peak is split into 2, 2 peaks here. They are carbon 13 satellites, you understand. So this is this simple molecule boron 11 gives you about 13 peaks. Of course why we did not see the boron 10 NMR of this molecule? It doesn't matter one or two examples to show. Boron-10 NMR can also be done and especially the coupling to proton and fluorine also can be seen.

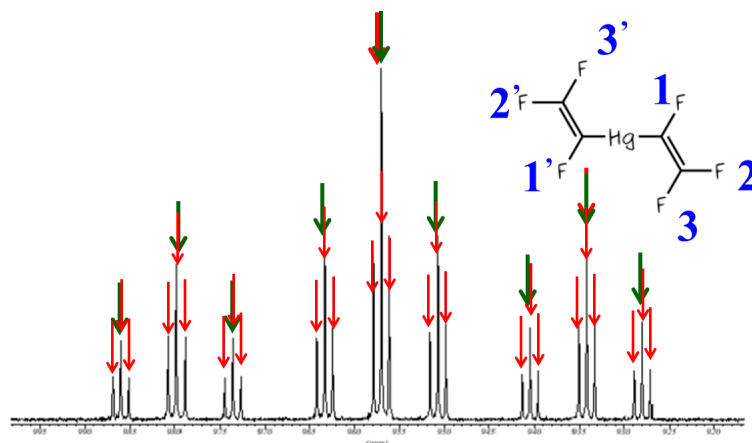
You go to another example mercury NMR. Interestingly mercury has 7 stable isotopes out of which only 2 are NMR active; that is mercury 199 and mercury 201. Both are NMR active and especially mercury 199 is always a preferred choice, not 201 and that is because this mercury 199 a spin half nucleus abundance is close to 16.7 percent, about 17 percent abundance is there. So fairly easy to detect so that's why mercury 199 is a preferred choice, when you have to detect mercury NMR, Hg NMR.

This is an example of dimethyl mercury 199 NMR.



Now you see a very single peak we are going to get carefully if you see it is proton decoupled remember there is no coupling you are reading breaking all the coupling of mercury proton but not with carbon so if you look at it carefully what are these these are carbon 13 satellites carbon 13 coupled to mercury is split like this. So if you measure separation from this to this, you get one bond carbon mercury coupling. We have broken proton couplings here so you get a single peak, with carbon 13 satellites. What happens if you look at the proton coupled one. For the mercury NMR proton coupled. How many protons are there now? two methyl equivalent six protons, so six into half into plus one you have how much you are going to get so you are going to get two into six into half plus one. You are going to get seven peaks. You count there must be seven peaks here. One two three four five six seven, because two N plus one rule you have to apply. Now N is equal to six, two into 6 into spin is equal to half for proton plus one. You get seven peaks. You get seven peaks and a separation of any of these adjacent lines if you take, it gives you mercury 199 and proton coupling, which is fairly large about 100 Hertz. You are going to see, this is a proton coupled 199Hg NMR of dimethyl mercury. It is not dissolved in any solvent, it is a neat sample is taken, neat means it is not dissolved in any solvent, that is what we do. And what happens if you do the proton decoupled spectrum of this molecule see earlier we took only proton coupled, now mercury NMR with proton decoupling if you do we are going to see carbon 13 satellites, what we saw here in the example. This has been expanded here very clearly you can see about 686.2 Hertz, which is coupling between one bond mercury and carbon 13. The same experiment what we saw in the previous two slides back, but only thing is expanded pattern with a better experiment and acquired with more scans to see the satellites. Here the interest was only to see boron signal, it was not acquired for a long time. Here you can see satellites with enhanced intensity; and if you measure the separation you get one bond carbon with mercury coupling of 686 Hertz. Okay.

This is another interesting molecule when you are analyzing multiplicity pattern in proton I showed this as an example. Here if you look at this in the vinyl group all the three fluorines are equivalent. This is inequivalent, this is inequivalent; this is inequivalent.



But if you take the whole molecule with respect to mercury there is a symmetry this is symmetric with respect this, these two are symmetric equivalent, these two are equivalent and this and this are equivalent, each of these symmetric with respect to fluorine because of their equivalence. When it couples with mercury they will split into a triplet. Take for example how we can do that. Here I will show you here first consider mercury as a single peak; now these two fluorines are equivalent splits this into a triplet. And these two are equivalent split each of this into a triplet, you get nine lines. Further each of these lines is split into a triplet because of this coupling equivalent fluorines. You know the chemically equivalent two fluorines, so the symmetric fluorine makes this a complex spectrum. Let us see how. It is of course center of this multiplicity correspond to chemical shift of mercury Hg 199. The chemical shift is a center, okay I will remove that, so that you will know that this is the triplet, a large triplet because of coupling between mercury and two bond fluorines, here large triplet. As I said now this and this are chemical equivalent makes each of them into triplet one two three so each line of the triplet is becoming a triplet. Further see it is large. Look at this one, this one triplet and each of them is another triplet, now these two makes each of these lines into a triplet like. One triplet, two triplets and three triplets. So this is nine lines, nine lines, nine lines. so totally how many lines we expect? 27 lines with this mercury coupled to symmetric fluorines. Each fluorine is individually chemically inequivalent, but because of the symmetry these two fluorines are equivalent; these two are equivalent; these two are equivalent. As a consequence you are going to get 27 lines, which is triplet of triplet of triplet which is called ttt. That is what you are going to get.

On the other hand if one of the fluorine is replaced with a CF₃ group now, look at the molecule same previous molecule one of the fluorine is replaced with the CF₃. This is replaced by CF₃ group; everything remains same, because all are chemical inequivalent and with respect to mercury these two are equivalent, these two are equivalent and these are equivalent, now without even looking at the spectrum we should say what is the pattern we are going to get? This mercury splits because of these two fluorines into a triplet, 1:2:1 triplet equal coupling, okay. Further it also splits because of these into triplet of triplets. That is also fine. But there is a long range coupling of this fluorine with this mercury one two three four one that is a equivalent CF₃ groups. Then this triplet of triplets nine lines are there, each of these nine lines is further split by CF₃ groups. It will be a septet. Very complex molecule spectrum you are going to get. See this is a triplet of

triplet of septet, because this is the chemical shift of mercury. One triplet is because of these two, each there the triplet is split in another triplet because of this coupling and then if you carefully see each line of this nine line is a septet because of coupling with two CF_3 . This pattern is called triplet of triplet of septets. So the intensity pattern we can easily work it out how we get, we already done it earlier. We have already discussed the septet pattern this is 1:6:15:20:15:6:1 pattern. But unfortunately they are not resolved it is very noisy spectrum. But if you carefully do a good experiment and get a better resolution and better signal to noise ratio each of them will be seven line pattern. So this entire pattern for this mercury is triplet of triplet of septets. This is what it is. Since the time is up, I am going to take up nitrogen 14 and nitrogen 15 NMR in the next class. But right now in this today's class we continued with our discussion with a phosphorus I showed you taking an example of PCl_3 when the phosphorus is attached to chlorine, that chlorine has two types of isotopes, chlorine 35 and chlorine 37 with abundance 76 percent and 24 percent and you can think of different possible combinations of isotopomers, when all the three chlorine are 35, two are 37 and one 35. Two 37 and one 35 and all are 37. How many possibilities are there we can work out and then we can find out four different types of isotopomers are there. Of course two isotopomers have three such possibilities, the intensity gets multiplied by three times so when similar to $CFCl_3$ molecule we have observed PCl_3 also gives four peaks and intensity peak correspond to statistical distribution of the populations of each of these isotopomers. With that we continued further with boron NMR and I took example of boron 10 and boron 11, boron 11 has been $3/2$ gives 4 peaks of equal intensity when coupled to spin $1/2$ nucleus, and with 80 percent abundance boron 10 spin is equal to 3 gives 7 peaks when it is coupled spin half nucleus. We took the example of BH_4 and then we looked at boron 11 and boron 10. The equivalent protons split each of them into a pentet and we could get the boron 10 proton, and boron 11 proton couplings. We took few other examples of the boron molecules also. Then we went into mercury, several examples were taken. The mercury is again has seven isotopes; two of them are stable which are NMR active 199 is always a important thing; that is a thing, which we have to consider. $Hg\ 201$ we do not need to consider that generally nobody is going to study because it is going to be a broad peak. So mercury 199 is a preferred choice. we took example of two to three molecules including dimethyl mercury. Looked at the mercury spectrum, proton decoupled and proton coupled and we saw how many peaks we are going to get everything so we could immediately see. We could measure mercury carbon couplings from the satellites. Also we took the example of silicon and a tetramethylsilane we saw and we see silicon proton couplings, silicon carbon couplings, by doing decoupling experiment; few such examples we took. So three different nuclei we could study today. We could get the analysis spectrum of phosphorus, silicon, boron and mercury. All four we could do in this class. Several examples we took, and analysis I did by taking one or two simple examples. But then there will be more complications, when you go to a particular molecule but what I

gave you was only a idea how to go ahead, do that so. With this I am going to stop here we will come back and continue with remaining nuclei in the next class. Thank you very much.