

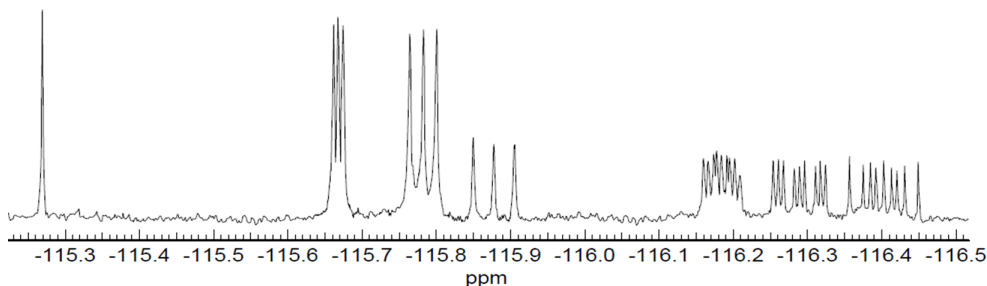
One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
Prof. N. Suryaprakash

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

Lecture 29: ^{31}P NMR

Welcome all of you. Now, we have started discussing heteronuclear NMR spectra since last class. Of course, we discussed extensively carbon 13. In the last class, I showed you how we can utilize DEPT and experiment in carbon 13. Three different types of experiments you can do with the last flip of the proton as 45 degree, 90 degree and 135 degree. Based on that, we can identify the different carbons attached to different number of protons. And I also showed you how we can utilize this DEPT experiment to identify the correct structure of some small molecules like monoterpenes. Two such examples we saw. Extending further, we started analyzing spectrum of other nuclei. We took the example of fluorine NMR. Fluorine is 100 percent abundant, spin half nucleus, very friendly nucleus. We started doing that. And we analyzed spectra of many of the molecules. Couple of examples I took. How we can see fluorine-fluorine coupling, fluorine-proton coupling and how the multiplicity pattern arises, we understood. Analyzed simple example couple of molecules. And we also analyzed example where some other dilute spin can appear and give rise to satellites, like in proton spectrum. So, we took the example of molecule containing molecule. Here, mercury coupling to fluorine appear as satellites on either side. Separation of that if you measure, you will get mercury-fluorine coupling. This is what happened. So, afterwards, another interesting observation I wanted to tell you was the fluorine is very sensitive to isotopic substitution. We took the example of simple molecule, di-fluorobromomethane where just substitution of bromine 79 and 81 gives a small change in the chemical shift position because there will be four different types of isotopomers in that molecule corresponding to bromine both in 79, both in 81 and one 79, other 81 with two such possibilities. We got the statistical distribution of populations, which gives different intensity peaks. Same thing we observed for CFCl_3 . CFCl_3 is a simple molecule. Fluorine NMR should give a single peak, but it gives four peaks of intensity, 100, 95, 30 and 3. And this we could explain the intensity pattern based on the statistical distribution of the populations of different isotopomers of molecule containing different chlorines. Chlorine 35 and chlorine 37 are there. Chlorine 35 is 76 percent abundant. Chlorine 37 is 24 percent abundant. Find out all the possible different isotopomers present and then we could get the information and number of populations of each of the isotopomers and statistical distribution of that gives different chemical shifts and we were able to get all the peaks, we can assign and also the intensity pattern.

Continuing further, today we look at isotopic effect because of deuterium, an another example of a deuterated molecule called vinyl fluoride. We look at this molecule now.



J. Am. Chem. Soc. 1992, 114, 7127

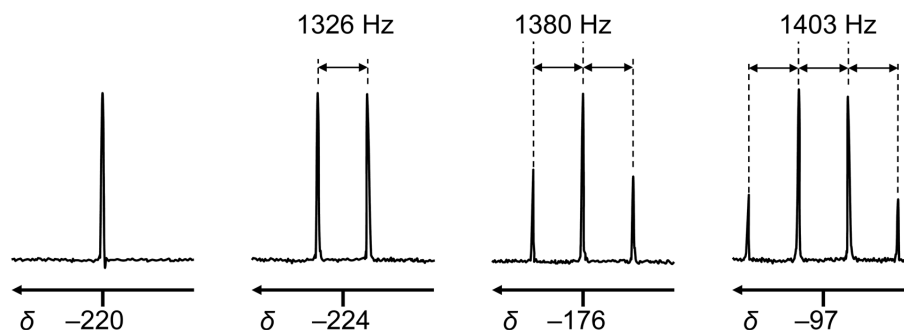
For example, the vinyl fluoride if you take only fluorine without any deuterium substitution, we are going to get a singlet peak. This is a single peak. But there are different deuterated analogs of that. What are the different deuterated analogs? I can show you this is only fluorine. Of course, here proton is being decoupled. And here we have a deuterium in this position. Then fluorine coupled deuterium gives rise to three lines pattern of equal intensity. I showed you like CDCl_3 and the others. When a spin half nucleus is coupled to spin one nucleus, you get three peaks of equal intensity. Again, the deuterium here it is trans to this fluorine, we get three line pattern. Again this is deuterium geminal to this fluorine. Now, of course, there are two deuteriums. Both could be trans, one cis, one geminal, one cis and one geminal, one cis, varieties of possible combinations we can see. If you carefully look at it, you can understand one thing from this spectrum. Remember, when the deuterium is there in the geminal position, the separation is larger. Then, it comes to trans and then comes to cis. What do you understand from that? The J coupling between fluorine and deuterium is larger for geminal coupling, then trans, then cis. It is completely a reverse phenomena or a different phenomena compared to what we observe in protons. In protons, we saw trans coupling is larger, then cis coupling, then geminal coupling. But here, you see, geminal coupling with fluorine and deuterium is larger than trans than cis. This is the phenomena. So, two bond chemical shift also is larger, more for that of the trans three bond chemical shift and this one. Similarly, J coupling, J geminal is larger than J trans, than J cis. So, not only chemical shift, the chemical shift of two bonded is larger than trans three bonded and cis three bond chemical shift. That means, two bond chemical shift means, that is one, which is J geminal. So, geminal chemical shift is larger than trans chemical shift than cis chemical shift. That is what it is. Similarly, we also got the information about J couplings. This idea, we will see how we get the pattern.

Of course, when two deuterium are present, one is trans, other is cis. What is the pattern

we get? First, it is going to be three lines pattern of equal intensity, and each of them is split into three three lines because of second deuterium. If you come to this pattern, of course, geminal coupling, as I said, is larger. That is the first one, large three line pattern and each of these lines is split into three three lines like this. That is the other one. Go to the last one, geminal and trans. Geminal coupling is large and trans coupling is next one. So, this is like this. Each of them will be three three lines, like this. Multiplicity pattern can be very easily assigned. But the only thing is, you see the difference in the chemical shift positions, each of them because of deuterium substitution, whether it is monosubstituted, due to di-deuterium substitution, whether it is cis, trans and geminal makes a lot of difference in not only appearance pattern, but also in the chemical shift positions. That is what I wanted to tell you. Now, from this, we can get J_{FD} coupling, deuterium fluorine coupling. Can we get proton fluorine coupling from this? Of course, remember, I explained to you when I discussed about the magnetical equivalence, HH coupling, I deuterate one of the hydrogen atom, HD coupling you get and we could get HH coupling by using the ratio of the gammas. Exactly here. Now, use this value, ratio of the gammas and then measure the FD coupling, convert that into this one and you are going to get JFH. From measure JFD, you can get JFH. That is what we are going to get for all the cis, trans and other things, JFH can be measured here. That is about fluorine.

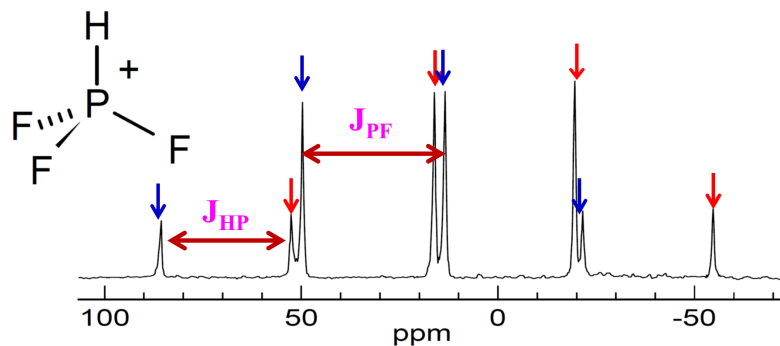
We will continue, keep going, otherwise, we will be stuck with only one nucleus for a long time. Let us look at the second nucleus, that is, phosphorus NMR. Another friendly nucleus, because it is 100 percent abundance, spin half, spin half nuclei is always friendly nuclei for us. Let us see four different types of molecules. Take an example like this.

^{31}P NMR spectra of the phosphorus(III) halides (a) PCl_3 , (b) PFCl_2 , (c) PF_2Cl and (d) PF_3

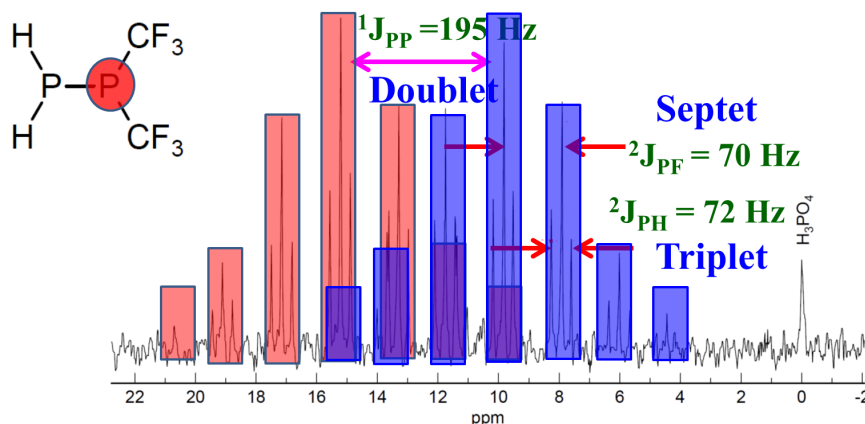


We see the phosphorus NMR of that. Each of them is coupled to fluorine. First one is PCl_3 , no fluorine. Chlorine is a quadrupolar spin. Generally, it would not come, it would not come. Ignore it. Quadrupole coupling is enormously large. It is coupling for this is not seen. The PCl_3 gives a single peak, fine. PFCl_2 gives a doublet, two peaks. PF_2Cl ,

because two fluorine is chemically equivalent, gives a triplet. PF₃, see, slowly, we are removing one chlorine and adding one fluorine. PF₃, three fluorines are chemically equivalent, makes this phosphorus a quartet, four lines of intensity 1331 is a quartet. This is another interesting example.

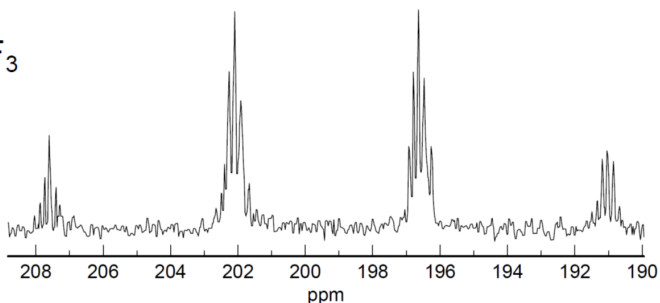
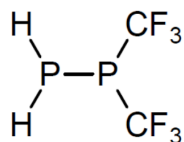


Let us look at the ³¹phosphorus spectrum of this molecule, HPF₃ in CDCl₃. What are the couplings we can see for fluorine and for phosphorus? For phosphorus, there are two couplings. One is phosphorus proton coupling, other is fluorine phosphorus coupling. There are two types JHP and JFP. There are two couplings and JHP coupling is quite large, generally. That will be a doublet, very large coupling. That will be a doublet. Initially, it is going to be a doublet because of JHP coupling and each line is this thing is going to be a quartet like this. Some of the quartet lines are overlapped. It is going to be a quartet. What are these things? We can now identify very easily. This is JPF coupling, three fluorines are present is a quartet. Any two adjacent line of the quartet if you take, it will give you PF coupling. What is the HP coupling here? HP coupling is here. See, this is HP coupling and subsequent lines, you can consider this one. You take these two, this line. That is HP coupling. Again, this to this you take, you get HP coupling. Very easily you can get HP coupling. HP coupling is easily obtainable. It is a doublet and each line of the doublet is a quartet because of this thing. So, this is how you are going to get two quartet, one quartet for one of the doublets of HP, other quartet is for other doublet of the HP coupling. So, this is called quartets of doublet.

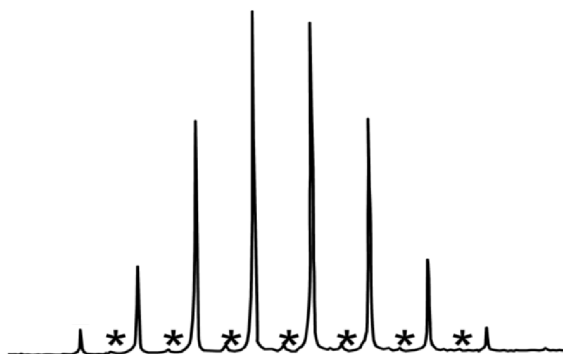


This is a simple molecule. It is not full spectrum. Partial spectrum is shown here, but remember it is proton coupled. It is very explicitly written here. What is the meaning of that? Now, there are two phosphorous. Both are chemically inequivalent. This phosphorous is different. Each of these phosphorous can experience coupling with protons and fluorine. My question is what is this phosphorous? This is a partial spectrum; I mean partial spectrum of the entire ^{31}P spectrum pertaining to only one of the phosphorous. Now, this corresponds to which phosphorous? Very interesting to observe. First of all, you please note this phosphorous can couple to this phosphorous also. They are chemically inequivalent. So, coupling can be there. One bond PP coupling is there and then, two bond HP coupling is there. In addition to that, we have one two bond PF coupling also. If you come to this phosphorous, one bond HP coupling is there, one bond PP coupling is there and one two three bond PF coupling is there. Each of these fluorine can experience different couplings. Looking at the pattern, I would say this correspond to this phosphorous, because for this phosphorous to have coupling to this 3 fluorine, 1 2 3 4 5 bonds away, 4 bonds away to become a quaternaries, very weak, quite unlikely. That is my first guess. So, I would say this is for this phosphorous because this phosphorous can experience direct one bond coupling and two bond coupling and also three bond coupling; all the three can be present here. So, I would say this is this phosphorous and it is a direct one bond PP coupling, which is quite large about approximately 195 hertz. It is a doublet. It gives us a doublet. Then, what will happen? Each of this line is split into a septet like pattern because these two fluorines are equivalent, two CF_3 groups. So, it is like 6 fluorines coupling to this phosphorous, $2NI+1$ we have to apply, 2 into N is equal to 6 into half plus 1. So, it is going to be 7 line pattern. It is going to be a septet pattern. This separation is a septet. Each of this is a septate pattern, 1 2 3 4 5 6 and 7. You can count. There will be 7 such lines. It is a septet and that coupling separation is 70 hertz. That is also fine. And interestingly and each of this septet line is split into a triplet because of this PH_2 protons. So, this phosphorous experience three couplings. PP coupling is a doublet. Then, it is a septet because of two CF_3 groups and it is also each line of the septet is a triplet because of PH_2 group. So, this is one septet of triplets for one of the doublet peak. This is another septet of triplets for another doublet peak. So, the total pattern is doublet of septet of triplets. So, this can happen only for this phosphorous. I hope it is clear for you. Let me repeat. For this phosphorous, this is a one bond coupling. It is a doublet which is here. This peak and this peak, center of that and each of this doublet splits into 7 line pattern and we have to see. There will be overlap. There will be 7 lines from the center, 3 this side, 3 this side. Similarly, for this 3 septets are here, 3 septets are here. This septet is coming because of these two CF_3 groups. That is not all. Each of the septet line is split further by PH_2 group. That is a triplet. So, it is going to be septet of triplets. So, each doublet is going to be septet of triplets. So, there are two such things. As I said, this is one septet of triplets. This is another septet of triplets. There are

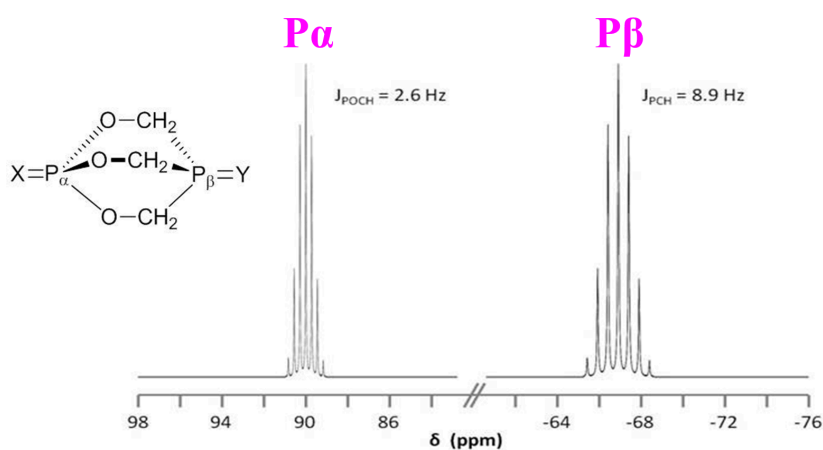
two such septet of triplets. Some of the lines are overlapped here and the total pattern is doublet of septet of triplets. Very easily you can do that.



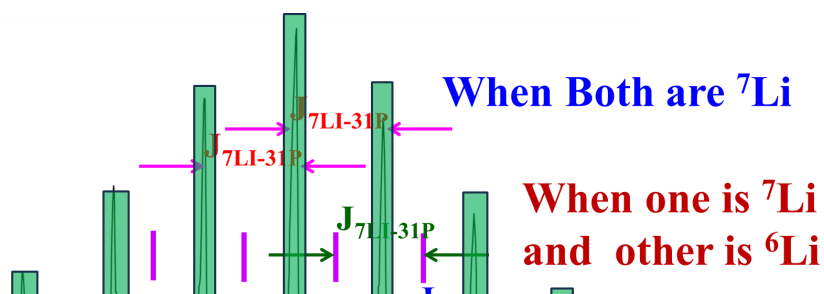
Now, this is the next phosphorous. Obviously, this is the pattern. This is something very interesting. How can we get? This is again some funny pattern here. We will see what it is. Looks like a quartet of some septet of a quintet like that. How do we get that? It is written here. Remember, J_{PH2} and J_{PP} is approximately equal. What is J_{PP} ? Here I saw J_{PP} is 95 Hz. That means, J_{PH2} and J_{PH2} both are of that order. As a consequence, what happens? One will be a doublet and each line of the doublet will be a triplet. Then, it can overlap and gives us a quartet. How? Remember, when we understood the multiplicity pattern, we discussed this at stretch. Look at this one. This is this phosphorous triplet of doublet of septet. Why do we get this one? First, it is a pH coupling. We call it a triplet. Does not matter. Then, each line of the triplet is a doublet because of this. Center lines will overlap and appear like a quartet. Each line of the quadruplet is now split here because of two CF_3 s as a septet. So, it is triplet of doublets of septet. Triplet coupling is slightly larger than this one. Approximately equal, but this is little larger. As a consequence, we have to say first triplet coupling is larger as triplet. Then, each of the triplet is a doublet and each line of this doublet is going to be a septet. So, it is triplet of doublet of septet is a pattern for this phosphorous. You understood? A simple molecule, phosphorous spectrum if you take, there will be two groups, two chemical shifts, one for each phosphorous and the multiplicity pattern is very much different. For one of them, it is going to be a different pattern doublet of triplet of septates. Other is different pattern we saw. So, this is how it is.



We go to the other molecule $\text{PO}(\text{CH}_3)_2$. How many peaks we expect for this molecule? If I do not tell you how many peaks, if you do not read this, simply you can count the number of peaks. You are going to get ten lines because all the nine protons are equivalent. So, $2N + 1$ rule if you apply, 2 into 9 into half plus 1 , it is going to be 10 peaks. Are we getting 10 peaks? See here $1, 2, 3, 4, 5, 6, 7, 8$. Where are other peaks. One is here, one is somewhere here. You do not see it. Very weak in intensity. It is ten line pattern. This separation will give you pH coupling, phosphorous and proton coupling. Then what are these small small lines which are seen here, which is written star here? Remember this phosphorous can also have a coupling with carbon in natural abundance of 1.1 percent. Obviously, that will give satellites and that is what you are seeing. Phosphorous coupled to carbon is appearing as satellites.



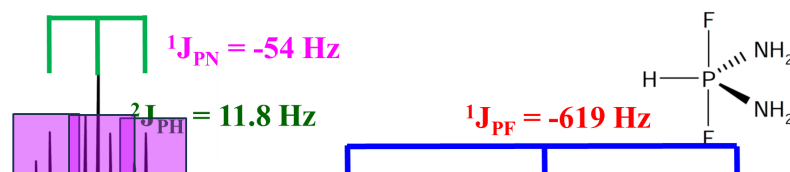
Simple another molecule. Here, only one type of proton is there, three CH_2 s, but there are two phosphorous, P alpha and P beta. See this P alpha can couple all the 6 protons which are equivalent. It will be a seven line pattern from same $2N + 1$ rule and for P beta also, it can couple to all the 6 chemically equivalent protons gives it a seven line pattern, but the coupling strength is slightly different. This is about close to 9 hertz. This is close to 2.5 hertz and very easily you can say why it is seven line pattern because all the CH_2 protons are equivalent 2 into 6 into $\frac{1}{2}$ plus 1 . You get seven line pattern. It is a septet pattern like what we saw in the previous example for CF_3 which we got septet. Exactly, we are getting seven line pattern septet and for two phosphorous, two septets are there and the couplings are different. So, separations are different. Very easily you can even assign this is P beta because this is large coupling, separation is larger. This is P alpha. So, from the coupling, from the separation, you can make the assignment of each of these phosphorous.



So, go to this molecule. This is something very interesting which I wanted to discuss little bit more. This is a molecule where we have phosphorous and lithium both are present. Remember, lithium has two isotopes, lithium 6 and lithium 7. Lithium 7 spin is $3/2$. Lithium 6 is spin 1. We already discussed about boron $3/2$ and boron 3. Here spin is 1, not 3. That is the difference. Lithium 7 spin is 1, when it is coupled to phosphorous, what is the type of spectrum you are going to get? Remember, it is proton completely decoupled. It does not couple to proton. Only we are looking at lithium phosphorous coupling. Carbon is very weak due to natural abundance. Forget it. You will see satellites. So, when you are looking at phosphorous lithium coupling, lithium 7 has abundant 92 percent, quite large. Lithium 6 abundance is 7.4 percent appear like a satellite. One appears like abundant spin coupling, other appears like a satellite peak, which is which? We have to understand. We will see this. There are two possibilities you can think of. One possibility is both the lithium could be 7. That is possibility is there. When both the lithium is 7, what will happen? One lithium splits phosphorous into four lines of equal intensity. That is what we saw for $3/2$ spin. Because spin is $3/2$, we have four lines of equal intensity, 1 1 1 1. What does second lithium do? It will split each of these lines into again 4 lines. From the center I wrote 4 lines. Now, add up the intensity. It is 1 2 3 4 3 2 1 and that is the pattern you should get. When both the lithium are lithium 7, which has spin $3/2$, when it is coupled to phosphorous, you get 7 line pattern of intensity 1 2 3 4 3 2 1. That is exactly what we got here. See here, 7 peaks, 1 2 3 4 3 2 1. This is 7 line pattern coming because of coupling of both the lithiums to phosphorous. When both the lithiums are in lithium 7 spin state, both are lithium 7, then you get this one. So, we could explain strong intensity big in big peaks 7 lines, intensity pattern we explained. When phosphorous coupled to both the flow with lithium in $3/2$ state. Then what about these small small lines? What about the other one? Now, we will try to understand this one. This is very easy. Of course, what is the intensity pattern? When both are lithium, I say 92 percent abundant. Both 92 percent abundant if you multiply 85 percent intensity. So, those intensities are 85 percent and the remaining has to be 15 percent. And you measure the separation there, large intensity 7 line pattern. Any adjacent peak if you measure, you get the coupling between lithium and phosphorous. Lithium 7 and phosphorous to be precise, that is 45 Hz. It has been measured. You

understood the phosphorous. Now, it is coupled to both the lithiums. Both lithiums one could be lithium 7, both other could be lithium 6 and both could be lithium 6 also. Both lithium 6 is you know abundance is very small. In both one is lithium 7, other is lithium 6. What is the probability you can think of? When one is lithium 7, that splits into 4 line patterns equal intensity that we have been discussing because spin 3/2. Now, what is happening? It is also coupled to lithium 6. What is its spin? Its spin is 1. So, when spin is 1, each line is split into 3 lines of equal intensity. That is what we have been explaining, discussing in CDCl₃, everything we discussed. In CDCl₃, we just showed that it deuterium when its coupled to spin one will be 3 lines of equal intensity. So, it will be 3 lines. This will be 3 lines. This will be 3 lines. This will be 3 lines and then, this coupling is only 16.7 hertz. As a consequence, what happens? There will be 12 lines of equal intensity. Most of them do not overlap. This separation is 45 hertz and this is only from here 16 hertz. So, as a consequence, these lines are very well separated. The overlap is not there because you see, one is here, other is here. This is 45 hertz and from here, they have 3 lines of 16 Hz. So, there is no question of crossover or overlap with the other peaks. All 12 lines should be visible. See here, if you see that this is one, both are lithium are 7. Now, we start looking at this peak. Start looking at this one. When one is lithium is 7, other is 6. First, it will be 4 line pattern and each line is split into 3, 3 like this. You see, but unfortunately, some are overlapped and you do not see it. See, of course, I have highlighted this in green, but you see 3 peaks here. If you remove this, you will be clearly see these 3 peaks here, 3 peaks here, 3 here, 3 here. So, all 12 peaks can be easily assigned and this adjacent separation of this gives you lithium 6 to phosphorous coupling. This is lithium 7 to lithium phosphorous coupling. So, we understand this is a simple molecule. Spectrum appears very simple, but you need to use isotopic abundance, spins of different isotopes and get the multiplicity pattern to make the assignment. So, we could easily assign both the peaks coming because of coupling to lithium 6 and lithium 7 with phosphorous. So, this is done very easily. You could do that.

Next, we will go to another simple molecule, very simple molecule. Can you imagine a simple molecule, this phosphorous I am looking, will give enormously complex spectrum, hard to believe right, looking at simple molecule and interestingly, you should also see nitrogen 15 is labeled. What do you mean by labeled? We have made it 100 percent. Otherwise, abundance is 0.37. If it is natural abundance, we do not bother about it. It gives satellite peaks, we do not even see it. It is such a small intensity 0.37 percent abundance. We generally ignore it unless you are specifically interested to see the satellites, enhance the intensity and acquire for a long time; data you have to acquire for several hours to see that, but it is labeled here. So, you should treat it like an abundance like proton and fluorine and phosphorous.



So, nitrogen is also like abundance spin now because of labeling. So, this phosphorous can experience four different couplings. It can experience coupling with proton, it can experience coupling with fluorine, it can experience coupling with this nitrogen, it can also experience coupling with this part, this proton. Four different types of couplings it can experience. Pattern is very difficult to understand even in such a simple molecule. It can experience four different couplings, one heteronuclear, another heteronuclear, another heteronuclear and then another heteronuclear.

So, three different types of heteronuclear couplings are there for this phosphorous. Very interesting example I am giving you. Please understand this one very carefully. Now, we are looking at the phosphorous NMR. This phosphorous can have one heteronuclear coupling, another heteronuclear coupling, another heteronuclear coupling here because of nitrogen labeling and also another heteronuclear coupling like this. Four different heteronuclear couplings and I have given you the values of this approximately, where, analysis has been done. I do not want to measure and keep on spending time to analyze the spectrum for you. One bond pH coupling, this is 836 Hz, very very large, very large; and one bond PF coupling is also large and one bond nitrogen phosphorous coupling that is also quite large 50 Hz and one bond, I am sorry not one bond, two bond pH coupling H2 to this H2 group can couple to phosphorous that is also quite reasonably large about 12 hertz. So, all the four couplings are quite large and reasonable especially one bond coupling is very large and this one bond PF coupling is very large and one bond PN coupling is also very large. Some have a negative sign, do not worry about that.

That we will see later and this is the typical spectrum for the phosphorous. Very interesting, you can see this in the book. I have taken this from the book of inorganic molecular chemistry. Fantastic book, when you read that I saw this very interesting

example I have taken from that. I thank the author for I was able to take the spectrum from that book. So, very interesting example. Look at this, how do we get this multiplicity pattern? Can we explain this? First, let us say this is the chemical shift of phosphorous that is well known. It will always be at the center of the multiplicity. Only a single phosphorous center of this multiplicity is the chemical shift and this is the large separation is a doublet 836 hertz. I will call it as JPH coupling. And from this each of them is coupled to fluorine and it will be a doublet. Please understand this is one doublet. I will say one is here, one is here. This is pH coupling and each of the doublet is further split by fluorine into triplet because there are two fluorines triplet. So, 1:2:1 triplet is there. So, one intensity, two intensity and one intensity is one triplet. This separation gives you FH, FP coupling. This is another triplet. Another triplet is because you look at this one triplet from this one two and one another triplet. You understood the thing. Let me repeat this is one doublet because of phosphorous proton coupling and from the center of this doublet there is a triplet pattern 1:2:1 intensity, one two and one. This center peak anyway will not change the position. That is there only. This is because of P coupling with two equivalent fluorines. Similarly, this also split into a triplet and this coupling is again 619 Hz. So, we got doublet of triplets. Fine. Now, we will explain one of them here. When I explain one of them there is also one PN coupling. This coupling, there are two nitrogens which are equivalent. So, that will split again into a triplet similar to this fluorine. Two nitrogen are splitting each of this line into triplet, we get doublet of triplets. First there was a doublet and each line is a triplet. So, there are six lines here doublet of triplet and each of the six lines here you see one two three four five six lines. Each of the six lines is split into a triplet because of PN coupling. That is one two one triplet. Interestingly, this also coupled to two H₂'s two equivalent protons. There are four protons. Two equivalent protons two, two each. Then each of them is split this into a quintet pattern like this. See two pH coupling it is like this one quintet, one another quintet. There are three such things very interesting. Let me repeat it for you to understand how such a simple molecule can give rise to a complex spectrum. This is center of the chemical shift of phosphorus. It will doublet because of pH coupling. Each line of the doublet is split into a triplet because of PF₂ and each line of this triplet of doublet is split into another triplet because of PN coupling and each line of the triplet is further split into quintet because of two groups of H₂s. So, four protons and that is a quintet. So, this is what it is. So, what is the total pattern? Total pattern is doublet of triplets of triplets of quintets. So, doublet of triplets of triplets of quintet or pentet whatever you call. So, totally how many peaks you get? 90 peaks. A simple molecule one phosphorus spectrum if you take the spectrum without doing any decoupling all of them are coupled you are going to get 90 peaks very complex spectrum. Still we can interpret the multiplicity pattern. So, I think time is getting up. I am going to stop it here.

Today, we discuss a lot about fluorine NMR, phosphorus NMR, lots of examples I took. I could analyze the fluorine spectrum of several molecules. I showed you isotopic effect especially with chlorine substitution CFCl_3 , deuterium substitution of vinyl fluoride molecule with a single monodeuterium substitution, di-deutero substitution in the ortho position in the cis position, geminal position or trans position and how the coupling varies. And I showed you geminal coupling of FD is larger than trans. So, this part we also observed that and we measured the chemical shift also; how the chemical shifts are changing due to isotopic effect, very easily we could see. And I took the example of another molecule you know how different fluorines coupled to different types of fluorine present gave rise to a septate. From the septate separation I could measure coupling and identify the phosphorus. In another example of a molecule like this we have plenty of things phosphorus coupled to proton, 2 equivalent fluorines, 2 equivalent nitrogens and 4 equivalent protons and we got 90 lines and a pattern was doublet of triplet of triplets of quintets, fantastic and if you have the idea of how the pattern comes we can make the assignment. So, this is what I wanted to explain to you. I will stop here already I have taken a lot of time today. We will continue with the discussions in the subsequent classes not only an example of phosphorus and some other heteronuclei also. Thank you very much.