One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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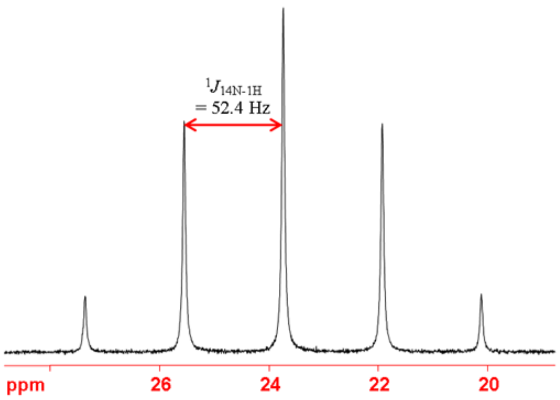
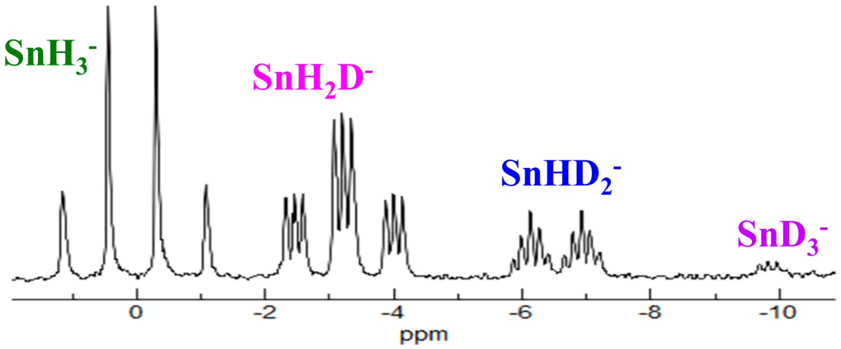
Lecture 31: Analysis of Spectra of Heteronuclei

Welcome all of you, since last 2 3 classes we have been discussing about analysis of the heteronuclear spectra, spectra of varieties of nuclei like fluorine, phosphorus, boron, silicon, mercury, etc. The varieties of examples we took. And we knew how we can extract the couplings, especially for abundant spins like phosphorus, fluorine. How to get the coupling off the abundant spins and from the satellites we could get the coupling between abundant and the rare spins. And then I took the example of boron. We have 2 isotopes boron 10 and boron 11; and boron 11 is going to give you 4 peaks of equal intensity because of spin 3/2. Boron 10 gives 7 peaks of equal intensity when it is coupled to spin half nuclei like, proton carbon or fluorine like that. That is what we observed. And we could get the coupling between boron and proton, fluorine etcetera. Similarly, silicon NMR we took example of couple of molecules we could see 1 bond silicon coupling, 2 bond silicon coupling how the spectrum can be complex. We can get the proton coupled silicon spectrum, proton decoupled spectrum; and we can get when we do proton decoupled silicon spectrum, coupling to other dilute spin like carbon. You could get carbon silicon coupling like that. So, many such examples we took, and we can go ahead with few more nuclei. Of course, there are several isotopes in the NMR periodic table. All the elements and all the examples we cannot take. Few more examples which you routinely come across, I am going to discuss, because all these things when you do bio NMR, in chemical applications and material science we come across these things. So, I am going to take few more examples of some standard nuclei. We will start today with what is called nitrogen-15 NMR and nitrogen-14 NMR. Nitrogen 15, of course, is spin half nucleus, the abundance is 0.37 percent. The nitrogen 14 is spin 1 abundance is large 99.63 percent. So, interestingly this is quadrupolar nucleus, very rarely we are going to get sharp peaks there. But we will see what to do. I am going to look at the ^{14}N spectrum of NH_4Cl.



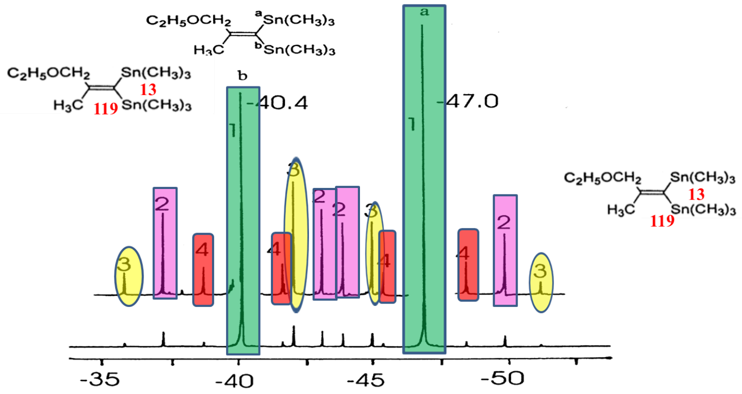
I am looking at 14N NMR coupled to equivalent 4 protons like we saw you know in BH4. What is the type of spectrum you are going to get? 4 protons are equivalent and coupled to spin 1, does not matter whatever the spin of this coupled nuclei, but these are chemically equivalent 4 protons spin half. Then 2 Ni plus 1 if you apply, 4 into half into plus 1. You get 5 peaks, exactly you are going to get 5 peaks. And measure the separation. This is going to give you ^{14}N and ^{1}H coupling. Remember it is one of the rare example, because nitrogen-14 is a quadrupolar spin and you would generally get broad signal. But here is an example. In NMR jargon we call it as AX4 spin system because nitrogen proton are heteronuclei, with 4 equivalent protons we call it as AX4 spin system; and we are looking at A part of AX4. It is going to be a quintet like this; and directly we can measure the separation and get the nitrogen-14 proton coupling.

Of course we can also look for the ^{15}N NMR of a simple molecule like ethylene diamine you see remember taking nitrogen 15 NMR spectrum in natural abundance is a fairly a difficult task because nitrogen 15 abundance is 0.37 percent; very difficult to see that unless you are labeling the system. And also further it has a negative magnetic moment we have to do lot of NOE, etcetera. I will discuss later for enhancing the signal, but usually nitrogen 15, is although the spin half nucleus, is fairly difficult to detect because of its sensitivity. But nevertheless, we can still do it and this is an example of ethylene diamine in CdCl3 and it is a spectrum there are 2 spectra here that given one is proton decoupled other is proton coupled. In the case of proton decoupled you can clearly see we are going to get a single peak because there is a symmetry here there are only 2 nitrogens here, both are chemically equivalent. So, we are going to get a single peak. But how many couplings you can get, if you want to look for the coupling. You can have one bond proton coupling and then this CH2, this is 2 bond and this can also have 3 bond coupling. So, you have 3 different couplings if you look at the proton coupling and there is also proton coupled spectrum given here, and this is a very funny pattern of quintet. Why do you get this quintet? this can happen only when this is also equivalent. These 2 are equivalent couplings, gives triplet of triplet, and so that some of the lines are overlapped. We have we have taken the example of the spectral analysis of the multiplicity pattern, it is triplet of triplet, both the couplings are equal somehow. As a consequence you are going to get a quintet. You ask me a question what happened to one bond coupling? why I am not seeing that? one bond coupling has to be large in this. But in this case one bond coupling is absent due to rapid exchange. Thus we do not see one bond coupling here, we are seeing only 2 bond and 3 bond couplings, which are almost are equal, approximately. A a consequence the proton coupled 15 Nitrogen spectrum is a quintet for this molecule. Of course, usually you know if you look at the nitrogen 15 NMR spectrum they are very simple because in a given molecule hardly there will be few nitrogens, 2 or 3 or 4 nitrogens will be present, unless you go to protein etcetera, where there are too many amino acids present. Then each amino acid has an NH proton, then you will have lot of nitrogens. If you go to a big protein there will be too many nitrogens, but in small organic molecules, simple molecules, like this hardly there will be 2 or 3 nitrogens. So, we have 2 nitrogens in this molecule. This is a proton decoupled NMR spectrum of nitrogen 15. you are going to get only a doublet, very simple you got a doublet, very easy to interpret.



With this now will go to tin NMR. Tin is also another interesting nucleus. Tin has 3 isotopes tin 119; tin 117; and tin 115. All are spin half isotopes. All are NMR active, but only thing is all have negative magnetic moments, similar to nitrogen -15. It does not matter as far as the detection is concerned. Lt us not worry about it at the moment. Tin 115 has very low natural abundance, since it is 0.68 compared to carbon 13 if it is taken as 1. So, practically we can ignore tin 115. We will worry only about sn 119 and sn 117. Bothsn 119 and sn 117 have nearly equal natural abundance, very interesting you see, almost 7.7 and 8.6 take as both have natural abundance of 8. Sensitivity of sn17 is 19.9, about 20. Sn 119 sensitivity is 20.5, take it 26. These are all some information to analyze the tin NMR spectrum. Let us analyze the tin NMR spectrum of $SnH3^-$ and its deuterated analogs in liquid ammonia. You remember, the statement tells me deuterated analogs. I take $SnH3^-$ as my molecule. Its deuterated analogs means we do not know how many deuteration is possible. It can be SnD3, SnH2D, SnHD2, SnH3. All isotopomers are possible. So, this spectrum is a combination of all those things. Now our job is to identify which is which and analyze it. Of course, if you carefully look at it there is a lot of isotopic effect here. You can see that isotopic effect is such that peaks have been shifted quite a bit. Look at this one, this is a taken from the paper Chem comm published in 1987.

First of all SnH3 you consider. How many peaks you expect if you look at a tin NMR. The tin 119 we are looking at. You will get only a quartet because all the 3 protons are chemically equivalent. So, it will be a quartet of intensity 1331. This I would say is $SnH3^-$ without any difficulty. What are the other combinations we can think of? SnD2H. That is also possible. We will see what are the possible combinations? what are the isotopomers we can assign? This I would say SnH2D. Why did I say that? remember these 2 protons split this into a triplet, it is a triplet here. The center of this to center of this, center of this one is 1:2:1 triplet. And each line of this triplet is split because of deuterium which is spin into 3 lines of equal intensity. See you got this. I would clearly say this can be assigned to SnH2D^{-}. Wha about the next one? next one I would say is SnHD2; why? because this is a doublet because of proton coupling. So, tin will split into a doublet and then each line of the doublet is split because 2 equivalent deuterium into a pentad like this 1, 2, 3, 2, 1, which we saw earlier when we saw 2 equivalent deuteriums when it splits spin half nuclei it will make it 1, 2, 3, 2, 1 pentet. That is what you get. This doublet is because of SnH coupling and each of this pentet is coming because of deuterium coupling. So, that is also possible. We could analyze what is the next alternate possible next isotopomer. We can think of or next analog of this molecule next is SnD3^{-}. No proton at all. Then how many peaks you expect for in that? put it into your equation 2NI plus 1. So, I is equal to 1. So, 2 into there are 3 deuterium 6 plus 1. There should be 7 lines. Here all are not resolved, all are not clearly visible, it is a poor signal to noise ratio also. In reality if you get a good spectrum it should give rise to 7 peaks. And I would say this is because of SnD3^{-}. So, all the group of peaks can be easily assigned to different analogs of SnH3. This is sn119 where you get proton tin coupling; and tin deuterium couplings. Both are present here. An example you can see clearly, the isotopic effect on the chemical shift is enormous. This is for H3 and replace one of the protons by a deuterium; and this has shifted by this much. And if you go in the ppm approximately about 3 to 3.2 ppm it has shifted, huge shift in the chemical shift. So, this is because of isotope effect.

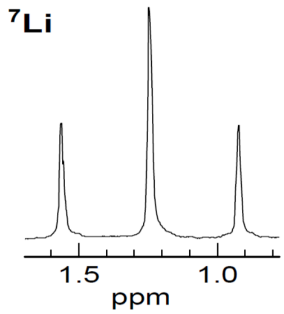


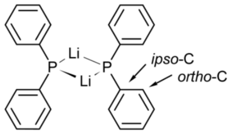
All right we will go to the another example of a molecule tin 119 spectrum of this simple molecule like this. Look at this molecule and every line here is a genuine peak and this group is expanded, this group is expanded here, this group is expanded here. And there are only two tins here they are non equivalent two tins are there and we are getting so many peaks here how do you analyze this? every peak has to be assigned.

So, how do we do that? we will start with the simple example of the analysis of the tin spectra. First these two individual peaks can be there. And possibility one both can be individual for tin two signals for tin 119 in two different environments of A, that is it could be 115. Let us say that will not couple at all; there is no coupling between these two individual spins you get the peaks, there is a possibility. So, both will give individual peaks here and it pertains to two different molecules tin 119, for one when it is A, one it is B. There are two peaks, both the peaks correspond to possibility one for A and one for B and from two different molecules. So, strong peaks, we can assign. There is no coupling with anything else. That is one possibility all other couplings are ignored.

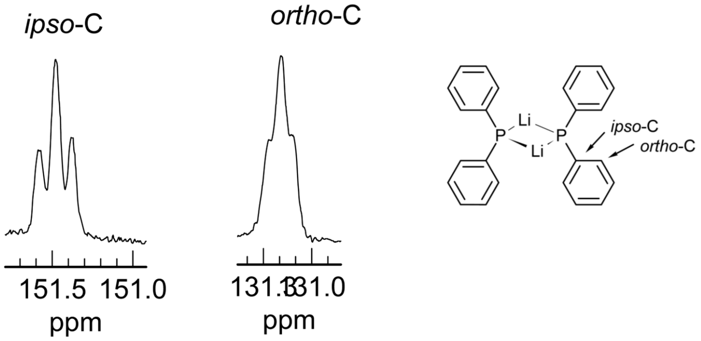
I have already discussed, just because in future for the analysis of this molecule we come across AX spin system. And the AX spin system is there we get two four peaks; two for A and two for X. That we have been discussing. This separation gives you a doublet. It is symmetric you know when A is coupled to X, X is also coupled to A, the interaction is mutual. So, both will be doublets. The separation of the doublets in A or X will give you J coupling between A and X. With this we will consider what is the possibility? There is a possibility molecule contains one Sn 119 other is Sn 117. There are two isotopomers. But remember both of them have abundance, I said 7.6 and 8.26, both of them are almost equally abundant. There could be a coupling between them. We cannot stop that and both of them may have a different resonating frequency, the tin resonating frequency 119 and 117 are far apart, megahertz away. See frequency here it is written they differ by 8.3 MHz and coupling is very small. So, they are weakly coupled AX spin system and at 500 MHz spectrometer the chemical shift is almost 8.3 megahertz separation and coupling between them is very small. So, If I consider both one is 119 other is 117, it forms a coupled AX spin system. Tin 119 can coupled to tin 117, it forms AX spin system. The AX spin system should give two doublets, one doublet for A and doublet for X. In this possibility there are two such possibilities like this. One is this is 119, this is 117 that is one molecule. Other molecule, this is 117 this is 119 that is also possible there are two such possibilities. So, that means two AX spin systems; two AX spin system means how many lines you expect? Eight peaks. 2 you get for tin 119 and 4 you get for tin 119. 4 for tin 117. For each of this AX two lines will be there, for this one from one AX another two lines from other AX. Similarly four lines here for Sn 117 when you detect Sn 117, you get four peaks, but now we are detecting 119. So, of the two AX spin system, four peaks should there and we should be able to see them here. And this is what it is. This already we have assigned, for this possibility I said one is A other is B I have written this is A this is B. So, this is one doublet because of the AX spin system, it has to be doublet one doublet, and other doublet where it is going to be seen? in tin 117 resonance. we are not seeing that 8.3 megahertz away. The other one this possibility is another doublet equal intensity exactly from the center you can see. So, four peaks you have assigned. The remaining four peaks if you want to see, go to tin 117 NMR, fine. So, one doublet is detected for this, other with other thing. What happened to other peaks? Of the four peaks of AX if they are seen, it is in tin 117.

Now what is the possibility three? both can be 119 why we have taken this 117 and this is 119. Why not both can be 119? that is definite possibility. In which case it forms AX spin system. One AX spin system and there exists a coupling between this and this; and only one such possibility. So, this is a molecule with possibility three; both tin could be 119. Now that possibility should give rise to two doublets symmetrically placed for each of these two strong peaks A and B. So, we analyze this, we analyze four doublet peaks here. Now what is left over, is one doublet, this is another doublet, which is coming because of this one. So, we could easily make assignment of these four peaks, the doublets coming because of coupling with a situation where both are tin 119 which forms AX spin system. Gives doublet at the chemical set of both A and X. Another possibility this is Sn 119 this is carbon 13, and this is Sn 119 this is carbon 13. There can be a coupling between them in which case again it again forms two AX spin system; and four sets of doublets you get. Two doublets at 119. And where do you get the other set of two doublets? It is seen in carbon 13 NMR. So, the two doublets are seen each for A and B. And this we assigned, this we have assigned, this we have assigned, and these are the four peaks very weak. So, with that also we could get four peaks; each of them is giving two, two peaks doublets; that is done. Next what happened other set of two doublets they are seen at the 13C resonance. What is the last possibility? not last the fifth possibility. Both could be 117 you do not see that in the tin 119 NMR, because you have to go to tin 117 resonance which is 8.3 megahertz away. Then you will see all those peaks. What is the other possibility? this is Sn 117 this is carbon 13; this is Sn 117 this is carbon 13. That is also possible that you will see again in tin 117, fantastic you see. So, beautiful, a simple molecule each peak can be assigned by looking at varieties of possible isotopomers. You could assign every peak, every peak is genuine.

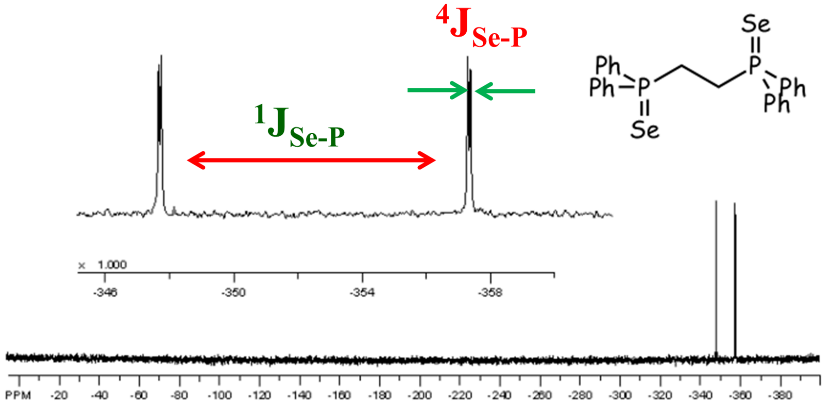




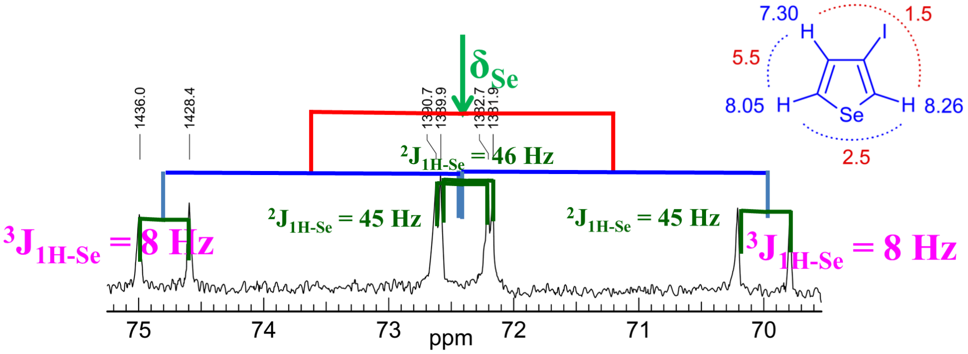
Next, we will go to the example of a lithium NMR. For lithium NMR, consider this molecule. We can see lithium, 31P, 13C all NMR spectra of this molecule lithium diphenylphosphide dimer (Ph2PLi)2. If you look at the lithium NMR, here I am going to get a triplet. Why we are getting a triplet? See lithium is coupled to phosphorus equivalent, both are chemically equivalent, equally coupled to two phosphorus. As a consequence, it is a triplet that we know. When there are two equivalent spins coupled to another spin, it will be a triplet. And this separation gives me lithium phosphorus coupling. Very easy.



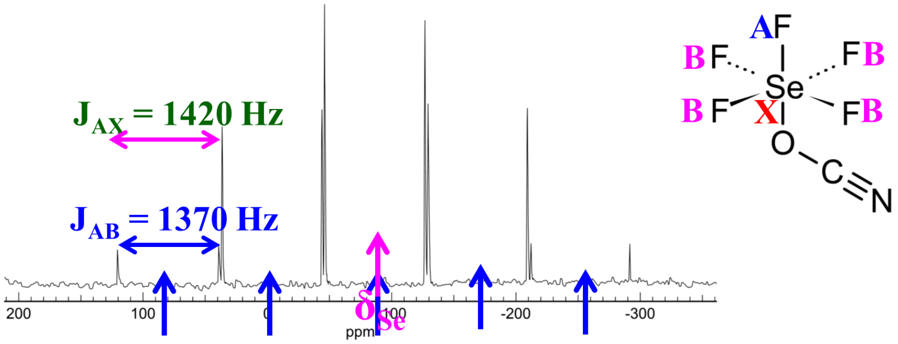
And if I look for the carbon-13 NMR of it with proton decoupling you must get only phosphorus carbon coupling. I am decoupling proton, I am looking at carbon and the two carbons are closeby. One is directly bonded to it, it is a ipsocarbon. Other is this one. These are all far away, other carbons here. So, we will expect at least two carbons; one is ipsocarbon and ortho carbon. Each of them is a triplet. Why? JPP is very large two carbon 13 forms an ABX spin system and coupling between them AB is there and it is called ABX spectrum and we are looking at the X part of AB. So, this is what is happening. As a consequence, each of them is going to be a triplet. The JPP is so large about 200 Hz, as a consequence we get triplet for each of them. And 13C appears as a triplet because of this. Alright and of course, remember we are breaking the coupling between proton and carbon. We are going to get only phosphorus coupling and lithium coupling; both we could see, both of them.



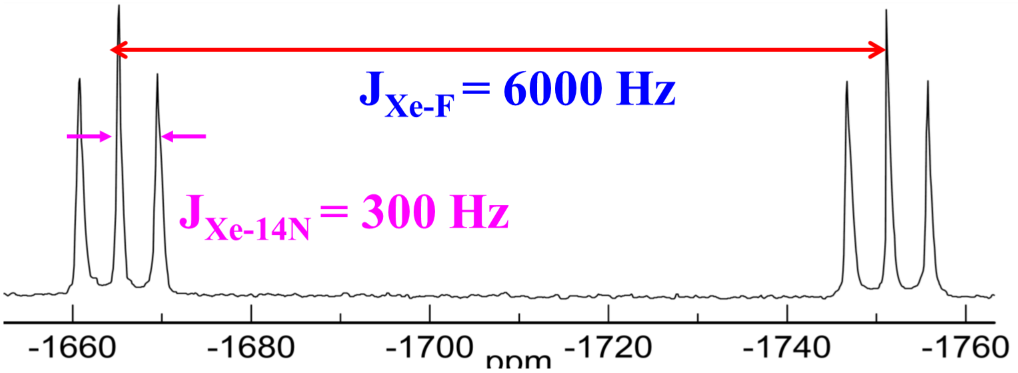
Selenium 77 NMR we can think of. What is the selenium 77 NMR? It is a spin half nuclei, the natural abundance is only 7.6 percent. Let us look at this molecule. How many peaks you can expect for this? It is a very big molecule, this is a big name for it. And we can see one bond selenium phosphorus coupling and we can see 1, 2, 3, 4 bond selenium phosphorus coupling also; both are possible. Simply record the spectrum of it with proton decoupling you are going to get two peaks. What are these two peaks coming from? we can measure them. This is coming because of one bond selenium phosphorus coupling. Why two peaks? actually there is a symmetry. Only one selenium is you have to consider, but there is a phosphorus coupling one bond that makes it a doublet. So, that is why this is a one bond selenium phosphorus coupling. Further there is a multiplicity. Why is it coming? It is coming because of selenium coupling with phosphorus which is four bonds away. And why there are no proton couplings? you have broken the coupling between selenium and proton, the decoupled spectrum, all right. So, as a consequence we see only that.



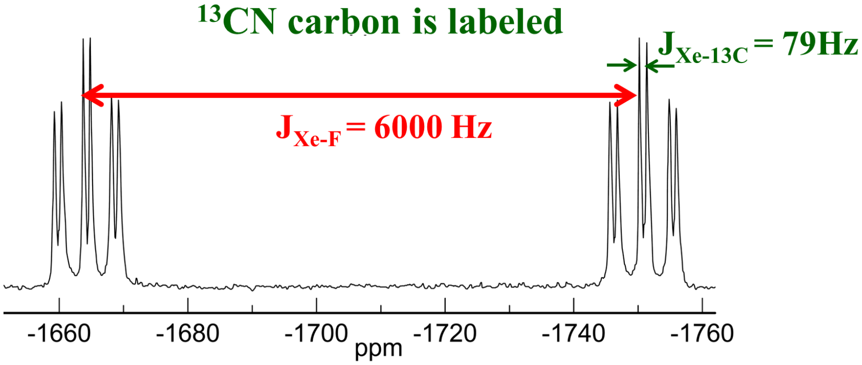
What about the analysis of the selenium spectrum of iodo selenophene. You look at it, it is a simple molecule. We analyzed the proton spectrum of it, if you please remember, when I analyzed the proton spectrum with only one selenium. There is actually two bond selenium proton coupling. It will be a doublet and there is also another proton coupled to selenium. Each line of the doublet is going to be another doublet. So, doublets of doublet and further what is happening is each line of the doublet is split by three bond proton selenium coupling. This is iodine, three bond selenium proton coupling. This you see one doublet, one doublet, one doublet and one doublet. Each of these four lines is split into further doublets doublet. So, it is going to be doublet of doublet of doublets ddd. We are going to get eight line pattern. From the separations you can measure one bond selenium proton coupling, and three bond selenium proton coupling.



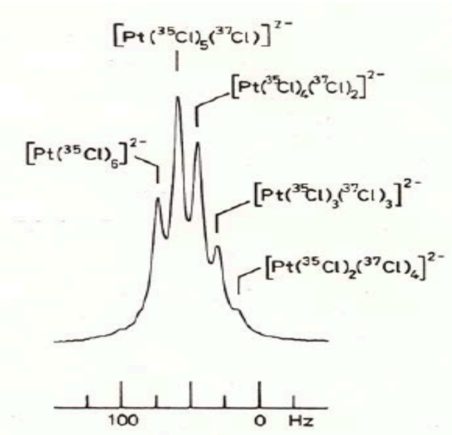
And similarly we can look at the selenium NMR of this molecule; what is that you are going to get if you look at the selenium NMR of this molecule? see this is the structure. It is what is called AXB4 spin system we are looking at the selenium X part of it. This is a differnet fluorine. These four fluorines are equivalent. These four equivalent fluorines split it into a quintet and then each like the quintet is split into doublets because of this coupling. Please understand, we are looking at the selenium. These four equivalent fluorines split this into a quintet and then each line of the quintet is split into another doublet because of coupling with another fluorine and this how it is. This is a quintet of doublets. I say quintet because this coupling is larger, you see JXP is larger than this. We always have to take the larger coupling. So this how it is. This is the center and then this is one peak, and other peak coming because of this. From the center there is going to be 5 peak pentet and each of this is split into a doublet like this you see. Ss a consequence it is going to be pentet of doublets and this separation gives you this coupling.

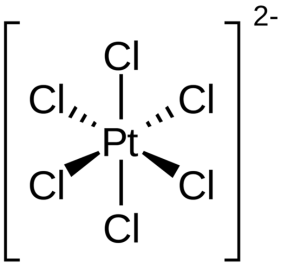


Of course, you can also use xenon NMR. Xenon-131 has spin 3/2; and the abundance is 21 percent; xenon 129 spin is half, its natural abundance is 26.4 percent. There are 7 other isotopes we do not need to worry, but look at this xenon NMR spectrum of [CH3CN-Xe-F]$^+$AsF6$^-$. The one bond xenon fluorine coupling is there. The xenon is directly bonded to fluorine. This is spin half nucleus. The xenon 129 if you do, it is going to be 6000 Hz coupling. You see large coupling, and each of them is further split because of nitrogen-14 coupling of intensity 1:1:1. So this is xenon-14 nitrogen coupling of 300 Hz.

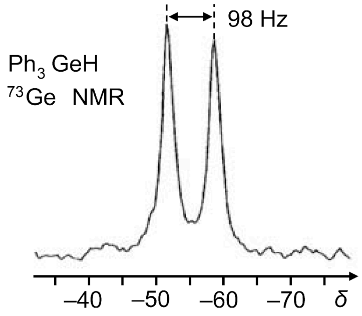


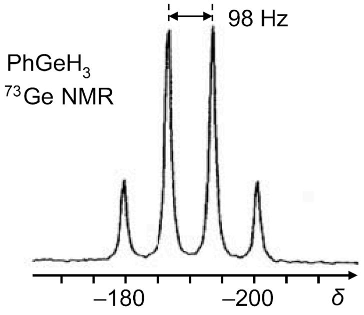
And in case what happens, interestingly if you are going to label the system, carbon 13 is labeled. Then in which case what will happen this xenon coupling is there. This is xenon-14N coupling. And each each line of this triplet of triplet a doublet of 3 lines of equal intensity. 3 triplet is further split into doublets because of carbon coupling. See this is 6000 hertz 300 hertz this is 79 Hz. And this is what the pattern you are going to get. And if you look at the nitrogen 14 NMR of this molecule it is very broad because of nitrogen 14 relaxation. All these things do happen.





Of course this is a platinum NMR, similarly you can do that, there is no issue. [PtCl6]2-if you look at it, due to chlorine it has different types of isotopomers like we saw in PCl3. Varieties of isotopomers are present. Each of them is going to give you a peak. This is the situation where all chlorine are 35, one is 35 others of 37, like that all isotopomers you can consider for this molecule. And you get different peaks 5 to 6 peaks all peaks intensity can be calculated based on the population of the distribution of the different types of isotopomers. Same thing you can do for bromine. That means when halogens are substituted, this type of isotopic effect is going to be dominant.





And the last example is germanium NMR. Its spin is 9/2 and when it is coupled to proton germanium is going to be doublet. This is the spectrum of Ph$_3$GeH and PhGeH$_3$; it is 73Ge spectrum. Obviously it is a doublet because of Ge-H coupling. I am not worried about the pH_3 part if it. We take GeH$_3$. It has to be a quartet we got it. Ph part we are not worried about the coupling, that is far away. So, this is germanium spectrum, spin is 9/2. Quadrupolar spin coupled to spin half nucleus, and we can analyze that and get the coupling from this. This is a germanium proton coupling of 98 Hz; about 100 close to 98 hertz. So, this how we can analyze germanium NMR. We saw xenon NMR etcetera lot of examples we took today. So, in summary I told you today in this class we have taken several examples of different nuclei like selenium, xenon, platinum and germanium, etc. Various examples we took, and we also looked at nitrogen 15, nitrogen 14 NMR several examples we took and we could easily assign the peaks, based on the multiplicity pattern and get all the coupling information. So, with this I have given you fair idea about analysis of the spectra of varieties of heteronuclei, which you commonly come across in material chemistry, biochemistry, in biological studies, bio NMR or simple organic chemistry, organic molecules where you could think of proton, carbon, nitrogen 15, phosphorus, fluorine, varieties of nuclei. So, at least you got a fair idea when you have a different nuclei spin half coupled to spin half; spin half coupled to spin one, the quartipolar spin, when you detect in the quadrupolar spin which is coupled to spin half, or which is coupled to spin one or other quadrupolar spin what is the pattern you are going to get, and how you can interpret it. Looking at the pattern how we can get the couplings and we saw over the period the coupling strengths could be enormous in for example, xenon, xenon-proton coupling was 6000 Hz. The coupling strength can be different, enormously different. It could be few Hz to several thousands of Hz. So, all those things we observed, when we studied different nuclei. So, I thin you got the fair idea about analysis of not only proton spectra, carbon spectra, also varieties of abundant and dilute spins, both spin half and quacdupolar spin. So, further we can continue,but lot of nuclei are there, lot of isotopes are there, which we can continue and do it. Yhere is no issue for that. But I cannot keep on covering all the nuclei, I took several examples already. I am going to stop here. From the next class we will go to a completely different topic. Thank you very much.