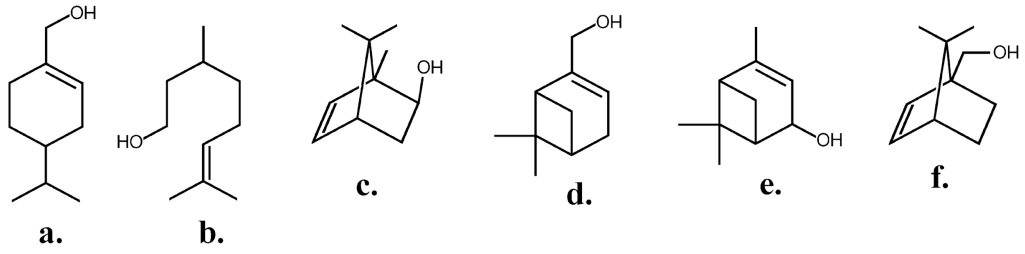
One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
Prof. N. Suryaprakash

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

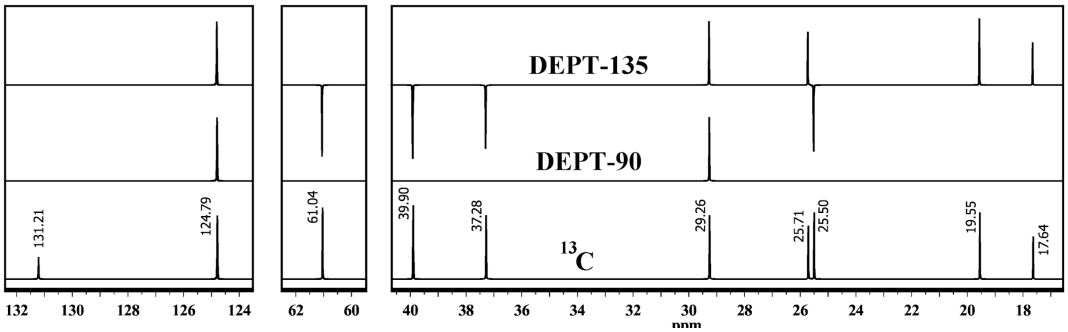
Lecture 28: Analysis of 19F spectra

Welcome all of you. In the last class, we did discuss extensively and we analyzed the carbon 13 NMR spectra. I took lot of examples, where we could analyze the spectrum based on the chemical shift and coupling information. And I showed you the spectrum of carbon 13 coupled with the heteronucleic, abundant spins like, phosphorus, fluorine, etcetera. And we could clearly see the multiplicity patterns, in several of the examples we took,the CH3 group coupled to carbon will be a quartet and then we have 2 bond couplings, 3 bond couplings, like that. And we were able to assign most of the peaks. When you are directly detecting the carbon, the question of dilute spin does not arise at all, that is what I have been telling you. So, in the spectrum, the analysis of the spectrum directly gives you coupling of carbon 13 with abundant spins. What happens if there are dilute spins in the molecule apart from abundant spins? For example, selenium, silicon like that. But you are detecting carbon; that itself is the dilute spin, but when you are detecting that, do not worry about that dilute spin. The other dilute spin can appear as a satellite for this. This is a very interesting example. We took this as an example with tin and I took the example and showed how the satellites of the tin gets reflected, especially tin 117 and 119, 2 tin isotopes give rise to satellites with 2 different coupling strengths. And intensity was approximately equal, corresponding to their abundance of 7 or 8 percent; both of them are nearly equal to 7.8 and 8.4 of that order. So, intensity also agreed. You are able to get the heteronuclear coupling from the satellite spectrum, that is fine. And when we have a complex multiplicity pattern, identification of the carbon even after decoupling protons is a difficult job. Even though you simplify the spectrum by decoupling, but still, how do you assign which carbon is which, like whether the CH3 carbon, CH2 carbon, CH carbon and quaternary carbon, how do you make their assignment? Of course, you have to break the coupling and still assign. Otherwise, you know if there is a coupling, CH3 is a quartet, CH2 is a triplet like that. In spite of complexity, somehow we can work, with enormous difficulty. We can identify at least to some extent. But here, decoupling is there. Removing the carbon-proton coupling, still we have to assign the carbons based on the attachment of protons to different carbons. How many number of carbons are CH3, CH2, CH like that, how do we do that? For that, I said DEPT experiment. DEPT is a simple pulse sequence, where the carbon 13 has 2 pulses on the carbon 13 channel. Proton has 3 pulses. The last pulse on the proton is a flip angle pulse. I said with that flip angle of the pulse, we can do 3 experiments, 45, 90 and

135 degree flip angles. When it is DEPT 90, only CHs will be there, all positive. In DEPT 135, CH and CH3 are positive, CH2s are negative. In the conventional spectrum, all carbons will be present. So, with combination of all these things, you can see identify which carbon is which. Very fairly, it is easy to do that. And I showed the example in a complex molecule like cholesterol, how DEPT experiment helps us in identifying the carbons based on the number of protons attached to it. That is what we did. Going further, I also said using carbon 13 NMR, we can even make the structural assignment of some molecules. We took an example of one molecule and showed how based on the number of carbons, with observed coupling with fluorine, we could even get the structure of the molecule. That was easy. Can we extend it further, the DEPT? I will give another one important application of DEPT. How we can utilize DEPT to get the structure of the molecules? Here, I am taking example of two monoterpenes, identifying the correct structure of monoterpenes is our challenge. Let us see what we do. The challenge is, I have to use the DEPT experiment to identify the correct structure of these things.



There are about 6 molecules, all are monoterpenes. We want to find out what is the correct structure of it by using DEPT experiment. And DEPT experiment was done for this thing. It is a conventional carbon 13 experiment. This is DEPT 90 and DEPT 135.

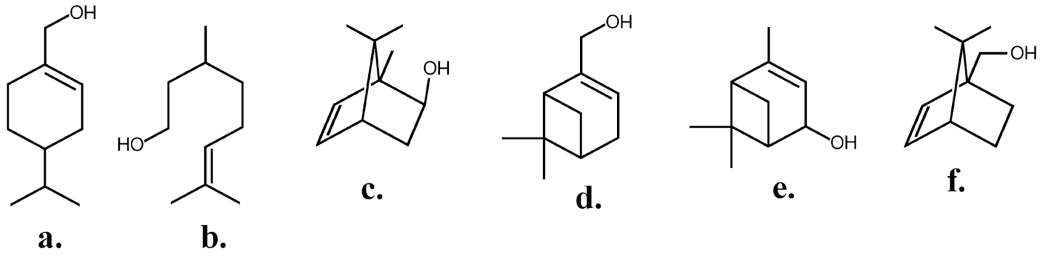


Already, I told you DEPT 90 gives you only CH positive, and DEPT 135 shows you CH and CH3 are positive, CH2 are negative. Just look at it and then, leftover peaks are the quaternary, can be identified from the conventional NMR spectrum.

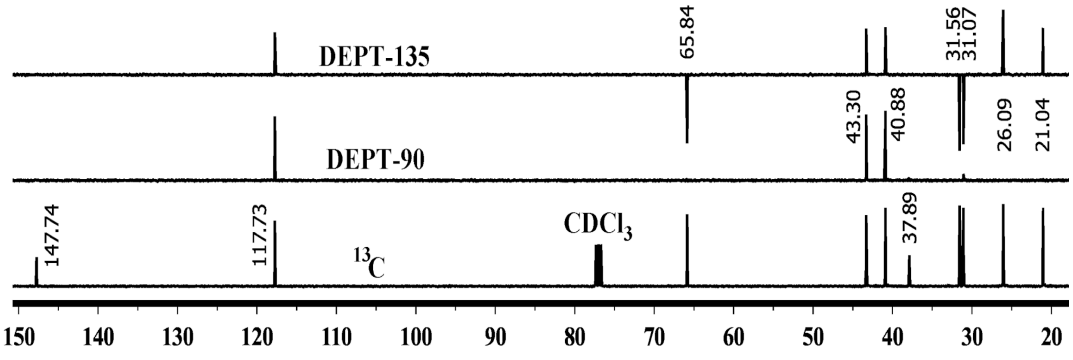
We can easily identify. Look at it. There are 2 CH3s which are positive, CH3 has 2 peaks, which are positive here. And, CH2, if you look at it, 1, 2, 3, 4 CH2s, because of negative

intensity in DEPT 135, I know these are CH2s. And, if you look at the CHs, we have 1, 2 and 3 CH peaks. And, from the conventional carbon 13 spectrum, there is only one peak which is left here. That is a quaternary carbon. I know quaternary carbon is 1.

There are 2 CHs, 2 CH3s and 4 CH2s and 3 CHs. This is what the conclusion I draw from the DEPT experiment. Now, our job is to identify which of these terpenes coreesponds to this, from the DEPT spectrum, that is it corresponds, which of these terpenes. If I know that, I can identify the correct structure. Using this information, we will go further. Now, if you go further, our job is to identify the molecule 2 CH peaks, CH3 peaks and 4 CH2 peaks. All these things we have to identify. Look at the molecule 1 here. Here, you have 3 CH2s. See what is highlighted here. But, what we require is 4 CH2. So, that is not the structure. Look at this one. Again, 3 CH3s. That is not our structure. Go to the next one. 3 CH2s. That is also not our structure. Because, here we needed 2 CH3s. Here, we needed 4 CH2s. Come back to this one, 3 CH3s. That is also not our structure because experiment shows only 2. Come to this, again, 3 CH3s ruled out. That is not our structure. And, come to this. You have 2 CH3s, 4 CH2s, 3 CHs, Perfect. That means, from the DEBT experiment, I can conclusively say, this is the structure of this monoturpene.



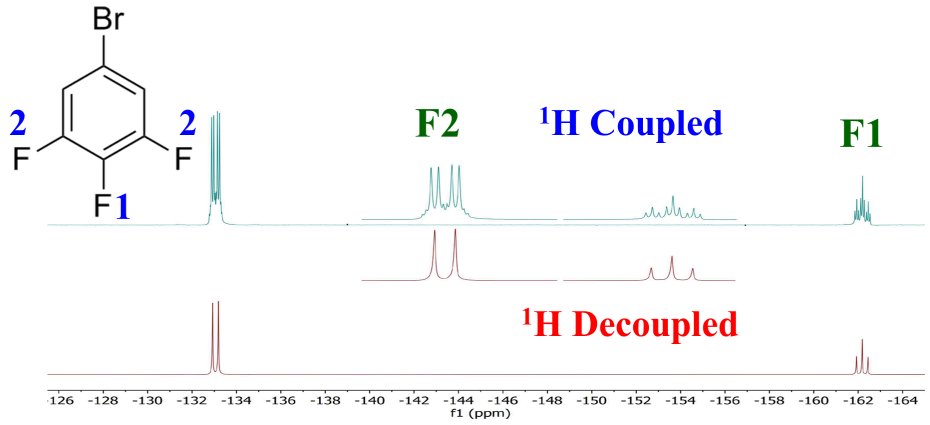
Go further. Another experiment has been done, DEPT experiment, where you can see here, 2 CH3 peaks you can see and 3 CH2 peaks, 3 CH peaks and 2 quaternary peaks here and here. From the normal carbon 13 spectrum, you see 2 quaternary peaks and 2 CH3 peaks, 3 CH2 and 3 CH peaks. This is what we have observed from the DEPT experiment, DEBT-90 and DEBT-135 and the combination of normal carbon 13 NMR.



What is the possible structure now? We will try to analyze this one. Of course, there are 4 CH2s that is ruled out because according to that, we need to get only 3 CH2s. So, that is ruled out. What about this? This is 4 CH2. That is also ruled out. This one, 3 CH3. That is ruled out because we wanted only 2 Ca3s. That is also. Look at this one. This is 3 CH3. That is ruled out. This is also ruled out. Finally, what is left with this molecule is 2 CH3, 3 CH2, 3 CHs and 2 quaternary. That must be the structure of the molecule. So, using the DEPT experiment, from the carbon 13 very easily, we can even make the assignment and get the correct structure of small molecules like this.

I showed you two examples of terpenes. Very interesting examples, taken from the book of Niels Jacobsen. So, it is a very good example. I think with this, I have covered quite a bit about carbon 13 NMR. About 3 or 4 classes, we discussed at stretch and I showed several examples, several applications of carbon 13 NMR, DEPT experiment, problems we encountered in the experiment, If we are mistuning the 90 degree or j coupling is not correct; and also how we can utilize DEPT experimental information to get the correct structure of small molecule like this. So, with this fairly large enough information I have given you on carbon 13. we will continue further with the analysis of the spectrum of different heteronuclei. I took extensively large time, long time for carbon 13 because it is another extensively used nuclei apart from proton. Other heteronuclei, you know some of these are used, know in our chemistry, material chemistry, etcetera, but not extensively used like proton and carbon. Nevertheless, we can analyze lot of such heteronuclei NMR spectra and get something, some information from these things.

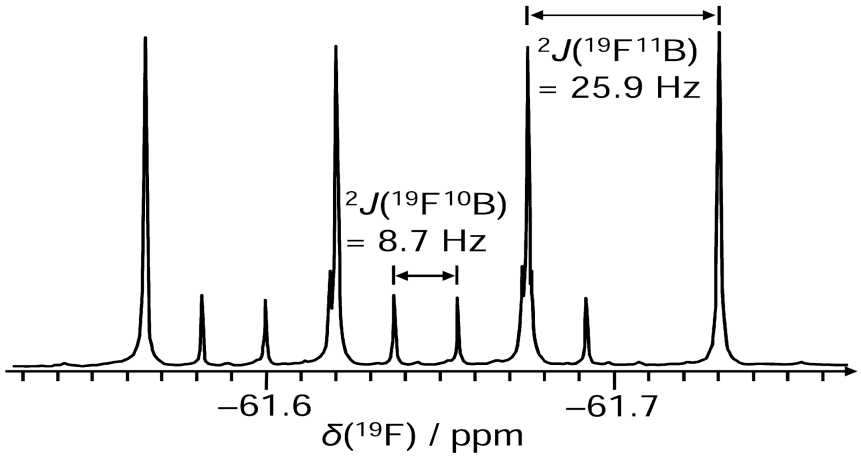
We will start with the analysis of 1D spectra of selected heteronucleic. We start with the fluorine NMR. Of course, fluorine is 100 percent abundant, spin half nuclei, very friendly nucleus like proton. Spin half nuclei are always friendly nuclei, very easy to get the spectra and easily understandable. Further it has 100 percent abundance. So, experimental spectrum we can obtain very fast without much difficulty.



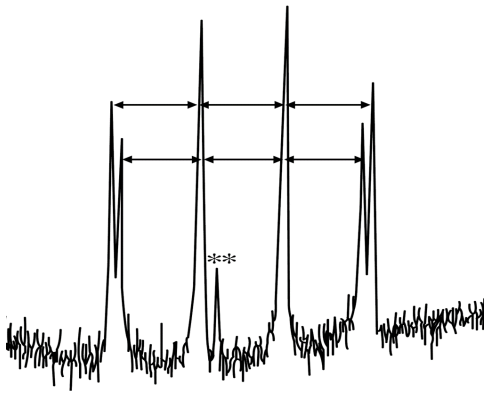
This is a fluorine 19 NMR spectrum of the molecule C6F3H2Br. Now, we have to make the assignment of fluorine. How do you make the assignment of fluorine? I would clearly say this is the fluorine 1 and this is fluorine 2. Why? Remember, I explained to you about the multiplicity pattern you get in the phenyl protons. Now, if you look at this fluorine and this fluorine, there is a chemical equivalence, but this couples with this fluorine equally because one ortho coupling of this fluorine to this fluorine and this fluorine to this fluorine is identical. It gives rise to a triplet like pattern, doublet of doublet, two center lines overlapped. It is going to be a triplet. At the same time, we also have the coupling because of two remaining protons here. They are also chemically equivalent. These two protons are also chemical equivalent. They will split this fluorine equally. Then, it is going to be triplet of triplet. Again, each line of the triplet is further split into triplet because of protons. So, this fluorine experiences fluorine fluorine coupling and also fluorine proton coupling. Coming to this fluorine 2, interestingly, they are chemically equivalent. You can split with one of these fluorine, become a doublet. Similarly, it can split with another proton and it can become a doublet. So, this fluorine 2 has to be doublet of a doublet. Exactly, look at this. So, I can make assignment. This is fluorine 1 and this is fluorine 2. To confirm further, we can do one more thing. We can decouple protons, observe fluorine. What will happen? All FH couplings are removed. Only FF couplings are retained and when we do that, this is a proton coupled spectrum and this is a proton decoupled spectrum. When you decouple proton, all FH couplings are removed. These are only FF couplings retained. FH coupling is removed and FF couplings are retained here. So, very simply, you can see this multiplicity. Triplet is because of this fluorine coupling to these two equally and these two fluorines become a doublet. So, very easily, you can identify. I showed you the advantage of decoupling of the heteronuclei when you are seeing such type of spectra. If there is a complexity, you can do selective decoupling or broad bond decoupling of the heteronuclei.

What happens if there is a coupling to other nuclei like boron? Boron has two isotopes, spin 3 and spin 3/2 and abundance is approximately 20 : 80. Abundance of Boron 10 is 20, and that of boron 11 is 80. Boron 11 has spin 3/2, boron 10 has spin 3. When it coupled to spin half nuclei, what will happen? Boron 10, when it is coupled to a spin half nuclei, let us say, 1 nuclei spin half, 2 into half plus 1, it is going to be 2 into 2; 4. Of course, we have only 1 spin, 1 boron we are taking into account. 2 into 1 into 3 plus 1 is going to be 7 lines. Go to boron 11, n is 1, I is equal to 3/2, 3 by 2 into 2, it will become 3 plus 1, 4. So, if any of the spin half nuclei like fluorine is coupled to boron 11, it gives 4 lines. If it is coupled to boron 10, it should give 7 lines of equal intensities. 7 lines are of equal intensity and 4 lines are of equal intensity. But the intensity ratio between these will be 1: 4 because abundance is 20 and 80. If both the boron isotopes are present, then what will happen? You have coupling because of both boron 10 and boron 11, one gives you 4

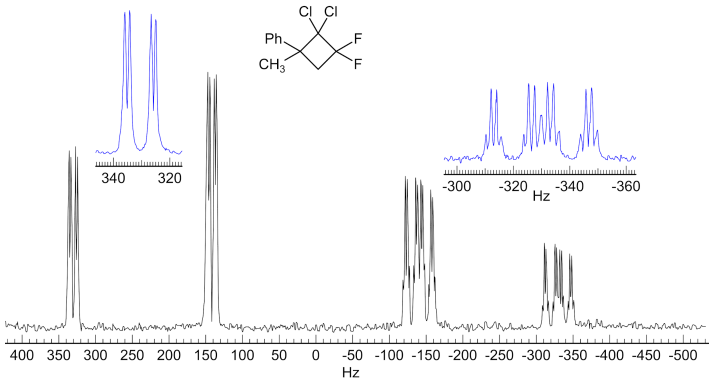
lines, other gives you 7 lines. See, this is exactly what happens. This is NaBF4 molecule in D2O. Now, boron spin 3/2, it is going to give 4 lines. Abundance is 80 percent, boron spin is 3, it gives 7 line pattern. Intensity ratio is 1:4. And the separation of this gives you boron 11 fluorine coupling. This boron 10 fluorine coupling you are going to get. And this coupling is quite large compared to this one. Very easily, you can analyze coupling of quadrupolar nuclei to fluorine. And this is information you will get. Center of this to center of this gives you what is called isotopic shift. When the boron isotopic change from 10 to 11, see this is the shift you are going to see. Always, I told yesterday also, heavy isotope always shift the chemical shift to the higher field.



Another molecule, fluorine NMR, again boron coupling. Here, it is a potassium bromine CF3 4 times, K[B(CF3)4]. Now, we are looking at the fluorine. So, it does not matter. What we have to worry about is the coupling with boron. Now, for boron, as I said, there are 2 isotopes, boron spin 3/2 gives 4 lines of equal intensity. And then, boron 10 couples to fluorine gives 7 lines of equal intensity. So, intensity ratio is 1:4 between this and this. And this separation gives you boron 11 fluorine coupling and say adjacent separation of any of these 2 peaks gives you boron 10 and fluorine coupling. Very easily, you can do that.

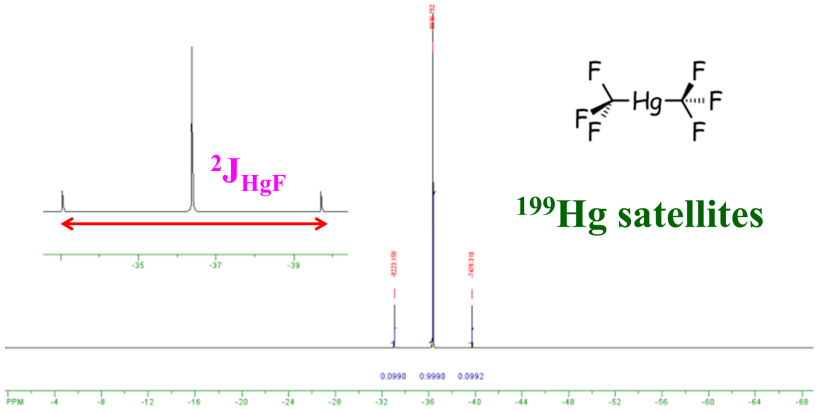


Of course, we can also have a bromine. There it is boron. Now, it is bromine. Bromine has 2 isotopes, Bromine 79 and Bromine 81. And interestingly, both of them are almost of nearly equal abundance 49.5 and 50.5 like that. And both are spin 3/2 nuclei. Now, in this case, what will happen? You will get 4 lines of equal intensity and both of them will give 4 lines. Bromine 79 and bromine 81 will split fluorine into 4 lines of equal intensity. And equally, not only equal intensity among these four lines, also between bromine 79 and bromine 81 peaks. So, this is what is happening. And now, we are going to see 4 lines here, strong 4 lines. This is one bond J coupling of bromine 81 fluorine. This is one bond J coupling of bromine 79 and fluorine. Small change in the coupling is there, 1695 Hz and 1570, Hz. There is some difference. And usually, this type of broadening is not observed. It is very broad because of bromine. So, it appears as if we are not resolving peaks here, but there are peaks, which is not completely resolved. So, you can get all the coupling information very easily.



Go further. Now, let us look at the fluorine spectrum of a molecule like this. And this has two possible conformations. This conformation could be like this. When the conformation is like this, there are two fluorines. Interestingly, we have a fluorine-fluorine coupling here. That is quite large. Fluorine-fluorine coupling is quite large. And it gives us a doublet. And there are two fluorine with a two different chemical shifst. This is F 1 and F 2. And each of them will be a doublet because of large separation is because of FF coupling. This fluorine splits this into a doublet first. This also splits into a doublet. Further, if you go to the fluorine 1, fluorine 1 experiences three different types of couplings. One is FF coupling. Other is this fluorine 1 can a couple to this proton and also to other proton. So, it experiences two different couplings. Both are single protons, as a consequence, this is going to be one doublet because of fluorine and other doublet of doublet because of two other protons, which is 3 bond coupling. $^{3}J_{FH}$ couplings are there. Two $^{3}J_{FH}$ couplings of almost nearly equal strength. Small difference is there. So, as a consequence, large doublet is because of FF coupling and doublet of doublet is because of two FH couplings, which is slightly differing in the strengths. Let

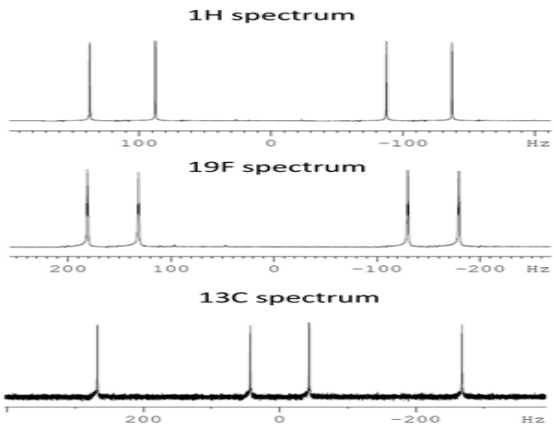
us come to this one. This fluorine 2 is very interesting. This has a large coupling because of fluorine doublet, but each of them has two couplings because of $^{3}J_{FH}$. Like here, 3 bond proton fluorine couplings are there, two of them. So, each of them will split into a doublet. So, it is like here doublet of doublet. Further, interestingly, this fluorine also coupled to the CH3. 5 bond coupling is there and that 5 bond coupling because of CH3, 3 chemically equivalent protons. Each line of this doublet of doublet is going to be a quartet. So, what is the pattern you get for the fluorine 2? The pattern what you are going to get, first it will split into a doublet, and each line of the doublet is split into doublet of doublets because of two $^{3}J_{FH}$ couplings and each line of this 4 line pattern, doublet of doublets and also this 4 line pattern, will be a quartet because of 5 bond coupling with CH3 protons and fluorine. So, it is going to be the pattern you are going to get. Largest coupling is doublet, doublet of doublet of doublet of quartets. So, this is doublet of doublet of doublet, ddd pattern. Here, this is dddq and this is what the pattern is. Of course, when you are looking for the fluorine NMR, also you can get the satellites, carbon satellites. When I observe proton, I saw carbon 13 satellites. Now, fluorine is also 100 percent abundant spin, any other dilute spins coupled to it will give satellites.



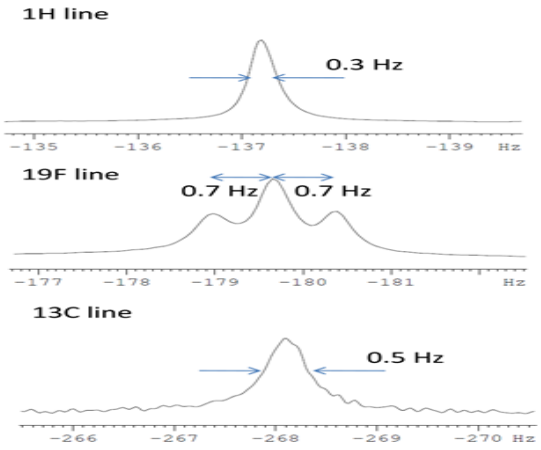
Exactly, if I take the molecule like this, this fluorine NMR gives a single peak, but this mercury, couples to these fluorines equally because there is a symmetry. As a consequence, you see on either side of this, two peaks. This is the expanded version here. You can see and interestingly, this mercury abundance is about approximately 16 percent or so. As a consequence, very strong intensity satellites you are going to see. The intensity of the satellites can give you a rough idea about the abundance. This compared to carbon is quite large, and we know this abundance of mercury is about 16 percent. That is what it is, and we can get from the satellite spectrum and this separation if you measure, you will get mercury fluorine couplings. You understand? From the satellite spectrum you can get for fluorine, similar to proton where dilute spins give rise to satellites. And measuring the separation gives you j coupling between fluorine and the

dilute spin. With this, we will go to another interesting topic called isotopic effect. This you must remember because whenever you have to do fluorine NMR, be careful. Fluorine is a very very interesting nucleus. Its chemical shift is very very sensitive to isotope effects. Replace, for example, proton by deuterium, the effect is seen. We already saw that. Similar to that, in the case of fluorine chemical shifts, the isotopic effects will be dominated. We will see an example like this. Whenever you have to analyze the fluorine spectrum, you have to be extremely careful.

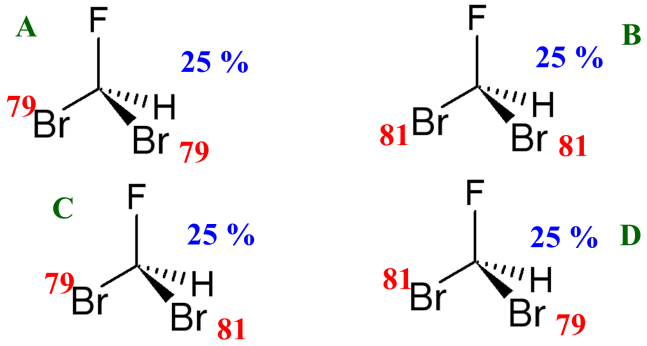
Look at this carbon 13 labeled bromofluoromethane. This carbon is 13 labeled here. So, there are three abundant spins, proton and fluorine and carbon which is labeled. So, it is also abundant 100 percent we can say. So, these are all three heteronuclear weakly coupled AMX spin system.



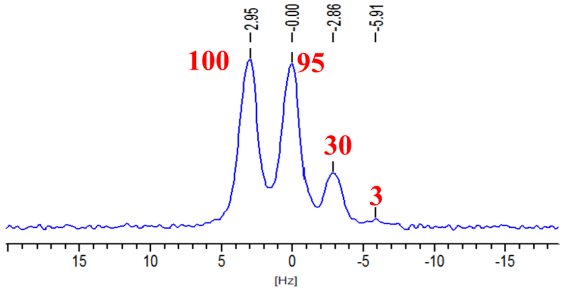
This is the proton spectrum. If I analyze this, I will get JCH and JFH, and this CF is a passive coupling. All those things we have discussed and here also, proton spectrum JCH we do not get, other two couplings we get. If you go to proton 13 spectrum, we get JCH and JCF, JHF we do not get, that is a passive coupling. This we have been discussing quite a bit. That is also not an interesting thing.



What is interesting thing is, the expansion of one of the peaks here. Any one of these peaks, we have expanded for all the three. And it is a fairly a very good spectrum, very good line width. If you carefully see, proton is a very very sharp line, single line and line width is 0.3 hertz. Similarly, for carbon also. Whereas look at this fluorine, it appears like a triplet. Where is this triplet coming from? Why fluorine peak is a triplet? But it is a genuine peak. There is no other way protons or anything for it to couple to give a triplet. Usually, we say if it is coupled to CH2, some other CH2 or CF2 group, we can say it is a triplet. But there is no such thing here. Then why fluorine 19 peak is a triplet? We will understand that. For that, we have to go into what is called isotope effects. Bromine 79 and bromine 81 and both has been 3/2. Both have a natural abundance of equally, 49.5, 50.5, I will say 50:50. Both of have equal abundance. Both are spin 3/2. That is what I told you when I analyzed the bromine coupling to fluorine in the previous example. Let us see what are the isotope elements present in this molecule.



One thing is, both the bromine could be 79. There are two isotopes, equal abundance. There is a possibility both bromine could be 79. That is fine. There is another possibility. This could be 81 and this could be 81, both could be 81. That is also possible. Another possibility, this is 79, this is 81. One more possibility, this is 81, this is 79. But what is the difference between this and this? You cannot make out. So, C and D are equally probable. If I say there are 100 molecules, 25 percent of 25 molecules will be both bromine 79. 25 molecules will be both bromine 81. 25 molecules with one bromine 79 and this bromine 81. 25 molecules will have this bromine 81 and this bromine 79. As I said, C and D are indistinguishable. They are overlapped. So, what happens? You get three peaks. In reality, there are four molecules, four spectra. But this spectrum of these two molecules are indistinguishable. They overlap. As a consequence, you get one peak for this, one peak for this, two peaks overlapped will be a triplet like pattern. So, one, two and one intensity ratio you get. Actually, there are four peaks from four different isotopomers and the peak positions have changed here because of the isotopic substitution. That is the important point. You understood. Now, we can understand why we got a triplet for fluorine. You may ask me a question, why not we see for proton and carbon similar effect. Fluorine is more sensitive for this, not other two nuclei. Alright.



We will take another example of CFCl3, where we can see the isotopic effect dominant here. Again, fluorine. CFCl3, if I take the spectrum, how many peaks we expect? Take CHCl3 chloroform. If you take proton NMR, how many peaks we get? There is only one proton. I told you single nucleus gives only one peak. No other coupling. Forget about carbon 13, dilute spin coupling. Abundant spin is proton, we get only one peak. C-12 attached to proton, we will get only single peak. Similarly, CFCl3 also should give single peak, because this also similar to proton, 100 percent abundant with spin half. So, fluorine NMR of CFCl3 also should give a single peak. Fair enough to assume and it is true. It has to be a single peak. But interestingly, we get four peaks here. One peak here, one peak here, one peak here, one peak here. This intensity is 100 percent. One is 95, 30 and 3. True spectrum, real spectrum. How do we get these four peaks? Why not you get single peak like CHCl3? This is where isotopic effect comes into the picture. Forget about carbon 13 is natural abundance. So, interpretation we can do like this. Before that, you should remember, the chlorine 35 is 76 percent, chlorine 37 is 24 percent. Like bromine, we got you know 79 and 81, 50, 50. Here also, we should consider the abundance. One is 76 and other is 24. There are various isotopomers we can think of. What is the possibility one? Possibility one is all the chlorine could be 35 possible. So, 76 percent abundance, 76, 76, 76, all three are present. Then, if you take the population of this, it is 0.438, multiply 0.76, it is 0.438. I will say this is 100 percent intensity peak. Make it as 100 percent, normalize it for 100 percent intensity. So, if I take a molecule, if all the three chlorines are 35 in this molecule, CHCl3, then I get a one peak. I call this intensity 100. What is the possibility two? Possibility two, these two chlorines could be 35, this is 37. Again, three such possibility. These two, 35, this is 37 and these two, 35, this is 37. There are three such possibilities. Now, what is the population of each isotopoomer? One is 0.76 and this is 0.76, these two and this is 0.24. I already told you, chlorine 35 is 76 percent abundance, chlorine 37 is 24 percent. So, for each of these molecules, what is the population? 0.76, 0.76 and 0.24. So, this is 0.138. But that is not all. There are three such possibilities. Like we saw in the other example bromine, there were two such possibilities. The overlapped, the intensity added up. So, there are three such possibilities. So, it gets multiplied in intensity. So, 0.138 into 3, you get 0.415. If this is 0.415, what is this intensity compared to the previous peak? The previous peak, I took it at 100 percent. Normalize with respect to that. This turns out to be 95 percent. Fair

enough. You could assign the second peak. Now, what is the another possibility? Two chlorines are 37, one is 35. There are again three such possibilities. These two can be 37, this is 35. These two, 37, this is 35 and these two, 37, this is 35. Three possibilities are there. Now, what is the population? Only one is 35 and the other two 37. So, multiply as 076 percent, 76 percent for 35, 24 percent for these two, it is 0.044. Again, three such possibilities, 0.132. Normalize that with the first one, it turns out to be 30 percent. Very interesting. So, we got the third peak also of 30 percent intensity. What is the last possibility? Last possibility, all the chlorines are 37. Calculate the population. There is only one such possibility, 0.0134 and normalize it with the other one, first one, it is 3 percent. So, what is the intensity ratio you get? 100, 95, 30 and 4. So, there are four peaks coming because of different isotopomers. So, the intensity of the peak is due to the statistical distribution of isotopomers. Remember, the intensity of the peaks is due to statistical distribution of isotopomers. Isotope shifts are expressed always in ppb, and this is what you are going to see. Very dominant isotope effect of fluorine. So, I took two examples and then, I showed how the statistical distribution of population gives rise to this. So, this is the time is getting up. I am going to stop here, but I want to summarize what we discussed today. We continued with carbon 13 and then, I showed you I can use the knowledge of DEPT, find out the number of CH3 carbons, CH2 carbons, CH carbons and quaternary carbons and use this knowledge to identify certain structure of small molecules. I showed with the example of terpenes, 5 or 6 different monoterpenes were there, which is which we do not know. But I took the advantage of DEPT experiment, identified number of CH3 is present, number of CH2 is present, CH present and quaternary carbons and find out which molecule matches with that and we could identify that.Then, continuing further, we started analyzing the spectra of many other heteronucleic. Next, we took fluorine. Fluorine is again spin of nuclei, 100 percent abundant. I took several examples of fluorine. Fairly easily, we could assign fluorine-fluorine coupling, fluorine-proton coupling and multiplicity patterns. How we get when there are different heteronucleic present? Fluorine coupling, fluorine-fluorine, fluorine-proton coupling, everything, we analyze that. Interestingly, I also pointed out one more thing. Satellite pattern, satellite peaks also we see in fluorine NMR. I took the example of CF3HgCF3 and we could see fluorine NMR coupled to mercury. We get mercury coupling as satellites. That also we understood. Most important point if you remember is, fluorine is very sensitive to isotopic substitution. We took two examples and showed how different isotopomers can give rise to different peaks and there is a shift in the positions. It is very confusing. See, simple example of CFCl3 should give you a single peak, but it gives you four peaks of different intensity, 100, 95, 30 and 3 and we could identify each of them and explained the intensity pattern based on the population of the isotopomers. The intensity comes because of the statistical distribution of different isotopomers, population of different isotopomers. So, this is what we understood. I will

stop here. We will come back and continue the analysis of fluorine and other heteronuclear in the next class. Thank you very much.