One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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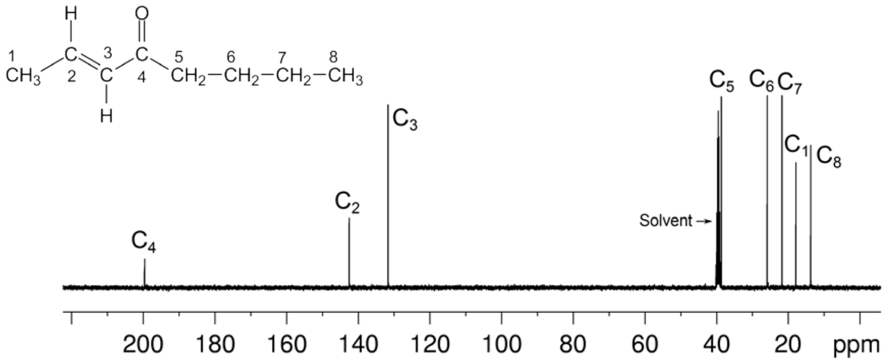
Lecture 26: 13C-NMR-III

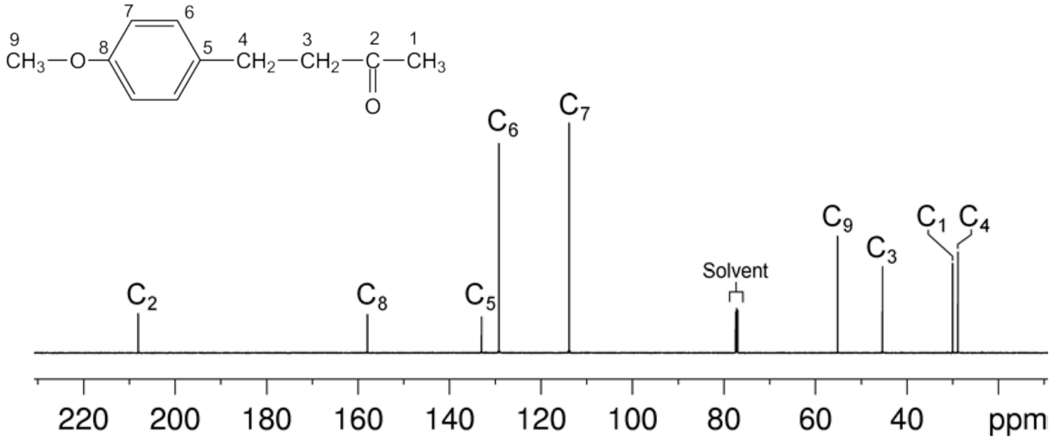
We have already been discussing carbon 13 NMR since last two classes. I discussed varieties of things about carbon 13 NMR. Especially, I said we are going to record the carbon 13 NMR in a decoupled manner. That means, we break all the couplings of carbons with all other protons. Then, the spectrum what you are going to get corresponds to single peak for each chemically inequivalent carbon. And what are the types of decoupling? We can have types of decoupling like completely broadband decoupled with NOE, without NOE, coupled with NOE, decoupled all combinations we discussed. And I said basically what you do is you have to do the decoupling with NOE. That is a conventional carbon 13 NMR spectra recorded always. When we record such type of spectra, I showed that all carbons will not be of equal intensity. It could be because of symmetry. Symmetry will also givex rise to different intensitites that is understandable. When there is a symmetry two carbons are overlapped, that will have double intensity, fine. But the remaining carbons which are attached a single proton or not attached to any proton should have identical intensities. But it normally not happens. This is because not only symmetry, the relaxation plays a dominant role. Especially the protonated carbons relaxes very fast. Non-protonated carbons like quaternary carbons, Ipso carbons which are present in the molecule, relax very slowly. Carbons attach to protons ensure that these carbons relaxes faster. As a consequence, they will have signal intensity more than other carbons. I showed that to record the carbon spectrum with identical intensities, what you have to do is to record the spectrum with relaxation delay or delay between the subsequent pulses which you apply should be 5 times that of the longest T1 of the carbon of your molecule. If a molecule has different carbons with different T1 find out the carbon which has



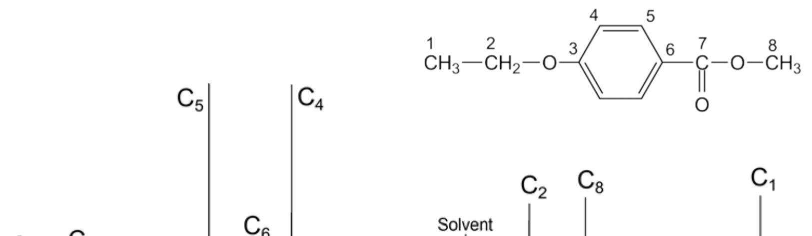
highest T1; longest T1. Use that value 5 times that one as the relaxation delay, then you will get all the carbons of equal intensity. That is what I said and continuing further from that today, this is an example of the spectrum where I showed you this Ipso carbon is weak in intensity, whereas these two carbons double the intensity whereas this para carbon is one intensity. In principle, these two will be of the same intensity, but because symmetry is there, two carbon peaks they are overlapped. It appears double the intensity. Only problem is this Ipso carbon, this one whose intensity very small, because as I told you, the non protonated carbons relax very slowly. As a consequence by the time you apply the next pulse, the magnetization of that particular carbon would not have relaxed back, or not achieved thermal equilibrium. It would not have come back to Z axis as a consequence completely. Thus its intensity is weaker. So, how do you analyze the carbon 13 spectrum? It is fairly simple. You do not need to break your head. All you have to do is apply your knowledge like how you use your knowledge to analyze the proton spectrum, in the same manner. As I told you, the parameters which affect the proton chemical shifts, will affect the carbon 13 chemical shift also in the same manner. So, very easily you can start assigning.

Take an example of the molecule like this. Look at the CH3 proton. We all know CH3 comes at the very high field. This could be CH3 and of course, there is another CH3 here. This CH3 and of course, this CH3 have different chemical environments. If you look at the table, where I have shown here, where the different chemical functional groups resonating in the carbon 13 spectrum, you can find out CH3 which attached to the CH will be almost around this range only, and it would be slightly deshielded compared to this one. So, I would say this is carbon 8 and this is carbon 1. Then the remaining is simple. We have three more CH2s. Among three more CH2s, which carbon is which is another thing, which you need to understand. That is a different question. There is a way to do that. We will discuss that when you go further in the INADQUATE experiment. And of course, you come to the solvent. This is a solvent which is used. One solvent peak is here in addition to these three. And if you come here, there are quaternary carbons here, I think that is C4. C2 is this one and this is C3. These are all CHs. C2 and C3 are CHs and C4 is quaternary. Quaternary is very weak in intensity because it relaxes slowly. Whereas, C2 and C3 you see should have been attached to single protons, should have been of equal intensity, but somehow this C2 has a very long relaxation compared to C3. It is relaxing slowly. But basically, you can assign more or less a sort of each individual peak to a particular carbon and when there is difficulty with too many CH2s are present which carbon is which, which CH2 carbon correspond to which peak, that is more of detail. We will do that when you go further.

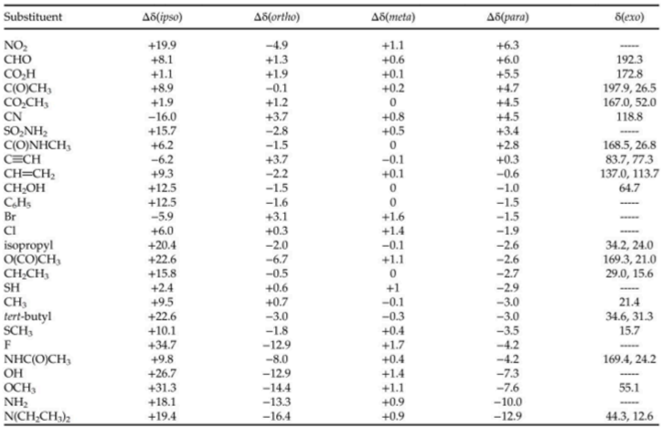
Take an example of another molecule. It is a carbon 13 proton decoupled of this simple molecule. Here, it is fairly easy for you to understand.



Obviously, we have two carbons which are two CH3s here, one is CH3 and OCH3. OCH3 is here that comes to the down field that we know. So, CH3 (1) is here, OCH3 is down field. This is CH3. Of course, this is also C=O attached, but this is directly O attached. So, this is C1, this is C4. Then, there are two CH2s, 3 and 4, this is C4 carbon coming to the very high field and especially, the C8 carbon which is OCH3 is coming here. This is CH2 and C double bond O carbon, this carbon and this carbon, they are not attached to proton. They are very weak in intensity. This is solvent. Solvents are always quaternary. They are not attached to any proton usually. So, as a consequence, the solvent peaks are generally weak in intensity unlike proton spectrum where solvent peaks are huge, but here in carbon 13 spectrum, solvent peaks are very low in intensity. Of course, these two are protonated C6, C7 double the intensity because of equivalence. this is equal to this, this is equal to this. Because of the chemical equivalence, you can clearly identify these two carbon signals are double the intensity for two carbons which are overlapped or which are having symmetry. This is how it is. You can easily interpret this one.

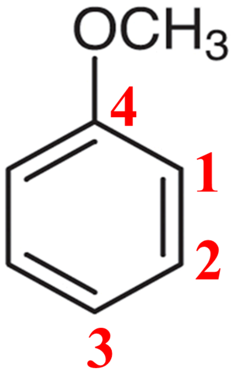


Go further, another simple molecule. Here, it is easy to do that. Where do you get C8? There are two CH3s. One is C8 attached to CH2. Another is OCH3. OCH3 comes down field. It is here. Then, we have a CH2 that has to be here and then, there are four aromatic carbons. Two aromatic carbons here. This carbon, this carbon is equivalent. This and this are equivalent. So, we have two carbons of equal intensity and then, remaining C3, C7, C6 carbon, this one, this one and this one, there are quaternary carbons very weak in intensity. So, very easily you can identify and do the analysis; and the interpretation is easy, but then, here I made some rough estimate of these chemical shifts. What is the guarantee that what I have done is correct? That is my analysis is correct? How do we know the assignment is correct? Especially, when you have phenyl groups. These are all CH3, OCH3, we will not generally get confused. Whereas, in the proton here, which is C4, which is C5, I do not know. But there is a way to predict the carbon 13 chemical shifts. This is what is called the effect of the substituents on aromatic carbon chemical shifts. Depending upon what is the type of substitution, you have different proton chemical shifts especially for aromatic carbons. We can easily predict, very simple rule like we can do for the protons, we can also do for the carbon 13.



Substituent	Δδ(*ipso*)	Δδ(*ortho*)	Δδ(*meta*)	Δδ(*para*)	δ(*exo*)
NO_2	+19.9	−4.9	+1.1	+6.3	-----
CHO	+8.1	+1.3	+0.6	+6.0	192.3
CO_2H	+1.1	+1.9	+0.1	+5.5	172.8
$C(O)CH_3$	+8.9	−0.1	+0.2	+4.7	197.9, 26.5
CO_2CH_3	+1.9	+1.2	0	+4.5	167.0, 52.0
CN	−16.0	+3.7	+0.8	+4.5	118.8
SO_2NH_2	+15.7	−2.8	+0.5	+3.4	-----
$C(O)NHCH_3$	+6.2	−1.5	0	+2.8	168.5, 26.8
$C\equiv CH$	−6.2	+3.7	−0.1	+0.3	83.7, 77.3
$CH{=}CH_2$	+9.3	−2.2	+0.1	−0.6	137.0, 113.7
CH_2OH	+12.5	−1.5	0	−1.0	64.7
C_6H_5	+12.5	−1.6	0	−1.5	-----
Br	−5.9	+3.1	+1.6	−1.5	-----
Cl	+6.0	+0.3	+1.4	−1.9	-----
isopropyl	+20.4	−2.0	−0.1	−2.6	34.2, 24.0
$O(CO)CH_3$	+22.6	−6.7	+1.1	−2.6	169.3, 21.0
CH_2CH_3	+15.8	−0.5	0	−2.7	29.0, 15.6
SH	+2.4	+0.6	+1	−2.9	-----
CH_3	+9.5	+0.7	−0.1	−3.0	21.4
tert-butyl	+22.6	−3.0	−0.3	−3.0	34.6, 31.3
SCH_3	+10.1	−1.8	+0.4	−3.5	15.7
F	+34.7	−12.9	+1.7	−4.2	-----
$NHC(O)CH_3$	+9.8	−8.0	+0.4	−4.2	169.4, 24.2
OH	+26.7	−12.9	+1.4	−7.3	-----
OCH_3	+31.3	−14.4	+1.1	−7.6	55.1
NH_2	+18.1	−13.3	+0.9	−10.0	-----
$N(CH_2CH_3)_2$	+19.4	−16.4	+0.9	−12.9	44.3, 12.6

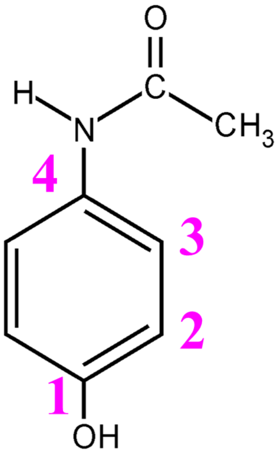
Take for example, this is a table where we have NO2 here. Remember, when I was telling you, I was trying to predict some of the chemical shifts in the substituted benzenes in the proton spectrum. Identically, here also, if you have different substitutions, you can find out the values or the contribution of each of these functional groups, substituent groups at different positions in the phenyl group. For example, I have a NO2 in a molecule, in phenyl group. One of the substituent is NO2. Then, for the ipsocarbon, this is the contribution. For ortho carbon, this is minus 4.9. For meta, this is 1.1. For para, it is 6.3. That means, you have to find out the contributions for each of them and then just do the co-addition of these things, you will get this value. I hope you still remember the phenyl protons also in the example of analysis of proton spectra, I took two or three examples and I showed you based on the substitution of NO2. Simply, first I took the example of the dinitrobenzene, where each proton has one ortho and one metanitro and I added that value and showed you basic value for proton chemical you have to take 7.28 and then add the substituent value to arrive at the approximate values of the predicted chemical shift for protons of the phenyl ring. Identically, you can do the same thing for carbon 13. All substituents are there, their values are given at different positions. All you have to do is, you have to simply take the value and add it up. And here, the base value is taken again for benzene. Here, carbon 13 chemical shift of 128.4 is the base chemical shift of carbon 13 of benzene. And then, different substituent values will be taken and co-added. That is what you have to do.



Take for example, this methoxybenzene, OCH3 is there. Here, there are four different carbons. There is a symmetry here and these are same, this and this are same. I can calculate or predict approximate chemical shifts for each of these carbons. Let us start with carbon 1. Carbon 1 has OCH3 group in the ortho position. Go back to your table. Where is OCH3 here? if you see, OCA3 is here. OCH3, if the carbon is in the ortho position, its value is -14.4. If it is a meta position 1.1; and para position -7.6 and ipso it is 31.3.

These values, we will remember. We will take these values and use them here. For carbon 1, OCH3 is in ortho position. I showed this value is -14.4 here. I have to add for that and I get this value. For 2, it is in the meta position. When I showed in the meta position, it is 1.1. Please add it up. It is 129.4. Similarly, for this one, the substitution in the para position, in fact, instead of adding, it is again subtracting. It is 120. For carbon, which

Ipso, directly attached, and this is the contribution. And this is the total chemical shift. Approximately, like we did for the proton chemical shifts in the phenyl groups, depending on the substituents, here also, depending upon the position of the substituents, different carbon chemical shifts can also be calculated and this is what it is. These are the values we have obtained, 114, 129.5, 120.8, 159.7. See here, all the experimental values are approximately equal. For I look at the last one, 159.51, here 159.7. So, close by. Of course, predicted values is predicted, not experimental. Authentic value is experimental, but to make the assignment easier, this is one way you can calculate. You can predict the carbon 13 chemical shifts and that is how all these things can be assigned very easily.

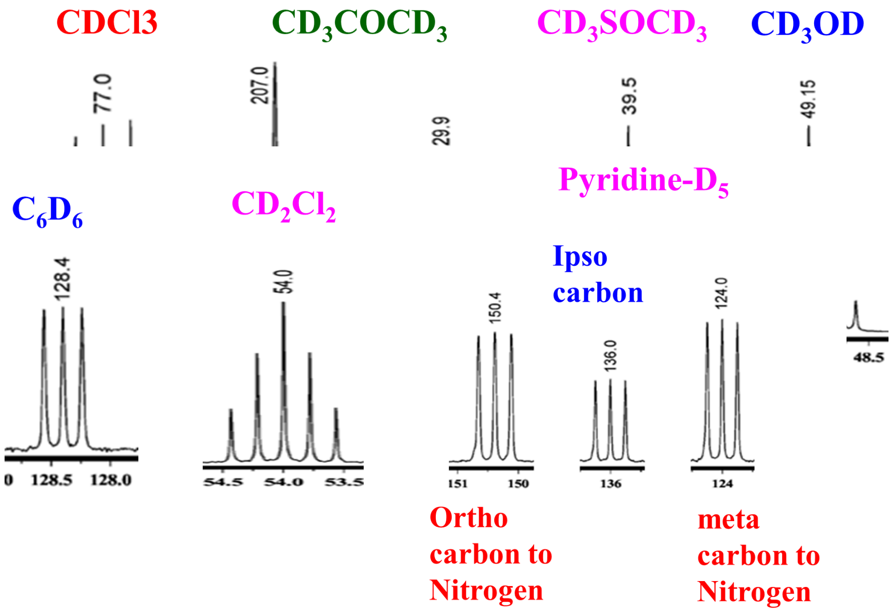


We go to acetaminophen, para acetaminophen. This is what we also try to analyze in the proton spectrum, I think. Look at this one. This group NHCO-CH3 group, this substitution, you have to see its value for ipso, ortho, meta and para. Of course, we also have a OH in para position, and you have to consider two parameters. Let us consider this proton 1. Proton 1 for ipso is OH and para is NCHCO-CH3 and those values are taken from the table. Ipso is 26.7 and para is -4.1 for this group and this group. Go back here and see the table for OH, for example, ipso it is 26.7 and para is -7.3. So, like this you can start putting NHCO-CH3 as also here. For NHCO-CA3 ipso is 9.8, para is 0.4. I have added this value here; ipso and in the other case, for the case of this OH, this carbon ipso is OH and para is this one. So, IPSO OH value is this, para value is this one. For carbon 2, this is ortho, this is meta, values are taken. Carbon 3 again, this is meta, but this is ortho. Carbon 4 is very interesting. IPSO is this one, this value is -9.8 for ipso; whereas, for para is -7.3 and this is the value you are going to get. You can calculate the carbon 13 chemical shifts with additive factor like this; and this is what it is. Look at this for a carbon, for example, 1, 2, 3, 4, all the 4, I am not worried about this and this because we are calculating only for the phenyl carbons, only 1, 2, 3, 4, if you see, this is 153. Go back to our calculation. This is C1 is 151. We are getting 153. For example, CO2 is 115 and we are getting 150. Very precisely, if not precisely, at least close by to the experimental value, you can calculate and this is what the idea you have to use for making the assignment.

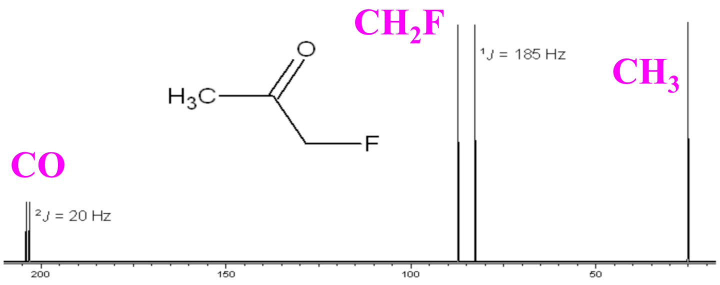
In the previous examples, when I took the assignment, I made a rough estimate based on the intensity and everything, but with that idea, use this table, calculate the substituent effect and then you can make the assignment very easily. So, you can go back with the meta and this thing. We analyze the spectrum of proton. If you remember, we calculate the proton chemical shifts based on its position and same thing we can do for all the 6 carbons here. There are 6 carbons. For this carbon 1, IPSO is NO2 and meta is COOCH3. You can do that. What is the value of Ipso for this one? What is the value for this from the table? Take it, simply keep adding everything and this is the value you are going to get. So, for all the carbons we have calculated and then if you see this value, what you calculated, of course, this is 148.3, the value calculated. Experimental is given as 148.23. Look at this one. This is calculated value. Experiment is very close by. There is not much difference. Look at this one, 131.4 is calculated. Experimental is 131.5. So, very easily you can start making the assignments. This is how you can use this value, but there could be deviations. I am not telling these are the accurate values, but they come close to the experimental value. You can use these as starting parameters. Your assignment will be fairly accurate plus you have to use the chemical shift ideas and then in case, wherever you require, you can do other techniques. So, this is the way you can start interpreting the spectrum.

We know how to analyze the spectrum. We know how to record the spectrum, how to interpret the carbon-13 spectrum, especially the phenyl carbons based on the substituents. Of course, there are several other tables for several other types of groups. Using the steric effect, we can calculate the chemical shift for linear chain molecules. There are aliphatic groups, for CH3 chemical shift, CH2, CH3 in a long chain also we can do. There are several tables for that. Using steric effect, for example, particular carbon, how many bonds away it has CH2, CH3, how many carbons are there, how many CH2s are there, how many CHs are there. Each of them, you can calculate, use the value and then get the additive value for a particular carbon and predict the chemical shift. It is possible for that also by using steric effects. I am not going to the details of that, but just I wanted to tell you that itself will take enormous amount of time if you want to discuss. In most of the books, the steric effect and the values are given like the table which I showed you is given in books. Simply take that, start using it for the analysis.

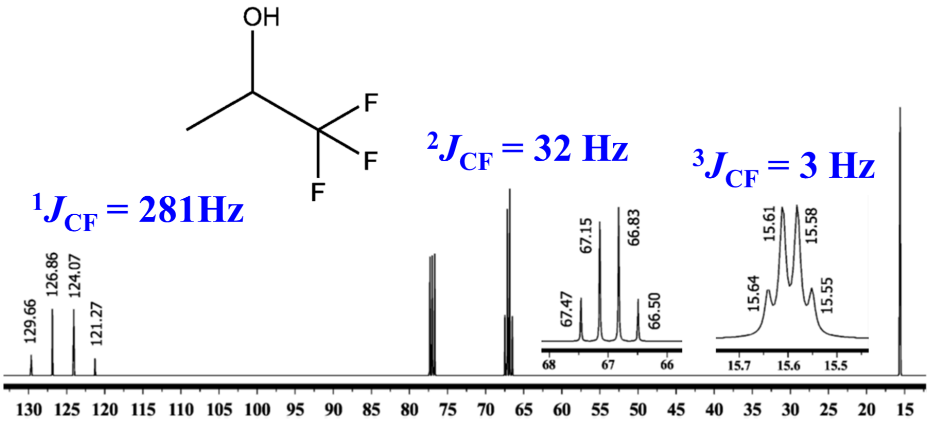
Next, we want to understand the coupling between the carbon and other spins. Carbon 13 can also couple to other spins like we saw in the proton case, proton-phosphorous, proton-fluorine, proton-carbon coupling we got. Carbon 13 can also couple. See, carbon 13 coupling usually we see, when you record the spectrum in deuterated solvent. What happens when carbon is coupled to deuterium? How many peaks we expect?



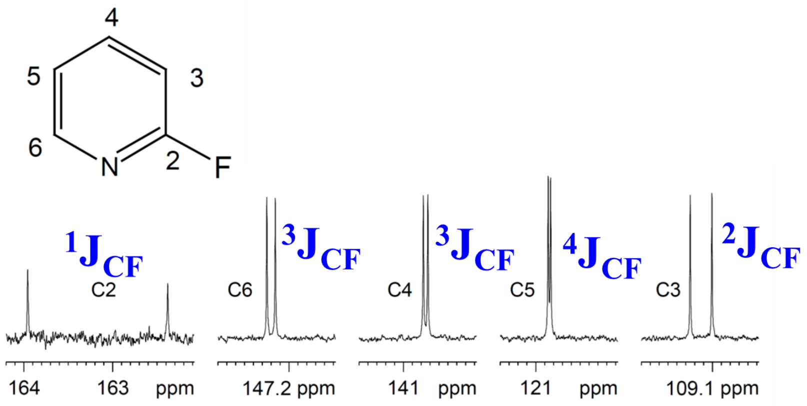
Remember, carbon 13 is spin half, deuterium is spin 1. So, obviously, we get three lines of equal intensity and usually the solvent peaks are not protonated. As a consequence, they will not relax faster, they are weak in intensity. Take for example, CDCl3. This is a solvent normally used for organic molecules and it comes at 77, you get three peaks of equal intensity. This separation gives you coupling between carbon and deuterium. Very simple. If you go to this CD3COCD3. CO carbon has no deuterium attached, gives a single peak. CD3, when three protons, three deuteriums are attached to a articular carbon, you can calculate the intensity pattern also. It is going to give you, see, even line pattern, 1, 2, 3, 4, 5, 6, 7, septet pattern we are going to get with different intensities, which can be worked out. So, when you have a dimethyl, CD3COCD3, this is the pattern you get. When you have a dimethyl sulfoxide like this, again seven line pattern, because there are three CD3s are present. CD3OD, you get pattern like that, again seven. C6D6, similar to CDCl3, you get three line pattern, because all carbons are equivalent and all deuteriums are equivalent, you get three peaks of equal intensity. CD2Cl2, there are two deuteriums present, you get only five lines. Unlike with three deuteriums you get seven lines, here you get five lines of different intensities. We also worked out once, when there are two deuterium coupled. Remember, when I was working out CH2D2 molecule in proton spectrum, when you simulated, we also worked out the intensity pattern. It is 1, 2, 3, 2, 1 intensity we got exactly five peaks. Similarly, because proton and carbon both are spin half, when it is coupled to two deuterium, intensity pattern remains same. Pyridine D5, pyridine has three different types of carbons, ortho carbon, meta carbon, ipso carbons, all will give rise to intensities. I mean triplet, we do not say triplet, triplet in NMR jargon is 1:2:1. I would say it is three lines of equal intensity. And especially, ipsocarbons, as I told you, the relaxation is slow, not attached to proton also, will appear it lower intensity. And when you want to record the spectrum, you can measure the coupling.



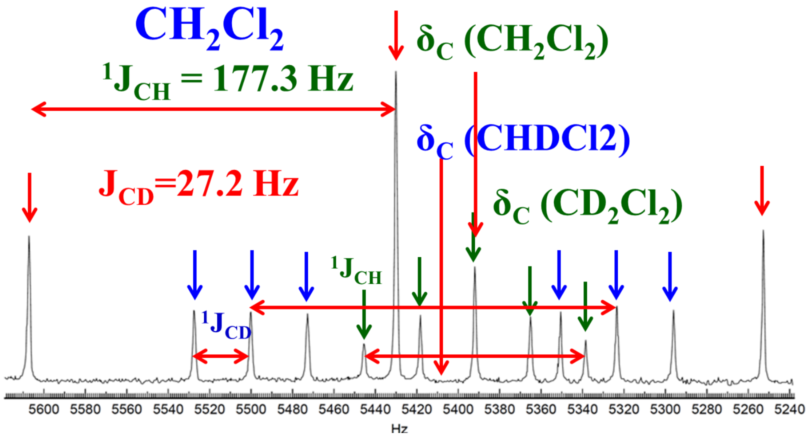
Let us look at the carbon 13 spectrum of this molecule. I am looking at the carbon fluorine coupling. Carbon can also couple to proton, that we can extract easily. When it is coupled to fluorine and also proton, both abundant spins are there, you will get complicated spectrum. Spectrum gets terribly complicated. How do you simplify that? I told you already, in the proton analysis, I told you at the end, we can break the coupling of one of them to simplify the spectrum. Do this, you break the coupling with proton, all protons coupled, all carbons are removed. But I told you, other nuclei are still coupled, so fluorine is still coupled. You are breaking coupling with carbon proton, but fluorine carbon coupling is still present. So, then how many different carbons are there? One is CH3, one, two, three. There are three different carbons, you have three different different peaks. This is a CH3 peak, this is CH2F, this is CO, and you see, this is the fluorine. This fluorine directly attached to this carbon. Of course, this is also there, one bond coupling is there, this is CH2F, and this CO has two bond coupling. This is three bond coupling, one, two, three bond coupling, this is CH3. This carbon of CH3 can couple to fluorine, but very weak coupling, three bond coupling, far away. Largest coupling is one bond, you know, this carbon to this fluorine, 185 hertz, and this is 20 hertz. Mind you, one bond, C-F couplings are always negative, but it is not written here, but it is negative. You can interpret that.



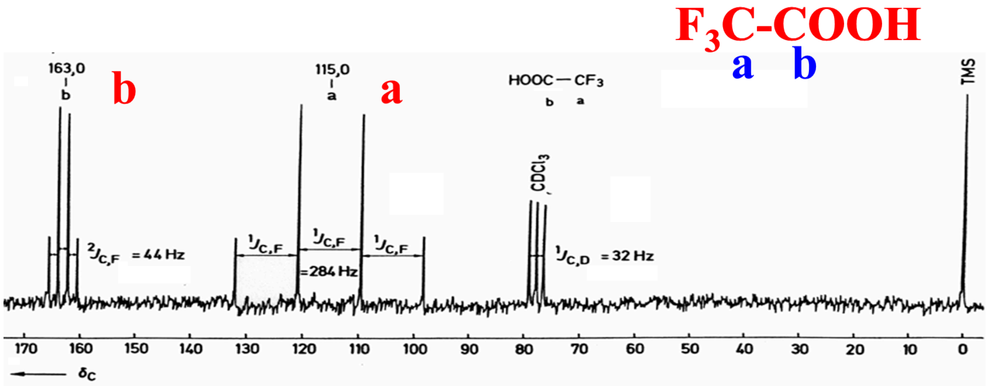
Another molecule, it is very simple. This is carbon 13 spectrum in CDCl3. How many peaks you are going to get for this? How many carbons are there which are chemically inequivalent? Look at it, one, two, and three. There are three different carbons. We will start interpreting this now. First, I would say this is this carbon. You know why? This is a large quartet. Large quartet of this comes because of carbon coupled to three equivalent fluorines, CF3. CF3 carbon is coming in this region, in the aromatic range. Usually, we get aromatic protons, aromatic carbon carbons around 120 or 130 ppm. But CF3 carbon is coming. Do not get surprised. All these things can happen in NMR. And you measure the separation, this is 280 hertz. One bond CF coupling is very large. So, I would safely put this as $^1J_{CF}$, and that is corresponding to this carbon. Go to the next one, $^2J_{CF}$, which is $^2J_{CF}$? This carbon can couple to this. This is 32 hertz, quite large. And that also has to be a quartet. Same three equivalent fluorines are coupled. So, you can see three equivalent fluorine coupling. And then 3J, this carbon can also couple to this and it is going to be a quartet. So, very easily you can understand all those things. This is the spectrum, a simple molecule, where we are looking at only carbon-fluorine couplings. Of course, proton coupling we are not seeing. And what is this peak? At 78 ppm, why it is coming? Those three peaks of equal intensity is because it is a recorded in $CDCl_3$. Carbon is coupled to deuterium and giving three peaks of equal intensity. This is a solvent peak. So, like this you can start interpreting.



Go to this molecule. This is a fairly simple molecule, 2-fluoropyridine. And there are different carbons. There is no symmetry because this fluorine is here. All five carbons are different. There is no symmetry because this is not proton, this is fluorine. So, pyridine has symmetry, 2-fluoropyridine has no symmetry. So, all carbons, five carbons are chemically inequivalent. What is the largest coupling we can think of? Largest coupling we can think of is the one bond, this one. Look at this. It is a doublet. Again, proton decoupling, you will get only carbon-fluorine couplings. The second largest is what? Look at it, two bond coupling. Which is the two bond coupling? This carbon to this fluorine, quite large. I can assign this as carbon 3 and I can assign this as carbon 2. The numbering starts from 1 as nitrogen. So, this is carbon 2, this is carbon 3. What is the next one? Next is three bond coupling. There are two three bond couplings, this one and this one, C4 and C6. And one of them is, this is quite large compared to this. Both can be interpreted. And the last one is this one, this carbon. This carbon has a four bond coupling, very weak. And these values have been measured. You can see it, one bond coupling, two bond, three bond coupling, four and five bond couplings. As the number of consecutive bonds increases, interestingly here, couplings are coming down. Systematically, they are coming down. One bond is larger, then two bond, then three bond, then four bond.



We look for carbon 13 spectrum of a simple molecule, not simple molecule, mixture of molecules, not one molecule, three molecules. That is CH2Cl2, dichloromethane, CHDCl2, and CD2Cl2. See, three molecules are present. Of course, CH2Cl2 spectrum, we will consider first. Three molecules are CH2Cl2, CHDCl2, CD2Cl2. When I look for CH2Cl2, how many peaks we expect? I am not decoupling. It is proton coupled. See, here simply written 13C. If it is decoupled, I would have written in flower bracket ^{1}H. Here, that is not written. That means proton is not decoupled. It means carbon is coupled to proton. When this carbon is coupled to proton, how many peaks we expect for carbon 13 of CH2Cl2? Already, I told you there are two equivalent protons. It has to be a triplet. Can you see a triplet pattern here? Obviously, this large triplet gives you one bond CH coupling. This corresponds to one bond CH. That is CH2Cl2 triplet. Very clear. There is no confusion about it. I can put it as this one. Then, go further. This gives me one bond coupling. Go further. I will take other molecule now. Other molecule is CHDCl2. What is the pattern we expect for



CHDCl2? You should remember, this carbon splits into a doublet because of proton coupling, and each line of this doublet will be 3 lines because of deuterium coupling. And, where do you get that pattern? If you look at the spectrum, you can identify that pattern like this. Identical, but it is not exactly at the center of CHCl3 chemical shift. It has moved a bit. Chemical shift has moved a bit. This is because of isotopic substitution. This is called isotopic effect. Because one proton is replaced by deuterium, its chemical shift has moved a bit because identical environment is not there. The CH2Cl2 has one environment. CHDCl2 has a different environment. As a consequence, its chemical shift has moved. But remember, substitution of a heavy atom always moves the peak to the right. So, this chemical shift is coming to the right. Please remember, substitution of heavy atom moves the peak to the right. This is what happened. And, this is the chemical shift of CHDCl2. From the center of the chemical shift, there is a doublet. And, each line of the doublet is split into three lines of equal intensities. And, this is the doublet that corresponds to $^1J_{CH}$. And, each line of that is split into these three. Three lines of equal intensity. That gives rise to JCD coupling between carbon and deuterium. What is the last one you can think of? Last one is CD2Cl2. There are no protons here. Directly, carbon is coupled to D2. I told you already it gives rise to 1, 2, 3, 2, 1 intensity pattern, 5 line pattern because of two equivalent deuteriums are splitting this carbon. And, this is the pattern you are going to get. And, this is what it is. And, you see this is the chemical shift. It has again moved from this and also moved from this to the right. That is what I said. With substitution of heavier isotope, chemical shifts always move towards the higher field. And, the separation of any of these five peaks you take, adjacent peaks you take that gives you JCD. So, very easily you can analyze this also. From this, the carbon deuterium coupling has been obtained as some value. So, there is an isotope shift. Isotope shift mind you is always expressed in ppb, in fact, lower value. It will be expressed in ppb. But, in this case, it is quite large and expressed in PPM; how much it is you can calculate. So, we can start analyzing one more molecule before you go further and then we can stop; and then discuss many other things in carbon 13 later.

It is a simple molecule. Carbon 13, proton, broadband decoupled, which is very nicely written. I should have written here ^1H in a flower bracket. What is the type of spectrum you are going to get for this molecule? Very simple. First, it is TMS. That is a reference, TMS carbon. And, of course, what are these three peaks which are coming? Equal intensity, CDCl3 solvent and this corresponds to coupling between carbon and deuterium. That comes at 78 ppm approximately. That is also fine. Now, we have to understand these peaks. What are these peaks? Why are they coming? If you see carefully, it is a large quartet. You can measure the separation of this quartet. That is a huge value, large separation and value is about 284 hertz. Where it can be? It can be from which carbon? Obviously, it is from CF3 carbon. CF3 directly attach carbon fluorine. These three fluorines will split this into a quartet. This is a CF3 group. But simultaneously, this carbon is also coupled to this fluorine. You understand? Simultaneously, COOH carbon is also coupled to fluorine. Again, three fluorines chemically equivalent split this carbon also into quartet, two bond coupling. This is a two bond carbon fluorine coupling. This is a one bond carbon fluorine coupling. And one bond carbon fluorine coupling is about 284 Hz and two bond is about 44 Hz. Very easily, you can interpret the spectrum. Here, you are directly detecting carbon. Question of satellite does not arise. Remember, you are directly detecting carbon. So, fluorine is abundant. When you are detecting the dilute spin, it is as good as you are seeing the abundant spin. So, when they couple to abundant spin, you will get splitings like this. Very easily, you can extract heteronuclear couplings in these molecules. I hope you got the point now. Now since the time is getting up, what I am going to do is, I will stop here. What we did in this class? We started understanding how to interpret the carbon spectrum, simple spectrum. I said intensity of the peaks depends upon chemical equivalence. How many carbons are chemically equivalent? If there are two equivalent, then intensity will be doubled. And also, I said quaternary carbons, IPSO carbons which are not protonated, usually will have very low intensity because they relax very slowly. And I said you have to give 5 times the longest T1 of the particular carbon as a relaxation delay, so that all the carbons will be of equal intensity. That is one thing. And also, I showed you how to make the assignment of different carbons based on the multiplicity pattern or using the chemical shift. The multiplicity pattern was not there because we decoupled protons, and only based on the chemical shift. But how do you know which is the chemical shift? Especially for the phenyl groups, we have a substituent effect. Like we did for the protons, the different substituent substituents in a phenyl group have a contribution to different sites, ortho, meta and para positions. And there is a table available for that. Use these values, start with the basic value of benzene. Whatever the basic value which I showed for benzene? 124 or something; that you take, that value, co-add with all these additive values of the substituents, then you get the approximate value of carbon chemical shifts for different carbons. And then use as a starting point to get the experimental value. Precise experimental values will be known. You can make the assignment. Then I also said protons can couple to abundant spins, like phosphorus, fluorine, etcetera. And we took the example of the carbon fluorine coupling and how the spectrum gets complex. Of course, we do the decoupling and remove proton couplings, but still heteronuclei like fluorine, phosphorus, others, if they are present, they are coupled. So, how do you analyze that? And we took the example of one or two molecules. And we measured the carbon fluorine couplings. And we saw how this multiplicity comes with one bond coupling, two bond coupling. We can have the carbon couplings up to three bonds, four bonds. We saw in the example of 2-fluoropyridine up to four bond couplings. So, in some other molecule also we saw up to three bonds and four bond couplings. So, couple of examples we took to understand, analyzed and extracted the heteronuclei coupling between carbon and fluorine. With this, I am going to stop here. We will continue with the next class where I will give you some other information, some more things about how you can use carbon-13 to get the structural information. Thank you very much.