One and Two Dimensional NMR Spectroscopy for Chemist
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Lecture No: 37
Coupled and Decoupled 13C-Spectra

Welcome back. In the last class I started discussing carbon 13 NMR where, I introduced some salient features of carbon 13 spin. Where we discussed. as I have been telling all along, the gyromagnetic ratio of carbon is four times less. As a consequence the energy separation is less, sensitivity is less, in addition to that carbon-13 has an abundance of only 1%. Taking all those factors into account, we discussed and I showed, that carbon-13 is nearly 5700 times less sensitive compared to that of protons, that is one point. Secondly, I also said when the carbon 13 is only 1% abundant. In a molecule containing one carbon, the possibility of seeing carbon 13 in that state is only 1%. That if there are 100 molecules there may only 1 molecule which has carbon-13. So the probability of seeing that is 1 in 100, and I said if there are two carbons it is going to be 1 in 10000. And then extended the logic and I said if there are, let us say 6 carbons in the molecule, this is not uncommon in most of the organic compounds, you will see there are a large number of carbons present.

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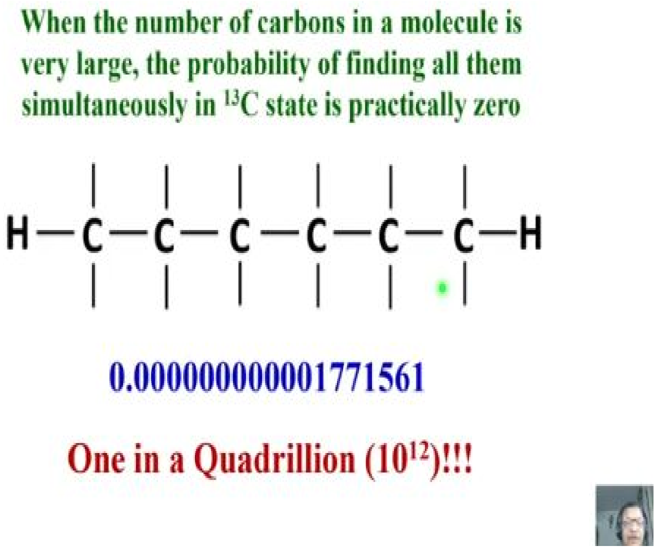

When the number of carbons in a molecule is very large, the probability of finding all them simultaneously in ^{13}C state is practically zero

0.000000000001771561

One in a Quadrillion (10^{12})!!!

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I just took a simple example, just to point out, if a molecule has 6 carbons, what is the probability of finding all the carbons in carbon-13 state? This is 1 in 100, 1 in 100, 1 in 100, each of them is 1 in 100. The joint probability of seeing them is a product of all these things, that is, it turns out to be be 1 in 10 to the power of 12.   It is one in a quadrillion, look at this number, Such a very very small number. It means the probability of seeing all the carbons in the carbon-13 state at a time is practically 0, you will not be able to see all the carbons as carbon-13.

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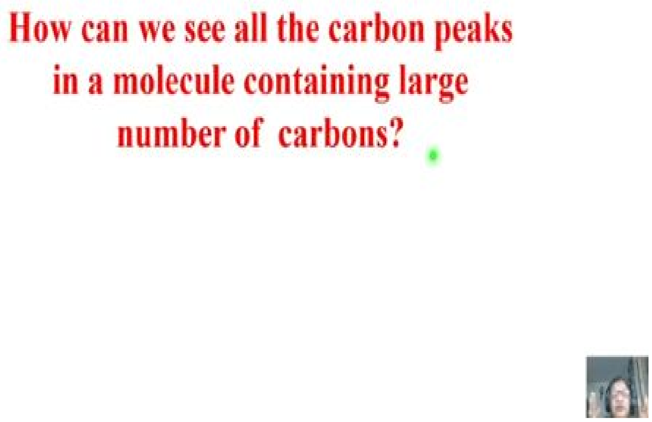

How can we see all the carbon peaks
in a molecule containing large
number of carbons?

Then the question can be asked, if that is the case, how can we see all the carbons in a molecule containing a large number of carbons. This is a valid question which we need to answer: how can we get all the carbon peaks, in spite of the fact that the probability of seeing all of them in the carbon-13 state at a time is practically 0?

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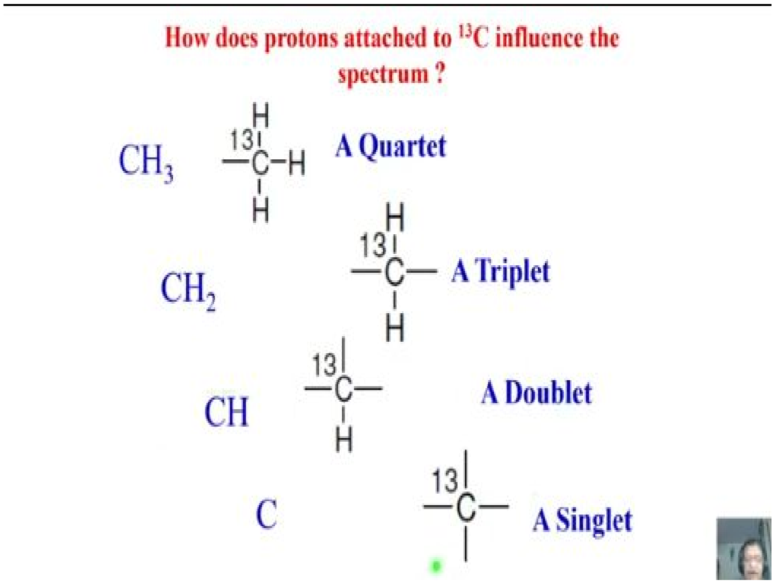

How does protons attached to ^{13}C influence the spectrum ?

CH_3 A Quartet

CH_2 A Triplet

CH A Doublet

C A Singlet

So before going to that let me introduce, of course we will come to that point, we will answer in one or two slides. Before that let me point, out how does protons attached to carbon-13 influence the spectrum? This we should know so that we can go ahead and answer many questions. How does protons attached to carbon 13 influence the spectrum? Remember there may be CH3 groups in the molecule, there may be CH2 in the molecule, there is a CH and also a quaternary.

All different types of carbons we can think of; only these 4 types of carbon, which you can normally think of in any given molecule. If there is CH3 carbon present in your molecule, the carbon 13 signal will be a quartet. Why is it a quartet? Because carbon 13 probability of seeing all the carbons in carbon 13 is practically 0, I pointed out. So each carbon now will not be seen by the other carbons for interaction, they will be seeing only the protons which are attached to that or the protons attached to the next carbon.

First let us see this carbon, it is seeing protons attached to that. There are 3 equivalent protons, chemically equivalent, then what is going to happen? Just apply 2NI+1 rule, There are 3 chemically equivalent spin half nuclei coupled to carbon. What you will see? It has to be a quartet of intensity 1, 3, 3, 1. Clear Right? Now, what about CH2 carbon? Exactly I say these two protons are equivalent, again apply 2NI + 1 rule, this carbon will be a triplet.

And what about the carbon attached a single proton? This we have come across many examples, like $CHCl_3$ and what you are going to see is, this is coupled to only a single proton which is bonded to it. As a consequence , this is going to be a doublet. The quaternary carbon which is not attached to any of the protons directly, there is no directly bonded proton, it will be a singlet. This is the general pattern you expect for any carbon in the carbon spectrum.

Of course, you ask me a question about what happened to the long range coupling? which we saw in protons. Of course it will be there, we will come to that later. But by and large, generally there are two types of spectra recorded in carbon 13, one is fully coupled, other is fully decoupled. Of course, sometimes we used do off-resonance decoupling, where you ensure only the carbons which are coupled to directly bonded protons, that coupling pattern is seen.

For example, the experiment is done in such a way, this carbon will only couple to these three protons and we are going to see only coupling of CH_3, the carbon with 3 protons. So it will be a quartet, similarly it will be a triplet, there it will be a doublet and no coupling at all. This is a type of spectrum normally used to be seen. And if you want to do a fully coupled spectrum, definitely a possibility, this carbon not only can see the protons coupled to it, it can also see the protons which are two bonds away or three bonds away, that is also possible.

But at the moment we concentrate on this. When directly bonded protons there are, CH_3 is a quartet, CH_2 is a triplet and CH carbon is a doublet and a quaternary carbon or any carbon, a CO carbon like that which are not attached to any protons will always be a singlet. This is a point which we must remember.

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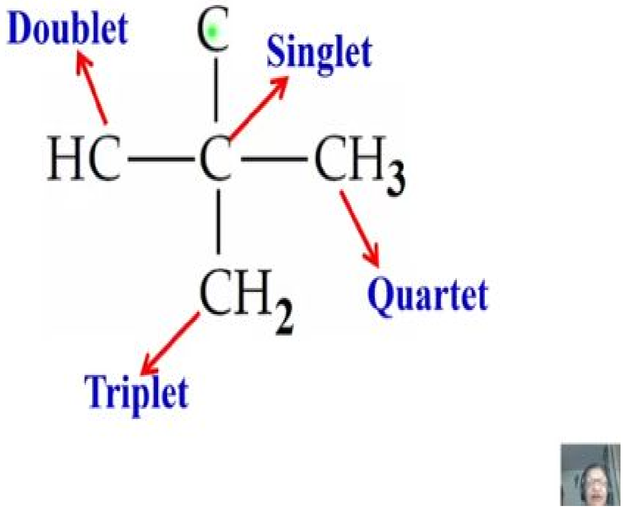

Now take a simple hypothetical example of the molecule, let us say I have a molecule like this; hypothetical molecule, do not go by practicality of these things, that type of molecule exists or not, I do not know. I am just for the discussion purpose I am taking. If I have a hypothetical molecule like this, in the carbon 13 spectrum, I get that quartet for this, I get a triplet for this, I get a doublet for this, I get a singlet for this. Of course depending upon the substitution here we get particular pattern, you understand?

The carbon 13 spectrum cannot have any other pattern apart from this. Only I am considering directly bonded proton coupling, that is all. These are the only 4 patterns you can think of.

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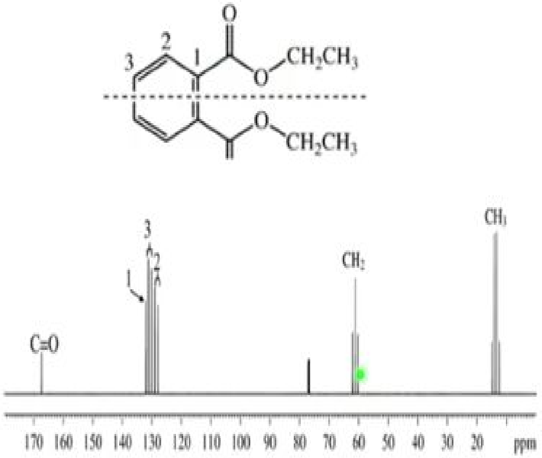

Now look at this spectrum of this molecule. We have a molecule like this, it is a realistic spectrum, we have a CH2 and a CH3, what were we seeing in the proton spectrum? These 3 protons coupled to these 2 protons and this made it a triplet, these 3 protons made this as a quartet. There was a coupling between the 2 protons through chemical bonds. Now we are not worried like that, when I am looking for this carbon, this carbon is coupled to these 3 protons only. As a consequence you see, it is as a quartet.

This carbon sees these 2 protons, so it is going to be triplet. Now look at the other carbons here, each of these carbons you can see, this is a doublet because it is only one proton attached to it, it is a doublet this is a doublet and this carbon is not coupled to anything and it is a singlet. It is a very nice example to see in a realistic spectrum, you can see all possible carbons present, all types of carbons, like CH3, CH2, different types of CH's the aromatic CH's and also have a quaternary carbon, unattached to proton.

You also have a CO carbon etc, so all of them are seen here. This is the pattern normally expected.

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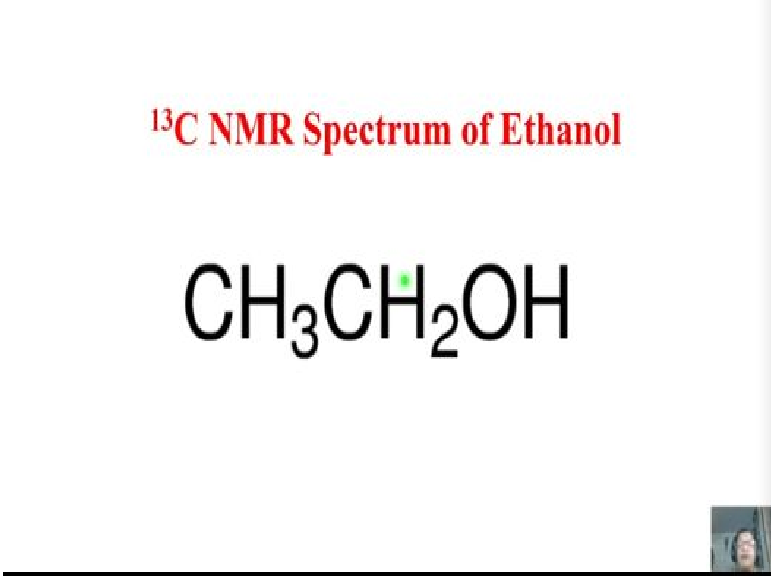

^{13}C NMR Spectrum of Ethanol

CH_3CH_2OH

Now let us look at the carbon 13 spectrum of ethanol. It is all well known as CH3CH2OH. What did I say? We always see this carbon coupled to this proton, this carbon coupled to this proton. So you must get a triplet and a quartet, quartet for this carbon and a triplet for this carbon, that is fine. Please keep this into mind, the type of pattern we are going to get for different carbons.

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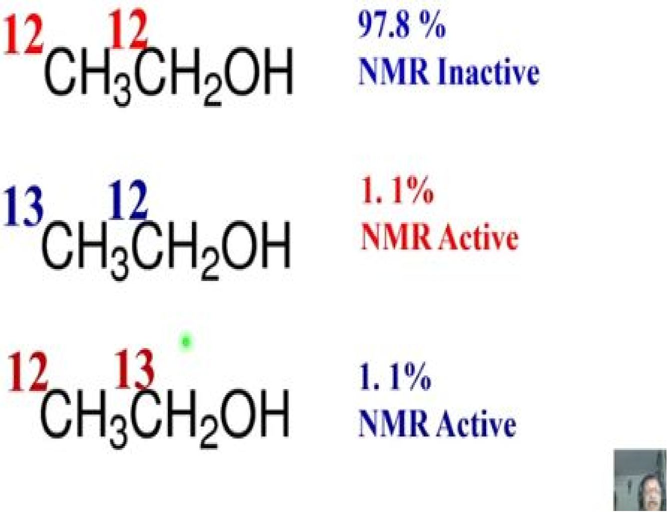

$^{12}CH_3{}^{12}CH_2OH$ 97.8 % NMR Inactive

$^{13}CH_3{}^{12}CH_2OH$ 1. 1% NMR Active

$^{12}CH_3{}^{13}CH_2OH$ 1. 1% NMR Active

Now, let us try to understand again the probability of occurrence of each carbon in carbon-13 state and carbon-12 state. This is discussed and we said in a large molecule of containing six carbons, the probability of seeing all the carbons in carbon-13 state at a time is one in the quadrillion that is what we said. Now, let us go slowly, I will ask a few questions for which we have to get the answer, and then our carbon 13 spectrum becomes more clear for us. Now in ethyl alcohol, what are the possible isotopomers we can think of?

The possible isotopomers you can think of are, this carbon can be carbon 12, this carbon can be carbon 12. I said this probability is 97.8%, it is NMR inactive. This can be carbon 13, this can be carbon 12, it is only 1.1% NMR active. These I have said it, and I am repeating again to make you understand. There is another isotopomer, this is carbon 12, this is carbon 13, this is only 1.1% NMR active.

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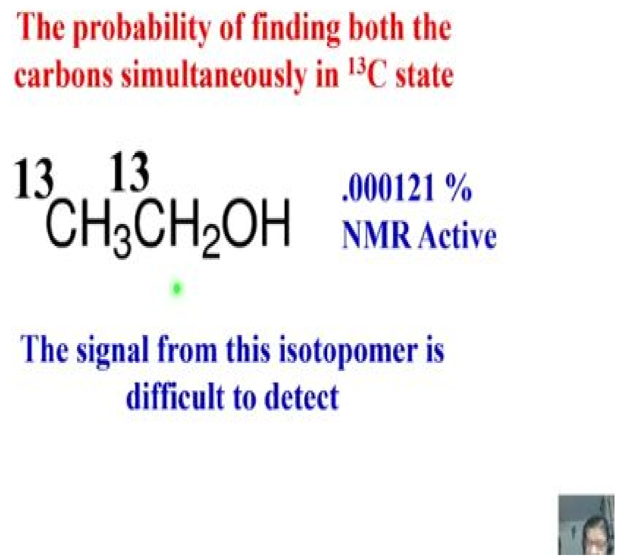

The probability of finding both the carbons simultaneously in ^{13}C state

$^{13}CH_3{}^{13}CH_2OH$ .000121 % NMR Active

The signal from this isotopomer is difficult to detect

And the probability of finding both the carbons simultaneously in carbon-13 state in this ethyl alcohol is 0.000121% this also I showed. This is NMR active and only this isotopomer is totally NMR inactive. The signal from this isotopomer is very difficult to see, we already saw, probability of seeing this is so difficult you will not see. Carbon-13, carbon-13 both simultaneously present, this isotopomer peak is not seen, very difficult to detect.

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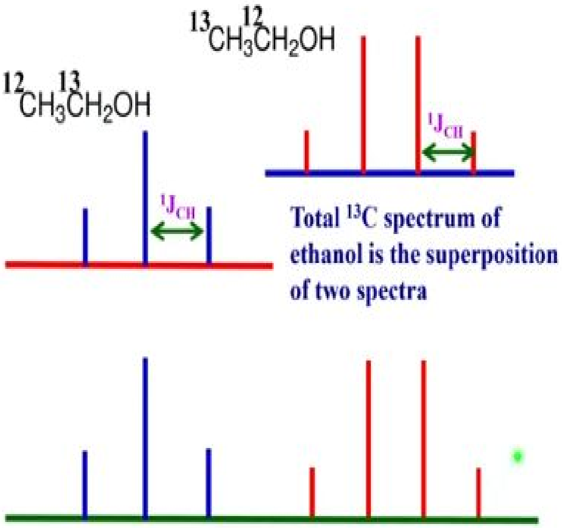

Total ^{13}C spectrum of ethanol is the superposition of two spectra

Now, let us get this spectrum of carbon 13. Now I consider this isotopomer, what is the type of spectrum I am going to get? That is why it introduces the carbon spectrum when it is coupled to 3 protons. When CH3 is there, I get a quartet for this isotopomer. Perfect, This is what we understood when carbon is coupled to 3 protons, you get a quartet. Now, what about this isotopomer? It gives a triplet, but in reality in the given sample, take your sample in the NMR tube, take this spectrum, you have 1% of the molecule in this state; 1% of the molecule in this state.

For example; if you take, let us say, 100 molecules, one in hundred molecules will be this, and one in 100 molecules will be this, that is a probability. Since there are 2 different types of carbons, you have to take 1 in 10000 will be this, or 1 in 10000 will be this, 1 in 10000 is for 2 carbons. So now when I see this carbon, this separation gives me one bond J carbon proton coupling, coupling between carbon and 3 protons, understand? This separation gives me coupling between carbon and proton. What about this triplet? This separation gives me one bond coupling between carbon and this proton. Now in a realistic situation when I take the NMR spectrum, all these isotopomers are individually present, right? and NMR spectrum will not distinguish what is what. It is simply gives the spectrum of every isotopomers at a time.

Now the total spectrum is a superposition of these two, you understand? The real carbon-13 spectrum, if you take of ethanol, you get a spectrum from this isotopomer and you get the spectrum from this isotopomer and together this is a realistic spectra, what you saw; and this is what you are going to see.

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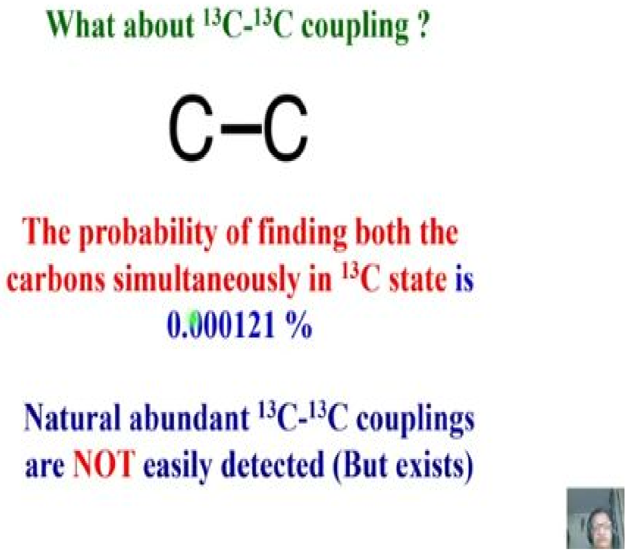

What about ^{13}C-^{13}C coupling ?

C–C

The probability of finding both the carbons simultaneously in ^{13}C state is 0.000121 %

Natural abundant ^{13}C-^{13}C couplings are NOT easily detected (But exists)

Now the question is what about the carbon-13, carbon-13 coupling, probability of finding both of them is 1 in 10000 you can ignore it. Natural abundant carbon-13, carbon-13 couplings are not seen also. But remember molecules having carbon-13, carbon-13 both simultaneously, in principle, you may get the carbon-13 spectrum of that, but the probability of finding in so low, you can ignore.

So basically, what you are going to see is the spectrum for each isotopomer individually, they just superimpose. And carbon-13, carbon-13 couplings in natural abundance is not detected because again this is low probability, but does not mean coupling is 0, that does not mean it is non-existent, it exists. Only thing is we do not see it, that is all. I hope the point is clear now.

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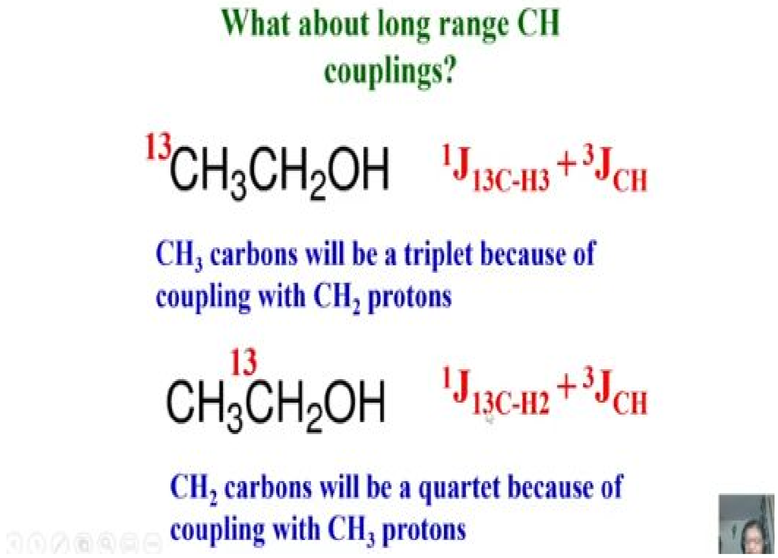

What about long range CH couplings?

$^{13}CH_3CH_2OH$ $^{1}J_{13C\text{-}H3} + {}^{3}J_{CH}$

CH_3 carbons will be a triplet because of coupling with CH_2 protons

$CH_3\overset{13}{C}H_2OH$ $^{1}J_{13C\text{-}H2} + {}^{3}J_{CH}$

CH_2 carbons will be a quartet because of coupling with CH_3 protons

Now we will ask you another question, what about long range proton proton couplings which are affecting the carbon? But remember when I was looking for this ethyl alcohol spectrum I saw these 2 protons coupled to this one makes it a triplet, these 3 protons couple to this proton makes it a quartet. That was in there proton spectrum; and just because you are now looking at the carbon-13 NMR, it does not mean that this coupling does not exist. It exists right?

That coupling also exists. Now what about those long range proton-proton couplings, what happened to do that? How do they get reflected in the spectrum? Let us look at it. Now if I look for this carbon-13 isotopomer, we got carbon 13 proton couplings here, which was a quartet, but at the same time these two protons are also coupled to this, and as a consequence carbon-13 spectrum is going to be a triplet because of the CH2 carbon, CH3 carbons will be a triplet because of CH2 protons, you get the point.

This is quartet is because of these 3 protons and this triplet is because of this coupling, this carbon is also coupled to this and also coupled to these 2 protons. Remember, these 2 protons do not think when this proton is coupled to this, you cannot say this is not coupled to this, the long range coupling. So this carbon is not only a quartet because of this, it is also coupled to this one and further gives additional triplet, because they are equivalent to protons. Remember I am looking for carbon now, then you may ask me a question what happened to proton-proton coupling? Again do not get confused. They are passive spins, so proton-proton couplings you are not going to see here. You see only coupling between the active spin and passive spin you get coupling of this carbon to these 3 protons, which is a quartet; coupling of these carbons with these two protons will be additional triplet.

So that will be coming into the picture. I am sorry this is a mistake, which is made. It is not 3JHH, it is 3JCH we will come to it. So similarly this is also 3JCH. This not HH will not be seen, I said HH will not be seen. And this is what it is, it is 3 bonds CH coupling is also seen; and similarly here also if I look for this CH2 carbon you are going to get a coupling of this carbon to these two protons, will be a triplet and addition to that these three protons also coupled to this carbon. Is it clear now? So carbon can experience simultaneously coupling to other protons also.

Earlier I said you will see only quartet but I am now bringing in the long range, it is CH coupling. So long range CH couplings are also getting reflected here. Now CH2 carbon will be quartet because of this coupling and CH2 carbon will be a triplet because of this, and also because of CH3 protons it is going to be an additional quartet.

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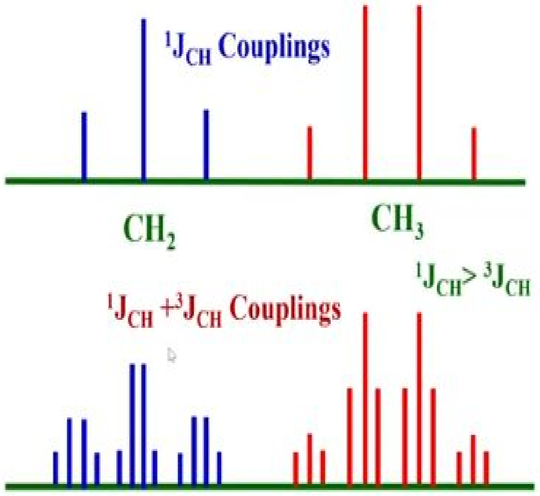

Let us look at this spectrum very carefully. What is 1JCH? This is this spectrum, this is CH3 and this is CH2. You understand? We are seeing these things. Now if again this is a 1 bond coupling, Now this realistic spectrum, where CH3 carbon is coupled to 3 protons and is a quartet, CH2 carbon is coupled to 2 protons and it is a triplet. Now, there is a long range 3JCH coupling, the protons also coupled to this carbon. For these 2 protons there is also coupling with these 3 protons, these 3 protons coupled to this carbon. What will happen now?

Each line of the triplet is going to become a quartet. Is it clear now? Each line of this triplet is going to become a quartet. Similarly, here also directly bonded carbon to three protons will give a quartet. It is only a stick plot, I am giving to make you understand. Directly bonded carbon to protons will give rise to a quartet, but there is also a remotely bonded proton to this carbon. What will happen? Then each carbon line, which is a quartet, is going to be a triplet.

So what is happening is, the long-range CH couplings are also possible, if I look at this molecule. Like this we have a directly bonded carbon proton coupling, which makes this a quartet and it is also having a long range protons coupling to this carbon, which makes each line of quartet be a triplet because of this, exactly same here it will be a triplet of a quartet, it will be a quartet of triplets.

That is the real spectrum, you see. If a carbon 13 spectrum is real spectrum is obtained bringing all protons coupled to all the carbons. It is a fully coupled carbon 13 spectrum. Assuming this long-range couplings are seen, now this carbon if you see CH3 carbon is going to be a quartet of triplets. Hope you are all clear, what I am telling. So large coupling, the quartet is because of direct CH coupling and the triplet is because of a long-range carbon proton coupling. Similarly it is going to be a triplet of quartets.

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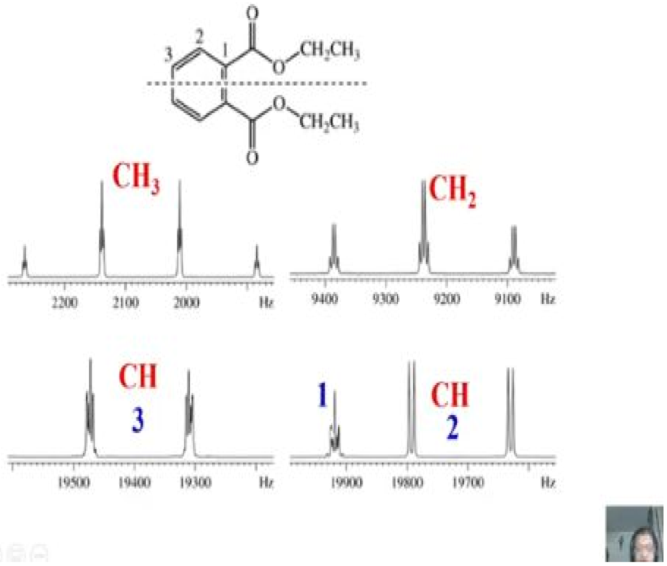

This is exactly what we are going to see in the realistic spectrum, if you see all protons coupled to all the carbons. This is what it is, look at this CH3 carbon. This CH3 carbon is a quartet because for 1 bond CH coupling; will be the quartet and these two protons are also coupled to this carbon, long range proton carbon coupling. Then what is happening? Each line of this quartet is a triplet. This CH2 if you look at it, this carbon proton coupling is a triplet and this carbon is coupled to these 3 protons; as a consequence each line of this triplet is a quartet.

You understand? Similar to the proton spectrum, but here we are observing carbon-13, we are seeing carbon protons coupling one bond and carbon proton two bonds couplings or 2 or 3 bonds coupling. This is what you are seeing; and that is what if you can see the spectrum of other carbons also you can interpret like that.

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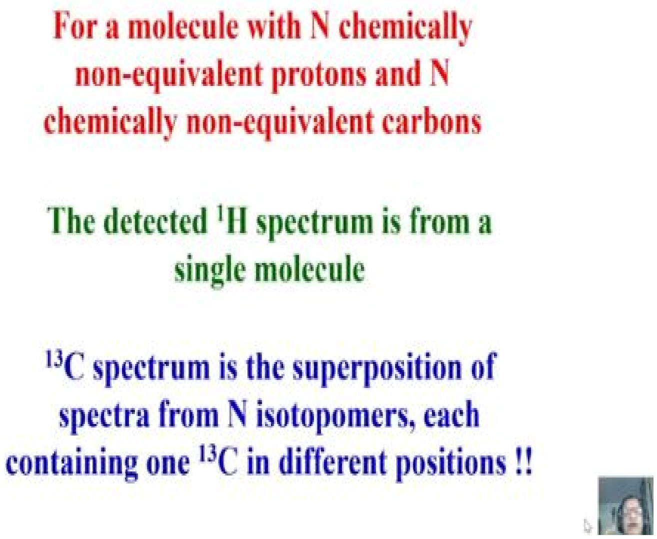

For a molecule with N chemically non-equivalent protons and N chemically non-equivalent carbons

The detected ^{1}H spectrum is from a single molecule

^{13}C spectrum is the superposition of spectra from N isotopomers, each containing one ^{13}C in different positions !!

So what do you understand from this? For a molecule containing N chemically non-equivalent protons, and N chemically non-equivalent carbons, the detected protons spectrum is from a single molecule. Because all the protons are 100% abundant and simultaneously you can see all the protons present in the molecule, you can get the spectrum directly, all the peaks from all the protons can be obtained from a single molecule, no doubt at all.

What about carbon 13? Carbon-13 spectrum is the superposition of spectra from N isotopomers, each containing one carbon in different positions. If there are 10 carbons in the molecule, in the real carbon-13 spectrum what you see? It is not one spectrum, it is 10 spectra, each corresponding to different carbons, they get superimposed and that is what you are seeing in the carbon-13 spectra. You understand, please remember. You are not seeing the spectrum from a single molecule in carbon-13.

Every carbon in this carbon 13 position will be an isotopomer, 10 carbons have 10 isotopomers and then the individual spectrum of each of them are the there, like I gave the example of a ethyl alcohol, all of them would be superimposed. As a consequence, the carbon 13 spectrum is not from a single molecule or single isotopomer. It is always what you see is the superposition of spectrum from different isotopomers corresponding to the number of equivalent carbons.

So a simple formula you remember, if there are N chemically inequivalent carbons in your molecule, there are 10 NMR spectrum corresponding to each carbon in carbon-13 state, that is they are all superimposed, and that is what you are seeing. Please remember that.

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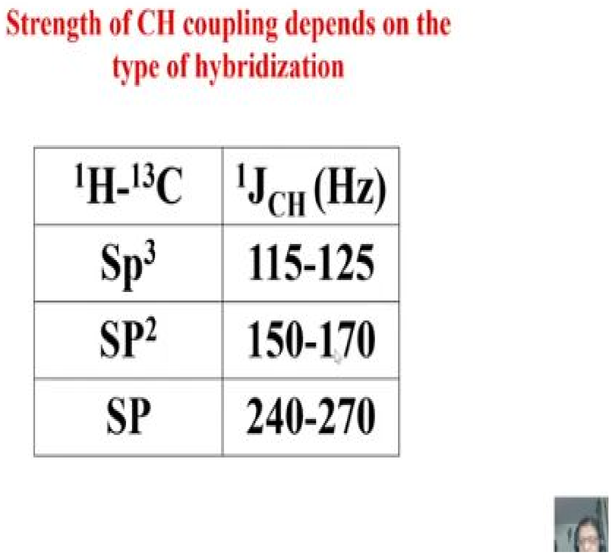

Strength of CH coupling depends on the type of hybridization

^1H-^{13}C	$^1J_{CH}$ (Hz)
Sp^3	115-125
SP^2	150-170
SP	240-270

Now, we will come to the strength of CH coupling. What is the approximate value of the carbon coupling which you should have an idea. Like proton proton coupling as I said 1 bond coupling, 2 bond couplings, 3 bond couplings, etcetera. In the case of, CH coupling 1 bond carbon proton coupling if it is Sp3 hybridized carbon, it is around 115 to 125 hertz. If it is Sp2, it is still larger, Sp carbon is 240 to 270 hertz.

One bond coupling, remember, 1 bond 1JCH. So depending upon the type of hybridization, if you go to Sp hybridized carbon the carbon proton 1 bond coupling is 240 to 270 hertz, quite large. For Sp3, it is much less and Sp is the largest and Sp2 is in between. This is the important thing you should know when you are analyzing the carbon 13 spectrum.

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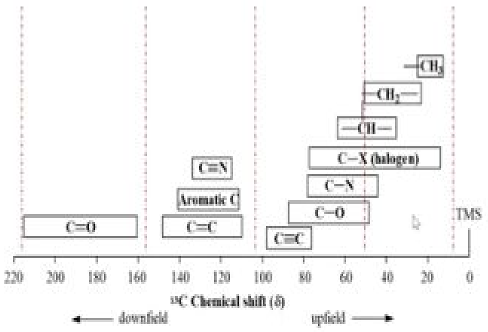
^{13}C Chemical Shifts



Similar to the proton spectrum I showed you by different functional groups of the carbon, also there are varieties of groups for which the chemical shift ranges have been more or less identified. Suppose you have a carbonyl carbon, I have to see the peak somewhere around 160 to 220 ppm. I told you carbon 13 goes from 0 to 300 ppm unlike proton. If I have to see aromatic carbon, I will see the spectrum from somewhere around 100 to 140, 150, like that.

If I see a CH3 carbon it is somewhere around 20 ppm. Exactly the chemical shift pattern that we saw in the proton, similar trend is there also. There whatever the factors which affect the chemical shift of protons, will also affect the chemical shift of carbon in the same manner, there is no difference. So that is why you can look at this chart and then from the chart you can identify which carbon is coming where ,and the interpretation becomes much easier.

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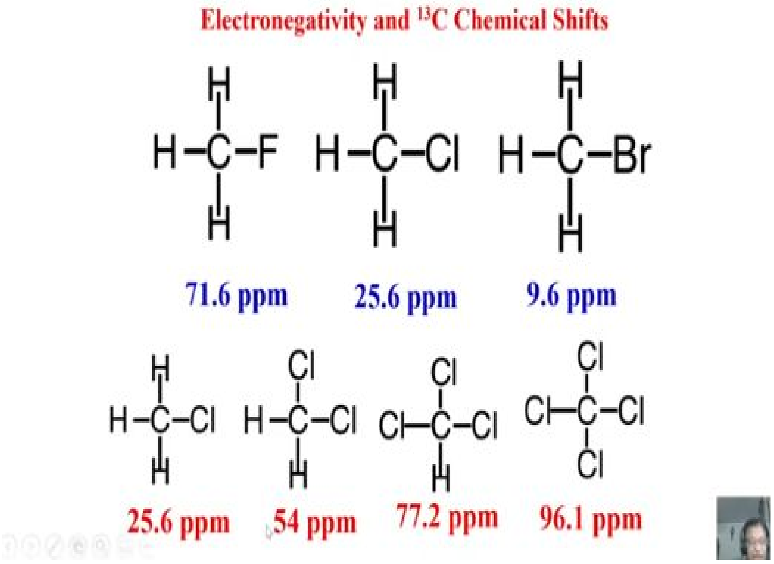

Electronegativity and ^{13}C Chemical Shifts

71.6 ppm 25.6 ppm 9.6 ppm

25.6 ppm 54 ppm 77.2 ppm 96.1 ppm

Similarly, if you look at the electronegativity and carbon 13 chemical shifts, exactly what you saw in case of protons. Now take an example of a molecule CH4 where one proton is knocked off and fluorine is substituted. This comes at 71.6 ppm, instead of fluorine if I put chlorine you get at 25.6, instead chlorine if I put bromine it comes to 9.6 ppm. What does it tell you? Again, more the electronegativity it withdraws electrons from the carbon as a result that carbon shift downfield.

That is exactly what you observed in protons right? The logic is the same, the phenomena is not different. So depending upon the electronegativity of the substitution, the chemical shift of the carbon starts changing like this. Bromine is least electronegative compared to carbon, much less compared to chlorine, it is 9.6. Chlorine is less electronegative compared to fluorine comes at 25.6 and the fluorine is the most highly electronegative atom when it is attached to these it comes at 71.6.

Now you can see that here also, as you saw CHCl3, CH2Cl2, CH3Cl, CCl4 we observed in proton, of course, we do not see CCl4 but now let us see what happens as we see the number of chlorines which are bonded to carbon keeps increasing in the molecule, like this. If one of the protons is replaced by a chlorine it comes at 25.6 ppm. If two chlorines are bonded to the same carbon here, it comes at 54, when three are there it is at 77.2 and all the 4 protons are replaced by chlorines it comes at 96.1.

It is exactly what we saw in proton, depending upon the number of electronegative atoms that are attached to particular carbon, more the electronegativity atoms substituted, what will happen, it will get more de shielded and starts moving to the low field. So that means towards the higher ppm value it goes, exactly the trend we have observing.

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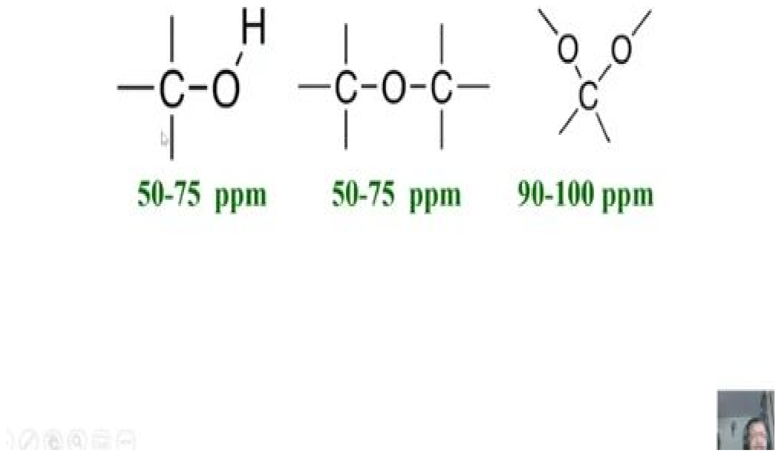

So we have different groups like this, if I have a carbonyl carbon, these are all the given in the chart which I showed you earlier, or many you can see these type of information is available in the literature quite a bit. If I look for the carbon like this which is attached to 2 oxygens like this, the chemical shift may be approximately around 90 to 100 ppm. For carbon like that, which is bonded to an oxygen atom, it is around 50 to 75 ppm. Similarly, this carbon attached to OH group is around this range.

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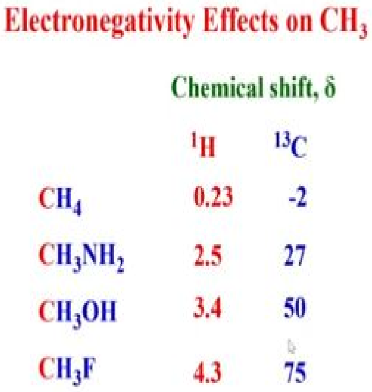
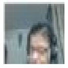


Electronegativity Effects on CH_3

Chemical shift, δ

	^1H	^{13}C
CH_4	0.23	-2
CH_3NH_2	2.5	27
CH_3OH	3.4	50
CH_3F	4.3	75



So like this we have a variety of things; electronegativity effects in the carbon can also be seen. For example, especially for CH3 examples I took as an example. If I have CH4, you take this molecule, in the case of proton, we saw this highly shielded 0.23 ppm, now in carbon also CH4 is highly shielded, it goes beyond TMS, -2 ppm. Similarly, if one of the protons is replaced by NH2, then it comes to 2.5 in the case of proton, this CH3 proton, whereas in carbon 13 it goes to 27 ppm.

Similarly if I go to CH3OH, this proton attached the carbon comes at 3.4 ppm in proton, whereas carbon comes at 50 ppm, this carbon highlighted, all colored in red. Now CH3F, these three protons in the proton NMR comes at 4.3 ppm, whereas in carbon 13, it comes to 75. Exactly the trend is same; see there, if a proton is coming to the down field, the carbon attached to the same proton also follows the similar trend. That is what I wanted to say.

The electronegativity effects on the particular CH3 group, how it affects the proton spectrum, in the like manner the carbon 13 chemical shifts are also affected. But the only thing is the range is here 0 to 10 ppm, here the range is from 0 to 300 ppm, the correspondingly chemical shift values are quite large here. That is the only difference.

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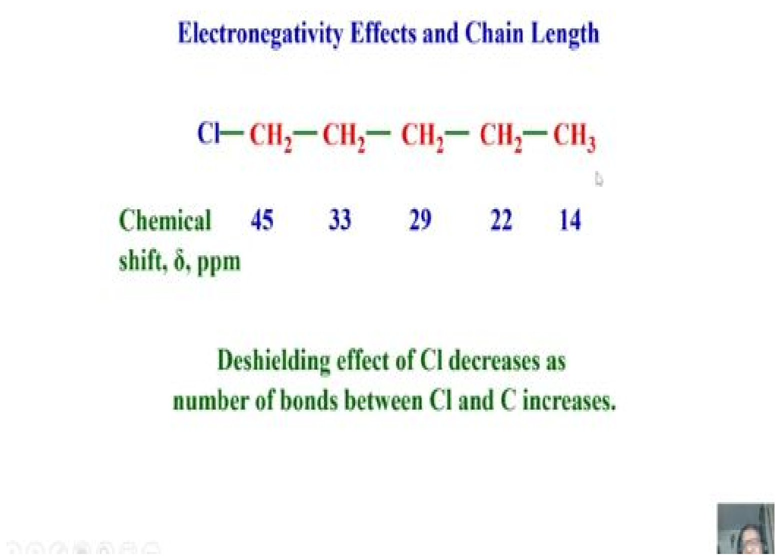

Electronegativity Effects and Chain Length

$Cl-CH_2-CH_2-CH_2-CH_2-CH_3$

Chemical shift, δ, ppm 45 33 29 22 14

Deshielding effect of Cl decreases as number of bonds between Cl and C increases.

We saw what happened as a chain length increases, we saw the induction effect when we substitute the electronegative atom; how it affects, we saw that in protons also. Now a long chain molecule is taken; an hypothetical molecule, do not worry what is attached, what is this molecule. Now one of the protons is replaced by a chlorine here, now this carbon comes at 45 ppm, this carbon comes at 33 ppm, 29 ppm, 22 ppm and 14 ppm, only I am concentrating on the carbon here.

The carbon chemical shift, sees what happens to the one which is directly attached to the electronegative atom, that carbon is lowest; comes almost downfield, at highest ppm value, that is 45 ppm. As you keep on going this way, the next neighbour, next neighbour like that, the induction effect keeps reducing and if you come to this CH3 carbon, practically its effect is quite a bit reduced and it still comes at high field.

So this is what I wanted to show: the electronegative effects also have the same inductive effect as you in protons, the trend also similar, it keeps reducing as the chain length increases. The deshielding effect of chlorine is very clearly seen with the increase of the number of bonds.

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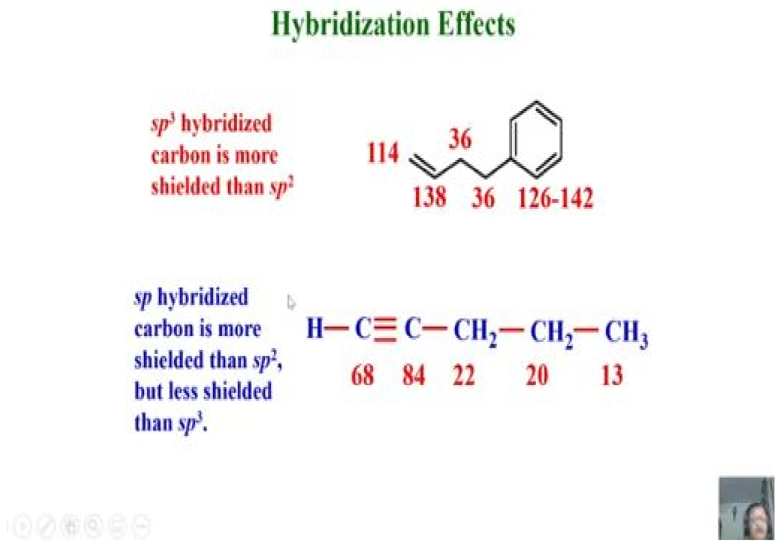

Hybridization Effects

sp^3 hybridized carbon is more shielded than sp^2

sp hybridized carbon is more shielded than sp^2, but less shielded than sp^3.

$\mathrm{H{-}C{\equiv}C{-}CH_2{-}CH_2{-}CH_3}$

68 84 22 20 13

What about the hybridization effect? Same; look at the hybridized carbon here, these different types of carbons, sp3 carbon is more deshielded than sp2. There is a simple formula you remember. It is a general trend, sp3 hybridized carbon if it is there, that is more shielded than a sp2 carbon. Now similarly sp carbon is more shielded than sp2; but less shielded than sp3. Order you remember now, which is more shielded? sp3, then sp2, then sp.

The shielding effect on the chemical shift if you want to see; the first more shielded is sp3, then sp2 and sp. So sp3 carbon comes at high field, then sp2 carbon, then sp. That is the way the trend follows. So sp3 carbon is more hybridized than sp2; and the sp hybridised is more shielded than sp2; but less shielded than sp3.

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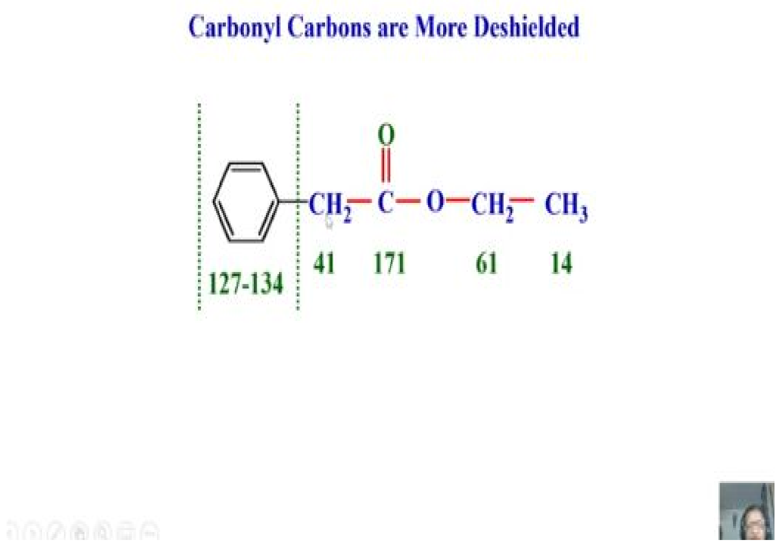

Carbonyl Carbons are More Deshielded

So carbonyl carbons are more shielded we can see here. Generally, and in a molecule like this you all different types of carbons, the aromatic carbon comes around 120 to 140 ppm, carbonyl comes at 170 and CH3CH2 will come similarly here, CH3 generally comes between 10 to 20 ppm, this is 20 to 30 or 40 ppm; like that. So these are all similar trends to the proton chemical shifts.

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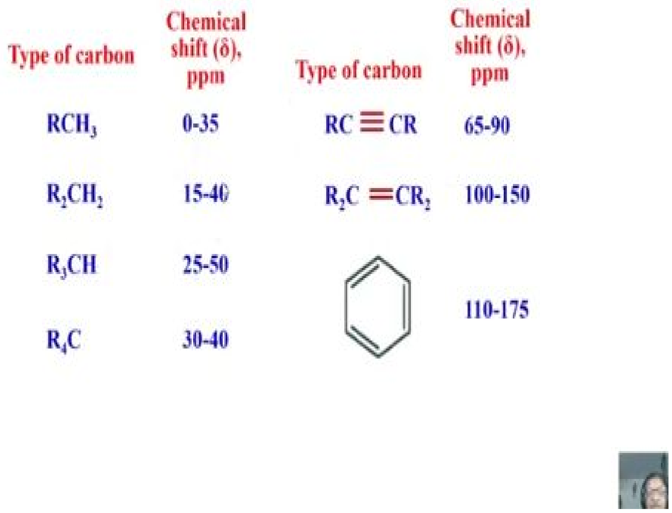

Type of carbon	Chemical shift (δ), ppm	Type of carbon	Chemical shift (δ), ppm
RCH_3	0-35	$RC\equiv CR$	65-90
R_2CH_2	15-40	$R_2C=CR_2$	100-150
R_3CH	25-50		110-175
R_4C	30-40		

Look at the different types of carbons when it is attached to the R group, the type R group that you are to have, the chemical shift varies like this.

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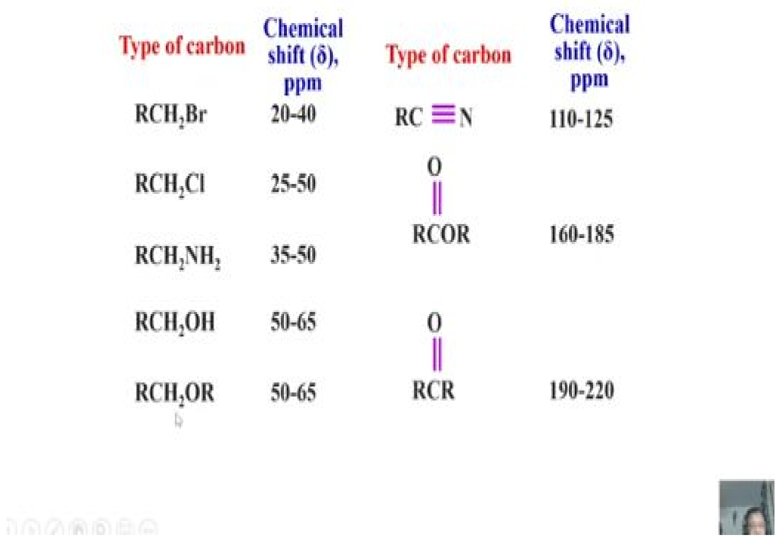

Type of carbon	Chemical shift (δ), ppm	Type of carbon	Chemical shift (δ), ppm
RCH_2Br	20-40	$RC\equiv N$	110-125
RCH_2Cl	25-50		
RCH_2NH_2	35-50	$R\overset{\overset{O}{\|}}{C}OR$	160-185
RCH_2OH	50-65		
RCH_2OR	50-65	$R\overset{\overset{O}{\|}}{C}R$	190-220

So these are all general ideas, and some information. I take a carbon like this, type of carbon RCH2Br bromine, fluorine, this is what we saw for a CH3 group. Similarly, if you have an R attachment like this how these carbon chemical shifts are affected; it is same trend, follows the similar trend you can see. If I have a RCH2Br and if I have R group is this one then chemical shift of particular carbon, this carbon is around 110 to 125 ppm.

Extend the logic like this, if you have a RCH2OH, if R group is, let us say, if the R group is C double bond O; and R is the on either side, this and this; this carbon comes very down field at 190 to 220ppm.

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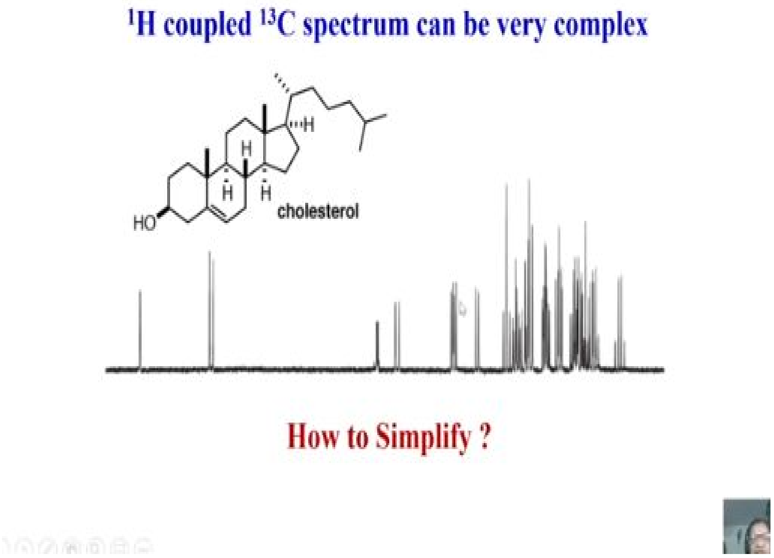

^{1}H coupled ^{13}C spectrum can be very complex

How to Simplify ?

So this is the type of information we get especially for different chemical shifts of carbon. So in a realistic example we get a spectrum this like this, For a big molecule this is a carbon 13 spectrum. Now your job is to analyse. First you have to simplify this spectrum, to identify number of carbons. Remember it is a carbon spectrum you have to assign peaks to each carbon; how you do that? This is a problem by irself. You understand this is now,we will start analysing the carbon 13 spectrum.

So I today I will stop here. Today I gave you an idea about how carbon 13 spectrum is affected. When there are directly bonded protons how the carbon peak is split, how it splits because of the remote bonded protons; what are the types of factors that influences the chemical shift; the range of chemical shifts of carbon and also pointed out the factors that affects the chemicals shift of proton also affects chemical shift of carbon similarly, etc. So, I will stop here, in the next class will start analysing the spectrum of carbon 13.