Advanced NMR Techniques in Solution and Solid-State

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Module-09
Analysis of NMR Spectra and Their Analysis
Lecture - 09

Welcome back, in the last class we discussed a lot about scalar couplings, multiplicity patterns; everything we understood. We also tried to analyze some of the spectra, by using a family tree approach. It is not a realistic spectrum, used the hypothetical molecule with a hypothetical values for the couplings; we wanted to simulate the spectrum synthesize and see how the spectrum comes for a given molecule.

The classic example we took was CH_2D_2; where carbon 13 proton and deuterium all the 3 different nuclei are there. One is natural abundance of 1% other 2 are labeled. The deuterium is 100% and at the same time one is spin one nuclei; other are spin half nuclei. We could get this multiplicity pattern very easily. And we also understood quite a bit about varieties of multiplicity pattern and what is the nomenclature adopted in naming the multiplicity? That we see when 1 spin is coupled to varieties of other spins, both chemically equivalent or nonequivalent. We understood quartet, doublet, triplet, septet, pentet and multiplicity like doublet of a quartet; multiplicities like a triplet of triplet, triplet of quartet, all those things were understood. We are using the idea now to analyze some of the simple molecules, simple spectra of proton and other nuclei.

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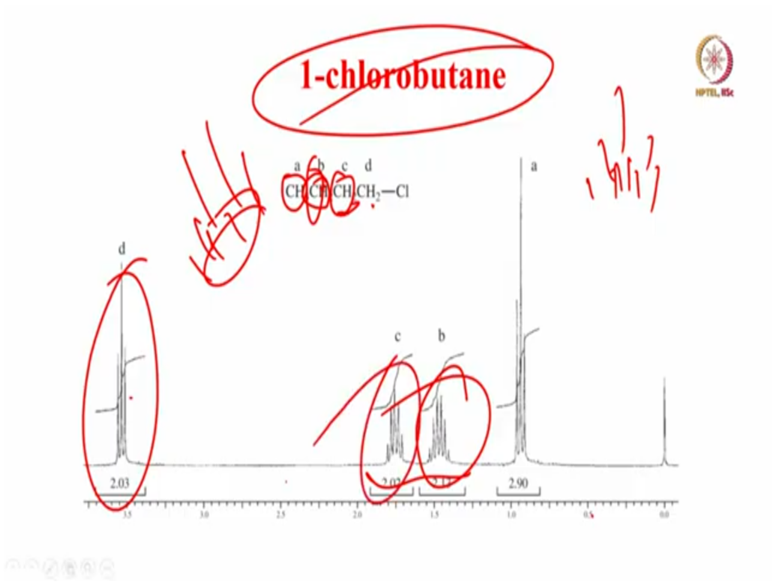

So, today we will come back and start with what is called the analysis of the spectrum. I think the simple molecule 1-cholorobutane is a very simple molecule whose structure is given. It is a realistic spectrum, it is not synthesized. So, now looking at the molecule we can say there are 4 different groups of protons. Obviously you must get 4 different groups of proton peaks, of course this is a reference TMS.

Now the basic knowledge tells me CH3 group generally comes in the high field region, around 0 to 0.5 to 1 or 1.5 ppm; CH3 group will come. So, this is my first guess; if this is a CH3 then it is a triplet, why is it triplet? It is because you can see that this is coupled to CH2; because this is coupled to CH2; though that CH3 has become a triplet that is correct.

Now what is happening? After that another easiest thing to understand is the CH2 which is attached to chlorine; because chlorine is an electronegative atom it withdraws the electron from the CH2 and comes to the downfield. So, this must be a CH2 protons attached to chlorine; and why it is a triplet again? Because this is adjacent group is again CH2 and it is a triplet; very easily we understood.

Now the remaining 2 groups, how do you understand that? Very easily you can understand remember, here one important thing you should go by the multiplicity pattern here. See if you go by the multiplicity pattern here; now consider a and proton b. If I take proton b the proton b complexity is much more than proton c the reason is this proton b is coupled to CH3 and CH2 both.

So, because of CH3 is going to be a quartet and then futher the quartet is going to be a triplet because of CH2; it is a more complex pattern. Whereas, on the other hand proton, c is coupled to 2 CH2; it is going to be triplet of triplets. That is what we understood earlier in the multiplicity pattern. So, the one which is more complex should be proton b; see this is more complex. I would say this is proton b; and this is proton c. This is how based on the chemical shift, based on the multiplicity pattern because of the scalar couplings, you can make the analysis of the given spectrum.

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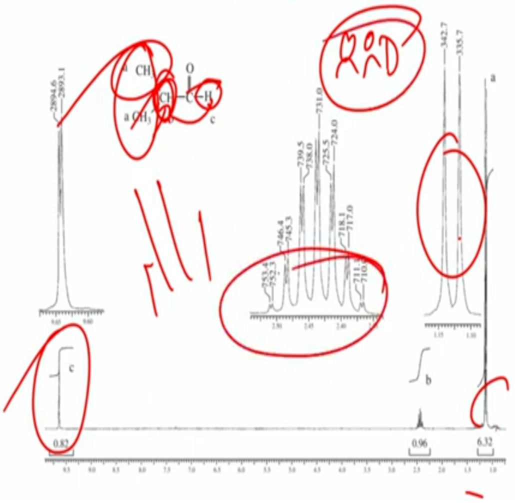
^{1}H spectrum of 2-methylpropanal (isobutyraldehyde).



Now we look at another molecule 2-methylpropanal. It is a very easy to analyze; very simple molecule. Looking at the molecular structure given here. One is CHO; adehydic group is there CHO; this because of this CO, will come to downfield. So this must be CHO proton. And of course this is going to be a triplet; why it is a triplet? If you look at these why it is a triplet, very easily from the spectrum; from this structure you know this CH has a long range coupling with this CH proton; because of that long range coupling this is going to be a doublet; because of coupling with this proton, this proton splitting this into a doublet. Now let us see what will happen to these 2 CH3s, these 2 CH3s are here, are they equivalent? they are not equivalent; but this will couple to this proton and become a doublet and that has to be well resolved. This in principle is going to be doublet of doublets as a matter the resolution is poor. Look at the CH proton here; the CH proton; each of these 2 methyl groups are chemically inequivalent and each of them is split this into a quartet and each line of the quartet is further split in the quartet with CH3 group; but also it has a long range coupling with CH. So, it will become quartet of a quartet of a doublet; and a very complex pattern. You can look at it here; this is a very complex proton spectrum. And of course you can analyze, it is not so difficult. One can start looking at it analyze very easily.

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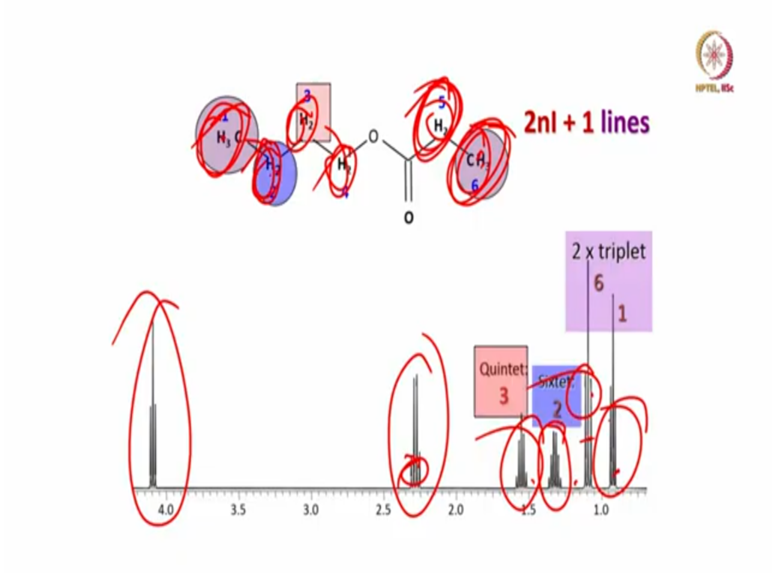

Now we look at this; it is another one, easiest way to understand; very simple spectrum. There are 6 groups of protons here 1, 2, 3, 4, 5 and 6; there should be 6 groups of peaks; you can see here; the 6 groups of peaks. Now go by the multiplicity pattern, that is what I just now said. And here this CH3 is coupled with this CH2 that is a triplet; this could be 1 let us say.

There are 2 CH triplets here which is which we will see later. This one is a triplet and the CH2 has to be a quartet because of this CH3. We have the quartet here; this is the only quartet and there is no other coupling possible because they are separated by several bonds 1, 2, 3, 4 bonds away; coupling is almost 0; so you will not see. So, this has to be a quartet this has to be a triplet. Two groups are identified, then you come here this CH3 has to be a triplet because of the CH2.

So, another triplet is there and then this CH2 is quartet and then also become a triplet because of this; like I said in the previous example, this is a very complex one; is going to be like this. Whereas this one is going to be triplet of triplets like this; whereas this is the only isolated

CH2 group which has coupling only with this; not any of the other protons. So, this is going to be a CH triplet, where easily you can make the analysis.

Now the question is which triplet is which? whether this or this? What you have to see look at the separation here, the coupling which one matches with this one; this or this? You can identify because this is quartet is coming because of this; then you know this coupling has to match. It should be identical from that; you can identify whether this CH3 is this one or this one? So very easily you can do that. This is how analysis can be done.

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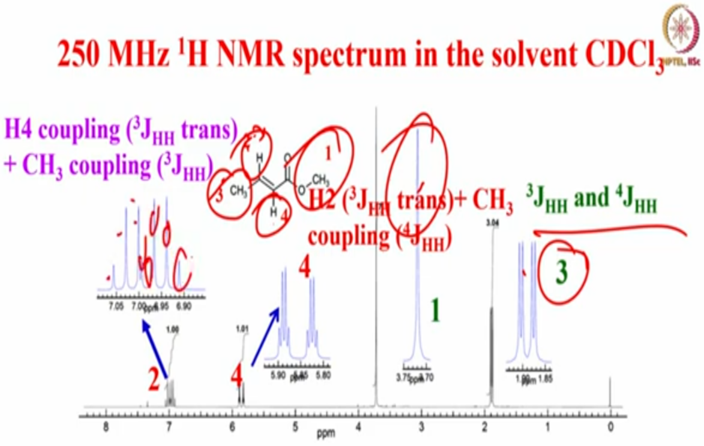

250 MHz ^1H NMR spectrum in the solvent $CDCl_3$

Now of course this is another very simple molecule; look at the proton here CH3 there is no other coupling for this proton CH3 proton. All the 3 protons are equivalent, and the other remaining protons are far away situated. So, what is the pattern you expect for this? A singlet that is what you get; that is simple I can assign this for CH3 group. Next look at this one this is I call it as 3, because this is CH3 group which is coming high field; at the same time it is going to be a doublet because of this proton. And another doublet because of this proton it is going to be doublet of doublets with 2 couplings between these 2 protons. So, I can safely say this is proton 3. Very good; then what is the other thing, which I have to understand. The only remaining 2 protons you know. So, which are the remaining 2 protons? I will say this is proton 2; this is because this has 1, 3 bond coupling with trans and also CH3 coupling. For 1 coupling this is a proton 4; now this is proton 2. In the case of proton 2, this is coupled to proton 4 and it is going to be a doublet and each doublet is going to be quartet because of

CH3; see 1, 3, 3, 1 quartet 1, 3, 3, 1 other quartet 2 quarters are overlapped. So, this has to be proton 2 and this has to be proton 4.

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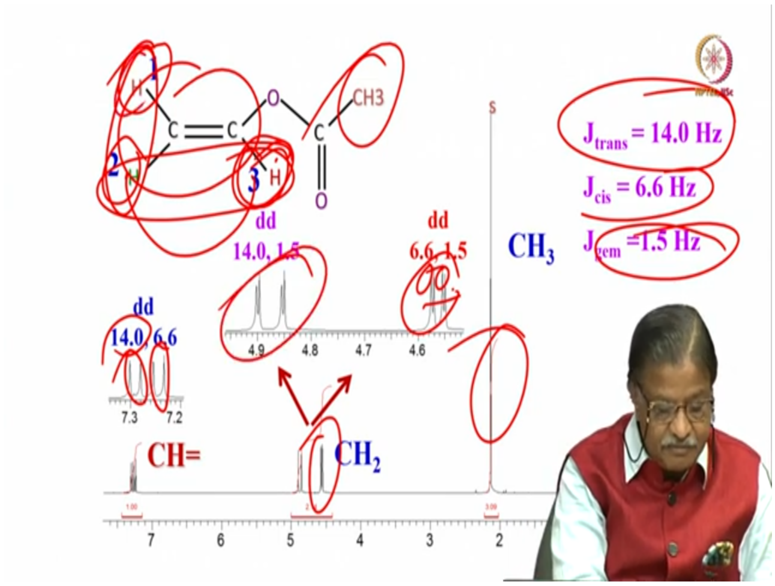

$J_{trans} = 14.0$ Hz

$J_{cis} = 6.6$ Hz

$J_{gem} = 1.5$ Hz

Like this you can start making these assignments. So, we can keep on talking about these things there is no end for it. I will go into another spectrum where you are going to use the knowledge of cis and trans coupling. I will take this example; this is where I told you know it is trans coupling; in this double bond ethylene group like this. I told you trans coupling is larger than cis coupling; and cis is larger than geminal coupling. That idea can be utilized to analyze which proton is which here.

For example the CH3 is isolated single peak. It is a singlet, no coupling at all that is clear. Now between these 3 protons which is which very easily you can understand. Look at the CH proton 1; CH proton has a trans coupling and cis coupling. Which is that one? this CH3 proton has a trans coupling, this is a large coupling 14 hertz; trans coupling is 14 hertz, and also cis coupling both are simultaneously present; and the cis coupling is 6.6 hertz.

So, it is a large doublet and each line of the doublet is going to split into the doublet of doublet like this. So, this has to be this proton. Using the knowledge of cis and trans couplings I could assign this. Now the remaining 2 what about this proton? This proton experiences a trans coupling with this and a geminal coupling with this. The geminal coupling is very small, where is it? we can see this is the only possibility is here, the large coupling and a small coupling of 1.5 hertz. So, this has to be this proton; or what about this proton? This proton experiences cis coupling here. At the same time, it experiences geminal coupling with this; that is very easily we can start analyzing every things.

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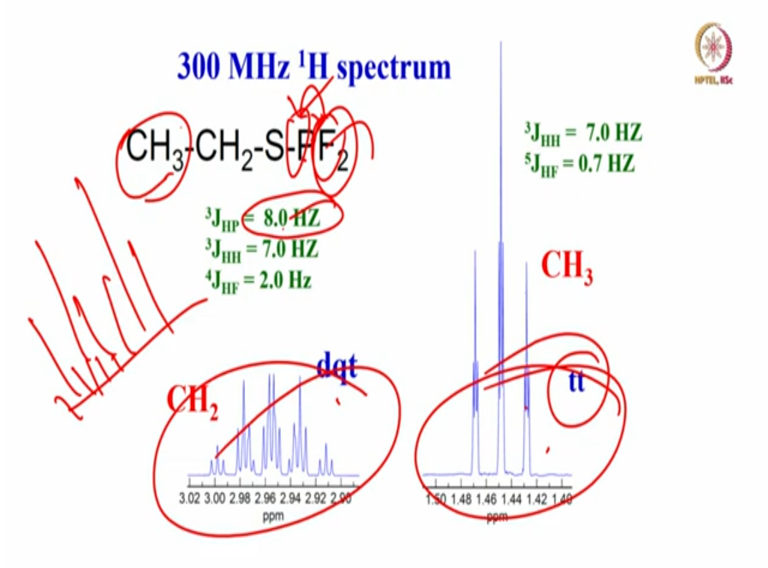

300 MHz ^1H spectrum

CH_3-CH_2-S-PF_2

$^3J_{HP}$ = 8.0 HZ
$^3J_{HH}$ = 7.0 HZ
$^4J_{HF}$ = 2.0 Hz

$^3J_{HH}$ = 7.0 HZ
$^5J_{HF}$ = 0.7 HZ

So, now I will go to a molecule where there need not be only proton coupling; you can observe in the proton spectrum the hetero-nuclear couplings also. For example in this proton spectrum of this molecule; there are 2 proton groups CH2 and CH3; but each of them has a coupling with phosphorus which is spin half nucleus; and fluorine which is again spin half nucleus. Both of them are 100% abundance.

So, it is quite likely there is a coupling of CH3 to CH2, phosphorus and fluorine. Similarly this can couple to this and this. You see the pattern now. Now the common sense tells me, as I have been telling you, in the high field region methyl comes. This methyl proton is here; this has to be a triplet here, because of this first it is a triplet; very clear. At the same time it is also another triplet of a triplet; because of the fluorine coupling, very clear. What about phosphorus coupling? it is not there; that coupling is 0. That is why CH3 proton gives triplet of a triplet. It has one triplet because of this CH3, proton another triplet because of 2 fluorines. So, we are going to get to triplets of triplets. Whereas, come to this group, this CH2 group, the CH2 becomes a quartet because of CH3. I will erase that and you will see that now. This CH2 becomes a quartet because of this CH3; that is correct.

So, now because of this, it is a quartet. At the same time, you see it is also has a coupling with phosphorus and also coupling with fluorine. But with the coupling information given here, you see a proton phosphorus coupling is quite large. So, it is going to be firstly large doublet of 8 Hertz because of phosphorus and proton coupling. The second is proton, proton coupling, this coupling. Then it will become a triplet.

Further each line of this triplet of triplet become triplet because of fluorine; each of them will be triplet like this. So, you will get a complex pattern like this, this is pattern. This is why I gave a lot of examples of multiplicity patterns. It is doublet of a quartet of a triplet. So, in this example I deliberately took; you have proton coupling and also coupled with 2 other hetero nuclei. you may not be observing. What about the PF coupling then?

Remember I explained to you these are passive nuclei, passive coupling is not going to be seen when we are observing proton. So, this passive coupling between phosphorus and fluorine is not seen here. So, you will get only proton coupling; active coupling with passive spins proton to phosphorus, proton to fluorine, proton to proton you see; but not other couplings. So, this is very useful information you can start analyzing this. So, I do not think this I will explain.

(Refer Slide Time: 14:20)

^{13}C NMR

Another extensively utilized NMR nuclei

Now I will go to the carbon 13 NMR, carbon 13 is another extensively utilized NMR nuclei. Most of the time, in organic chemistry or biology by people use carbon-13, nitrogen 15 and proton phosphorus-31. These are extensively studied nuclei. Let us see how does the carbon-13 NMR spectrum looks?

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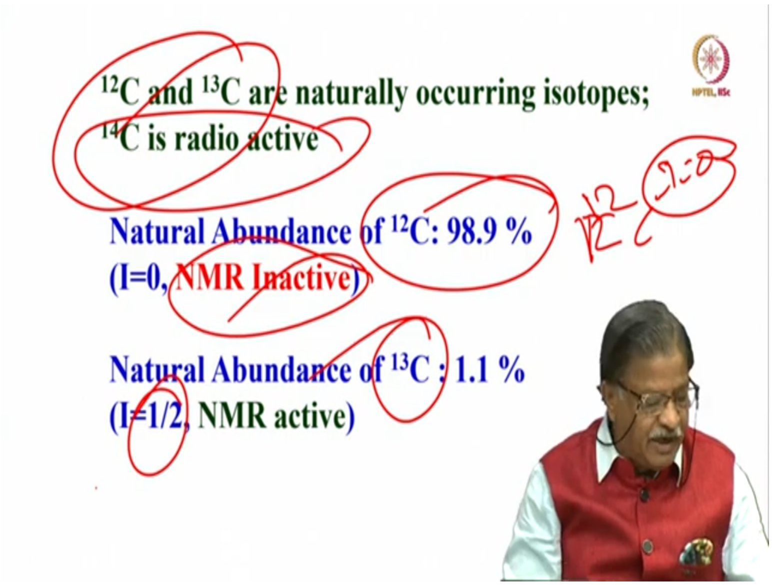

^{12}C and ^{13}C are naturally occurring isotopes; ^{14}C is radio active

Natural Abundance of ^{12}C: 98.9 %
(I=0, NMR Inactive)

Natural Abundance of ^{13}C : 1.1 %
(I=1/2, NMR active)

First of all remember there are 3 isotopes for carbon; 12, 13 and 14, 14 we ignore it is radioactive, we do not see it. The good thing in the nature is carbon 12 is 99% abundant almost 99% but we will not see that. You know why? I explained to you carbon 12 has spin equal to 0. So, magnetic moment is 0; it cannot give NMR. So it is NMR inactive, they are NMR silent nuclei. Now on the other end carbon 13 is 1% abundant that is NMR active. interestingly it is the spin half nucleus, very easy to study; very easy to understand the behavior of spin half nuclei.

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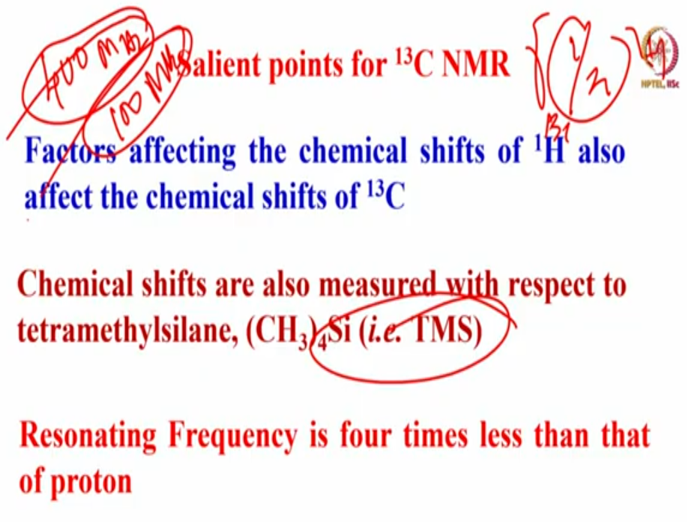

Salient points for ^{13}C NMR

Factors affecting the chemical shifts of ^{1}H also affect the chemical shifts of ^{13}C

Chemical shifts are also measured with respect to tetramethylsilane, $(CH_3)_4Si$ (*i.e.* TMS)

Resonating Frequency is four times less than that of proton

So, another salient point is whatever the factors that affect chemical shift of protons which we discussed, the same thing is applicable for carbon 13 also. Here also use TMS as the reference, like in proton. And only thing is gamma of carbon is 1/4 that of the proton; gamma of carbon. As a consequence, the resonating frequency is 4 times less than that of proton.

That is what we discussed last time. If I have a spectrometer of 400 megahertz; that means for a proton resonating at 400 megahertz; carbon 13 comes at 100 megahertz; that is what it is.

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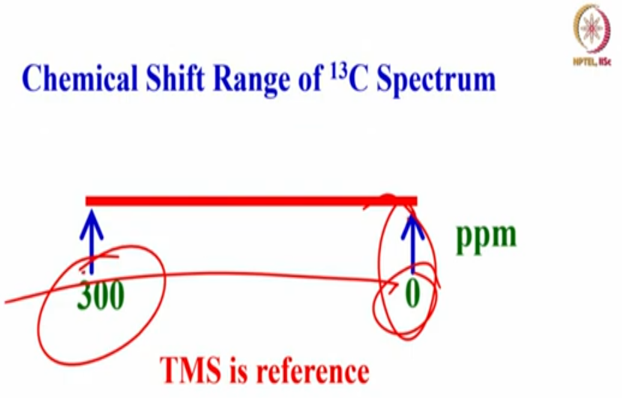

Chemical Shift Range of ^{13}C Spectrum

TMS is reference

But the chemical shift range if you look at it, the chemical shift range of carbon 13 is also 0 to 300 ppm; it is not 0 to 10 ppm like proton. This chemical shift range is much larger here. So, take TMS as the reference put it at 0 ppm and you will have peaks anywhere from 0 to 300; and of course in special cases you can get go beyond 300 also. I am just taking by and large in most of the cases it is between 0 to 300 ppm so this is a chemical shift range of carbon 13.

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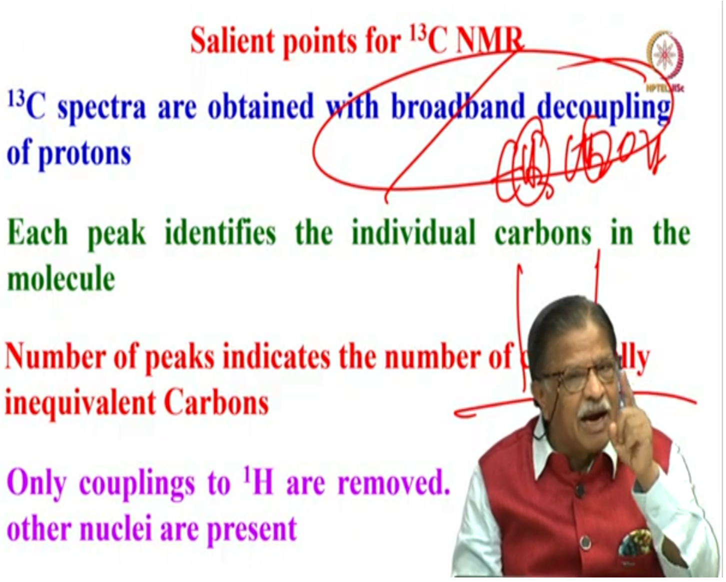

Salient points for ^{13}C NMR

^{13}C spectra are obtained with broadband decoupling of protons

Each peak identifies the individual carbons in the molecule

Number of peaks indicates the number of lly inequivalent Carbons

Only couplings to ^{1}H are removed. other nuclei are present

Now another thing is, carbon 13 we always obtain by decoupling proton. @hat is the decoupling? I have not discussed but for that please go back to my previous course.

Broadband decoupling means simultaneously we break the coupling of all carbons with all other protons. That means in a given molecule there may be n number of carbons; each carbon coupled to n number of protons which are chemically inequivalent; and some equivalent groups which are present elsewhere in the molecule.

But that will give rise to complexity; One carbon, if it is a CH 3 carbon, it will become quartet. If it is coupled to another CH2 protons then it will become quartet of triplet; all this complexity will come. And already carbon 13 is less abundant, 1% sensitivity; is 4 times low gamma compared to proton. So, it is very difficult; why should we have multiplicity pattern which complicates the situation? So, always carbon 13 NMR is recorded by doing what is called a broadband decoupling, where protons coupled to all the carbons are simultaneously decoupled. How do we do that is a different question? that we have discussed in the previous course; Then what will happen? there is no coupling of carbon with protons at all. What does it mean? If I have CH3CH2OH; ethyl alcohol and I look for carbon 13, I break the coupling of carbon with protons. So that means there is no coupling between carbon proton for CH3, I get 1 peak; for CH2 we get 1 peak, that is all. It means for each chemical individual carbons we get only 1 peak. So, if there are n number of peaks, you can simply say there are n carbon is present in the molecule; that is the simple thing. The salient points of carbon 13 NMR is, it is done with broadband decoupling, which removes all the proton carbon couplings.

As a consequence if there are a number of carbons in the molecule, there are number of peaks there are n numbers of peaks, very easy to identify. But then you may ask me a question like hetero-nuclei in the previous example, we saw proton, carbon, fluorine, phosphorus were there. You remove the coupling of carbon and proton by broadband decoupling, but not with other nuclei.

You can do special experiment by removing everything that is a different question, but if you are broadband decoupling proton with carbons, if the fluorine is present or phosphorus is present they are still coupled. Remember that we are not removing; the multiplicity still can be present.

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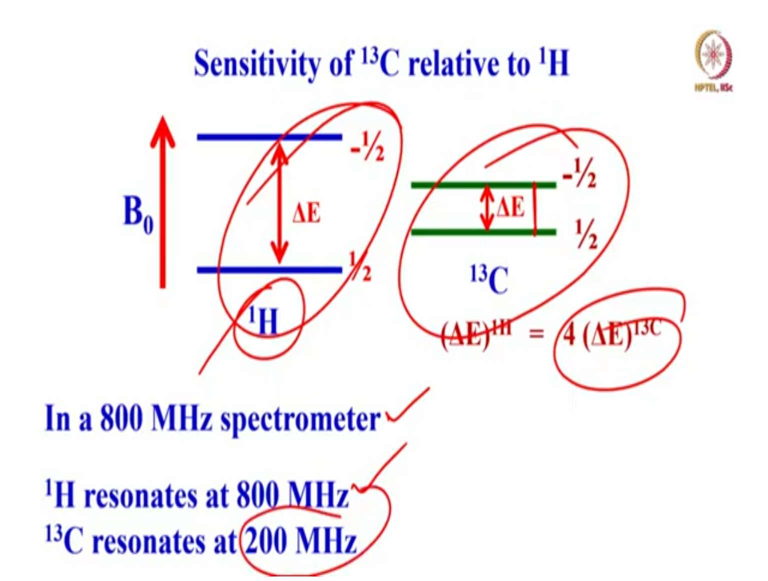

Sensitivity of ^{13}C relative to ^{1}H

$(\Delta E)^{1H} = 4\,(\Delta E)^{13C}$

In a 800 MHz spectrometer

^{1}H resonates at 800 MHz

^{13}C resonates at 200 MHz

So, we will take some examples; as I said Zeeman interaction energy separation is larger for proton because it is more 4 times more gamma than that of carbon. As a consequence energy separation is less 4 times less here compared to proton. So, sensitivity is much, much less here; So in an 800 megahertz spectrometer I get proton at 800 megahertz and carbon 13 comes approximately at 200 megahertz.

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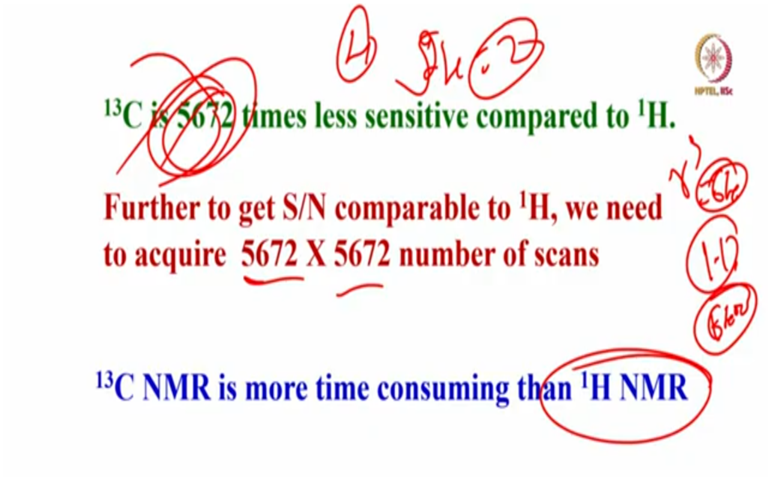

^{13}C is 5672 times less sensitive compared to ^{1}H.

Further to get S/N comparable to ^{1}H, we need to acquire 5672 X 5672 number of scans

^{13}C NMR is more time consuming than ^{1}H NMR

So, more details about carbon 13, which has sensitivity in principle 5670 times smaller. In the previous class we saw that taking into account teh gamma it goes to a cube of gamma and by taking natural abundance we showed that it is gamma cube of approximately 64 we took. And then 1.1% in abundance; if you consider it is 64 into 100, 6400 we said approximately. So, if you precisely calculate this is number of times less sensitive compared to proton.

But signal to noise ratio goes by square of the number. If I acquired 4 scans then signal to noise ratio will be root of 4; it is going to be 2. So, I have to multiply this by this, to get good signal to noise ratio. All these things tell me carbon 13 NMR is more time consuming than proton NMR. That it is very, very time consuming; very less sensitive; very difficult to detect.

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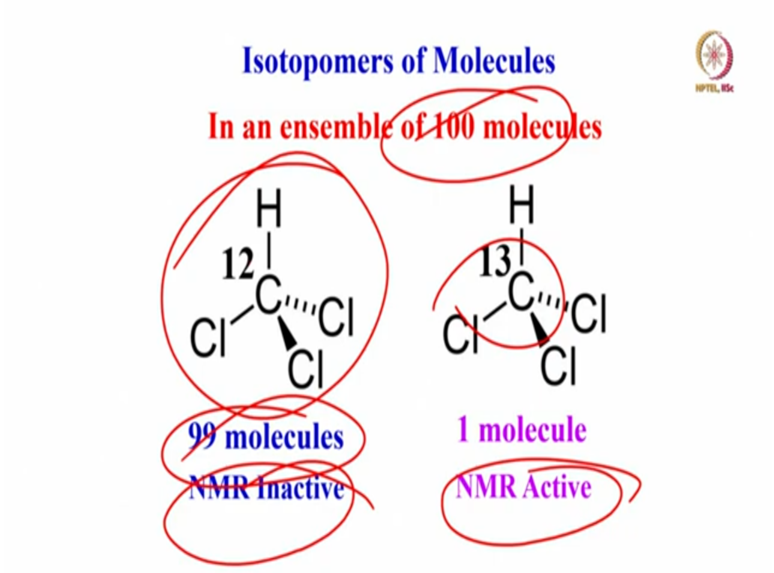

Isotopomers of Molecules

In an ensemble of 100 molecules

99 molecules

NMR Inactive

1 molecule

NMR Active

Now I will give you some salient points and interesting features about carbon 13 NMR. Let us consider an example of a molecule like CHCl3. We will talk about isotopomers of the molecule. I consider 100 molecules are there in my sample tube; an ensemble of 100 molecules. According to me the abundance of carbon 13 is only 1%, abundance of carbon 12 is 99%. So, in an ensemble of 100 molecules we have 99 molecules that are carbon 12. And only 1 molecule has carbon 13; but 12C is NMR inactive and 13C is NMR active.

So, you will see only 1 carbon in its carbon 13 state. All other molecules are carbon 12 which does not give NMR at all.

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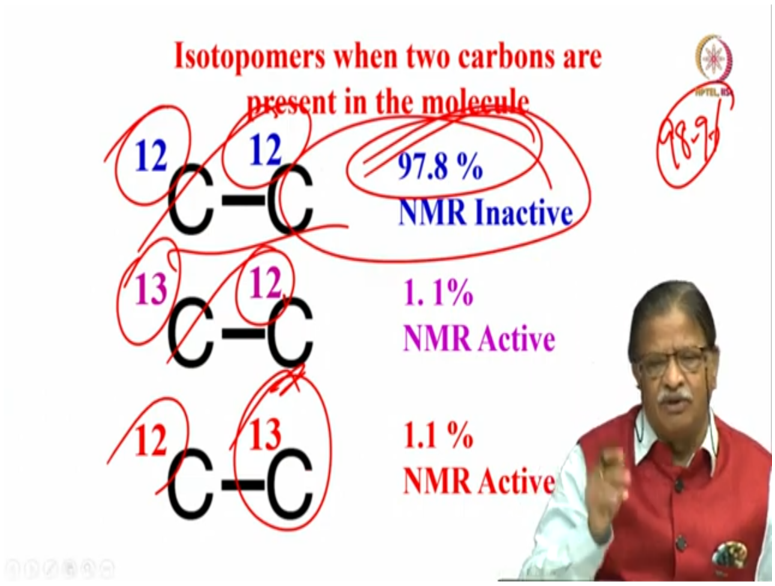

Isotopomers when two carbons are present in the molecule

$^{12}C-^{12}C$ 97.8 % NMR Inactive

$^{13}C-^{12}C$ 1. 1% NMR Active

$^{12}C-^{13}C$ 1.1 % NMR Active

98.9

So, now what happens if I have a molecule with 2 carbons present? Let us consider what will happen? I consider a situation some hypothetical molecule with 2 carbons are present. I have not completed the structure of the molecules do not worry. Now there is a possibility both carbons can be in carbon 12 that is 98.9% present. So, if you take this factor, multiplication of this gives 97.8% of the molecules are in this state.

So that means majority of the molecules what you are observing are NMR inactive. Whereas consider the situation, one of the carbons is in carbon 13 state, other is carbon 12; that is also possible but this is only 1.1% abundant because this is carbon 12 is inactive. Think of another possibility this is carbon 13, this is carbon 12; again it is 1% this is NMR active. So, there are 2 molecules with 1% NMR activity and then 98% of the molecules with 2 carbons in carbon 12 state are NMR inactive; they are NMR silent.

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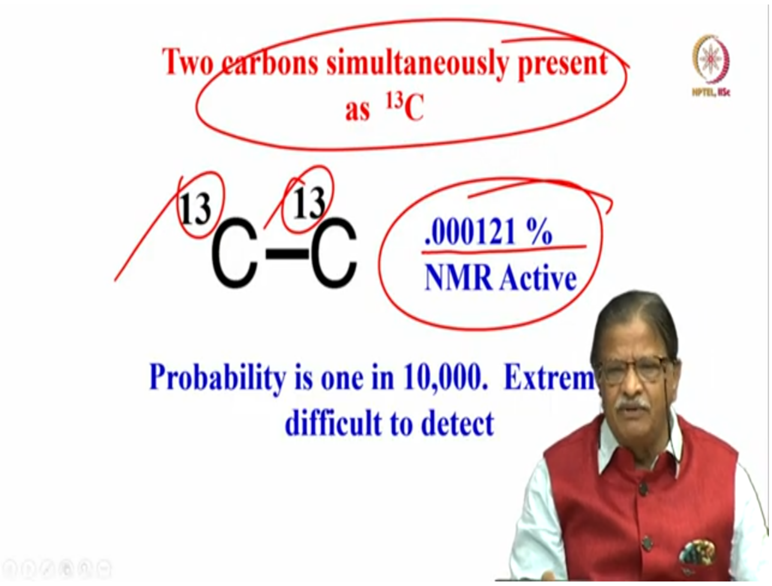

Two carbons simultaneously present as ^{13}C

$^{13}C-^{13}C$

.000121 %
NMR Active

Probability is one in 10,000. Extrem
difficult to detect

So, what is the possibility of 2 carbons simultaneously present as carbon 13? That is a very interesting question; can there not be 2 carbons simultaneously in carbon 13? Of course it is a possibility but then remember 1.1% of this and 1.1% of this; 1 in 100 will be in this position 1 in 100 will be in this position. The joint probability of both the carbons in carbon 13 state is 1 in 10000. So, if you take 1.1% as the abundance factor, it turns out to be 0.000121% that means in 10000 molecules you will see 1 molecule which is NMR active where both the carbon are in carbon 13 state. So, probability is 1 in 10000. This is extremely difficult to detect at all.

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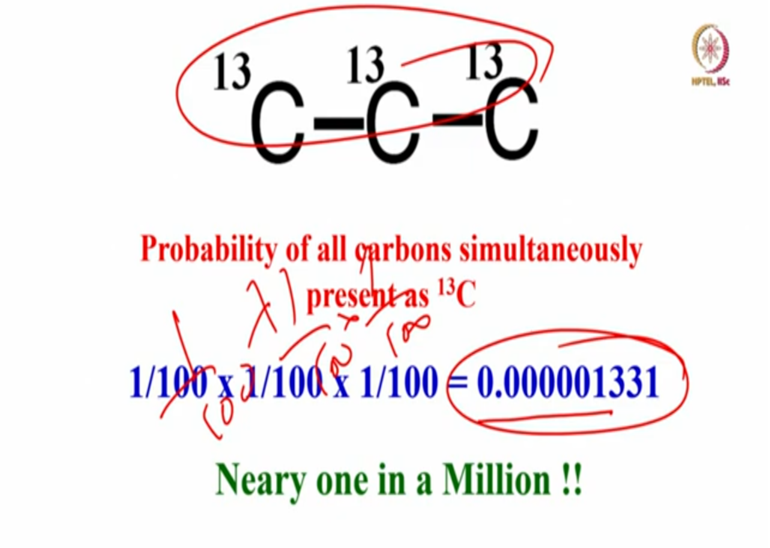

$^{13}C-^{13}C-^{13}C$

Probability of all carbons simultaneously present as ^{13}C

$1/100 \times 1/100 \times 1/100 = 0.000001331$

Neary one in a Million !!

Now take the other example of the molecule, what is the probability all the 3 carbons are in carbon 13 state? We can immediately understand 1 over 100 into 1 over 100 into 1 over 100. So what is the probability? It is 0.000001331 that is 1 in a million. If you have million molecules in your sample only in 1 molecule there is a probability where all the carbons are in carbon 13 state.

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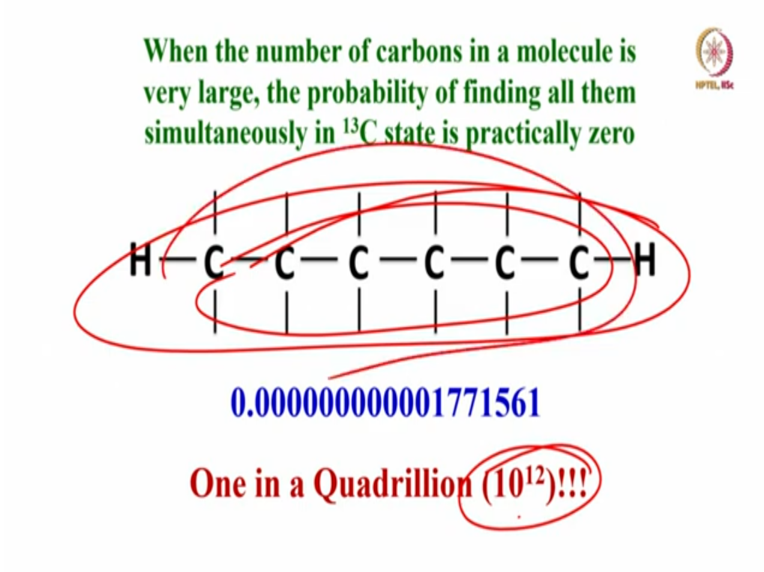

When the number of carbons in a molecule is very large, the probability of finding all them simultaneously in ^{13}C state is practically zero

0.000000000001771561

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

Now extend the logic; I do not want to keep on do on the arithmetic. Go to a very big molecule with 6 carbons are present, an hypothetical molecule. They are all different with substitutions, do not worry there is no symmetry in this molecule. All carbons are inequivalent, and there are 6 carbons. What is the probability of seeing all the 6 carbons in carbon 13 state?

It is such a small number; 1 in a quadrillion; 1 in 10 to the power of 12. So many number of molecules if there are present; millions and millions of molecules, 10 to the power of 12 molecules if we can think of, there may be one possibility where only 1 molecule has all the carbons in carbon 13 state.

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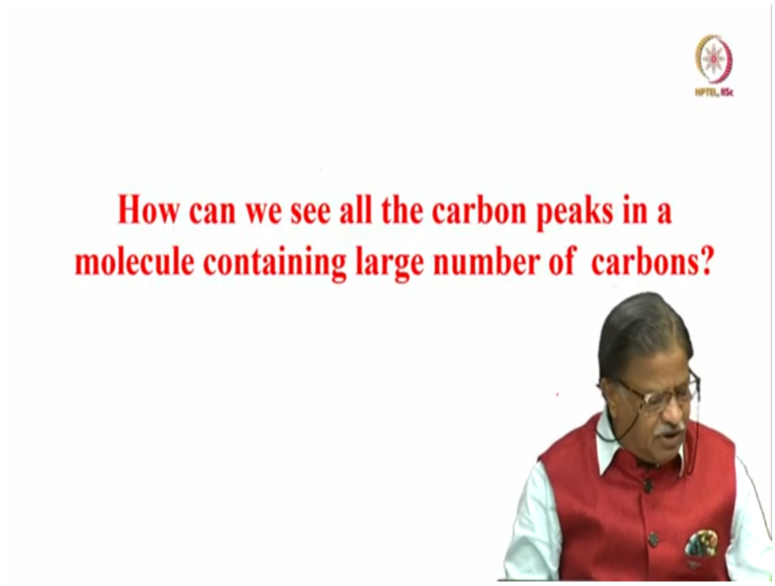

How can we see all the carbon peaks in a molecule containing large number of carbons?

So, now the question I am going to pose is, how can we see all the carbon peaks in a molecule continue large number of carbons? true we have seen carbon 13 spectrum. Take your molecule, put in a magnet and record the NMR spectrum. You see carbon 13 spectrum with 10 or 20 lines or 30, 50 lines present. How can we see, when the probability like this is so low? Even for 6 carbons I said it is 1 in a quadrillion. If there are a large number of carbons, 10 or 20 or 30 carbons present in your molecules, how can you see the carbon 13 spectrum? it is a difficult question one need to answer.

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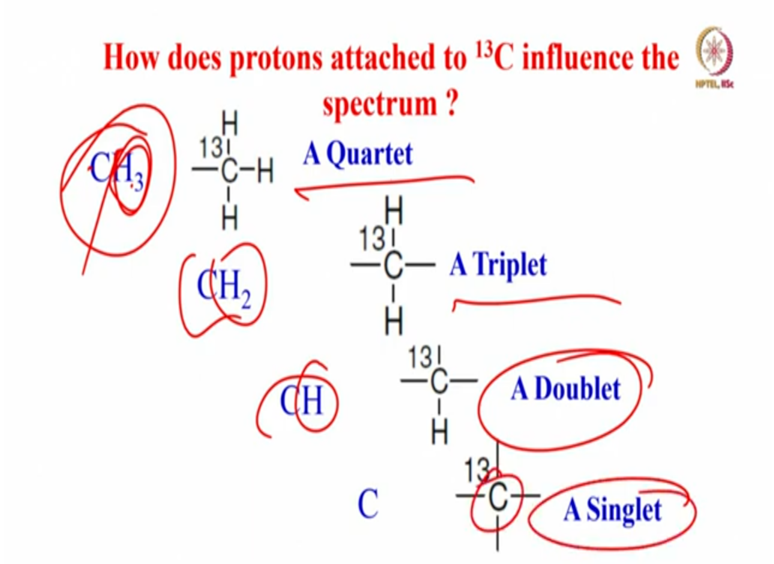

How does protons attached to ^{13}C influence the spectrum ?

So, next before going further to understand that, let us see how does the protons attached to carbon 13 influence the spectrum. If proton is attached to carbon CH3 proton; there are 3 equivalent protons I told you it has to be a quartet, because there are 3 equivalent protons coupled to this; 1:3:3:1 intensity. If there are 2 equivalent protons coupled, it will be a triplet with only 1 proton coupled it will be the doublet; If there is no proton coupled, each carbon is going to be singlet.

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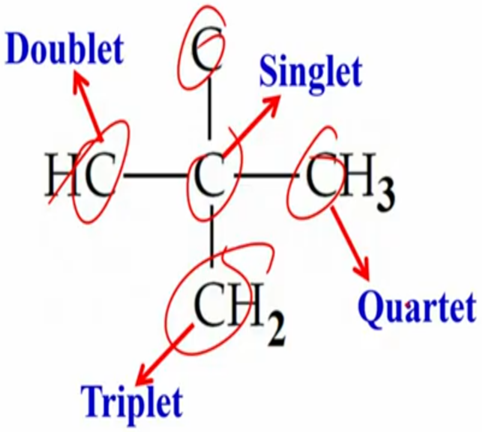

So, imagine if all the different functional groups are present in a molecule like this you will get quartet, singlet, doublet, triplet, very the complex spectrum you are going to get. Now my question is how we got all the carbons peaks in a straightforward way; in spite of the fact the abundance or the probability of seeing all the carbons in the carbon 13 state is 1 in 100. If that is the situation how do we see carbon 13 spectrum?

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^{13}C NMR Spectrum of Ethanol

CH_3CH_2OH

We will understand by taking a simple molecule ethyl alcohol; The two carbons are present here; we already discussed what are the possibilities of carbon that can be present here?

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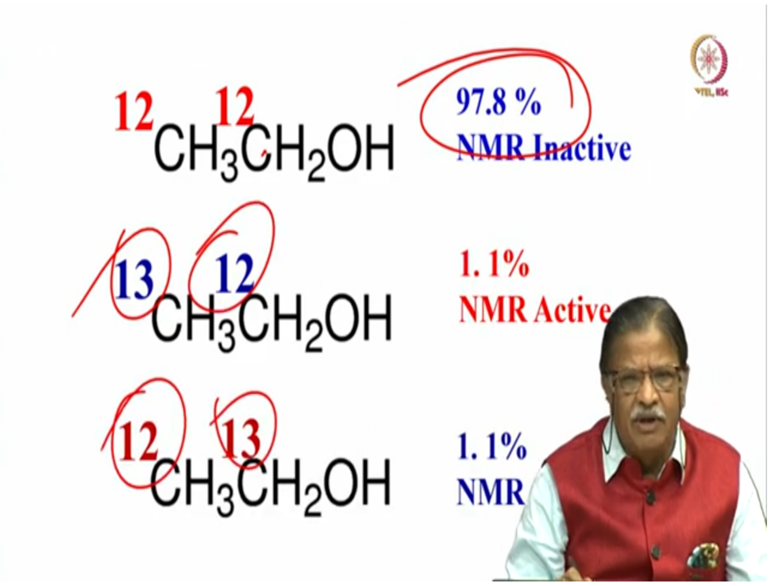

$^{12}CH_3{}^{12}CH_2OH$ 97.8 % NMR Inactive

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

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

We said this is carbon 12 this carbon 12, I mean both are carbon 12, 97.8% NMR silent nuclei; carbon 13 this one this is carbon 12, 1.1% NMR active. This is carbon 13 this is carbon 12 1.1% NMR active.

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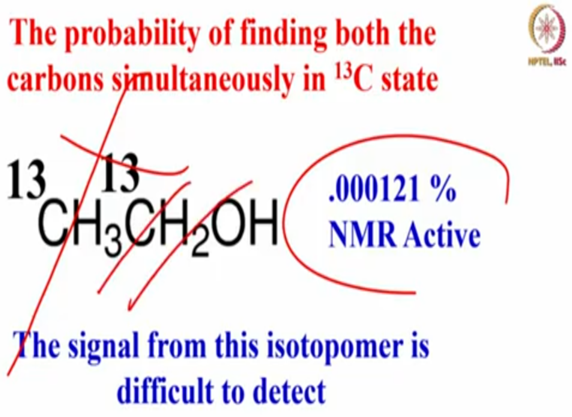

The probability of finding both the carbons simultaneously in ^{13}C state

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

The signal from this isotopomer is difficult to detect

And now probability of finding both in carbon 13 say is 0.000121% which is NMR active. So, the signal from this isotopomer I am not detecting at all. Remember this signal is not coming from this molecule, I can ignore this isotopomer, I can ignore now. I have only two isotopomer to deal with; which are they? I can ignore this one, it does not give NMR only this gives 1% NMR active, 1% NMR active. Whereas this I will ignore because abundance is too small.

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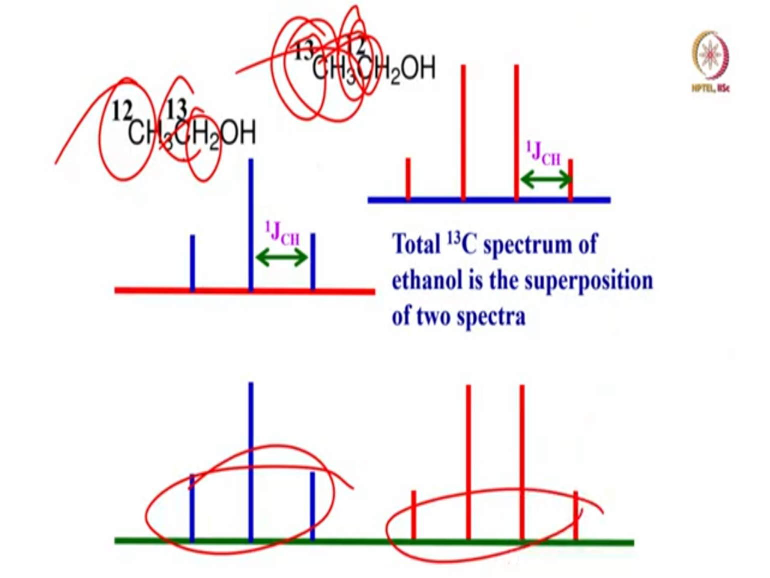

Total ^{13}C spectrum of ethanol is the superposition of two spectra

So, I have to consider only 2 isotopomers. Let us look at this problem of 2 isotpomers; how does it come? First consider this molecule where this is carbon 13 this is carbon 12; this carbon; what is the type of spectrum you get? I just now showed you there is CH3 group present, you will get a quartet, perfect; you will get only quartet for this. The spectrum for this carbon will not give signal because the carbon 12 state is NMR inactive.

Now I will consider other molecule this is carbon 13; this is carbon 12. What is the pattern you get for this? I just now showed to you for CH2 group, the carbon has to be a triplet because it is attached to 2 equivalent protons. Now in reality in an ensemble of molecules that are present in the NMR tube both these molecules are simultaneously present; the spectrum is a superposition of both the spectra.

So, we are going to get a quartet, and you got to get a triplet in when you take the spectrum of this molecule. In reality you will get a spectrum like this, this is a realistic spectrum, you get a quartet and triplet. You are not separating the molecule like this one for CH3 and one for CH2 like this. In a given tube both are present. So, you get the superposition of both the spectra.

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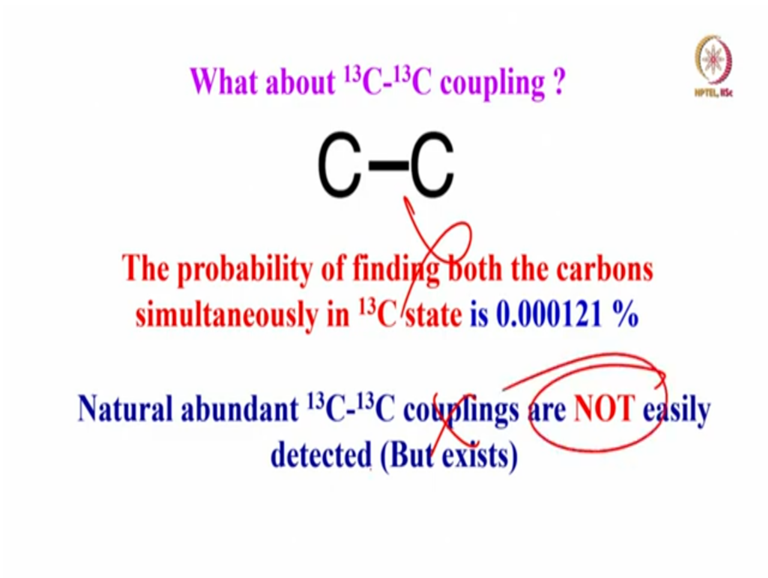

What about ^{13}C-^{13}C coupling ?

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)

So, what about C13-C13 coupling? As I told you we do not see it, we can ignore. But remember coupling is not 0, coupling exists, not 0; but you do not detect it, because of very low probability of seeing such type of molecules.

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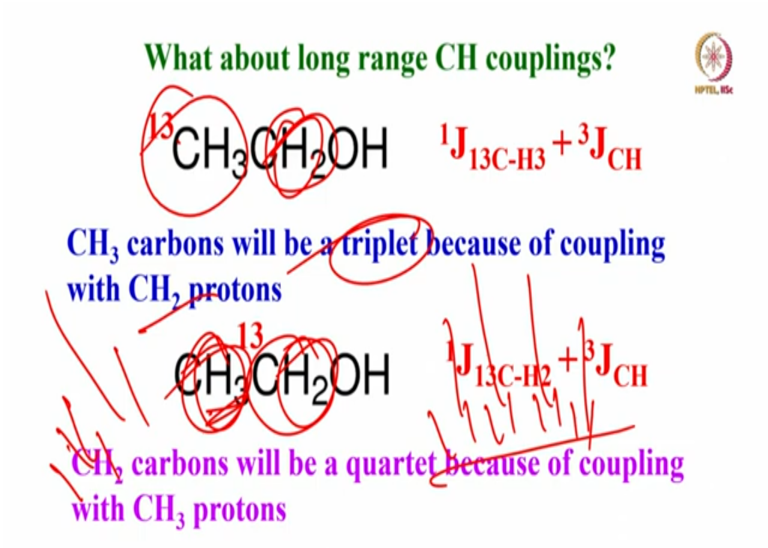

What about long range CH couplings?

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

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

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

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

So, now we can ask a question; we discussed carbon 13 spectrum like this, this is a quartet this is a triplet everything. But what about this proton coupled with this carbon? Can these 2 protons couple with this carbon? can these 3 protons couple to this carbon? Why not? It should be possible, it is possible. So, in principle what you are going to see is, you will see long range proton carbon couplings also. You will see everything actually. So, CH3 carbons will be a triplet because of the CH2, CH3 carbon is going to be further split into the triplet because of CH2 protons. Very important, it is the additional triplet coming because of CH2 protons. So, it is going to be a quartet and each quartet is going to a triplet because of coupling with CH2 protons, very easy.

So, now what about this one? This is going to be a triplet because 2 protons and each line of the triplet is a quartet because of long range coupling with CH3 protons. So, what you are going to get? CH2 carbons will be quartet because of coupling with CH3 protons. So, first it is going to be triplet because CH2 protons and it is going to be further split into quartet because of CH3 protons.

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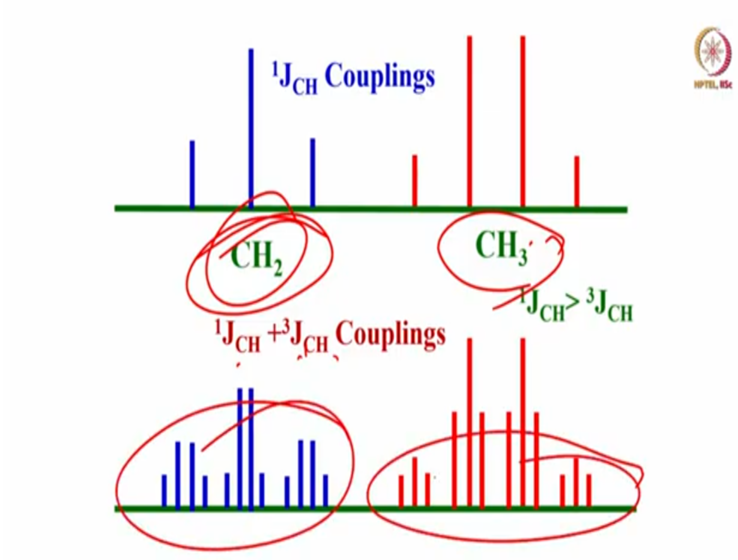

So, the pattern taking into account only J CH coupling 1 bond proton carbon coupling. If you consider for ethyl alcohol CH3 will be a quartet, CH2 will be a triplet. Now if you take proton and carbon it is a CH coupling; 1 bond CH and 2 bond CH couplings. If you consider remote carbon proton couplings also, then you get triplet of quartets and quartet of triplets. This is a real spectrum what you should see for a ethyl alcohol if you take the spectrum.

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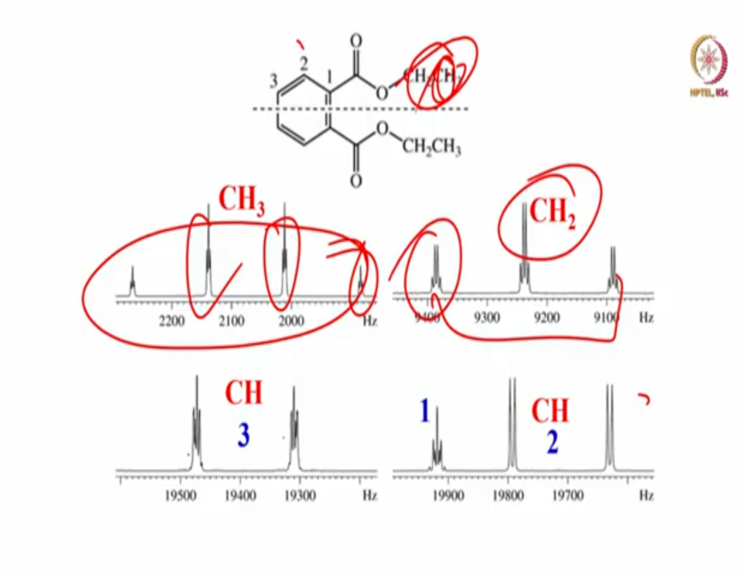

So, this is a realistic molecule you can see, For a molecule like this a CH2 is a large triplet and each line of the triplet is a quartet because of CH3; and the CH 3 is a quartet because of 3 protons and each line of the quartet is a triplet because of this CH2. And then similarly the aromatic protons you can see doublet and quartets; everything will come; depending on long range couplings; very easy to understand.

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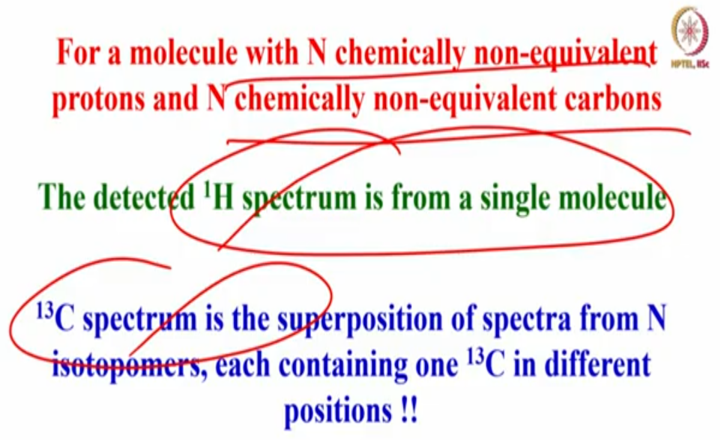

For a molecule with N chemically non-equivalent protons and N chemically non-equivalent carbons

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, remember the statement; it is very, very important statement. For a molecule with N chemically nonequivalent protons and N chemically nonequivalent carbons present. Consider and big molecule with N chemically nonequivalent protons are there. So, N groups of protons are there; N chemical nonequivalent carbons are. There are N carbon peaks which are coupled to protons. So, in reality the protons spectrum is obtained from a single molecule. All the peaks are coming from one molecule, because of 100% abundant. Whereas, carbon 13 spectrum is a superposition of the spectra from N iosotopomers, and each isotopomer containing at least 1 carbon in different carbon 13 state. That is the important point, remember carbon 13 spectrum is not from a single molecule. It is from N number of molecules that have N carbons, in which each spectrum corresponds to one molecule where one carbon is in carbon 13 state; That is an important point.

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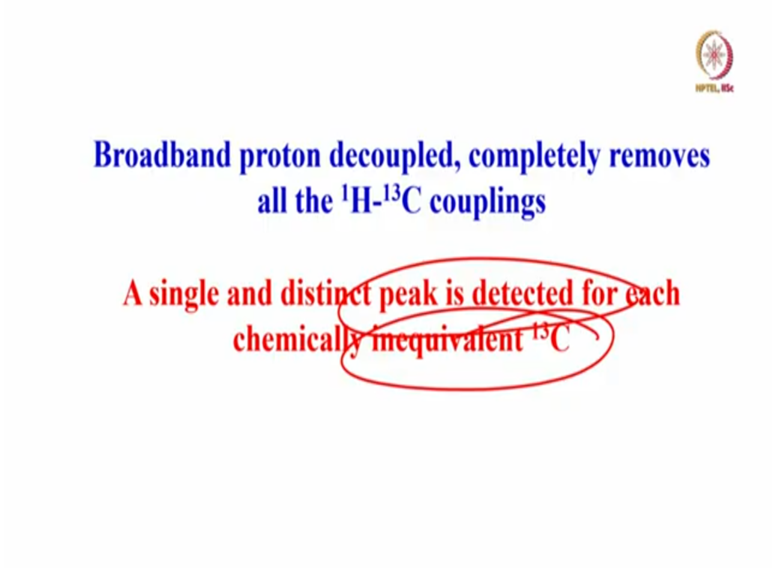

Broadband proton decoupled, completely removes all the ^{1}H-^{13}C couplings

A single and distinct peak is detected for each chemically inequivalent ^{13}C

So, now the question is generally you get a carbon 13 spectrum like this; how do we simplify this? If you get like this you know with all couplings or long range proton carbon, one bond proton carbon coupling like this, then it is very, very complex. This is as complex as a proton spectrum to analyze; but I said in the beginning carbon 13 spectrum we record with a broadband decoupling where all couplings of the carbon to protons are simultaneously removed.

If you do the broadband decoupling, you get only 1 peak for each chemically inequivalent carbon. That is what we do in carbon 13; it is always recorded or usually I would say recorded, by broadband decoupling.

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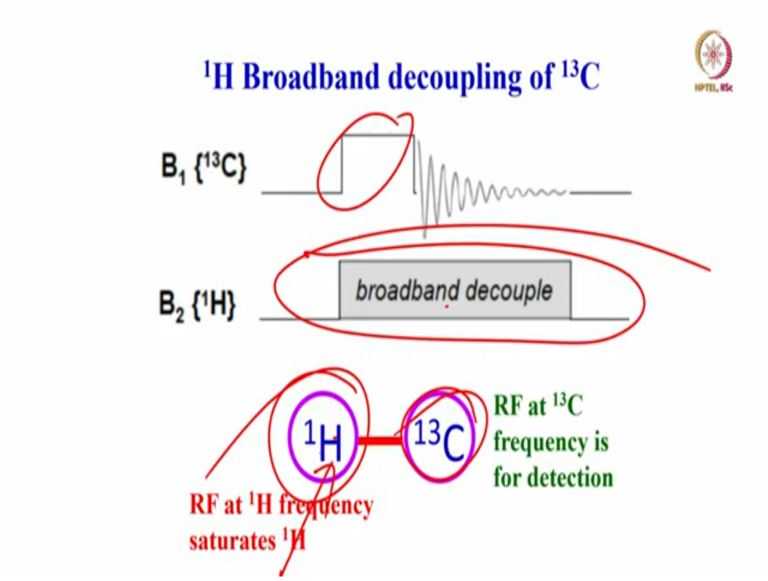

^{1}H Broadband decoupling of ^{13}C

So, when you do the broadband decoupling in a simple way; this is what we discussed in the previous course, you have 13C and apply the decoupling power, radiofrequency pulse simultaneously on the proton channel continuously to saturate the protons. The carbon 13 you are detecting will not see this proton in either alpha state or beta state. As a consequence, the coupling between carbons and protons are broken.

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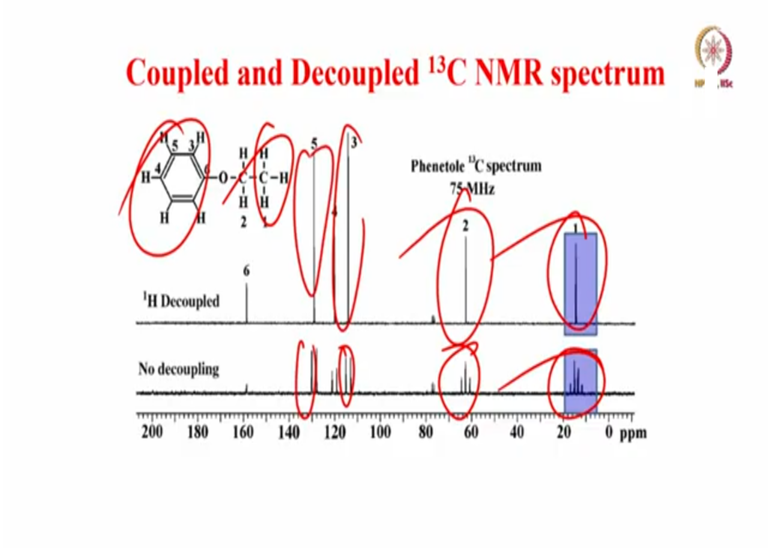

Coupled and Decoupled ^{13}C NMR spectrum

And this is how this spectrum gets simplified. Look at this, it is a quartet a CH3 group. Now broadband decoupling makes it a singlet. It is a triplet, the broadband decoupling makes it a singlet. Each doublet like this for aromatic protons become singlets, like this it is very easy to understand.

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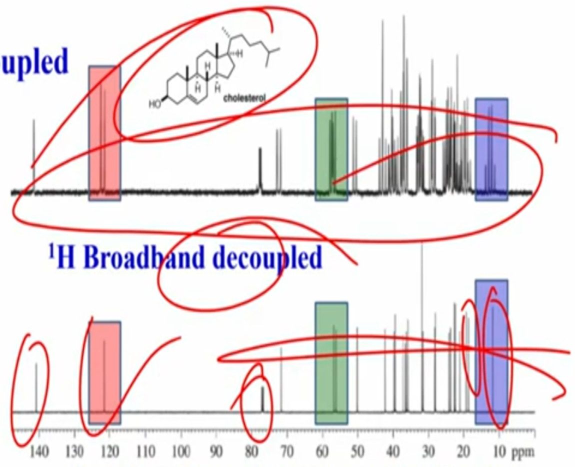

^{1}H coupled

^{1}H Broadband decoupled

Broadband decoupled spectrum identifies the number of carbons in the molecule

So, in a complex molecule which I showed you, cholesterol molecule which is so complex how do you simplify now? do the broadband decoupling; what is the advantage? Each peak corresponds to one carbon. Measure the number of carbons, number of peaks present here, except this which is a solvent chloroform, then you can find out the number of carbons present in this molecule, if there are no other hetero-nuclei which are coupled to it.

So, in this case there is no other hetero-nuclei fluorine, phosphors etcetera which are coupled. So, as a consequence just count the number of peaks 1, 2, 3 like that, that many numbers of carbons are presents in the molecule that is easiest way to understand.

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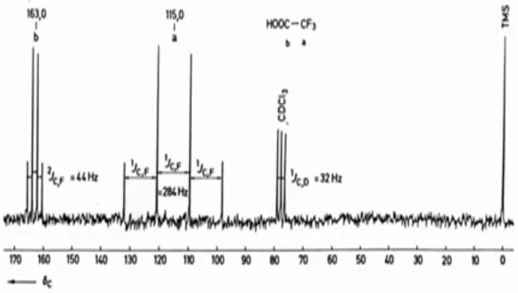
Heteronuclear Coupling Constants

^{1}H broadband decoupled F_3C-COOH



So, what I am going to do is I think time is up I will stop here. We will continue the analysis of the remaining spectra in the next class. But what basically I want to tell you is this one, you would have understood by now. We understood lots of NMR interaction parameters. Now in this class we understood how to analyze the spectrum; different proton spectra based on the multiplicity, based on the chemical shifts; where they come, different functional groups where they resonate, depending upon the neighboring groups which are adjacent to that. How the multiplicity arises, we try to interpret the spectrum. Couple of examples we took. In the carbon 13 we know carbon 13 abundance is only 1%; carbon 13 is NMR active, carbon 12 is NMR silent. As a consequence, we also understood if there are N number of carbon simultaneously present in the molecule. There is a probability that all carbons can be in carbon 13 state but it is extremely small. There is a large number of carbons. It is almost impossible to see all carbons in carbon 13 state; but then we can think of isotopomers. Each carbon in carbon 13 state can be present, where remaining can be carbon 12. So, we can consider the number of isotopomers. So, we understood the carbon 13 spectrum is the one which is a superposition of the spectrum for each individual molecule; where in each individual molecule at least 1 carbon is in carbon 13 state.

And then generally, I said, carbon 13 spectrum is the superposition of the spectra of all the carbon 13 isotopomers. You can get long range couplings in addition to one bond coupling. But that we can remove by decoupling; that is what also I said. So, whereas the proton spectrum is from a single molecule, the carbon 13 is from the superposition of spectra. And we tried to understand some of these spectra like this. We will stop here, come back and continue the analysis further. With that will go to the different topic later. Thank you.