One and Two Dimensional NMR Spectroscopy for Chemist
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Lecture No: 36
Basics of 13C-NMR

So in the last couple of classes we have been discussing extensively about the analyses of the proton NMR spectra of different types of molecules, where I told you, sometimes the types of tricks that you have to adapt in looking at the pattern and making the assignments. You might look at the intensity, you might look at the chemical shift position, you have to look at the multiplicity pattern, sometimes you have to measure the frequency separations; all those tricks you have to adapt and then make the assignment of each peak to the particular proton in a molecule. That is the basics required for the utility of NMR spectrum. First thing you have to make is the assignment of all the peaks, and this is how we started the analysis and before I end this analysis of the proton spectrum; and in the last class I gave an example where there was a fluorine coupling. I will continue with this, a proton can experience simultaneously coupling with multiple heteronuclei, I will show that example.

And I also discuss about sometimes, it may appear to you that peak is missing. It cannot be missing it will be still present there but you should know how to extract it. Like that one or two examples I will give and then we will go to carbon-13 NMR.

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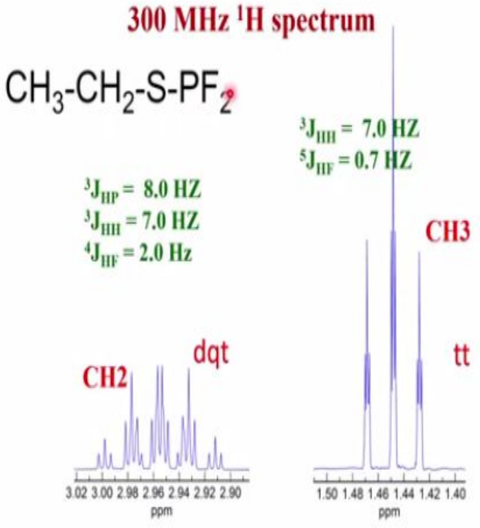

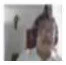

Let us look at the spectrum of this molecule, CH3-CH2-S-PF2. Now observable NMR nuclei for detecting, we have 3 here. I am not bothered about this sulphur, I am looking for phosphorus, I am sorry phosphorus, fluorine and proton, all the three I am seeing. I have a CH3 group, a CH2 group, forget about sulphur but it is the molecule, I have phosphorus and fluorine. As far as I am concerned there are 1, 2 and 3, abundant hetero nuclei, remember abundant.

All these couplings can be clearly seen in this spectrum. Of course, this is NMR active, this is NMR active, there are less abundant carbon 13, so you will see them as satellites. So, we will not worry about satellite analysis at the moment. Right now, let us concentrate on analysing the proton spectrum of this molecule. When I see proton, I get essentially 2 groups; one for CH3, other for CH2; of course that is very clear.

And now this CH3 comes where? In the high field region, that is also clear, and CH2 comes in the low field region, that is also correct. Now this CH3 has to be a triplet because of CH2, that also we have been utilizing this idea for quite some tims. So it is a triplet, but each line of the triplet is additionally a triplet. How is it possible? This can happen only when the CH3 can have a long range coupling with fluorine. So this 1, 2, 3, 4, 5 bond coupling. 5 bond coupling between this CH3 protons and 2 fluorine's which are equivalent give rise to triplet of triplets. Remember this is a magnetically equivalent applied 2NI + 1 rule then triplet of this because of this CH2, it is triplet and now because of this F2 each line of this triplet is a additional triplet. So this is a triplet of triplets you are going to get. Now I may ask you a question. Phosphorus is 100% abundant that is also spin-half nuclei. Where is that coupling?

See this 4 bond phosphorus fluorine coupling is very weak. Hence as a consequence you are not seeing it here. Otherwise it could have even complicated much more, each of this 9 liens pattern would have become 18 lines pattern, because each of them would have further spit into doublet because of this phosphorus. We are not seeing that coupling; so it is only triplet of triplets.

Now coming to CH2, it is very interesting. What type of coupling pattern you expect for CH2? First thing CH2 can couple to CH3, it is a quartet, very clear. But this can also couple to phosphorous, it is 1, 2 and 3, coupling, it is present. 3 bond phosphorus proton coupling is reasonably good value, 8 hertz. Only 4 bond coupling we did not see here that is all; the 3 bond coupling is there. In addition to that, this CH2 protons can also experience coupling with 2 equivalent fluorines. So it experiences coupling with protons, phosphorus and fluorine all the 3. It is a very interesting example, that is why I wanted to show you the protons can simultaneously experience the coupling with 3 different hetero nuclear spins. And in the very first example analyse giving you same points of scalar coupling, you remember I said each nuclei can experience multiple heteronuclear couplings at the same time.

It is a classic example how this CH2 is experiencing coupling with proton, phosphorus and fluorine; all the 3. Once you know that, this analysis becomes fairly simple. Now first thing is CH3 coupling big quartet and this is large coupling is about 7 hertz. Interestingly 3 JHP coupling is much larger, so this will be a first a doublet and then each line of the doublet will be split into a quartet because of this, will get 8 length pattern. And each line of this is going to be triplet because of this F2, chemically equivalent fluorine. That is what you are seeing it is a doublet of quartet of a triplet. You can see 1, 3, 3, 1 one quartet, 1, 3, 3, 1 one quartet - two quartets and of centre this quartet to centre of this quartet correspond to doublet and each of these lines is a triplet, see. With many overlaps you are not seeing all the lines, carefully;

But you can see very easily you can understand, first the doublet is from centre of this to centre of this; and now the quartet comes because of CH3 1, 3, 3, 1 one quartet 1, 3, 3, 1 another quartet overlapped and each line of this is a triplet which you can clearly see. Very nicely all multiple nuclear heteronuclear couplings can easily be extracted from this. But remember do not expect coupling between phosphorus and fluorine here, it will present, but you will not see remember, you know why I am telling you? I told you a long back, this is an active spin when I am seeing that and this is passive, this is passive, this is passive. At the site of the active chemical shift you see coupling between active spin and passive spins. That is what you are seeing here. Coupling among the passive spins like P, F, you will not see because they are passive couplings. That is why you see only coupling of this with this, this and this and nothing else; and that is the way you can analyse.

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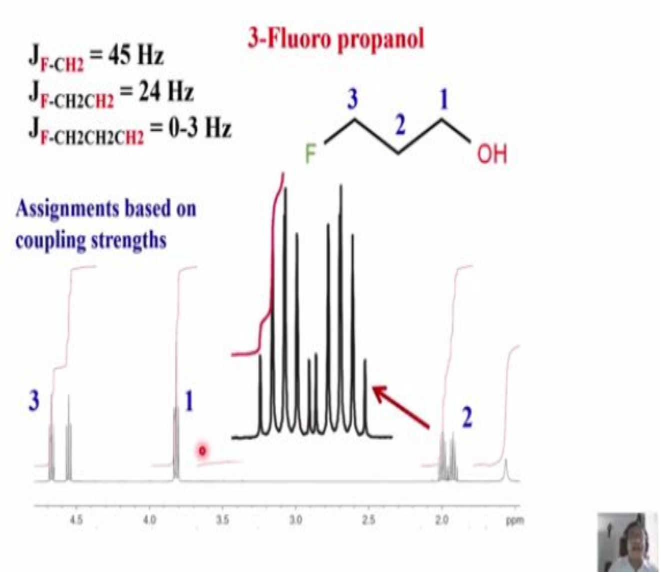

3-Fluoro propanol

$J_{F\text{-}CH2} = 45$ Hz

$J_{F\text{-}CH2CH2} = 24$ Hz

$J_{F\text{-}CH2CH2CH2} = 0\text{-}3$ Hz

Assignments based on coupling strengths

Another simple molecule you see, this is a 3-Fluoro propanol. Now this fluorine is present, this is CH2, CH2, CH2, OH. Very easy; when it is coupled to CH2 with this fluorine, then what will happen? This CH2 has to be a doublet because of this; and then it is also coupled to CH2, it will become a doublet of triplets. But remember 1 bond FH coupling is quite larger compared to 2 bond; and this is larger compared to 3 bond.

I will give you the coupling values; 1 bond fluorine proton coupling is 45 hertz. Now, which is that you can see; a large doublet and each line of the doublet must be a triplet, where do you see the spectrum here? Look at this, this is a bunch. A large doublet, each line of the doublet is a triplet, then this has to be proton 3. Also, it is attached to electro negative atom. So it comes down field, that is another way. But I am assigning based on the coupling strengths.

And what about this one? This is 1 2 and 3; 3 bond couplings will be 24 hertz. Look at this one, where is that, this one will be a doublet because of this. Each line of the doublet is split by into triplet because of this, an another triplet because of this, very complex pattern. That means quintet or septet whatever it is, two set patterns should be there. So it will be a doublet of sextet or septet.

Where can you see that? It is here, the expanded portion of that if you see, you can 1, 3 pattern here, see. It is a pentet like pattern; It is a pentet like pattern. Centre of this to centre of this correspond to a doublet and each line of the doublet is split by this CH2 and this CH2 giving rise to pentet patterns. See this is 1, 2, 1 triplet, 1, 2, 1 triplet, 1 2 1 triplet. So overlapping giving rise to a pentet. So this is also assignable, this correspond to proton 2.

Then what is proton 1? Proton 1 is far away and long range coupling to fluorine is 0 to 3, hertz sometimes you may not get it resolved, may not be able to see that, no problem. Then it is coupled only to the CH2 which is neighbour to it. As a consequence, proton 1 is a triplet. So assignments based on the coupling strengths, you can make easily. This a simple analysis of molecule based on the hetero nuclear coupling strengths, you can also do.

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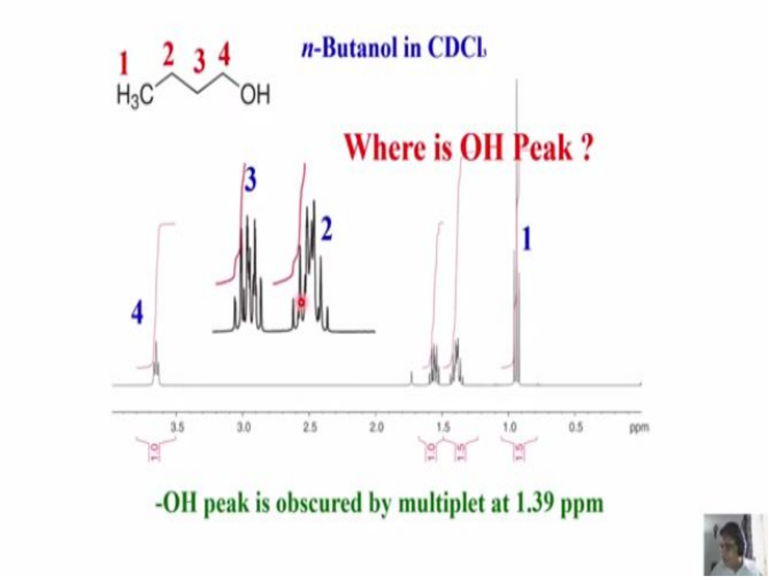

n-Butanol in $CDCl_3$

Where is OH Peak ?

-OH peak is obscured by multiplet at 1.39 ppm

Sometimes you come across a situation like this. It is a very simple molecule I have taken. CH3 CH2 CH2 CH2 OH, n-Butanol; it is done in CDCl3. CH3 you know, it is a triplet because of this. This CH2 is a quartet and a triplet, a complex pattern somewhere here; and this CH2 is a triplet of a triplet because of these two, somewhere here;, and this is a triplet because of this one, that is here.

Now my question is we have 5 groups of protons including OH. Where did that OH go? My question is I assign this 1, 4, 2, 3. Now the question is where is OH? It must be there somewhere in this spectrum. Sometimes what happens OH peak is obscured by the multiplet at 1.39 ppm. What is at multiplet at 1.39? This one. see OH is hidden here, look at it. You can see broad OH peak is below this.

OH peak is broadened; in addition to that it is hidden below this peak, gets obscured. Then how do you know it is OH? How to get that out? You will not get it out, at least you must be able to say this is OH peak. How do you do that? There are certain tricks adapted for this.

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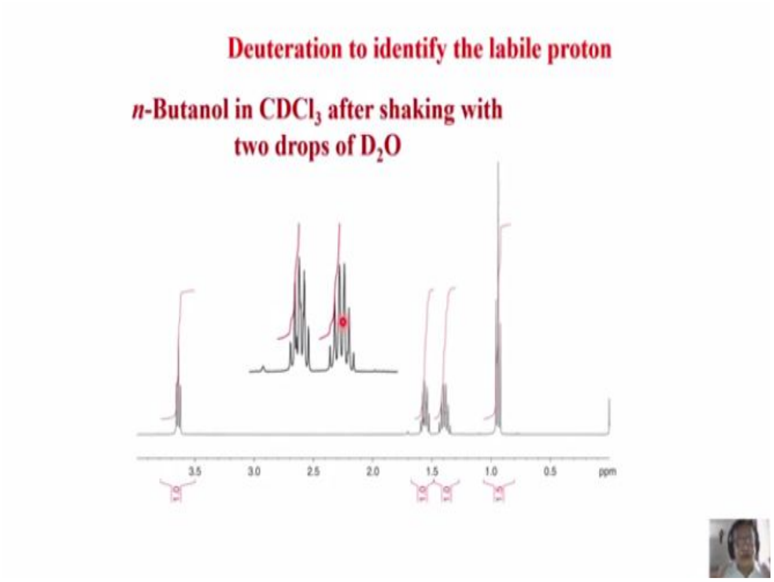

Deuteration to identify the labile proton

n-Butanol in $CDCl_3$ after shaking with two drops of D_2O

Take a small amount of, less than 10 mg or 15mg of D2O, less than a small micro drop; one drop of D2O. You add to this solution in a NMR tube, shake it for some time. Add one drop, shake the NMR tube for some time. Sometimes depending upon the exchange rate, it will go fast or sometimes after 2, 3 minutes or 5 minutes or sometimes half an hour, no problem. Then record the spectrum after some time. Look at this, it became a very clear pattern now, compared to this. Earlier you see, the OH peak was obscured by this bunch. Now OH has disappeared. We get very clear multiplicity pattern here. What happened to OH then? When you add D2O, OH will become OD. It is not protonated anymore, it is deuterated. Because it is deuterated you do not see in the proton spectrum. As a consequence, OH peak is not seen but at least you identified where OH was hidden here.

So these are some of the tricks of the trade you should know, looking at the spectrum where to identify OH, where it is hidden and based on the coupling strength how to analyze. Now, I took an example today where one proton can experience coupling with three different hetero nuclei – proton, fluorine, phosphorus like that, and how do we get the coupling information, how to analyze this spectrum? I showed all those things.

So, I hope you all have the idea of what to do everything; and of course NMR is a big ocean. You should start analysing large number of spectra. This is a reasonably small molecule, too small complex molecules I have taken. Go to bigger and bigger Molecules, real experts start analysing the spectrum of proteins, very big macromolecules, also. That comes with little bit of experience, once you start doing this work, it is a matter of time; in a few months, you will become an expert to analyse even the complex molecule.

So with that, I will stop about analysis of proton spectrum. Now, I will go into, go to the other one; that is analysis of the carbon 13 spectrum, I will start, another nucleus. We will start here afterwards, the analysis of the carbon 13 spectrum.

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^{13}C Another extensively utilized
NMR nuclei

Why I took carbon 13? Because for the chemists; especially organic chemists, carbon 13 is another extensively utilized NMR nuclei. Because all your molecules contains carbon; I am not talking about inorganic chemists. They also have different exotic nuclei, we will come to the later when we do multinuclear NMR. Now I am concentrating on carbon 13. Generally most of the organic chemists come to us and say I want carbon 13 NMR. Because they synthesize the molecule, they want to see proton NMR, carbon 13 NMR. So after proton, especially for the chemists, this is second most sought after nuclei.

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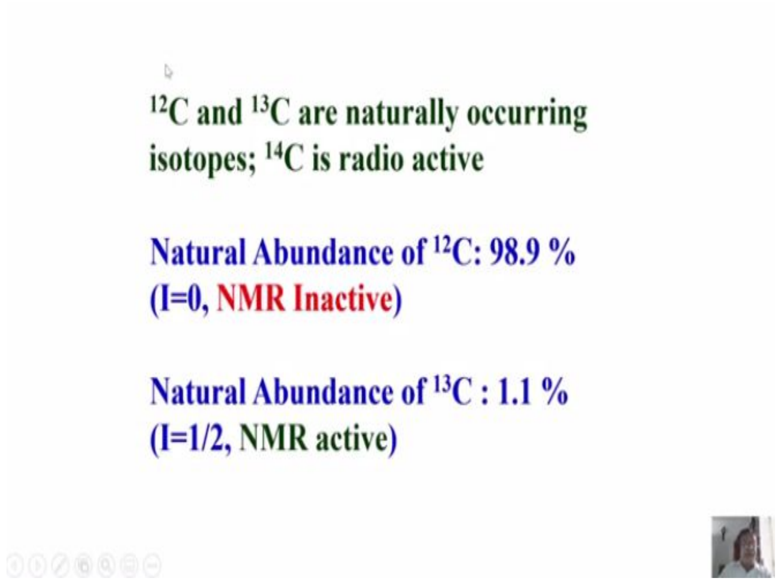

^{12}C and ^{13}C are naturally occurring isotopes; ^{14}C is radio active

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

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

Some important points about carbon 13. Carbon has two naturally occurring isotopes – C12 and C13. C14 is also there but that is radioactive, ignore it, it is unstable. We concentrate only on carbon 12 and carbon 13. If you remember the very first class, when you worked out the spin of the nuclei, I said carbon 12, because of the even atomic mass and even atomic number 12, 16 its spin is 0.

That is what I said. So spin is 0, magnetic moment is 0; when magnetic moment is 0; there is no interaction at the magnetic moment with the external magnetic field. So no Zeeman effect, no splitting up of energy levels, no NMR. That is what I said when the spin value is 0, such nuclei NMR inactive. So carbon 12 is NMR inactive. Interestingly this has 98.9% abundance and carbon 13 is only 1.1% abundance.

You see this thing, you know nature is helping us, you take it as an advantage for us. If carbon 12 were to be 100%, let us say abundance is 100%, in all the organic molecules you have so many carbons, your spectrum would have been so complex, NMR spectrum, probably impossible for us to analyse easily. Now we have to struggle a lot and to get analysis of this because they are coupled with all protons - proton proton coupling, proton carbon coupling, carbon carbon coupling; everything would have been there.

Fortunately nature is helping us. As a consequence we do not see carbon 12 at all; because they are NMR inactive and we concentrate only in carbon 13. Interestingly it is also very good for us because it is spin half nuclei. I told you in beginning, you remember? Spin half nuclei are relatively easy to study compared to nuclei with spin greater than half.

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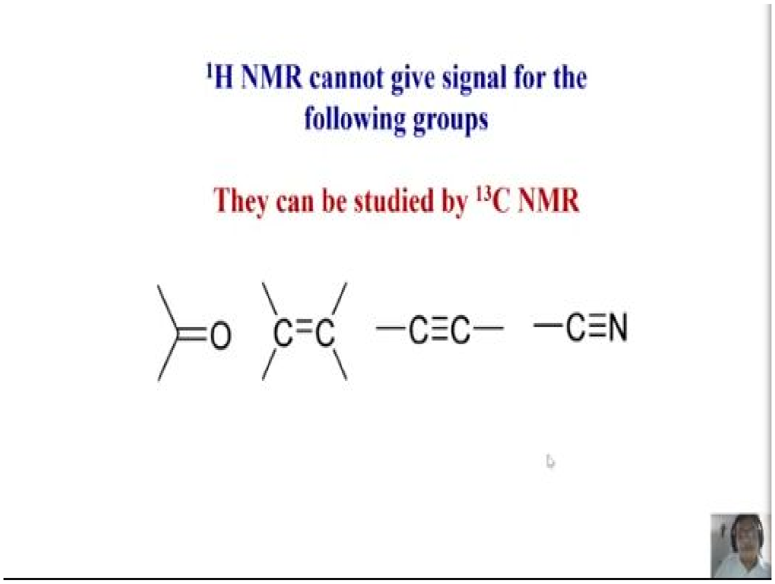

^{1}H NMR cannot give signal for the following groups

They can be studied by ^{13}C NMR

When do you make use of carbon 13 NMR, look for proton NMR? If I have a CO groups; C double bond C, C triple bond C; or CN group like that, if I want to get information about such type of groups present in a molecule, proton NMR cannot give you. Where is the chance for proton NMR to give that information, there are no protons here, and on the other hand I can study carbon here, I can get this.

I can study carbon and all these groups, functional groups present can be identified. So carbon 13 NMR is also very useful. Whatever, sometimes, the information which you cannot get for certain functional groups in the proton NMR, you can get from carbon NMR.

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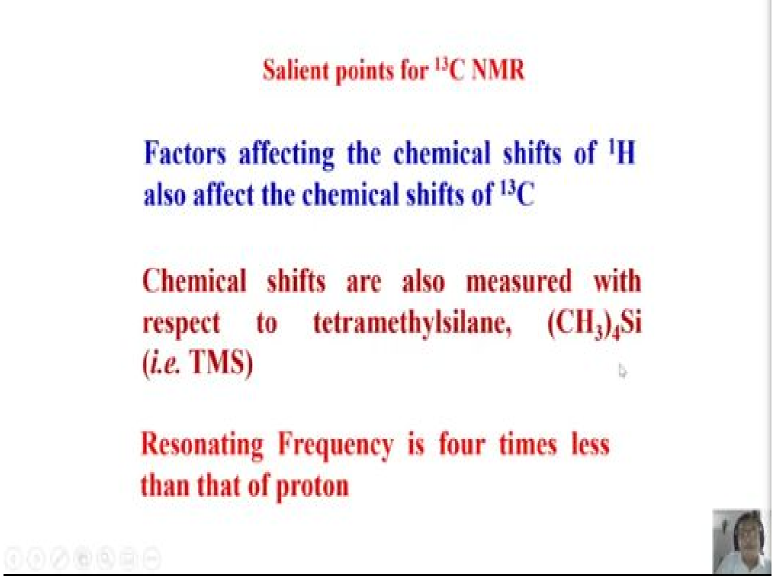

Salient points for ^{13}C NMR

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

And now salient points you should also remember, when you are analysing the carbon 13 spectrum, remember the factor which affects the chemical shift of proton also affect the chemical shift of carbon 13 same, there is no difference. Similarly, if I say CH3 proton is coming at high filed, CH3 carbon is coming at high field. If I say CH2 proton comes next down field, CH2 carbon also comes next. By and large it follows the trend, more or less it follows the trend.

So the factors that affect the chemical shift of protons also affect the chemical shifts of carbon. Next question is, I told you when I use the reference as TMS, this TMS, tetramethylsilane as carbons, protons and silicon. As I said, there are 4 carbons all are chemically equivalent here; and I said it is a very good reference for carbon 13 NMR. So the reference used for carbon 13 is again TMS, like what we use in proton.

Resonating frequency of carbon is 4 times less than that of proton. I hope you do not have to ask me questions, I hope you know the answer, why? The reason is gyromagnetic ratio of carbon is four times less than that of protons. As a consequence resonating frequency is four times less. Of course it also mean sensitivity is 4 times less. We will come to the later.

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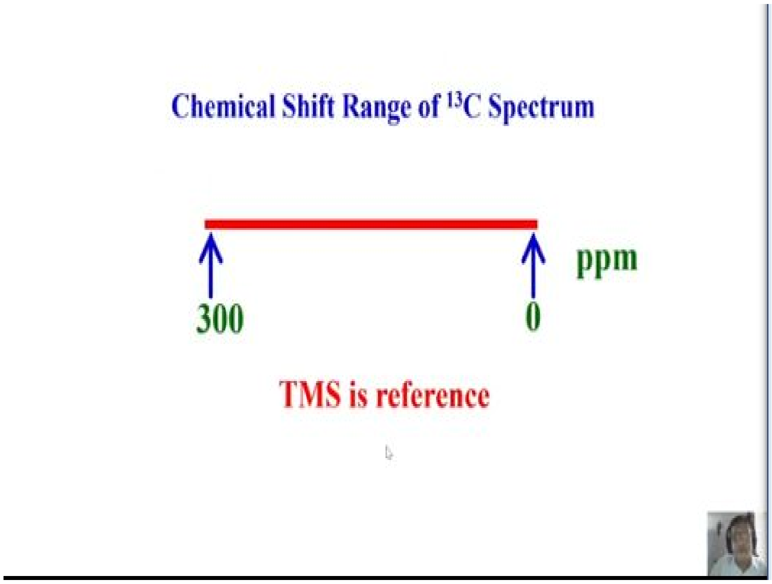

Chemical Shift Range of ^{13}C Spectrum

300

0

ppm

TMS is reference

Now, if you look at the chemical shift range of carbon 13, here it is. Measured with reference to TMS, proton is 0 to 10 ppm, but carbon is 0 to 300 ppm, very interesting. Remember, if I have a 500 mega hertz spectrometer, if I want to study proton, 10 ppm, so I will cover only 10 X 500; 5000 hertz. That is all my range of observation. That is the width of spectrum I want to see, called spectral width.

If I have to see the carbon 13 at the same 500 mega hertz, it is 125 mega hertz is the carbon, now 125 X 300, it is 37500. It becomes huge, spectral width becomes quite large, you know. So this is are the important points you have to remember, when you are looking for proton and carbon.

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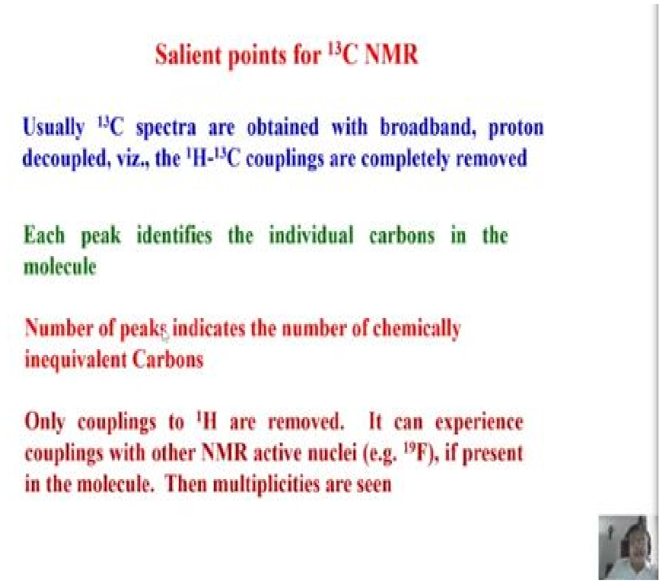

Salient points for ^{13}C NMR

Usually ^{13}C spectra are obtained with broadband, proton decoupled, viz., the ^{1}H-^{13}C couplings are completely removed

Each peak identifies the individual carbons in the molecule

Number of peaks indicates the number of chemically inequivalent Carbons

Only couplings to ^{1}H are removed. It can experience couplings with other NMR active nuclei (e.g. ^{19}F), if present in the molecule. Then multiplicities are seen

Another point is most of the time carbon 13 spectra are obtained with broadband, proton decoupled. May be you are wondering, what is this decoupling? I have not introduced yet, I will introduce that to you later. But please remember, in the case of carbon 13, we break the coupling of all carbons to all protons. Then what will happen? We will see later. When there is no coupling; all carbons will give single lines.

Carbon-carbon coupling we do not see, only carbon proton coupling we see, that we will remove. When we remove that, you get only individual carbons, individual peaks. And each peak then can be identified for different individual carbons. So, in a carbon 13 spectrum, you take a proton decoupled, broadband decoupled carbon 13 spectrum. If I have a molecule five different carbons, we will get only 5 peaks, very simple, 1, 1, 1, 1, 1 line you get, no multiplicity, 1, 1, 1, 1, 1 line you get, 5 lines.

If I have molecule with 10 carbons, do proton decoupled carbon 13 spectrum, if we take, we will get only 10 peaks, that is all, easy to understand. No breaking of head; Analysis of the carbon spectrum is much easier than that of the proton. But you took the example of phosphorus fluorine coupled spectrum; we saw in the proton you know; just few minutes before. There you had a phosphorus and fluorine ,CH3CH2 group.

If I take carbon 13 spectrum of it, you will remove carbon proton couplings, but what about phosphorus, fluorine? No, that you do not remove. See remember, very interesting thing about NMR is, selectivity you can break the coupling of one nuclei with other, but other hetero nuclei coupling you can retain also. That is a very interesting thing you know. Nowadays with the present day spectrometers, we can do decoupling of one spin, one nuclei, two nucleus simultaneous like that, many things are possible. So I can decouple one nuclei at a time, all protons can be decoupled with carbon. I can get proton fluorine and carbon fluorine, phosphorus carbon, all couplings I can see, very interesting. Or I want to retain carbon proton coupling, I want to remove fluorine coupling, I will remove fluorine coupling.

It is possible, I can play with this, this is beauty of NMR. I can play with nuclei, I can remove the coupling of the specific nuclei and observe that. That is what broadband decoupling of heteronuclei, I will come to that later.

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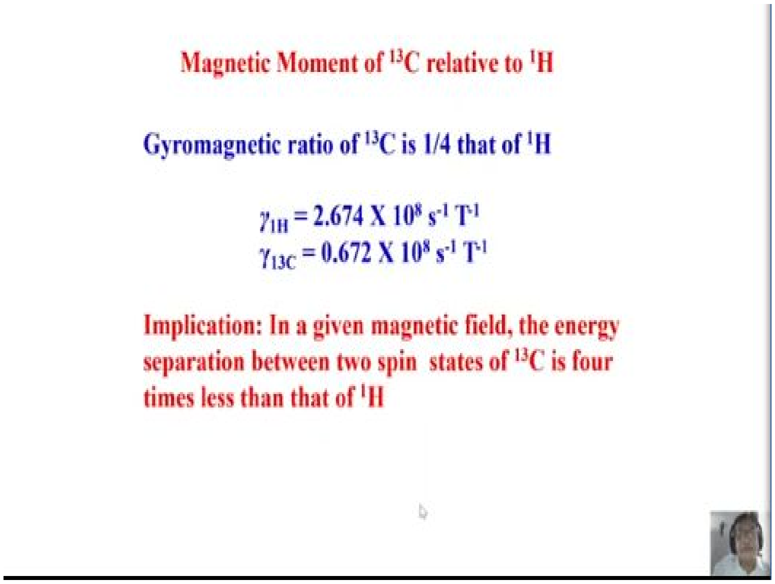

Magnetic Moment of ^{13}C relative to ^{1}H

Gyromagnetic ratio of ^{13}C is 1/4 that of ^{1}H

$\gamma_{1H} = 2.674 \times 10^{8}\ s^{-1}\ T^{-1}$
$\gamma_{13C} = 0.672 \times 10^{8}\ s^{-1}\ T^{-1}$

Implication: In a given magnetic field, the energy separation between two spin states of ^{13}C is four times less than that of ^{1}H

Another interesting point you must know is, the magnetic moment of carbon 13 is relatively four times less than that of proton. That is because gyromagnetic ratio is four times less, I told you. Gamma of proton I said 26.74 into 10 to the power of 7. Similarly carbon is 6.724 into 10 to the power of 7. I told you radians per tesla per second. There must be radians here, it is expressed in radians.

What does it mean? Gamma is 4 times less means, in the very first class in spin physics we discussed. That means energy states of carbon is four times smaller than that of proton.

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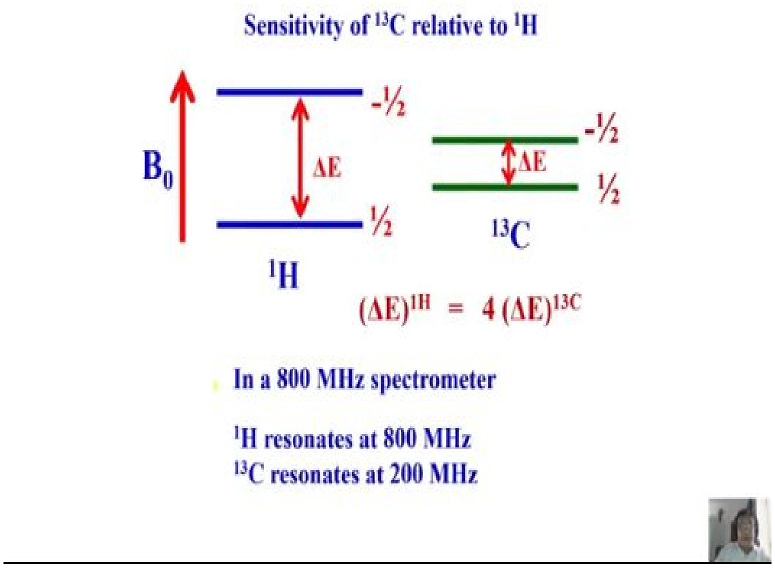

Sensitivity of ^{13}C relative to ^{1}H

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

In a 800 MHz spectrometer

^{1}H resonates at 800 MHz
^{13}C resonates at 200 MHz

Now this is the energy separation of proton and this is the energy separation of carbon, this is 4 times less. Remember I said, this is also spin half nuclei, okay? This also has two possible orientations; alpha beta. But this is less sensitive compared to this because of less gamma and energy separation is 4 times smaller. I told you about sensitivity when we discussed.

The sensitivity depends upon magnetic field which in turn is responsible for this energy separation. As a consequence, carbon 13 is less sensitive compared proton. So in a 800 mega hertz spectrometer I will take, if I say proton comes at 800, where does carbon come? If proton comes at 800 mega hertz, carbon comes at 200 mega hertz. You understand this one very clearly.

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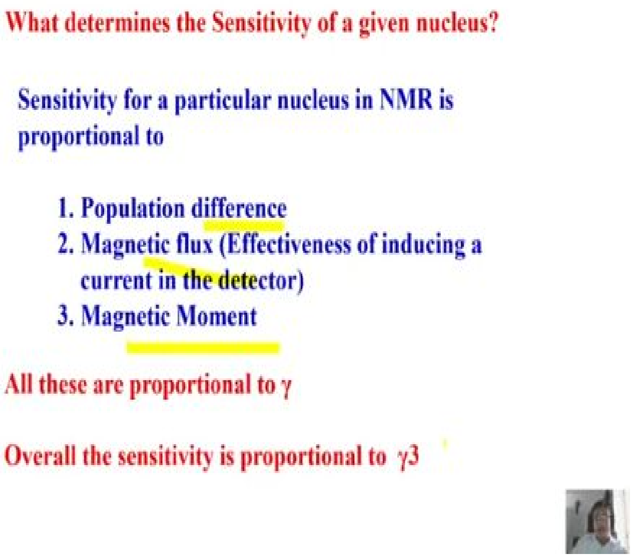

What determines the Sensitivity of a given nucleus?

Sensitivity for a particular nucleus in NMR is proportional to

1. Population difference
2. Magnetic flux (Effectiveness of inducing a current in the detector)
3. Magnetic Moment

All these are proportional to γ

Overall the sensitivity is proportional to $\gamma 3$

Now I told you about the sensitivity of the nuclei gamma cube everything I discussed, I do not think I have to go again. Sensitivity of the nuclei depends upon 3 factors I said, population difference and magnitude flux and magnetic moment, all are proportional to gamma I said, it is gamma cube. Remember you worked out the sensitivity for carbon and nitrogen related to that of proton. In one of the classes I showed in this slide. I guess you remember all those things. Do not forget that sensitive factor we calculated.

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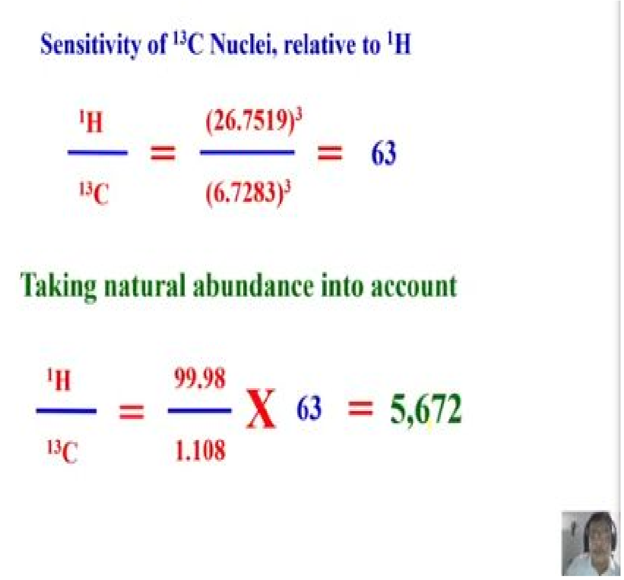

Sensitivity of ^{13}C Nuclei, relative to ^{1}H

$$\frac{^{1}H}{^{13}C} = \frac{(26.7519)^3}{(6.7283)^3} = 63$$

Taking natural abundance into account

$$\frac{^{1}H}{^{13}C} = \frac{99.98}{1.108} \times 63 = 5{,}672$$

Again I am showing it here, sensitivity of the carbon 13 relative to proton, if we take only gamma cube into account, it is 63, almost 64 times. Whereas if I look at this sensitivity, take into to account abundance also; we saw it is 5672, nearly 5700 times less sensitive than that of proton.

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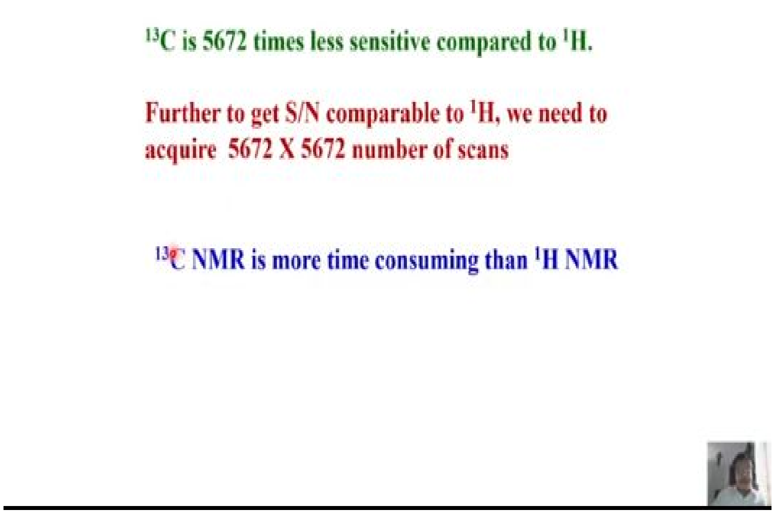

^{13}C is 5672 times less sensitive compared to ^{1}H.

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 it is 5672 times less sensitive means, if I have to get the signal to noise ratio comparable to proton, we need to acquire 5672 x 5672 number of scans, because signal to noise ratio goes by root of square, which takes me enormous amount of time. So carbon 13 NMR is more time consuming than proton. So this is the situation.

This is 5672, that is in one scan, one accumulation, when I send one RF pulse, I will get a proton spectrum of particular signal to noise ratio. For the same signal to noise ratio, if I have to get for carbon 13 taking sensitivity, gamma and abundance into account, I have to acquire this many number of times scans, I have to send that many number of pulses and collect the signals. Of course, further assuming various other parameters are there in NMR, like relaxation etcetera identical. If it is not, it is a different question again. But does not matter, all this tells me the carbon 13 NMR is more time consuming than proton NMR. Understood the point? Carbon 13 NMR is more time consuming than proton NMR.

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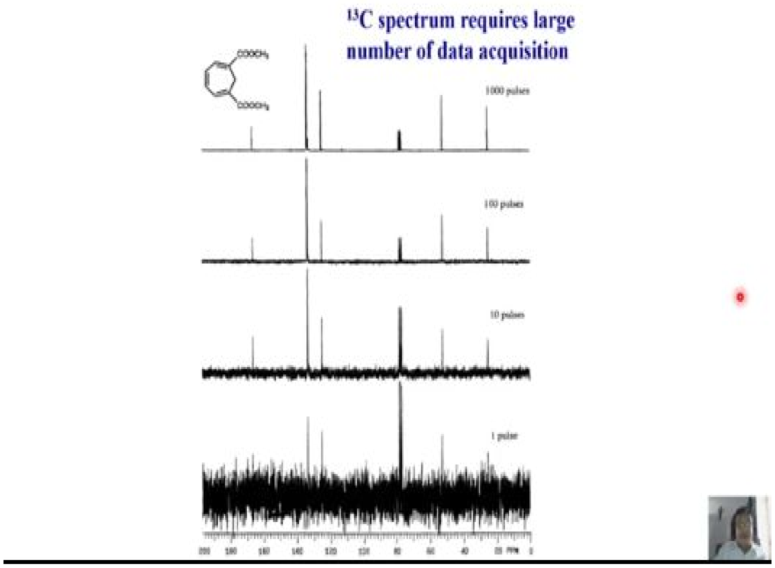

^{13}C spectrum requires large number of data acquisition

That is why we keep on adding the data, due to signal averaging. I will tell you what is signal averaging when I come to practical applications, how to get this spectrum, how to process the data everything I will discuss, in one of the classes. But till then keep this point in mind, we have to keep on adding the data. If I send only one pulse and collect the signal, this is the NMR spectrum, carbon 13 spectrum of this molecule.

What can you make out of this, if I give you this spectrum? It is very difficult, right? So look at the spectrum, with a single pulse; sending one radio frequency pulse, if I collect the carbon 13 spectrum it looks so noisy, it is very difficult to get any meaningful picture out of this. What can you get out of this? Look at this, many peaks are not even visible. On the other hand, we can do the co-adding of the data.

Instead of one pulse, I will send 10 pulses. One after the other, send a pulse, collect the signal. And afterwards send one more pulse, collect the signal, send one more pulse, collect the signal. And then keep on adding the data every time you collect one above the other, like this. So it is a one accumulation, we call it as accumulation - accumulation of the data, one pulse accumulation or signal averaging.

So you apply one pulse, send one pulse acquire. Now apply hundred times, thousand pulses you apply. Every time co-add the data, what is the change you are seeing? Look at it, it is very noisy, the noise reduces, it is much less, much less and see all these peaks which were not visible here, especially this peak; and look at this signal to noise ratio of this peak, we can clearly see all peaks.

So carbon 13 NMR requires lot of data acquisition, enormous time it requires; compared to proton. I give you a simple example, of course nowadays things have become better with a high frequency spectrometers, and electronics is difference, see there is a change in electronics; NMR methodologies or doing the experiment types, so many sophisticated experiments we could do, we can do faster, no problem, But still if I take proton spectrum in one minute, carbon 13 will take at least 15 minutes to 30 minutes depending upon the concentration and the number of carbons you have in the molecule. So yes basically, relative to proton carbon is time consuming.

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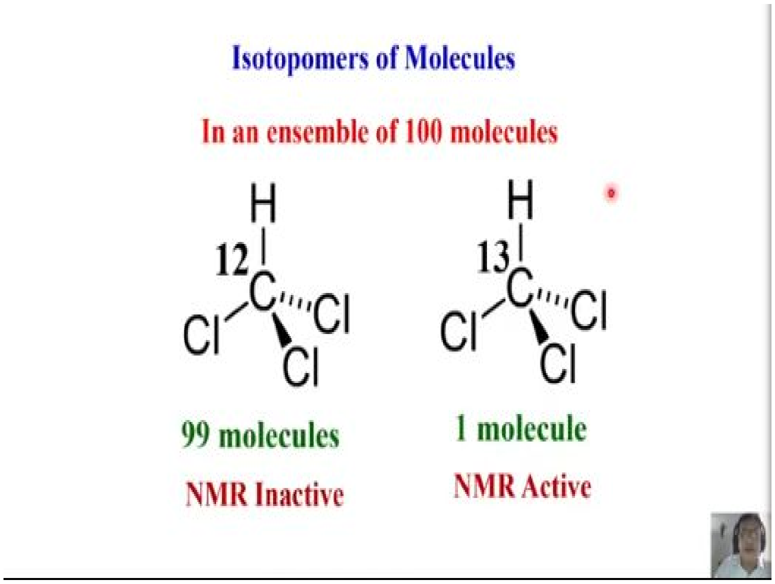

Isotopomers of Molecules

In an ensemble of 100 molecules

99 molecules

NMR Inactive

1 molecule

NMR Active

Now I will introduce a word called Isotopomers of molecules. This you would have come across in chemistry, I do not have to explain to you. I will take the example of CHCl3, chloroform. I will take 100 molecules, 99 molecules contain carbon twelve. That is major abundant spin. Abundant which is 99%, carbon 12 is abundant. Only one molecule is carbon 13 because its abundance is only 1%.

So in 100 molecules and a statistical average if I take, 99 molecules are a carbon 12 attached which are NMR inactive. C12 is NMR inactive because spin is 0. Whereas C13 is NMR active and spin is half.

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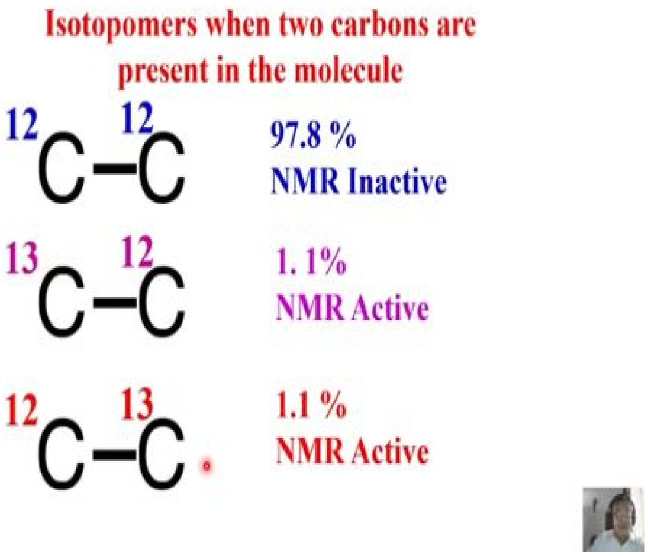

Isotopomers when two carbons are present in the molecule

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

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

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

With this idea let us see what happens if there are two carbons in the molecule. I consider a situation there are two carbons. How many isotopomers you can think of? There is one possibility, there are two carbons which are bonded, I am not worried about the complete structure ;just considering only the C-C fragment. This carbon can be 12, this carbon can be 12. What is the probability of that? This is 99.8%, this is in 99.8%, together the probability of both of them carbon 12 is 97.8, NMR inactive. That means if I have hundred molecules are present, 98 molecules are with both of them carbon 12, it will not give a spectrum at all. It is NMR inactive. On the other hand think of this possibility, this is carbon 13, this is carbon 12. It is quite likely, you can see that. What is the abundance of this carbon? Only 1% and this is 99%.

So this is NMR active. What is, the other isotopomer we can think of this one, this is carbon 12, this is carbon 13, that is also possible. That is also 1.1% abundant and NMR active. So in the molecule containing two carbons, 98% of the molecules contain carbon 12 which do not give us the signal at all. Carbon signal it will not get, you will not get carbon signal at all. Only this will give carbon, 1% of this small isotopomer, 1% of this isotopomer will give signal.

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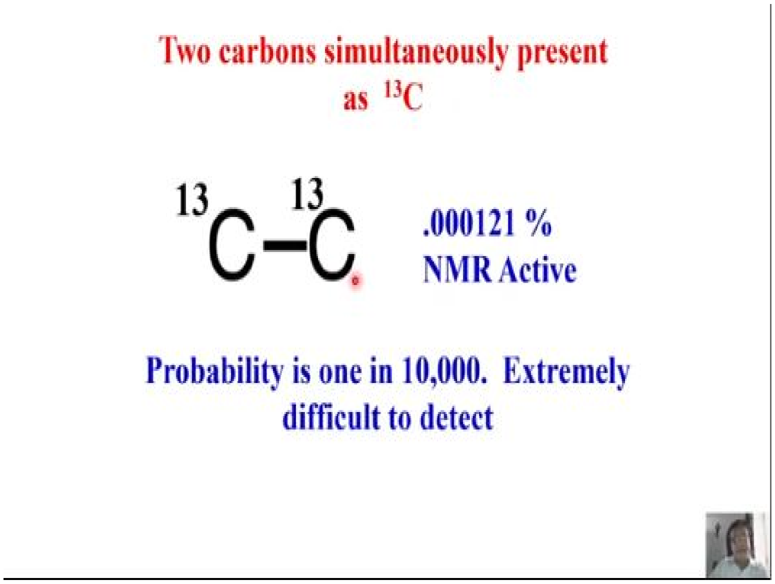

Two carbons simultaneously present as ^{13}C

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

.000121 %

NMR Active

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

You may ask me a question, what is the other probability when both are carbon 13? Sure, both are NMR active. Now what is abundance of this? This is 1%, this 1 in 100, together the joint probability is always a product, one over 100 into one over 100, one over 10000. So this is 0.000121%. In 100 molecule probability of seeing this is almost 0, you will not see that.

All are NMR active, you will not see that. So probability is one in 10000, extremely difficult to get a molecules isotopomer both carbon in carbon 13 states, that is fine.

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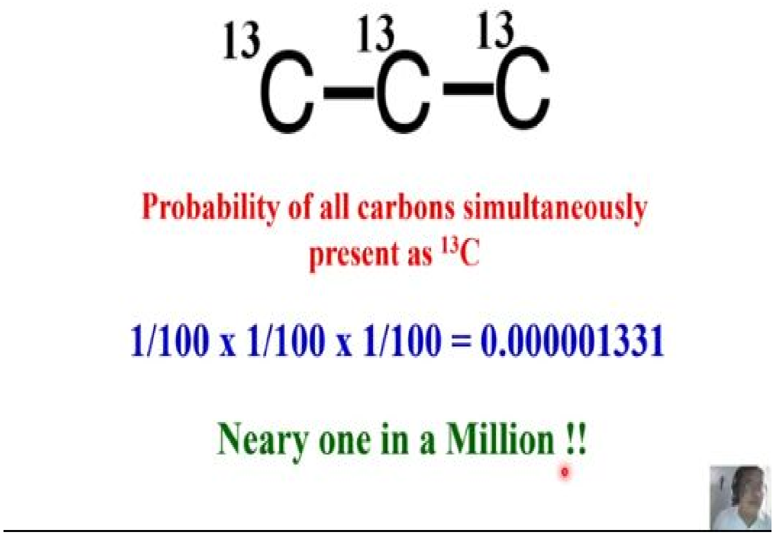

$^{13}C-^{13}C-^{13}C$

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

1/100 x 1/100 x 1/100 = 0.000001331

Neary one in a Million !!

Now I will go to carbon 13 with three carbon presentd in a molecule; simultaneously bonded like this, sequentially. What is the probability of all 3 to be carbon 13 now? Up to this you know, 1 in 10000. Now another one in 100% you have to add. Now joint probability is 1 over 100 into 1 over 100 into 1 over 100, it is even small, 0.000001331. It turns out to be a sort of in nearly one in a million.

One in a million, remember for all the three carbon to be seen in the state of carbon 13. Even more difficult. Even two carbons in carbon 13 is one in ten thousand, that was difficult. Now it is one in million.

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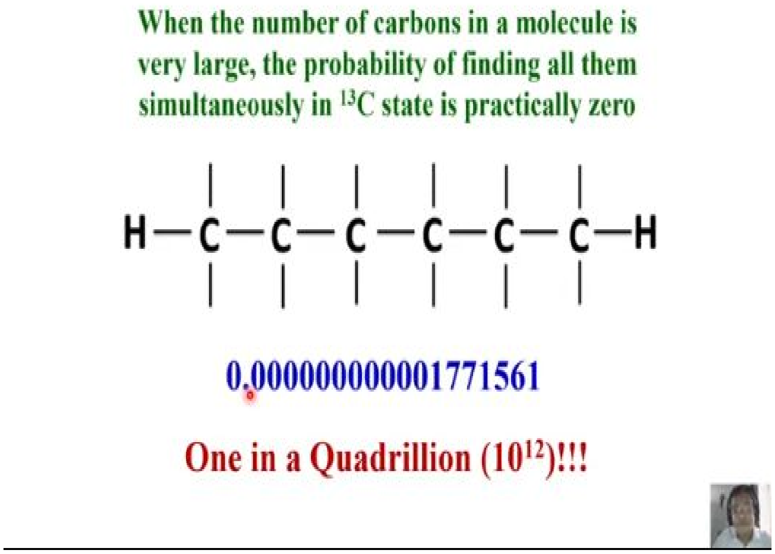

When the number of carbons in a molecule is very large, the probability of finding all them simultaneously in ^{13}C state is practically zero

0.000000000001771561

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

Extend the logic, in some of the molecules you come across several carbons in a chain. You know polymer you have a lot of carbons in a chain like this. I have taken an example of six carbons because up to this we know it is one is million and now another one in million. So 1 in 10 to the power of 12, one in a quadrillion. Probability of all the carbons, 6 carbon to be present in the carbon 13 state is one in a quadrillion.

Can you think of that in a realistic situation? Impossible, very, very difficult or practically 0. So in a given molecule all the carbons present at a time in the carbon 13 state is practically 0. You understand; Now the question is how do you detect carbon 13? Now will go ahead further. I will stop for the day, I will come back tomorrow. I will tell you more about how we get carbon 13 spectrum in spite of the fact abundancy is low and probability of seeing all the carbons in the carbon 13 state in a big molecule is so low or practically 0. So we will meet tomorrow.