Advanced NMR Techniques in Solution and Solid State
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Module -10
Heteronuclear NMR
Lecture - 10

Welcome back. Today let us continue with the analysis of the spectra of some other nuclei. In the last class, we understood about the multiplicity pattern, we understood how to analyze the proton spectrum, based on the multiplicity pattern; because of coupling with the neighbouring groups it could be both homonuclear, heteronuclear. And we took several examples, how we can analyze the spectrum and we synthesized the spectrum also, at the same time, we took the realistic spectrum and tried to analyze, based on the multiplicity pattern.

So, that is what we did. So, we got some hang of how to analyze the spectrum, what is useful information we require for this is the coupling and also chemical shift. The knowledge is essential to make the analysis of the spectrum. So, we came to the carbon 13, we discussed carbon 13. We also understood carbon 13 is 1.1% abundant, very difficult to see all the carbons in carbon 13 simultaneously in a given molecule. We discussed and understood it is superposition of the spectra of N different molecules, each corresponding to one carbon in a carbon 13 state. Whereas, the proton is 100% abundance, and you get from a single molecule. And we also said, for carbon 13 the discussion is generally only based on the broadband decoupling. Carbon 13 spectrum is recorded only with broadband decoouplint most of the times, unless you are interested in carbon proton couplings. That means simultaneously, all protons coupled to all the carbons will be removed.

That is called broadband decoupling; in which case you will see individual carbons for each carbon one peak. If there are N peaks in the carbon spectrum N chemically in equivalently carbons are present. But mind you, you are not removing the coupling with other heteronuclei; like if the molecule has fluorine present, phosphorus is present, which are all 100% abundance, that can couple with carbon. That we are not removing; only proton coupling of carbon can be removed.

Of course, in the present a spectrometer it is possible to decouple various nuclei simultaneously. We can break the coupling with different nuclei also, it is possible. But generally this is what is done in the carbon chemistry; broadband decoupling. And then we wanted to analyze some of the carbon 13 spectrum, after understanding how carbon 13 broadband spectra for some big molecules are seen. We saw small molecule and also big molecule. We will see how we can analyze that.

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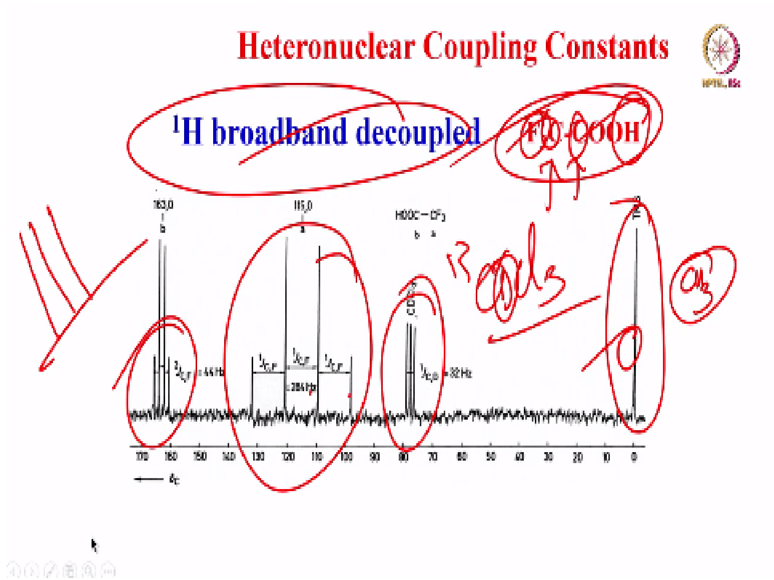

Heteronuclear Coupling Constants

^{1}H broadband decoupled

F3C-COOH

I will take a simple example of a molecule like this; it is called acetic acid F3C-COOH. Now, it is the carbon 13 NMR spectrum, I have told you the broad band decoupled; meaning there is no coupling of carbon with proton. Of course, there is only one carbon is here COOH, but that also is not coupled to carbon. And there are 2 chemical in equivalent carbons here; COOH carbon and CF3 carbon. Now what is the type of spectrum we are going to get for this? very simple spectra we have got, we have to interpret it.

Look at this one, this is a TMS. This is what is used as a reference; we will ignore it. Here TMS has CH3 protons, but remember broadband decoupled; the single peak, no carbon splitting at all.

You come to this peak there are 3 peaks of equal intensity; what are they coming from? This is the solvent we use; what is called CDCl3. The carbon 13 is coupled to deuterium, deuterium is spin 1; as a consequence you get 3 lines of equal intensity. That is why this is a solvent peak. But now look at this one. This is CF3.

Of course, in this case what is happening is we are get large quartet why this quartet coming? There are another quartet with the small separation. There are 2 quartets coming; what are they? why are they coming? Remember, this carbon is directly attached to 3 protons here. So, as a consequence what is going to happen is exactly similar to what you see in proton NMR like proton couplings.

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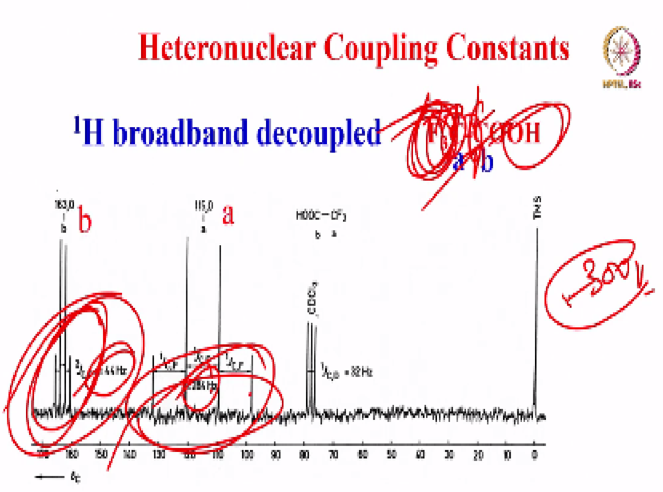

Heteronuclear Coupling Constants

^{1}H broadband decoupled F_3C-COOH

a b

So now, this carbon can be coupled to this fluorine. As a consequence, the 3, chemically equivalent fluorine split this carbon into a quartet. And interestingly, CF coupling is very large, it is of the order of nearly 300 hertz; 284 hertz. One bond carbon-fluorine coupling is so large, it is around 300 hertz and with a negative sign. So, this large quartet with large separation must be this carbon attached directly to proton, sorry fluorine. That is fine. What about this carbon? why it is quartet?

Remember this carbon has long range coupling with this fluorine. These 3 fluorines simultaneously couple to this carbon also. As a consequence, this carbon is going to be quartet, because of these 3 fluorines. And this coupling is very small 44 hertz. That is why in the quartet you see the adjacent separation is small here compared to this. So, these 2 quartets are because of 2 different carbons which are split into quartets, because of 3 equivalent fluorines. The directly attached fluorine carbon has a larger separation, larger quartet and this is a smaller quartet. Very easy to interpret. If there used to be a proton coupling then he would have brought coupling with OH protons and all those things.

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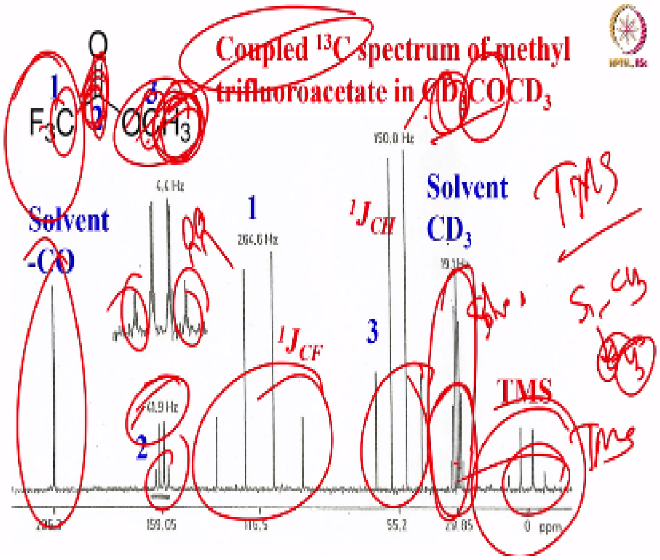

Coupled ^{13}C spectrum of methyl trifluoroacetate in CD_3COCD_3

Now, we will go to another molecule like this. It is a very simple molecule; it is trifluoroacetate in CD3OD. Now it is very difficult; Looks like it is very complex. And remember again this is carbon coupled, not broadband decoupled. This is the interesting thing, that why this example is chosen to tell you. Now carbon is coupled to proton, very interesting thing should happen. What is the structure of this molecule? It is like this CF3COOCH3, a very simple molecule.

How many carbons are there; 1 carbon, 2 carbon and 3 carbon; there are 3 different carbons, but see 123456, different peaks are there. where are they coming from? why are they coming? What are those peaks? We have to understand that first. Remember, at the reference 0 we have a quartet. This is what is the reference we use; TMS. TMS has a Si with 4 CH3 groups; and this carbon is coupled to 3 equivalent protons and gives rise to a quartet. As a consequence at a 0 reference, you have a quartet. This is TMS, easy to interpret.

Then this multiplicity pattern coming because of coupling with deuterium, it is the solvent peak, this is a solvent carbons of the solvent CD3COCD3, which is the coupling to deuterium; D3. And it may not be from 100% D3. It could be CD2HCDH2, verities combinations will be there; different isotopomers. As a consequence you get a complex pattern. This is from the solven, that also we understood. Now, how do you understand 4 different patterns? 4 different patterns, you see one of them has the large quartet separation.

In the previous example, we saw these must be CF3, where carbon is directly bonded to fluorine equivalent fluorines. So, it is a CF3 carbon. Then this carbon, this is carbon is directly attached to the proton, is also a quartet, fine; that is also understandable. What about this carbon? This carbon is coupled to this fluorine, two bond coupling is there, 40 Hertz. We saw in the previous example. So, this is quartet. But remember if I expand this, each line of the quartet is a further quartet; it is a quartet of a quartet.

What does it mean? That means this carbon is also coupled to these 3 protons. So, this is quartet because of all these 3 fluorines, and each line of the quartet is further split into quartet because of these 3 protons. So, this is also understood; this carbon. Now what is this isolated peak which is coming here? Where is it coming from? Remember, this is the carbonyl peak of the solvent, CD3 COCD3 is there; this is CD3 carbon, whereas this is a CO carbon of the solvent. That is how you can interpret the spectrum very easily.

So, now all carbons can easily be assigned, solvent, everything. And you can measure directly CF coupling and also CH coupling, because it is not proton decoupled. So now, with this carbon, of course, a lot more things we can discuss. There is no time to spend so much on these things. What we will do is we will take some simple examples of spectra of few other heteronuclei. That is very important to understand the spectra of few other heteronuclei; that can give us an idea as how to analyze the spectra?

Generally of course organic chemists concentrate on the proton and carbon. If you go to inorganic chemistry people, they have different other exotic nuclei, they will be interested in studying different types of nuclei. Let us take the example of other some heteronuclei to analyze.

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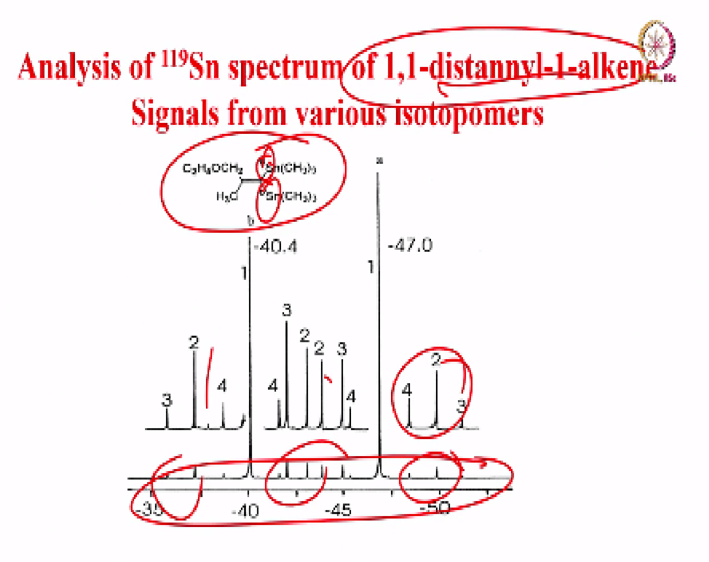

Analysis of ^{119}Sn spectrum of 1,1-distannyl-1-alkene

Signals from various isotopomers

We will start with analysis of spectrum of a molecule like this. Its name is like this; and the structure is very simple, there are only 2 tins present here. I am looking at a tin-119 NMR Remember, I am looking at tin-119 NMR of this molecule. And this is the complex spectrum you have got; and these regions are expanded here, this is a vertical expansion given, to make it lines very clearly visible. Now, we have to analyze this; why the spectrum is so complex? there are only 2 tins here; there are only 2 tin nuclei here; but the spectrum is very complex.

But remember none of them are impurities or anything; there are real peaks from the sample. Now, how do you interpret it?

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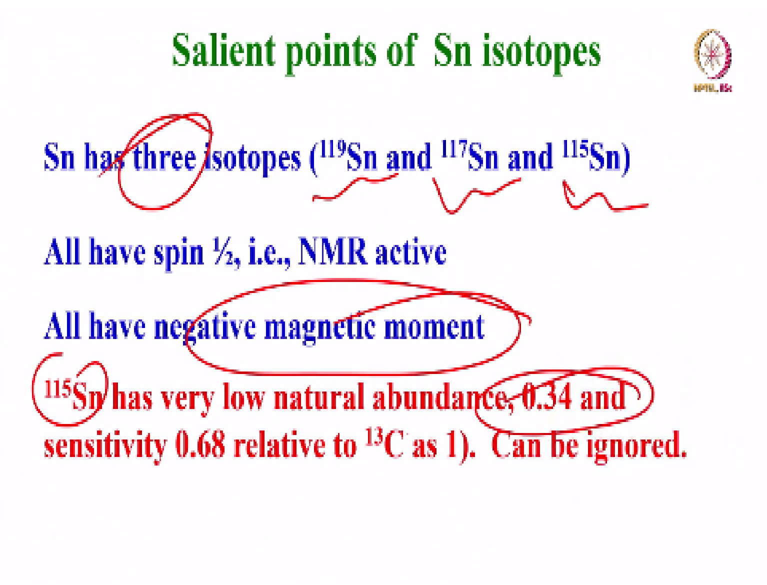

Salient points of Sn isotopes

Sn has three isotopes (^{119}Sn and ^{117}Sn and ^{115}Sn)

All have spin ½, i.e., NMR active

All have negative magnetic moment

^{115}Sn has very low natural abundance, 0.34 and sensitivity 0.68 relative to ^{13}C as 1). Can be ignored.

So, first thing before you understand; what are the salient points of the tin isotopes? tin has 3 isotopes tin-119; tin-117 and tin-115. Interestingly all are NMR active; all are spin half nuclei. Also the interesting point is all of them have negative magnetic moment; what does it mean? I explained to you, remember if it has a negative magnetic moment, the sense of the precession is opposite. The protons are precessing like this in the magnetic field, the tin will process in the opposite direction; that is all the difference.

But if you consider tin115, its abundance 0.34, it can practically be ignored and sensitivity is also very, very small. So, practically we can ignore it, we do not have to worry about it.

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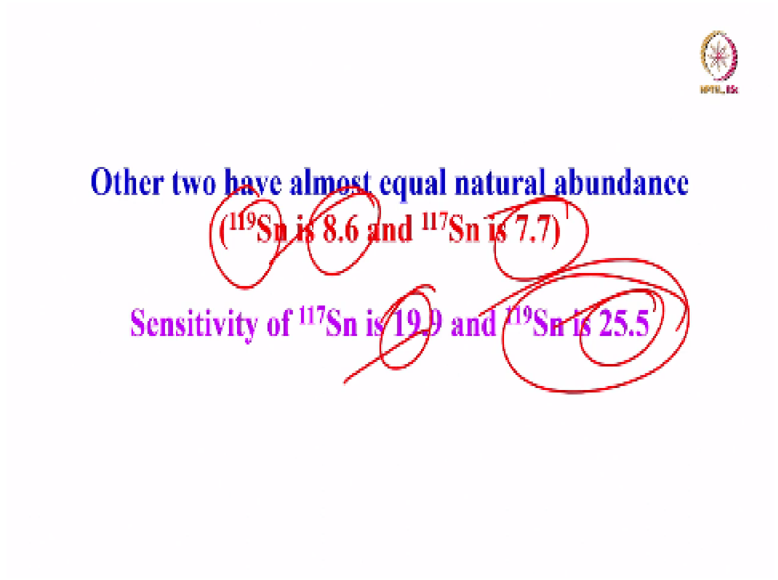

Other two have almost equal natural abundance

(^{119}Sn is 8.6 and ^{117}Sn is 7.7)

Sensitivity of ^{117}Sn is 19.9 and ^{119}Sn is 25.5

But we consider other two tin isotopes, which have equal natural abundance, remember tin 119 is almost 8.6%; this is 7.7%; on an average both of them around 8% abundance. So, both are equally abundant almost, and sensitivity of one is about 20 and other is 25; the sensitivity of 117 is 20; the sensitivity of 119 is 25. Good, that is why we got the tin-119 spectrum, the sensitivity is better and spin half nuclei. Now, our challenge is to analyze the spectrum and interpret. You have to say which peak is coming from which tin?

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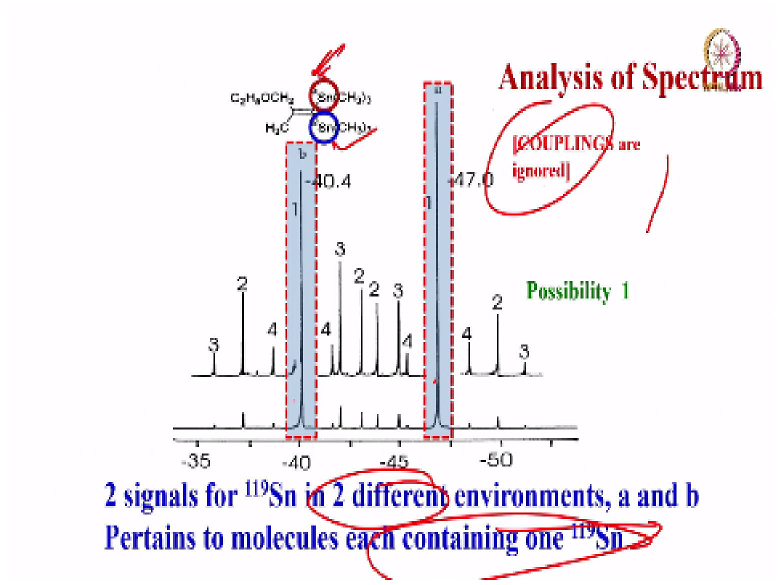

Analysis of Spectrum

[COUPLINGS are ignored]

Possibility 1

2 signals for ^{119}Sn in 2 different environments, a and b

Pertains to molecules each containing one ^{119}Sn

Each peak we have to make the assessment very clearly; no peak should be left out. We will start analysis like this. See, now we know there are 2 tins present. Here the concept of isotopomer you have to think. For example, there is one possibility where there are 2 tins which are present; and one is 119 other is 115, whatever it is. There is no coupling with any other thing, there are 2 independent tins which are present.

So, they are the peaks 2 signals for 2 tin-119 in different environments; A and B and pertain to each containing only one tin 119; and there is no coupling with any of these things. Couplings are ignored here; there is no other coupling. So, that was 2 peaks here, strong peaks we can assign for 2 different tin molecules containing tin-119 in different environments. In one case, this is-119; other case this is-119. This is from 115 or so, which is not visible, not coupled at all, that is fine.

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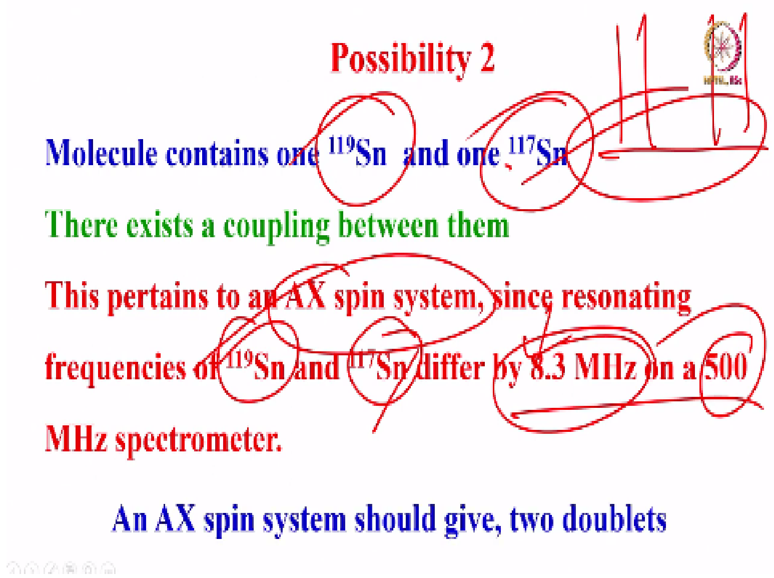

Possibility 2

Molecule contains one ^{119}Sn and one ^{117}Sn

There exists a coupling between them

This pertains to an AX spin system, since resonating frequencies of ^{119}Sn and ^{117}Sn differ by 8.3 MHz on a 500 MHz spectrometer.

An AX spin system should give, two doublets

Now, consider the possibilities. Varieties of possibilities you can think of. Consider one possibility where the molecule contains one-119 and other tin-117. There are 2 tin isotopes, and both are NMR active and both are spin half, both are equally abundant, almost equal and both have very good sensitivity. That means there exists a coupling between these two. These two are you know adjacent to each other. There may be a coupling between these two, when they have a coupling between these two, we call it as an AX spin system.

I will not introduce the spin nomenclature; I will come to that later, but remember it is called a AX spin system. AX spin system is too weakly coupled system; each of them will give rise to a doublet. Simple logic; we discussed this when we understood the multiplicity, when one proton is coupled another proton, this will see this in alpha and beta positions and become a doublet and this will see this in alpha and beta position become a doublet. So, like that, when 2 spins are weakly coupled, you get 4 peaks.

That is exactly what we should expect. And then another interesting thing is tin-119 and 117; they are separated by large chemical shift, in the sense I know at 500 megahertz spectrometer, the relative frequency difference is 8 to 9 megahertz, so you do not see both of them together. See only one nucleus at a time. You can see tin-119 NMR only in 119 NMR. tin 117 peaks you do not see. For that you have to go to tin-117 resonance by shifting the resonating frequency a bit. So, now we are considering the tin 119; although the molecule is present as tin 117 with one of the tin. So, what are the possibilities?

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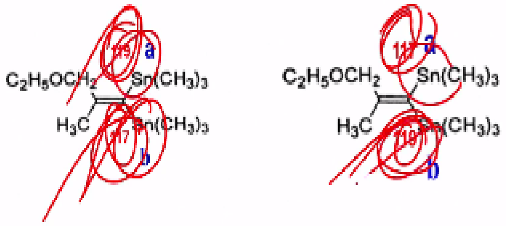
Possibility 2

There are two such possibilities



Two AX spin systems should give eight peaks

We can consider 2 such possibilities like this. One, this could be 119, other this could be 117. Or this could be 117, this could be 119. There are 2 molecules. Further now, both are different. And there is a coupling between them. As I said, this will be a doublet, this will be a doublet, this will be a doublet, this will be a doublet. How many doublets we expect? 4 sets of doublets we should get for two AX spin system, you should get 8 lines. But remember, this is tin-117; that coupling is seen, but this doublet will seen only in tin-117 NMR. So, you will get only one doublet for this and one doublet for this tin-119. That is all you are seeing.

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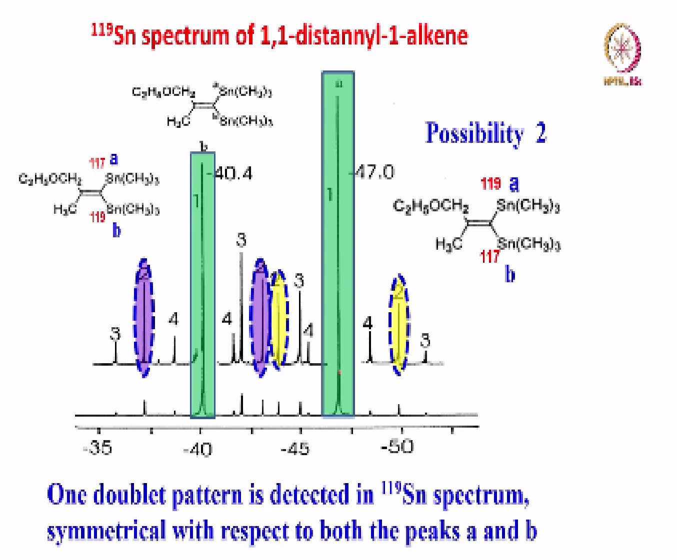

^{119}Sn spectrum of 1,1-distannyl-1-alkene

Possibility 2

One doublet pattern is detected in ^{119}Sn spectrum, symmetrical with respect to both the peaks a and b

So, now, this we have already analyzed and then each tin give rise to one doublet because of its coupling with tin-117. Two isotopomers; this could be one of them, two doublets on either side; and other one these are the two doublets on either side. So, 4 peaks were identified. The remaining 4 peaks, where are they? They are seen in the tin-117 NMR.

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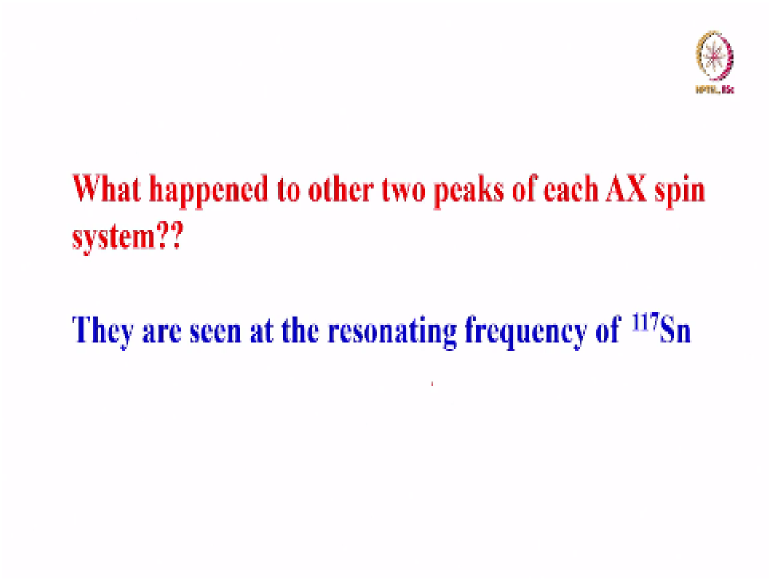

What happened to other two peaks of each AX spin system??

They are seen at the resonating frequency of ^{117}Sn

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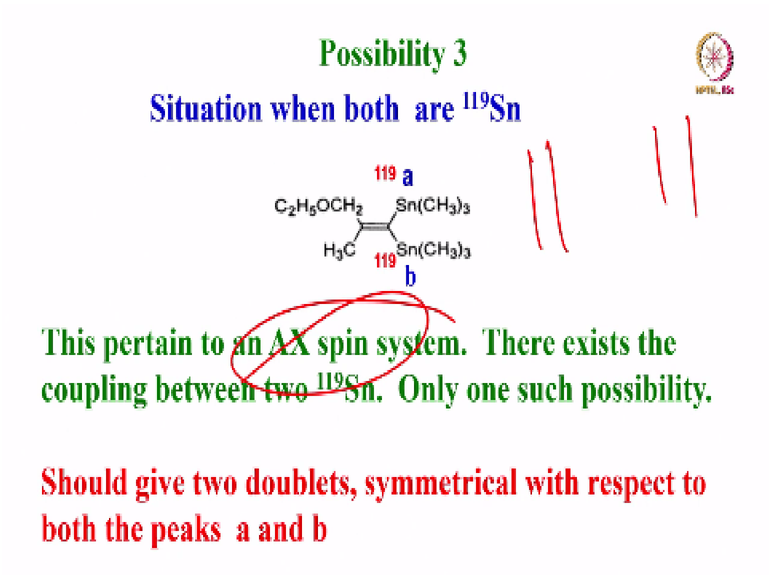

Possibility 3

Situation when both are ^{119}Sn

This pertain to ~~an AX spin system~~. There exists the coupling between ~~two ^{119}Sn~~. Only one such possibility.

Should give two doublets, symmetrical with respect to both the peaks a and b

Remember that two peaks we have already assigned in the possibility 2. Now possibility, 3 why cannot we think of both tin-119? this pertain to an AX spin system. Again 2 tins are coupled; and each of them will be a doublet. So, what will happen then? you should get how many peaks? you should get two doublets. Two doublets for each tin, on either side, we should get 2, 2 lines. It is symmetrically placed with respect to both the tin peaks.

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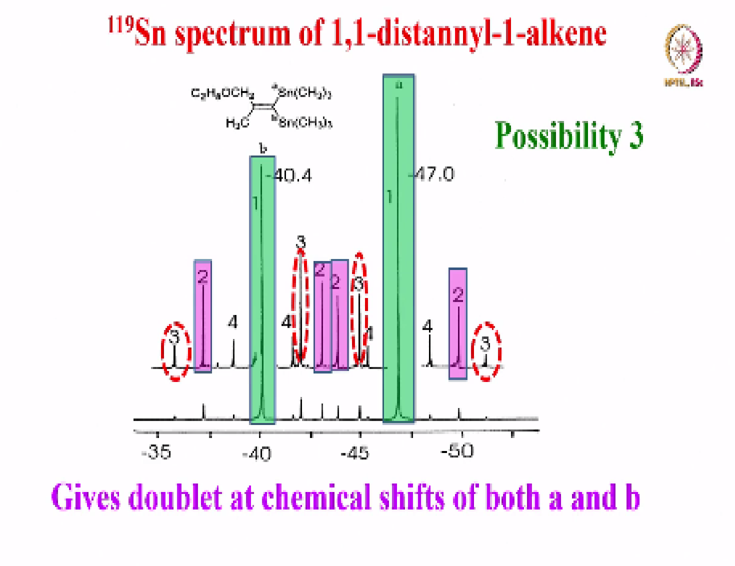

^{119}Sn spectrum of 1,1-distannyl-1-alkene

Possibility 3

Gives doublet at chemical shifts of both a and b

So, this we have analyzed, and this peak we analyzed; these 4 peaks. Now, what is left? See this is one doublet; this is another doublet which is symmetrically placed on either side. This is another doublet which we are trying to see, why the intensities are small? That is a different question. We will not worry about it. Again, this is little bit of involvement in discussion. We will keep it pending, do not worry, these peak assignments are correct. So, we assigned 4 peaks.

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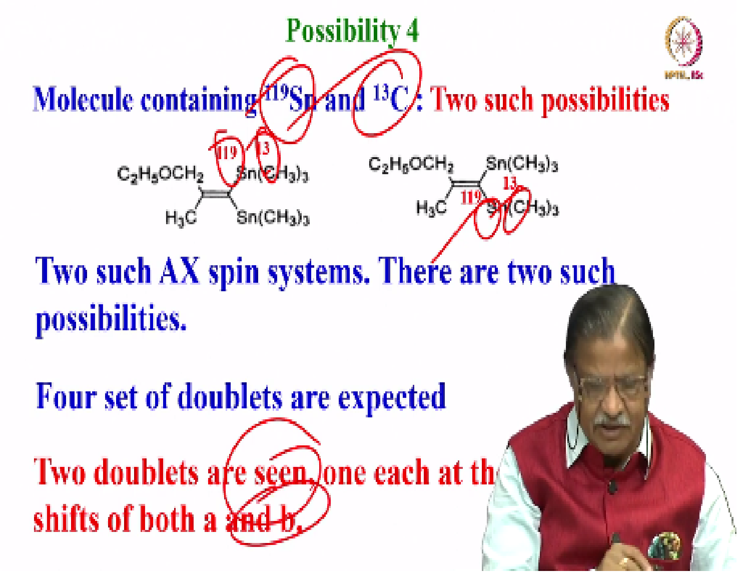

Possibility 4

Molecule containing ^{119}Sn and ^{13}C: Two such possibilities

Two such AX spin systems. There are two such possibilities.

Four set of doublets are expected

Two doublets are seen, one each at th

shifts of both a and b.

Now possibility 3 is over. What is the possibility 4? One can be tin-119, and other can be carbon 13. This is possible; for example, this can be tin-119, this is carbon 13. Can there be a coupling?

why not? Carbon 13 is 1.1% abundant. It couples to tin and give rise to multiplicity. It can become a doublet, it is possible. And another molecule this is 119 this is carbon 13. That is also possible. So, there are again 2 is AX spin systems. There are two such possibilities; and you should get 4 doublets; 8 peaks are there.

But remember out of the 8 peaks, 4 peaks are seen in this case, in this 119 spectrum. The remaining 4 peaks are seen in carbon-13 spectrum; that is the difference. So, 2 doublets are seen here at the chemical shifts of a and b.

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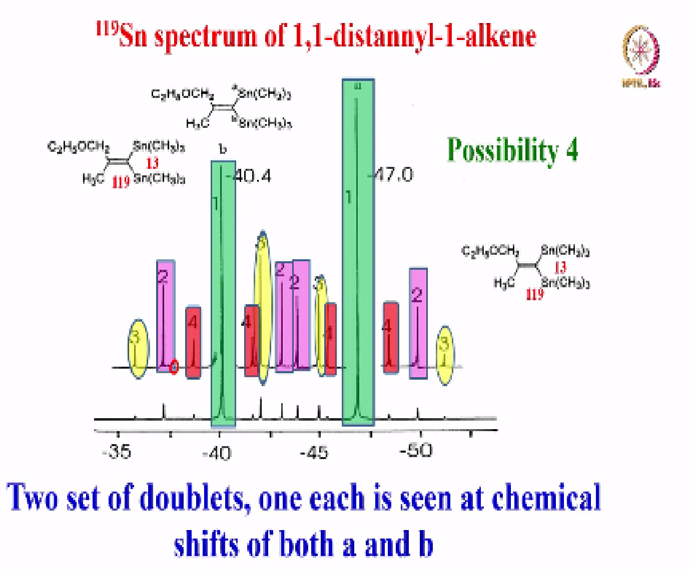

^{119}Sn spectrum of 1,1-distannyl-1-alkene

Two set of doublets, one each is seen at chemical shifts of both a and b

And now we analyze this, you analyze this, we analyze this and now these 4 lines are analyzed. Fantastic; all peaks have been analyzed, all the 4 peaks. So, none of them are impurities, except the small, small cases which are not from this molecule. So, 2 sets are doublet one each seen at chemical shift of a and b. Now, what happened to another set of 2 doublets now; that is seen in the carbon 13 specctrum.

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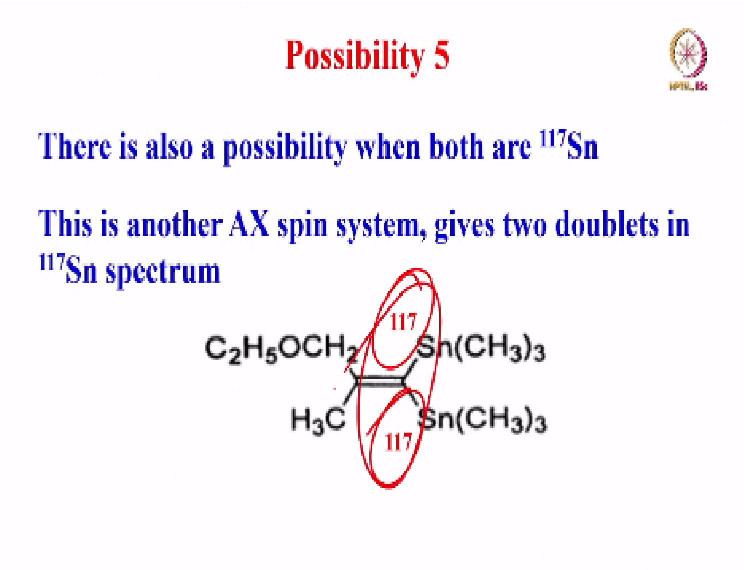

Possibility 5

There is also a possibility when both are ^{117}Sn

This is another AX spin system, gives two doublets in ^{117}Sn spectrum

There is a possibility; another possibility, what is another possibility? Both could be tin-117. It is also possible, but remember you do not seen them in tin-119 NMR, because it is a passive spin. If you see want to see this, you have to go to tin-117 NMR. Remember, you record tin-117 NMR identical spectrum we are going to see for that also. And that is why we are not going to see this in tin-119 NMR. So, this will be seen in resonance of tin-117.

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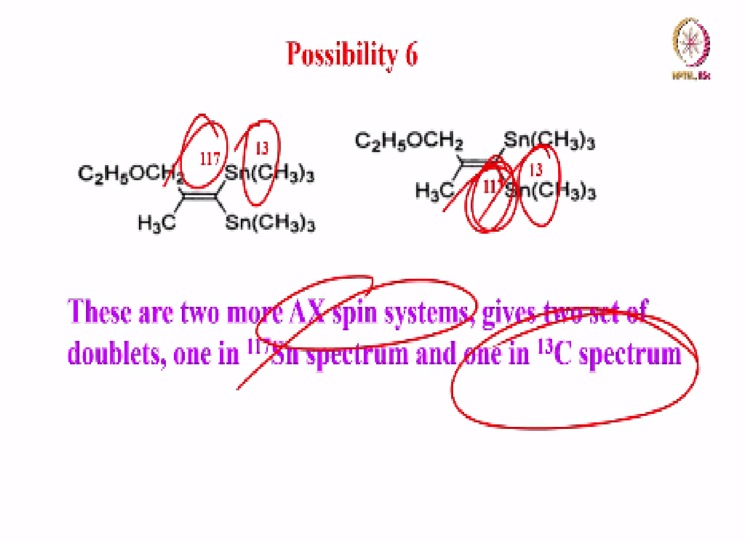

Possibility 6

These are two more AX spin systems, gives ~~two set of~~ doublets, one in ^{117}Sn spectrum and one in ^{13}C spectrum

Now what is the possibility 6; very confusing. Now this could be 117, this could be carbon 13. Or this could be 117, this could be carbon 13. Again, you get 2 AX spin systems; 2 AX spin system, each will give rise to 4 peaks. There will be 8 peaks actually, 4 is seen in tin 117 NMR and the remaining 4 are seen in carbon 13. In both of them we do not see in tin-119 spectrum, this is the possibility. So, very simple molecule, look at the complications. Only there are 2 tin atoms are present in the molecule. But because of the isotopes abundance and different isotopomers are present in the molecule, so many possibilities we can think of; and each peak can be clearly assigned. This is the beauty of NMR. Where small microscopic perturbations, at the site of one of them, because of isotopic substitution, is clearly visible in the NMR spectrum, That is how by understanding the isotopomer spectrum, we were able to analyze this tin NMR.

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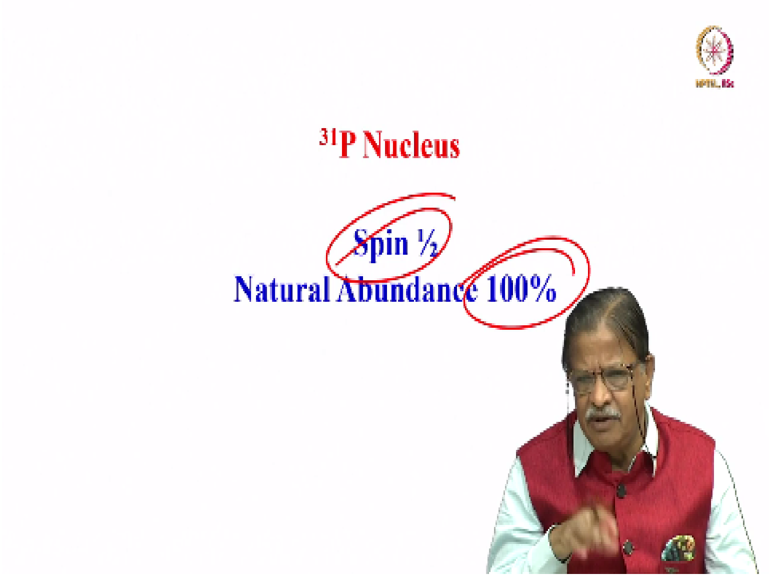

^{31}P Nucleus

Spin ½

Natural Abundance 100%

Now, we will go to another exotic nuclei; Phosphorus NMR. This is something which most of the time biology people use, they study 31P NMR. Interestingly, it is a spin half nuclei; friendly nuclei for us; also 100% abundance, very easy. The Phosphorus, fluorine and protons, they are all friendly nuclei to study because of 100% abundance and spin half nuclei.

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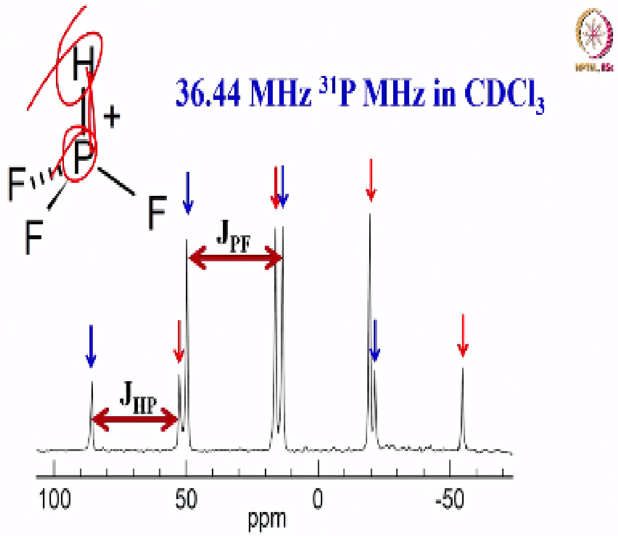

36.44 MHz ^{31}P MHz in $CDCl_3$

Look at this molecule, it is a very simple molecule and it is PF3H. There is one proton and 3 fluorines. Now, these 3 fluorines are equivalent, then how what is the pattern we expect? Remember you are looking at phosphorus NMR. phosphorus can couple to this proton. What will happen? it will become a doublet and then it is also coupled to 3 equivalent fluorine atoms. Then what will happen? each one of these doublets will become a quartet. You can see that; there are 2 quartets here; one quartet is this, this, this and this; and the other is this, this this and this; there are 2 quartets.

And the separations, one large separation correspond to HP coupling, other separation of the quartet gives rise to PF coupling. So, this is a case where in the heteronucleus phosphorus has coupling with 2 other heteronuclei. As a consequence, what we are going to see is two doublets of 2 quartets. here you are going to see, well this is one quartet, this is other quartet; see very easily, you can see the 2 quartets, which I will show you again. See, what I have marked here, this is one quartet which are marked in red arrows, other is another quartet which are marked in blue arrows. So, very easily you can analyze the phosphorus spectrum.

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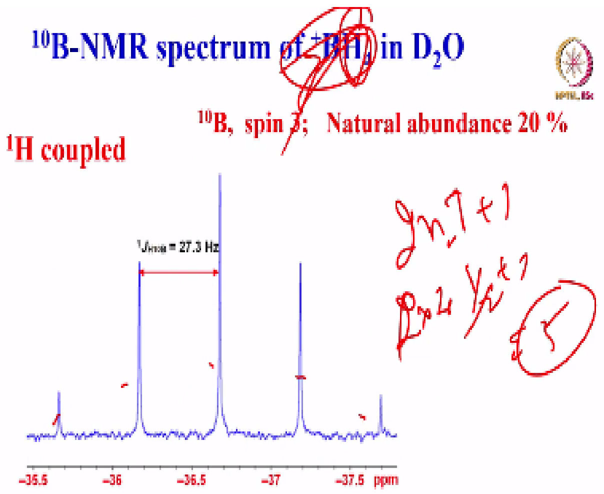

^{10}B-NMR spectrum of $^{+}BH_4$ in D_2O

^{10}B, spin 3; Natural abundance 20 %

^{1}H coupled

You look at the boron NMR; something interesting. Boron has 2 isotopes, boron-10 and boron-11. Boron-10 has spin 3; natural abundance is 20%. Now I am looking for the boron NMR with its coupling with protons; of this molecule, BH4. You should know that by now, there are 4 chemically equivalent protons present, what is splitting pattern you expect for boron? boron 10 Spin 3; 2nI + 1 you add up this one; say we have now 4 protons coupled; 2 into 4 proton spin is half + 1 you will get 5 peaks; exactly we see 5 peaks. This is because of proton coupling, this is the boron-proton coupling, you get by measuring these adjacent peaks separation.

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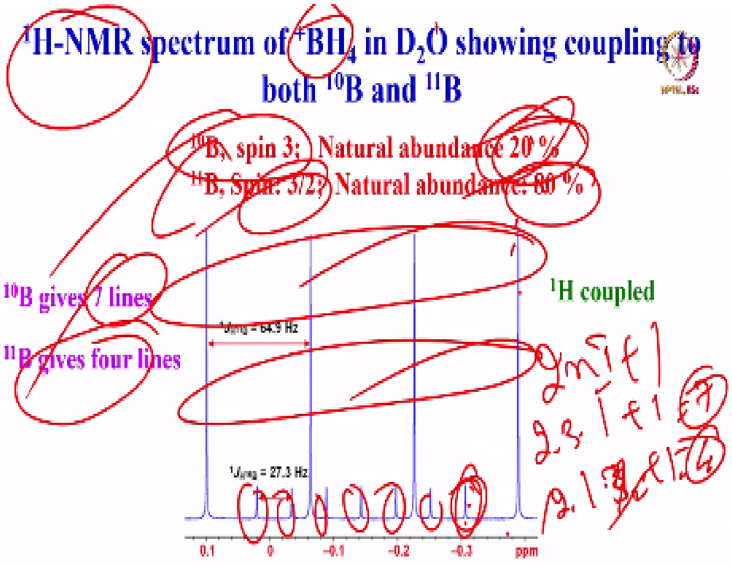

^{1}H-NMR spectrum of $^{+}BH_4$ in D_2O showing coupling to both ^{10}B and ^{11}B

^{10}B, spin 3; Natural abundance 20 %
^{11}B, Spin: 3/2; Natural abundance: 80 %

^{10}B gives 7 lines

^{11}B gives four lines

^{1}H coupled

Why not we do boron 11 NMR? it is possible for the same molecule you do boron-11 NMR, again it is coupled to 4 equivalent protons, identical five line pattern you get; only thing is the coupling is different now, because boron 11 proton coupling is 65 Hertz in the previous example, it is about 27 hertz here. The pattern is the same, it is five line pattern. So, intensity pattern again goes by the Pascal's triangle you can see that. Now, what happens in a molecule like this, if I take proton NMR, I am not looking at boron NMR; roton NMR of this molecule. You can see very very interesting things do happen. Boron-10 has spin 3; the abundance is 20%; the boron 11 has spin 3/2 abundance is 80%. Now, how many peaks you expect for Boron-10? Put the 2N + 1 formula very simple, in the case of boron spin is 3, 2 into 3 into boron spin is 3 and there is only 1 boron is there plus 1; 7 peaks you get. In the case of boron 11 2 into 1 into spin is 3 / 2 + 1. So, how many peaks you get? You get 4 peaks, so boron 11 gives you 4 peaks. Boron 10 gives you 7 peaks because of different spins. Boron 10 spin is 3, you get 7 peaks you will see 1 2 3 4 5 6 7, 7 peaks you see; easily you can say they are from boron 10 because of the multiplicity, at the same time natural abundance is 20%. See their intensity is 20% less than this. This is 80%; if we take this as 100; this is 20% of that. That is intensity ratio 1 is to 4. That is intensity 1, this should be 4; intensity ratios 1 is to 4 here. So, very easily you can say these 4 peaks are coming because of boron 11; and these 7 peaks are because of boron 10.

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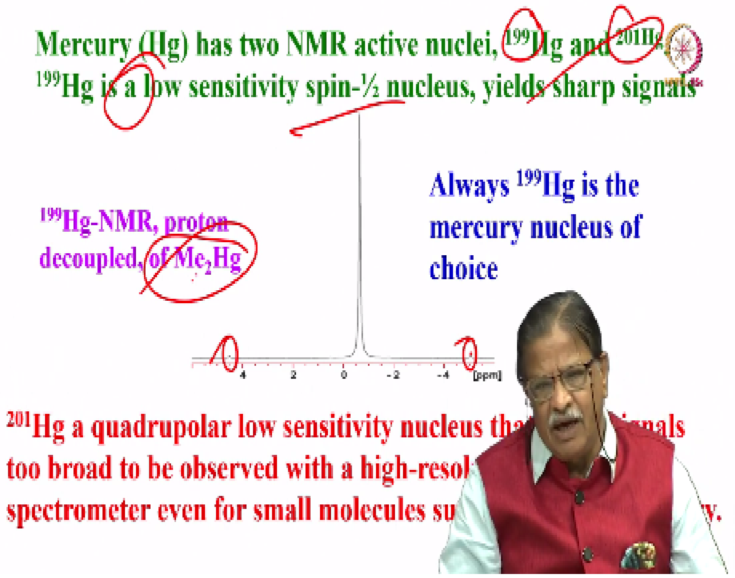

Mercury (Hg) has two NMR active nuclei, ^{199}Hg and ^{201}Hg.
^{199}Hg is a low sensitivity spin-½ nucleus, yields sharp signals

^{199}Hg-NMR, proton decoupled, of Me_2Hg

Always ^{199}Hg is the mercury nucleus of choice

^{201}Hg a quadrupolar low sensitivity nucleus th
too broad to be observed with a high-resol
spectrometer even for small molecules su

So, now I will take the example of mercury NMR. Mercury has 2 NMR active nuclei. Mercury 119 and mercury 201. 119 is low sensitivity, spin of half nucleus and give sharp peaks. Let us take Mercury NMR of this molecule, dymethyl mercury. When we take the mercury NMR, you get a very, very sharp and single peak. But there are these chota peaks here, what are these peaks? they are satellites, they are the peaks which are coupled to carbon or proton; we will see which is bit later.

So, now if you see these, these give peaks, also coupled to either carbon of this or protons either of them.

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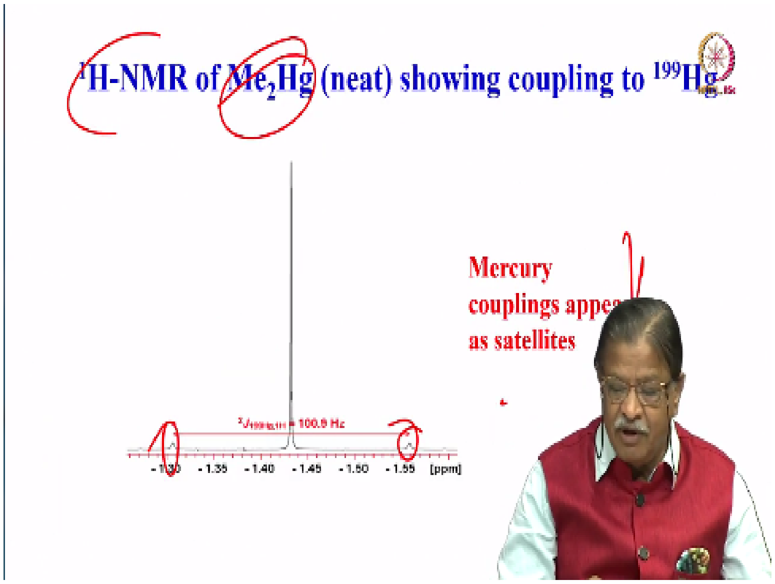

^{1}H-NMR of Me_2Hg (neat) showing coupling to ^{199}Hg

Mercury couplings appe
as satellites

We can see now, you can measure the separation from the other spectrum and understand. Now if you take the proton NMR of this methyl mercury, di methyl mercury, and you can see Mercury couplings appear as satellites here, this is what I said; we are going to see mercury satellites. Measure the separation 100 hertz, go back here, measure the separation, we will find out what are they; so, this is the mercury coupling; 2 bond coupling of mercury with proton. So, in the proton spectrum, mercury appears as satellites.

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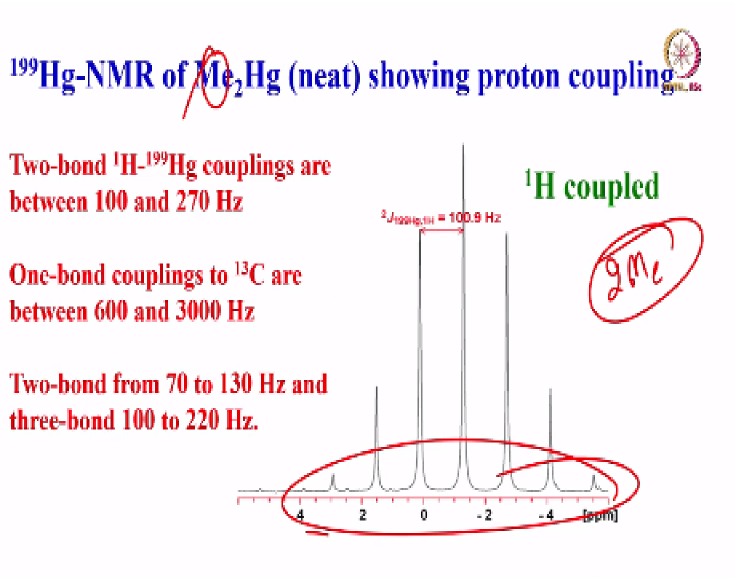

^{199}Hg-NMR of Me_2Hg (neat) showing proton coupling

Two-bond ^{1}H-^{199}Hg couplings are between 100 and 270 Hz

One-bond couplings to ^{13}C are between 600 and 3000 Hz

Two-bond from 70 to 130 Hz and three-bond 100 to 220 Hz.

^{1}H coupled

Of course, you can also see proton coupled, proton coupled how many you expect? we saw that mercury very easily we can work it out, there are 2 methyl groups represent; when 2 methyl groups are present you work out the pattern. See when mercury will split into quartet, because of 1 methyl and each line of the quartet become another quartet because of another methyl. So, what is the pattern you are going to get? a septet; that we observed; that you know.

We worked out in the proton spectrum, the multiplicity pattern. That is why explicitly we took example to see when one spin is coupled to 2 methyl groups of equal coupling, you see the pattern you are going to get; it is the proton coupled spectrum.

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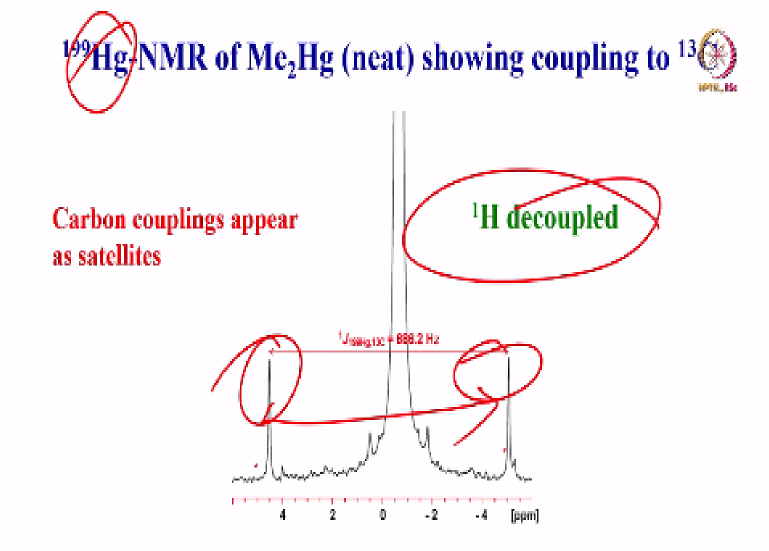

^{199}Hg-NMR of Me$_2$Hg (neat) showing coupling to ^{13}

Carbon couplings appear as satellites

^{1}H decoupled

The same thing you can see mercury NMR, but proton decoupled, break the coupling with proton; then you are going to get see 2 peaks here. What are these 2 peaks? you are breaking coupling of mercury proton, but not mercury with carbon. So, these are the carbon mercury couplings, which because carbon is 1% abundant each come as a satellites; here is the mercury carbon couplings. So, this is how you can understand the mercury spectrum.

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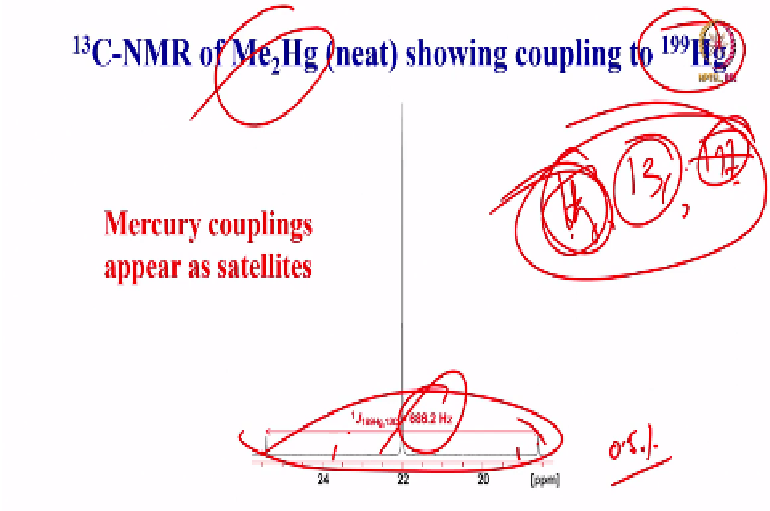

^{13}C-NMR of Me$_2$Hg (neat) showing coupling to ^{199}Hg

Mercury couplings appear as satellites

But you can ask me why not we see carbon 13 NMR? Because this methyl mercury, you have mercury, you have carbon and you also have proton; these are different nuclei, you can study proton nuclei with carbon coupling, and you can see mercury satellites or you can see carbon by coupling with proton or decoupling with proton to see this one. You can see mercury resonance and then decouple proton; varieties of possible experiments you can do.

So, now, if you see the carbon 13 NMR of dimethyl mercury, and you are seeing the mercury 119 coupling, you see here these 2 are the peaks, and the intensity pattern tells you the percentage of abundance of mercury. If it were to be carbon-13 it is 1% and 1% split into 2 it is 0.5%. But here you see much better; the intensity is much better; the abundance of this mercury is much better than that of carbon. So, from carbon 13 NMR you see mercury satellites and from this you get mercury carbon coupling. Sometimes huge coupling; remember J coupling of nearly 700 hertz you see between mercury and carbon. So, like this, what I wanted to say is n numbers exotic hetero nuclei can be studied. We can take a lot more nuclei. I can give you an example without even showing the spectrum. Common we see tetra methyl silane; go to Silicon NMR the proton NMR we see single peak, usually the reference; in carbon 13 NMR, you get a single peak because we did broad band decoupling and used as a reference.

Now go to Silicon NMR, again do broad band decoupling. Carbon is one percent natural abundance, you do not see satellites, let us say, you get single peak. Now I do one thing. I will bring in the coupling of proton to silicon. How many peaks you expect, very interesting you understand for example, tetra methyl silane in CH3, CH3, CH3 and CH3 are there. So, now, there are 12 protons, equivalent protons.

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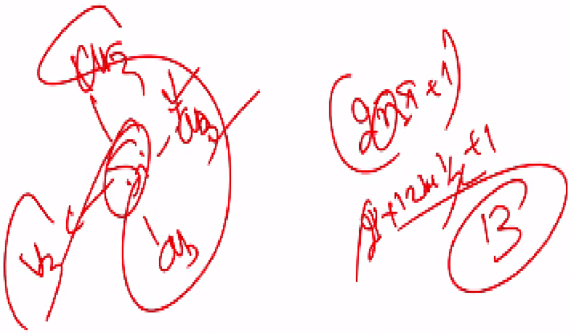

If it is coupled to silicon, how many peaks you expect? Remember 2nI + 1, n is 12 here; 2 into 12 into half + 1. So, it is 13 peaks we expect. Go back and record the silicone NMR of Tetra methyl silane with proton coupling, you will see 13 peaks. So, that is how looking at the multiplicity pattern, using the simple formula I gave you, when you have equivalent spins when they are non equivalent spins; using the family tree approach and depending upon the coupling strength, chemical shift information, and depending upon the abundance and everything, for a given molecule you can get varieties of NMR spectra and correspondingly you can use all of them to get the information. In a molecule like this you can do carbon 13 NMR, proton NMR, silicon NMR; In silicon NMR you can do proton decoupling, in carbon 13 NMR you can do proton decoupling; you can do proton coupling, all these, verities of experiments you can do depending upon the information you want to derive.

So, this is a basically broad view I wanted to give you about the analysis of the spectra of molecules, different types of molecules, and different heteronuclei. I hope you got the idea of how we can go ahead and analyze different spectra. But remember, all these things I explained in detail, with number of examples in the previous course. This is only to take you along with me, I explained this. Those who want to get more information, please go back to the previous course.

So, I stop here now, but remember today what we discussed, in this class, we analyzed verities of spectra, proton spectra; carbon spectra; nitrogen spectra and then we understood how we get the pattern; boron spectra for example, if we take BH4, look at the boron NMR coupled to proton, you will get boron 10 isotope, boron 11 isotope couplings will be there; one gives you 7 lines pattern of 20% intensity; other gives you 4 lines of 80% intensity.

So, depending upon that, isotopes depending upon the abundance, you can see how many peaks you are going to get, each of them can be interpreted within knowledge of the coupling; with the knowledge of the chemical shift, knowledge of the abundance; knowledge of the sensitivity, if you use, any spectra, which is given can easily be analyzed for any molecule, of any nuclei. So, I hope with this you can go and practice with more spectra from more number of books available, you will be able to get a lot of information and you will become a master. So, I will stop here at this stage today. And in the next class will go for a different topic. Thank You.