One and Two Dimensional NMR Spectroscopy for Chemist

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Lecture No: 43
Analysis of spectra of other nuclei

Welcome back, in the last class we discussed something about multi nuclear NMR, and some isotopic shifts, effects of substitution of different isotopes on the NMR spectrum. I discussed quite a bit, and I showed you how important it is, just by mere substitution or replacement of one proton by deuterium has a tremendous effect on the spectra and the peak moved quite a bit.

Similarly, especially we saw and discussed that halogen substituted like fluorine, chlorine, bromine had a tremendous effect in giving rise to isotropic shifts, and I showed couple of examples like dibrofluoromethane, one molecule; and CFCl3, PCl3, PtCl6, and etc. so many molecules were there, and we showed the example of couple of them and we worked out the intensity pattern, how it comes based on the population distribution of different isotopomers. So this is a very important point, please remember, we need to understand this.

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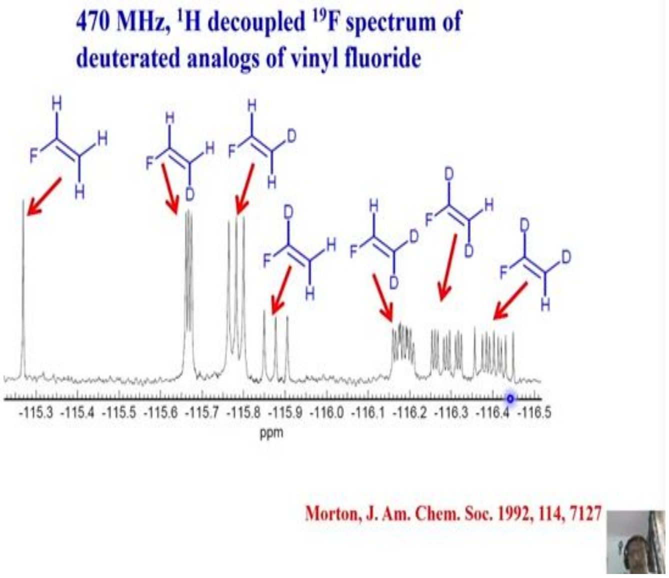

470 MHz, ^{1}H decoupled ^{19}F spectrum of deuterated analogs of vinyl fluoride

Morton, J. Am. Chem. Soc. 1992, 114, 7127

And then in the last slide, I did not get time, I was in a hurry, so let me go slowly and taking one or two minutes today. This is the spectrum of deuterated analogs of vinyl fluoride. Remember. I took the SnH_3^- spectrum, I showed Tin119 NMR spectrum, where I took its deuterated analogs also. Then we could interpret the NMR spectrum of that so easily taking into account what happens if one, deuterium is substituted, two deuterium are substituted, all are 3 deuterium, etc. we could explain the multiplicity pattern.

Now this is a similar molecule, there it was a 119 Tin NMR, now it is a 19F NMR and this is the molecule. Remember, it is proton decoupled. I am looking at fluorine NMR with proton decoupling. So completely all the proton couplings are removed. So if this is the molecule, when only one fluorine is substituted, and no other couplings are there, of course, do not worry about, carbon 13 satellites, we do not worry about it, and all the protons are completely decoupled; how many peaks we expect? Only one peak; exactly this is what we see. Now the deuterated analogs of this was taken; in the sense di deutero analogs, we will take first, first go to mono and then go to di. If one of the protons is replaced by deuterium, one of the protons, how this spectrum affects, you will see. First one, let us consider this molecule very, very interesting you see here what is happening?

Now as for this fluorine is concerned, it is 3 bonds away and 3JFD coupling is there, but it is cis 3 bond vicinal coupling, It is vicinal coupling, it is a cis coupling; it is a cis orientation and the coupling you can easily measure. This deuterium, because it is spin 1, splits this fluorine resonance of into 3 lines of equal intensity; and we measure the separation of adjacent peaks of this three lines, you are going to get a fluorine coupled spectrum corresponding to vicinal cis configuration 3J coupling, 3JFD coupling; that is fine.

Next, we will go to another one. Now this deuterium is in trans position, not in cis position; again 3 bond coupling; but it is moved from this position to this position. Look at the pattern what does it tell you? the J coupling is is much more. Now the trans coupling is much more, see quite large. So we are going to see FD coupling quite larger like this.

What is this one? this is the situation where deuterium is geminal to fluorine. In the sense it is only 2 bonds away, 2 bond FD coupling is much larger than 3 bond coupling. See the separation here quite large; now measure the peak separation between this and this, you get JFD, 2 bond

JFD, Try here, you measure this separation between these, you get 3 bond FD here you are getting 2 bond fluorine deuterium coupling, very easy. So that is what you are going to observe when you have a single deuterium, with different analogs where deuterium substitution position is varied.

Now look at this molecule; now we are looking at 2 deuterium substitution, deuterium substituted two positions, one here one here. Interestingly, what happens is one of the deuterium splits fluorine into 3 lines of equal intensity, like here. But what the other deuterium does? Remember, they are non-equivalent you cannot use 2NI+1formula, here because they are non-equivalent.

First one of them splits into 3 line pattern of equal intensity. Second deuterium, splits each line of these three lines into 3 three lines of equal intensity, understand? It is a deuterium fluorine coupling; because of spin one, deuterium gives rise to 3 peaks and each line of this three line further split into three, three lines because of coupling with another deuterium. So we are seeing 9 line pattern. Here 9 lines are there.

Exactly the same pattern you will see in this position, when the deuterium is 2 bonds away and fluorine is experiencing 2 bond deuterium coupling; and 3 bond deuterium coupling, see this is what it is. One of them is a 2 bond coupling other is a 3 bond coupling. How do you identify 2 bond coupling? Simply take the centre of this to centre of this, or centre of this to centre of this, it will exactly match, with this two bond coupling.

And then each line of this 3 line is further split by another, deuterium into 3, 3 lines, very clearly 9 lines you can see. That is the beauty of coupling with the second deuterium. Now, this is the another analog of that, Another very interesting thing; now we have a geminal coupling. I am sorry, I would say 2 bond coupling of fluorine and deuterium and 3 bond coupling of deuterium which is in trans position and you see again 9 line pattern.

Analysis of that gives me 2 bond FD coupling and 3 bond FD coupling, trans to fluorine, very nice. You see the most interesting you have to understand how the deuterium substitution has a dramatic effect in the chemical shift position, because of isotopic substitution in the position. Secondly here 2 deuteriums are substitute;d here with no other substitution, with one substitution the different positions shifted like this. With two substitution, even more it shifted so the dramatic effect of the substitution of deuterium you see on the chemical shifts of fluorine also.

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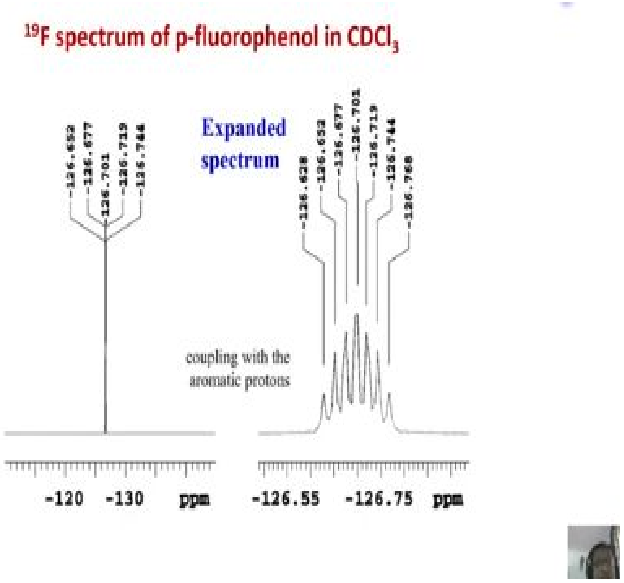

^{19}F spectrum of p-fluorophenol in $CDCl_3$

With this now, we will try to analyze some of this spectra of different nuclei. I wanted to make you understand heteronuclear NMR, extensively I have covered carbon, proton everything, that is more than sufficient for you, because with that knowledge you can analyze. But some tricky situations will be there, like we saw isotope shifts or varieties of other things will come, some of the problems once in a while, when you come across.

So let us see some of the spectra; other than proton and carbon; some heteronuclear spectra. Heteronuclear in NMR jargon is anything other than proton, that is called hetero nuclei. Of course heteronuclei means anything, when carbon is observed, proton is heteronuclei; does not matter but in NMR colloquially we say I am looking at heteronuclear spectrum means other than proton, this is just a convention, of course not that you should not see proton.

Now let us look at the fluorine spectrum of para fluorophenol, phenol is C6H5OH, and para position in the 4th position, we are having fluorine. If you see the fluorine spectrum of it , it is fantastic, you know it is beautiful single line you are going to see. When the same thing is expanded, it is a multiplet. See why this multiplet is coming; see first thing fluorine is experience a coupling with these 2 protons which are ortho to it, they have the same coupling strength because of symmetry, there is C2 symmetry for the molecule same coupling strength, then it gives a triplet like pattern, because two peaks of the centre lines overlap. Each of these things experience coupling with meta protons of equal strength, both meta protons have the same coupling strength with fluorine. Now each of these triplet line patterns further split into triplet because of that. So you will get triplet of triplets, so you should get in principle 9 lines. We will try to understand 1, 2, 1, one triplet, 1, 2, 1, one triplet, 1, 2, 1 triplet, 1, 2, 1; so all the three triplet here overlap. And this is the fluorine spectrum if you analyze this, you can get which is the larger triplet which is smaller triplet, if you analyze you can get coupling of fluorine with ortho protons and also to meta protons. Very easy, this is a simple fluorine spectrum.

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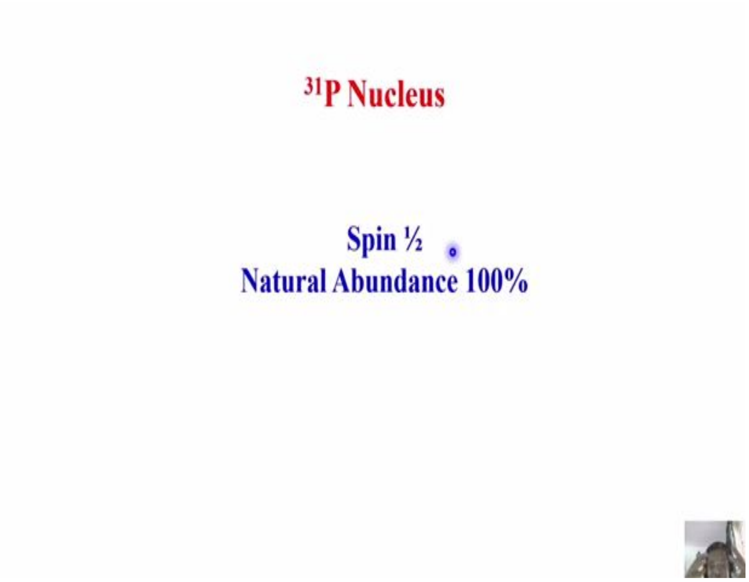

^{31}P Nucleus

Spin ½

Natural Abundance 100%

Now I look for the phosphorus 31, phosphorus 31 is this is spin half nuclei, and it is a another favourable nuclei; abundance is 100%. Easy to detect, as I told you earlier, spin half nuclei are really friendly for us; very easy to deal with them; unlike quadrupolar nuclear, that are spin greater than half, that spin 1, 3/ 2, 5 /2, 7 / 2 spin keeps increasing, you know it is very, very difficult for us to handle. So, it is more comfortable to work with the spin half nuclei, and also with 100% abundance, so that is one such nucleus P31.

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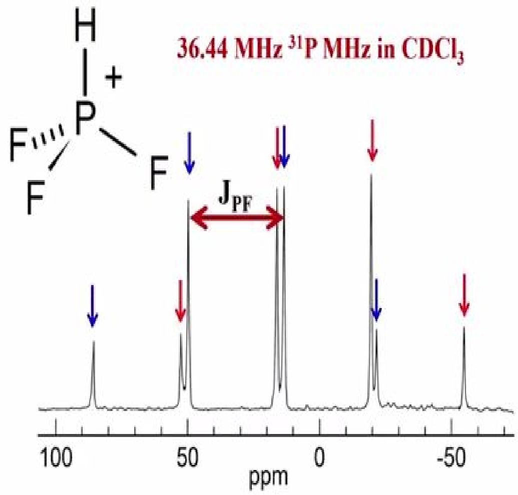

Now let us look at the P31 spectrum of this molecule, what type of spectrum we expect here? Look at this spectrum, you will try to understand. First thing all the 3 fluorines are equivalent; all the 3 fluorines are equivalent. That will split phosphorus into a quartet; remember it splits into a quartet; and then this phosphorus is also split by proton. What will happen when it split ? It splits each line of the quartet into a doublet, you understand?

Now, the question is which is larger? This FH coupling is larger or HP coupling is larger; accordingly, you will say doublet of quartets or quartets of doublets. See you understand now, look at this; which is larger here? See this is one, quartet is 1,3,3,1, this are two lines; 1,3,3,1, it is a quartet, each line of the quartet is a doublet like this, because of coupling with HP. Now what we have to see is, which coupling is larger?

Measure this coupling, this is a quartet or measure this to this one. Which of them is larger? if fluorine to phosphorus is larger, that coupling is larger than quartet coupling is larger; doublet is smaller than that. In principle take any of the peak, measure with respect to this. I can consider for example, I will take a highlighter, and I will show you this peak, this peak, this peak and this peak also a quartet; this, this, this and this from another quartet.

So, now this quartet if you take 1, 2, 3 and 4 find out the centre of that. Let us say this is centre and find out this quartet, and find out the centre of that, this is HP coupling. And this is PF coupling, which is larger? you find out, because it looks like more or less they are equal. Depending upon whichever is larger, you call it quartets of a doublet or doublets of a quartet that is what you should understand.

This is one quartet, this is another quartet this is JPF, this is JHP. Looks like JPF is larger than JHP, as consequence it is a quartets of doublet.

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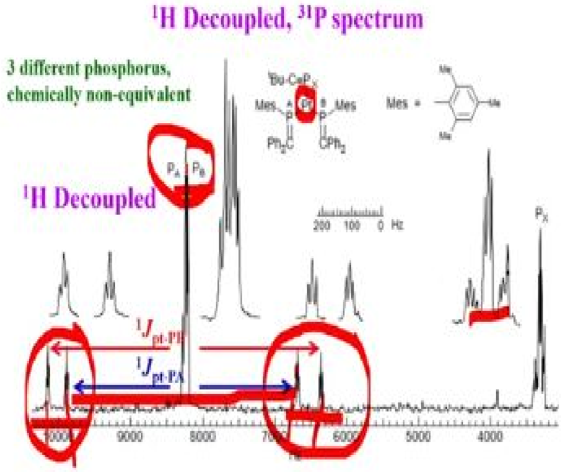

^{1}H Decoupled, ^{31}P spectrum

3 different phosphorus, chemically non-equivalent

Now look at the other phosphorus spectrum of another molecule which is proton decoupled 31P spectrum. How many phosphorus are there? If the phosphorus spectrum is you are looking at? This is one phosphorus, this is another phosphorus; and this, 3 phosphorus are there. And all the 3 phosphorus are chemically in-equivalent because, you see, if you look at the structure of the molecule there is no symmetry.

So all are chemically in-equivalent, there must be 3 phosphorus peaks we get; one is here Px one phosphorus; there are 2 phosphorus here which are overlapping both chemical shifts are there Pa and Pb, very small change in the chemical shift they are overlapped here. And you are not able to see that at all, you cannot identify what is what. But if you carefully see you, are going to see some peaks here; what are they? These are all coupling of phosphorus with platinum.

It couples to platinum, platinum abundance is small, then what do you get? satellites. You are going to get satellites, that is what happens. now this you are going to get satellites for this peak here, this is phosphorous; platinum coupling for this Pa and Pb you get 2, 2 satellites. How can we get 2, 2 satellites? That means we have 2 phosphorus chemical shifts, that are more or less overlapped; but interestingly its coupling to platinum are different; one coupling maybe this, other coupling maybe this.

Now to identify which is the chemical shift of phosphorus A and which is a chemical shift of phosphorus B, simply take this separation; divided by 2 that is chemical shift of 1 phosphorus. Take this separation and divided by 2; that is chemical shift of other phosphorus. So what you cannot distinguish the chemical shifts, very clearly in the phosphorus spectrum, you can make use of satellites, because satellites have better resolution here. You can make use of satellites and resolution and make the assignment of the individual phosphorus so very beautifully. Of course coupling patterns can be understood easily.

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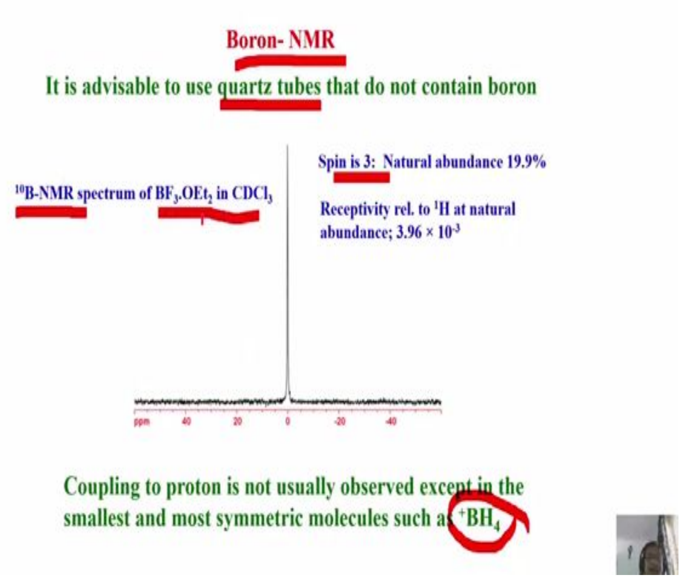

Boron- NMR

It is advisable to use quartz tubes that do not contain boron

^{10}B-NMR spectrum of BF$_3$.OEt$_2$ in CDCl$_3$

Spin is 3: Natural abundance 19.9%

Receptivity rel. to ^{1}H at natural abundance; 3.96×10^{-3}

Coupling to proton is not usually observed except in the smallest and most symmetric molecules such as $^{+}$BH$_4$

Now we will go to boron NMR, boron is something which you should know. Borosilicate glasses are there, NMR tubes sometimes contain boron as they are made up of borosilicate glasses. So if you are looking for boron, you should not use the borosilicate glass, because you get boron signal from the NMR sample tube. The advise for such situation is you have to use quartz tube, remember you have to use quartz NMR tube, when you want to study boron NMR.

One interesting thing is boron spin is 3, spin is 3 for boron 10, that is very interesting. So that is why if you want to see the boron NMR of, let us say BF3EtO2, you get a single peak. So you are going to get only one boron signal, of course it should couple to fluorine.

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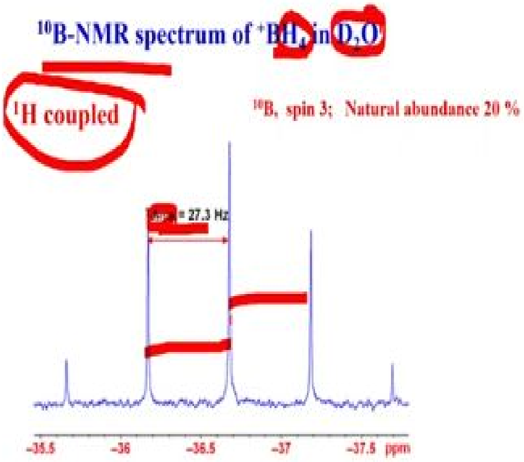

^{10}B-NMR spectrum of $^{+}BH_4$ in D_2O

^{1}H coupled

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

Let us see now, what is happening in the next one. The next one, is BH4 that was BF3EtO2 and it is the reference. Now you the B10 NMR. If I see B10 this H4 should couple to that, am I right? Go back here, remove everything look at it, coupling to proton is not usually observed here ,; in the smallest and symmetry molecule, except in this molecule. So you do not see coupling to protons, but look here; boron-10 NMR spectrum of this BH4, H4 is 4 chemically equivalent protons.

What you have to do? You have to apply 2NI+1 tule, when you apply 2NI+1 rule, follow Pascal triangle because proton is spin half. Boron when you are observing, you have to see the coupling with proton. But in this example, what we are seeing is a five line pattern, where it is coupled to boron-10, it is a boron-10 NMR; there is also boron-11; will come to the later about how that spectrum comes. In boron-10 NMR, boron is coupled to 4 protons. Using the Pascal triangle you get 1, 4, 6, 4, 1 intensity; these peaks adjacent separation gives you boron 10 and proton coupling.

So B10-H coupling, it is the proton coupled NMR spectrum. So why you got 5 lines? H4 2NI+1 you got 5 lines, for intensity pattern is Pascal triangle you apply and the adjacent peaks separation gives you J coupling. So boron 10 NMR spectrum of BH4 is easy to interpret, and also it is done in D2O, no question of solvent peak or anything here; very simple

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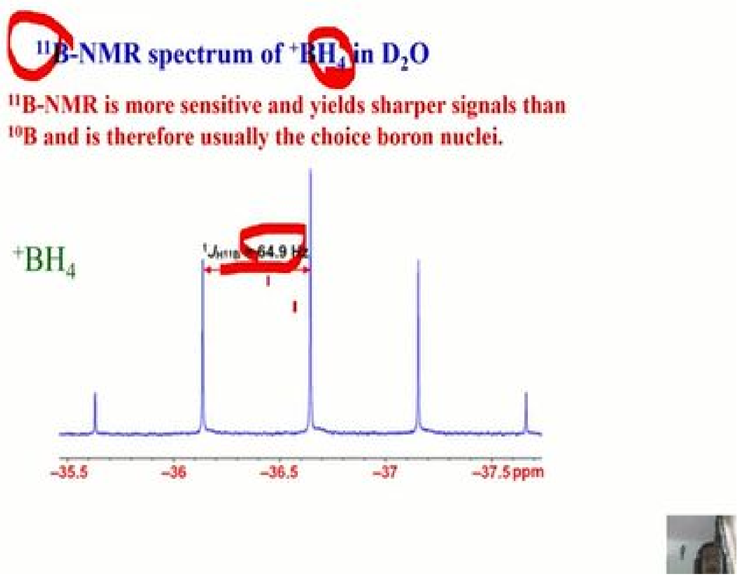

^{11}B-NMR spectrum of $^{+}BH_4$ in D_2O

^{11}B-NMR is more sensitive and yields sharper signals than ^{10}B and is therefore usually the choice boron nuclei.

Same thing; do boron 11 NMR, what happens so? Pattern remains same, it cannot change because, again does not matter what is the spin of the observing nuclei, this spin is different whereas, this spin is different, boron 10 has spin 3, this is spin 3/ 2 of boron 11; does not matter what is the spin of the observing nuclei; but what it is coupled that is proton. So again 4 equivalent protons, apply Pascal triangle, 2NI+1 rule, get the intensity 1, 4, 6, 4, 1, exactly same pattern what you saw here.

So you get B10 proton coupling here, you get B11 proton coupling here. See the isotope couplings are different; B11 proton is 65 hertz approximately this, this is 27.3 Herz. See difference B10 proton coupling is much more; almost half of it compared to 11B coupling. So, very easily we can see boron NMR and its coupling to proton, especially in this type of molecule you see; otherwise normally as I said the coupling to proton is usually not observed, except in symmetric molecules like that.

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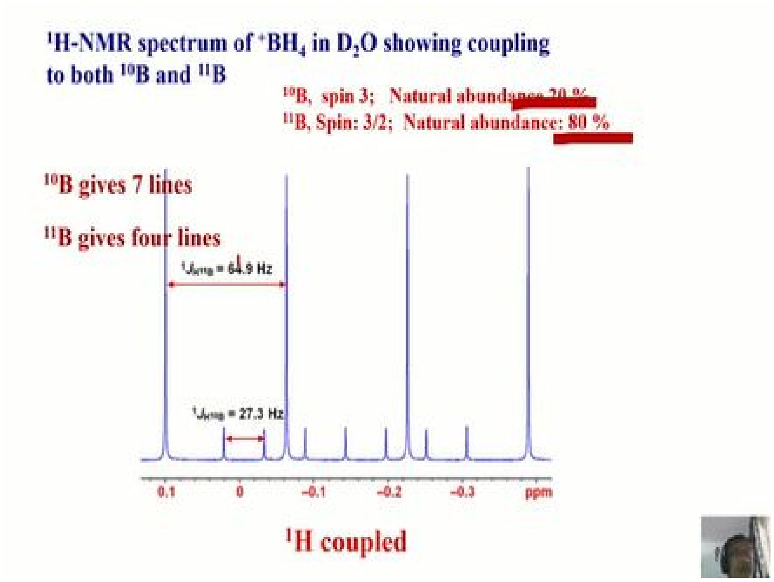

^{1}H-NMR spectrum of $^{+}BH_4$ in D_2O showing coupling to both ^{10}B and ^{11}B

^{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

Now, we saw boron NMR, let us not worry about it. Let us see proton NMR, what type of proton NMR spectrum we get? see very interesting thing, I am sorry, see what type of things we are going to see in the proton NMR. What we are seeing is 1H NMR, proton is coupled to boron when we are observing boron, we are seeing coupling to H4, we got that 1, 4, 6, 4, 1 intensity pattern.

Now, let us see, we analyze this spectrum. There are strong 4 peaks here, what are they? Why is it coming? What is this coming from? and there are also small peaks here of equal intensity, fantastic spectrum all peaks are of equal intensity here, if you carefully see these 4 peaks, I would say, it is because of the B11. B11 as you know has spin 3 / 2, so 2NI+1, if you put N is equal to 1, I is equal to 3 /2 so how many peaks you expect? This 2 and this 2 will get cancelled, and so 3+1 only you get 4 lines.

So for spin 3 / 2, 2 into NI+1 n is equal to 1, 2 into 3 /2 ; so 2 cancels, you will get only 4 peaks and these 4 peaks are for B11 and of equal intensity and the separation between adjacent lines gives you 11B- proton coupling.

What about B10? Spin is 3, you put 2NI+1 what happened? 2 into 6+1, 7 peaks you should get but remember, 7 peaks should see here 1, 2, 3, 4, 5, 6, 7, fantastic you see all the 7 peaks and have equal intensity.

But, what is intensity when compared between this and this? This is much larger than this; reason is B11 is 80 % abundant, B11 is 80% abundant and B10 is 20% abundant as a consequence the intensity ratio is 20 : 80, 2 : 4 intensity ratio should be there and that is what you are seeing. And this peak is boron 10-proton coupling, this what we observed when you observe the boron resonance right, the same couplings were measured.

We did two experiments. We have to do boron 11 and boron 10 experiments. On the other hand in one proton NMR experiment, all the couplings of boron 10 to proton, boron 11 to proton can easily be seen.

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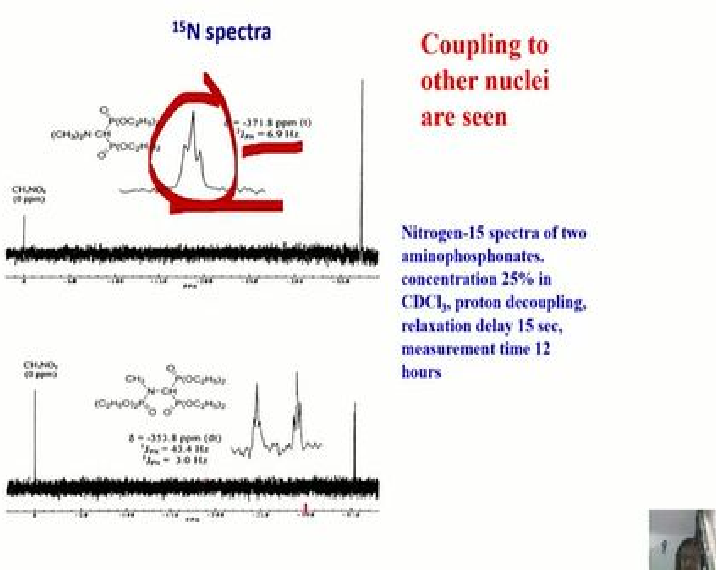

^{15}N spectra

Coupling to other nuclei are seen

Nitrogen-15 spectra of two aminophosphonates. concentration 25% in $CDCl_3$, proton decoupling, relaxation delay 15 sec, measurement time 12 hours

Let us go to nitrogen 15 spectra something difficult to observe you know. You can see nitrogen 15 NMR here; and you can see coupling to other things, generally it is very weak peak. This is the nitrogen spectra of amino-phosphates very, very weak; because nitrogen has very low abundance, so you need to acquire more scans; and of course majority of these problems have been solved now, because you have different types of highly sophisticated, very sensitive probes for detection of an NMR signal, like cryoprobe and etc. Even nitrogen 15 in natural abundance detection is also not difficult. I just wanted to show you the nitrogen 15 natural abundant can also be seen and this nitrogen coupling to other nuclei can also be measured.

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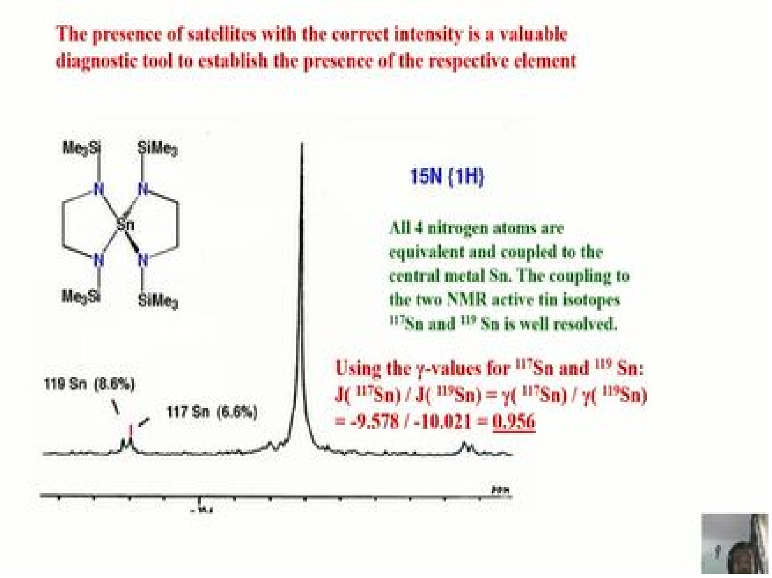

The presence of satellites with the correct intensity is a valuable diagnostic tool to establish the presence of the respective element

15N {1H}

All 4 nitrogen atoms are equivalent and coupled to the central metal Sn. The coupling to the two NMR active tin isotopes ^{117}Sn and ^{119} Sn is well resolved.

Using the γ-values for ^{117}Sn and ^{119} Sn:
$J(^{117}\mathrm{Sn}) / J(^{119}\mathrm{Sn}) = \gamma(^{117}\mathrm{Sn}) / \gamma(^{119}\mathrm{Sn})$
$= -9.578 / -10.021 = \underline{0.956}$

And, especially in this case this is a fantastic example, there are 4 nitrogens attached to tin here, 4 nitrogen are attached; all 4 are equivalent; and then if we do nitrogen 15 NMR, proton with decoupling, 4 nitrogen are there, all are equal, so hene it is much better no problem. But you see 2 short lines here, what are these lines? They are satellites; but not carbon 13 satellites like this; they are satellites of Tin.

Tin has two isotopes, of course in principle there are 3 isotopes; we will ignore 115tin. 117tin and 119tin; there are two isotopes. Each of them can couple to nitrogen, when nitrogen-15 itself is a diluted spin, very low abundant 0.37. But when you are observing that we will not worry about, but with respect to this, this is a low abundance spin. These appear as satellites. Look at this, when you are detecting nitrogen, 2 peaks are appearing here, which are satellites; one corresponds to 119Tin- nitrogen coupling, other is tin 117- nitrogen coupling.

So that is the important thing. Now by using the ratio of these peaks, one can find out the presence of percentage of different isotopes more percent, because intensity is very precise here. If you measured very precisely you can find out the percentage of 119tin and percentage of 117tin. Both are almost equal here.

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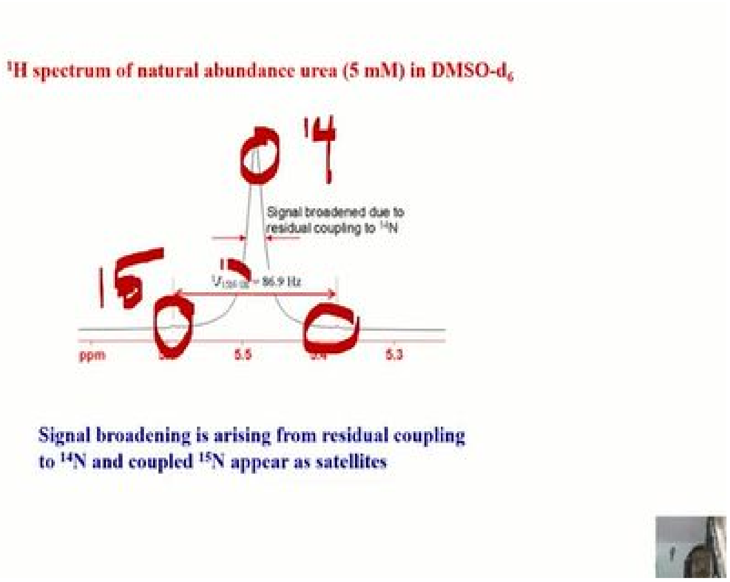

^1H spectrum of natural abundance urea (5 mM) in DMSO-d_6

Signal broadening is arising from residual coupling to ^{14}N and coupled ^{15}N appear as satellites

Now we will see 1H NMR spectrum of natural abundant urea, what is the urea? It is a simple molecules CO(NH2)2, I think. Look at the 1H spectrum of that, this is a very broad peak coming. What is that coming from? Urea contains NH2 group; nitrogen has 2 isotopes; N14 and N15, N14 is a quadrupolar spin, generally it relaxes very fast and gives a very, very broad signal like this. This is because of N14, and you will not be able to see other couplings at all here, so broad.

Whereas nitrogen 15 is low abundant, 0.37%, but still it is spin half nuclei and that gives rise to a doublet. Nitrogen 15-proton coupling you can see in the proton spectrum. NH proton here, this is also NH proton, but this is N15-H proton, This is N14 H proton. The majority of the peaks like carbon 12 attached proton, and the large peak is coming because of 14N attached proton, this is 15N attached proton. So, as a consequence, they are very weak in intensity and nevertheless measurement of the separation gives you proton-nitrogen 15, J coupling. That information is easily obtainable.

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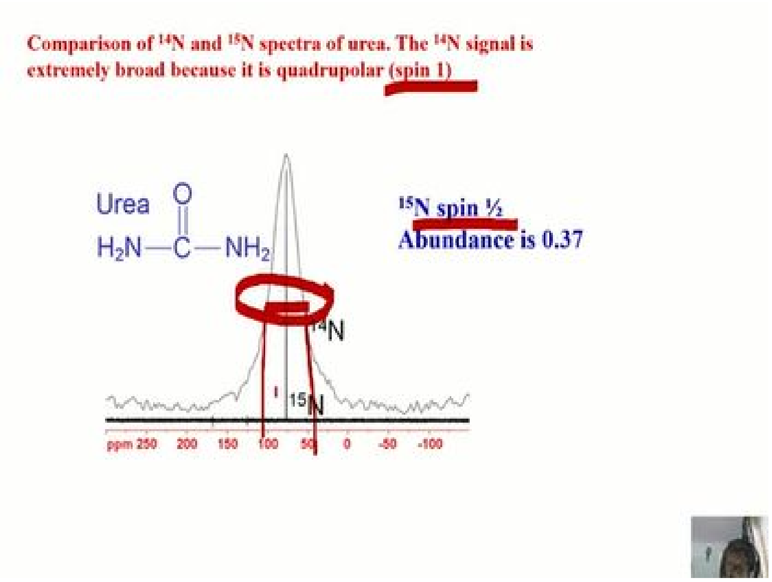

Comparison of ^{14}N and ^{15}N spectra of urea. The ^{14}N signal is extremely broad because it is quadrupolar (spin 1)

^{15}N spin ½
Abundance is 0.37

Now we can compare the N14 and N15 spectra. you can also record spectrum of this urea CO(NH2)2. Now, N14 spectrum if you record, it is very broad. Look at the width, it starts from somewhere here, let us say take the mid here to here, you will take half width, peak width approximately 50 ppm, which is a large line width. N14 is really broad because of quadrupolar nature of the spin. It is N14 spin 1, where the central peak is N15.

N15 is spin half, it is a spin-half nuclei, and that is why you are getting a sharp peak. see compare N14 spectra with N15 spectra. The N14 is many, many orders of magnitude broader than N15 spectrum; this happens actually.

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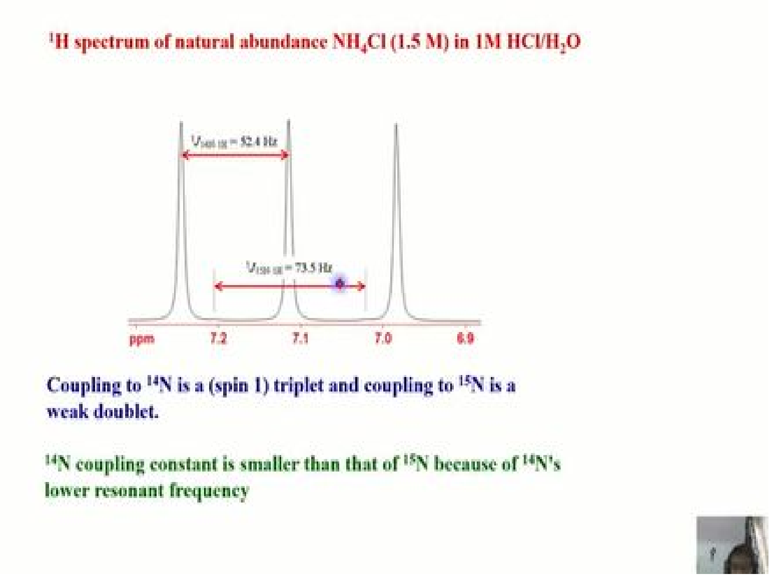
^1H spectrum of natural abundance NH_4Cl (1.5 M) in 1M HCl/H_2O

Coupling to ^{14}N is a (spin 1) triplet and coupling to ^{15}N is a weak doublet.

^{14}N coupling constant is smaller than that of ^{15}N because of ^{14}N's lower resonant frequency

So, if I look for the proton spectrum of NH4Cl again, you see N14 can couple to H4 proton, and give rise to 3 lines of equal intensity like similar to deuterium coupled to carbon in CDCl3 you know. Similarly, now N14 is coupled to proton you get 3 lines of equal intensity. N15 coupled to this and you get small peaks of low intensity, that is for 15N proton J coupling, all these things are very easy.

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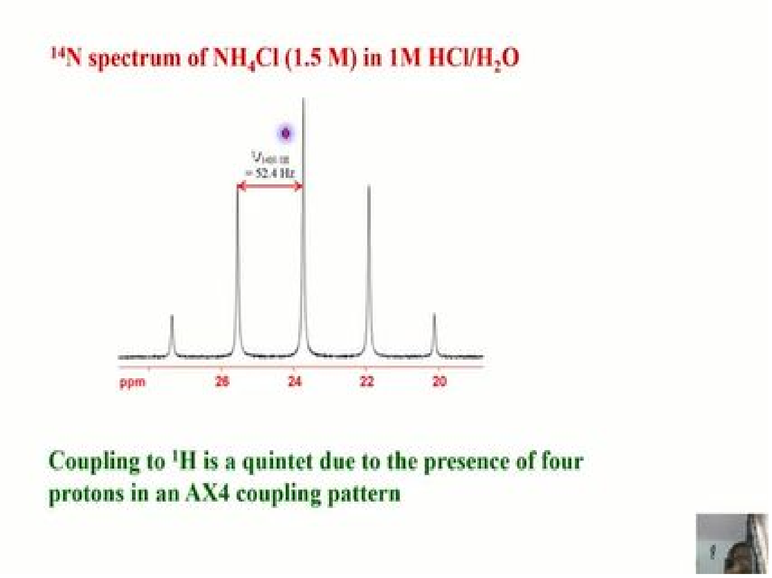
^{14}N spectrum of NH_4Cl (1.5 M) in 1M HCl/H_2O

Coupling to ^1H is a quintet due to the presence of four protons in an AX4 coupling pattern

Now, N14 spectrum of NH4Cl it is something very interesting, N14 spectrum; if you look at this 14N is coupled to proton, 4 protons as I said earlier, you must get according to Pascal triangle and 2NI+1rule, you get 5 lines, 1, 4, 6, 4, 1, intensity. Very beautiful spectrum, measure this separation you get 14N proton J coupling, you understand? Similarly, we dsicussed this example earlier also.

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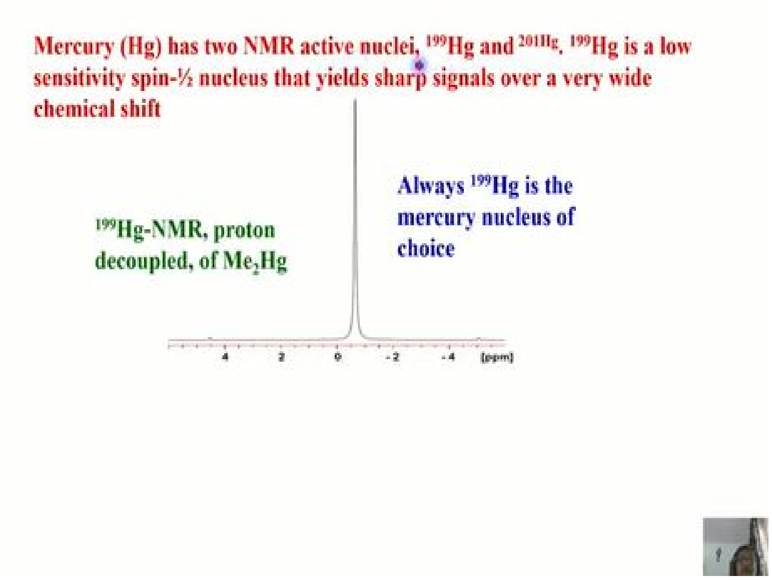

Mercury (Hg) has two NMR active nuclei, ^{199}Hg and ^{201}Hg. ^{199}Hg is a low sensitivity spin-½ nucleus that yields sharp signals over a very wide chemical shift

^{199}Hg-NMR, proton decoupled, of Me$_2$Hg

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

Mercury is another interesting nuclei, it has two isotopes 199 and 201, but most of the time what people use is 199; because 199 is a spin half nuclei and 201 is quardrupolar spin that normally not studied. So the most favorite nuclei for all of us if you are studying mercury is mercury199.

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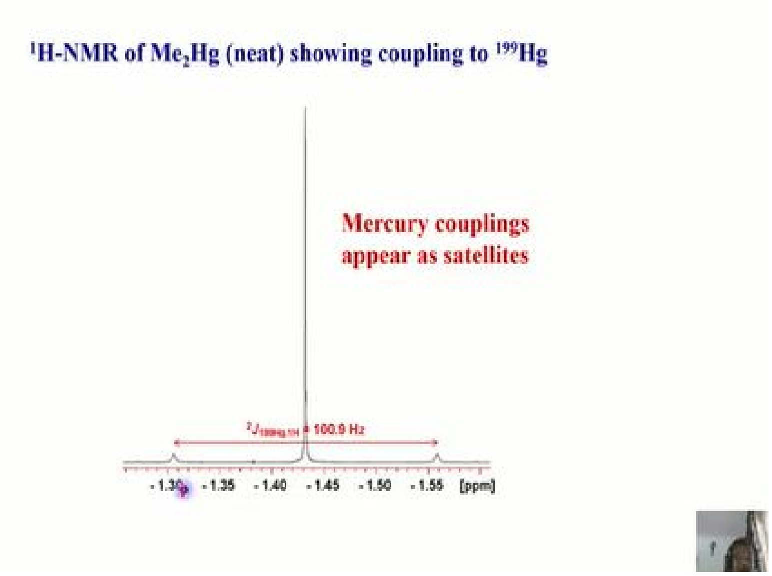

^{1}H-NMR of Me$_2$Hg (neat) showing coupling to ^{199}Hg

Mercury couplings appear as satellites

So, now it is a proton NMR spectrum of dimethyl mercury is taken, neat sample, it is dissolved in any solvent, mercury 199 in spectrum, you see, you get a sharp protons spectrum, you get a sharp proton peak, because of methyl protons are equivalent. But mercury is there, that is coupled here and you see the mercury has very small abundance and as it is appearing as a satellites here. This gives you mercury to proton coupling, you understand? This gives mercury to proton coupling as satellites.

I am just giving an example of simple molecule, 2 methyls are equivalent, proton spectrum gives a single peak and coupling to it is only mercury, whose abundance is small, and gives satellites.

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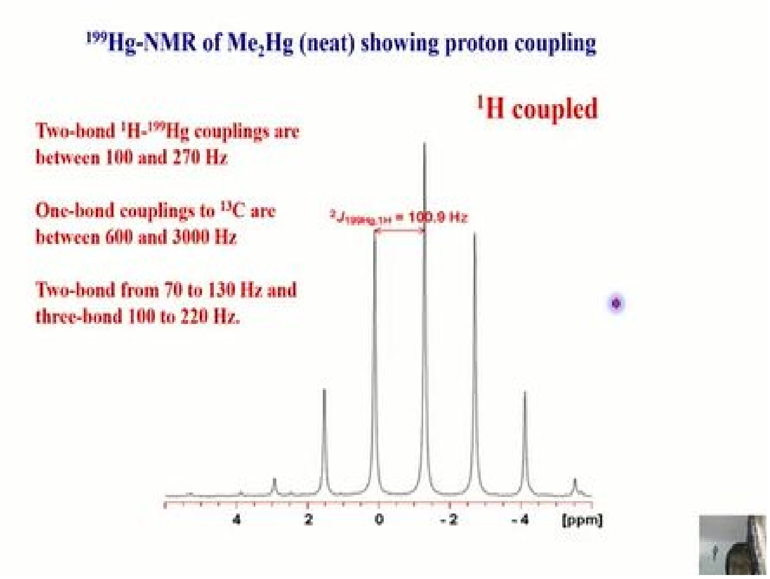

^{199}Hg-NMR of Me_2Hg (neat) showing proton coupling

^{1}H coupled

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.

Now, instead of satellite observation, I can do an Hg NMR also. If I do mercury NMR, when protons are coupled, you are going to get 1, 2, 3, 4, 5, this many peaks; why? Remember, it is coupled to 2 methyls, each methyl is going to split this into it quartet. One methyl will splits this into one quartet, each line of the quartet is split into another quartet because of another methyl, as a consequence you are going to get 1, 3, 4, 1, 2, 3, 4, 5, 6, 7 octet, which we worked out earlier, remember this is what the pattern you are going to get.

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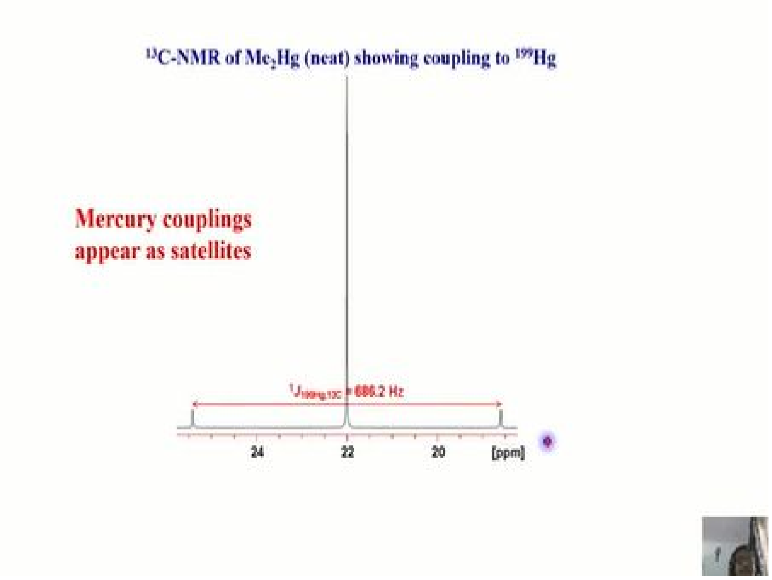

^{13}C-NMR of Me_2Hg (neat) showing coupling to ^{199}Hg

Mercury couplings appear as satellites

And, the same mercury NMR; when you see that you can see mercury 199, if you do the decoupling of proton, you can see carbon satellites now. Another interesting thing, look at this one; here mercury NMR, proton coupled; here we decouple protons, no proton coupling, so in principle it must be singlet, but there is a CH3 group attached to it, it gives rise to carbon satellites, carbon to mercury coupling is seen.

So beautiful, simple molecule you can see proton NMR, you can see carbon, you can see mercury in a proton NMR or in mercury NMR you see, carbon satellites, in the proton NMR you can see a mercury satellites. All possible things can be measure to get information. Very beautiful thing. On the other hand we can do carbon 13 NMR also, if you do carbon 13 NMR what is going to happen? again proton decoupled, there is no splitting, you get mercury satellites.

Completely we are decoupling proton, carbon is only coupled to methyl now, this is the single peak of carbon, and these two are mercury satellites.

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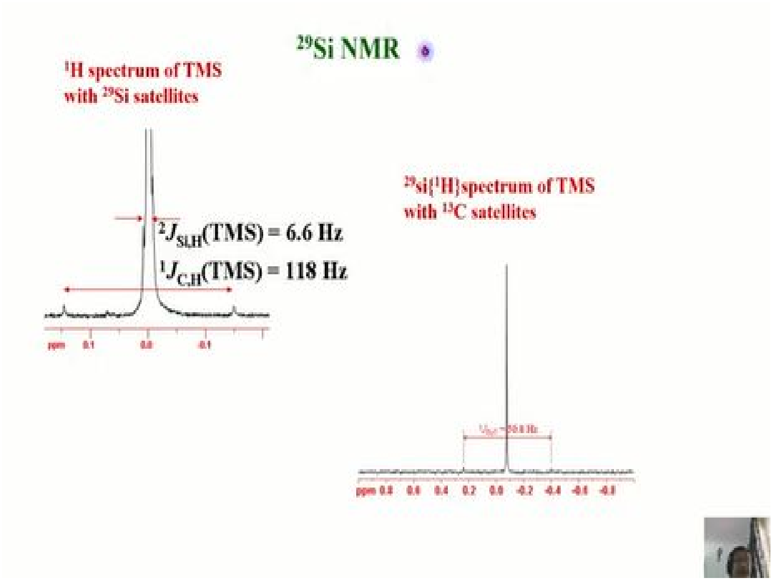

^{29}Si NMR

^{1}H spectrum of TMS
with ^{29}Si satellites

$^{2}J_{Si,H}$(TMS) = 6.6 Hz
$^{1}J_{C,H}$(TMS) = 118 Hz

^{29}Si{^{1}H}spectrum of TMS
with ^{13}C satellites

So silicon NMR of course tetramethylsilane I showed you once, this is the proton signal, these two are carbon 13 satellites, and these two are silicon satellites. On the other hand I can see silicon NMR with proton decoupling, then I get carbon satellites very interesting right? In TMS, the tetramethylsilane I can see silicon NMR, it is also possible. In this case of proton NMR, we get silicon satellites and carbon satellites, In silicon NMR with proton decoupling we see carbon satellites.

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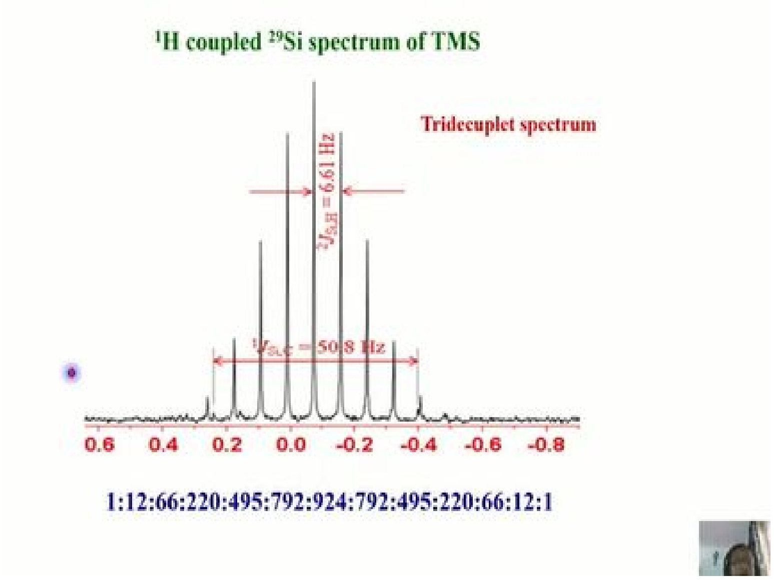

^{1}H coupled ^{29}Si spectrum of TMS

Tridecuplet spectrum

$^{2}J_{Si,H}$ = 6.61 Hz

$^{1}J_{Si,C}$ = 50.8 Hz

1:12:66:220:495:792:924:792:495:220:66:12:1

Very interesting things, on the other and I can see proton coupled silicon NMR, how many peaks I should expect? There are 12 protons all are equivalent; remember, apply 2NI+1rule you should get 13 peaks, it is called tridecuplet spectrum, tridecuplet means 13 peaks spectrum. In principle you count here there are 13 peaks, here is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, so may be 2 peaks are hidden somewhere here because of lower intensity.

And according Pascal triangle you can get intensity pattern, huge, you can work out, you understand? So, I am just quickly going through lots of nuclei many, many spectra can be analyzed, basically what you need is a foundation for analysis of the proton spectrum and carbon spectrum, how they are coupled. And another thing is when dilute spins are coupled, weak abundant spins, I told you it gives rise to satellites and you should know how to analyze the satellite spectrum.

The classical example is dimethyl mercury; in that you can see mercury spectrum with proton decoupling will get carbon 13 satellites, you can see carbon NMR with proton decoupling get mercury satellites, you observe mercury NMR you can get proton couplings. All possibilities you can see. So, this is a beauty of NMR when you want to do multinuclear NMR varieties of possibilities you can think of, varieties of experiments you can do and get lot of information.

So with this I think I am going to stop multinuclear NMR. In the next class we will start going to different topics. So analysis part of NMR of proton, carbon, multinuclear, multiplet analysis, all detailed information is given. Now we should start going to more advanced topic from next class.