One and Two Dimensional NMR Spectroscopy for Chemist

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Lecture No: 42
Coupling among magnetic equivalent nuclei and isotope effect

Welcome back. In the last class we discussed several heteronuclear interactions and we did even analyze a couple of heteronuclear spectra like fluorine spectra, carbon spectra, varieties of things. I also gave an idea about the coupling strengths of heteronuclei involved, how to analyze this spectrum, varieties of information was given to you.

Today what I am going to do is, I will continue with this heteronuclear interactions. Introduce some interesting things which you can come across in the NMR; like how when heteronuclear is there, how it can affect your NMR spectrum from isotopic shifts, isotopic effects in the NMR spectrum, and then we will analyze couple of spectra of different nuclei. With that then you can go to a different topic.

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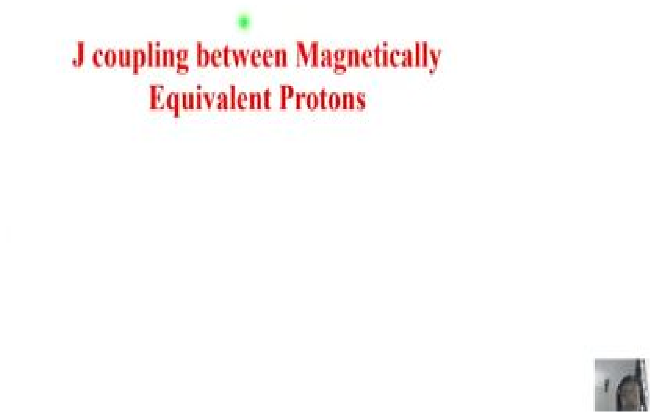

J coupling between Magnetically Equivalent Protons

Now one important thing we should know is the J coupling between equivalent spins, that is what we should know.

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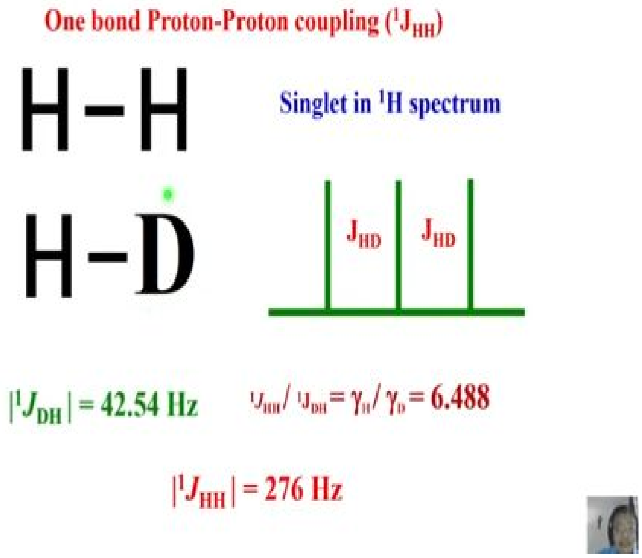

One bond Proton-Proton coupling ($^1J_{HH}$)

H–H Singlet in ^1H spectrum

H–D

$|^1J_{DH}| = 42.54$ Hz $\quad {}^1J_{HH} / {}^1J_{DH} = \gamma_H / \gamma_D = 6.488$

$|^1J_{HH}| = 276$ Hz

For example consider proton-proton 1JHH, that is I said, is in the molecule hydrogen. There are two protons joined by a single bond. I mean, two hydrogen atoms joined by single bond. Now if I take the NMR spectrum of that we get a single peak. Now the question is how do I get the J coupling information? Remember, I gave an example, by doing satellite analysis in the case where proton NMR will not give me the coupling information among equivalent spins.

For example in the cis and trans of di substituted ethylenes and others we saw, symmetrical disubstituted, the protons are chemically equivalent gave a single peak. However we looked at the carbon 13 also, included carbon-13 also into the molecule at the natural abundance, when that was brought into the picture, we broke the symmetry molecule. Automatically symmetry gets broken; instead of A2 spin system, it becomes AA'X spin system.

As a consequence, we are going to get if I have a single proton peak coming because of carbon 12 attached protons, there are satellites on either side, comes because of carbon-13 isotopomer of the molecule. This we saw. Especially in the molecules which we discussed in the last class where cis, trans protons have chemical equivalence; whose coupling was not showing in the proton spectrum. We saw that in the satellites because it became AA'X.

And we could get AX coupling; A'X coupling everything. So we were able to get proton- proton coupling information from the satellite analysis. So homonuclear coupling which is not reflected in the proton spectrum, in the 1 dimensional proton spectrum, we could extract them in one way. Now I am posing a question like this; it is a hydrogen molecule, here where is the question of carbon. I cannot break the symmetry like in the previous example, by bringing carbon-13.

Now, both are protons, what do I do? I have to break the symmetry to get the HH coupling? So one thing is of course to retain the molecule as such, the nature of molecule. Best thing is why cannot we substitute proton, one of the protons by a deuterium? Now what is going to happen in the NMR spectrum? This HH coupling is not reflected in the spectrum, ie. Proton-proton coupling. But what about HD coupling? Remember deuterium is spin one nucleus, this is spin half nucleus. Now I am observing proton. What will happen to the proton peak? Remember we discussed in CDCl3, spin half nucleus coupled to spin one nucleus; what is going to happen? then this proton will split into three peaks, three lines or three peaks of equal intensity 1:1 : 1, because deuterium spin one, has three energy states minus 1, 0, +1, you understand? As a consequence we are going to see 3 peaks in the proton spectrum because of H-D coupling. Sure we are going to get three 3 peaks like that. What do the separation of peaks gives me?

If I measure the separation from this peak to this peak; any two adjacent peaks, if I take, I am going to get JHD, J coupling between proton and deuterium. So how does it solve my problem? Remember, in the carbon 13 satellites when you were analyzing, you were directly getting JHH from teh satellite analysis, but we analyze this and we get JHD. So how does it solve my problem? There is a formula; there is a way you can get, when the isotope substitution is there in a molecule like this. When I know HD coupling, HD scalar coupling because deuterium is isotope of hydrogen, there is a simple formula. If I know the gyromagnetic ratio of this, the gyromagnetic ratio of this; then I can get the J coupling between proton and proton, If I know this or if I know this, I can get this, very easy. Because that is going to by a simple expression for 1JHH; because we are looking at 1JHH here divided by1JHD is equal to gamma HH or gamma HD.

What is gamma HH? We know that; it is 26.75 into 10 to the power of 7 radians per Tesla per second; that we should not forget. Remember I told you also, the gamma of deuterium is 6.42 times smaller, when I was explaining to you the table of NMR active nuclei with their properties

In the first or second class, in one of the classes, I discussed this and told you gamma of deuterium is 6.425, whatever it is. You can get the approximate value or the exact value from the one of the good books. So the gamma of this is different from proton by this amount; this is smaller by this amount. So, according to this formula if I know the ratio of JHH to that of JHD. This is proportional to; or equal to gamma H divided by gamma HD. So what do I know here?

I don't know JHH, I want to find JHH. I know this JHD, I measured from the spectrum. I know gamma of proton. I know gamma of deuterium, which is, this many times smaller than gamma of proton. Simply plug in the values for gamma plug in the value of measured JHD; what you are going to get is JHH. Very easy right? In equivalent spin systems you can do that.

Of course, you can do the same thing in the previous molecule what I showed you. The three bond HH coupling in cis and trans substituted ethylenes we saw that you know. In such cases also you can do that. You can get HH coupling by making deuterium substitution. But there is one small difficulty there. What is the difficulty? Remember 1 bond JHD itself is so small, of the order of 6.4 times as 6.45 times. Smaller than that of proton if I go for 3 bond, It may be negligibly small; sometimes you will not be able to measure it also. This coupling will be hidden within the line separation of 3 bond 4 bond HD coupling; and you will not be able to see, because of low gamma of these things 6.45 times lower than that of proton. So that is why that was not a practical situation, there. So what we did was, we looked at the carbon 13 satellites.

In proton NMR we get carbon 13 satellites because proton is coupled to carbon-13. Of course, in the proton spectrum satellites are called carbon 13 satellites, because they are coupled to carbon 13. So we brought in carbon 13 in natural abundance for the molecule to break the symmetry; that was feasible in that molecule, but in this molecule there is no carbon 13 at all, first thing. So we have to use a different method and this is the procedure which is adapted; by changing the proton to deuterium and measure the HD coupling and obtain JHH by using this formula.

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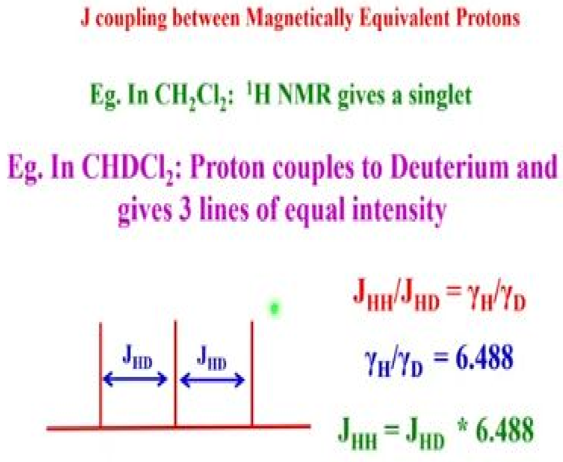

J coupling between Magnetically Equivalent Protons

Eg. In CH_2Cl_2: ^1H NMR gives a singlet

Eg. In $CHDCl_2$: Proton couples to Deuterium and gives 3 lines of equal intensity

$J_{HH}/J_{HD} = \gamma_H/\gamma_D$

$\gamma_H/\gamma_D = 6.488$

$J_{HH} = J_{HD} * 6.488$

So now we will see how to get the J coupling between magnetically equivalent nuclei, in other example like this. This is CH2Cl2. What I can do is; of course, I can bring in carbon 13 here. Look for the carbon 13 NMR, that I am going to see because it is coupled to two protons carbon 13 has to be triplet. What does it give me JCH? but, does it give me JHH, no it does not give me JHH again.

So in this case, I cannot use carbon 13 also. I cannot even break the symmetry or how do I break the symmetry here; I change the proto into deuterium, both of them or one of them. Then you get 2 bond JD, one bond CH coupling you will get, and one bond CD coupling you will get; and two bond HD coupling you are going to get if you break the symmetry; and it will be much smaller.

So one of the possibilities in this case, getting into instead of carbon 13, why cannot I deuterate one of the protons? You get, when you deuterate that, you get CHDCl2. This is another way, so I can see when I can see this CHDCl2; protons coupled to deuterium will be these 3 lines of equal intensity. I got 3 lines of equal intensity. What did I get? JHD here. Simply plug in the values what I gave you, now I got this, I will get this value.

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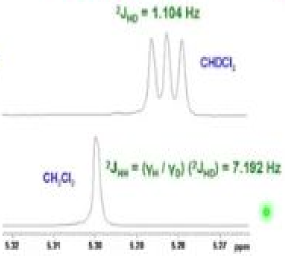
^{1}H NMR spectrum of $CHDCl_2$

$^{2}J_{HH}$ in CH_2Cl_2

$^{2}J_{HD}$ = 1.1 Hz



$^{2}J_{HH}$ = 1.1 * 6.488 Hz

$^{2}J_{HH}$ = 7.14 Hz

And literally this CHDCl2 molecule, the real NMR spectrum when it is recorded, you see two bond HD, it is very small, 1.1 Hertz. Now if you want to go to 3 bond, how do you measure three bond HD? that is why in such molecules it was not practically feasible. So it is 1.1 hertz does not matter it is 1 bond coupling, 2 bond coupling, 3 bond coupling, but this formula is valid. Now plug it into this formula and you are going to get JHH of 7.1 hertz; just plug it in these parameters.

So we know in systems where we have magnetical equivalence, we will be able to get HH coupling; which is invisible in the proton spectru; by using either carbon 13 satellites or making isotopic substitution, and we see the HD coupling and from that we can get HH coupling.

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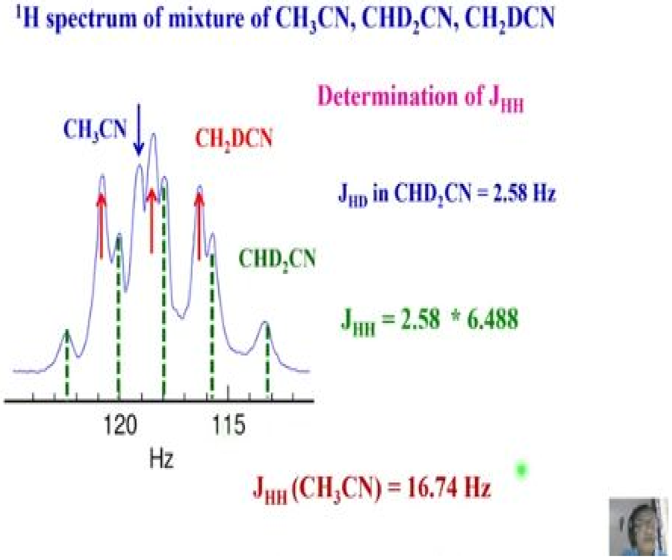

^{1}H spectrum of mixture of CH$_3$CN, CHD$_2$CN, CH$_2$DCN

Determination of J_{HH}

J_{HD} in CHD$_2$CN = 2.58 Hz

J_{HH} = 2.58 * 6.488

J_{HH} (CH$_3$CN) = 16.74 Hz

These all well known, now let me take the example of other one. I took CH3CN, of course, no problem at all we get a single peak. But I want to get the J coupling in that, what do I do? there are two or three possibilities for me. I can think of various options. Can I use carbon 13 here? why not? In the proton itself look for the carbon 13 satellites see whether you can break the symmetry; see whether you can measure the J coupling using the satellites.

Or look for the carbon 13 spectrum you get only CH coupling. Sometimes it is always advantages to have isotropic substitution, very simple sometimes. Look at this molecule CH3CN, I can make it CHD2CN or I can make CH2DCN, what did I do here? Removed one of the protons and put D here, in this case removed 2 protons and put D2 here. Now we have 3 different isotopomers; three different molecules. Now take the proton spectrum of this; and this is a CH3CN a single peak.

It has to give a single peak. Now if I take CH2DCN how many peaks I expect/. So when this deuterium is coupled to proton, CH2DCN does not matter whether it is CH3 or CH2 or H3 does not matter to single deuterium, so what will happen? We get 3 peaks of equal intensity 1: 1 : 1. Please remember. I said this is coupled to spin one nucleus as a consequence these two protons are split into three lines of equal intensity due to spin one deuterium, fine.

So you can get this; and this is here, you can already see there is an isotope shift because of substitution of deuterium. Next alternatively, why cannot I see this molecule? That is also possible right? That also will couple to this one, and I can get HD coupling here also. Once again HD coupling I can convert to JHH using the formula, do that. If I take the spectrum of that, I took the mixture of all the 3.

Now look at it, you are going to get when two deuterium are coupled to proton, in one of the examples we worked out, it is going to give a pentet with intensity pattern 1, 2, 3, 2, 1. Any how, I will remember I said this. I hope you remember in one of the classes, a couple of classes before, I mentioned to you when spin of nuclei is coupled to 2 equivalent spin 1 nuclei, you get a pentet of this intensity 1, 2, 3, 2, 1. There is a pascal triangle also for this, you can work out. But in fact, I worked out by a family tree approach and showed you how you get 1, 2, 3, 2, 1 intensity, does not matter. You remember we have got it now. So where is the center of this, center of this is here? We CH3CN is there, this is the chemical shift. When I substitute for one deuterium, this is the chemical shift. When I substitute with two deuterium, this is the chemical shift. What is happening? because of heavy atom substitutution, because of isotopic substitution; there is a shift in the chemical shift position. This is what I said isotopic effect. How much it shifts per one deuterium if it is this? two deuterium substitution if it this? if you have 3, 4 like that, it can linearly change like that only.

You can easily find out the shift because of isotopic substitution. Normally it is expressed in parts per billion or sometimes if it is large value parts per million. Now coming back to our J calculation, I can measure JHD here from the spectrum, either this one or this one; any of them you take, and that is the measured value is about 2.6 hertz; multiply with the gamma deuterium, and the coupling what you get for CH3CN, proton-proton coupling is 16.74 Hz. Indirectly we got the JHH between the protons in CH3CN, although in the proton spectrum it gives a single peak.

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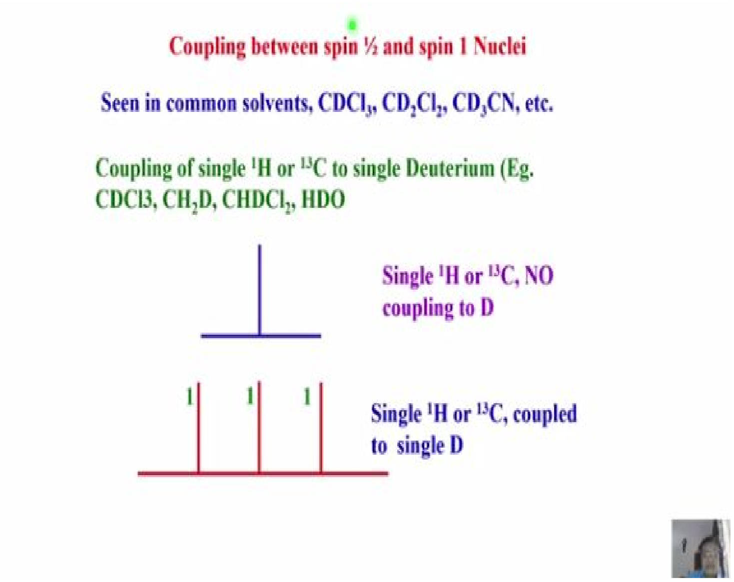

Coupling between spin ½ and spin 1 Nuclei

Seen in common solvents, $CDCl_3$, CD_2Cl_2, CD_3CN, etc.

Coupling of single ^1H or ^{13}C to single Deuterium (Eg. CDCl3, CH_2D, $CHDCl_2$, HDO

Single ^1H or ^{13}C, NO coupling to D

Single ^1H or ^{13}C, coupled to single D

This is a very important point. Now, I will discuss something about what is called isotope effects. Of course just now we discussed isotopic effect, there no point in going for this. CDCl3 is one thing which gives 3 peaks

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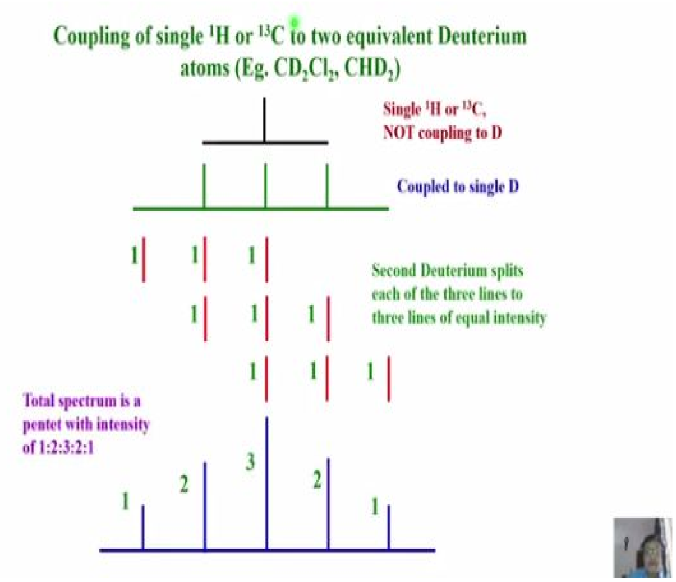

Coupling of single ^1H or ^{13}C to two equivalent Deuterium atoms (Eg. CD_2Cl_2, CHD_2)

Single ^1H or ^{13}C, NOT coupling to D

Coupled to single D

Second Deuterium splits each of the three lines to three lines of equal intensity

Total spectrum is a pentet with intensity of 1:2:3:2:1

I explained already and if you add another deuterium for that I showed you just few before. I repeated, so I am showing you, you get 1, 2, 3, 2,1 and when I have 2 deuterium and 3 deuterium you get peak intensity of 1 3 6 7 6 3 1.

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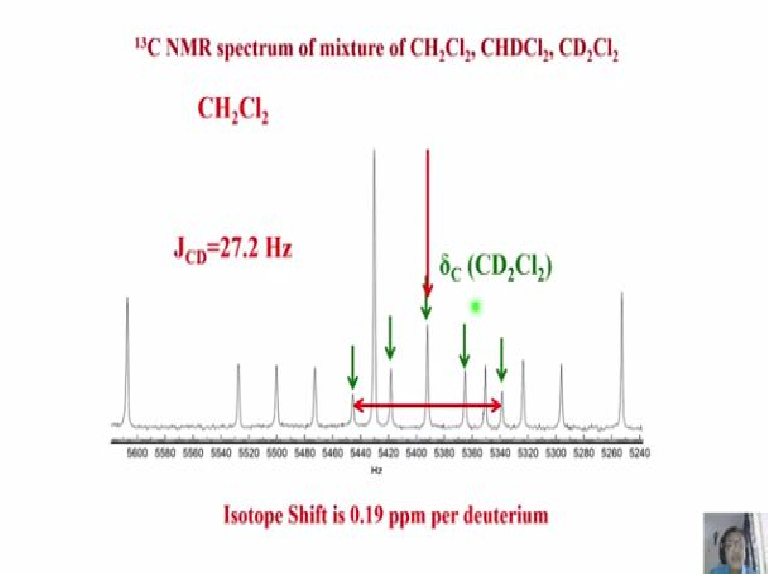

^{13}C NMR spectrum of mixture of CH_2Cl_2, $CHDCl_2$, CD_2Cl_2

Isotope Shift is 0.19 ppm per deuterium

And then we also saw how much is the shift in the peak position? Isotopic shift because of deuterium; this was explained in the morning so I did not remove the slide possibly. So I am repeating, I am quickly going through; this a triplet because of, CH2Cl2. I am looking at carbon 13. This is one JCH, this is a delta of carbon chemical shift. Now this is when 1 deuterium is present. See what is happening is this will be a doublet because of CH. And 1 deuterium makes each of them into 3, 3 lines of equal intensity; each line of the doublet will become 3, 3 lines of equal intensity. If you take the center of this, it is moved by this much. So this is the isotropic shift because of substitution of 1 deuterium. Now if I have 2 deuterium and this is what it is; 1, 2, 3, 2, 1. So now what is the chemical shift here? this one.

You see from here to here, by substitution of 2 deuterium, all this is because of isotopic substitution. Please remember, in many examples the chemical shift will shift when you make isotopic substitution. This is the important point which you must remember. Now isotopic shift is 0.19 ppm for deuterium, one deuterium is here, 2 deuterium, 3 deuterium is here, it keeps on changing. So what does it tell you?

I also told in the morning, by the substitution of a heavy atom, the peak is shifted to the high field. This small concept, you should remember. Just by substitution it shifted to the high field.

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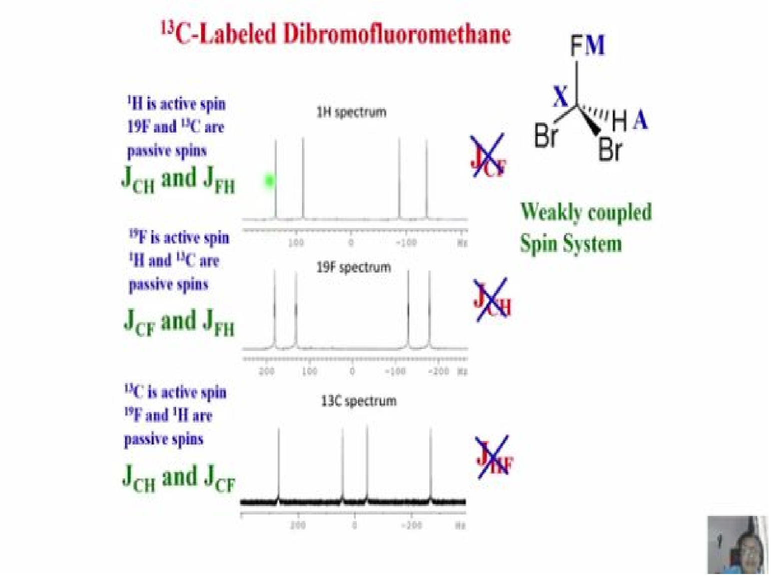

^{13}C-Labeled Dibromofluoromethane

^{1}H is active spin
19F and ^{13}C are passive spins
J_{CH} and J_{FH}

$\cancel{J_{CF}}$

^{19}F is active spin
^{1}H and ^{13}C are passive spins
J_{CF} and J_{FH}

$\cancel{J_{CH}}$

^{13}C is active spin
^{19}F and ^{1}H are passive spins
J_{CH} and J_{CF}

$\cancel{J_{HF}}$

Weakly coupled Spin System

Now I will take another example of very good molecule. While explaining to you active and passive couplings, in one of the classes, I showed this molecule. Where, I said carbon 13 is labeled in which case in this molecule there are 3 heteronuclei A, M and X. I said it is weakly coupled AMX spin system, where I explain to you about active couplings and passive couplings, you know that, you do not forget that.

In the proton spectrum, when I see, it is the active spin; fluorine and carbon 13 are passive spins We get from this spectrum these 2 couplings; and we do not get that. this we have discussed, so I am going quickly. Similarly in the fluorine NMR, fluorine is active, these two are the passive spins and what we are able to get is JCF or JFH and we do not get JCH in this spectrum.

Similarly, in carbon 13 NMR, carbon 13 is active and F, H are passive spins. So you get these things from this analysis, but you want to get this, This is what we said. But one important point. I kept there. I did not explain I was waiting for this time. If I do one thing, I carefully expand one of the peaks of the fluorine. Look at all this spectrum, each peak is very well resolved and gives sharp peaks. This is sharp peak carbon, look at the fluorine there is something here. If you carefully see here, what is that? let us expand and see.

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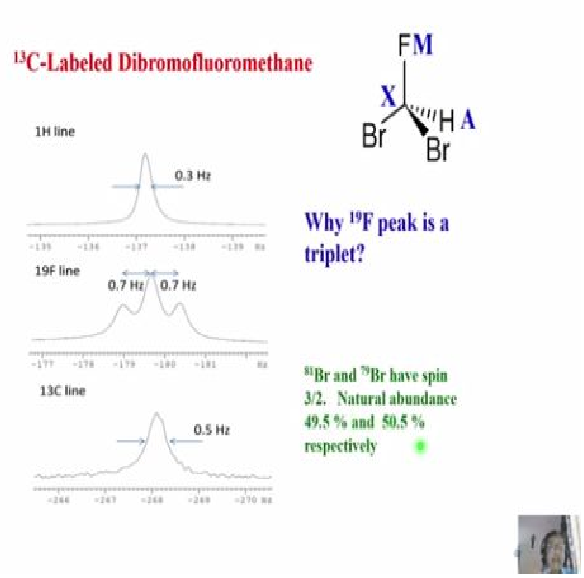

^{13}C-Labeled Dibromofluoromethane

Why ^{19}F peak is a triplet?

^{81}Br and ^{79}Br have spin 3/2. Natural abundance 49.5 % and 50.5 % respectively

If we expand the proton spectrum where the linewidth is quite good 0.3 hertz, that is small value, whereas carbon 13 is 0.5 hertz, but it is not a artifact or inhomogeneity it is there you see. Each peak is behaving like that, we cannot ignore that, you understand why? Why it is happening? why fluorine is a triplet? What makes fluorine a triplet in this molecule? Of course, do not tell me there are two bromines that have become a triplet. Ofcourse, bromine will not couple and also it is a quadrupolar spin.

So what makes it triplet? In the 1D NMR we saw which is active spin and which is passive spin. We know what are the types of spectra we are going to get? But still it is a triplet, and it is a genuine spectrum, nothing is wrong in that. How do you analyze that? What we do is, the clue is bromine has isotopes; bromine 81 and bromine 79 and both have spin 3 /2. Bromine has 81 and 79; and both have spin 3/2.

Interestingly the natural abundance of both of them are 49.5 and 50.5. So almost 50-50 we can say, do not worry about 0.5% both of them are equally abundant. 50-50. Very interesting. Bromine two isotopes, both are spin 3/2 and both are equally abundant more or less.

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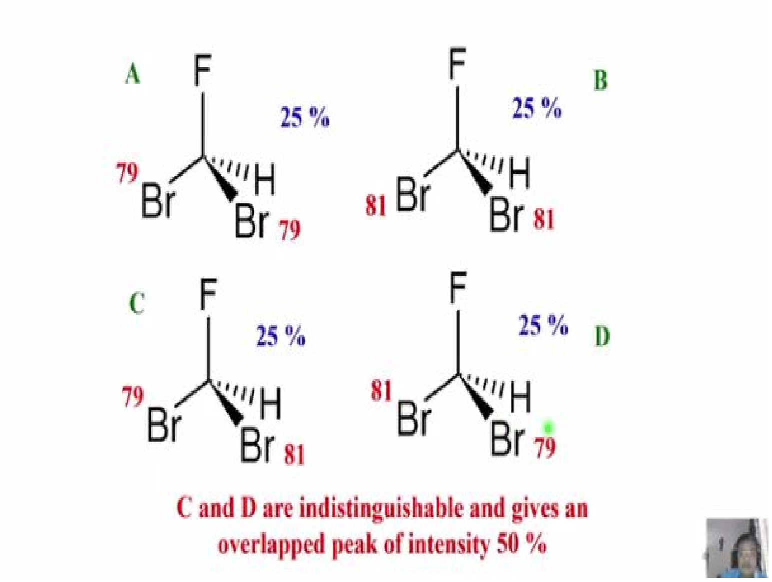

C and D are indistinguishable and gives an overlapped peak of intensity 50 %

Now, let us look at what are the possible isotopomers you can think of in this molecule. First situation, both the bromines can be 79; it can exist as bromine 79, there is one possibility. There is another possibility, both the bromines can exist as bromine 81, correct, that is also possible. Think of another possibility; this bromine exists as 79, and this bromine exist as 81. Is there any other possibility? of course one more possibility this bromine can be 81 and this bromine can be 79; and these two are indistinguishable; you cannot distinguish, there are two possibilities here. So how many isotopomers are there? in this molecule. Four different isotopomers, and what is the possible probability of each of them? Because of equal abundance, if there are 100 molecules this is 25% is 25% this is 25% and this is 25%.

All are equally probable, now if you carefully; see C and D are indistinguishable, that is whether bromine 79 is here are 79 is here, whether bromine 81 is here or 81 here; does not matter because they are indistinguishable of isotopomers. So if you look at the fluorine spectrum, So now before going let me complete this, because of that what you are seeing is 4 peaks corresponding to four different isotopomers.

This fluorine spectrum gives one fluorine peak for this; one for this isotopomer; one for this and one for this isotopomer. But as I said these two isotopomers have equal probability, and they are indistinguishable and these two peaks overlap. As a consequence, in your fluorine spectrum, it appears like a triplet 1, 2, 1 intensity, but in reality it is not, 1 :2: 1 intensity; it is 1,1,1,1 intensity of four isotopomers.

Each isotopomer gives a single fluorine peak. Each peak should be singlet, but because of isotopomers it becomes 4 peaks, 4 isotopomers. These 2 being indistinguishable, they overlap and appear like a triplet, that is the reason why you got a triplet, you understand the logic? How a small change in the isotopic substitution the, bromine is 81 here, becomes 79 here, the small change in the atomic weight, already spectrum is slightly different. See this is the beauty of NMR, that is what I said the beginning itself.

The beauty of NMR is, you study even the microscopic perturbation at the site of the nucleus. So we can understand what is happening at the site of the nucleus just by microscopic change in the electronic charge distribution, and that gets reflected in the spectrum, that is what I wanted tell how I isotopic effect is affecting.

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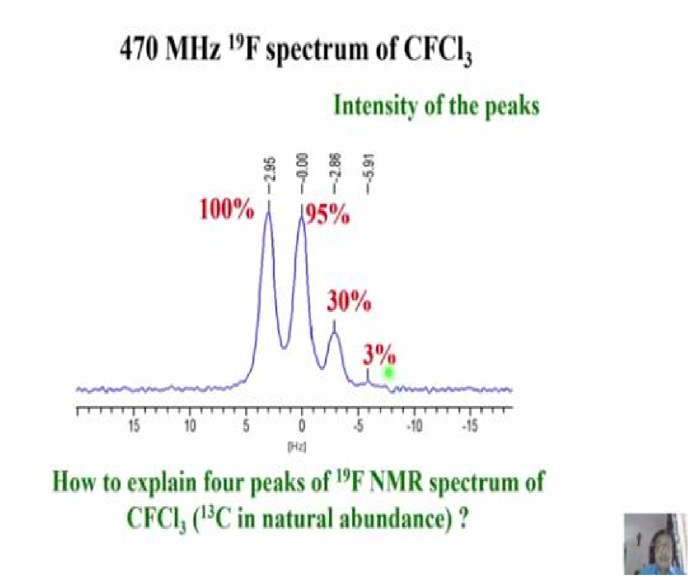

470 MHz ^{19}F spectrum of $CFCl_3$

Intensity of the peaks

How to explain four peaks of ^{19}F NMR spectrum of $CFCl_3$ (^{13}C in natural abundance) ?

Now next this molecule, this we already discussed, I said there are 4 possible peaks we get for the CFCl3. 100%, 95%, 30%, 3% of intensity.

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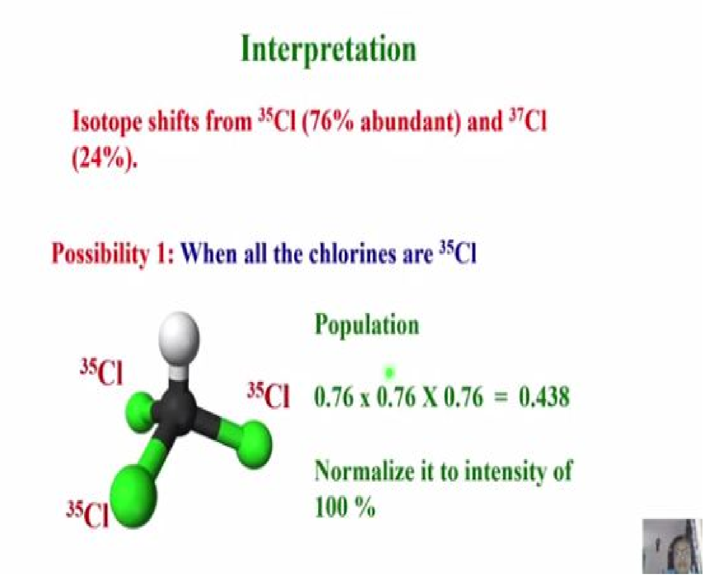

Interpretation

Isotope shifts from ^{35}Cl (76% abundant) and ^{37}Cl (24%).

Possibility 1: When all the chlorines are ^{35}Cl

Population

$0.76 \times 0.76 \times 0.76 = 0.438$

Normalize it to intensity of 100 %

Now how to understand this? I explained this to you. There is a possibility of all the chlorine could be 35 with 76% abundance and I worked out and showed you this is the intensity and normalized to 100%

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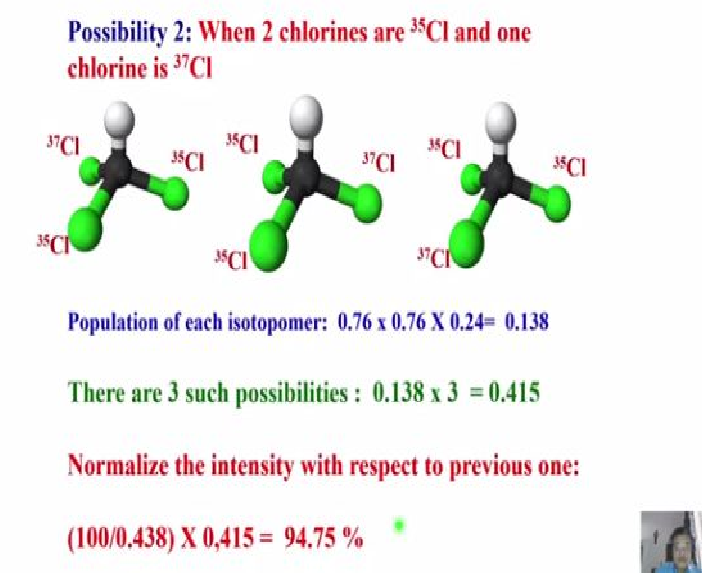

Possibility 2: When 2 chlorines are ^{35}Cl and one chlorine is ^{37}Cl

Population of each isotopomer: $0.76 \times 0.76 \times 0.24 = 0.138$

There are 3 such possibilities : $0.138 \times 3 = 0.415$

Normalize the intensity with respect to previous one:

$(100/0.438) \times 0,415 = 94.75$ %

And next possibilities, 2 chlorine are 35 and one chlorine with 37; this and this are 35, this and this is 35, this and this is 35. 3 such possibilities and I showed you this is the intensity you are going to get when the intensity is normalized with the first molecule.

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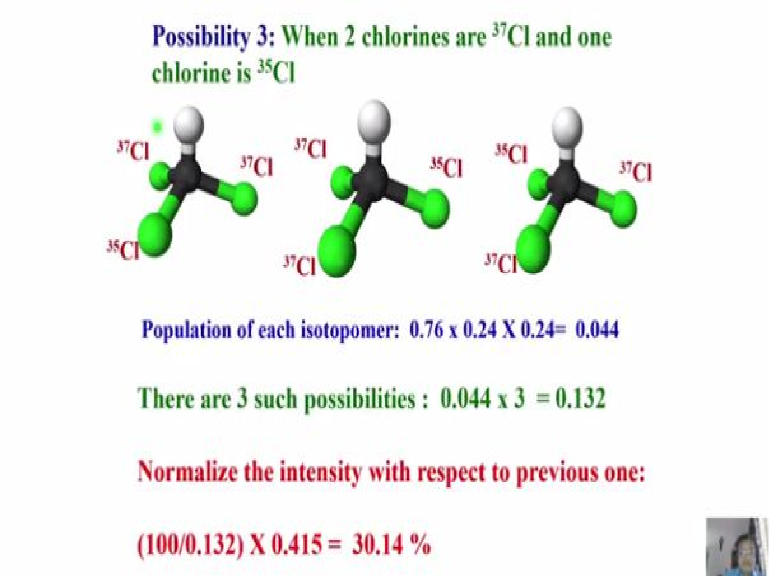

Possibility 3: When 2 chlorines are ^{37}Cl and one chlorine is ^{35}Cl

Population of each isotopomer: 0.76 x 0.24 X 0.24= 0.044

There are 3 such possibilities : 0.044 x 3 = 0.132

Normalize the intensity with respect to previous one:

(100/0.132) X 0.415 = 30.14 %

Same way we saw for the molecules with 2 chlorines are 37 and one is 35, this I do not want to repeat, this is already talked in one of the classes before.

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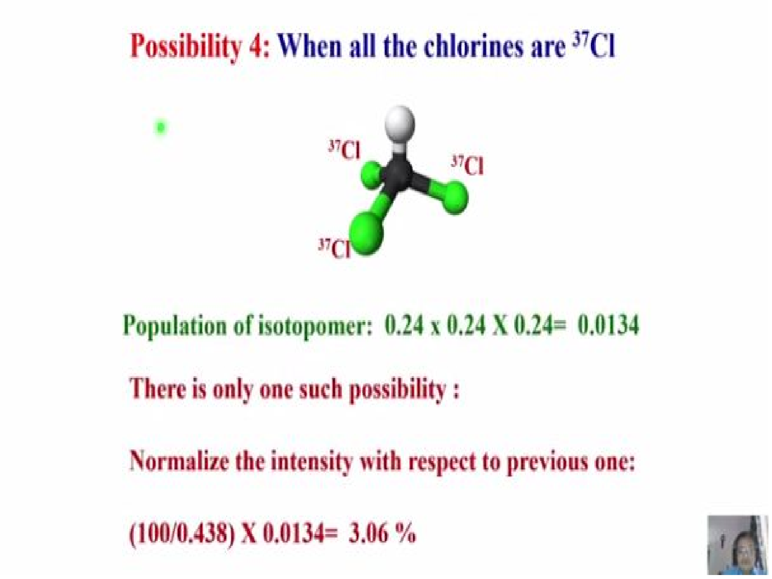

Possibility 4: When all the chlorines are ^{37}Cl

Population of isotopomer: 0.24 x 0.24 X 0.24= 0.0134

There is only one such possibility :

Normalize the intensity with respect to previous one:

(100/0.438) X 0.0134= 3.06 %

And we also saw the probability for chlorine all 37 and we have found out the intensities 3%.

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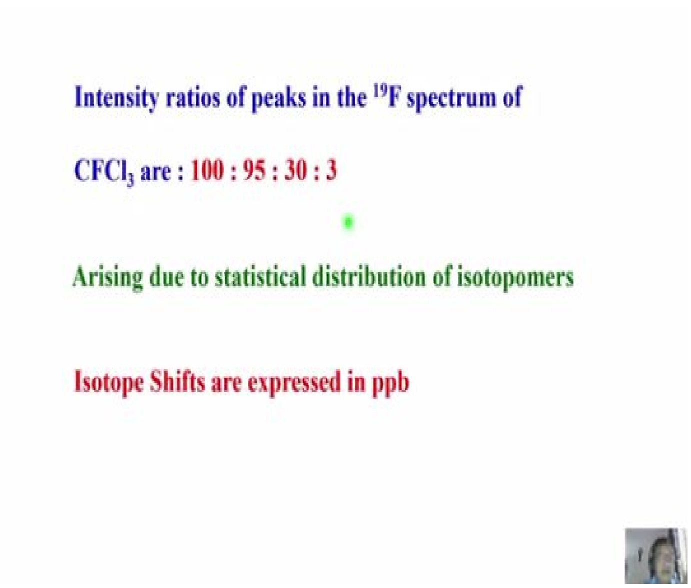

Intensity ratios of peaks in the ^{19}F spectrum of

$CFCl_3$ are : 100 : 95 : 30 : 3

Arising due to statistical distribution of isotopomers

Isotope Shifts are expressed in ppb

As a consequence, we knew the intensity ratio of the peaks in CFCl3 are 100, 95, 30, 3 and I remember when we understood a single spin system giving multiple peaks we discussed this isotopic effect. I did not say the isotopic effect explicitly there, but now it is of course. I think I mentioned but in any case I am explaining to you now we calculated intensity everything.

We worked out the intensity pattern you also discussed why you are getting different types of isotopomers finally the intensity is because of statistical distribution of isotopomers and that is what happens. But remember another interesting point. I want to tell you is there is a shift in the peak position as an effect of substitution of different chlorines, so this is all chlorine 35; this two 35 one 37; this is one 35 two 37; this is all 37 so in this case what is happening?

The shift to the high field is for the chlorine which is 37. Same thing we observed earlier also, In the isotopic substitution when you think heavier atom is substituted, it shifts to the high field; that is what we observed in the earlier example also. But this is isotopic effect; moment you make a substitution or another isotope is present, the probability of distribution of populations are there, then you get multiple peaks. And you have to carefully analyse them.

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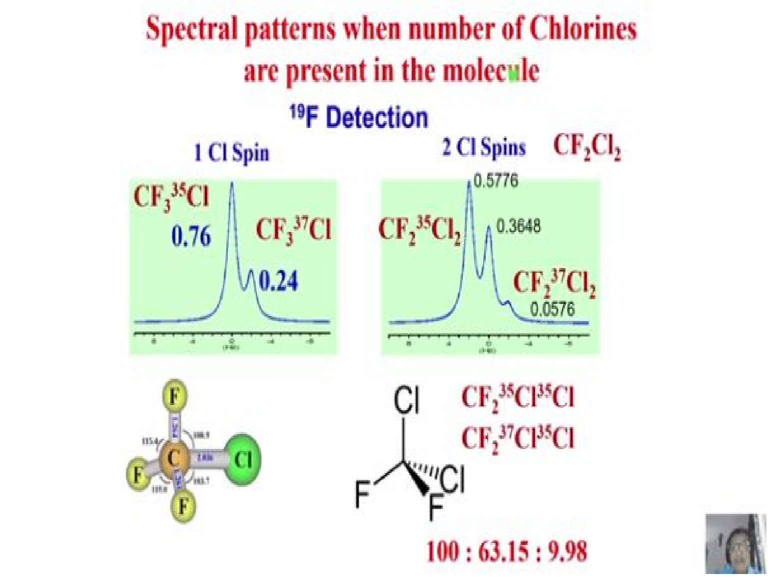

Spectral patterns when number of Chlorines are present in the molecule

^{19}F Detection

$CF_2{}^{35}Cl^{35}Cl$

$CF_2{}^{37}Cl^{35}Cl$

100 : 63.15 : 9.98

Now you can work out varieties of patterns like this, instead of CFCL3; what happens if it is CF2Cl2; if it is CF3Cl; work out, I gave an example for CFCl3. The same way if I ask you, I give you a molecule CF2Cl2. Chlorine , I tell you has 76%, 24% abundance, work out for all different isotopes of chlorine, calculate all the intensity of the peaks, number of peaks that are possible, you can work out, take the possibility in the CF2Cl2.

First all are 35; in this case all are 37; in this case one 37 and other is 35; so all these things you find out the ratio of the populations you will get intensities easily. Now you do not have to worry about what the intensity you get experimentally, you can theoretically calculate, simply by looking at population distributions, how statistically they are distributed.

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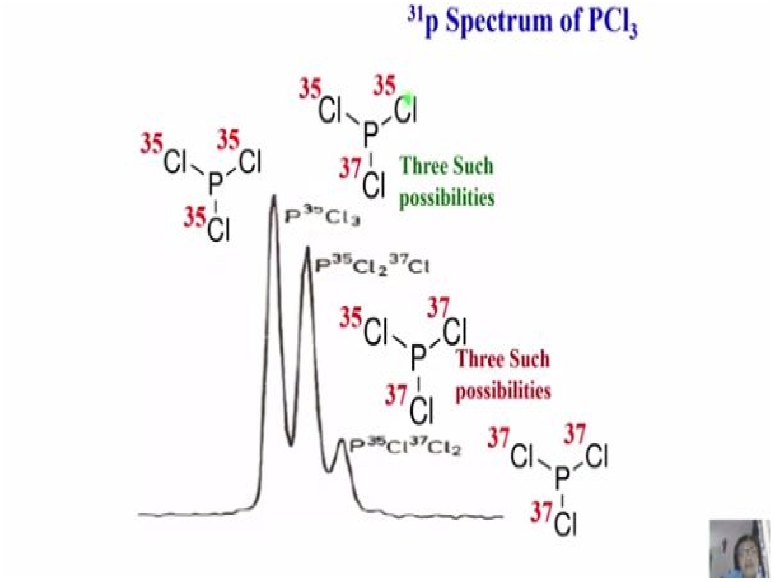

^{31}p Spectrum of PCl$_3$

This is what I wanted to tell you; and see here the same thing in the phosphorus 31 NMR. Very interesting thing happens. see always these halogens, fluorine, bromine and chlorine are substitueted, this type of isotopic effects are largely seen, we saw that in the first example in the fluorine related molecule with bromine substitution then CFCl3 now in PCl3.

Generally this type of isotopic effects and the isotropic shifts are dominant in halogen substituted molecules like this. So now in the PCl3 also we can work out all the chlorines can be 35; like similar to CFCl3. Here I am observing the phosphorus NMR, you can calculate all the intensities very nicely exactly it obeys same intensity pattern.

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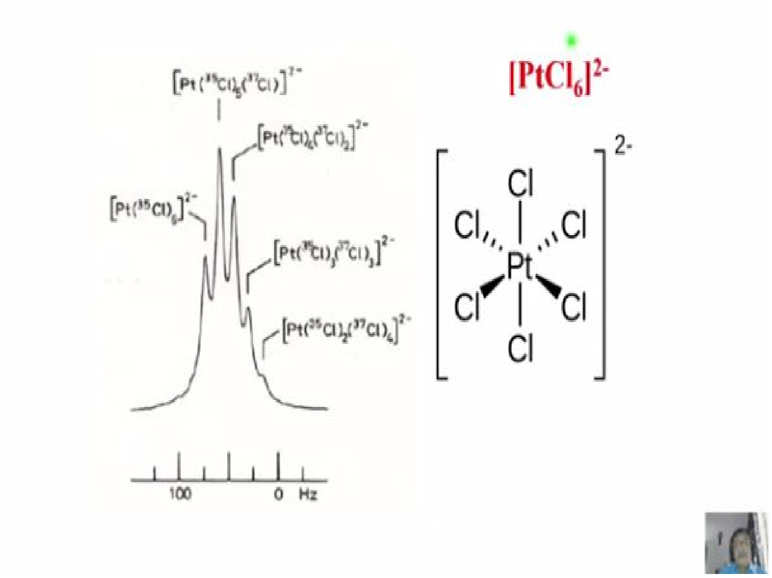

What is intensity pattern, what you got for CFCl3; 100, 95, 30, 3 and you will get; and you can see this effect, especially when you have a platinum with 6 chlorine complex, you see and many peaks you are observing. Actually in principle, in the platinum NMR if you see you must see only single peak, but varieties of isotopomers are present here. As a consequence, different peaks you are going to get. In principle you can calculate what are the possible isotopomers you find out and calculate the intensities.

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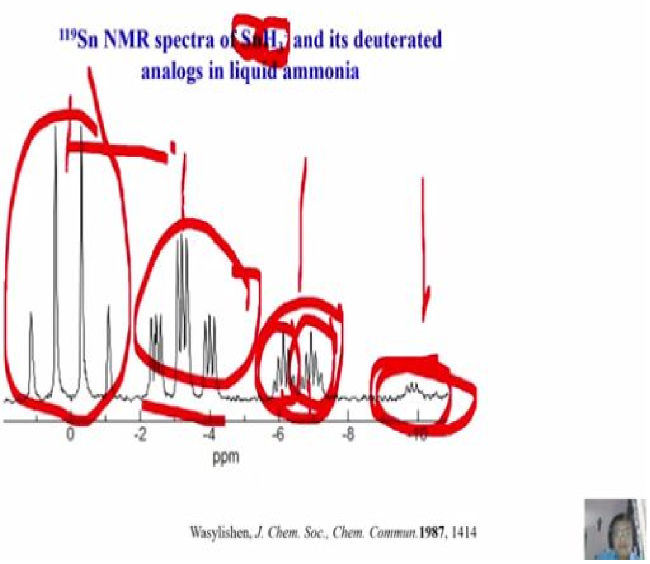
^{119}Sn NMR spectra of SnH_3^- and its deuterated analogs in liquid ammonia

Wasylishen, *J. Chem. Soc., Chem. Commun.* **1987**, 1414

Now I will take another simple example. This is a very nice example. I like it. Look at this spectrum, this is a Tin NMR I am doing, Tin NMR spectra we are SnH3 - and its deuterated analogs in liquid ammonia, see this statement, spectrum taken from Chem. Commun. What is tin119 NMR? because it is spin ½ nuclei remember, Tin 119 and it is NMR active, and the abundance is about 7, 8% that does not matter. So now we are looking for the Tin 119 NMR.

The answer lies in the statement here, deuterated analogs in liquid ammonia, how many deuterated analogs you can think of? There is one possibility $SnH3^-$ everything is protonated; or one deuterated SnH2D; two may be deuterated, SnHD2, and all the three protons can be deuterated SnD3. So there are 4 different types of isotopomers possible. Because of substitution of deuterium, four different types of molecules, you can think of. Now we can analyze the spectrum, if you understand what are the deuterated analogs here.

Are you all with me? Please understand, now consider the first one, $SnH3^-$; when there are 3 equivalent protons are there what happens to tin NMR. The signal will become a quartet, like a magnetically 3 equivalence means like CH3 you saw in the carbon NMR. CH3 carbon will become a quartet because of 3 protons; exactly tin peak will become a quartet. This is exactly corresponding to SnH3-.

Now we take the next one; next one is SnH2D. What happens now? H2, it is analogous to CH2, then it will split this peak into a triplet. Because there is one deuterium what will happen? each line of the triplet is split into three lines of equal intensity by deuterium, this is what we understood, you know, and we were understanding CD3Cl, CD2CN, all those spectra, we discussed, even CDCl3 if you look at it, carbon 13, it is split into three lines of equal intensity because of deuterium. So exactly, first tin is going to be split into triplet by 2 protons and 1 deuterium makes each of these triplet line into 3 lines of equal intensity, this is also understood.

Then next is this one, what is this? This is a possibility SnHD. When one proton is there, it is like a CH proton and the carbon is split into a doublet by proton. Similarly, tin is going to split to doublet here, by this one proton. But there are two deuterium, two of three protons are replaced by deuterium. What that will do? that will split each line of the triplet into 5 line pattern which you also worked out for intensity, very recently. 1, 2, 3, 2, 1 we got.

What is the last possibility? All the three can be deuterium. It is SnD3^{-}. When three deuteriums are there we found out, it splits into seven lines; we saw that, you know you. put in 2NI +1, n is equal to 3; I is equal to 1, 3 into 2; 6, +1 seven lines you will get and you also calculated the intensity and we observed the CD3CN spectrum.

So you will get seven lines, but it is a poor quality spectrum; you are not seeing seven lines. But what I wanted to tell you is, look at it isotopic effect. Just by changing one of the hydrogen to deuterium, then drastically you can see the effect on the spectrum; and also peaks, how much can be shifted by 1 deuterium, 2 deuterium, 3 deuterium. And you can in fact find out the chemical shifts difference between here to here, and this to this centre, and this to this center, and this to this center. In fact all are equal.

So you can find out when there is one deuterium substitution, what is isotopic shift? Because one heavy about atom substitution what is isotopic shift? When there are two heavy atoms, when there three atoms substituted, etc. So all these things can be easily calculated, these are all the effects of isotopes you can see here.

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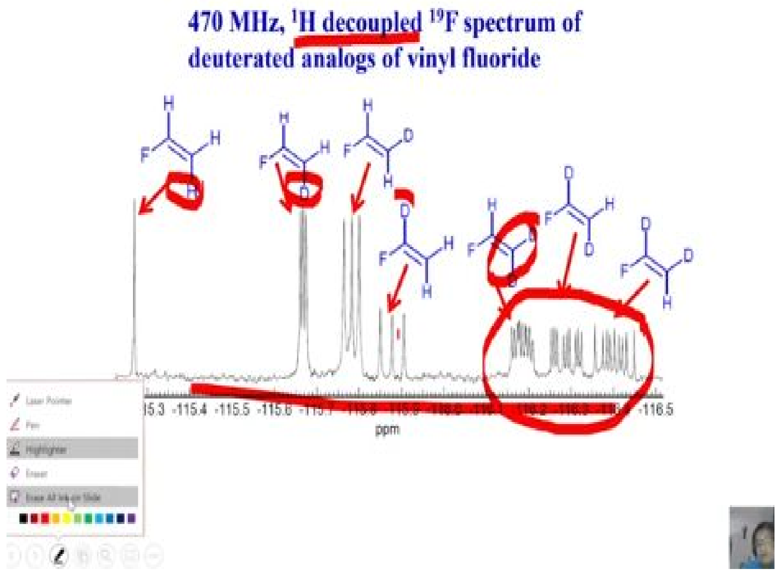

470 MHz, ^{1}H decoupled ^{19}F spectrum of deuterated analogs of vinyl fluoride

Now I am going to give you a last example of this. Now look at the fluorine NMR spectrum of vinyl fluoride. This is a vinyl fluoride. When there is single fluorine, proton decoupled remember, so no proton fluorine coupling you get a single peak. what about, if I have deuterium here. Instead of proton, I replace one of the proton by a deuterium, it becomes three lines.

Now I put deuterium here. Very interesting because it is a trans coupling, this is cis coupling you are going to get this. When the deuterium is here, you get this thing; when the deuterium is here; 2 deuterium are there you get this; and 2 deuterium in the trans position, so 2 deuterium will be geminal position and 2 deuterium in the cis position, fantastic spectrum, you see, so beautifully you can understand the effect of substitution of deuterium.

Not only isotropic shift, how the spectrum is getting affected, whether there is one deuterium is there or two deuterium is there, depending on whether it is a geminal, vicinal, trans or cis, based on that entire pattern changes. I hope we can understand may be if there is a, 5 minute time in the next class or 2-3 minutes I will see and explain to you and then afterwards we go to multinuclear analysis. So I stop it today.