One and Two Dimensional NMR Spectroscopy for Chemist
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Lecture No- 41
Heteronuclear couplings and satellite analysis -2

Welcome back today let us continue with the heteronuclear interactions. In the last class I introduced so many interaction parameters as for the heteronuclear interactions are concerned, between abundant spins, between abundant spin and rare spin, varieties of interactions you can see and we also came to the level of understanding the satellite spectrum. I explained what is a satellite spectrum, how do you extract information for the satellite spectrum, especially in cases when proton NMR cannot give the information like a single peak for a molecule like di substituted ethylene, cis or trans, does not matter, the symmetrical di substituted molecules, if you take, because of the molecule symmetry, you get a single peak. But how do you know, what is the coupling between them, there exists a coupling between two protons. How do you see that? So some cases, in symmetric molecules, you will not be able to see the coupling information so easily. In which case, the satellite spectrum, the analysis of the satellites provides a lot of information.

I took the example of Si_2H_6, where we found out one bond silicon proton coupling through satellites, two bond silicon proton coupling; and three bond proton-proton coupling we could see. So this is what I wanted to say, a lot of information you can derive from the same proton spectrum, but if you carefully look at the analysis of satellites, let us continue further today.

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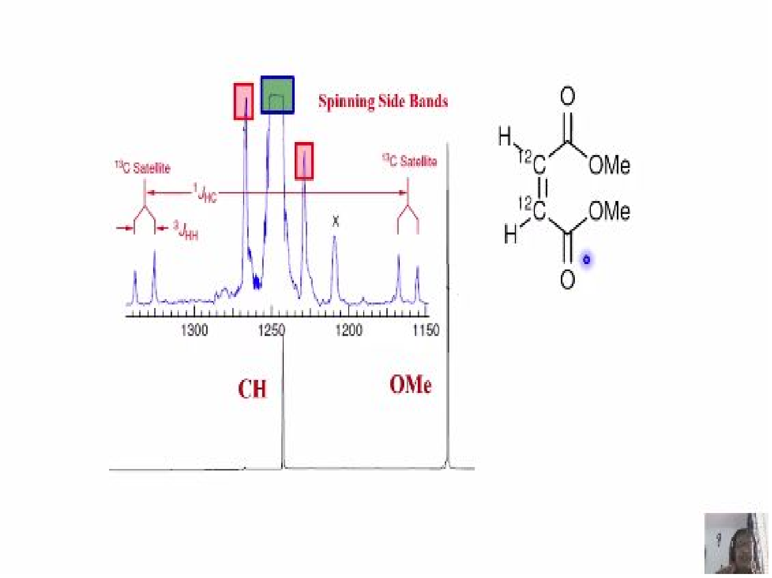

See this is a molecule. It is a perfectly symmetric molecule. There are two carbons here, both carbons can be in the carbon-12 state. They exist as carbon-12, no problem. In which case, you get only a single peak, that is precisely what you are seeing. It is only a single peak but I know there is a coupling between these, how do I do that? As I just now explained to you, record the spectrum of this molecule.

This I am now concentrating on which one? This, I am looking at this carbon. So when I look at this carbon, of course, you can also look for the OMe peak later. I am not looking, this is the OMe peak. you can also see this satellites of the OMe peak. But now I am concentrating only on this peak because I am interested in getting HH coupling. So this spectrum is enhanced with a larger vertical scale increased. Then you see some other things, forget about this and this, what it comes because of some side bands, spinning side bands, etc. When you want to see 1% of intensity of the peak, there is quite likely sometimes you might see impurities, other peaks also. But apart from that if we carefully analyse, you see there are two peaks here. What did we do? why these 2 peaks are coming now? these are the spinning side bands.

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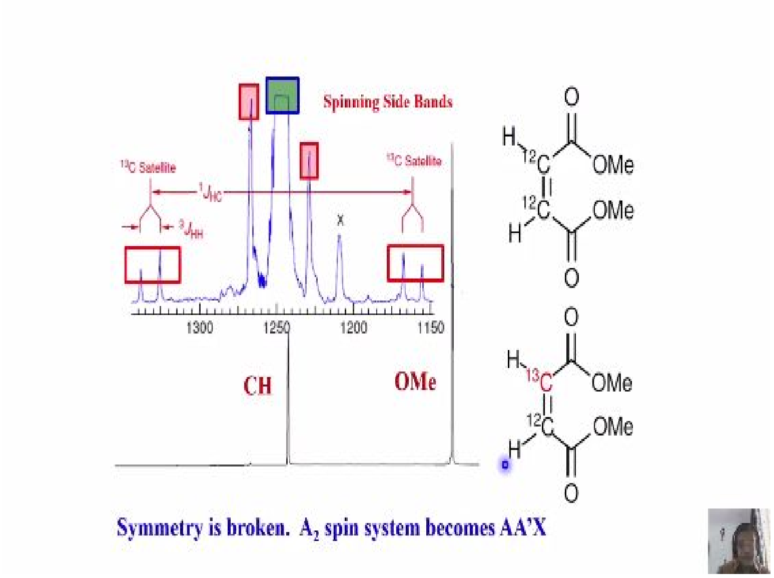

Symmetry is broken. A_2 spin system becomes AA'X

This is because, now we are looking for carbon-13 of the molecule. Now I am consider this molecule where carbonexists as C13, so carbon here exists as C13, in this molecule carbon here exists as C13. In which case, you have broken the symmetry. In instead of A2 spin. now AA'X, like in the previous example. This center to this center gives you one bond CH coupling, and separation of these 2 doublets gives you 3 bond proton-proton coupling. Now I know whether this is cis or trans. I can analyse I can get the coupling information very easily by just looking at the satellite spectrum.

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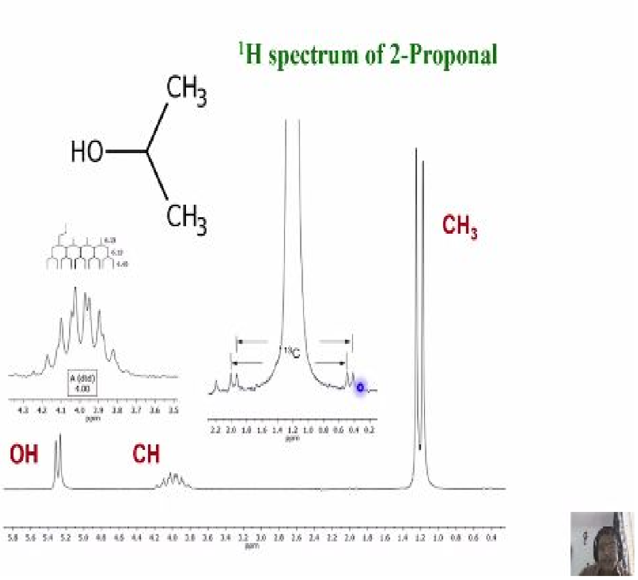
^{1}H spectrum of 2-Proponal



Now look at the spectrum of 2 propanol see it is a very interesting molecule. We have CH and 2 CH3'. This CH3 is a doublet because it is coupled to CH proton. Now what we can do is, we can enhance this intensity and see carbon 13 satellites here.

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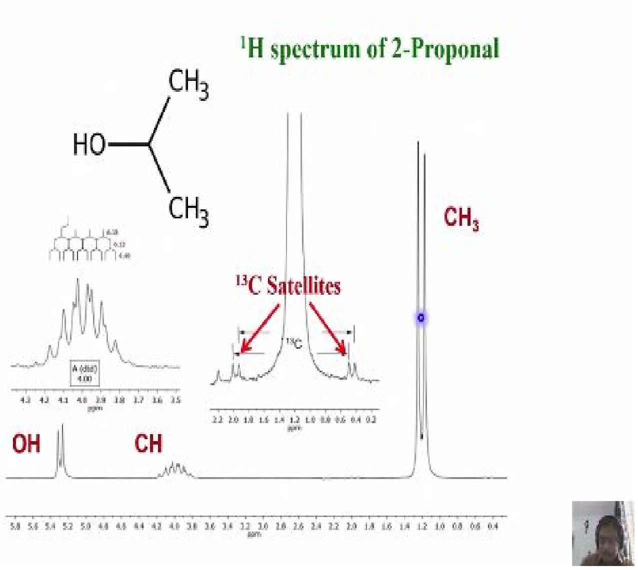
^{1}H spectrum of 2-Proponal

These are the carbon-13 satellites. I can measure this and get this CH coupling. Of course, this HH coupling is already visible here itself, but you can see here also. In this case, the question was symmetry does not come, because this is coupled to this equally and it is a doublet.

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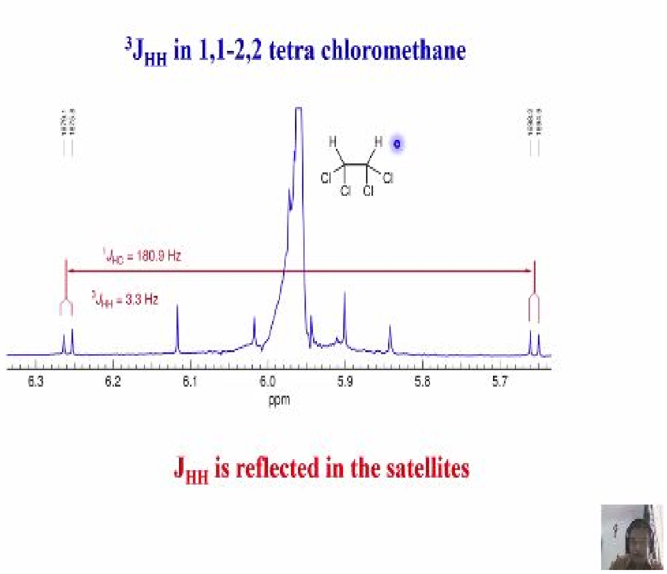
$^3J_{HH}$ in 1,1-2,2 tetra chloromethane

JHH is reflected in the satellites

This is another molecule 1,1-2,2 tetra chloroethane. In this molecule, now if you look at the protonated molecule, this is what it is; there are other impurities etcetera you do not worry, and This side satellites are these two. Centre of this to centre of this gives you CH coupling, and analysis of the doublet of the satellites gives you HH coupling. Very clear right? So we were able to get CH coupling HH coupling and all those things. All you have been doing is to analyse the satellites.

So, satellite when you look at it more often you will break the symmetry, as a consequence some of this information which you do not get from 1D NMR you can start getting.

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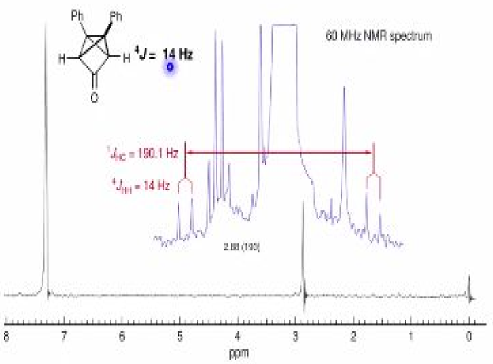
$^4J_{HH}$ in symmetric tricyclic system



You see an example, where 4 bond HH in the symmetry tricyclic system can be measured from these satellites. This is a spectrum which you have enlarged in intensity, you see a doublet here and here. These doublets correspond to coupling of this proton to this proton. Because of symmetry, you do not see in the main peak, you will see only a single peak. But when you look at the satellites, this separation to this separation, center of this to center of this, you see CH coupling and this doublet separation gives you 4 bond proton-protron coupling which is of the order of 14 Hertz.

Remember, when I was mentioning to you about the strength of the coupling, homonuclear couplings, I did mention in this type of molecules, you can get long range couplings, even of the order of 20 Hertz also. Remember I showed this particular example also, I think;

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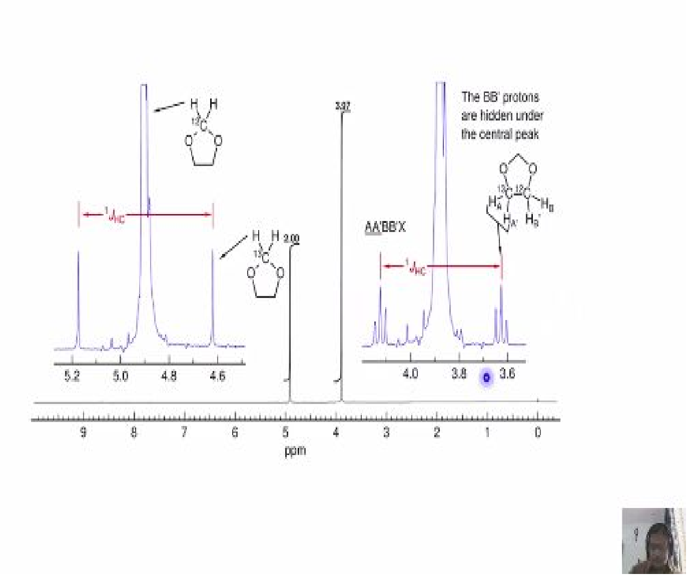
The BB' protons are hidden under the central peak

So, we can extend this logic for more carbons present in the molecule, how do you analyse these thing everything. See in a molecule like this, now I have a molecule like this; and I have I have two protons here. You understand. To make it simpler there are three CH2s. These two CH2s are here and one CH2 peak is here. Now, If analyse this proton spectrum, this CH2 gives a single peak. I enlarge it in higher intensity you are going to get protons-carbon coupling. I am going to see proton carbon coupling, forget about other things geminal coupling, later. Now if you come to this part, now if I break this symmetry, by taking one of them is in carbon-13 state and other is in carbon-12 state, if I assume, now you have broken the symmetry. Otherwise it would have been A2B2, now because symmetry is broken, it is AA'BB'X. What is X? X is carbon 13.

This is what you are going to see. It is AA'BB'X now. The analysis of this, you can take this spectrum I did not give the analysis of AA'BB'X spin system, you can analyse and get all the coupling information.

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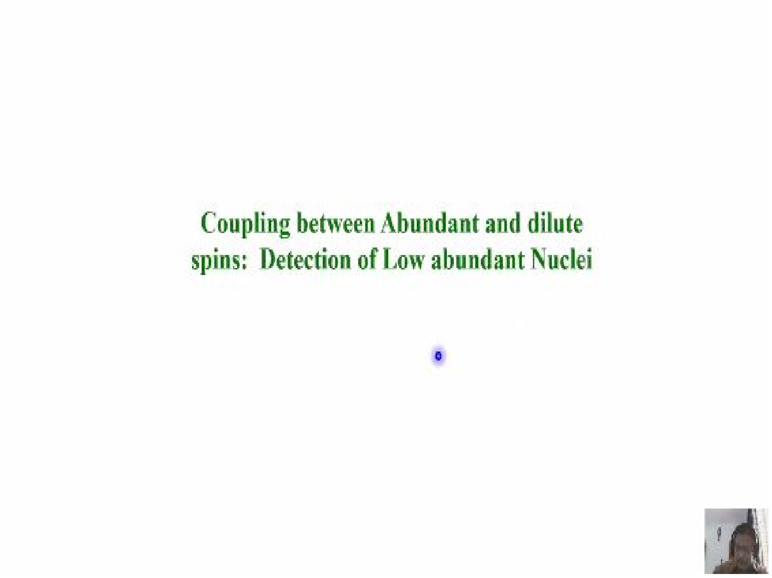

Coupling between Abundant and dilute
spins: Detection of Low abundant Nuclei

Now that is just for the satellite analysis; one of the examples I gave. When we go ahead we can get number of such examples, we come across, need not be for coupling extraction, but for some other purpose. We will see that. Now I will give you an example of coupling between abundant spin and dilute spin. Dilute spin means low abundant spin; and I am looking at low abundant spin. So what I meant is, this we already discussed, if you carefully remember in the carbon-13 and number we did not look at the carbon-fluorine coupling?

Carbon is a low abundant nucleus, we detected carbon, and observed carbon-fluorine, carbon proton coupling, everything. The same example here I am giving. The abundant spin is proton or fluorine are phosphorus. That can couple to carbon, tin, mercury etcetera. Then we can analyse that. But we are detecting carbon, low abundant nuclei. So if you observe carbon 13 spectrum, you analysed all CF coupling CH coupling etcetera.

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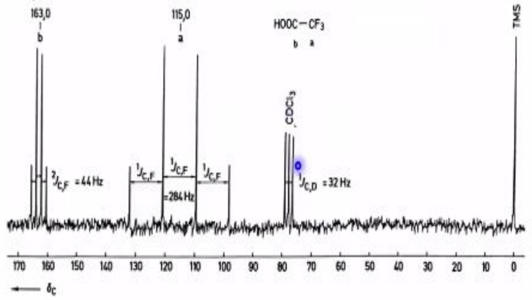
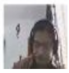
Heteronuclear Coupling Constants

^{1}H broadband decoupled ^{13}C spectrum of trifluoroacetic acid

F_3C-COOH





Exactly same thing, in trifluoroacetic acid we analysed this carbon spectrum and got coupling between low abundant spin to high abundant spin, while I was detecting low abundant spin. In previous examples, I was detecting abundant spin. So the same thing, this also we discussed, you analysed this, I do not want to see this again; there is no point in going again.

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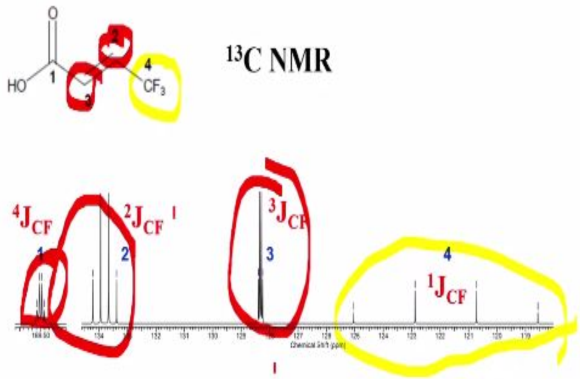

^{13}C NMR

Now this part we will see, this I did not explain. This is a simple molecule. I am looking at carbon-13 NMR, low abundant spin. Carbon now can couple to fluorine and also to proton. How do you simplify the carbon spectrum? First thing, do the broadband decoupling. Remove all proton carbon couplings. So what are you left with? Only carbon fluorine couplings. As I said one bond CF coupling is quite large. This carbon, what is the pattern expect? It must be a quartet. A large quartet you see, 1, 3, 3, 1 quartet. What is this one? This large quartet has to be this CF3.

Now, we can go ahead further, what is the next one? Next carbon is this; this carbon can also couple to fluorine. Again it has to be a quartet. So how many bonds it is separated. This carbon to this fluorine only two bonds; so this coupling is much larger, you see a better quartet; may not be resolved like this, because this coupling is larger. This is one bond coupling but it is still it is a quartet.

What about this one? The next carbon 3. This is 1, 2, 3 bond coupling. This is also much better and 4 bond carbon coupling is here. Very easily you can identify all the carbons based on their splitting pattern and the coupling strengths. So this is what the information which I wanted to tell you. Coupling between abundant spin and a dilute spin can be there, you can detect the dilute spin and observe lot of things.

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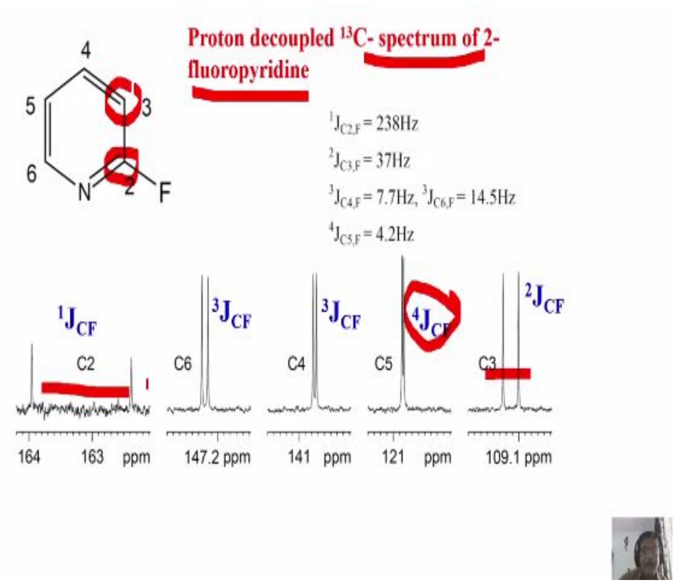

Proton decoupled ^{13}C- spectrum of 2-fluoropyridine

$^{1}J_{C2,F} = 238Hz$

$^{2}J_{C3,F} = 37Hz$

$^{3}J_{C4,F} = 7.7Hz$, $^{3}J_{C6,F} = 14.5Hz$

$^{4}J_{C5,F} = 4.2Hz$

Now, coupling between carbon and fluorine also we saw. Both are spin half nuclei in a molecule like this. This I think we observed, we saw that, I think. I explained to you proton decoupled carbon spectrum of 2-fluoropyridine. I do not know whether I explained to you. If I decouple all the protons here, you get only CF coupling, One bond CF coupling is larger, this is that one, C2. And then two bond is next one, Which is this carbon? Three this much larger then, 3 bond, 4 bond so only based the carbon fluorine couplings, you can start analysing. Here completely protons are decoupled. So 3 bond coupling of this we observed 2 bond, last if you take this one, 1, 2, 3, 4 bond coupling very weak, you see. This has to be carbon 5. So depending upon the coupling strength you can make the assignments.

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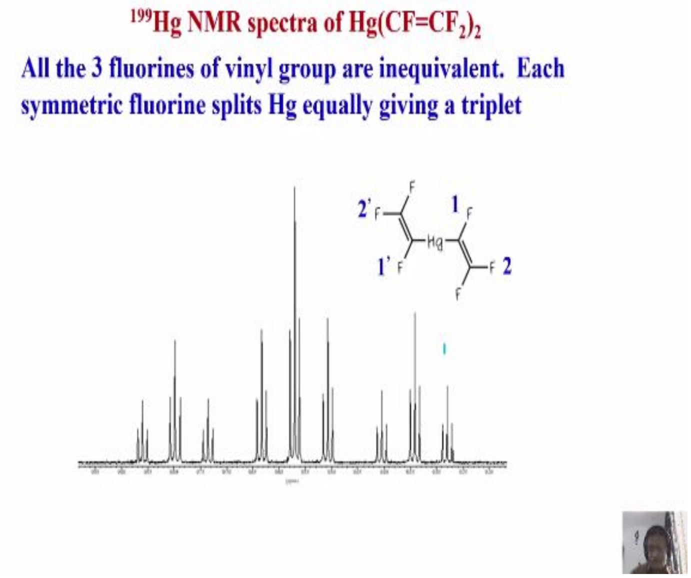

^{199}Hg NMR spectra of $Hg(CF=CF_2)_2$

All the 3 fluorines of vinyl group are inequivalent. Each symmetric fluorine splits Hg equally giving a triplet

This is a classic molecule which I showed you, in the example of multiplicity pattern called triplet of triplets, when I was analysing. I showed you this. Now, all fluorines of vinyl group chemically inequivalent, these 3 fluorines are inequivalent. Each symmetric fluorine splits mercury equally. It means, these 3 fluorines are not identical. These 3 fluorines are not identical, but interestingly what is going to happen is? This fluorine will split this mercury, both at equal extent, same coupling strength.

Similarly, with these 2 fluorines, will split this mercury by the same amount; because coupling same to same. Similarly, this coupling to these 2 fluorine coupled to this mercury again has the same strength. What I try to say is, each of this symmetric fluorine which are chemically equivalent like this and this, coupled to mercury by same extent. So what happens? If this is coupled to this, and this is coupled to this, but the same coupling strength, what pattern you will expect?

I told you it has to be doublet of doublets, central two lines overlap and you get a triplet. So that is the thing what you are going to observe when you do that. See these two split mercury into a triplet like pattern, like this. Only 3 peaks you get nothing more. Further then we have a coupling to another fluorine; this fluorine we will take, and it will couple to this one by the same extent. Each line of triplet will become another triplet, because coupling between 2' and Hg and 2 and Hg are same. So each line of triplet becomes another triplet. Now, it is coupled to these two fluorines again with the same coupling strength. Now what will happen? Triplet of triplet will become another triplet. Each line of triplet of triplets become triplet. So how many peaks you get? You get 27 peaks, totally.

Pattern is simple, this is called triplet of triplet of triplets. You should call this as TTT, Triplet of Triplets of Triplets.

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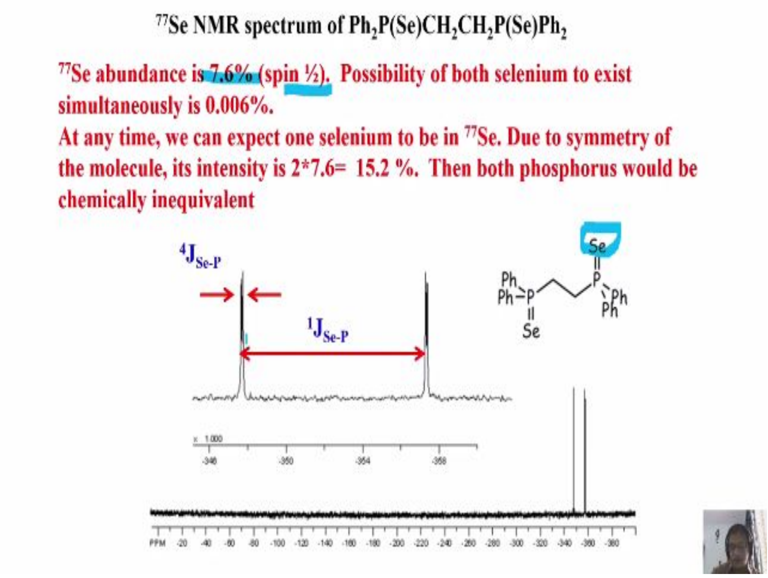

^{77}Se NMR spectrum of $Ph_2P(Se)CH_2CH_2P(Se)Ph_2$

^{77}Se abundance is 7.6% (spin ½). Possibility of both selenium to exist simultaneously is 0.006%.

At any time, we can expect one selenium to be in ^{77}Se. Due to symmetry of the molecule, its intensity is 2*7.6= 15.2 %. Then both phosphorus would be chemically inequivalent

Similarly, now we can look for the Selenium NMR. Abundance is only 7.6% here, spin half nuclei. Now, you can look at this, there are two seleniums here. If you see any Selenium at any given instant of time, like we saw in carbon-13 satellites, symmetry is broken. When symmetry is broken, you get selenium phosphorus coupling; very easily we can measure that.

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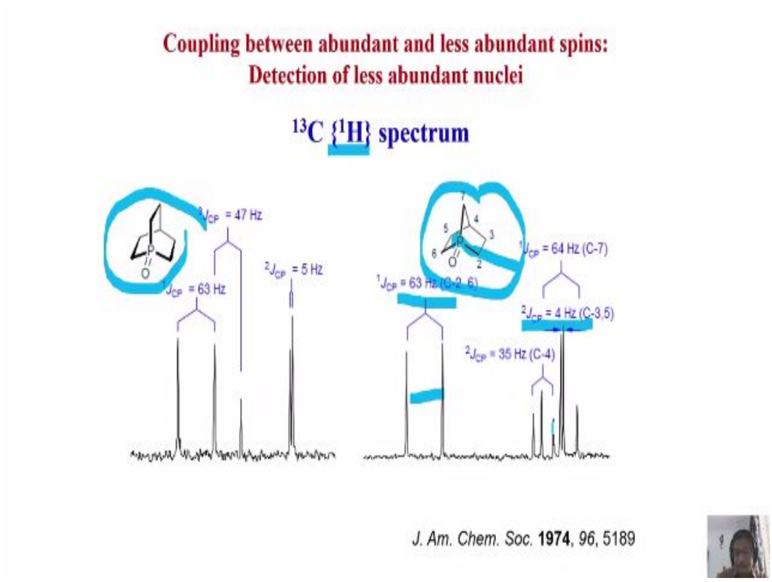

Coupling between abundant and less abundant spins:
Detection of less abundant nuclei

$^{13}C\{^1H\}$ spectrum

J. Am. Chem. Soc. **1974**, *96*, 5189

Of course we can see coupling between phosphorus and carbon in this simple molecule; you can see it. Now, the phosphorus one bond coupling to this and two bond coupling to this, three bond coupling to this, all those things we can see. Very clearly you can see that, one bond carbon phosphorus coupling is seen. Of course, protons are decoupled here. Then two bond Carbon phosphorus coupling are seen, but one thing you should see; these coupling strengths are much smaller unlike in fluorine.

Remember one bond carbon fluorine was nearly 300 hertz but here it is much smaller, carbon phosphorus coupling. But nevertheless, you were able to analyse, you can see all those things and clearly it could be this molecule or this molecule; both the type of molecules you can make the assignment easily.

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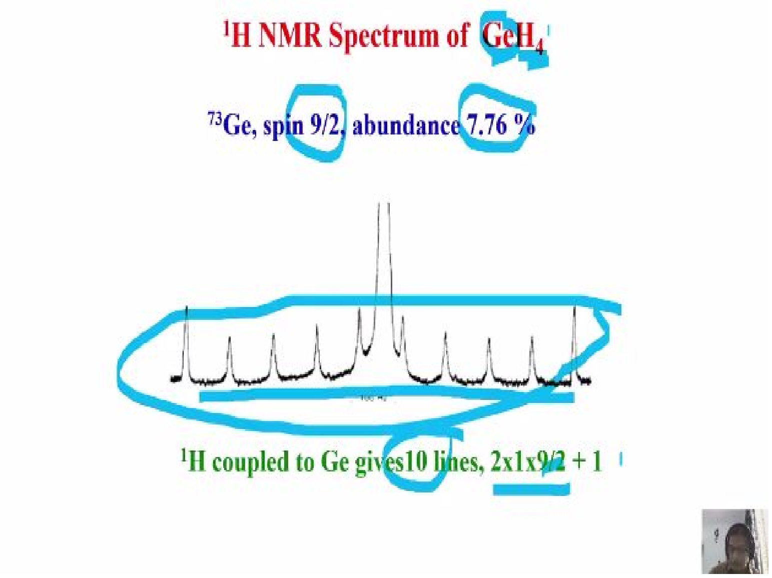

^{1}H NMR Spectrum of GeH_4

^{73}Ge, spin 9/2, abundance 7.76 %

^{1}H coupled to Ge gives10 lines, 2x1x9/2 + 1

This is another molecule where I am looking at the heteronuclear interaction. I am looking at the proton NMR spectrum of GeH4. Germanium H4; Germanium has spin is 9/2; but I am looking at proton and Germanium is 7.76% abundant. That is another thing. Assuming I am seeing only proton, of course germanium is low percent small abundant, what is its largest peak I should get, most intense peak? Only H4 peak.

But if I enhance the intensity larger, then I see germanium coupling to proton also, they are seen a satellites. But why so many peaks? Now, we know germanium spin is 9/ 2. This is the quadrupolar spin. I wanted to show you how quadrupolar spin splits and then give this spectrum, complex like this. This is 9 /2 spin, and just put it in into 2NI+1 equation. Now only one germanium is there, spin is 9/ 2 and 2 into 1 into 9/ 2 + 1, it gives 10 lines.

Count: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 all 10 lines are seen here. You understand? So these are again satellites. when we analyse this satellite spectrum, you get germanium proton couplings.

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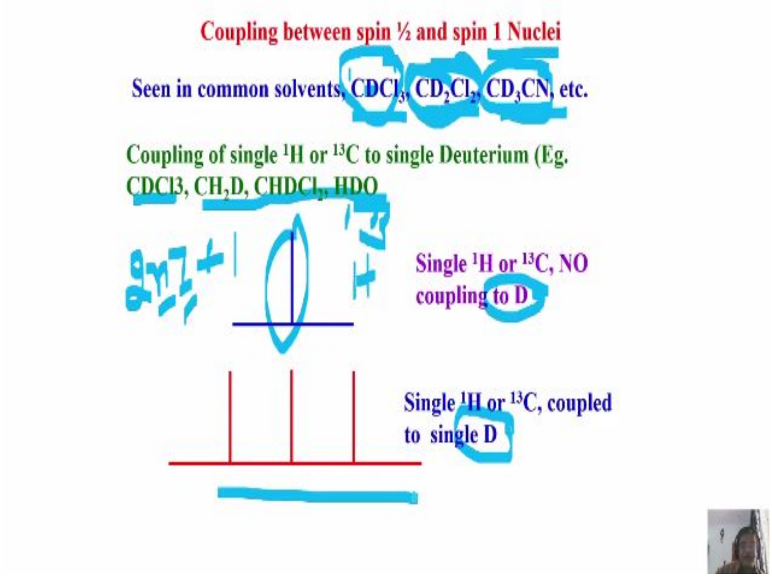

Coupling between spin ½ and spin 1 Nuclei

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

So now coupling between spin ½ and quadrupolar nuclei, what I said here. Now, we can see this here again. Now quadripolar spin I am considering here, ofcourse abundant quadripolar spin. This was satellites here. Now, I am looking for the abundant, abundant is Deuterium, let us consider. What are the solvents we normally use? CDCl3, CD2Cl2, CD3CN. But have you ever taken the spectrum of pure solutes. Please try take the spectrum of pure solutes. Then you will see, you will get residual proton peaks.

If you take pure CDCl3 solvent, it will not be100% pure, there will be some percentage of CHCl3 also. It will give you a peak at 7.2 ppm. Similarly, dichloromethane what is CD2Cl2? dichlomethane, whatever it is. I do not know the name of the molecule. You people know, chemistry people should know. This is, again there is a residual protonated solvent, and you are going to get proton peak. Similarly, CD3CN, Interestingly, this has several isotopomers.

It can have CD2HCN, CD3CN, CHD2CN, CH2DCN and all those things you can get. So all this isotopomers have residual proton peaks. Here CH2Cl2, that is present. CHDCl2, CD2Cl2 all these isotopomers will be there. The protonated compounds will give you residual proton peaks in the proton NMR. Now in such cases, you can also see coupling of carbon to Deuterium or even proton to Deuterium.

Spin half nuclei can couple to spin 1 nuclei like this. Now, I will take the example of some of these things and we will see how the pattern comes. Now, let us take any one of this molecule containing single proton or single carbon. For example, CHCl3 or CDCl3, carbon will give a single peak, without any coupling to deuterium. I will not bring in coupling. Then we will get only single peak.

Now we bring in the coupling. Whether it is CHCl3 or CDCl3, it does not matter. So now when I have a, what I am seeing, I am looking for proton or carbon does not matter. I see proton NMR of carbon 13 NMR, I get a single peak. Now I am bringing Deuterium coupling to it. You understand, whether it CHCl3, or CDCl3, I look for carbon 13 or Proton, does not matter. I get only a single peak. Moment, I bring in the coupling, I get triplet. Not triplet, triplet is a wrong word because triplet is 1 : 2 : 1 in NMR. It is 3 lines of equal intensity. Why 3 lines? Because, Deuterium has spin one. When it is one, when you put it into a equation, 2NI+1, then simply will understand how many peaks you are going to get. N is equal to 1, I is equal to 1. What you will get, 2+1, 3 peaks, and of equal intensity. This is the advantage, you know, in this case of deuterium, of course, we also have a Pascal triangle for this.

I will show you when we go forward later, but you please remember there is one single Deuterium is coupled to either proton or carbon you will get 3 peaks of equal intensity, 1:1 :1 intensity.

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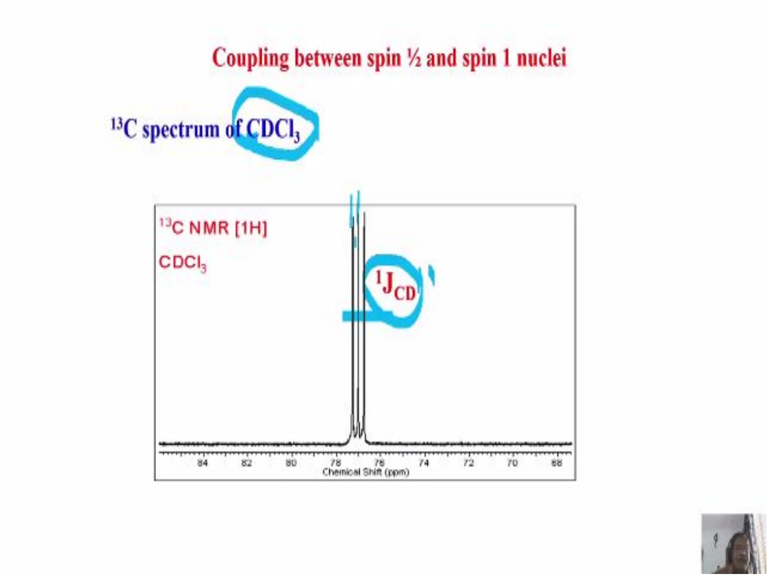

Coupling between spin ½ and spin 1 nuclei

^{13}C spectrum of $CDCl_3$

Here is a classic example you see in the carbon 13 NMR, when you take CDCl3 carbon-13 spectrum, there will be three lines of equal intensity. It is due to 1 bond carbon deuterium coupling., You measure the separation between this and this. What are you going to get? Carbon deuterium, J coupling. Carbon deuterium J coupling can be easily measured by measuring these adjacent peaks separation. So you can very clearly see coupling between spin half nuclei and spin 1 nuclei.

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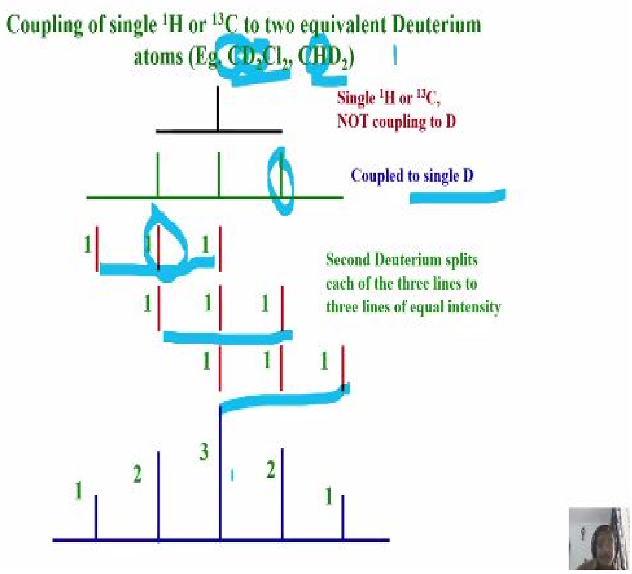

Coupling of single ^{1}H or ^{13}C to two equivalent Deuterium atoms (Eg. CD_2Cl_2, CHD_2)

Single ^{1}H 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

Now, what happens, when I take CD2Cl2 or CHD2. These are all the molecules, I am looking for carbon here, I am looking for proton here, or carbon also, does not matter. Here also you can see, one carbon is there, no proton. Now, what is the intensity pattern you get, how many peaks you are going to see? We will understand. When a single proton or single carbon, not coupled to deuterium you will get a single peak.

When it coupled to one deuterium as just now I said, we get three peaks of equal intensity, we got it. Now bring in another deuterium now. First it was coupled to single deuterium, now with that two deuterium, I have to take into account the intensity pattern, it is coupled to both. Remember you worked for CH2 group, CH3 group, multiplicity pattern for equivalent spins. Exactly, for spin 1 nuclei we can work out, you can get the diagram and splitting pattern from the family tree approach and I can generate the intensity pattern. When 2 deuteriums are coupled, 3 deuteriums are coupled to a spin ½ nuclei. So now when second deuterium is coupled; each line is going to be further split into 3 lines of equal intensity. Because the center line of the three lines always coincide with this. The central line of these 3 lines coincide with this; and this is again split into 3 lines again central line will coincide, this will again split into 3 lines again central line will coincide.

Like you did for the spin half nuclei, I am doing the same thing. I knew it will split into 3 lines of equal intensity. When I bring the second deuterium central line will remains same, there will be two lines on either side. Again here central line remains same, two lines on either side because the coupling strengths are equal, they are magnetically equivalent. Now all these intensities will overlap, 1 is to 1 is to 1 is to 1, etc. . Finally, what do you get? 1,2,3,2,1 this intensity we got. A pentet.

Remember, when I started analysing this spectrum of CH2D2, I showed this one. I said two deuteriums when coupled to proton, I said it give rise to a pentlet like this. 1,2,3,2,1 intensity. That is how we generated now. You got the point, how to generate this splitting pattern, when spin half nuclei is coupled to spin 1 nuclei. Whether it is one spin or two chemically equivalent spins, it could be 3 also. Now you can generate for 3 also later.

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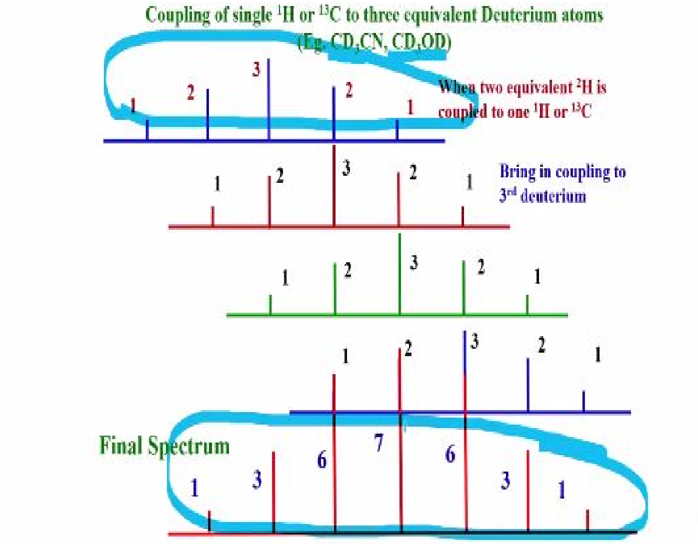

Coupling of single ^{1}H or ^{13}C to three equivalent Deuterium atoms (Eg. CD_3CN, CD_3OD)

Now example of CD3CN or CD3OD, let us see when two equivalent D is coupled to one proton or one 13C, we got already this one; 1,2,3,2,1 intensity. Now, I am bringing the third deuterium. What will happen when I bring the third deuterium? You must understand each of these lines will be like this. Each of these will split into 3 lines of equal intensity. Now, similar to this, we have 3 patterns.

Final spectrum will be overlap of all these, and it is 1, 3, 6, 7, 6, 3, 1. When 2 deutrieums are coupled, intensity pattern is 1, 2, 3, 2, 1; when three deutrieums are coupled intensity is 1, 3, 6, 7, 6, 3, 1. This is the pattern you are going to get. This is pentet. This is; 1, 2, 3, 4, 5, 6, 7 this is septet. You understand, the spin one nuclei when it coupled a spin half nuclei, if it is a single spin 1 nuclei, we have 1 : 1 : 1 intensity. If there are 2 spin 1 nuclei, 1, 2, 3, 2, 1 intensity. If there are 3 spin 1 nuclei, we get, 1, 3, 6, 7, 6, 3,1 patterns

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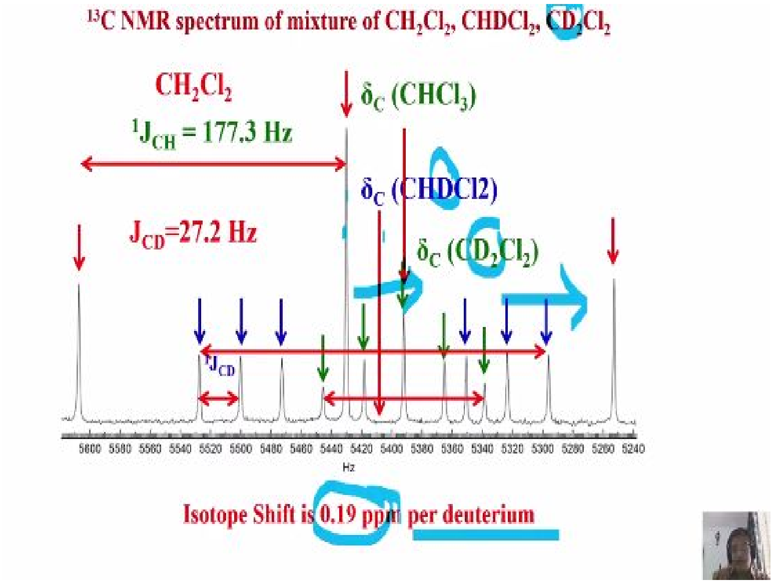

^{13}C NMR spectrum of mixture of CH_2Cl_2, $CHDCl_2$, CD_2Cl_2

Isotope Shift is 0.19 ppm per deuterium

Exactly that is what we get. Now we can analyse the spectrum. You will understand what is really happening. Now, I am looking for the carbon-13 spectrum of mixture of these three. CH2Cl2, first we will take that. What is the pattern we expect? I am looking for carbon-13 NMR in the mixture of three different molecules, do not get confused, the mixture of three different molecules.

This CH2Cl2, if I consider, in carbon 13 NMR what pattern we will get? Of course, chlorine will not couple. It is a large triplet; 1, 2, 1 intensity, it is a triplet correct? CH2Cl2 will be a triplet. What about CHDCl2? Let us think carefully. Start thinking carefully now. In the case of CHDCl2 carbon will split into this doublet because of proton, it is a doublet. And each line of the doublet will become 1 : 1 : 1, 3 line pattern. So all you will get 6 lines, because of CHDCl2, because of coupling with H and D, this carbon will be 3 lines here, 3 lines here. It will get 6 line pattern, that is what it is. This separation, of course, I forgot to tell you, gives you JCH; this is a chemical shift. Now when look at this, compared to this, it is not exactly at the center, it appears the peaks have moved to the right, is it not?

We can calculate. This is exactly the center, that means, this is moved by certain amount. What is that certain amount? This is what is called isotopic shift in NMR. Remember this is isotopic shift in NMR. Because one deuterium is substituted, carbon peak is moved by this thing, moved to the right by this much amount. This always expressed in parts per billion. You understand, it always expressed in parts per billion.

Now coming to the situation of another molecule, CD2Cl2. How many peaks you expect? Two deuterium are coupled, we already worked out, 1, 2, 3, 2,1 pentet, this is what it is, you see. So all the peaks are assigned. Carefully see now, go back, I want to make you understand. First, CH2Cl2 is a triplet, this separation gives you J coupling between carbon and proton and this is the chemical shift.

Second molecules CH2Cl2, first, it is a large doublet because of proton coupling and each doublet is 3, 3 lines because of deuterium coupling and there is a shift from the center, because of the isotopic shift. Next molecule is CD2Cl2, it gives a pentet, since these 2 deuterium are chemically equivalent. And you see, this is also shifted by certain amount. So what do you understand by that?

If you measure this separation to this, this separation to this, you can find out isotopic shift with addition of isotope. With only one isotope is there, this much is shifted. If 2 isotopes are there it is shifted by this much. If third one is there, it is shifted by some more. Another important point you should appreciate, when the heavy isotope is substituted the peaks are always shifted to the right, It is shifted to the right now.

And the peaks, when one heavy isotope is there, from here it shifted here. When two isotopes are there from here it shifted here. So more the heavy isotopes are substituted, larger the shift of the spectrum to the high field. This what you should understand. So you can calculate per deuterium substitution isotopic shift is 0.1 to 0.19 parts per million ppm, large value.

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Coupling between two less abundant spins

Detection of one of the dilute spins

Now one more thing. I can talk about the coupling between two less abundant spin and you are seeing that, what I can do is, some more I have to tell you about other things about deuterium substitution etcetera. It takes some time. So what I will do is, I will stop here. Today, I was telling you something about heteronuclear interaction of varieties of spins, spin half to spin 1, spin half to spin 9/ 2.

How we get satellites analysis? How we get the information from the satellites spectrum which is normally do not get from proton, varieties of things we understood. So in the next class, little bit more about this thing I will say and then we will take specific examples of nuclei with silicon, fluorine, selenium and one or two examples; and literally will sit and analyse those spectrum.

Then you get the feel for how to analyse the spectra of the varieties of nuclei. I cannot cover 110 elements all spectra, I have covered major, proton, carbon, some of the heteronuclei like fluorine etcetera. So, some more interesting examples I will take in the next class and try to do it quickly and finish it. With that, then we will start going into, after analysing heteronuclear coupling, some more exciting topics like polarization transfer experiment, relaxation, spin decoupling and INEPT experiment; and all those things we should talk. Then we will jump to 2 dimension NMR. So I will stop for the day.