# One and Two Dimensional NMR Spectroscopy for Chemist

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## Lecture No: 40

## Heteronuclear couplings and satellite analysis

Welcome back, in the last couple of classes we extensively discussed proton NMR spectra, analysis of proton NMR spectra, carbon-13 NMR spectra and analysis and editing of carbon spectra based on the number of protons attached to different carbons, by carrying out experiments called DEPT-90, DEPT-45, DEPT-135, like that. And we discussed a lot about various things about chemical shifts possible and how we can assign the carbon spectra based on chemical shifts. And I said, the factors that affect the chemical shift of protons also affects the chemical shift of carbon, that is what I said.

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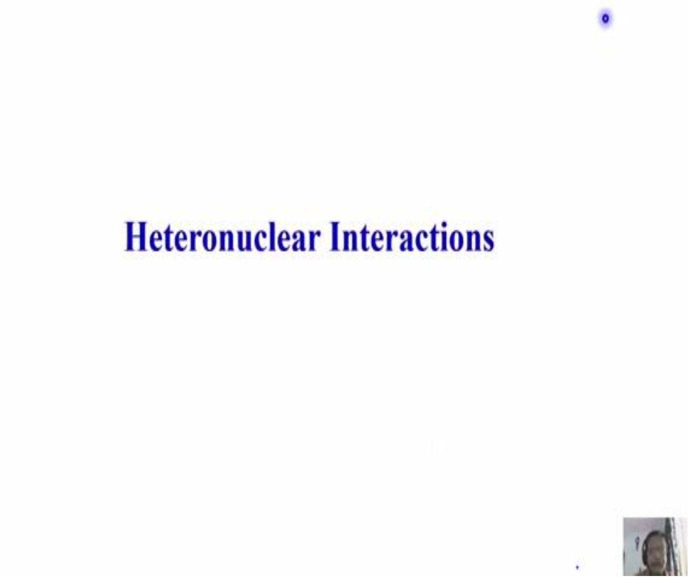

Heteronuclear Interactions

Now, let us continue today, a little bit deviating from carbon-13, some other heteronuclear interactions.

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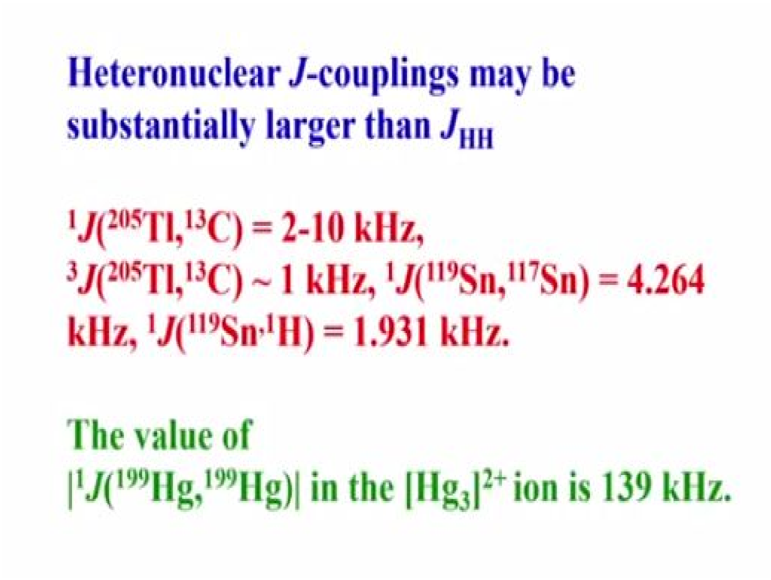

**Heteronuclear $J$-couplings may be substantially larger than $J_{HH}$**

$^{1}J(^{205}\text{Tl},^{13}\text{C})$ = 2-10 kHz,
$^{3}J(^{205}\text{Tl},^{13}\text{C})$ ~ 1 kHz, $^{1}J(^{119}\text{Sn},^{117}\text{Sn})$ = 4.264 kHz, $^{1}J(^{119}\text{Sn},^{1}\text{H})$ = 1.931 kHz.

The value of
$|^{1}J(^{199}\text{Hg},^{199}\text{Hg})|$ in the $[\text{Hg}_3]^{2+}$ ion is 139 kHz.

And I want to just give you a brief idea about various possible couplings you can think of. For example, among the heteronuclear couplings, they can be very large. For example, one point coupling between Thallium 205 and carbon-13 if you consider it can vary from 2-10 kilohertz, remember, 10 kilohertz. In fact in some of the nuclei like carbon etc., it covers almost half the spectral width.

In the 500 megahertz carbon13 will be about, let us say 30 thousand hertz or 35 thousand hertz is the spectral width, nearly one third of that or half of that is the spectral width. It is of the order of J coupling here. In exotic nuclei like these, sometimes chemical shift range will be very large, For example in nuclei like cobalt and others if you go, the chemical shifts can go upto 60000-65000 ppm. It is really large. Similarly, coupling is quite large in cases like this.

For example Thallium to carbon 13 three bond coupling is of the other one kilohertz, quite large. For example, one bond tin-proton coupling is very small, and tin - tin coupling can be there. Remember tin has 2 isotopes, we will discuss as we go ahead further. That can have coupling of the order of 4.267 KHz. We can even detect the coupling between two dilute spins whose abundance are very small, they are also called dilute spins.

So, we can see that in one example the mercury, mercury coupling, 199Hg-199Hg in this type of ion is 139 kilohertz, imagine? That is J coupling I am talking, not the chemical shift, not the spectral width. So it is 139 kilohertz is the J coupling.

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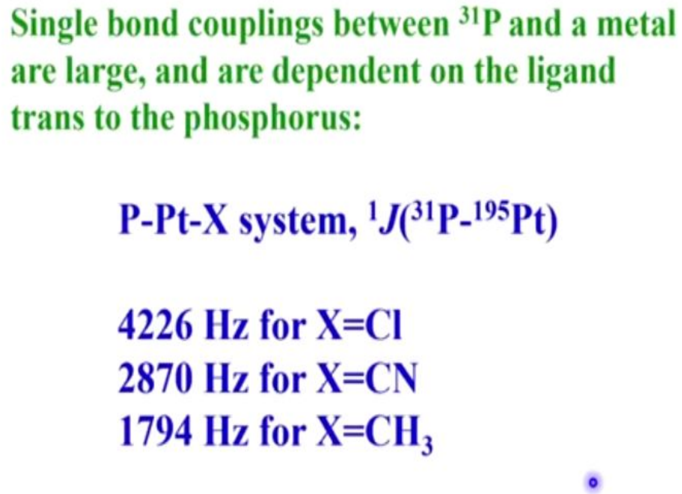

Single bond couplings between $^{31}$P and a metal are large, and are dependent on the ligand trans to the phosphorus:

P-Pt-X system, $^{1}J(^{31}P-^{195}Pt)$

4226 Hz for X=Cl
2870 Hz for X=CN
1794 Hz for X=$CH_3$

So, just to give an idea heteronuclear interactions, heteronuclear couplings can be substantially larger. So, that is what I wanted to tell you in this class and I wanted to give you few examples. In the case of platinum I consider a system like this 31P-Pt-X, we can look at platinum to phosphorus coupling; see phosphorus is spin half nucleus. So, if I look at that the coupling between phosphorus and platinum, where X is substituent, depending upon the substituent, if it is chlorine, it can be of the order of 4.26 kilohertz and if X is CN group, it is close to 2.9 kilohertz. That is the order of coupling. See so far we were discussing about proton and carbon, where the coupling constants is of few 100 hertz; in case of proton it is few tens of hertz, but when you go to exotic nuclei some of the rare nuclei, or the other hetero nuclei, they are so exotic the coupling constant can be of order of several kilo hertz, this point you have to keep in mind.

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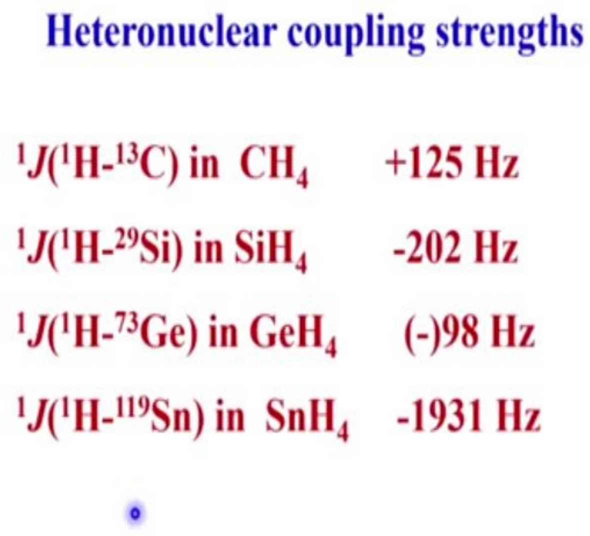

## Heteronuclear coupling strengths

$^{1}J(^{1}H\text{-}^{13}C)$ in $CH_4$ +125 Hz

$^{1}J(^{1}H\text{-}^{29}Si)$ in $SiH_4$ -202 Hz

$^{1}J(^{1}H\text{-}^{73}Ge)$ in $GeH_4$ (-)98 Hz

$^{1}J(^{1}H\text{-}^{119}Sn)$ in $SnH_4$ -1931 Hz

I just want to give you another example; take the methane, methane has carbon proton coupling which as I told you will not see it in either carbon spectrum or proton spectrum. Carbon spectrum I would say if I take coupled carbon 13, you will see it, I take back my sentence you will see that. In the case of the protons, you will not see proton-proton coupling; CH coupling you will see but it is very weak, and are satellites.

Now in the carbon proton coupling if you want to see this CH4 group it is of the order of 125 hertz; this is what I said, when we discussed about the carbon photon couplings. Now the same thing, instead of CH4, take SiH4, now proton to silicon coupling is 202 hertz; but it has a negative sign because silicon 29 has negative magnetic moment. All the nuclei which have negative magnetic moment, their signs of the couplings you have represent by negative sign.

For example, 1 bond 15N-1H coupling is 90 hertz. Many times people write 1JNH equal to 90 hertz. In principle you have to write as 1JNH equal to minus 90 hertz, because nitrogen 15 has negative magnetic moment. Similarly, in this case for example silicon has this one, of course sometimes even in the case of two nuclei with positive gayromagnetic ratio also, there can be a negative sign; that is a different question.

I took this example of silicon because, I know silicon 29 has negative magnetic moment. Look at Germanium, instead of CH4 if I get GeH4 it is -98 hertz with negative sign. And the other hand if it is SnH4 it is close to 2 kilo hertz. See these are the things which I wanted to point out, to keep it in mind.

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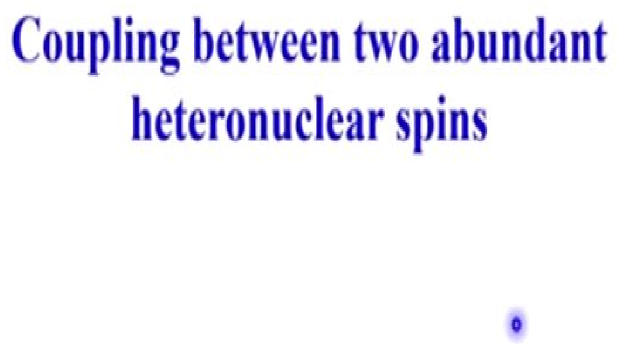

Coupling between two abundant heteronuclear spins

Now what you do is, we will understand the coupling between different abundant heteronuclear spins. How we can observe?

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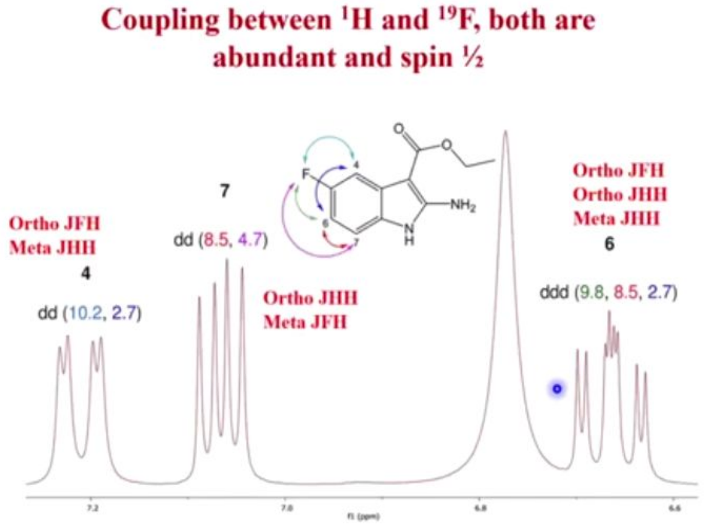

Coupling between $^{1}H$ and $^{19}F$, both are abundant and spin ½

Take a molecule like this. Now there is one fluorine here, of course, we saw that in the fluorine proton coupling everything earlier, but again, I want to brief it to you can get coupling between proton and fluorine, both are hetronuclei but both are spin half, both are abundant, almost 100% proton is 99.98, it is 100%. Take it both are 100% abundant. Now the fluorine is substituted in the molecule here, you can easily get coupling of this fluorine to this proton, coupling of this fluorine into carbon if you look for 13C NMR, all couplings are visible.

The coupling strength of fluorine to proton can be 2 bonds, can be 3 bonds, and you can see everything. Okay? So, if ortho fluorine proton coupling you have to see, this is generally of the order 8-10 Hz and meta is about 1- 3 hertz. Exactly similar to proton. In the phenyl ring I told you proton-proton coupling is 8 to 10 hertz, it can be 7-10 Hertz and meta coupling, I said is 1-3 Hertz; exactly same here. Just by substitution of the fluorine, the coupling range do not change much.

Similarly, here if you look at this proton 4 here, If you look for this proton 7 here, we have ortho HH coupling and we also have a meta FH coupling here. This experiences 2 couplings; one, of course homo nuclear and one heteronuclear; two couplings, it is experiencing both homo and hetero nuclear couplings. Same here also, proton 4 is experiencing both homonuclear and heteronuclear couplings. This is like the analysis of proton spectrum; more or less; like you analysed the proton spectrum, looking at this type of pattern.

There is not much of a difference here, especially in the ring system like this, between proton and fluorine the couplings are more or less similar to proton-proton coupling. Here again if you look at the proton 6, it experiences ortho FH coupling, Ortho HH coupling and Meta HH coupling; all the 3 couplings are expected here. See that is why this has a funny pattern like this we can interpret that and easily. I just want to show you, how we can analyze the spectrum. For example, you look at this proton 4; ortho coupling is about 10 hertz.

It is a large doublet and is also experiencing a meta coupling, which is about 2.7 hertz. So it is doublet of doublets. Now what about Para coupling? It is there but you are not seeing it, it is very weak so we do not see it. Now coming to proton 7, ortho coupling makes it a doublet; the meta coupling between fluorine and proton is about close to 4.7 hertz. So, it is a well resolved doublet of doublets. So, the analysis of this type of spectrum when photon, fluorine is coupled is fairly simple, is not that difficult.

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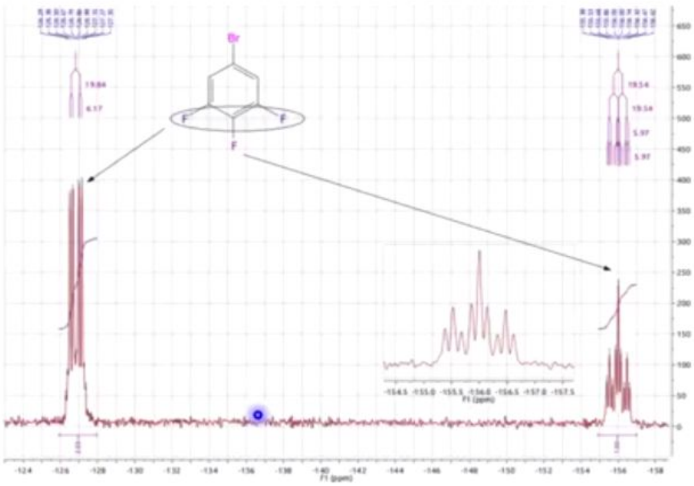
**The $^{19}F$ NMR spectra of $C_6F_3H_2Br$**



So, to extend this, if I look for a molecule like this; you have two fluorines and one fluorine here and if I look at this fluorine What is going to happen? It is coupled 2 fluorines almost equally. Because of the perfect symmetry they are chemically equivalent, coupling is also same; then it will become instead of doublet of doublets; the central lines of the two doublets overlap, it looks more like a triplet. Interesting right, it looks more like a triplet.

Interestingly these two protons are also coupled to this with equal coupling strengths, this proton to this fluorine and this proton to this fluorine, the meta couplings between proton and fluorine are both equal. Again, it looks like a triplet pattern because the couplings are equal; the central lines of FH couplings also overlap. So, what you are going to see is triplet of triplets for this fluorine. Very clear; see the interpretation is not difficult.

I hope you are all with me. Just to make you understand, I will repeat once again. Look at it; this fluorine is chemically inequivalent compared to these two fluorines; there is a perfect symmetry for this molecule. So, this fluorine and this fluorine are chemically equivalent. At the same time the coupling of this fluorine to this, this fluorine to this; are also equal. It means if I look at the splitting pattern of this fluorine, it should be doublet of doublets.

Because both the couplings are equal, remember we worked out the multiplicity pattern, when both the couplings are equal the central lines of two doublets; both lines overlap; as a consequence, it appears like a 1 :2 :1, triplet. Exactly 1 :2 :1, triplet. Similarly, this proton and fluorine coupling; this proton and fluorine couplings; these two meta couplings are also identical. And they are also a couple to this fluorine.

As a consequence again, it looks like a triplet. So, each chain of this triplet is further split into triplet of triplets, each line is a triplet. So it is going to be a triplet of triplets. Now on the other hand this one they are equivalent, you should treat like a single fluorine. So, it will couple with this fluorine and becomes a doublet; and again, it will couple with these 2 protons which are equivalent, again, it is a doublet. So, it is going to be doublet of doublets. You understand, what is the largest coupling? It is between this and this, FF coupling. It is about 19.84 Hz and this meta coupling is about 6.17 hertz, as a consequence it appears like the doublet of doublets. Are you all with me? This is easy to understand, very easy to interpret the spectrum, it is a very simple molecule; we have heteronuclear couplings and also homo nuclear couplings; between abundant spins.

But only thing is  HH coupling you do not see, in the 19F NMR, because I am looking at fluorine; that is what you should understand.

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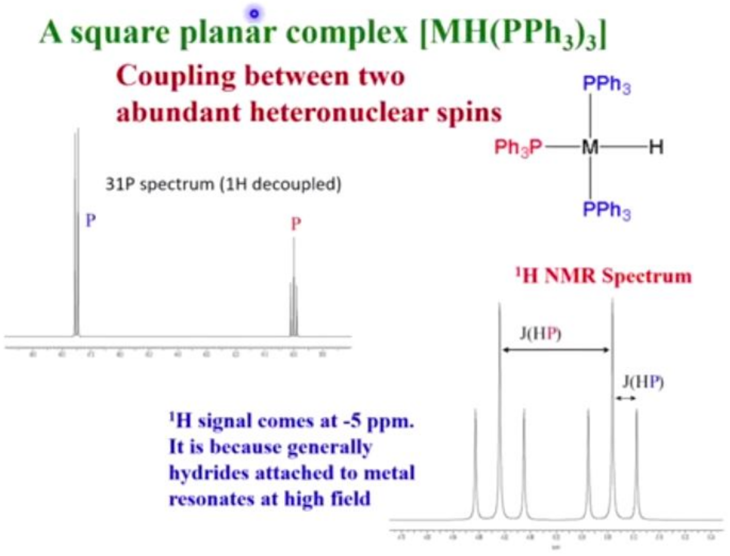

**A square planar complex [$MH(PPh_3)_3$]**

**Coupling between two abundant heteronuclear spins**

31P spectrum (1H decoupled)

**$^1$H NMR Spectrum**

**$^1$H signal comes at -5 ppm. It is because generally hydrides attached to metal resonates at high field**

Now I look for another example where two abundant spins are coupled. So, what is happening now? When two abundant spins are coupled, look at it, what are two abundant spins, phosphorus and proton; both are abundant. Let us look at the 31P spectrum of this molecule; a complex. How many types of phosphorus are there here, this is one phosphorus, this is one phosphorus and this is another type of phosphorus.

Because there is a perfect symmetry along this axis, it is a square planar, So, now what I am going to see is this phosphorus and this phosphorus are chemically equivalent; and this phosphorus is different. If I see phosphorus spectrum of this molecule, how many peaks I should expect? I must expect lot of peaks, remember, First phosphorus, phosphorus coupling is seen and phosphorus proton couplings can also be seen. To simplify this spectrum what is done here is protons are decoupled.

Remember I explained to the carbon-13 NMR, you can completely remove all the couplings of protons to all carbons by broadband coupling. Exactly you can do this, I said at that time also. This type of broadband decoupling is not restricted only to carbon 13. You can do this for all any nuclei of your interest now, now we are observing phosphorus decoupling all protons coupled to it. So, now we are seeing only there is no proton-phosphorus coupling. If at all, we see only phosphorus-phosphorus coupling. This also will not couple, this is a metal, that is different question. So, How many peaks you expect? two peaks, these two are equivalent to one phosphorus, it is another phosphorus. Very nicely you can see. But now, you understand the pattern this phosphorus is a doublets, why? This phosphorus they are equivalent coupled to this phosphorus. So, this phosphorus makes these two as a doublet.

It is like CH and CH2, CH coupled to CH2 proton. For CH2 will be a singlet. Right? Similarly two equivalent phosphorus is a singlet; and the other hand, if I see this phosphorus it experiences equal couplings between these two phosphorus. CH protons coupled to CH2 what do you expect? A triplet, exactly; this phosphorus is a triplet because of these two phosphorus couplings and this phosphorus these 2 are doublet, because of this coupling to this phosphorus.

So, these two are chemically equivalent; and center of this gives you chemical shift of this phosphorus, center of this gives you chemical shift of this phosphorus. What happens if I see the proton NMR of this that is interesting; proton NMR if you see what happens, this is coupled to this, this is coupled to this phosphorus and makes this a triplet. But at the same time this is also coupled to this phosphorus. You may be wondering what happened to your phenyl proton; that is far away and that is a long range coupling, you will not see. But this phosphorus can split with this.. Okay? this will make a large doublet, because the HP coupling is larger and each line of the doublet is split into triplet because of these two equivalent phosphorus; is it clear for you.

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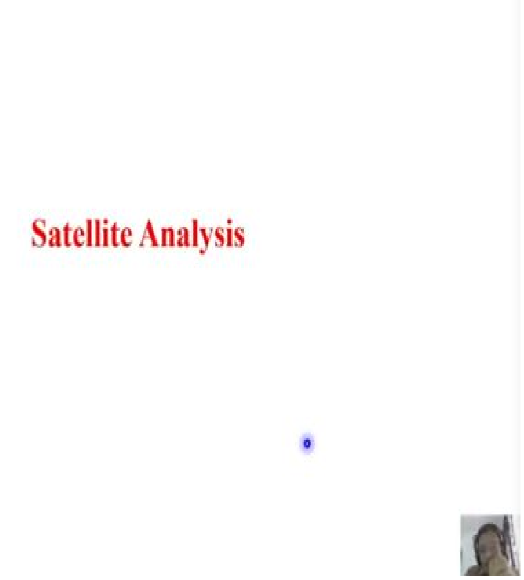

Satellite Analysis

Now, I will bring in another concept of satellite analysis. What is the satellite analysis?

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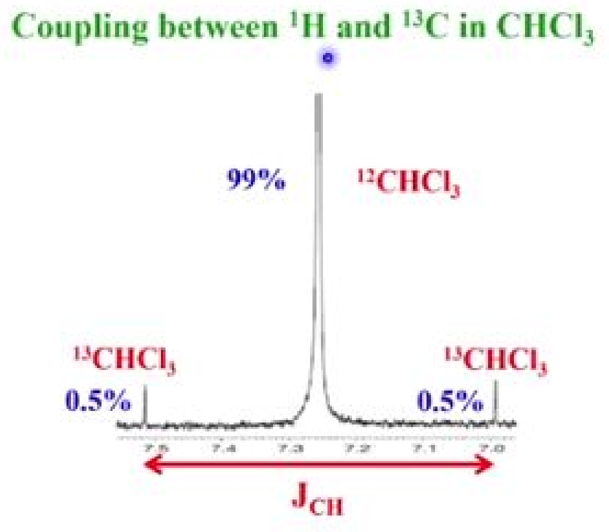

Coupling between $^1H$ and $^{13}C$ in $CHCl_3$

We will understand this now. Let us look at the proton spectrum of CHCl3, not carbon 13. I am taking proton spectrum. Remember when I analyze this spectrum; and I told you for a single spin half nuclei, when I was analysing the spin system, I said it will give a single peak for proton. True, no doubt about it. When I see carbon 13 spectrum, I see a doublet. It has CH carbon and gives a doublet I told you, remember, in the analysis of carbon spectra, I said CH3 is a quartet, CH2 is a triplet and CH carbon is a doublet. Correct?

If I see carbon spectrum it is a doublet and if I see the proton spectrum, it is a singlet. How is it possible? Remember, I also said interactions in NMR are mutual. So, proton is coupled to carbon, carbon is also coupled to proton. Then the question is, why protons spectrum is not a doublet, why only carbon is a doublet? The answer to this question lies in understanding the isotopomers, understand? You have to see what are the types of isotopomers.

Carbon 13 has two isotopes, carbon 12 and carbon 13. This abundance is 1% as I have been telling you. this abundance is only 1%, So, if I take 100 molecules of CHCl3, only one molecule is carbon 13. Remember in the carbon-13 spectrum analysis I discussed this in depth, we extensively discussed this abundance factor. So, it will be one molecule existing as carbon 13. 99 molecules among hundred molecules, will exist as carbon 12.

And what you see in proton spectrum, corresponds to 99% of the molecules, which are attached to carbon 12. 12CHCl3. What the magnetic moment of carbon 12? spin is 0. So, there is no magnetic moment, so this cannot couple to this proton. As a consequence, you will see only one single peak. But why did you see doublet in carbon 13 NMR. Because there you are directly looking at the carbon-13 isotopomer.

In the proton it is a mixture of both carbon 12, carbon 13 isotopomers, remember. So, in the proton NMR, we have mixture of isotopomers, where largest peak intensity correspond to this isotopomer. And what happened to 1% of carbon 13, that is present; and that splits because of carbon 13 into a doublet. You see, you take the proton NMR spectrum of CHCL3 enhanced intensity. You are going to see two small peaks on either side, it is at equidistant, of course most of the time it will be equidistant, but there is also called isotope effect, I will discuss later, as a consequence, a small difference could be there, but generally they are equidistant from the center of the peak.

But what is intensity of it? This is 99%; but this only 1% carbon? But that carbon is coupled to proton. What will happen to intensity of the peak? It will divide itself into two, because there are now 2 peaks. So, one peak became 2; remember this splitting pattern I explained, the intensity now reduced to half. So, what happens to the carbon 13 intensity, is only 0.5% compared to 99% of carbon 12, it is very weak peak. That is why these are called satellites, small peaks. Whenever you observe an abundant spin, if it come coupled to a low abundant spin, abundance of the order of 1% or 2%, or 5% like that, then that coupling gives satellite peaks.

Major peak is because of other isotopomer and I said satellites will come because of coupling to a low abundant nuclei. Now carbon-13 abundance 1% and you got a doublet because of carbon proton coupling with intensities of 0.5 and 0.5. Hence these are called satellites; remember that. And this separation gives me coupling between proton and carbon. If you go to carbon-13 spectrum and get the carbon spectrum coupled, carbon coupled spectrum with proton, you will get doublet with the same separation. Then there also you can get J coupling, here also you can get J coupling, understand? This is what it is. So, what I said interactions in NMR are mutual, it is valid. See here also you can see this coupling; you can also see carbon NMR. But why initially

I posed a question that we are not seeing, is because of this isotopomer; that is it for point. Please remember this point now.

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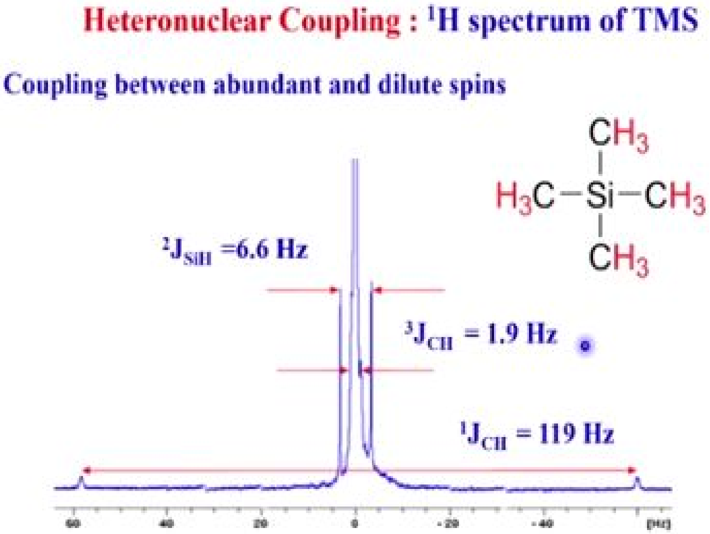

Heteronuclear Coupling : $^1$H spectrum of TMS

Coupling between abundant and dilute spins

Now, these types of satellite analysis I want to show you with one or two more examples. For example, look at tetramethylsilane. Now abundant spins are protons. Carbon is 1% abundant. Silica is also about 4% abundant. Okay? Very small percentage. Now where we should see silicon? We should see them as satellites. Now if I look at the proton NMR spectrum of tetramethylsilane.

Now the larger component of the proton signal comes because of carbon-12 attached to protons, this one. And carbon-13 coupled to proton appear as satellites here. The silicon-29 can also couple to proton; that is also because of less abundance appear as satellite here; you can see those satellites. This peak and this peak which is about 6 hertz separation, is silicon proton coupling; it is one and 2 bond coupling.

So, one bond CH coupling is 119 hertz. And two bond silicon proton coupling is 6.6 hertz, but it may so happen, remember, I was telling you in the carbon 13 NMR, this carbon can also couple to this proton, when I see the coupling. So, this 1, 2 and 3 bond proton carbon coupling also can be seen. There is only one such possibility; all are equal. If I see this carbon; this is 3 bond, if I see this carbon this is 3 bond, this is 3 bond; all are 3 bonds away.

So, there are 2 types of carbon couplings here, carbon proton, 1 bond carbon proton close to 119 hertz and 3 bond carbon protons close to 1.9 hertz; you can see here. Very weak in intensity and these are called as satellite peaks. But you can analyze, you cannot ignore them; you can analyse this measure separation, then I can get the J coupling between carbon and proton, I can measure one bond coupling, I can measure this separation, I can get 2 bond Silicon proton coupling. I can measure this separation; I get 3 bond carbon proton coupling. So, though these satellites are there with weak intensity, you acquire the signal, enhance the intensity to a larger height and then look for these satellite peaks. You can analyze; this is called satellite analysis. You can do that and get the coupling information.

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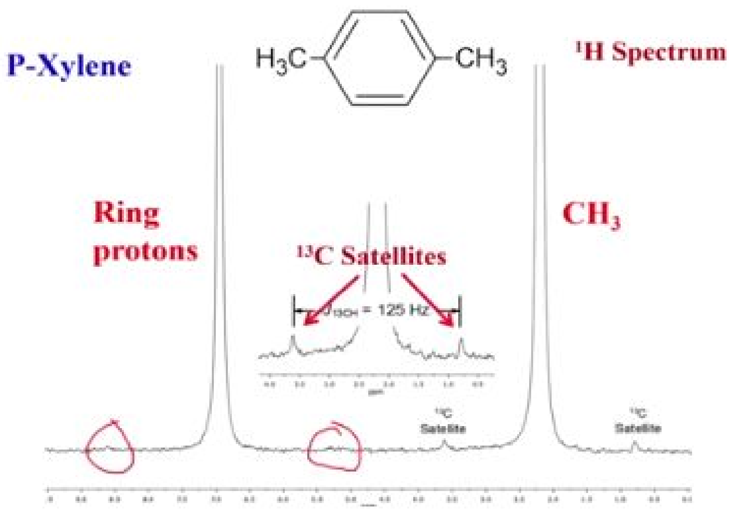

So, now I am asking you a question, this a para-Xylene, para-Xylene if look at it, we have ring protons, one peak, all are equivalent, we have 2 CH3s; they are chemically equivalent giving rise to a single peak. Now look at this proton, if you enhance the intensity largely; increase intensity by 3 to 4 times or five or ten times, these small peaks start coming up.

What are they? They are carbon13 satellites. Why is it a doublet? Because this proton is coupled to this carbon. As a consequence, this CH3 peak is a doublet, this proton peak becomes a doublet due to coupling with carbon spin half and gives the doublet. Measure this separation, what you will get? Carbon proton coupling. You asked me a question, why did we not see the same thing in ring?

Of course if you see carefully, if you do the experiment, acquire the signal for a long time and enhance the intensity, you can measure CH coupling for this ring carbons also. But I do not want to disappoint you, if you carefully see you will see a peak here and this peak. If I enhance the intensity a larger I will see the satellites, this coupling, this separation correspond to carbon proton coupling.

But this is not a good spectrum, signals are not acquired for a longer duration. So, you do not see it but if I acquire the signal for another half an hour then you see the satellites like this for this carbon also, understand? So with this now the satellite analysis hass become very clear for you.

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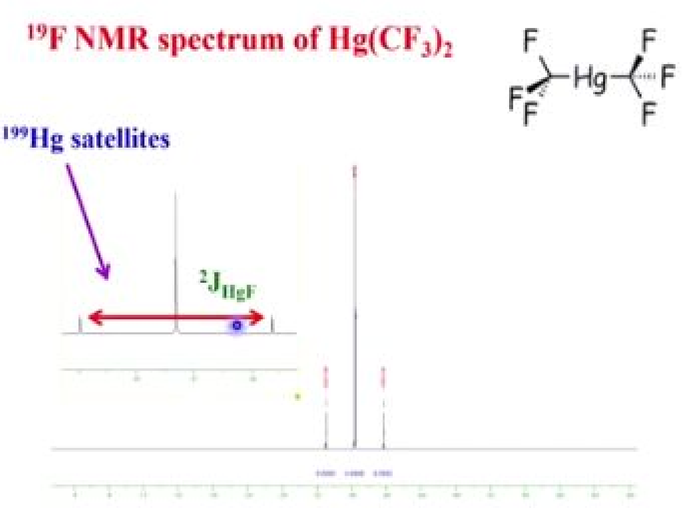

This satellites need not be restricted to only carbon. I said carbon is there, silicon is there; any of the low abundance spin can be see as a satellites. Now in this molecule, if you look at the fluorine NMR, How many peaks you expect for fluorine? There is a perfect symmetry, all fluorines are equivalent. As a consequence, you get only one peak for fluorine, we got only one peak. But what are these two peaks coming on either side? Extra peaks, this is because they are coupled to mercury, these 6 fluorines are coupled to mercury. As a consequence, what you are seeing is one and two, two bond mercury 199- fluorine coupling; and this intensity is quite large compared to carbon 13 satellites, carbon is only 1%. So, mercury abundance is much better than carbon. As a consequence, this intensity also is better. You please remember this point only for carbon we got weak intensity, because of less abundance.

You should not expect the same for all satellites. It depends upon the abundance of coupled nuclei. So, in this case mercury abundances is much better, than carbon. So, satellite peaks are reasonably good to analyze.

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Homonuclear couplings ($J_{HH}$) in Satellite Spectrum

Now I look for the homo nuclear coupling in the satellite spectrum. Now the question is if I analyze satellite spectrum what would I get? I will tell you if I analyze the satellite spectrum some information which you cannot get in the proton spectrum you will get, and we did solve this in one example. I do not know whether you remember, and the spin system analysis of AA'X coupled spin system, using Pople nomenclature I showed you how to distinguish between cis and trans isomers.

Remember where I showed you? Proton spectrum gives a single peak; taking carbon 13 into account you will break the symmetry and for the satellites peak we got, for cis and trans, one has a larger coupling, one has smaller coupling and identified cis and trans. I hope you are all with me. Please do not forget, keep following me regularly, that I discussed there.

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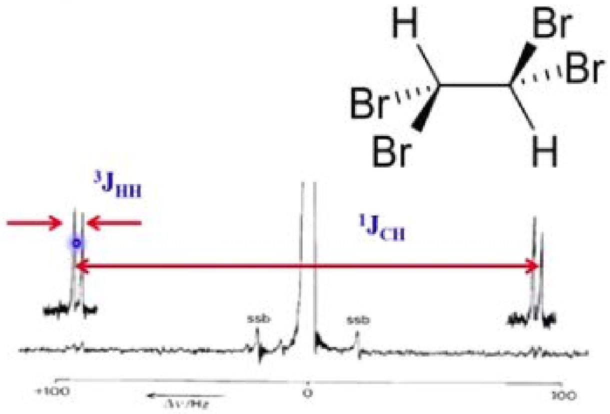
**$^1H$ spectrum of 1,1,2,2- tetrabromoethane**



**Symmetry is broken. $A_2$ spin system becomes AA'X**

Exactly you can do that to analyze and can get the homonuclear coupling which you normally cannot get in the proton spectrum. Look at this one, it is a case of tetrabromoethane 1,1,2,2. Now this proton and this proton are chemically equivalent; like an A2 spin system. So, what can you get here? if you take a proton NMR spectrum, you are going to get a single peak. But if I want to find out what is the coupling between this and this? How do I find out?

I told you this is a A2 spin system, that is why I introduce spin nomenclature, remember, before we came to analysis. Now I will consider this carbon in the state of carbon 13, if this carbon exits as carbon 13, now it is no more A2, symmetry is broken. Then what do you call it? Because coupling exists, now it is AA' coupling. They are chemically equivalent but coupling also exists, now it will become AA'X.

Why I call it AA'X because AAX coupling and AA'X couplings are different. So, it cannot be A2 now. It has to be AA'X spin system. This we analysed earlier. Now what I do is forget about this is a olden days experiment, they were spinning the sample and used to get artifacts, because of the inhomogeneity of the magnetic field, we will worry about it later. I will discuss when I come to practical applications.

So, now these are the satellites, plotted with the enhanced vertical intensity? What this separation gives you; this separations from center of this doublet to center of this doublet? What you get on either side? This is one bond CH coupling. And why each of them is a doublet. It is because it is 1,2,3 bond HH coupling, remember I am observing proton. So, this coupling is seen and this coupling is seen, both are seen.

So, we are going to see 3 bond proton-proton coupling in the satellites. So, satellite analysis gives me homonuclear couplings among chemically equivalent spins, which are not possible to get from the regular one dimensional NMR spectrum. So, what we did is; we did not do anything for this molecule. Only thing is, we took the NMR spectrum and started looking for the carbon 13 satellites. As a consequence, we know the symmetry of the molecule is broken and A2 spin system becomes AA'X spin system here, the analysis gives me both CH coupling and HH coupling.

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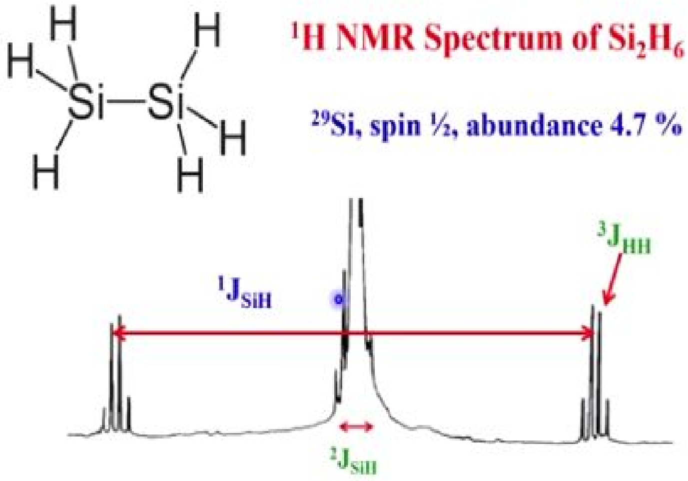

$^1$H NMR Spectrum of $Si_2H_6$

$^{29}$Si, spin ½, abundance 4.7 %

This is another example same. In the previous molecule it was bromine substituted tetra bromoethane, and now it is Si2H6 molecule. Here no carbon; but we can see SiH coupling and also HH couplings. Look at this one now; this silicon is spin half nuclei and is 4.7% abundant. When I do this proton NMR, I get a single peak. Coupling to silicon is only 4% intensity; because they are satellites. And that is seen because only 4% of the molecule are present as silicon-29.

But this separation to this separation gives me what? one bond silicon proton coupling. Center of this quartet, to centre of this quartet if I measure, I get one bond silicon proton coupling. At the same time, if you look at this one, what is this we are getting? This is HH coupling; this proton is coupled to this, because now you have broken symmetry. This CH3 group and this CH3 groups are not same. When I consider this silicon, they are different. So, this can split this, or this can split this. As a consequence, now these equivalent protons are split by SiH3 group and will be a quartet. So, satellites are appearing like a quartet. You analyze this, what you get 3 bond proton, proton coupling; this is one bond and of course if you carefully see, you can see 2 bond SIH coupling. But some peaks are hidden here. Okay? This also has to be a quartet, but it is hidden here, you can see 1,3,3,1 is hidden. So, we will not be able to extract clearly, but it is there. All coupling information will be easily extracted. You understand, you go the point as how to analyze the satellites,  how we analyze the satellite spectrum to derive the information, which is not possible to extract from the proton spectrum. Okay. I am going to stop now.