One and Two Dimensional NMR Spectroscopy for Chemist

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Lecture - 27
Geminal and Vicinal couplings

Welcome back, we have been discussing a lot about scalar couplings, coupling mechanism, varieties of splitting patterns when different chemical equivalent, inequivalent groups are coupled, intensity pattern and the nomenclature used for the splitting pattern like; doublet, triplet, quartet, sextet, quintet, varieties of nomenclature, everything we have discussed at a stretch and we also talked about varieties of coupling strengths possible.

Now continuing further quickly, no point in continuing further, see there is no end for it, we can keep on discussing on this scalar couplings itself for several hours. At some stage will have to put a stop. I hope I have given you an idea about what is the scalar coupling, how we can get information etcetera, but you will have to take it further by reading. Voluminous amount of literature is available, books are available you can continue.

But at the moment today, I will give you a few information about strengths of the coupling, little bit, varieties of coupling possible cis-trans, geminal etcetera and I am going to quickly end this and then we move over to analysis of this spectrum and define spin nomenclature etcetera.

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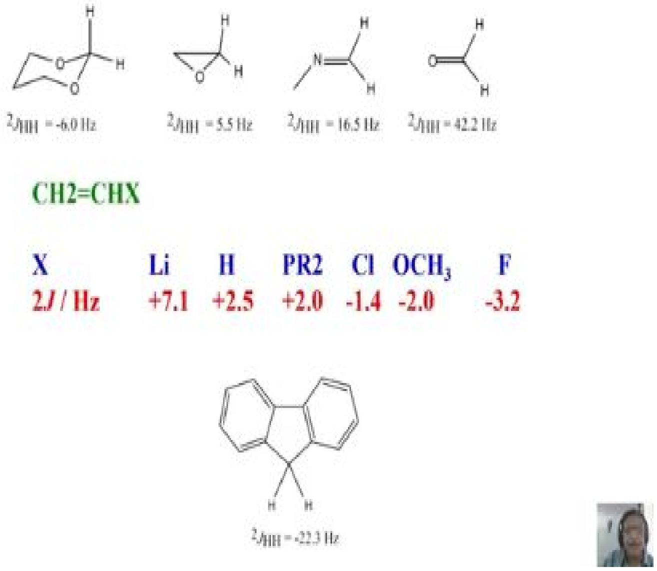

$^2J_{HH}$ = -6.0 Hz

$^2J_{HH}$ = 5.5 Hz

$^2J_{HH}$ = 16.5 Hz

$^2J_{HH}$ = 42.2 Hz

CH2=CHX

X	Li	H	PR2	Cl	OCH_3	F
2J / Hz	+7.1	+2.5	+2.0	-1.4	-2.0	-3.2

$^2J_{HH}$ = -22.3 Hz

So first thing is, of course look at the type of coupling we have. I already said we will start with one bond, two bond, three bond coupling. I discussed three bond couplings, if it is cis and trans, I also said trans coupling in many examples like olefins and substituted ethylene, etcetera, trans coupling is larger than cis coupling. Geminal coupling also has some interesting things. For example molecules like this, if I consider geminal coupling here, two bond coupling, it is -6 Hz.

Whereas in this molecule where C=O is attached the geminal coupling is 42.2 Hz. So we cannot simply say, a scale is there where you can say because of this, this is the coupling. Unlike cis and trans vicinal couplings, where by and large the trans coupling is larger than cis in many examples, which I am going to tell you today; the geminal couplings can vary like this and sometimes you can have a negative sign also.

That is important thing, you should see in this example, coupling starts from -6 goes up to 42.2 Hz by just mere change of the substitution. Look at this ring, and look at, this is only a small change here and here C double bond N is changed to C double bond O, the coupling changed drastically. Now similarly CH2=CHX type of molecule if I consider, now geminal coupling between these two protons if you consider and if it is nonequivalent, I am talking, in which case what happens if I have a substitution X? Depending on that, depending upon what is X? It can be lithium, proton, PR2, Cl, etcetera, it can vary from +7.1 to -3.2. Systematically it is changing, you can see that. The substitution has a tremendous effect on this geminal coupling including the magnitude and also the sign.

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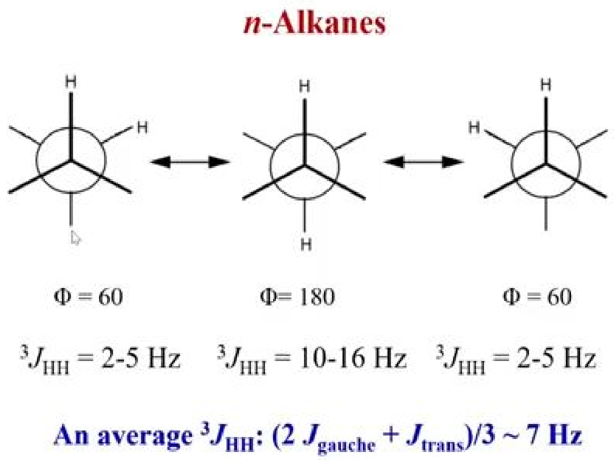

_n_-Alkanes

$\Phi = 60$ $\Phi = 180$ $\Phi = 60$

${}^{3}J_{HH} = 2\text{-}5$ Hz ${}^{3}J_{HH} = 10\text{-}16$ Hz ${}^{3}J_{HH} = 2\text{-}5$ Hz

An average ${}^{3}J_{HH}$: $(2\,J_{gauche} + J_{trans})/3 \sim 7$ Hz

And this is n-Alkanes, if you consider this type of molecules. This can undergo rotation like this which can have orientation like this, you can have a φ angle between this three protons and other one and between the CC bond, there can be a rotation; and if the angle of rotation if φ is equal to 60 degree, 3J coupling can be 2 to 5 Hz. If the φ angle between these two is 180 degrees, it is 10 to 16 hertz.

Look at this one, how when the interchange is going on between thes conformations; and for this conformation when phi is 180 coupling can be very large of the order of 10 to 16 Hz. So it can give information about the conformation. J coupling is used to get some information about alkanes.

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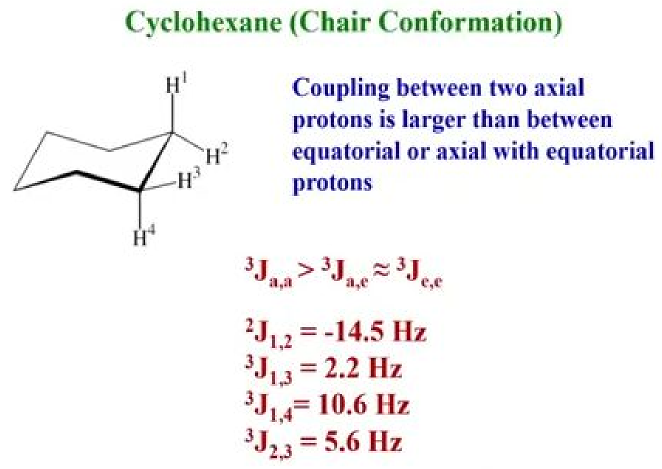

Cyclohexane (Chair Conformation)

Coupling between two axial protons is larger than between equatorial or axial with equatorial protons

$^3J_{a,a} > {}^3J_{a,e} \approx {}^3J_{e,e}$

$^2J_{1,2} = -14.5$ Hz
$^3J_{1,3} = 2.2$ Hz
$^3J_{1,4} = 10.6$ Hz
$^3J_{2,3} = 5.6$ Hz

For example, if I take Cyclohexane, I am just use chair structure conformation. Coupling between two axial protons is larger than between equatorial and axial and between two equatorial protons. Simply I tell you if I have three bond coupling between proton axial- axial protons, this is larger than axial-equatorial coupling, which is approximately equal to equatorial-equatorial coupling, remember this point.

Take an example of this 1, 2 coupling; J12, this can be 14.5 Hz with negative sign, whereas J13 between this and this can be 2.2 Hz. Between 1 and 4 here, this can be 10.6 Hz. So this coupling information can also give information and the strength of coupling can give idea about type of conformations in cyclohexanes also.

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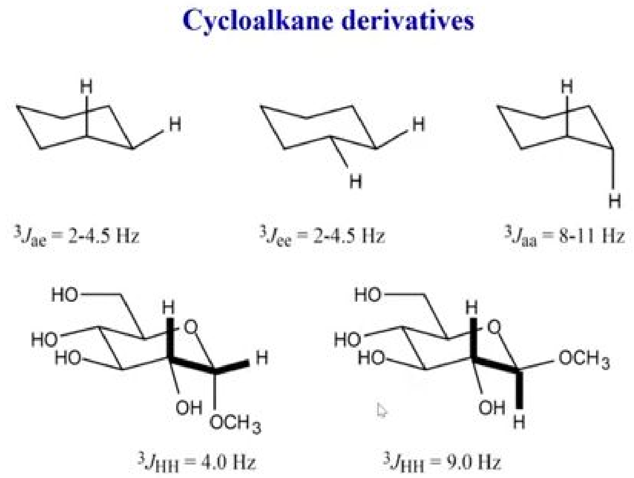

Cycloalkane derivatives

$^3J_{ae}$ = 2-4.5 Hz

$^3J_{ee}$ = 2-4.5 Hz

$^3J_{aa}$ = 8-11 Hz

$^3J_{HH}$ = 4.0 Hz

$^3J_{HH}$ = 9.0 Hz

And the same is true even in cyclohexane derivatives also. Look at this molecule if I take this one with axial equatorial coupling, is about 2 to 4.5 Hz. In this molecule on the other hand, it is 8 to 11 Hz. Most important you see the 3 bond coupling for this structure and this, this is cis and this is trans. 3 bonds cis coupling is 4 Hz, trans is 9 Hz. This can give you information about the conformation of cyclohexane derivatives also.

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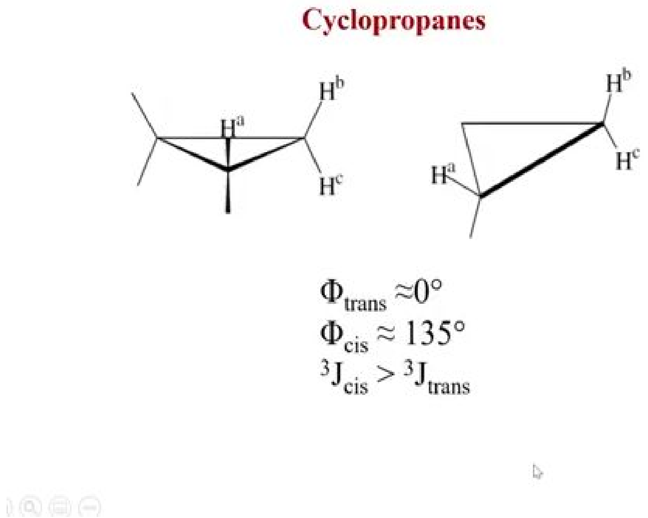

Cyclopropanes

$\Phi_{trans} \approx 0°$

$\Phi_{cis} \approx 135°$

$^3J_{cis} > {}^3J_{trans}$

Cyclopropane, it is another thing, a classic example in which cis coupling is larger than trans coupling. In trans is φ is approximately equal to zero degree. If it is a cis conformation, φ is approximately equal to 135 degree. Now find out the J coupling. The Jcis is quite large, then you know what is the angle of this. So very easily you can approximately get, from the coupling strength, whether it cis or trans, you can get the angle.

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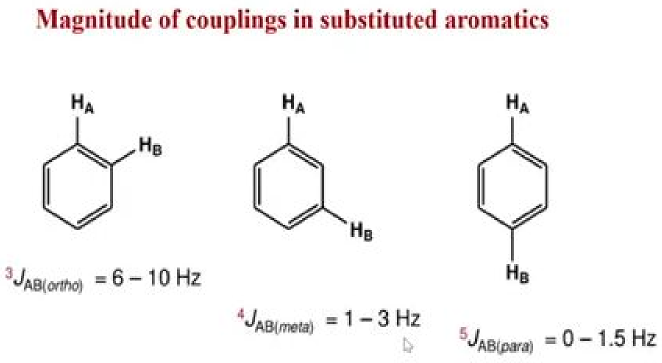

Magnitude of couplings in substituted aromatics

$^3J_{AB(ortho)} = 6 - 10$ Hz

$^4J_{AB(meta)} = 1 - 3$ Hz

$^5J_{AB(para)} = 0 - 1.5$ Hz

Another point is aromatic system. You always come across aromatic systems in your molecules. Look at this one, this is ortho coupling. You should not write, AB that is wrong. AB means strongly coupled. It is only a label not coupling number, not spin system nomenclature**.** Ortho coupling can be very large, 6-10 Hz. Remember in the case of substituted aromatic, I am talking, it can be have some substitutions here, and here, like that no problem.

Like benzene where I showed you ortho coupling varies from 6 to 8 Hz. Similarly, meta 1 to 3 hertz, para 0 to 1 Hz. Here also substituted aromatics also, ortho, meta and para couplings; 3 bond, 4 bond, 5 bond varies of this order. Here it is, ortho is 6 to 10, meta is 1 to 3, and para is 0 to 1.5 Hz.

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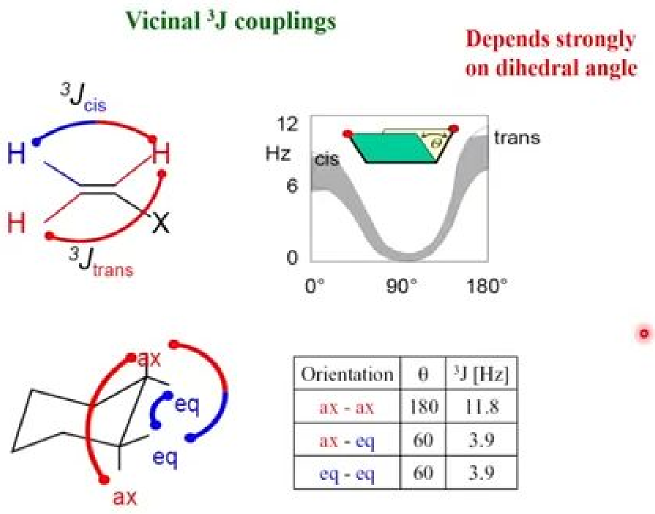

Vicinal ^3J couplings

Depends strongly on dihedral angle

Orientation	θ	^3J [Hz]
ax - ax	180	11.8
ax - eq	60	3.9
eq - eq	60	3.9

So vicinal coupling if you look at it, the vicinal coupling especially 3J coupling if you take, it depends strongly on dihedral angle, very strongly on dihedral angle. Look at this one, the dihedral angle is 90 degree, this coupling is close to 0. When it is cis orientation, it is any-where between 6 to 10 Hz. When it is trans orientation with 180 degree, the coupling can be quite large enough, it can start from 8 and go to 12 Hz.

So the 3 bond vicinal couplings gives an idea about axial-axial orientation, axial equatorial, equatorial – equatorial. Depending upon the angle theta, you have different coupling strengths. So you will get information about conformations of molecules.

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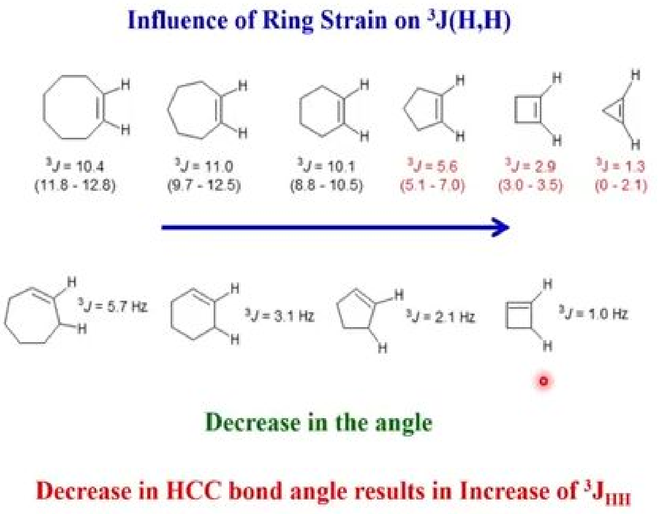

Influence of Ring Strain on $^3J(H,H)$

Decrease in the angle

Decrease in HCC bond angle results in Increase of $^3J_{HH}$

Another point is, some information I am giving you, just to get a feel for it. You do not have to worry about it, you do not have to even mug up or remember. It is just for the sake of giving an information, so that you should know when you are analyzing a spectrum, what are the points to look at. This information you can also get from the books. See, as the rings strain keeps on decreasing here from 8 membered, 7, 6, 5, 4, 3, except some anomaly here, steadily this coupling strength decreases, as you go down.

Same here also you see 3J coupling, ortho coupling here 5.7, 3.1, 2.1 and 1.0. As the size of the ring reduces the coupling strength steadily decreases. So decreasing the angle, HCC bond angle results in increasing 3JHH, this is an information.

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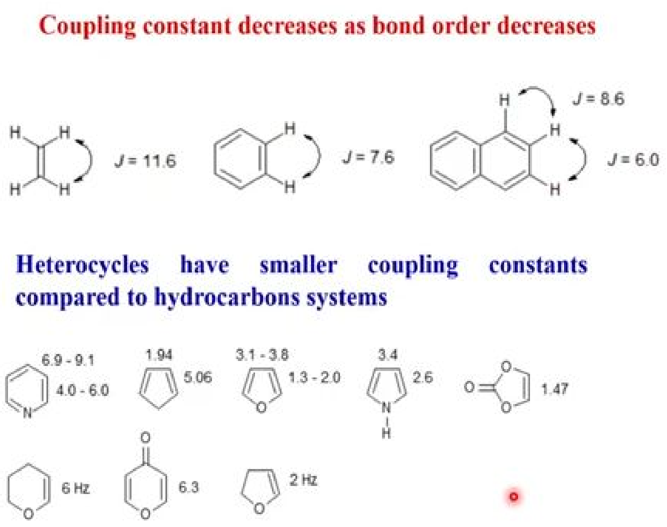

Coupling constant decreases as bond order decreases

Heterocycles have smaller coupling constants compared to hydrocarbons systems

Of course it also depends upon the bond order. In this case you remember, when the chemical shifts we were analyzing, I said all the four protons are equivalent. The ethylene proton comes at 5.29 ppm earlier. I told that, I hope you all remember. The coupling in this case is 11.6 Hz. You understand, you may ask the question, how do I got the coupling here? All are equivalent, it gives a single peak. Similar to benzene, it gives a single peak.

So the question is how did we get the coupling is a point will have to discuss later. I will tell you how to get the coupling information in equivalent spin system. For example, hydrogen molecule I told you 1 bond coupling is 276 Hz. How do I get that information? One of the classes I will discuss how to get the coupling in equivalent spin systems, where coupling is not reflected in the spectrum.

So now similarly here if you look at it this is 7.6 Hz, whereas in this case depending upon this, this is 6.0 Hz, this is 8.6 Hz. So like this heterocyclics also has smaller coupling constants compared to hydrocarbons.

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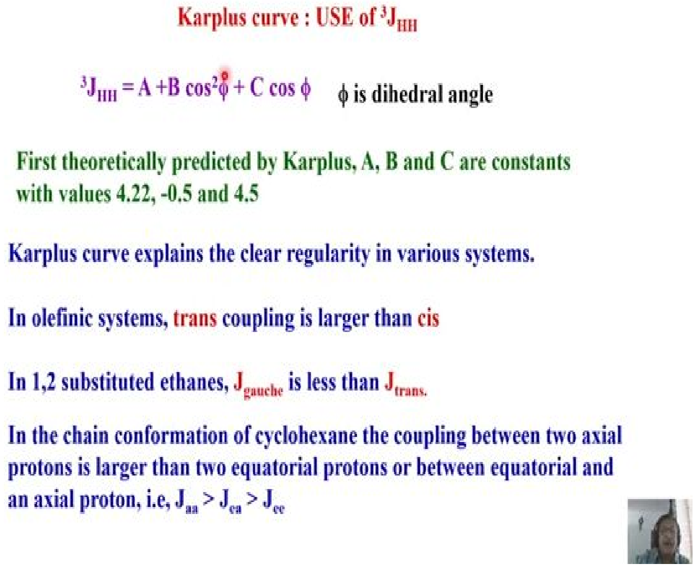

Karplus curve : USE of $^{3}J_{HH}$

$^{3}J_{HH} = A + B\cos^{2}\phi + C\cos\phi$ ϕ is dihedral angle

First theoretically predicted by Karplus, A, B and C are constants with values 4.22, -0.5 and 4.5

Karplus curve explains the clear regularity in various systems.

In olefinic systems, trans coupling is larger than cis

In 1,2 substituted ethanes, J_{gauche} is less than $J_{trans.}$

In the chain conformation of cyclohexane the coupling between two axial protons is larger than two equatorial protons or between equatorial and an axial proton, i.e, $J_{aa} > J_{ea} > J_{ee}$

These are all usea of Karplus equations, something very important. This is a very famous Karplus equation, a quadratic equation of cos phi, phi is dihedral angle. It will give you a lot of information about the varieties of systems. This is our first theoretically predictable Karplus, where the A, B and C are constants. Of course, now over the years this Karplus equation has undergone lot of modifications, and the coupling values people have derived depending upon different types of systems, different nuclei, etcetera. They have worried about 3 bond carbon proton coupling, 3 bond heteronuclear coupling and varieties of information about Karplus curve is available.

This is only basic equation I am giving you. All you have to remember is, it is the quadratic equation of cosine of phi, where phi is dihedral angle. The most interesting information you can get from Karplus equation is, the olefinic system if we know trans coupling, this information you should remember, trans coupling is larger than cis, In substituted ethanes, the gauge coupling is less than trans and similarly in other case, the cyclohexane we discussed.

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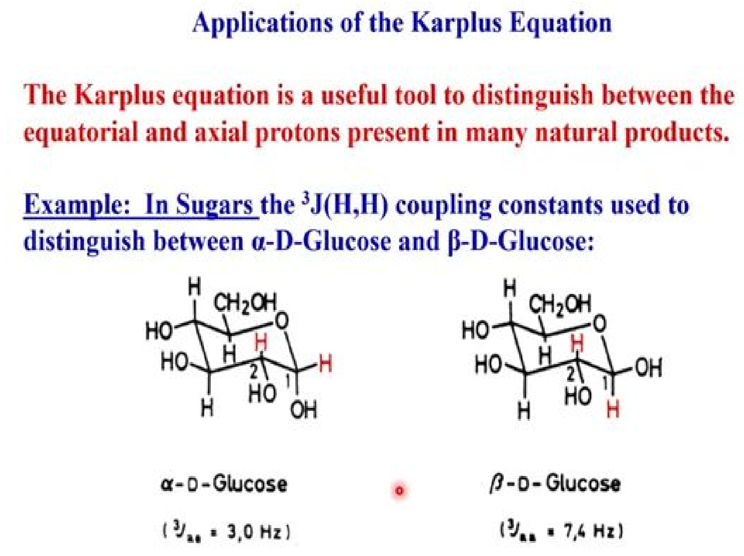

Applications of the Karplus Equation

The Karplus equation is a useful tool to distinguish between the equatorial and axial protons present in many natural products.

Example: In Sugars the $^{3}J(H,H)$ coupling constants used to distinguish between α-D-Glucose and β-D-Glucose:

α-D-Glucose

($^{3}J_{aa}$ = 3,0 Hz)

β-D-Glucose

($^{3}J_{aa}$ = 7,4 Hz)

Now the important application is Karplus equation will tell you, it can help you to distinguish between axial and equatorial protons, especially in some natural products based on the coupling strengths, really important information. In this molecule, this is alpha D glucose, this is beta D glucose. This is a cis orientation, this is trans orientation; or in other words this has an axial and equatorial coupling, axial and equatorial coupling, this is axial - axial coupling.

In other words axial-axial coupling I told you, is much larger, about 7.4 Hz. very interesting, right? So that is why looking at the coupling strength between these two protons, you can say whether this beta D glucose or alpha D glucose, fantastic application of karplus equation.

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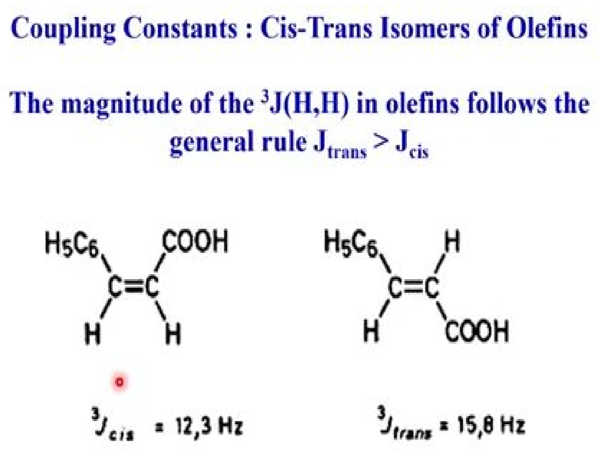

Coupling Constants : Cis-Trans Isomers of Olefins

The magnitude of the $^3J(H,H)$ in olefins follows the general rule $J_{trans} > J_{cis}$

$^3J_{cis}$ = 12,3 Hz

$^3J_{trans}$ = 15,8 Hz

It can also distinguish cis-trans isomers in olefins. As I told you trans coupling by rule, general rule, is larger than cis coupling. Look at this molecule, if these two protons are in cis configuration, the coupling is of the order of 12.3Hz. If it is in trans configuration, it is nearly 16 hertz, very large. So based on the coupling strength, you can distinguish cis and trans isomers. That is very useful information, okay?

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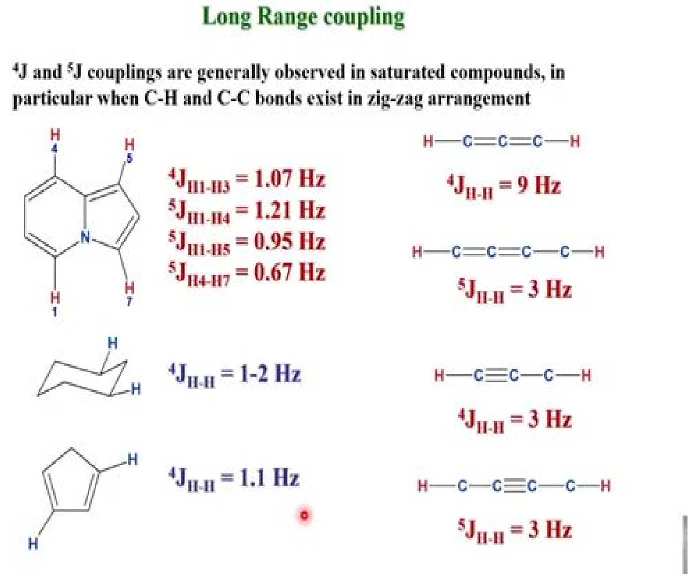

Long Range coupling

^4J and ^5J couplings are generally observed in saturated compounds, in particular when C-H and C-C bonds exist in zig-zag arrangement

$^4J_{H1\text{-}H3}$ = 1.07 Hz
$^5J_{H1\text{-}H4}$ = 1.21 Hz
$^5J_{H1\text{-}H5}$ = 0.95 Hz
$^5J_{H4\text{-}H7}$ = 0.67 Hz

$^4J_{H\text{-}H}$ = 1-2 Hz

$^4J_{H\text{-}H}$ = 1.1 Hz

$^4J_{H\text{-}H}$ = 9 Hz

$^5J_{H\text{-}H}$ = 3 Hz

$^4J_{H\text{-}H}$ = 3 Hz

$^5J_{H\text{-}H}$ = 3 Hz

Now we knew about 1 bond coupling, 2 bond coupling, 3 bond couplings, etc.. But in my one of the classes, when I was showing you the salient features of the couplings, I also said, the coupling strength decreases with increase in the number of bonds sequentially. Let us say for 1 bond coupling is quite large, we saw that in hydrogen molecule it is 276, 2 bond is smaller than that and 3 bond even smaller.

As you keep going far and far away, 4, 5 bonds coupling is much smaller. Coupling strength drastically reduces after 3 or 4 bonds. Most of the cases 4 bond couplings are very rarely seen, very small value. But, in some specific examples, especially when you have molecules which are linear like this, or molecules which are in zig-zag shapes like this, in which case very long range couplings have been observed, very long range coupling.

For example in this molecule, this proton and this proton are separated by 1, 2, 3 and 4 bonds. 4 bond coupling of 9 Hz is seen, it is really large. Four bond coupling, almost practically goes to zero. In some cases, and in this example you could see the long range coupling. You see in this molecule, again linear molecule, 5 bond coupling of 3 Hz is seen. That is also quite large, here in this molecule.

So in the zig-zag type molecule, you see, the 5 bond coupling is seen, 4 bond coupling is seen. So it is not that there are no deviations from the general rule. The general rule is couplings decreases with increase in the number of bonds, but does not mean there are no deviations. In many examples, we have observed long-range couplings of 4 bonds, 5 bonds, 7 bonds or 8, 9 bonds away.

I will show you one example today, for 2 protons separated by 9 bonds coupling has been seen, These are all very interesting. Of course these are rare examples, but what I am trying to say is, you have to be cautious while analyzing this spectrum. Do not be under the impression, okay after 3 bonds no coupling, it is practically 0; and this coupling is for a different reason, this peak is coming by different reason. No, there are deviations, you have to very careful, take all this factors into account while analyzing the spectrum.

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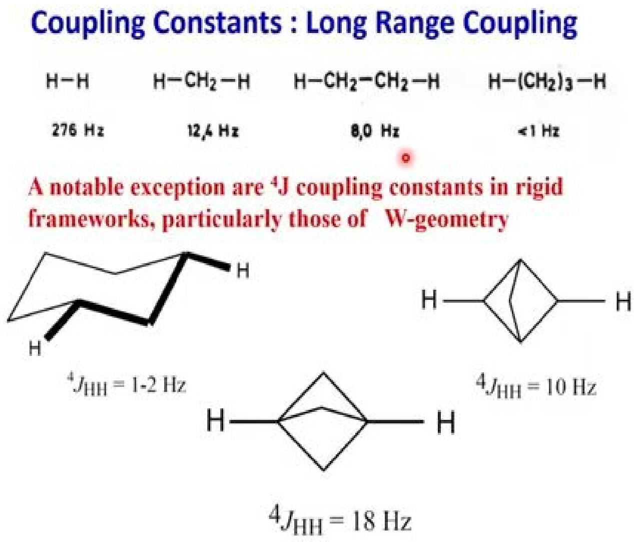

Coupling Constants : Long Range Coupling

$H-H$	$H-CH_2-H$	$H-CH_2-CH_2-H$	$H-(CH_2)_3-H$
276 Hz	12,4 Hz	8,0 Hz	<1 Hz

A notable exception are ^4J coupling constants in rigid frameworks, particularly those of W-geometry

$^4J_{HH}$ = 1-2 Hz

$^4J_{HH}$ = 10 Hz

$^4J_{HH}$ = 18 Hz

So this is a example, like this. In this type of molecule, 4 bond coupling is 1.2 Hz. Here you see four bond coupling of 18 hertz between this proton to this proton, enormously large, that has been seen.

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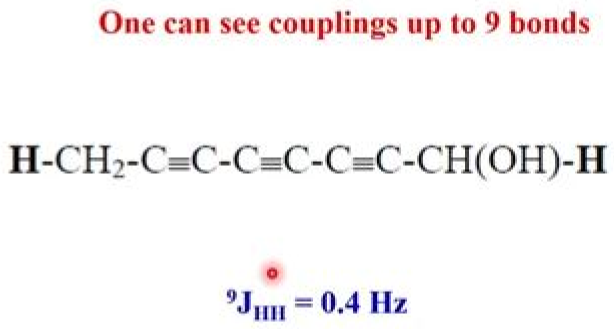

One can see couplings up to 9 bonds

$\mathbf{H}\text{-}CH_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH(OH)\text{-}\mathbf{H}$

$^9J_{HH} = 0.4$ Hz

And this is a classic example, in a linear chain like this, the coupling between this proton and this proton, of the order of 0.4 Hz has been seen. Remember this proton and this proton are separated

by nine bonds, 9JHH has been seen. A very rare example, but it is possible. So in NMR, many, many cases you cannot apply a general rule and as a dogma and say yes, this is what it is.
No, many, many interesting things do happen and you have to take all those things in to account before analyzing.

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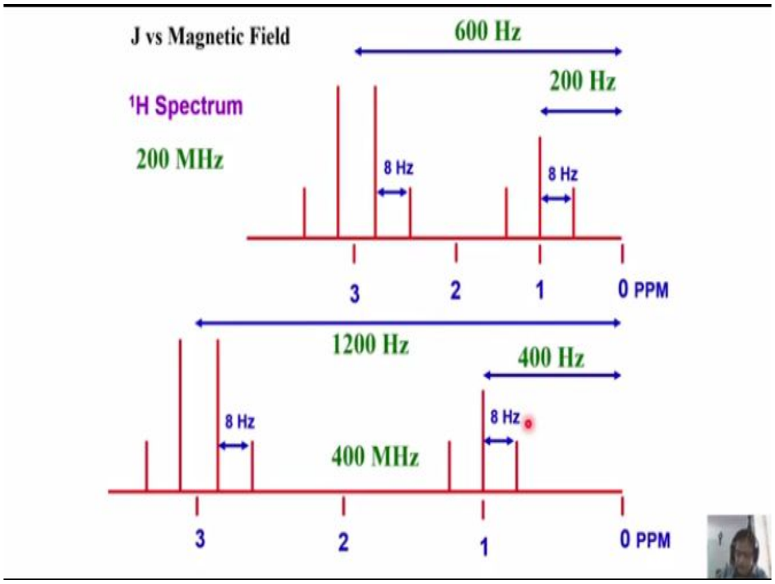

So far about the varieties of information I wanted to give you on scalar couplings, and coupling strengths etc. Now one more information, remember when I was giving the salient points, I also said J coupling is independent of the magnetic field, unlike chemical shift ,where chemical shift is linearly dependent on the magnetic field, J coupling is independent of the magnetic field.
Let us see this example. I have taken the spectrum of some hypothetical molecule.

Of course looking at this spectrum by now you must be experts, you must be able to say what is this molecule, hypothetical molecule. This is a triplet means it is attached to a CH2 group and this is a quartet means is attached to a CH3 group. It means it a molecule containing CH2 and CH3, some hypothetical molecule with other substitution. Now this is spectrum in 200 megahertz. I will measure this in frequency. In 200 megahertz 1 ppm is 200 hertz. What is 3 PPM? 600 Hertz. Now if you measure this separation between adjacent peaks, you are going to get coupling constant. What is the separation? I measure it is 8 hertz, that is a 8 hertz coupling, coupling constant we measured.

Let us do one more interesting thing. We will now go to higher frequency spectrometer. Same molecule we will record its spectrum at 400 megahertz. What is going to happen now?
Same 1 PPM measure, 400 hertz, remember PPM to frequency conversion we have done a lot of examples. 1 PPM is 400 hertz. What is 3 PPM? 1200 hertz in 400 megahertz. Measure the J coupling. Fantastic it is not changing. It is very interesting, right? The chemical shift is changing but J coupling is not changing at all. The separation between the peaks split because of J coupling do not get altered with the magnetic field.

This is the information I wanted to give you. Remember when you are measuring the couplings, irrespective of the magnetic fields, irrespective of the spectrometer you record, that remain same.

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Splitting pattern : A Family Tree Approach

Applicable to weakly coupled spin systems

Okay next, we will analyze one spectrum. Instead of analyze, I will say we will generate a spectrum, we will build a spectrum using family tree approach.

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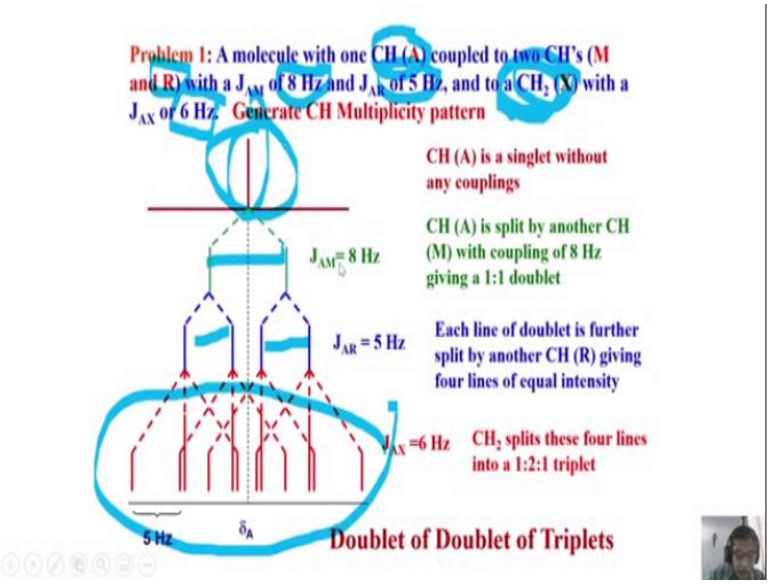

Problem 1: A molecule with one CH (A) coupled to two CH's (M and R) with a J_{AM} of 8 Hz and J_{AR} of 5 Hz, and to a CH_2 (X) with a J_{AX} of 6 Hz. Generate CH Multiplicity pattern

CH (A) is a singlet without any couplings

CH (A) is split by another CH (M) with coupling of 8 Hz giving a 1:1 doublet

Each line of doublet is further split by another CH (R) giving four lines of equal intensity

CH_2 splits these four lines into a 1:2:1 triplet

Doublet of Doublet of Triplets

Let us take this, I give you a problem. I will take one molecule which contains a CH proton. Read this question very carefully. I take a molecule which contains a CH proton and 2 CH's M and R and remember the coupling constant is 8 hertz and 5 hertz. What is the coupling constant? The coupling constant of 2 CH's with respect to this with respect to this CH, i.e, the coupling constant of CH with M and R are 8 Hertz and 5 Hertz.

Interestingly, it is also coupled to CH2 with a coupling strength of 6 hertz. Now my question is we have to generate a spectrum, theoretical spectrum in a stick plot. We will take a stick plot of this one. Now generate the spectrum. How do we do that? Simply adopt family tree approach. Take this CH proton A, without any coupling it has to be a singlet, correct, it is a singlet. Now it is coupled 2 CH's; M and R with couplings of 8 Hz and 5 Hz.

You may also remember, I told you when you, under analysis of the multiplicity pattern, the order of coupling which you take does not matter, it is immaterial. Now we can take this coupling first and make it as a doublet, or, this first and make it as the doublet, does not matter, so both we can take. First we will take coupling with M, it is 8 hertz. You can take R also, no problem. I took M and its separation is 8. So this CH proton is split this into a doublet.

Now what about this proton R? That also will split each of the line into doublets. Now what happen? It was doublet, now it became doublet of doublet, DD; it is DD now. That is not the end, this proton is also coupled to CH2, these protons that means each line of this doublet of doublet; What will happen? when it splits with CH2? Remember, magnetically equivalent spins you have to use 2 NI +1 rule. What is going to happen now? Each of line of the doublet of doublet splits into triplet. So, what you call this pattern? This is doublet of doublets of triplets. So, this is how we can generate the multiplicity pattern, understand? How easily we can do? This is, we generated theoretically, you know, assuming hypothetical molecule. But in real spectrum you have to go backwards, you will be given only this multiplicity pattern. Start analyzing and finally arrive at the chemical shift and all these coupling values. That is your job, that is what finally analysis that you have to do, Alright? So, I think I have given a lot of information about scalar couplings, and now we also took an example how to generate the multiplicity pattern, theoretically as an example.

Now we will go to analysis of spin systems using Pople notation and the spectrum. That is the next step. So I will stop this, and then we will go into the next one, which is called Pople nomencature.

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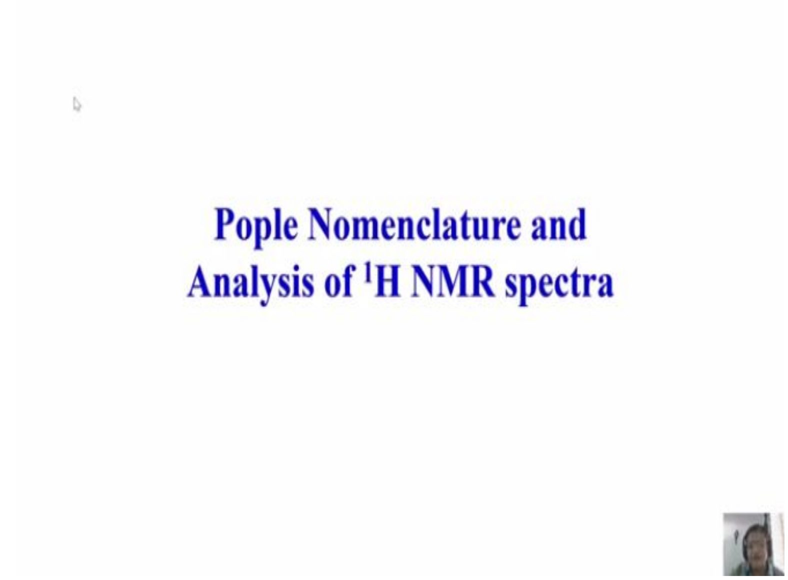

Pople Nomenclature and
Analysis of ^{1}H NMR spectra

I will continue this in this class today, because this is very important. Most of you will come across this, analysis part. I do not know whether you people have heard of weak coupling and strong coupling, I did mention it, and if you really get deeper and deeper into NMR analysis, if you become a hardcore NMR spectroscopist, you must know all these Pople nomenclature, analysis of the spectrum of different spin systems, etc. We will start what it is now.

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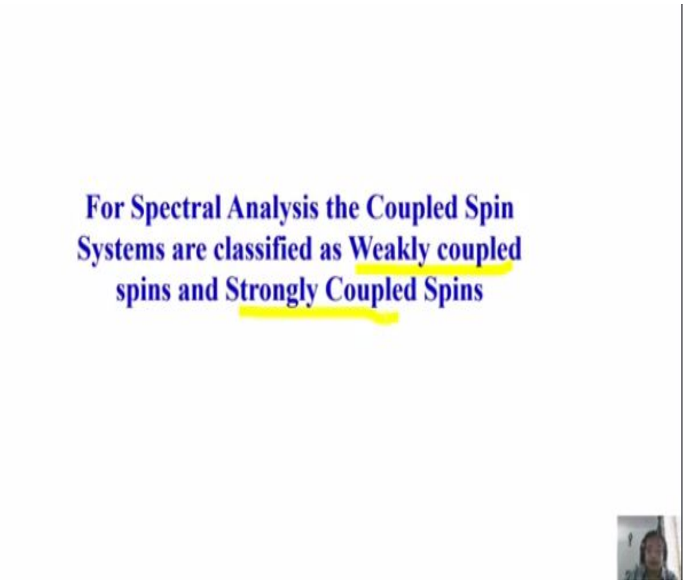

For Spectral Analysis the Coupled Spin Systems are classified as Weakly coupled spins and Strongly Coupled Spins

First, if I have to do this spectral analysis using Pople notation, first thing you should know is whether, what is the spin system; whether it is strongly coupled or weakly coupled. It is a very important aspect you should remember. Unless you know whether it is strongly coupled or weakly coupled, you cannot analyze this spectrum so easily. This is weakly coupled, this is strongly coupled.

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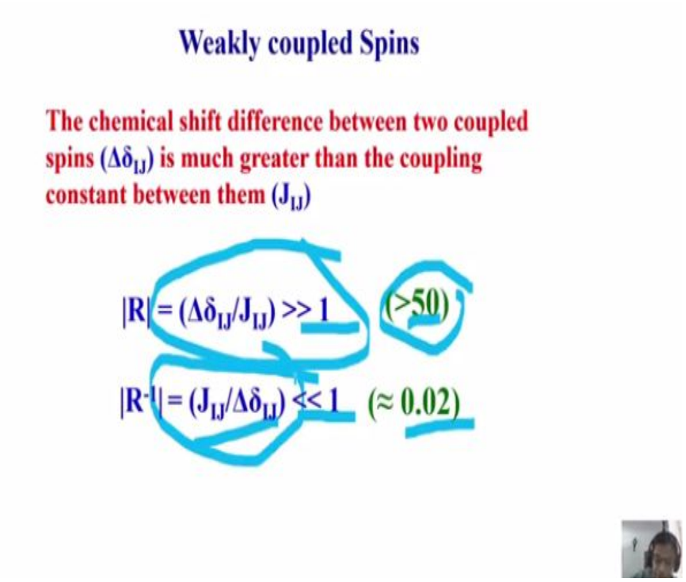

Weakly coupled Spins

The chemical shift difference between two coupled spins ($\Delta\delta_{IJ}$) is much greater than the coupling constant between them (J_{IJ})

$|R| = (\Delta\delta_{IJ}/J_{IJ}) >> 1$ (>50)

$|R^{-1}| = (J_{IJ}/\Delta\delta_{IJ}) << 1$ (≈ 0.02)

Now the question is what is weakly coupled spin system and what is strongly coupled? I have already told you in one of the classes what is a spin system, what is a strongly coupled spin, see what are strongly coupled spins, what are weakly coupled spins. I gave a quick description about those things. I hope you remember otherwise now you see the understanding of what is that now.

I will take the example of what is a weakly coupled. Remember, weakly coupled spin system is the one where the chemical shift separation must be much, much larger than the J coupling. I consider two spins, let us say, one proton is here with a coupling like this, and other is here with a coupling like this, what is the chemical shift separation between this and this? This is, let us say, delta. I will measure this as delta, this separation are called delta, delta, no problem.

If this value is sufficiently larger than this, this is J coupling; okay, this is sufficiently larger than the J coupling, then you call it a weakly coupled spin system. How much should be the larger is the next question. If this is 10 hertz, if this is 11 hertz, is it okay? No. There is some empirical rule. There is no hard and fast rule, but some empirical rule. It is the ratio of the chemical shift separation between these spins and to its coupling constant should be very much greater than 1 and that should be at least greater than 50 times, you understand?

Now let us take a simple example. I have two protons coupled J give rise to doublet each. The chemical shift separation between this and this, let us say is 500 hertz. The J coupling between these two is only 10 hertz. Now, what is my R? 500 divided by 10, it is 50. So, it is the weakly coupled spin system. On the other hand, I will take this chemical shift separation is only 20 hertz. My coupling is also 20 hertz of 10 hertz, what happens? 20 by 10 is only 2, so it has to be sufficiently larger, since the ratio is not very large, you call that spin system as strongly coupled.

Remember, a weakly couple situation is one where this chemical shift separation divided by its coupling constant, should be at least 50 times, more than 50. Some books write in a different manner. You understand, some books write inverse of this. There are J over delta delta in which case get the inverse of this.

In which case this formula is used then this has to be very much smaller than 1, like after add a 0.02. Some books follow this, some books follow this. You do not have to worry about it, but just remember one thing, conceptually the chemical shift separation should be sufficiently larger than coupling constant, then the spin systems are weakly coupled, clear for you?

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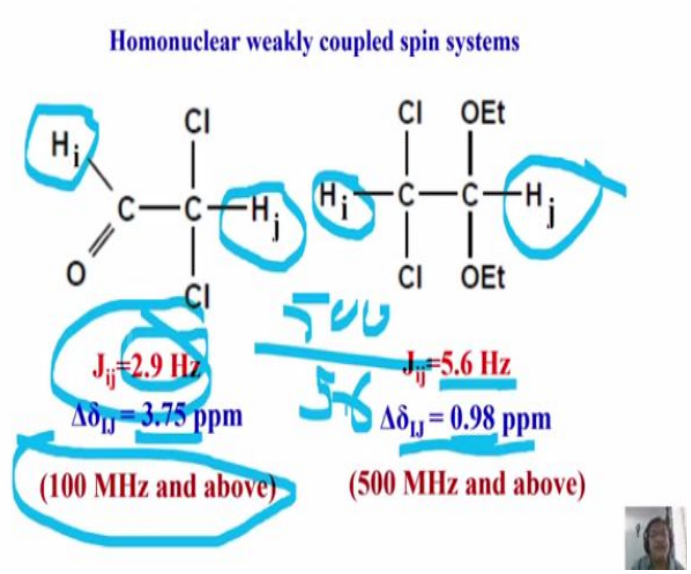

Homonuclear weakly coupled spin systems

J_{ij}=2.9 Hz
$\Delta\delta_{IJ}$ = 3.75 ppm
(100 MHz and above)

J_{ij}=5.6 Hz
$\Delta\delta_{IJ}$ = 0.98 ppm
(500 MHz and above)

Now we will see what are homonuclear weakly coupled spin system and heteronuclear weakly coupled spin system. Now consider a molecule like this, this proton H and this proton, the chemical shift separation is 3.75 ppm. You know when it is expressed in ppm you know how to convert to frequency. Let us say I am recording this spectrum at 500 mega hertz. For purpose of calculation, let us make it 4, easy to multiply. 4 into 500 is 2000 hertz. What is J coupling? 2.9.

2000 by 3, let us take it 3, 2000 by 3, close to 600; that means it is very, very weakly coupled spin system. Understand? Now take another example. Between this proton and this proton, chemical shift separation is 0.98, take 1 ppm. In 500 megahertz 1 ppm is 500 hertz. What is the coupling? 5.6. Now 500, you have to take it, divided by 5.6. What is this? Close to 100, that means, this is also weakly coupled spin system.

So very easily you can understand what is strongly coupled and what is weakly coupled and this can happen weakly coupling only in 100 megahertz. Remember the chemical shift separation depends strongly on the magnetic field. One important point I wanted to tell you, if your nuclear spin coupled are very strongly coupled, that means chemical shift separation is not much large compared to J coupling. Let us say, you are recording this spectrum at 100 megahertz.

What you will do to make it weakly coupled? You have to go to very high magnetic field. Let us in 100 megahertz if it is strongly coupled, I will go to 800 megahertz. Chemical shift becomes very large. Then it becomes weakly coupled. So the field has its tremendous influence on converting strongly coupled to weakly coupled or vice versa, okay? This is important point you must remember.

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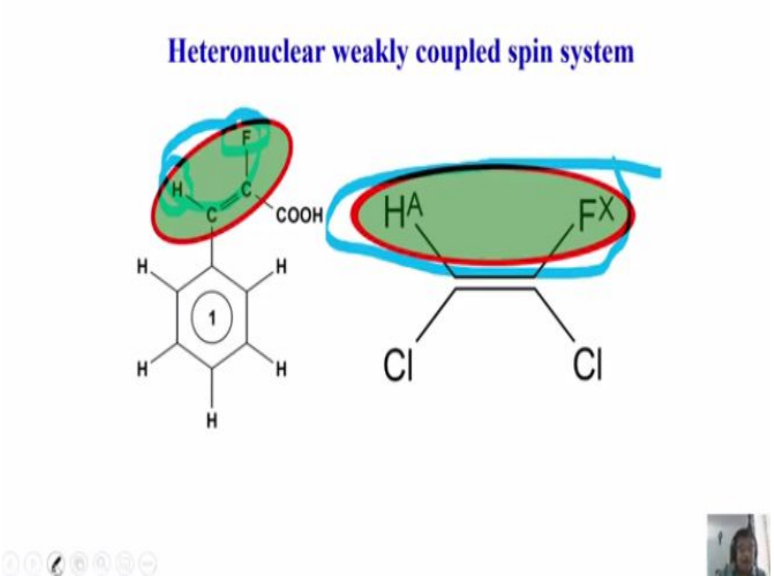

Heteronuclear weakly coupled spin system

In the case of heteronuclear, another interesting thing, take this molecule proton and fluorine. The question is are they homonuclear? Are they strongly coupled, weakly coupled? I do not have to tell you. You will be in a position to answer yourself now, because remember proton and fluorine have large separation in the resonating frequency. Proton in 500 megahertz comes at 500 MHz, whereas fluorine comes somewhere around 470 MHz. 30 megahertz difference is there.

Huge separation, you can call it as chemical shift separation of the order of 30 megahertz. What is this coupling? Only 10 hertz or 15 hertz. This means heteronuclear systems are invariably weakly coupled. Please remember when I give the example for heteronuclear spin system and I ask you whether it is strongly coupled or weakly coupled, immediately it should come to your mind, this type of heteronuclear systems cannot be strongly coupled, they always have to be weakly coupled. This very important point; heteronuclear case never be strongly coupled.

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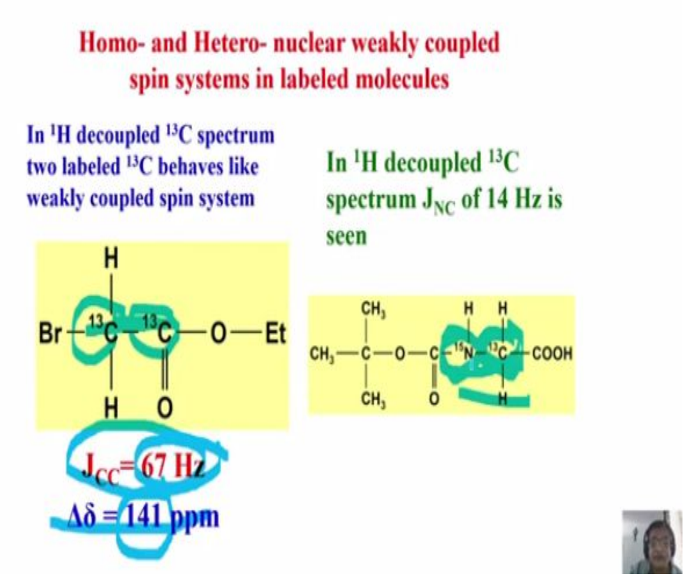

Homo- and Hetero- nuclear weakly coupled spin systems in labeled molecules

In ^{1}H decoupled ^{13}C spectrum two labeled ^{13}C behaves like weakly coupled spin system

In ^{1}H decoupled ^{13}C spectrum J_{NC} of 14 Hz is seen

J_{CC}= 67 Hz

$\Delta\delta$ = 141 ppm

So now I will give you an example of homo and hetero nuclear weakly coupled spin system in labeled molecules. Take an example like this. I will take this carbon and this carbon both I will label. Label means chemistry, I will do in chemical synthesis, somehow I make it 100% abundant instead of 1%. When I say 100% abundant, it is like proton or fluorine. Then you can see the coupling between these two.

That happens when they observed the coupling it is 67 hertz; but chemicals shift separation is 141 ppm. It is quite large. So let us take 600 megahertz. 600, easy to calculate. I will take 800 megahertz what is carbon resonating frequency? We have been discussing for so many times, 4 times less gamma, so 200 megahertz, that is why I took that example. Now, what is 1 ppm of carbon in 800 megahertz? 200 hertz. 200 into 141 ppm, very large, whereas the coupling is 67 hertz. This is a homonuclear labeled systems, they can also be weakly coupled. Take for example this molecule, nitrogen 15 is there and carbon 13 both are labeled; and this coupling is only 14 hertz. Now the question is, is it strongly coupled or weakly coupled? I do not have to tell you, you know the answer, because they are far away separated in resonating frequency.

In the 300 megahertz, carbon comes at 75 MHz, Nitrogen comes at 30 megahertz or 20 megahertz, whatever it is, it is 10 times lower gamma, 30 megahertz. Now what is the difference? Where is 75, where is 30 Mhz? Such a large chemical shift separation, and the coupling is only 14 hertz. That shows heteronuclear system like this, it is always weakly coupled. You get the point now I hope you understood everything.

So now I will stop here for the day. In the next class I will bring in the strongly coupled spin system. So far we were discussing our weakly coupled, then we look at the spectrum of strongly coupled, and weakly coupled 2 spin, 3 spin, 4 spin, etc., how to analyze and how to give the nomenclature for these using Pople, so that we will continue in the next class.