Advanced Transition Metal Chemistry_Spectroscopic Methods
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Module - 12
Lecture - 58
NMR Spectroscopy

Hello everyone. Once again, I welcome you all to MSB lecture series on Transition Metal Chemistry. We are almost in the last stages of this course. This is the fifty-eighth lecture. And in my previous lecture, I started discussion on NMR spectroscopy to make you familiar with interpretation to solve the structure of some simple molecules that you come across to make yourself familiar with NMR.

As I mentioned, if you are more interested, it is a wonderful topic and wonderful subject for studying and also doing research. And if you are more interested, always you can go to fully dedicated NMR spectroscopy courses and also the books I showed you in the beginning of my fifty-seventh lecture. So, let me continue from where I had stopped. In my previous lecture, I was telling you about spin-spin splitting and how NMR is so powerful in interpreting data and structure determination for molecules containing NMR active nuclei. I was telling you about Pascal triangle for I = ½; so, this is the one.

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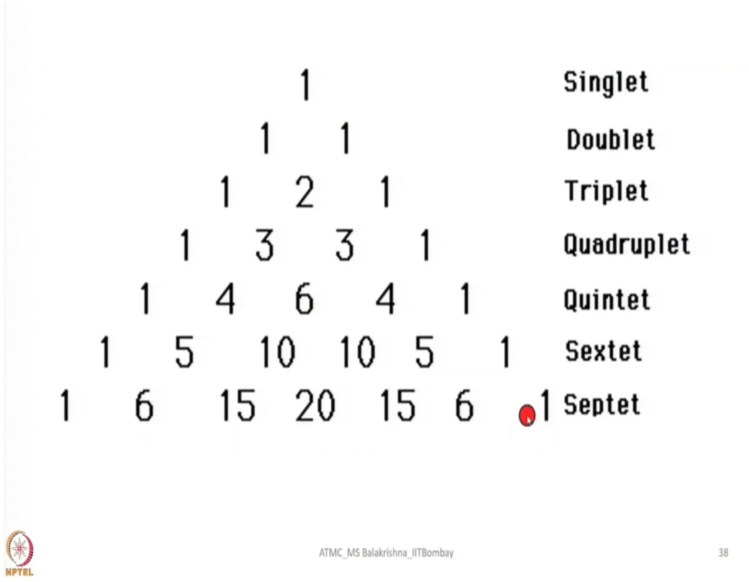

1	Singlet
1 1	Doublet
1 2 1	Triplet
1 3 3 1	Quadruplet
1 4 6 4 1	Quintet
1 5 10 10 5 1	Sextet
1 6 15 20 15 6 1	Septet

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I said it is unique for each nuclear spin; this is for I = ½. If we have 7 lines, we will be having intensity ratio of 1:6:15:20:15:6:1, because you can also examine this one by considering 6 equivalent protons or 6 arrows and start arranging them. All 6 are first upward; and then 5 are upward, one is down; and then one can be fifth one, sixth one or first one, second one; like that you have 15 options are there.

And then when you have two upward spin, low spin and 4 upward spin, you have 20 options. And again it repeats in the same sequence here and we end up with 7 signals 7 lines in a multiplet of septet having this intensity. As I mentioned, I told you that I will show you in case of isopropyl. That is coming I think; I would show you about how 7 lines are coming. Their range of magnetic coupling we will see now.

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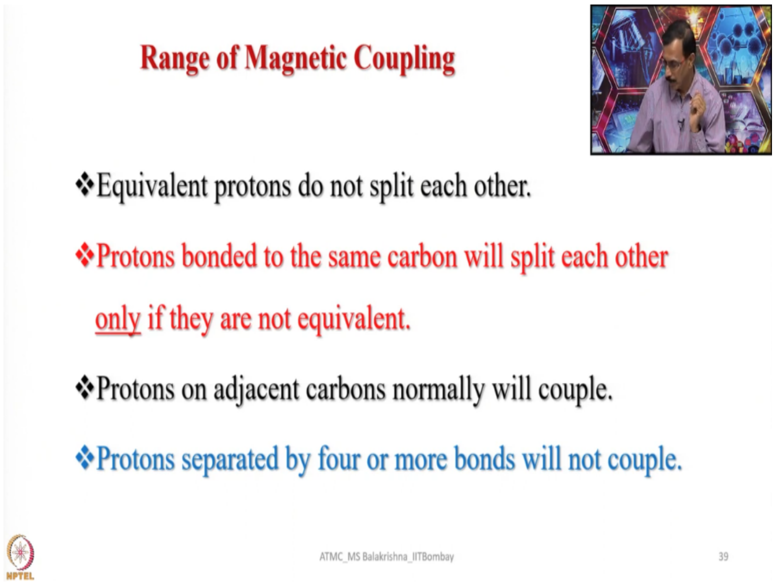

Range of Magnetic Coupling

❖Equivalent protons do not split each other.

❖Protons bonded to the same carbon will split each other only if they are not equivalent.

❖Protons on adjacent carbons normally will couple.

❖Protons separated by four or more bonds will not couple.

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Equivalent protons do not split each other. For example, if we look into ethanol, CH_3CH_2OH, in CH_3, protons, they do not split each other. Same way, methylene protons, they do not split each other. Protons bonded to the same carbon will split each other, only if they are non-equivalent. If the two hydrogen atoms present on the same carbon atom will split each other, only if they are not equivalent.

So, those cases are there; I can show you. And then, protons on adjacent carbon normally couple. When you look into two groups say CH_3 and CH_2 group or CH, they normally couple and show spin splitting accordingly. So, protons separated by 4 or more bonds will not couple, because, when you move further, the influence of the magnetic field generated by those will be less.

As a result, what happens, they do not couple. That is the reason we do not see very long-range coupling. For example, one CH_3 is here; after CH_2, there is one more; so, really it does not have much influence or its magnetic field generated in the same magnetic field, when we keep it, it does not have influence on the radio frequency of this one. As a result, they do not couple.

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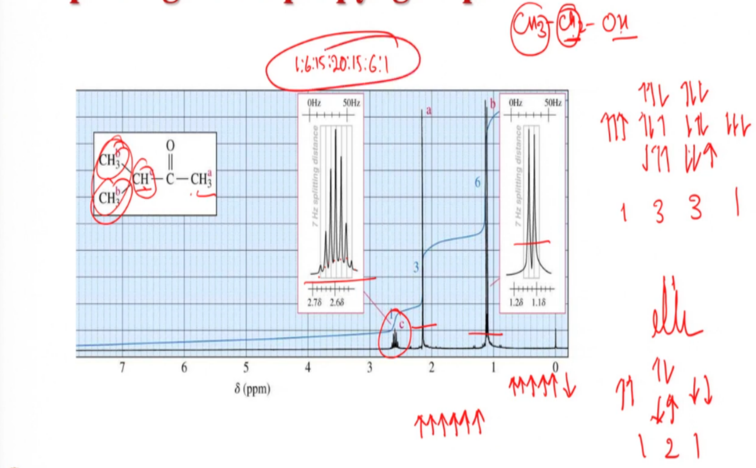
Splitting for isopropyl groups



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So, now, splitting for isopropyl group I showed you. So, your structure is shown here. Now, these two are equivalent; and now this is different and then this is different here. So, that means in this one if you see, this CH_3 is not coupled; it will show a singlet here. And now, this one is split by these 6 into 7 lines that is shown here. And of course, it is expanded; you can say, 1, 2, 3, ..., 7. The ratio, if you see, it is 1:6:15:20:15:6:1.

So, that means 1:6:15:20:15:6:1; you can examine that one. And then, for these 2 will be under the influence of this one; it splits into a doublet here. So, this is how it is splitting. And as I mentioned, in case of ethanol I should show you, CH_3CH_2OH. So, let us not worry about this one. Now, this one will be split by these 3. So, first these all the 3 will be in this fashion. And now what happens, we will be having 1, 2 like this and 1 like this.

And now, this one can have now 1 like this. This one like this and this like this. And now what will happen? It can be here and these 2 will be here like this. So, this is 1 set, 3 are there. And now what happens, 1 is like this, 2 are down, and then 1 down up like this or like this and like this; you cannot have anything else. Now, we have all the 3 down like this. So, now if you see, 1:3:3:1. So, that is the reason.

So, this one will show a signal something like this. On the other hand, this one would be under the influence of these 2. So, these 2 will be 1 like this, 1 is like this, 1 is like this, 1 is like this, 1 is like this, and 1 will be like this; 1:2:1. So, this is how you can also write for 6 also. 6 if isopropyl is there, we have to write like this; 1 like this, 3, 4, 5, 6. Now you consider 1, all the 5 and 1 like this; and one keep on shifting here.

And then you write for 2, 3, like that. So, then you will end up with this ratio here. So, this is how you can calculate the spin multiplicity and also their relative intensities. And this one simply you can do it from looking into Pascal triangle.

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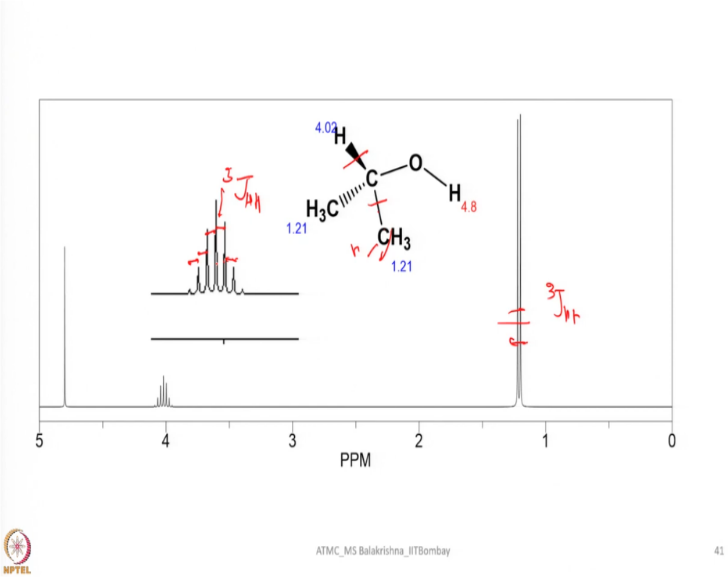

For this isopropanol spectrum, I have shown here, a septet is there and OH is coming around 4.8; and then, this is coming around 4.02; and then, these 2 are coming as a doublet around 1.21.

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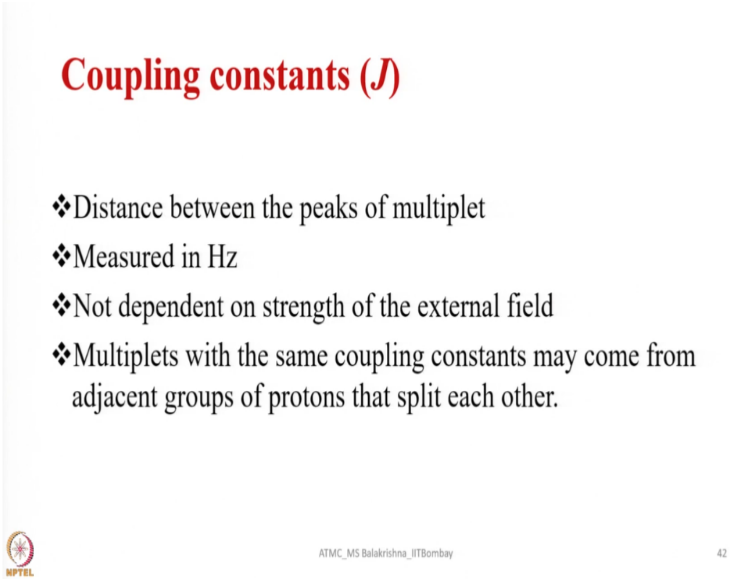

Coupling constants (*J*)

- Distance between the peaks of multiplet
- Measured in Hz
- Not dependent on strength of the external field
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

What is coupling constant now? Another term is coming. So, difference between the peaks of a multiplet is called coupling constant. If you go back to here, if you see the separation between these 2, this is same as this separation; this same as this separation; this separation is same; and this separation is called J, coupling constant. And in this case, what happens here, if you consider this one, 1, 2, 3.

So, if I write here like this, this is 1, 2, 3 bond coupling, $^3J_{HH}$ coupling. And of course, for this also it is the same; this also 2 is there; this also $^3J_{HH}$ coupling. This separation is same as this separation that indicates they are coupled to each other. This is called coupling constant. And distance between the peaks of multiplet; measured in hertz; not dependent on strength of the external field, you should remember.

Since it is measured in hertz, it is independent of magnetic field strength. Whether I record in 60 megahertz or 300 megahertz or 600 megahertz, the coupling constant remains same and chemical shift in ppm remains same. Multiplets with the same coupling constant may come from adjacent group of protons that split each other.

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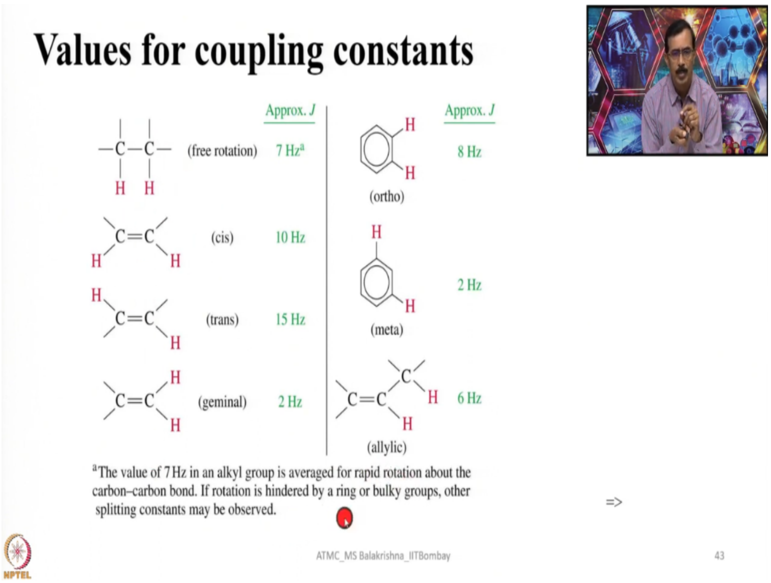

Values for coupling constants

	Approx. J		Approx. J
(free rotation)	7 Hz[a]	(ortho)	8 Hz
(cis)	10 Hz	(meta)	2 Hz
(trans)	15 Hz	(allylic)	6 Hz
(geminal)	2 Hz		

[a] The value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon–carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

=>

So, now, values for coupling constant is given here. For this one what happens, when free rotation is there, this is 7 hertz; and hear the cis coupling is 10 hertz and trans coupling is larger, 15 hertz on the same carbon. Due to some reason if molecule is unsymmetric, and then the hydrogens on the same carbon will split. Then that is called geminal coupling that is 2 hertz, very small, because they have very similar Larmor frequency, 2 hertz.

And then, in case of ortho coupling, in case of aromatic group, it is 8 hertz; meta, it is 2 hertz because farther and normally you do not see para, they are too far; and in allylic it is 6 hertz. The value of 7 hertz in an alkyl group is averaged for rapid rotation about the carbon-carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constant may be observed.

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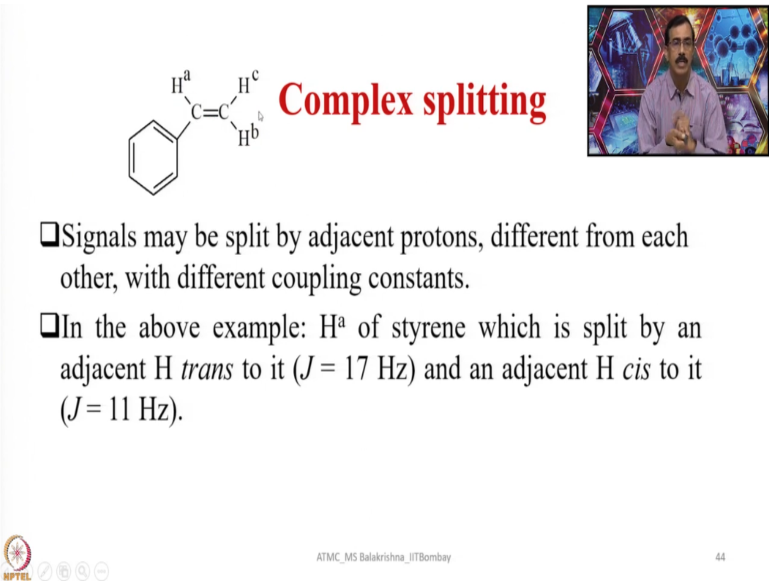

Complex splitting

❑Signals may be split by adjacent protons, different from each other, with different coupling constants.

❑In the above example: H^a of styrene which is split by an adjacent H *trans* to it ($J = 17$ Hz) and an adjacent H *cis* to it ($J = 11$ Hz).

And complex splitting, as I mentioned, geminal coupling you can see here because this molecule is not symmetric. And now the relationship between H_b with H_a is different from relation with H_c and H_a because these 2 are trans and these 2 are cis. As a result, they are not very similar. They are chemically equivalent, but magnetically they are not equivalent.

As a result, what happens, both of them will show different signals, but the margin is very less, but they show coupling with this H_a. So, signals may be split by adjacent protons different from each other with the different coupling constants. Once when we look into spectrum, we should be able to assign the signal due to H_a, H_b and H_c very readily. For example, in the above example, H_a of styrene is split by an adjacent H trans to it by 17 hertz.

This coupling is 17 hertz, whereas this coupling is 11 hertz. That means it shows a doublet of doublets. One is 17 hertz, first you should write, and this we call coupling or splitting tree. That we should be able to write it. I will try to make you familiar in writing this one. So, H cis to it 11 hertz; that means trans is more, 17 hertz. And first it will be split by trans to give 2 signals, and each signal will be further split into 2 each by H_c with 11 hertz.

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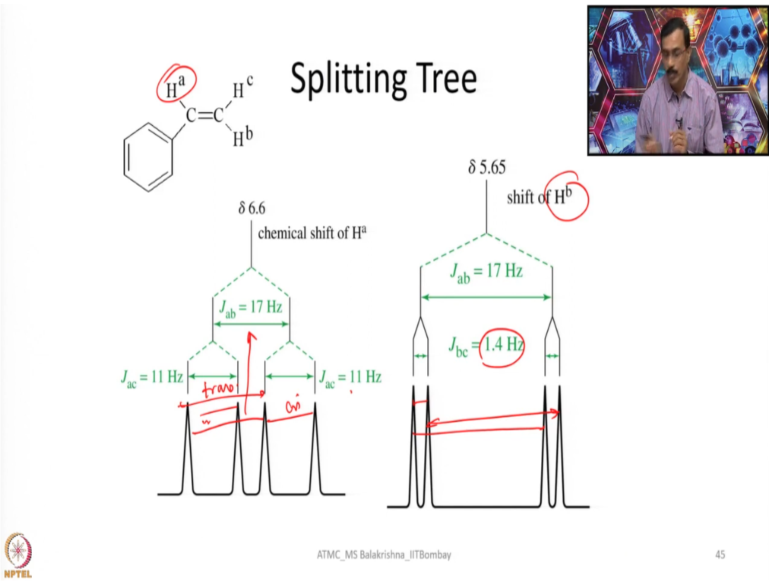

Splitting Tree

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You can see here 6.6 H_a; Ha, first you say 6.6. First it is coupled with this one, splits into a doublet and then each line is further split, because the coupling constants are different; it is stepwise you have to see the coupling. And then, this separation is 11 hertz; this separation is 11 hertz. Now, it will be a doublet of doublets. The separation, this one is shown here; and between this one and this one is shown here.

This is cis coupling and whereas this one is trans coupling. And same thing, this is for H_a; and then H_b what happens? Of course, H_b first it splits into larger coupling and then the smaller coupling is between this one, that is about 1.5 hertz, and now you can see the spacing. This is due to H_b and H_c coupling; weather this one you take or whether you take this one, this is due to J_{ab} coupling, 17 hertz.

So, now, with this one, we should be able to analyse the coupling constant for the other one also. This also shows the relationship between the mutually coupled protons, so that writing their geometry or structure or correct conformation is also very easy.

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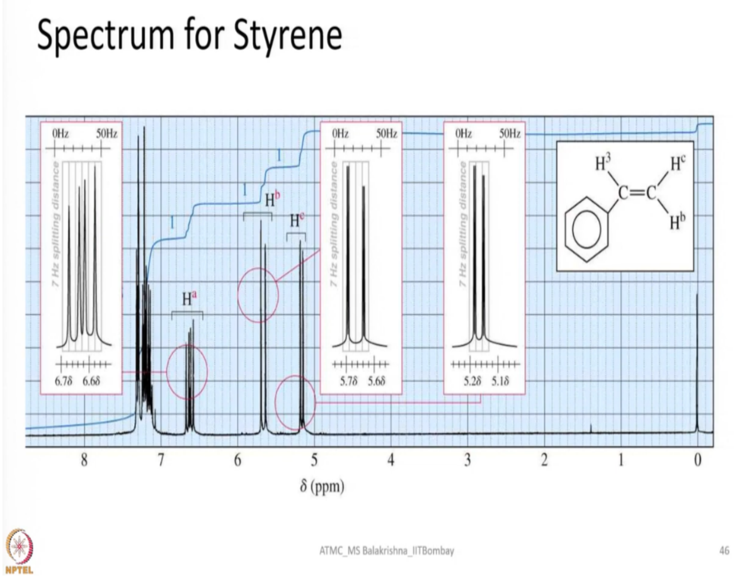

Spectrum for Styrene

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So, now, spectrum of styrene; this is how it looks like. This one will be showing a doublet of doublet. This one will also show a doublet of doublet. And all 3 are showing doublet of doublets. But wherever J_{bc} is there, the coupling is very small, 1.4 hertz. So, with this one, you should be able to make out which signal is due to which hydrogen atom; very simple.

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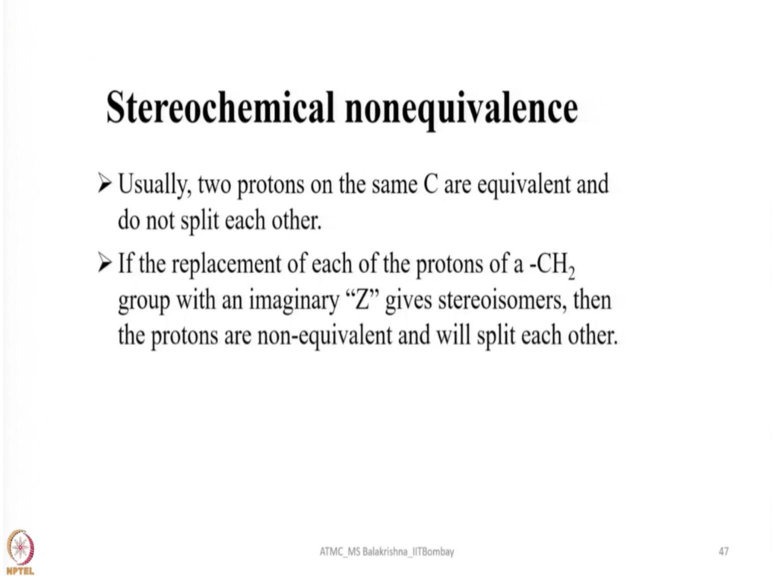

Stereochemical nonequivalence

- Usually, two protons on the same C are equivalent and do not split each other.
- If the replacement of each of the protons of a -CH_2 group with an imaginary “Z” gives stereoisomers, then the protons are non-equivalent and will split each other.

Now, let us look into stereochemical nonequivalence. What is the meaning of stereochemical nonequivalence? Usually, 2 protons on the same carbon are equivalent and do not split each other; I mentioned you. And then, if the replacement of each of the protons of CH_2 group with an imaginary Z gives stereoisomers, then the protons are nonequivalent and will split each other.

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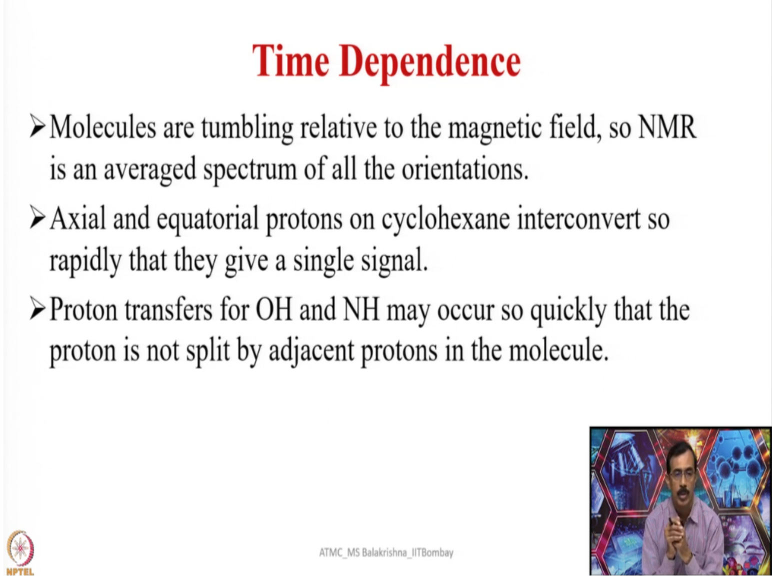

Time Dependence

- Molecules are tumbling relative to the magnetic field, so NMR is an averaged spectrum of all the orientations.
- Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal.
- Proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule.

Now, time dependence: Molecules are tumbling relative to the magnetic field, so, NMR is an averaged spectrum of all the orientations. Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal. For example, if you take NMR spectrum of cyclohexane at room temperature, what happens, they are rapidly converting axial into equatorial, equatorial into axial.

Because of this dynamic process what happens, the NMR timescale does not identify separately axial and equatorial and they appear as single signal; rapid tumbling is there. What would happen if we go for low temperature? Yes, if you go for low temperature NMR, in that case, you can arrest this dynamic process so that you can clearly distinguish between axial and equatorial protons and you will see separate signals.

So, proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in a molecule. What happens, they are very acidic. As a result, what happens, they will be exchanging these hydrogen atoms so quickly. As a result, what happens, at a given time, the neighbouring groups will fail to get influenced by the magnetic field of that one.

As a result, what happens, you do not see normally coupling due to OH or NH peaks, because, what happens, if they flipping, the flipping is so fast. The flipping is so fast; if it is much faster than NMR timescale of 10^{-8}, as a result, what happens, you cannot see the influence of those protons unless otherwise you make it static or stop the dynamic process.

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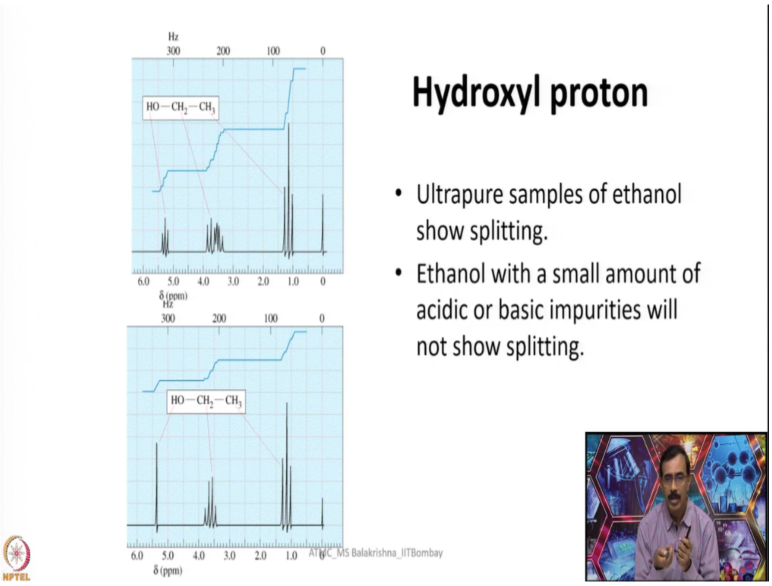

Hydroxyl proton

- Ultrapure samples of ethanol show splitting.
- Ethanol with a small amount of acidic or basic impurities will not show splitting.

For example, hydroxyl proton; if you see here, ethanol we have taken here. In ethanol, you can see this CH_3 will show a triplet because of N + 1 here. And then, this one should show a strictly speaking a quartet because of this one, but each quartet is split into a doublet. That means we are seeing each quartet is split into a doublet, the doublet of quartets. So, that means that is because of OH proton here.

That means, in very pure ethanol, if you take 100% pure ethanol, probably you can see, these kind of things, but rarely we will see it. On the other hand, what happens, normally you see something like this here. You will see a signal here and this is not influenced by this one. You see a quartet and a triplet here. Strictly speaking, one should get a signal like this. Of course, between OH and CH_3, no coupling, they are very far; but certainly CH_2 will be first coupled with a quartet here or it can be doublet if this coupling is more.

And then, each line will be split into 4 lines because of this one; so, a doublet of quartets or a quartet of doublets. So, you can see here. Whereas, this one is split by this one into triplet. Rarely you see this kind of spectrum. So, ultra-pure sample of ethanol can show splitting; very pure, 99.99 will not be enough; it should be 100%, 99.9999 you can keep on telling. So, that can show this kind of thing. And ethanol with a small amount of acidic or basic impurities will not show splitting at all here.

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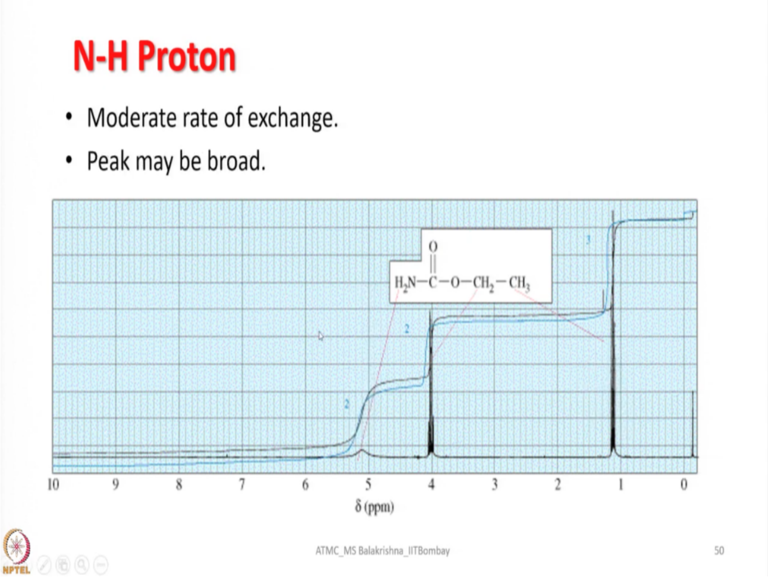

N-H Proton

- Moderate rate of exchange.
- Peak may be broad.

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And NH proton: Again, NH proton would be very broad here for the same reason, because of rapid exchange, and it will not show any coupling to any other groups present on carbon, but these 2 will split each other. So, this will be giving a quartet and this will be giving a triplet here. So, moderate rates of exchange and peak may be very broad.

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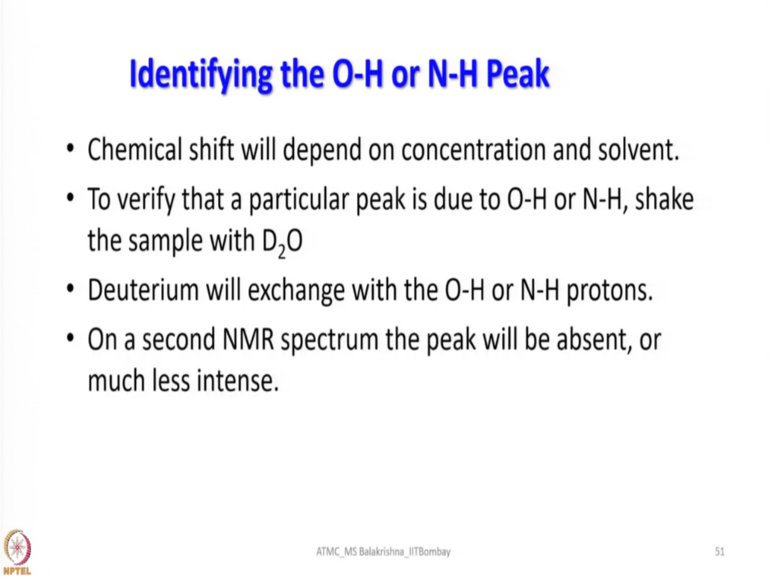

Identifying the O-H or N-H Peak

- Chemical shift will depend on concentration and solvent.
- To verify that a particular peak is due to O-H or N-H, shake the sample with D_2O
- Deuterium will exchange with the O-H or N-H protons.
- On a second NMR spectrum the peak will be absent, or much less intense.

So, identifying O-H and N-H peaks: So, chemical shift will depend on concentration and solvent; it is very important. And to verify that a particular peak is due to O-H or N-H, shake the sample with the D_2O, keep it for 24 hours and I record. And then the signal due to this one will be missing in the NMR. That indicates you have O-H or N-H group as I mentioned earlier. Deuterium will exchange with O-H and N-H to form OD and ND. On a second NMR spectrum, the peak will be absent or much less intense.

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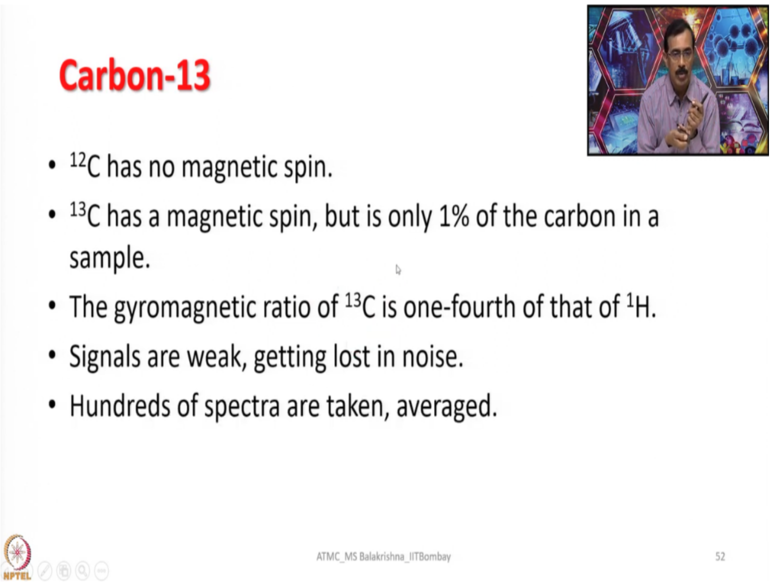

Carbon-13

- ^{12}C has no magnetic spin.
- ^{13}C has a magnetic spin, but is only 1% of the carbon in a sample.
- The gyromagnetic ratio of ^{13}C is one-fourth of that of ^{1}H.
- Signals are weak, getting lost in noise.
- Hundreds of spectra are taken, averaged.

Now, we will look into carbon-13. So, 12 has no magnetic spin, 12-carbon. And then, abundance of ^{13}C is only 1%. That means, if I take 100 molecules, out of 100 molecules containing carbon, 1 molecule have ^{13}C and remaining 99 would have ^{12}C; they are NMR inactive. So, whatever you will see signal, that is because of 1% ^{13}C. So, that means signals are very weak and you need large quantity of sample to observe ^{13}C NMR.

And gyromagnetic ratio of ^{13}C also, one-fourth of that of, almost approximately one-fourth of that of ^{1}H. That means 60 megahertz NMR for proton would be about 15 megahertz for ^{13}C or if it is 25 megahertz in case of 100 or 100 megahertz in case of 400 megahertz. So, signals are very weak, getting lost in noise. And if the signal to noise ratio is very high, you may not even see a signal due to carbon at all.

The sample should be very pure and it should be in larger quantity. At least 12% to 20% should be there in a carbon with NMR active; if not, at least it should be little bit more or probably have to run the NMR for a longer time. Hundreds of spectra are taken and averaged.

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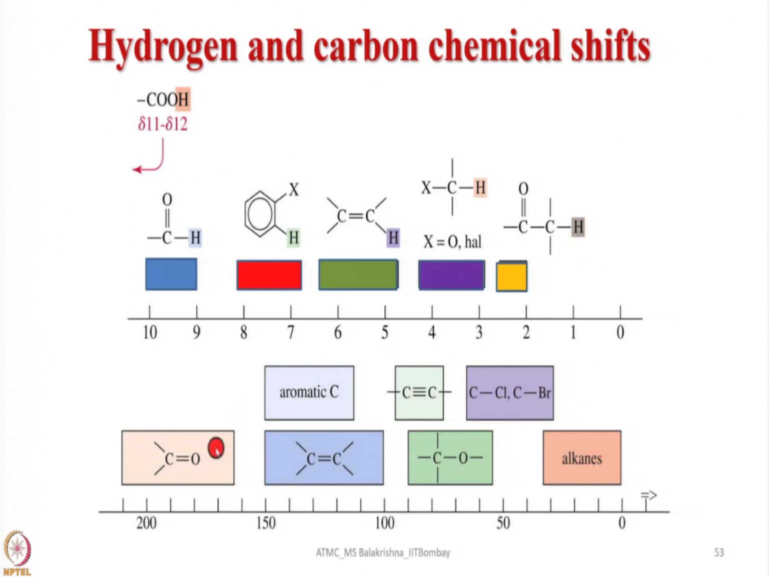

Hydrogen and carbon chemical shifts

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So, now let us look into hydrogen and carbon chemical shifts for various groups; already I showed you in previous ones. This gives some idea about the chemical shift range in both ^{13}C and ^{1}H for various groups here. For CH of aldehyde or ketone, it will be around carboxylic group; it is here. And when you have a halogen here, it will be having 7 to 8. And when you have an alkene bound one and then when you have a halo, it will be around 4 to 3; so, something like that. Similarly, one can also see for carbon also, corresponding where they appear.

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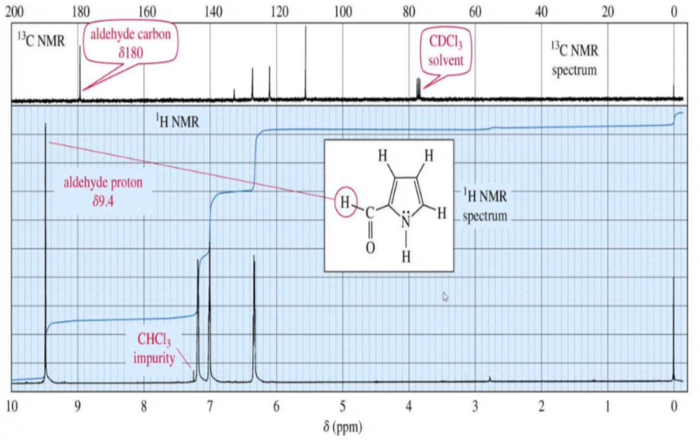
Combined ^{13}C and ^{1}H spectra



So, now, combined ^{13}C and ^{1}H spectra are shown here for this molecule. And this one is the ^{13}C spectrum. ^{13}C spectrum if you see, 1, 2, 3, 4, 5 carbon atoms. All 5 carbon atoms are very different. As a result, you will see 1, 2, 3, 4, 5 carbon atoms are very different. You will see 1, 2, 3, 4; one more should be here I think, probably it is here; so, 2 are there here.

In case of ^{1}H NMR, you can see this one is here much deshielded; and then NH proton is there; and then what we have is these 3 protons, we have these 3 signals here. And this NH is, it is somewhere here, the small NH, very weak signal because of exchange.

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Differences in ^{13}C Technique

- Resonance frequency is ~ one-fourth, 15.1 MHz instead of 60 MHz.
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.

So, differences in ^{13}C technique: So, resonance frequency, as I mentioned is one-fourth or 15.1 megahertz instead of 60 megahertz. And then, peak areas are not proportional to number of carbons. And carbon atoms with more hydrogen atoms absorb more strongly. That means it is very difficult to see signal due to quaternary carbon. If carbon has hydrogen, the possibility of seeing strong signal is more.

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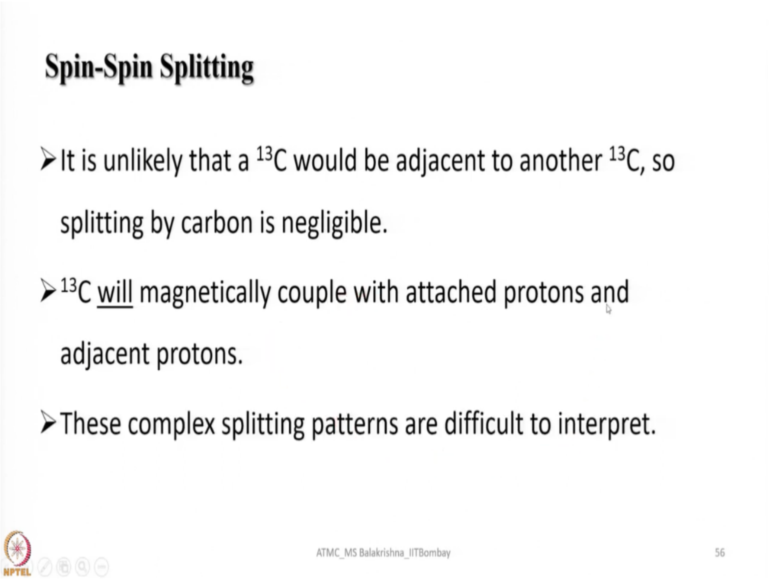

Spin-Spin Splitting

- It is unlikely that a ^{13}C would be adjacent to another ^{13}C, so splitting by carbon is negligible.
- ^{13}C will magnetically couple with attached protons and adjacent protons.
- These complex splitting patterns are difficult to interpret.

Let us look into spin-spin splitting here. So, it is unlikely that a ^{13}C would be adjacent to another ^{13}C; so, splitting by carbon is negligible. That means carbon-carbon splitting normally we do not come across unless it is enriched sample. If it is enriched sample means for example, if I take a methanol, all carbon atoms are ^{13}C. In such molecules like ethanol, CH_3CH_2OH, all CH_3CH_2 have ^{13}C, ^{13}C, then probably you can see coupling.

Otherwise you do not see it because what happens, if I take 100 here, 100 here and each one has NMR active and if I mix together, the possibility of seeing those 2 coming together to establish coupling is very rare and it is negligible. So, that is the reason we do not see carbon-carbon splitting at all. ^{13}C will magnetically couple with attached protons and adjacent. However, it can couple with other magnetically active nuclei such as hydrogen or phosphorus or fluorine or any other NMR active nuclei. These complex splitting patterns are difficult to interpret.

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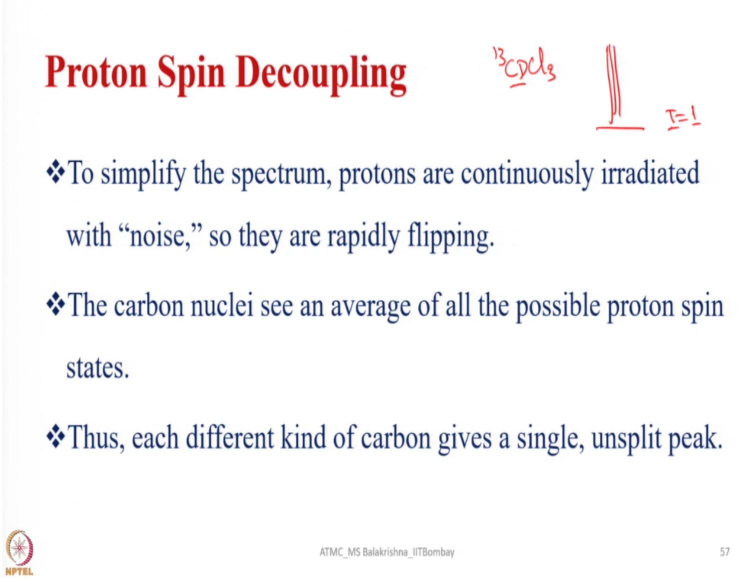

Proton Spin Decoupling

$^{13}CDCl_3$

I=1

- ❖To simplify the spectrum, protons are continuously irradiated with "noise," so they are rapidly flipping.
- ❖The carbon nuclei see an average of all the possible proton spin states.
- ❖Thus, each different kind of carbon gives a single, unsplit peak.

NPTEL

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Now, proton spin decoupling: What is this one, decoupling means? To simplify the spectrum, protons are continuously irradiated with noise, so, they are rapidly flipping. So, that means, when I am recording ^{13}C, to make it simple and interpretation is easy, all hydrogens present will be decoupled from the carbon atom so that you will see signals only due to carbon. Since carbon-carbon coupling is not there, what happens, you can just by looking into the local symmetry and you should be able to identify how many signals.

And if you see that many signals in NMR, yes, you can say you got your compound. So, the carbon nuclei see an average of all the possible proton spin states. And then, thus, each different kind of carbon gives a single unsplit peak. All show unique one, and in around 72.1, you may see a triplet of 1:1 is to intensity that is due to $CDCl_3$ sample we are using. $CDCl_3$, normally we use as a solvent; so, that one, the carbon is split with deuterium.

Deuterium is I = 1; if you use N + 1 rule, deuterium is I = 1. So, what basically you will see is 2nI + 1 the splitting is; so, you can see 2 into 1 into 1 plus 3, 3. And now you get a triplet here. N + 1 peaks will be there, but splitting will be 4. So, basically what happens, 4 lines will be there. So, here in case of deuterium $CDCl_3$, if you see ^{13}C $CDCl_3$ signal what happens, it appears like this one here. So, this is because this signal is coupled by this one, D. So, this is D is I = 1; so, you get a triplet, 2nI + 1 number of lines will be there.

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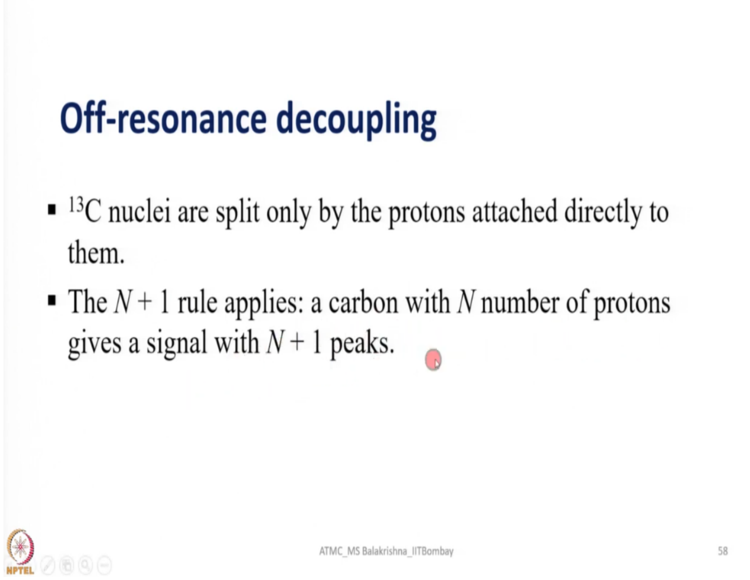

Off-resonance decoupling

- ^{13}C nuclei are split only by the protons attached directly to them.
- The $N + 1$ rule applies: a carbon with N number of protons gives a signal with $N + 1$ peaks.

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Off-resonance decoupling: So, what is that one? So, ^{13}C nuclei are split only by the protons attached directly to them. So, the N + 1 rule applies, a carbon with N number of protons gives a signal with N + 1 peaks.

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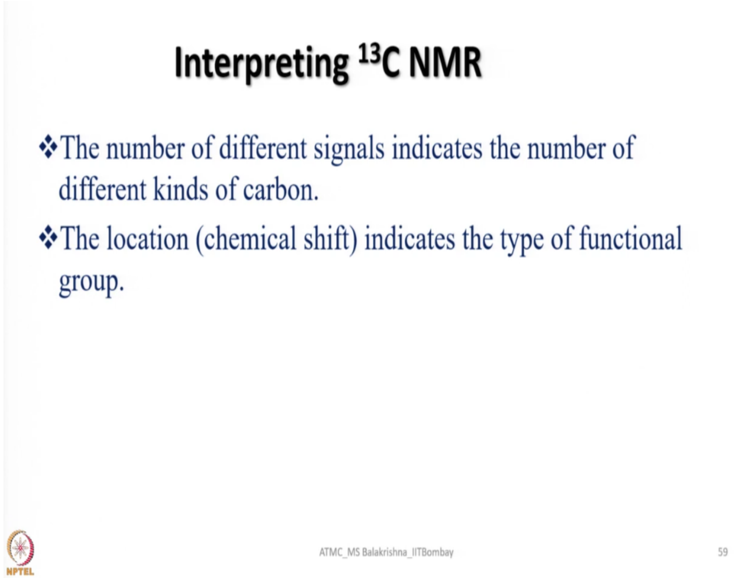

Interpreting ^{13}C NMR

- ❖The number of different signals indicates the number of different kinds of carbon.
- ❖The location (chemical shift) indicates the type of functional group.

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So, interpreting will be little bit complicated. As a result, what happens, we go for decoupled one.

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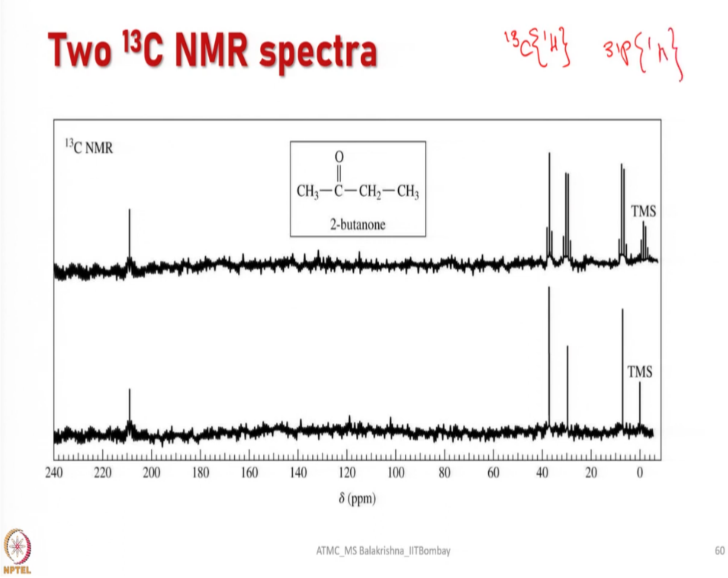

Two ^{13}C NMR spectra

$^{13}C\{^{1}H\}$ $^{31}P\{^{1}H\}$

You can see here, for example, this is a coupled NMR and this is a decoupled. Decoupled is very easy; we have 1, 2, 3, 4 carbons are there. You can see 1, 2, 3, 4 carbons plus TMS standard, whereas, here also we have 4, but you can see, because of hydrogen coupling, this one is also showing a quartet, and this is showing a triplet, and this is showing a quartet again. So, this is how it is, but we do not want that information.

Whatever the information proton comes from ^{1}H NMR, so, we do not want to complicate ^{13}C NMR. That is the reason what we do is, we nullify the coupling due to hydrogen and we call it as decoupled. ^{13}C we write in this one, decoupled one will be written like this, $^{13}C\{^{1}H\}$ in ^{1} H means ^{1} H decoupled. Similarly, in case of ^{31}P, we will write $^{31}P\{^{1}H\}$ something like this.

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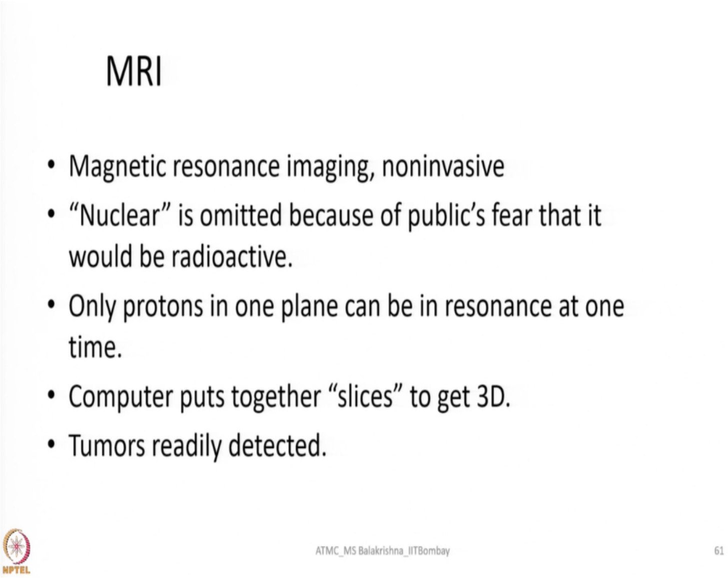

MRI

- Magnetic resonance imaging, noninvasive
- “Nuclear” is omitted because of public’s fear that it would be radioactive.
- Only protons in one plane can be in resonance at one time.
- Computer puts together “slices” to get 3D.
- Tumors readily detected.

Now, MRI, it is magnetic resonance imaging. It should have been nuclear magnetic resonance imaging, since the nuclear coming, people are worried that it may be radioactive, that is the reason that term nuclear is removed and simply it is called as magnetic resonance imaging. In this case what happens, only protons in 1 plane can be in resonance at 1 time and computer puts together slices to get a 3D information, 3D structure; tumours readily detected.

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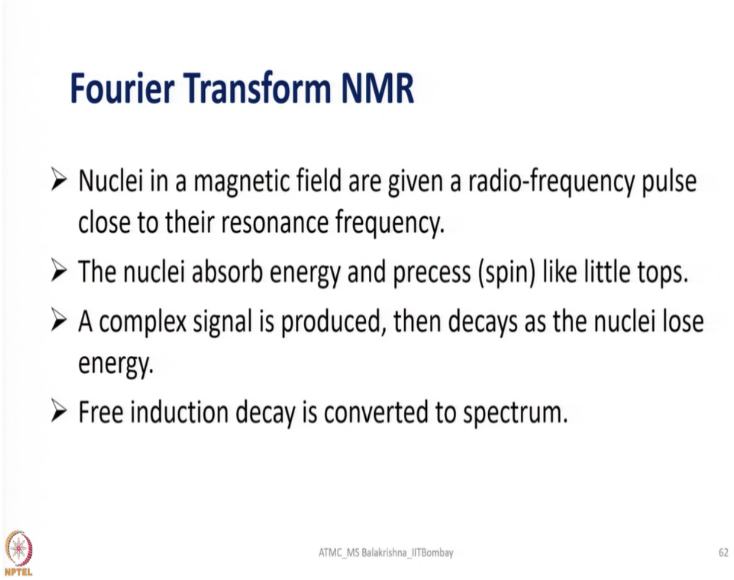

Fourier Transform NMR

- Nuclei in a magnetic field are given a radio-frequency pulse close to their resonance frequency.
- The nuclei absorb energy and precess (spin) like little tops.
- A complex signal is produced, then decays as the nuclei lose energy.
- Free induction decay is converted to spectrum.

And this is very important. What is FT NMR? Fourier Transform NMR, this is nothing but nuclei in a magnetic field are given a radio frequency pulse close to the resonance frequency. And then the nuclei absorb energy and precess, spin like little tops, like precess and then they flip. Then a complex signal is produced, then decays as the nuclei lose energy; that means when it comes back to the ground state. Free induction decay is converted to spectrum. These store FID and then later you can convert that into spectrum.

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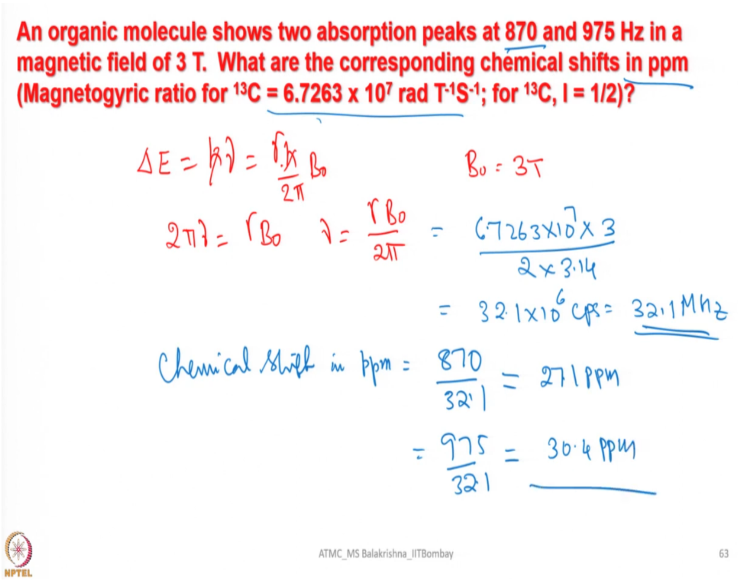

An organic molecule shows two absorption peaks at 870 and 975 Hz in a magnetic field of 3 T. What are the corresponding chemical shifts in ppm (Magnetogyric ratio for ^{13}C = 6.7263 x 10^7 rad $T^{-1}S^{-1}$; for ^{13}C, I = 1/2)?

$\Delta E = h\nu = \frac{\gamma h}{2\pi} B_0$ $\quad B_0 = 3T$

$2\pi\nu = \gamma B_0 \quad \nu = \frac{\gamma B_0}{2\pi} = \frac{6.7263\times10^7\times3}{2\times3.14}$

$= 32.1\times10^6$ cps $=$ 32.1 Mhz

Chemical Shift in ppm $= \frac{870}{32.1} = 27.1$ ppm

$= \frac{975}{321} = 30.4$ ppm

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So, now let us look into few problems here. An organic molecule shows two absorption peaks at 870 and 975 hertz in a magnetic field of 3 tesla. What are the corresponding chemical shifts in ppm? This is the question. And gyromagnetic ratio for ^{13}C, 6.7263 x 10^7 radians per tesla per second. For ^{13}C, I = ½; it is given. Also it is organic molecule we are saying, it is a ^{13}C.

So, now we have to see; what we have to do is, we have to calculate now ν correspond to this one, because 3 tesla is there. Corresponding to 3 tesla, what is the magnetic field strength, that we have to calculate. Once if you calculate magnetic field strength, then if you divide that one, the value 870 by that one, you get the corresponding value in ppm. So, let us do that one.

So, now, you should remember only 1 equation here, it is very simple, $\Delta E = h\nu = \gamma (h/2\pi).Bo$ Bo is the applied magnetic field and this is Planck's constant. So, now, if these 2 goes, then $2\pi\nu = \gamma Bo$. And then $\nu = \gamma Bo/2\pi$, this is the thing. So, now Bo is given, gamma is also given, let us apply here.

6.7263 x 10^7 x 3/ 2 x 3.14; approximately this comes around 32.1 x 10^6 CPS. That equals to 32.1 megahertz. This is the field strength now. So, calculate the chemical shift in ppm. So, what we have to do is, 870 is given here. First 870/32.1 and another one is 975/32.1 will give you corresponding in ppm. That one is 27.1 ppm; and then, this is 30.4 ppm. So, this is how one can do the calculation. Now, let us look into another example.

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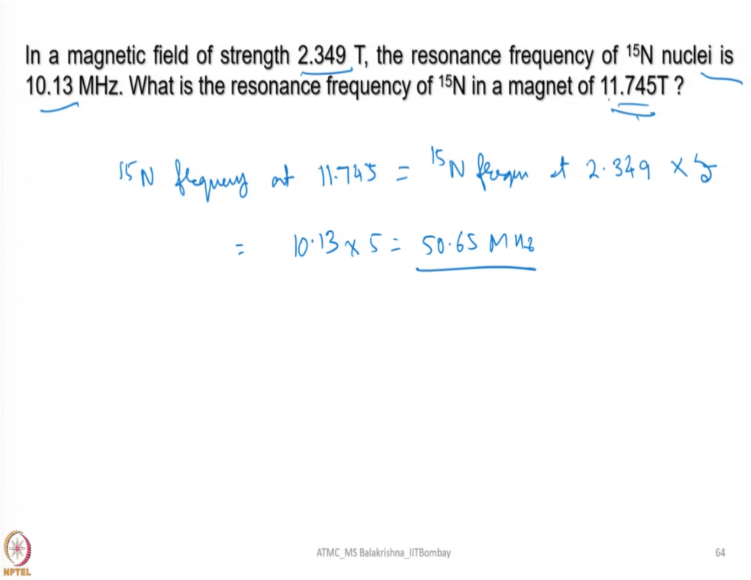

In a magnetic field of strength 2.349 T, the resonance frequency of ^{15}N nuclei is 10.13 MHz. What is the resonance frequency of ^{15}N in a magnet of 11.745T ?

^{15}N frequency at 11.745 = ^{15}N frequ at 2.349 × 5

= 10.13 × 5 = 50.65 MHz

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In a magnetic field of strength 2.349 tesla, the resonance frequency of ^{15}N nuclei is 10.13 megahertz. What is the resonance frequency of ^{15}N in a magnet of 11.745 tesla? So, now, we have to see ^{15}N frequency at 11.745 = ^{15}N frequency at 2.349 is 5 times. So, that means, basically, 10.13 x 5 would give you 50.65 megahertz; that is it. It is almost 5 times is there; so, you should be able to do that one. Magnetic field strength this one and this one is there; this is 5 times; that we know by simple calculation, so, 5 times. For this one, you should multiply and you get the answer.

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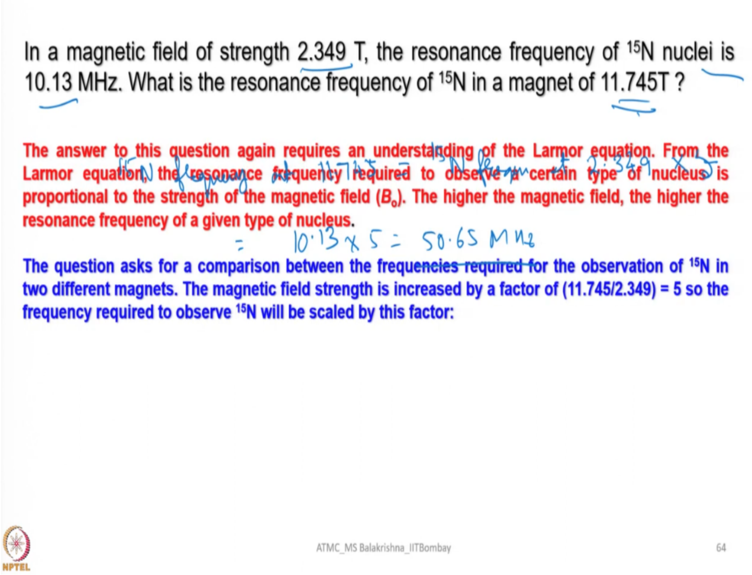

In a magnetic field of strength 2.349 T, the resonance frequency of ^{15}N nuclei is 10.13 MHz. What is the resonance frequency of ^{15}N in a magnet of 11.745T ?

The answer to this question again requires an understanding of the Larmor equation. From the Larmor equation, the resonance frequency required to observe a certain type of nucleus is proportional to the strength of the magnetic field (B_o). The higher the magnetic field, the higher the resonance frequency of a given type of nucleus.

^{15}N frequency at 11.745 = ^{15}N frequ at 2.349 × 5

= 10.13 × 5 = 50.65 MHz

The question asks for a comparison between the frequencies required for the observation of ^{15}N in two different magnets. The magnetic field strength is increased by a factor of (11.745/2.349) = 5 so the frequency required to observe ^{15}N will be scaled by this factor:

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So, this is the answer.

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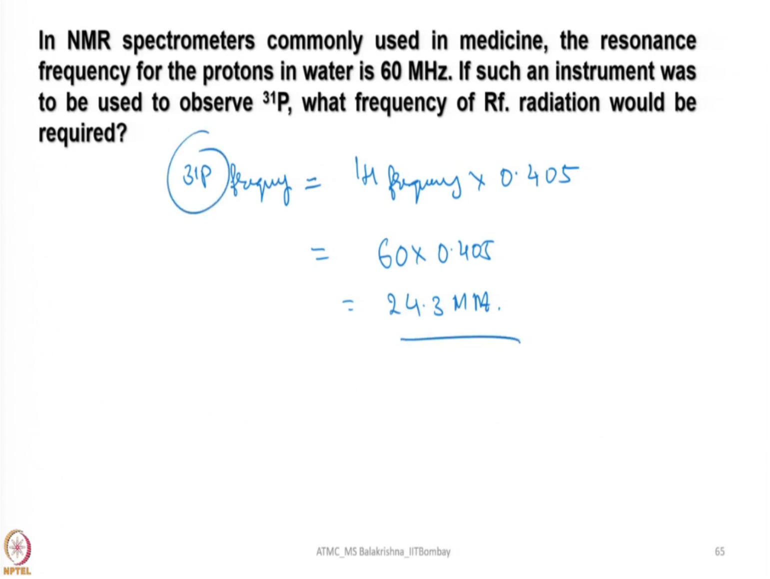

In NMR spectrometers commonly used in medicine, the resonance frequency for the protons in water is 60 MHz. If such an instrument was to be used to observe ^{31}P, what frequency of Rf. radiation would be required?

^{31}P frequency = ^{1}H frequency x 0.405

= 60 x 0.405

= 24.3 MHz.

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And then, in NMR spectrometers commonly used in medicine, the resonance frequency for the protons in water is 60 megahertz. If such an instrument was to be used to observe ^{31}P, what frequency of radiofrequency radiation would be required? This one; so, ^{31}P frequency we should know from gyromagnetic ratio, frequency equals ^{1}H frequency x 0.405. So, that means, if it is 60 megahertz we are using, 60 x 0.405 would give you approximately 24.3 megahertz for ^{31}P. So, this is how you can write.

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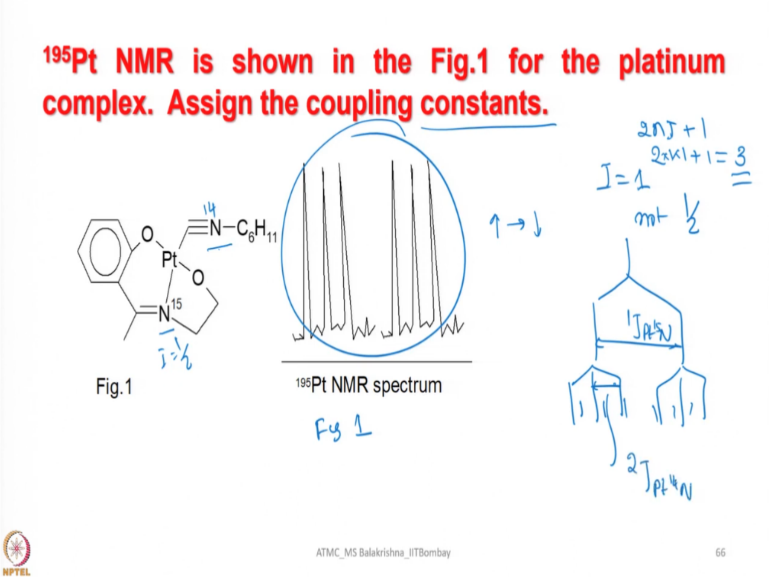

^{195}Pt NMR is shown in the Fig.1 for the platinum complex. Assign the coupling constants.

Fig.1

^{195}Pt NMR spectrum

Fig 1

$2nI+1$

$2\times1\times1+1 = 3$

$I = 1$

m_I $\frac{1}{2}$

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So, now, I have given one NMR, I have given the molecule, you have to interpret. ^{195}Pt NMR is shown in the figure 1; this is the figure 1; for the platinum complex, assign the coupling constant. Now, what you can see is, the structure is given and also this is ^{15}N and of course, it is not labelled means it is understood it is 14. Now, we have to see why we got 2 triplets and each triplet has intensity of 1:1:1.

And usually, a triplet with 1:1:1 has to do something with I value of 1, not half. ^{15}N means it has I = ½. That means there should be $^1J_{PtN}$. So, that means basically it first splits and this is due to $^1J_{Pt}{}^{15}{}_{N}$, this coupling, let us not worry about that when there is a coupling. And now, this will be split by ^{14}N. Why ^{14}N; so, N = 1, so, if you write 2nI + 1, so, 2 into 1 is there, nucleus; 1 into spin 1 plus 1; it will be 3.

Now, so, that means 3 of equal intensity. Why 3 equal intensity? I = 1; so, one will be like this, one will be like this, one will be like this. So, now intensity will be equal. So, now, we will see like this. So, intensity 1:1:1, 1:1:1. This is what we see here. Yes, we can interpret. So, it has coupling of both ^{14}N that is a ^{2}J coupling, this value is $^2J_{Pt}{}^{14}{}_{N}$. So, that is it. So, this is how you can interpret the spectrum. Very easy; we have to think little bit; you have to give some time, try to understand how the splitting looks like, what is the intensity, you should be able to do it.

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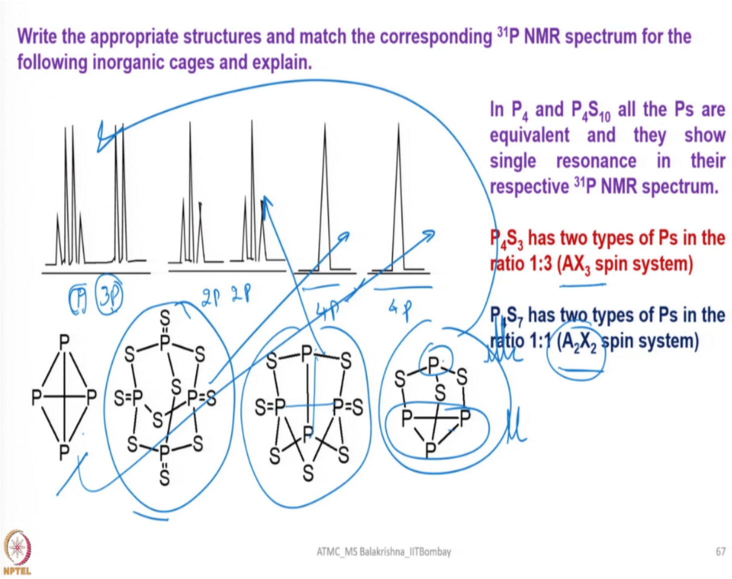

Write the appropriate structures and match the corresponding ^{31}P NMR spectrum for the following inorganic cages and explain.

In P_4 and P_4S_{10} all the Ps are equivalent and they show single resonance in their respective ^{31}P NMR spectrum.

P_4S_3 has two types of Ps in the ratio 1:3 (AX_3 spin system)

P_4S_7 has two types of Ps in the ratio 1:1 (A_2X_2 spin system)

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One more question I have given here. So, I have given 4 spectra here. Write the appropriate structures and match the corresponding ^{31}P NMR spectrum for the following in organic cages and explain. So, this is basically, the spectrum given is observed for a mixture of samples when white phosphorus was reflexed with certain quantity of sulphur. With sulphur what happens? very similar to white phosphorus reacting with oxygen to form phosphorus pentoxide are phosphorus trioxide, P_2O_3 or P_2O_5, here also you can get different compounds.

And now, based on what kind of compounds we get, by just looking to the spectrum, we should be able to identify. So, if you see here; and of course, here, chemical shifts I have not given; if you are familiar with chemical shift range, then you should be able to tell. In the absence of this one, still one should be able to speculate that there are two samples having one type of phosphorus atoms.

Assume in white phosphorus all the 4 phosphorus atoms are intact, so, P-P bonds are not broken, it is not fragmented, maybe insertion maybe there of sulphur. In that case, 2 cases where we have 4 equivalent phosphorus atoms; in this one what happens, we have out of 4, 2 of 1 side, 2 of 1 side, because they split each other into triplet. And here what we have is P and 3P. So, something like this we have.

So, that means 1 equivalent or 3 P and one is P. So, this one will split this into doublet and this will split into; now we have to write the structures. So, probably, just by looking to the ^{31}P spectrum of pure white phosphorus and comparing, yes, maybe a small quantity of white phosphorus is left unreacted. You can see here; yes, this is there; this can be one of them. And now, if we just look into this one, this is another product.

In this one, all phosphorus are equivalent and very similar to this one. So, this also shows a single signal. So, this is for this one, that is also, and this is for this one. And now here, these are of one type and this is one type. So, this will show a quartet and this will show a doublet. So, that means basically, so this one is for this one. And now the other one is left. If you see here, 2; this is of one type and this is of one type.

These 2 will split into triplet and these 2 will split this into triplet, and this is what this one. So, this is how you can very nicely interpret and it is very interesting. When you make a molecule or when you get a mixture of compounds and when you get a good NMR spectrum, you can really enjoy interpreting the data is wonderful. So, if you want to label them, this AX_3 spin system, it is A_2X_2 spin system.

Of course, why X? Why not A and B or something? That probably you should learn from fully dedicated NMR courses. As I mentioned here, it is only for interpreting, the sake of making you how to interpret without learning much basics; I am giving you only brief introduction to NMR spectroscopy. And of course, if you are more interested, you can also look into that one what would happen to the chemical shift difference, what happened to the chemical constant, coupling constant differences and all those things.

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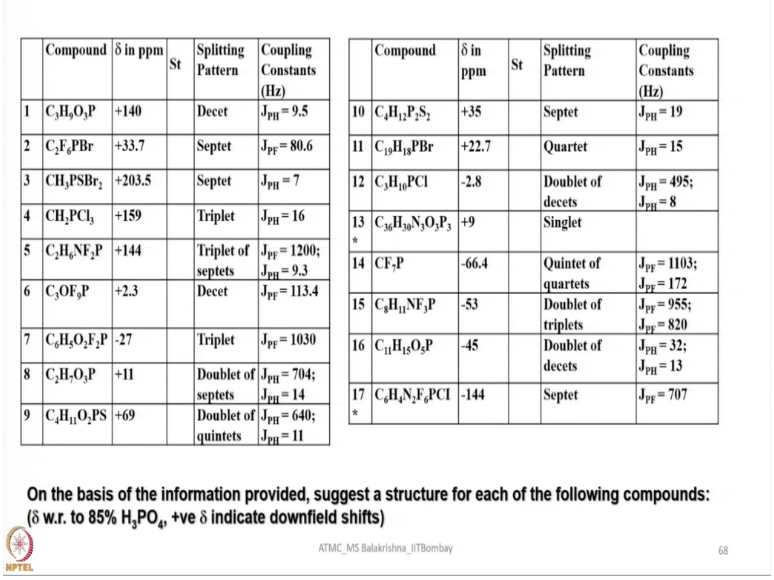

	Compound	δ in ppm	St	Splitting Pattern	Coupling Constants (Hz)
1	$C_3H_9O_3P$	+140		Decet	$J_{PH} = 9.5$
2	C_2F_6PBr	+33.7		Septet	$J_{PF} = 80.6$
3	CH_3PSBr_2	+203.5		Septet	$J_{PH} = 7$
4	CH_2PCl_3	+159		Triplet	$J_{PH} = 16$
5	$C_2H_6NF_2P$	+144		Triplet of septets	$J_{PF} = 1200$; $J_{PH} = 9.3$
6	C_3OF_9P	+2.3		Decet	$J_{PF} = 113.4$
7	$C_6H_5O_2F_2P$	-27		Triplet	$J_{PF} = 1030$
8	$C_2H_7O_3P$	+11		Doublet of septets	$J_{PH} = 704$; $J_{PH} = 14$
9	$C_4H_{11}O_2PS$	+69		Doublet of quintets	$J_{PH} = 640$; $J_{PH} = 11$

	Compound	δ in ppm	St	Splitting Pattern	Coupling Constants (Hz)
10	$C_4H_{12}P_2S_2$	+35		Septet	$J_{PH} = 19$
11	$C_{19}H_{18}PBr$	+22.7		Quartet	$J_{PH} = 15$
12	$C_3H_{10}PCl$	-2.8		Doublet of decets	$J_{PH} = 495$; $J_{PH} = 8$
13 *	$C_{36}H_{30}N_3O_3P_3$	+9		Singlet	
14	CF_7P	-66.4		Quintet of quartets	$J_{PF} = 1103$; $J_{PF} = 172$
15	$C_8H_{11}NF_3P$	-53		Doublet of triplets	$J_{PF} = 955$; $J_{PF} = 820$
16	$C_{11}H_{15}O_5P$	-45		Doublet of decets	$J_{PH} = 32$; $J_{PH} = 13$
17 *	$C_6H_4N_2F_6PCI$	-144		Septet	$J_{PF} = 707$

On the basis of the information provided, suggest a structure for each of the following compounds:
(δ w.r. to 85% H_3PO_4, +ve δ indicate downfield shifts)

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And here I have listed several compounds containing, about 17 compounds containing phosphorus and also I have given the chemical shifts for each one, and also the splitting pattern I have mentioned. Decet, for example here, decet means 10 lines. 10 lines are there; if you see here, it is trimethyl phosphite. 9 protons are splitting phosphorus into 10, decet line and PH coupling is 9.5, $^2J_{\text{PH}}$ coupling.

If you interpret and write the structure in each case, I am sure I can conclude that you know little more than 50% of ^{31}P NMR spectroscopy. You should be able to interpret any spectra that comes on to you with respect to ^{31}P NMR nucleus. Just try all those things; I am sure you should be able to get the correct structure in each case.

So, let me stop here. And few more examples I would continue in my next lecture before I move on to interpretive IR spectroscopy to understand IR spectra of coordination compounds with more emphasis for carbonyl groups. Until then, have a great time. And thank you for your kind attention.