Advanced Transition Metal Chemistry_Spectroscopic Methods
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Module - 12
Lecture - 57
NMR Spectroscopy

Hello everyone. Once again, I welcome you all to MSB lecture series on Transition Metal Chemistry. This lecture is fifty-seventh in the series. After this one, another 3 are left. So, in this one, let me begin discussion on NMR spectroscopy. As I had mentioned, I am not going to the details of NMR spectroscopy, but I would make you efficient in interpreting NMR data of multinuclear system, whether it is ^{1}H, ^{13}C, ^{19}F or any other NMR active nuclei. So, let us begin with first slide.

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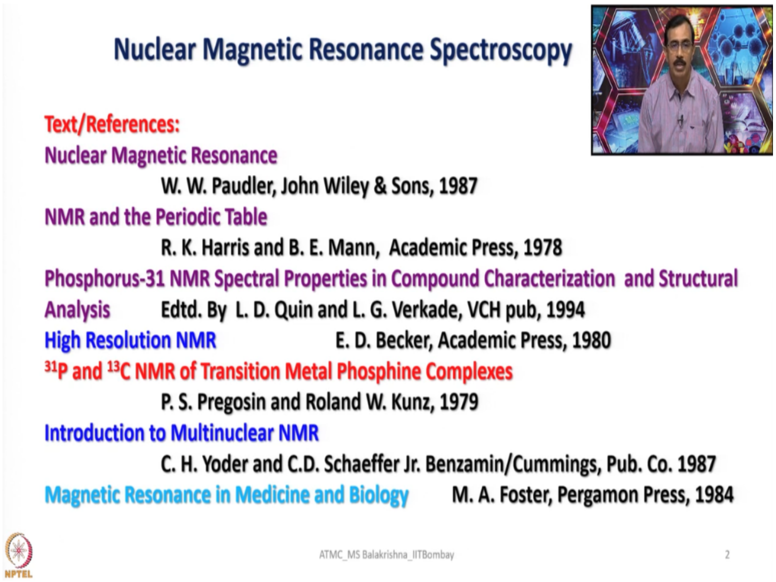

Nuclear Magnetic Resonance Spectroscopy

Text/References:

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R. K. Harris and B. E. Mann, Academic Press, 1978

Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis Edtd. By L. D. Quin and L. G. Verkade, VCH pub, 1994

High Resolution NMR E. D. Becker, Academic Press, 1980

^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes
P. S. Pregosin and Roland W. Kunz, 1979

Introduction to Multinuclear NMR
C. H. Yoder and C.D. Schaeffer Jr. Benzamin/Cummings, Pub. Co. 1987

Magnetic Resonance in Medicine and Biology M. A. Foster, Pergamon Press, 1984

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So, first slide I have given some reference books. If you are more interested in learning about nuclear magnetic resonance, you can refer to some of these books. These are all wonderful books and you can get wealth of information from these books. Please read and try to understand more about NMR spectroscopy.

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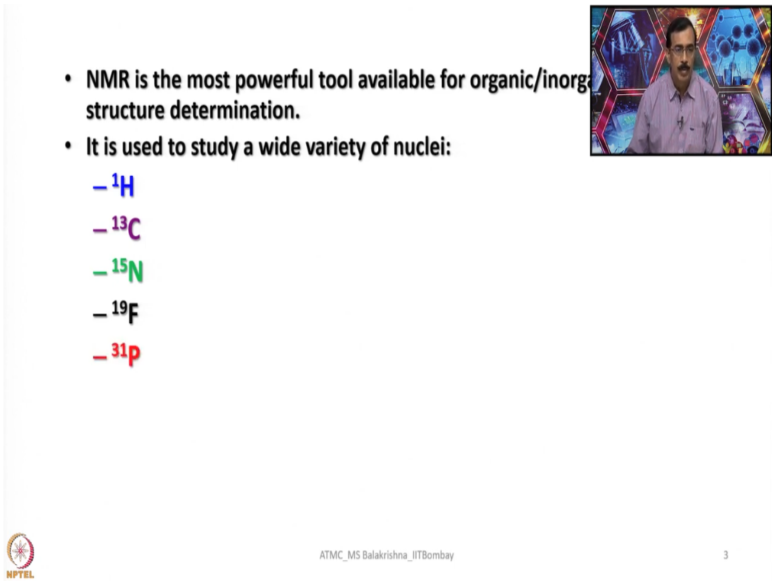

- NMR is the most powerful tool available for organic/inorg
structure determination.
- It is used to study a wide variety of nuclei:
  - ^{1}H
  - ^{13}C
  - ^{15}N
  - ^{19}F
  - ^{31}P

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So, NMR is the most powerful tool available for organic and inorganic synthetic chemists; not only for organic and inorganic, biochemist, material chemists, environmental chemists. In fact, all those who use chemicals, NMR is the most powerful tool to characterise those compounds and also to determine the structure. It is used to study a wide variety of nuclei. For example, ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P and many others.

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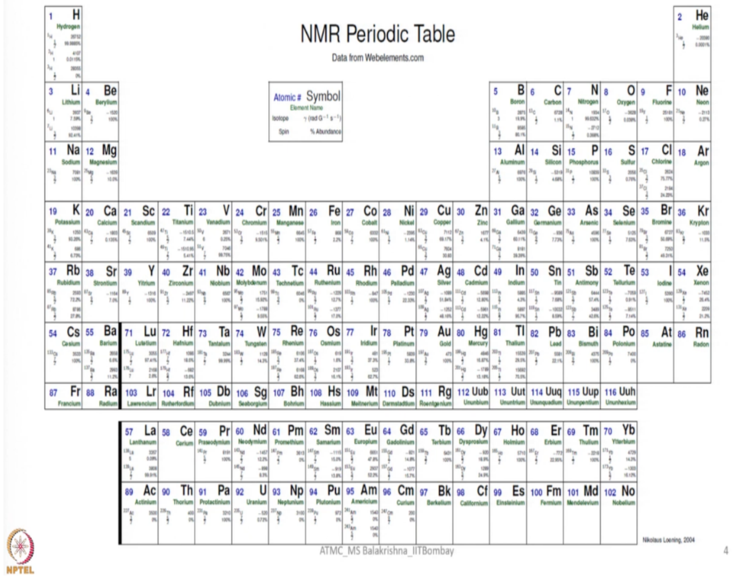

NMR Periodic Table

Data from Webelements.com

Nikolaus Loening, 2004

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This periodic table shows all possible elements which have NMR active nuclei. Plenty of them are NMR active. In fact, we can do NMR studies for most of these elements having isotopes which are NMR active. Of course, they may vary; all of them are not 100% but some of them are 100% or some of them are in trace quantity, some of them in 20, 30%.

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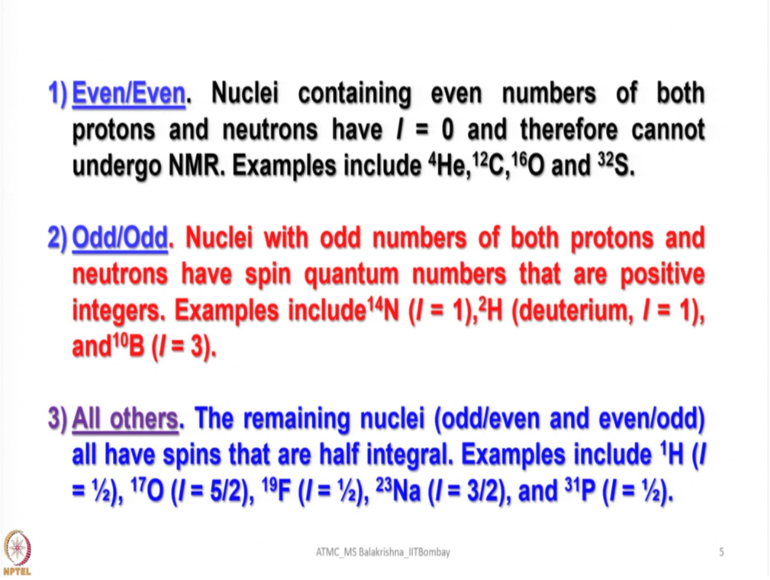

1) **Even/Even**. Nuclei containing even numbers of both protons and neutrons have *I* = 0 and therefore cannot undergo NMR. Examples include ^{4}He,^{12}C,^{16}O and ^{32}S.

2) **Odd/Odd**. Nuclei with odd numbers of both protons and neutrons have spin quantum numbers that are positive integers. Examples include^{14}N (*I* = 1),^{2}H (deuterium, *I* = 1), and^{10}B (*I* = 3).

3) **All others**. The remaining nuclei (odd/even and even/odd) all have spins that are half integral. Examples include ^{1}H (*I* = ½), ^{17}O (*I* = 5/2), ^{19}F (*I* = ½), ^{23}Na (*I* = 3/2), and ^{31}P (*I* = ½).

So, what we have to understand first is which are the nuclei which exhibit NMR. So, that means, let us consider nuclei containing even numbers of both protons and neutrons; have nuclear spin I = 0 and therefore cannot undergo NMR. That means, if you consider any nucleus having even number of protons and even number of neutrons, they have nuclear spin I = 0 and therefore cannot be used for NMR purposes.

For example, if you consider ^{4}He, ^{12}C, ^{16}O or ^{32}S, how would odd-odd, that means nuclear with odd number of both protons and neutrons have spin quantum number that are positive integers. For example, if you consider ^{14}N, nuclear spin I = 1; if you consider ^{2}H deuterium, I = 1; and also, if you consider a ^{10}B, I = 3. So, these are all having odd number of protons and odd number of neutrons and they are NMR active.

Rest of the nuclei having odd-even or even-odd combination of protons and neutrons have half integral values for nuclear spin. Example, ^{1}H, I =1/2; and ^{17}O, I = 5/2; if you consider ^{19}F, I = 1/2; ^{23}N, I = 3/2; and ^{31}P, I = 1/2; and many more. So, that means here if you consider, these are all even-even NMR inactive; whereas, odd-odd and rest of them, odd-even or even-odd combination of protons and neutrons are all NMR active. And of course, one should know how much such isotopes are present.

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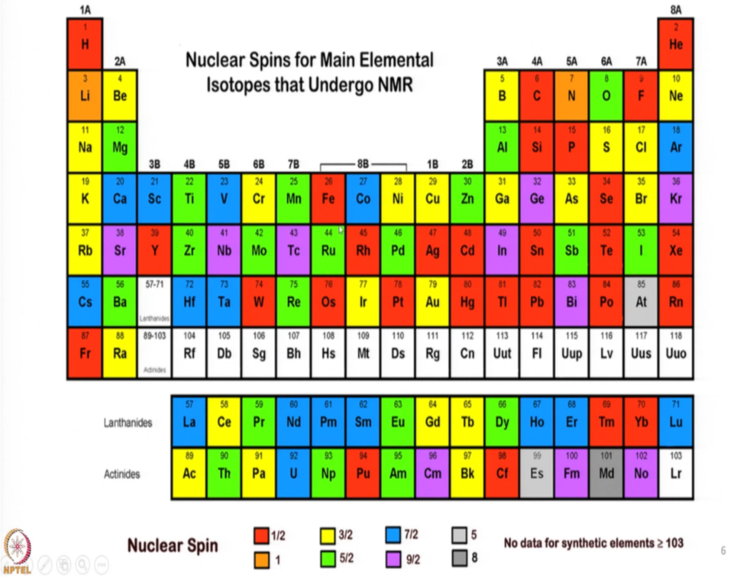

Nuclear Spins for Main Elemental Isotopes that Undergo NMR

Nuclear Spin 🟥 1/2 🟧 1 🟨 3/2 🟩 5/2 🟦 7/2 🟪 9/2 ⬜ 5 ⬛ 8

No data for synthetic elements ≥ 103

So, this one clearly gives you some idea about different types of nuclear spin we come across among elements in this periodic table. You can see, all those indicated in red colour have I = 1/2; and those which are in yellow colour have I = 3/2; and blue, 7/2; and then this orange one for lithium and nitrogen you can see; and also those in green colour, they have I = 5/2; and this in purple or violet, they have 9/2. So, that means you can see, a majority of elements do possess nuclei having NMR active I values.

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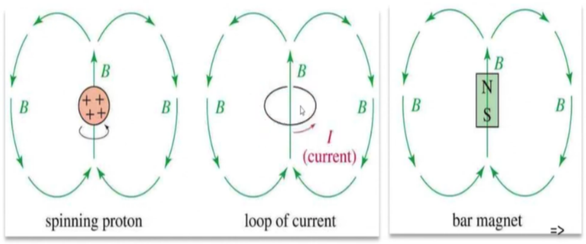
Nuclear Spin

- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.



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So, what is nuclear spin? A nucleus with an odd atomic number or an odd mass number has a nuclear spin. Now it is very clear from my previous slide, nucleus with an odd atomic number or an odd mass number possess a nuclear spin and the spinning charged nucleus generates a magnetic field. That is true. This information you must have learnt from physics also; any charged species generates a magnetic field when it is in circular motion.

So, for example, if you take, if you consider nucleus as a tiny bar magnet and if you keep in a magnetic field, it can be aligned with the magnetic field or it can oppose the magnetic field. So, that means spinning protons, they have haphazard way of arrangement. The moment you put them in a magnetic field, they are all aligned. Some of them are aligned with the field, some of them are aligned opposite the field. So, that means here, a loop of current is generated here, I.

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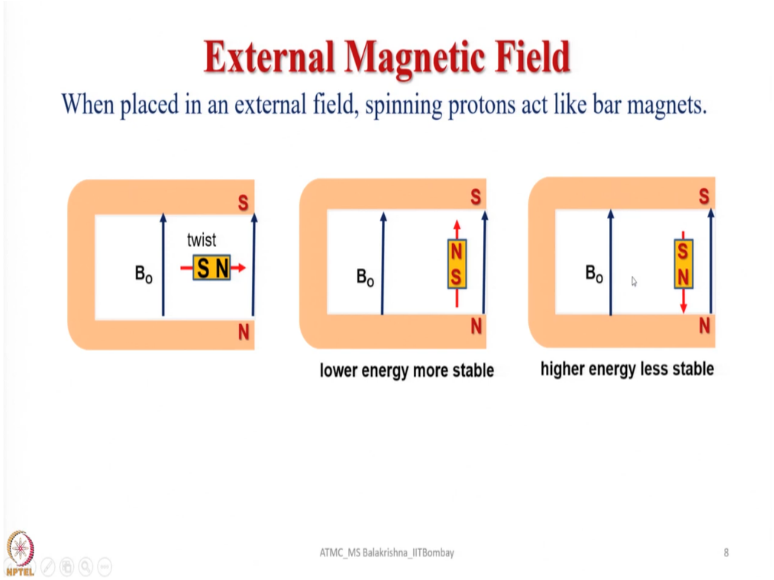

External Magnetic Field

When placed in an external field, spinning protons act like bar magnets.

lower energy more stable

higher energy less stable

That means, when placed in the magnetic field, spinning protons act like bar magnets. I mentioned you, it is in absence of magnetic field. In the presence of magnetic field what happens, some of them can be aligned in this way; they have lower energy and more stable; some of them can be aligned in this fashion and they have high energy and they are less stable. In fact, you can convert this one to this one by supplying energy equivalent to the energy gap between these two levels.

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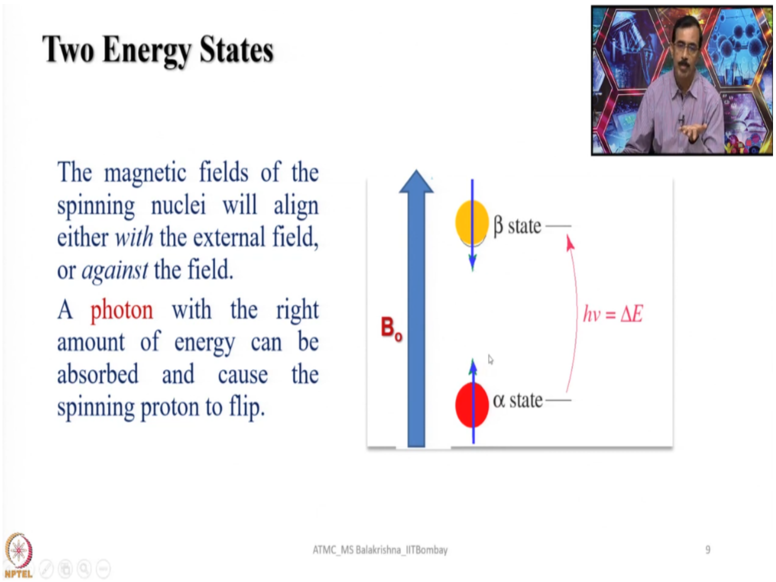

Two Energy States

The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.

So, you can see here, two energy states you can think of, alpha-state and beta-state. In alpha state, nuclei have aligned with the field; whereas, in beta state, higher energy, they have aligned against or opposite to the applied field. And the energy difference is given by h nu equals ΔE. If you supply the energy equivalent to this one, this can go to this one here.

The magnetic field of the spinning nuclei will align with either the external field or against the field. A photon with the right amount of energy can be absorbed and cause the spinning proton to flip. So, it is very simple. You try to imagine this spinning nucleus like a top you must have played with in childhood or someone will play even now. So, this is something like this.

(Video Starts: 07:08) A top is there and if it is rotating like this, what happens, when it is rotating steadily and looks almost static, when it is a perfectly balanced top, it will be rotating and it appears like it is standing; sometimes they say top is sleeping. In that case what happens, and now let us assume the applied magnetic field is in this direction along this axis of this top and then you apply another energy in this direction.

So, for example, you start playing a top and then try to touch it like this, perpendicular to that one, what happens, it starts wobbling. So, when the frequency of this one is suitable, then what happens, it will turn something like this, it will eventually wobble, and it becomes like this. That is what exactly happens in that case. **(Video Ends: 07:56)** So, this is called flipping.

That means that much energy it already gained when we supplied in the form of a photon in the radio frequency region. So, now, let us look into the relationship between this energy gap and the magnetic field strength.

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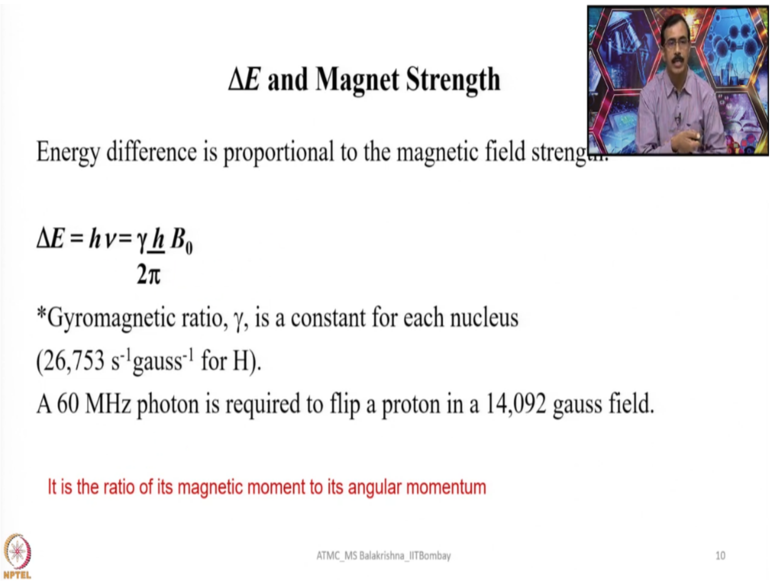

ΔE and Magnet Strength

Energy difference is proportional to the magnetic field streng

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

*Gyromagnetic ratio, γ, is a constant for each nucleus

(26,753 $s^{-1}gauss^{-1}$ for H).

A 60 MHz photon is required to flip a proton in a 14,092 gauss field.

It is the ratio of its magnetic moment to its angular momentum

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So, this is energy difference is proportional to the magnetic field strength. The energy gap is proportional to the magnetic field strength. That means energy gap can be increased by increasing the magnetic field strength, it can be decreased by decreasing the magnetic field strength. Now, that is given by this equation, $\Delta E = h\nu = \gamma (h/2\pi).Bo$.

So, this term (γ) is called gyromagnetic ratio. It is the ratio of its magnetic moment to its angular momentum; I am referring with respect to the nucleus. So, now, gyromagnetic ratio is a constant for each nucleus. It is a characteristic of each nucleus. It will vary from one nucleus to another one. And then for proton, this is 26,753 per second per gauss for hydrogen. A 60 megahertz photon is required to flip a proton.

That means, a 60 megahertz photon is required to flip a proton in a 14,092 gauss field. That means, if you keep a hydrogen or a proton in a magnetic field strength of 14,092 gauss field to flip it, the spin like this to become like this or to go to higher energy, you have to supply a photon equivalent to 60 megahertz. That is what this equation is telling you.

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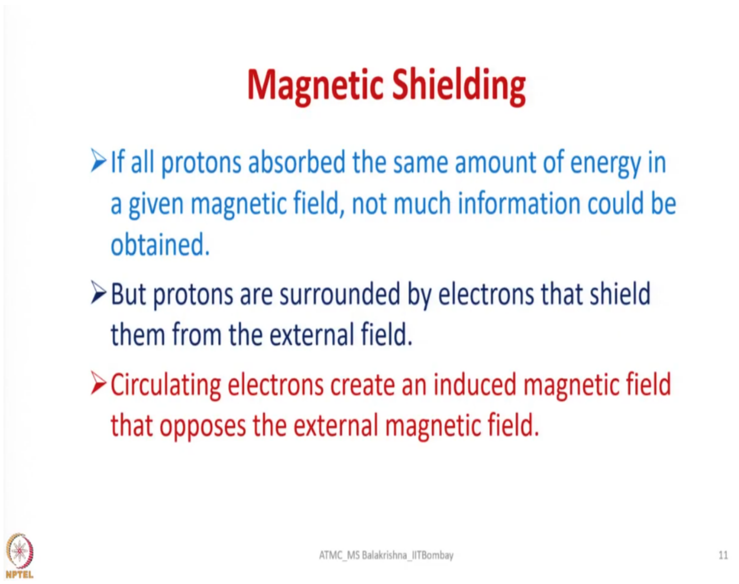

Magnetic Shielding

- If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.
- But protons are surrounded by electrons that shield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field.

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So, what is now, we have to look into another term, important term called magnetic shielding. What is it? If all protons absorb the same amount of energy in a given magnetic field, not much information could be obtained. That means, if you consider a molecule such as ethyl alcohol or isopropyl alcohol or acetaldehyde or anything, if all hydrogens absorb the same amount of energy to go to excited level, then probably NMR would not have been useful tool for determining the structure.

That means how it is different. So, but protons are surrounded by electrons that shield them from the external field. So, that means, when you place a molecule in a magnetic field, of course, if we have NMR active nuclei, what happens, the flipping of nucleus takes place. When it is taking place under the influence of a certain magnitude of magnetic field strength, you should remember that we are not putting a naked proton or naked nucleus without any electrons; since they are surrounded by electrons, they also generate a magnetic field.

So, that means the magnetic field generated by surrounding electrons varies from one nucleus to another one. As a result, what happens, they require a different amount of energy for flipping, that is called precession frequency. The circulating electrons create an induced magnetic field that opposes the external magnetic field. As a result, what happens, net magnetic field experienced by nuclei would vary.

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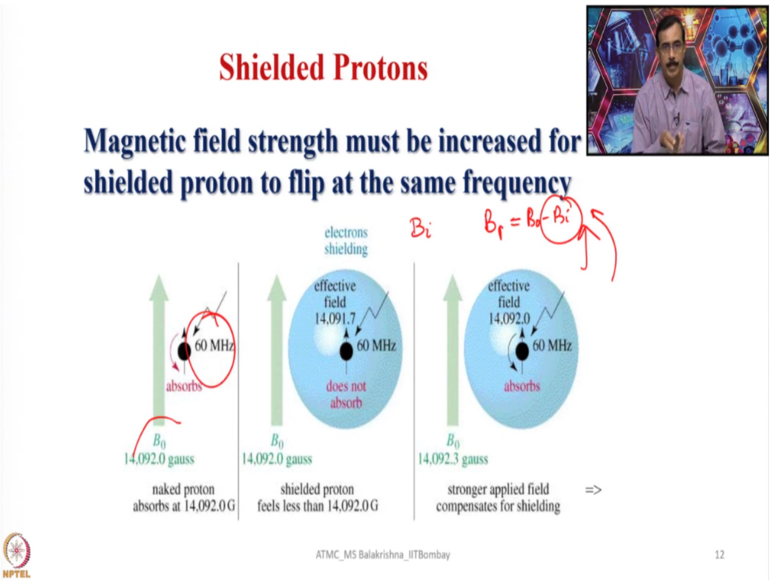

Shielded Protons

Magnetic field strength must be increased for shielded proton to flip at the same frequency

naked proton absorbs at 14,092.0 G

shielded proton feels less than 14,092.0 G

stronger applied field compensates for shielding =>

So, magnetic field strength must be increased for a shielded proton to flip at the same frequency. For example, let us say applied magnetic field strength is Bo. And because of the electron circulating surrounding the nucleus under magnetic field, they also generate a magnetic field, that opposes the applied magnetic field. As a result, that net magnetic field experienced by nucleus drops.

In that case what happens, if the radio frequency is fixed, then what you have to do is, you have to supply whatever the induced magnetic field generated by electron, equivalent. So, in that case what happens, again resonance occurs; you should remember. So, that means, in order to flip that one at the same frequency, there are 2 options are there, one can decrease the radio frequency for flipping, on the other hand, we keep that one constant, instead what we do is, we will try to match the loss of magnetic field by supplying extra magnetic field.

So, that is what we do. So, magnetic field strength will be increased; so, B nought must be increased for a shielded proton to flip at the same frequency. So, for example, if you take here, this is a 60 megahertz. It absorbs for flipping under the influence of Bo = 14,092 gauss. This is a naked proton. And if it is a shielded proton, what happens, net magnetic field experienced will be less because the magnetic field generated by the circulation of electron density would oppose.

So, then Bnet = Bo - Bi, net magnetic field experienced by nucleus; if I say the induced magnetic field say is Bi, resultant magnetic field experienced by the nucleus will be Bo - Bi. So, now, whatever the Bi is there, equivalent to Bi, we have to supply magnetic field so that resonance frequency remains same. So, that is what we do in each case. And in some cases what happens, in case of deshielding, we have to decrease it or we have to increase the frequency.

This is how the shielding influences. So, magnetic field strength must be increased for a shielded proton to flip at the same frequency. Stronger applied field compensates for shielding; so, that means whatever the balancing should be added so that the absorption frequency remains same.

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H_0	MHz
14100	60
23500	100
47000	200
58740	250
94000	400
117500	500

So, here I have given this radio frequency for different magnetic fields 14,100, it is 60 megahertz; this is with respect to hydrogen. And 23,500, it is a 100. So, this is how we have a 60 megahertz NMR, 100 megahertz NMR, 200 megahertz NMR, 250, 400, 500, 600 or even we have 1000 megahertz NMR now.

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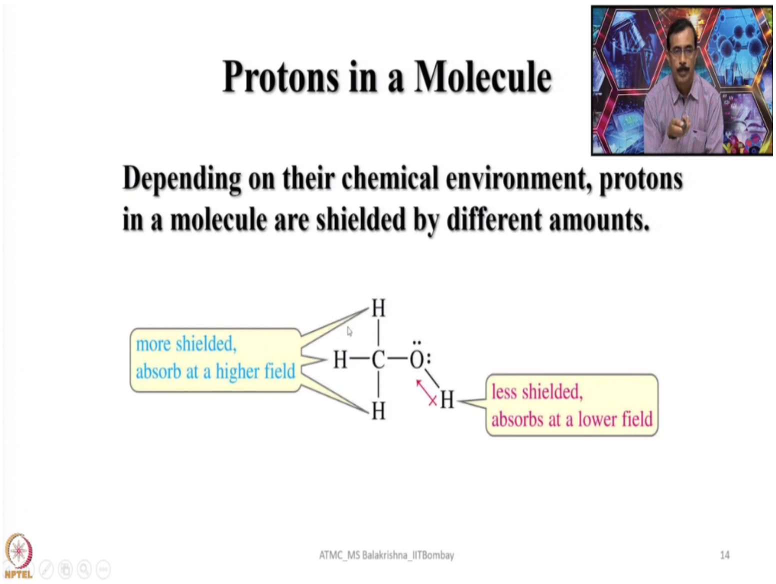

Protons in a Molecule

Depending on their chemical environment, protons in a molecule are shielded by different amounts.

more shielded, absorb at a higher field

less shielded, absorbs at a lower field

So, now, what would happen, protons in a molecule depending upon their chemical environment are shielded or deshielded; essentially, they will be shielded by different amounts. For example, if you consider a simple molecule such as methanol, if you see here, the electron density on hydrogen is pulled. You know that H is now almost like H^+; less electron density is there, it is less shielded, so, absorbs at a lower field, whereas here, they are more shielded, they absorb at a higher field.

So, now, this is how they have shielding and deshielding; makes the signals appear at different places. As a result, what happens, each functional group or each group is unique so that NMR is very helpful in determining the structure.

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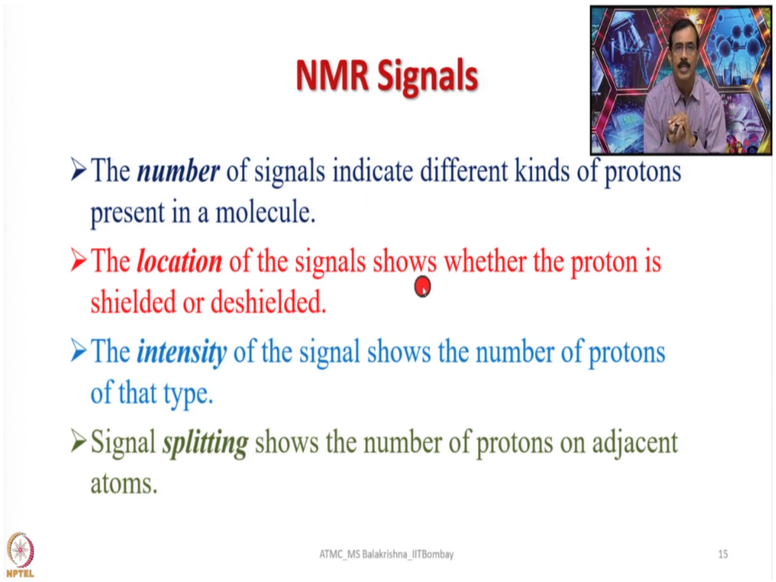

NMR Signals

- The ***number*** of signals indicate different kinds of protons present in a molecule.
- The ***location*** of the signals shows whether the proton is shielded or deshielded.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on adjacent atoms.

So, now, the number of signals indicate different kinds of protons present in a molecule. If we take ethanol; for example, ethyl alcohol we have CH_3CH_2OH. We get 3 signals that indicates 3 different kinds of protons are present in the molecule. The location of the signal shows whether the proton is shielded or deshielded. One is, it gives number of signals, indicates number of a set of protons available.

And then the location of the signal indicates, whether they are shielded or deshielded; accordingly, we can arrange them in the sequence. Or the intensity of the signal shows the number of protons of the type. Now, the intensity of the signal also tells in each group how many protons are there. And signal splitting shows the number of protons and adjacent atoms. Now, the splitting would tell you how many are there in the neighbourhood, in the next position or on adjacent atom.

So, that means here this NMR signal would give you all this information. First it would give you the number of different kind of protons present and the location would indicate whether the proton is shielded or deshielded. Again the intensity would indicate number of protons of that type are present. For example, CH_3CH_2OH if you consider ethanol, in CH_3, 3 are there, and CH_2, 2 are there, and OH, 1 is there. That information comes from intensity.

And then splitting; splitting would tell you CH_3 is next to CH_2, and CH_2 is in between CH_3 and OH, and OH is at the other end, next to that only CH_2 is there. So, something like that. This information, all information comes from NMR signals. This is how it becomes very easy to interpret the structure and determine the structure ultimately.

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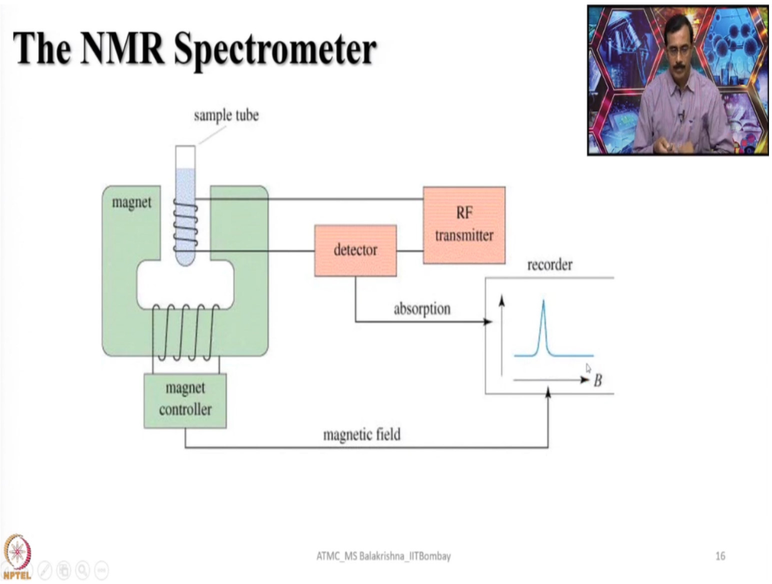

The NMR Spectrometer

This is the NMR spectrometer. So, this is that magnet, a Bo or whatever we tell. So, sample is inserted here; and then, a detector will be there and radio frequency will be applied here. And then, the signals would come; a detector is there and it will be then whatever the detector detects. And then, absorption will be shown on a recorded plot like this. And this one, this is the Bo; B, we say B is the applied magnetic field. So, it is always the increasing applied magnetic field is plotted in the direction; and absorption will be in this one, in this axis.

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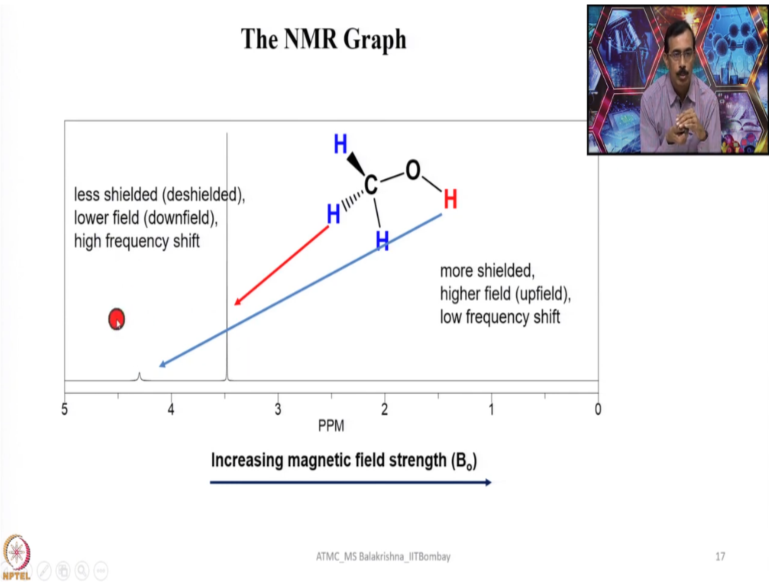

The NMR Graph

So, let us consider a methanol graph here. You can see, this is how methanol NMR spectrum appears like this. And now this one, these 3 protons are represented by this one here. And then here, the small one is due to H. So, that means, if the moment you see in this one, you can see a more shielded, higher field, low frequency shift for these things, whereas this one, less shielded, this H is less shielded and lower field, high frequency shift.

That means you can classify. So, when it is deshielded, we call it as; of course, here if we have used TMS as a standard I would tell you it is 0, with respect to that one, these signals are assigned the chemical shifts. So, this is less shielded, it is appearing left side and it is lower field. That is also called downfield shift and then high frequency shift, whereas here, once it comes on the right side, it is more shielded, these 3 and higher field and then low frequency shift.

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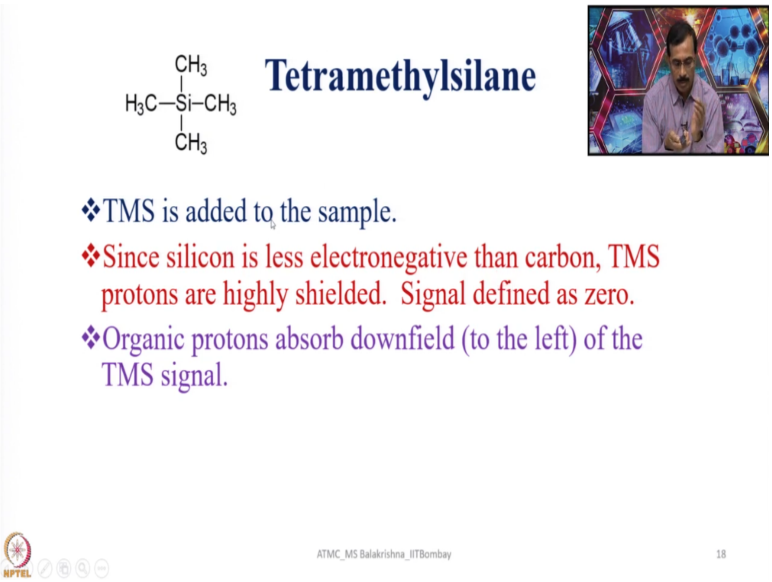

Tetramethylsilane

- TMS is added to the sample.
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.
- Organic protons absorb downfield (to the left) of the TMS signal.

So, now let us look into tetramethylsilane. So, this is the structure of tetramethylsilane. This is called TMS. It is added to the sample. Why it is added to sample? This is added as a reference. Since silicone is less electronegative than carbon, TMS protons are highly shielded because of so much electron density. So, signal defined as 0; whatever the signal it shows, that is calibrated to 0 value.

And now, we are recording NMR spectrum ^{1}H NMR for all molecules using this as a standard. So, organic protons absorb downfield to the left of the TMS signal. Most of the organic protons, they absorb downfield to the TMS signal. That means 0 if it is here, everything will be coming towards positive side, 0 to 10 or sometimes more.

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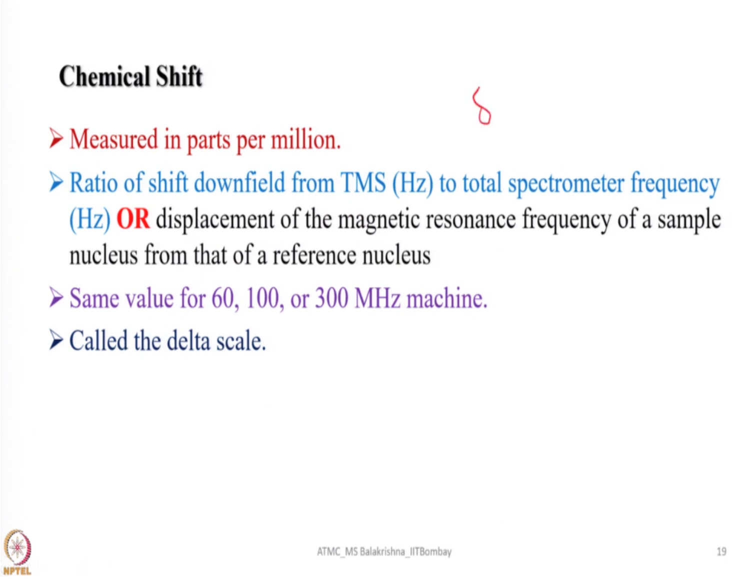

Chemical Shift

δ

- Measured in parts per million.
- Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (Hz) **OR** displacement of the magnetic resonance frequency of a sample nucleus from that of a reference nucleus
- Same value for 60, 100, or 300 MHz machine.
- Called the delta scale.

So, what is chemical shift? Chemical shift is measured in parts per million. I shall tell you why it is measured in parts per million, why not in hertz. Ratio of shift downfield from TMS to total spectrometer frequency will give you chemical shift in parts per million, or the displacement of magnetic resonance frequency of a sample nucleus from that of a reference nucleus.

For example, this is the same value, when you determine chemical shift in parts per million, it is independent of magnetic field strength. So, that is the reason we measure in parts per million. Whether you measure in 60 megahertz, 100 megahertz or 300 megahertz, it does not change. This is called δ scale. Whenever we write, we use this term δ.

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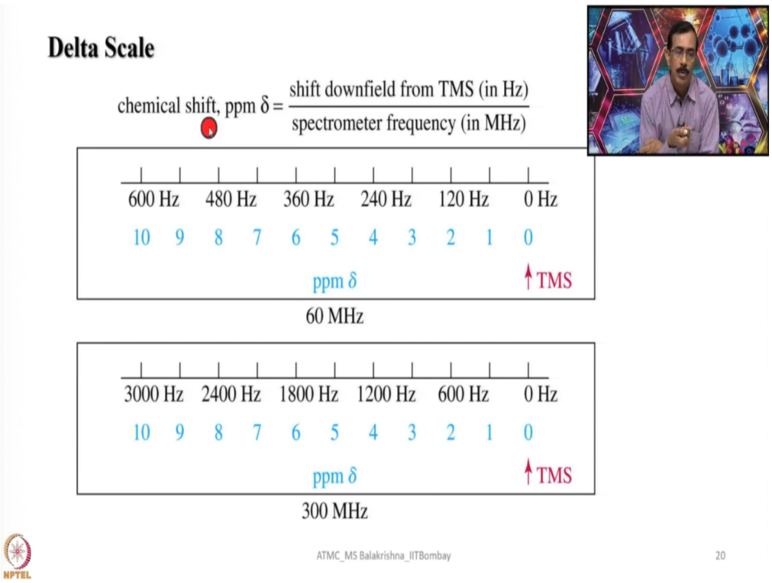

Delta Scale

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$

Now, this the δ scale I have given. I have again defined here what is chemical shift. A chemical shift in ppm is called δ. Either you have to write delta or ppm, there is no need to write both. The moment you write δ, it is understood that it is in ppm; or if you write it ppm, it is understood it is in δ scale. This is the ratio of shift downfield from TMS. That means, whatever the value that NMR spectrum shows, that one in hertz divided by spectrometer frequency will give you chemical shift in parts per million.

For example, you can see here 10 ppm for 600 megahertz divided by 10. So, here it goes like that. And similarly, this is in case of 60 megahertz; if you go for 300 megahertz also, you can see it is a 10; 300, 3,000 divided by 300 or here 600 divided by 60. So, this is how for convenience, to keep the NMR signal value constant irrespective of in which magnetic field we are measuring, so, it is given in δ scale or ppm.

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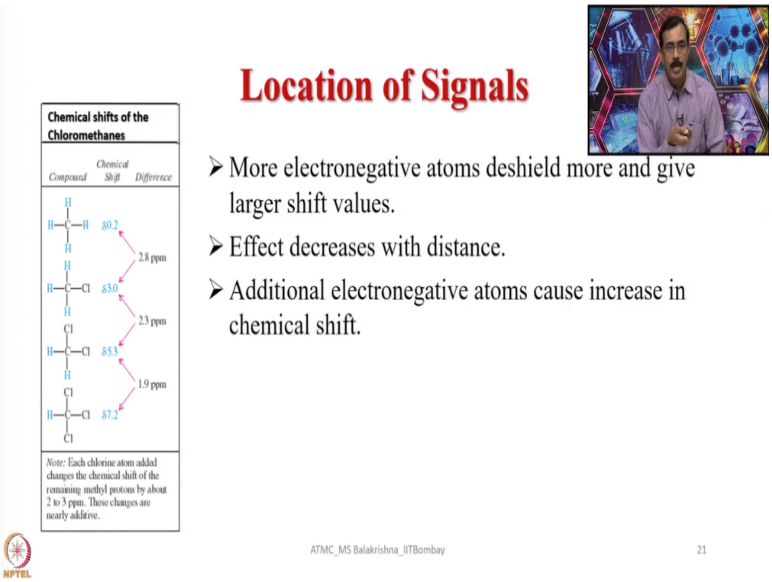

Location of Signals

Chemical shifts of the Chloromethanes

Compound	Chemical Shift	Difference
H H—C—H H	δ0.2	
		2.8 ppm
H H—C—Cl H	δ3.0	
		2.3 ppm
Cl H—C—Cl H	δ5.3	
		1.9 ppm
Cl H—C—Cl Cl	δ7.2	

Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

- ➢ More electronegative atoms deshield more and give larger shift values.
- ➢ Effect decreases with distance.
- ➢ Additional electronegative atoms cause increase in chemical shift.

So, location of signals now. So, I have given some, more electronegative atoms deshield more and give a shift values. For example, you can see here, values I have given. And then, effect decreases with distance, distance between 2 groups. Additional electronegative atoms cause increase in chemical shift.

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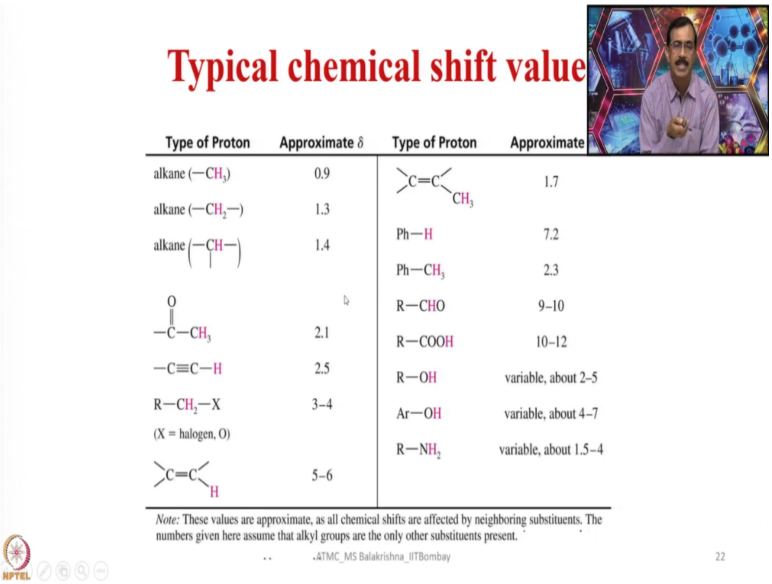

Typical chemical shift value

Type of Proton	Approximate δ	Type of Proton	Approximate
alkane ($-CH_3$)	0.9	$\mathrm{>C{=}C<_{CH_3}}$	1.7
alkane ($-CH_2-$)	1.3	Ph—H	7.2
alkane ($-\underset{\mid}{C}H-$)	1.4	$Ph-CH_3$	2.3
$-\overset{\overset{O}{\|}}{C}-CH_3$	2.1	R—CHO	9–10
$-C\equiv C-H$	2.5	R—COOH	10–12
$R-CH_2-X$ (X = halogen, O)	3–4	R—OH	variable, about 2–5
$\mathrm{>C{=}C<_{H}}$	5–6	Ar—OH	variable, about 4–7
		$R-NH_2$	variable, about 1.5–4

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present.

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For example, you can see here, alkane CH_3 would appear in 0.9 and alkane CH_2 will appear on 1.3. And if you go for CH tertiary carbon appears at 1.4. And in case of this one, when we have a CO group, it appears at 2.1; and alkane proton appears at 2.5. If you have a halide, then CH_2 appears around 3 to 4. And if you have something like this, this one will appear at 5 to 6.

And then, if you have a double group and then CH it appears at 1.7; and aromatic groups appear at 7.2. A phenyl, a methyl group on phenyl group appears around 2.3. Aldehyde group hydrogen appears around 9 to 10. Carboxylic proton appears between 10 to 12; and alcohol value around 2 to 5; and aryl alcohol H will be around 4 to 7; and amine will be around 1.5 to 4. So, this, the range is given. Again, there is a significance in giving the range.

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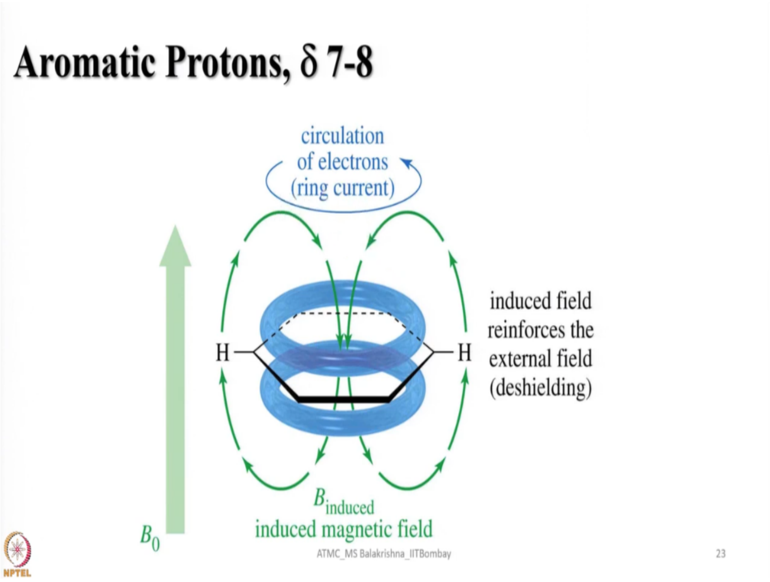

Aromatic Protons, δ 7-8

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So, now, aromatic protons, why they are so much deshielded? Let us look into it. The value is around 7 to 8. If you assume this or benzene group, say it is placed like this and with respect to the applied magnetic field. Then what happens, induced magnetic field, because of circulation of these delocalised electrons would generate a ring current. That generates a magnetic field that is aligned with the magnetic field.

If it is aligned with the magnetic field, what happens, it is more deshielded and it appears at higher frequency. So, that means here we call it, when it is aligned with Bi, induced magnetic field reinforces the external field. As a result, it is deshielded. The net magnetic field experienced by the nucleus is Bo + Bi, not Bo - Bi,. As a result, what happens, the radio frequency has been increased.

In this case, either you have to decrease the magnetic field; if you cannot do it, we have to increase the radio frequency. That is the reason they are appearing at deshielded region. We call high frequency shift for the same reason.

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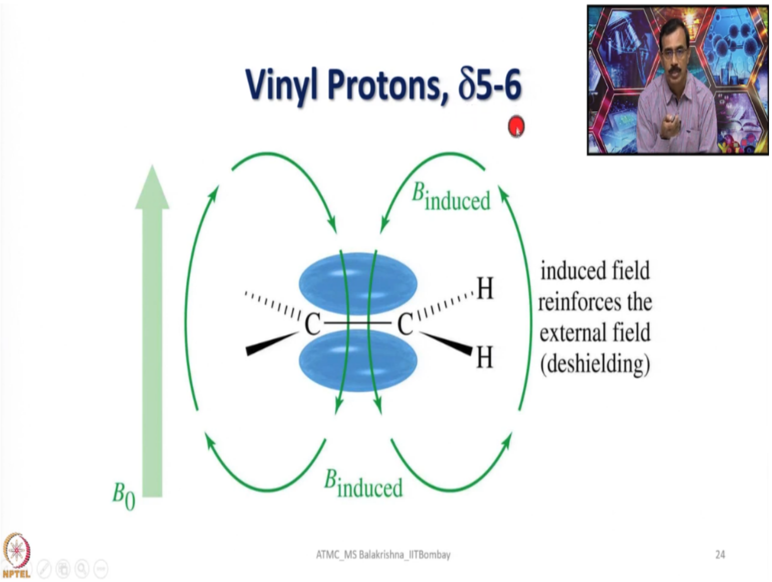

Vinyl Protons, δ5-6

induced field reinforces the external field (deshielding)

In case of vinyl protons, same explanation can be given. They appear between 5 to 6. So, induced field reinforces, but induced field generated here is in magnitude less than what we saw in case of acetylene.

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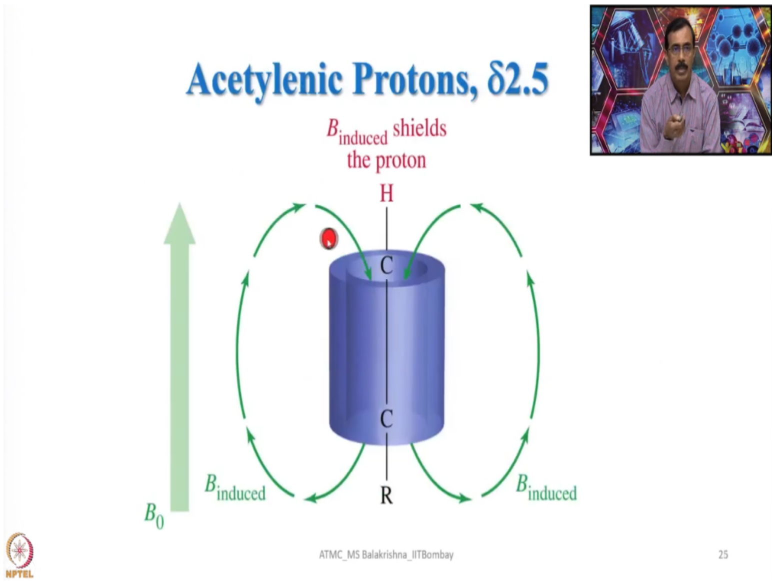

Acetylenic Protons, δ2.5

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Now, in case of acetylenic protons, what happens? it comes around 2.5. So, induced one is considerably less compared to those two groups here.

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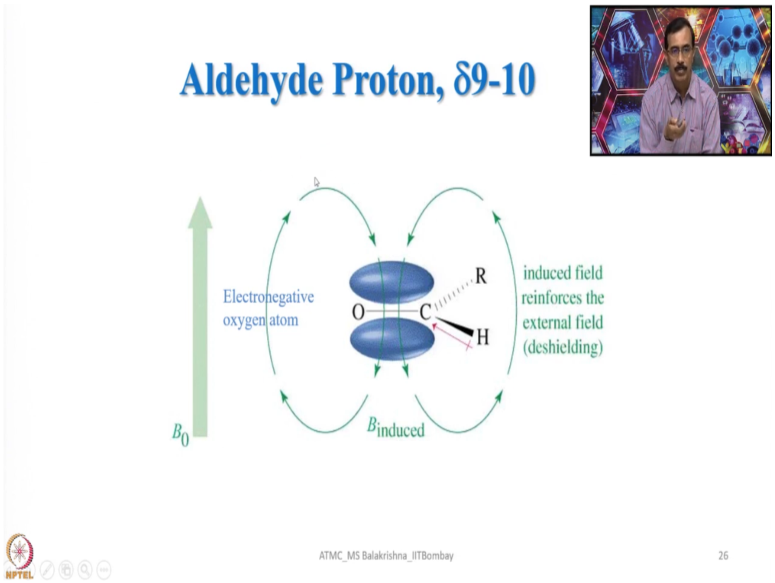

Aldehyde Proton, δ9-10

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In case of aldehyde protons, it is even more because of electronegative oxygen atom present here. As a result, what happens, it appears around 9 to 10. It is more deshielded and it is high frequency shift.

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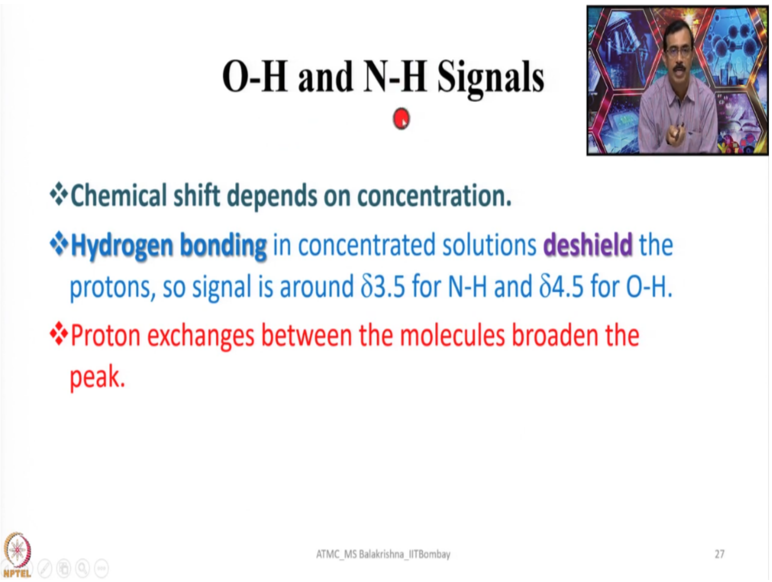

O-H and N-H Signals

- ❖Chemical shift depends on concentration.
- ❖**Hydrogen bonding** in concentrated solutions **deshield** the protons, so signal is around δ3.5 for N-H and δ4.5 for O-H.
- ❖Proton exchanges between the molecules broaden the peak.

And then, O-H and N-H signals, it is very important. Chemical shift here depends on concentration and hydrogen bonding in concentrated solutions deshield the protons, so, signal is around 3.5 for N-H and around 4.5 for O-H. This is very important; if hydrogen bonding is there how the chemical shift is affected. So, that means, due to the hydrogen bonding in concentrated solution that deshield the proton so that it goes around N-H proton would appear at 3.5 and OH proton would appear at 4.5.

So, proton exchange between the molecules broaden the peak. Another example is, these are very acidic, they can readily exchange. So, take this one and keep it in deuterium solvent and if it completely disappears and you may not see. Next day when you run NMR, O-H signal, that indicates that you have a O-H. So, that means you take this one, freshly recorded NMR in $CDCl_3$ or D_2O and then leave it for 24 hours.

After that one, all O-H have become O-D. In that case, this signal due to this H disappears, because in place of O-H, you have O-D. So, that indicates your compound has O-H. Same thing is true in case of N-H also. So, if sometimes confirming the presence of N-H is very critical, you can do this exchange process. Record freshly prepared sample and identify where N-H signal is coming, leave it for 24 hours, all N-H becomes N-D.

And then take NMR, this is missing. So, that indicates you have N-H. And of course, you can also confirm these things from IR spectroscopy by looking into O-H stretching frequency. That should be different, O-D will be there now.

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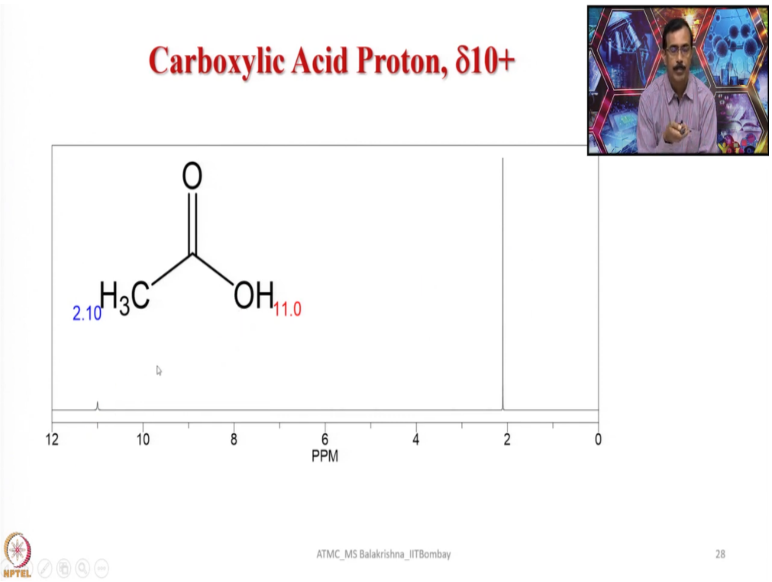

Carboxylic Acid Proton, δ10+

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So, now, carboxylic acid proton would come around 10. So, you can see here in this one, this is for CH_3 and this is for OH; is shown here.

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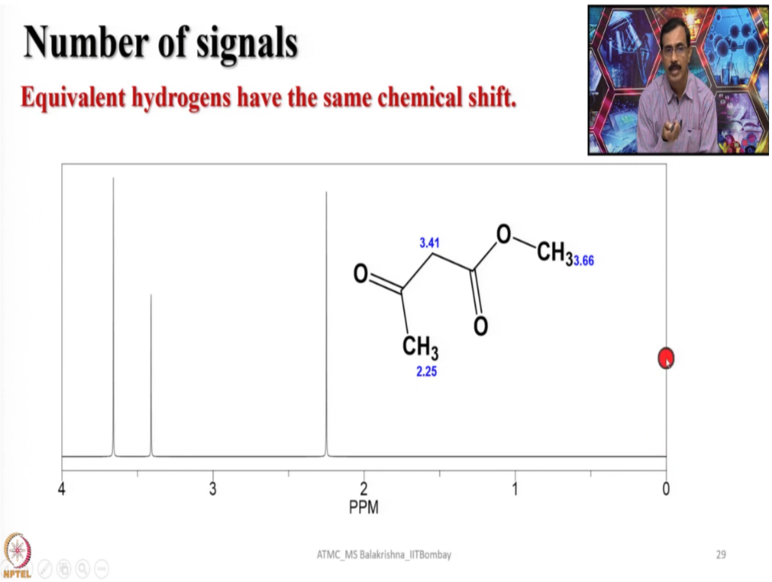

Number of signals

Equivalent hydrogens have the same chemical shift.

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And number of signals, we can see how many signals are there. 1, 2, and 3 signals are there because we have 1, 2, 3 are there. And relative chemical shifts also shown here. For example, this one is around 2.25 and this is 3.41 and this is 3.36. That means you can say relatively to what extent they are deshielded with respect to this 0 value of TMS.

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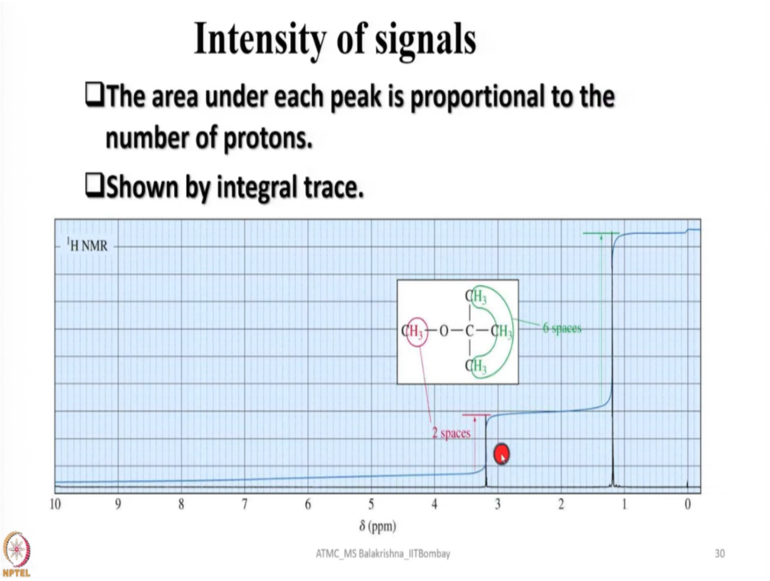

Intensity of signals

- ☐The area under each peak is proportional to the number of protons.
- ☐Shown by integral trace.

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Now, let us come to the intensity of signals. If you consider this molecule here, we have these 3 are equivalent. So, we have 9 protons and here we have 3 protons. So, when we get 2 signals, so, signal due to this one should have intensity 3 and then intensity of this one should be 9. So, that means it is 1:3. You can see here, the space taken is 2 spaces, 2; and then 6 spaces it has taken; that means 1:3.

So, this is how the intensity of the signal will tell you, how many identical or equivalent are there. Then now we can say without any problem, yes, there are 3 methyl groups are there and they are all on the same carbon atom. So, that means this is a quaternary carbon, can be identified here. Other one is, all the shifted which the function is next to CH_3 group. So, you should be able to tell it is an ethyl, something like that. So, intensity of the signal, I told you. Show by integral trace; this is called integral trace that will give you, number of equivalent protons present in a given molecule.

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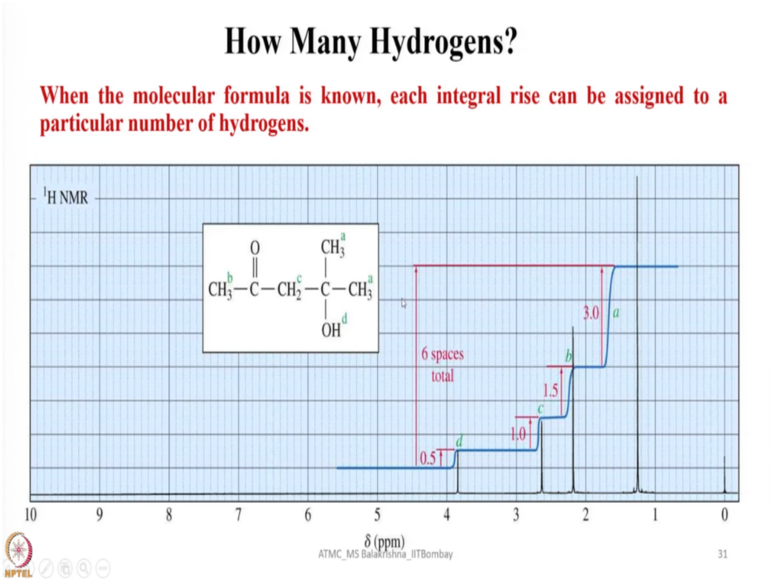

How Many Hydrogens?

When the molecular formula is known, each integral rise can be assigned to a particular number of hydrogens.

So, now, how many hydrogens? When the molecular formula is known, each integral rise can be assigned to a particular number of hydrogens. That is what I showed you here. You can see here. For example, here 1, 2, they are all, these 2 are identical; 4 type of protons are there; then we have 4 signals are there; and the ratio if you consider, this is 1:2:3:6. That means here 0.5:1:1.5:3.

So, that means basically, very nicely it will tell you how many similar types of protons are there. Then, segregating them as groups and then adding at appropriate place to arrive at the correct structure to understand it would be very easy.

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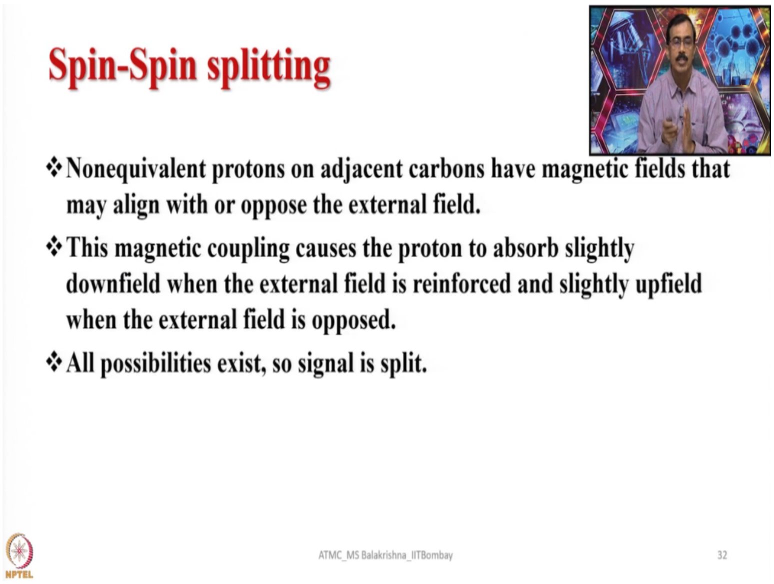

Spin-Spin splitting

- Nonequivalent protons on adjacent carbons have magnetic fields that may align with or oppose the external field.
- This magnetic coupling causes the proton to absorb slightly downfield when the external field is reinforced and slightly upfield when the external field is opposed.
- All possibilities exist, so signal is split.

So, now, let us come to spin-spin splitting. So, non-equivalent protons and adjacent carbons have magnetic fields that may align with or oppose the magnetic field. So, now let us look into, for example, if you take CH_3CH_2OH, CH $_3$ is there and CH_2 is there and OH is there. And CH_2 is adjacent carbon and 2 hydrogens are there. And how these adjacent hydrogen atoms influence the signal of CH_3 and same way how CH_2 get influenced by CH_3 protons; that we have to see.

That means, we should remember, when we are looking into the signal around CH_3, CH_2 also generates a magnetic field. Those 2 protons and they can also be aligned with the magnetic field or oppose the magnetic field. And depending upon that one, this signal will be split. So, this magnetic coupling causes the proton to absorb slightly higher downfield when the external field is reinforced and slightly upfield when the external field is opposed.

That means now, instead of giving 1 signal, it may show 3, 4 or 5 signals. And then we have to see what are the intensities. And then, after understanding 1 or 2 molecules, what we should do is, we should try to make it a general so that every time we should not calculate. The moment we look into a molecule, we should be able to tell how many lines will be there, how many signals will be there and how it is split; that we call it as spin-spin splitting. So, all possibilities exist, so, signal is split here. So, let us look into one example quickly.

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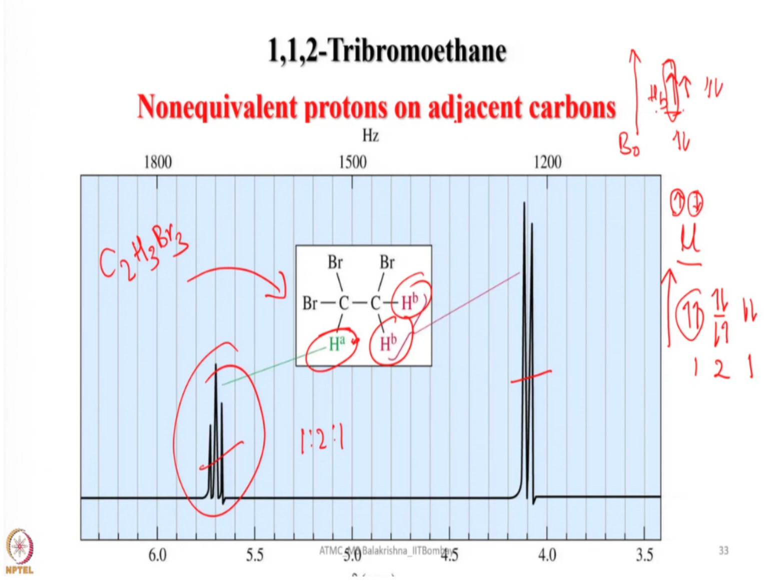

1,1,2-Tribromoethane

Nonequivalent protons on adjacent carbons

So, now let us look into 1,1,2-tribromoethane. So, non-equivalent protons and adjacent carbons are there. Now, these 2 are different from this one. So, now let us look into the signal of these 2. Signal of these 2 will be influenced by this one. That means, let me write here. This is the applied magnetic field, so, Bo. I am looking into this H_b; H_b should give a signal.

And now what happens, if H_b is something like this, now we have H_a, how it is going to influence? H_a would influence in this fashion. For example, it can be aligned in this way with this one; this is together, or it can be aligned something like this. So, as a result, what happens, one is here, one is here; this is low. So, we get 1 signal, and 1 signal in 1:1. So, this is how it is.

On the other hand; so, basically, it would be something like this. It can be aligned with the magnetic field, this one when we are talking about H_b signal or it can be opposite. So, that means, now it is influenced by 2 protons, 1 with the field, 1 due to the neighbouring one. So, with this one will give 1 signal, this one will give 1 signal, 1:1. We get a doublet here. Now, this is a triplet; how it is coming here?

So, now, we have something like this, two are there; both of them can be aligned with the magnetic field. Now, one can be aligned like this, one can be aligned like this. And this is true for this one also. Here we can have two arrangements. Now, this can be aligned like this and this can be aligned like this. And now, both of them can be aligned in this fashion. Now, what happens?

Now, 1:2:1, so, 3; this is coming, this is 1:2:1. So, this one is for this one. So, now, this one under the influence of these 2 here, what happens, it will be split into 3 with the intensity ratio of 1:2:1. So, this is how we can understand. Now it becomes very easy to write. For example, if the formula is given simply say $C_2H_3Br_3$, if it is given and if the spectrum is given here, and you should be able to write the correct structure here.

So, this is how one can use NMR very effectively with molecular formula. We should be able to write structural formula after looking into this one and analysing and interpreting. As I mentioned here, I showed you Ha reinforces field, this one for these 2.

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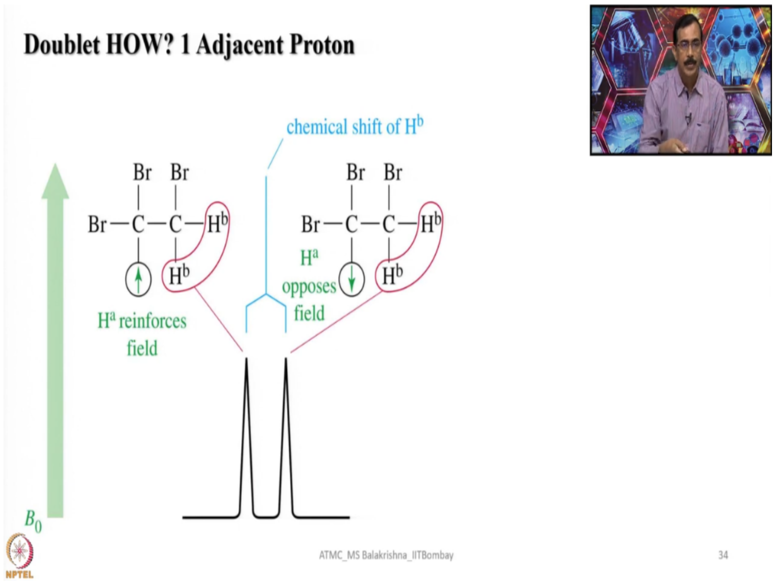

Doublet HOW? 1 Adjacent Proton

One is in this direction, this H is aligned with the magnetic field, this signal. And now, this one is opposite, aligned in the direction opposite to the applied field because it can have spin like this or it can have spin like that, when you are looking into the signal due to this one; so, 2 signals have come.

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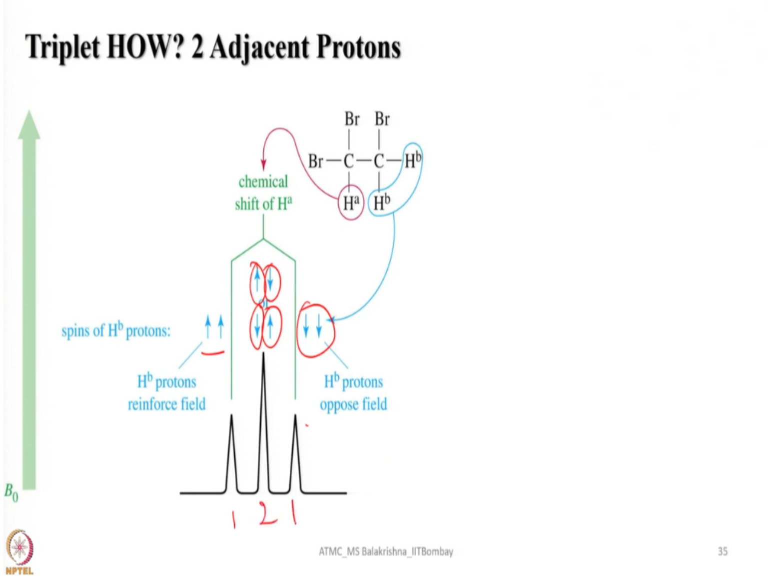

Triplet HOW? 2 Adjacent Protons

Now, if you see the other one, now when we are looking to signal of this one, these 2 have 2 small magnets; they can be aligned like this here, they can be aligned like this here. Now the field is increased, so, high field strength. Now, one is like this and one is like this and other combination is like this. So, and now both of them are down. So, this one signal is coming here; so, intensity is 1:2:1. So, this is how NMR understanding is simplified by looking into the spin-spin splitting.

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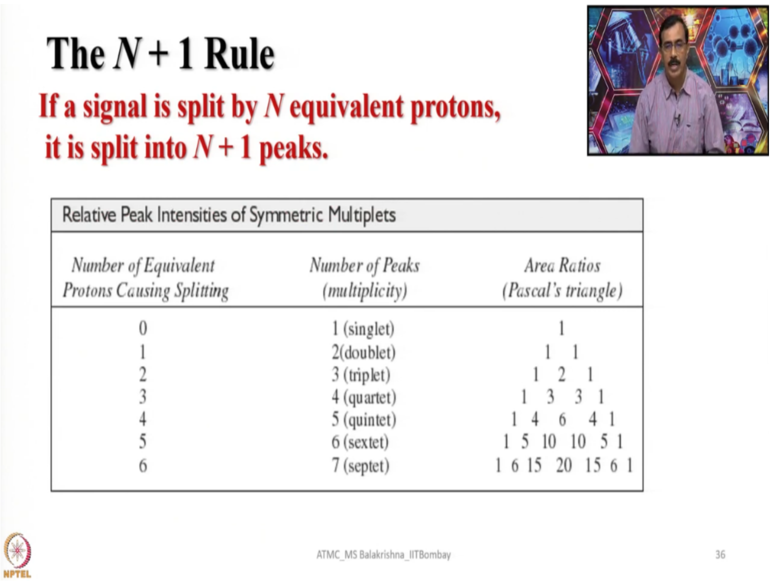

The $N + 1$ Rule

If a signal is split by N equivalent protons, it is split into $N + 1$ peaks.

Relative Peak Intensities of Symmetric Multiplets

Number of Equivalent Protons Causing Splitting	*Number of Peaks (multiplicity)*	*Area Ratios (Pascal's triangle)*
0	1 (singlet)	1
1	2(doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

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Then what happens, it becomes very tedious or laborious job to calculate how many signals are coming for each one every time you see. Sometime you may have 6 equivalent protons, 9 equivalent protons or 15 equivalent protons. Then what happens, it will be little bit cumbersome to understand or calculating every time. For that one, we have a simple rule here, a general rule that is called the N + 1 rule.

If a signal is split by N equivalent protons, it is split into N + 1 peaks. So, that means number of equivalent protons causing splitting 0 means 1 signal. In the neighbouring, you do not have anything means you get a singlet; and if you have 1, you will get a doublet; if you have 2, you will get a triplet; if you have 3, you get a quartet; if 4 are there, you get quintet; 4 + 1, 5; so, 5 + 1, 6; 6 + 1, 7, septet.

Then, to understand the relative ratio of these signals in a multiplet, we have to go for Pascal triangle. Pascal triangles will be unique for each nuclear spin. So, this one is for I equals half. The same pascal triangle, one cannot use, for I = 1 or I = 3/2, or I = 3, you have to write separate Pascal triangles first by writing the intensity of the first signal and you can continue writing.

This one is for nuclear spin I = ½ . So, this is the Pascal triangle that can tell you 7 lines septet means the intensity of these 7 lines will be 1:6:15:20:15:6. So, if you look into isopropyl alcohol, we can see that one. I will start my next lecture interpreting the NMR spectrum of isopropyl alcohol or isopropanol. So, until then, have excellent time understanding NMR. Thank you for your kind attention.