Advanced NMR Techniques in Solution and Solid – State
Prof. N. Suryaprakash
NMR Research Centre
Indian Institute of science – Bengaluru

Module 4
Internal Interaction Parameters and Chemical Shifts
Lecture - 04

Welcome all of you. In the last couple of classes we were discussing more about fundamentals of NMR, the concepts which are responsible that we have to understand, so that we can get NMR spectrum. That means we wanted to understand the concept of spin physics; where we discuss a lot about spin angular momentum, magnetic moment, magnetic quantum number, Zeeman interaction, and also we understood the sensitivity considerations, and magnetic field temperature which we can utilize.

For example at higher magnetic field we can get better sensitivity, at lower temperature we can get better sensitivity; it is because of Boltzmann population ratio, that also we understood; how the Boltzmann population depends. We understood more about where the NMR frequency comes in the electromagnetic spectrum, we did even calculate resonanting frequency for a given magnetic field, for different nuclei and what is the resonant frequency, etc. And we understood NMR spectroscopy comes in the radio frequency region of the electromagnetic spectrum. And we also understood how to get the resonance. We understood the bulk magnetization in thermal equilibrium and then we applied a radio frequency pulse in a direction perpendicular to the magnetic field, the bulk magnetization is static in thermal equilibrium and along Z axis. When you apply a radio frequency pulse in a direction perpendicular to it, we created non equilibrium situation and tilted the magnetization to the XY plane. And instantaneously there is a phase coherence and as time passes the spins will undergo decoherence and then at the same time start growing along Z axis, while inducing EMF in the receiver coil, which we detect as a function of time; which is called free induction decay.

We knew the time domain signal can be converted into frequency domain by doing a mathematical operation called Fourier transformation. And after that you can get the frequency domain spectrum. And for getting the spectrum we also understood what are the selection rules; we knew that changing the magnetic quantum number between any 2 states spin states by either 1 or – 1 are allowed transitions, as per the selection rules.

And also we saw what is the energy level diagram for the homonuclear couple spin system, 2 spin systems and also heteronuclear spin system. So, with that we got some basic idea about some of the important information or concepts that are required to understand NMR spectroscopy. Of course, in the previous course all these things were discussed in depth, some of you are in this course because to recapitulate that for the sake of the audience who are registered for the first time for this course; without prior knowledge or without attending the previous course. Thus I gave the gist of that course introduction to NMR, but little rapidly. So, those who want to understand more can please go back to the previous course. With that we will continue further I will introduce some interaction parameters in NMR. What is that? we will see today; I will introduce chemical shift.

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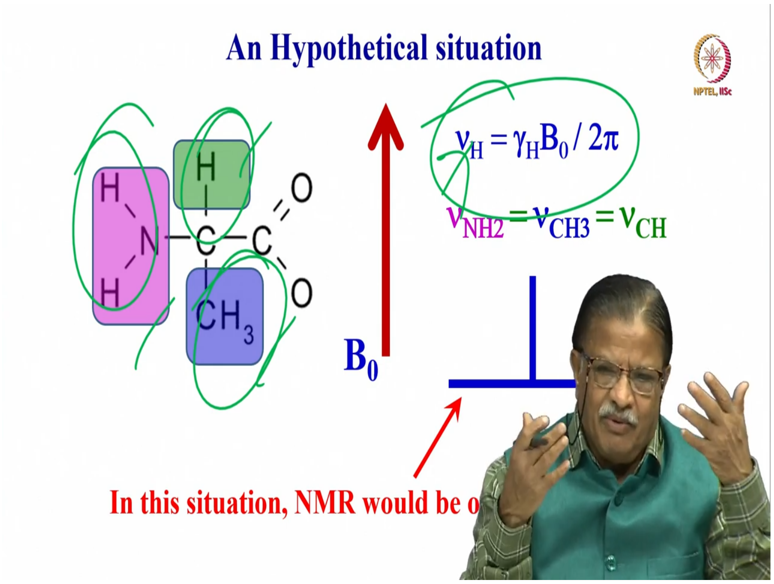

An Hypothetical situation

$\nu_H = \gamma_H B_0 / 2\pi$

$\nu_{NH2} = \nu_{CH3} = \nu_{CH}$

B_0

In this situation, NMR would be o

Consider the hypothetical situation, a molecule like this where we have highlighted 3 different types of protons in 3 different colors. As you can see we have CH proton CH3 proton and NH2 proton. In a magnetic field, if I insert this molecule and if I want to see the NMR spectrum, according to my resonance condition you remember, nu H = gamma H into B naught over 2 pi. Here gamma is constant for a given nucleus, that is for proton if I am going to detect, whether it is NH2 protons or CH3 proton or CH proton, gamma is same.

B_0 is a magnetic field which we are keeping constant, 2 is a constant and pi is a constant. Then what does it mean? What do you understand from this equation? It tells me whatever may be the molecule, you are going to get only a single frequency. That means you always get only one particular frequency in a given magnetic field. If that is the situation; it tells me the resonanting frequency of NH2 protons, CH proton and CH3 protons, all are equal.

So, we are going to get a one frequency, a single resonance peak. If this were to be the case NMR would have been of little interest for us. Nobody would have proceeded further in doing research in NMR. Fortunately what is going to happen is, there are so many interesting things in NMR and NMR is still a powerful technique. Then the question is what makes NMR a powerful technique. In spite of the fact I showed you by this equation, for any given nucleus in principle we should get a single resonance, still NMR is so useful. We will understand how it is useful.

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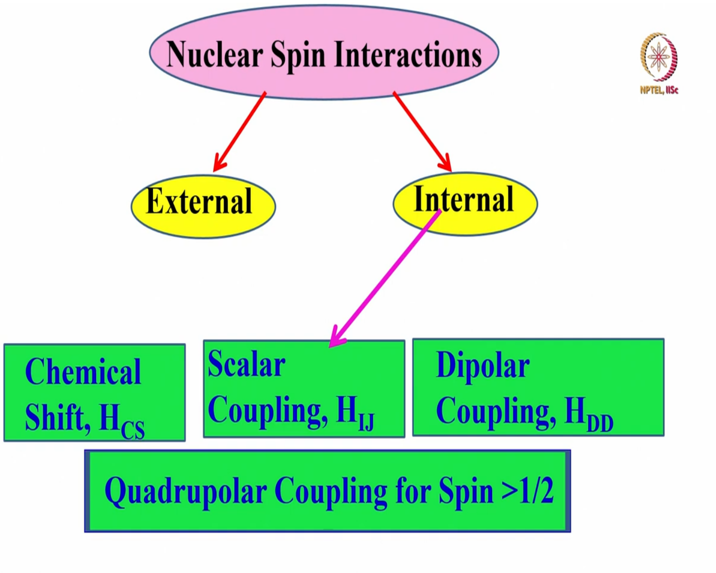

Nuclear Spin Interactions

External

Internal

Chemical Shift, H_{CS}

Scalar Coupling, H_{IJ}

Dipolar Coupling, H_{DD}

Quadrupolar Coupling for Spin >1/2

For understanding that we should know what are nuclear spin interactions? I would basically classify the interactions into two types. One is external interaction and the other is internal interaction. The external interaction is nothing but Zeeman interaction. That is what we discussed last time, the Zeeman interaction, interaction of the magnetic moments with the external magnetic field; and RF interaction that is the radio frequency pulse we are going to apply to detect the signal.

That is what we discussed. We said bulk magnetization we are going to tilt it by apply radio frequency pulse in a direction perpendicular the magnetic field. They are all external interactions. Also there are certain internal interactions which are inherently present in the molecules. What are they? They are chemical shifts, scalar couplings, dipolar couplings and quadrupolar couplings, if you are dealing with the nuclear spins which are greater than spin half.

As I said in the couple of classes before, for nuclear spin which is greater than half, they are quadrupolar nuclei and they give rise to what are called quadrupolar couplings. So, these are all internal interaction specific to the molecules.

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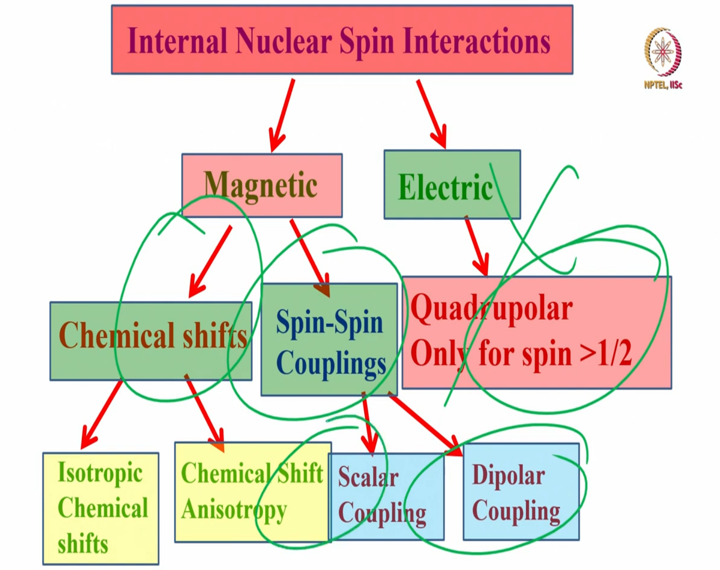

Internal Nuclear Spin Interactions

Magnetic

Electric

Chemical shifts

Spin-Spin Couplings

Quadrupolar Only for spin >1/2

Isotropic Chemical shifts

Chemical Shift Anisotropy

Scalar Coupling

Dipolar Coupling

NPTEL, IISc

Now if I go to internal nuclear spin interactions, again, I can classify them into 2 parts. One is a magnetic interaction, other is an electric interaction. Now if I go to magnetic interaction, further it can be classified into 2; one is chemical shift other is spin - spin coupling. And of course very important thing, these things we deal with very often. An electrical interaction as I said for the quadrupolar spins, the nuclei which have spin greater than half.

This is normally very difficult to detect, especially in the solution state, not difficult we are not good to see the quadrupolar couplings in solution state. We do not touch also in this course, we do not deal with quadrupolar for interactions also. Occasionally 1 or 2 times I may have to mention that, but we do not study quadrupolar nuclei we do not discuss this in this course. So, let us not worry about this one this interaction.

But if I go to chemical shift, it can be further classified into 2. One is isotopic chemical shift and another is chemical shift anisotropy. Remember all parameters in NMR are anisotropic; they are all tensors. So, Nevertheless, we go further and see can we detect everything or not. As we go ahead I will tell you if you go to the spin - spin coupling, again, I can divide into 2 types; one is scalar coupling other is it dipolar coupling. So, these are the internal interactions which you always deal with.

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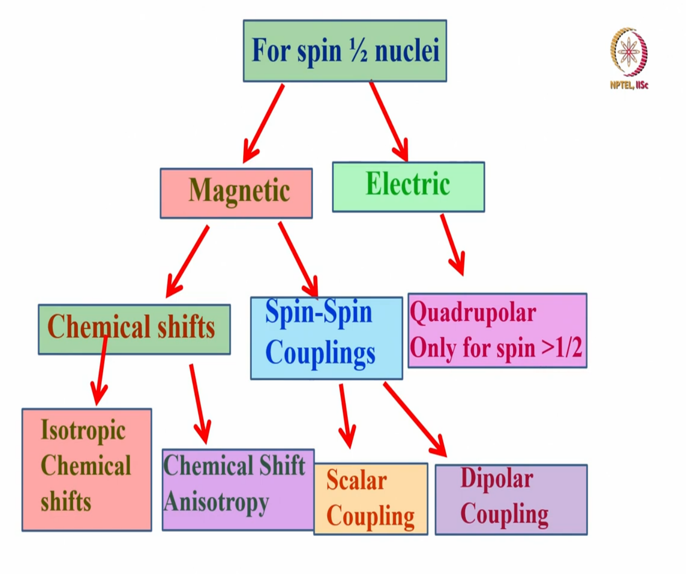

For spin ½ nuclei

Magnetic

Electric

Chemical shifts

Spin-Spin Couplings

Quadrupolar Only for spin >1/2

Isotropic Chemical shifts

Chemical Shift Anisotropy

Scalar Coupling

Dipolar Coupling

We are dealing with spin half nuclei as I told in the couple of classes before. In the entire course we do not touch upon nucleus with spin greater than half.

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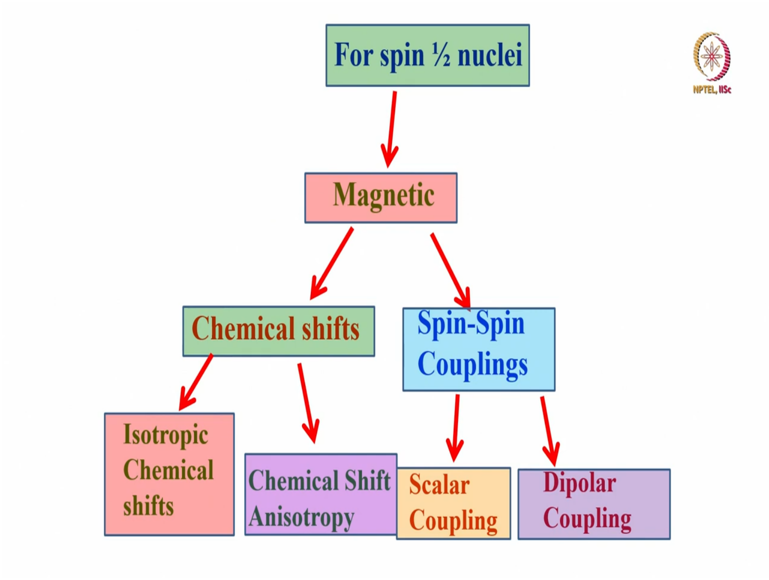

For spin ½ nuclei

Magnetic

Chemical shifts

Spin-Spin Couplings

Isotropic Chemical shifts

Chemical Shift Anisotropy

Scalar Coupling

Dipolar Coupling

So, we do not have to worry about electrical interaction at all. We concentrate only on magnetic interactions; that means; we deal with chemical shifts and spin - spin couplings.

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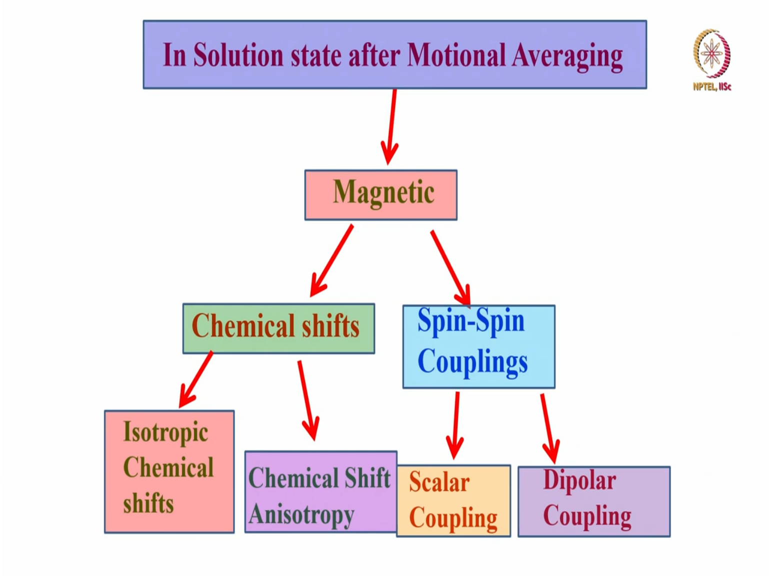

In Solution state after Motional Averaging

Magnetic

Chemical shifts

Spin-Spin Couplings

Isotropic Chemical shifts

Chemical Shift Anisotropy

Scalar Coupling

Dipolar Coupling

And further we are not dealing with solids at the moment; I come to the solid state NMR in the later part of the course. But at the moment when you are dealing with the solution state NMR there is a motional average going on, the nuclear spins are undergoing motion. As a consequence, what happens? Chemical shift anisotropy and dipolar couplings are averaged to 0.

So, basically in the solution state NMR of spin half nuclei we are interested in isotopic chemical shifts and scalar couplings. These are the 2 parameters which we deal with it.

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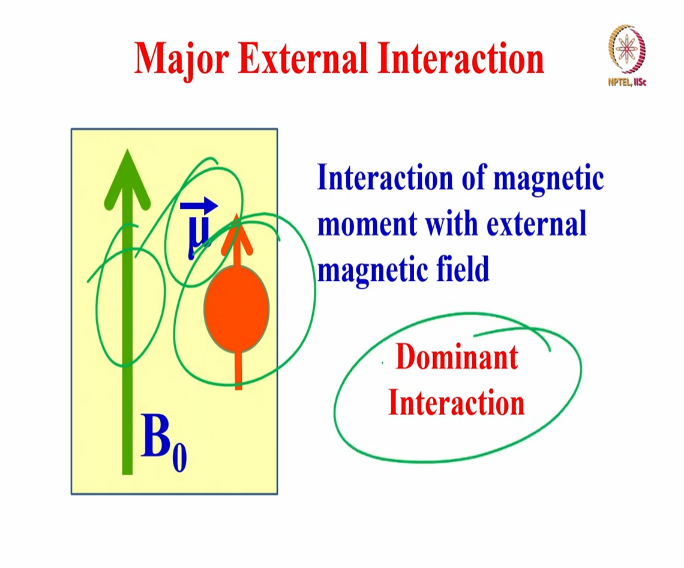

Major External Interaction

Interaction of magnetic moment with external magnetic field

Dominant Interaction

What are the other interactions? how it comes? Of course the dominant interaction is the Zeeman interaction; as I told you it is the nuclear spin which has a magnetic momen, ie. it can interact with the external magnetic field B_0 and because of that we are going to have a Zeeman effect, the splitting up of the energy levels. This is dominant interaction, remember in the spin half case, it is the dominant interaction largest; the strength of this interaction is quite large.

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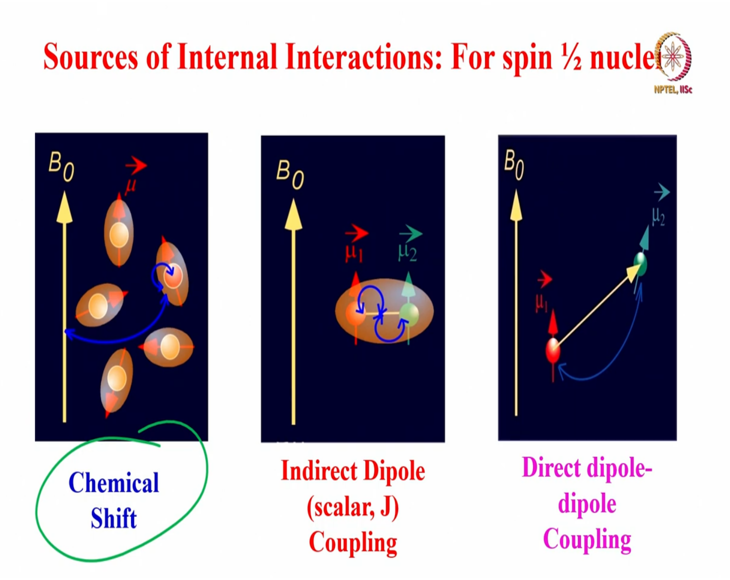

Sources of Internal Interactions: For spin ½ nuclei

Chemical Shift

Indirect Dipole (scalar, J) Coupling

Direct dipole-dipole Coupling

Now if you go to the sources of other Internal interaction for spin half nuclei, one is what is called the chemical shift. Please remember the nuclear spins are not bare nuclei; they are surrounded by electrons, the electrons also can be treated like tiny magnets, I told you. So, the electronic charge distribution at the site of nucleus has some effect. Because of the charge distribution at the site of the nucleus, we get certain interesting phenomenon which is called chemical shift; we will discuss this today.

And another interaction is the indirect dipolar coupling or scalar coupling; it is also called as J coupling. This arises because of interaction of the 2 nuclear spins mediated through a covalent bond. What happens is; we can consider a molecule, let us say 2 atoms are there; they are bound by covalent bond. The nucleus of one of them interacts with the electrons surrounding it; these electrons in turn will interact with the other electrons surrounding the neighboring atom that inter interacts with the nucleus spin.

This is a type of interaction where the magnetization or the polarization gets transferred from one nuclear spin to other nuclear spins mediated through covalent bond which is called scalar coupling or J coupling. And also we have what is called a dipolar coupling. It is an interaction of nuclear spins through space. For this there is no need of a covalent bond. In a 3 dimensional structure molecule can be very big and the two atoms may be separated by 5 or 10 bonds or even more; does not matter in the 3 dimensional structure.

It so happens, the 2 atoms or 2 nuclear spins come close by in space, special proximity is very important condition for this. When they come close in space; It is like bringing 2 magnets close to each other; then what happens? there is an interaction. This is through space interaction, and not through bond. It is through space interaction; this called a dipolar interaction and it is dipolar coupling.

So, this is another parameter; all these parameters can get reflected in the NMR spectrum. But in the solution state, as I said this dipolar coupling will not be seen. It is seen only in the solids or in the partially ordered systems which we will try to discuss in the later part of this course.

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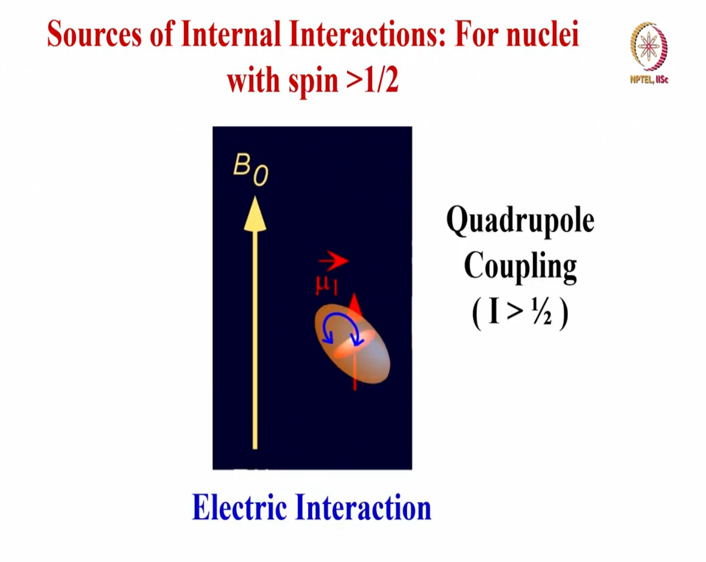

Sources of Internal Interactions: For nuclei with spin >1/2

Quadrupole Coupling
(I > ½)

Electric Interaction

As I said the quadrupolar interaction is an electrical interaction for spin greater than half. This we are not going to discuss but just to tell you it is an electric interaction.

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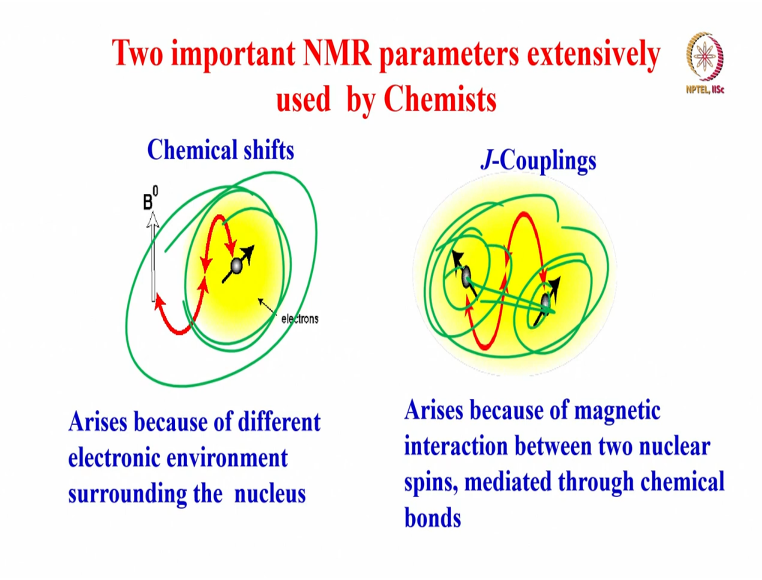

Two important NMR parameters extensively used by Chemists

Chemical shifts

Arises because of different electronic environment surrounding the nucleus

***J*-Couplings**

Arises because of magnetic interaction between two nuclear spins, mediated through chemical bonds

Now these are the 2 parameters which we will be dealing with in this class and in the next class. They are the 2 parameters which are extensively utilized both by chemist,s biologists and all those who extensively use NMR in this solution state. Of course as I already said chemical shift is the one which comes because of the electronic charge distribution, you can see here, it is around the nucleus. And of course this is the J coupling; as I told you, this nucleus will interact with this nuclear spin, mediated through covalent bond.

Because of the charge distribution around each nucleus, and there is a covalent bond between these 2; there the spin polarization from one spin to other spin gets transferred. This is called scalar coupling. These 2 are extensively utilized and we discuss this in detail today.

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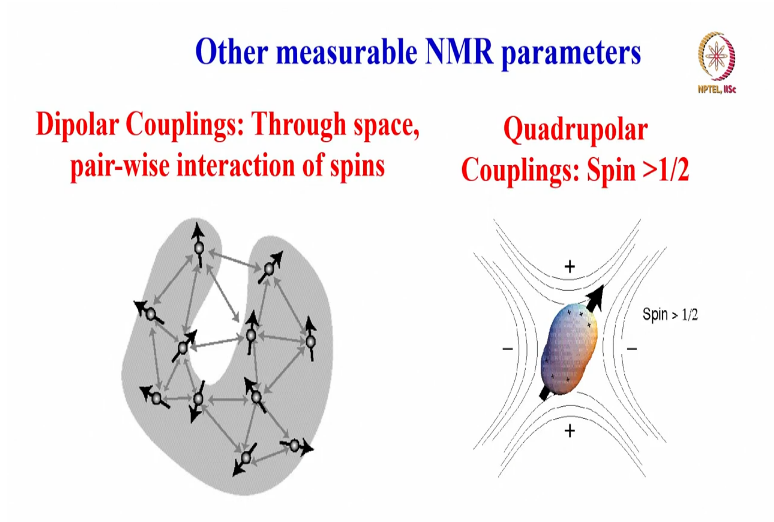

Other measurable NMR parameters

Dipolar Couplings: Through space, pair-wise interaction of spins

Quadrupolar Couplings: Spin >1/2

And of course, other measurable parameters I told you a dipolar coupling, a through space interaction; quadrupolar coupling we can also measure; we will not worry about it today.

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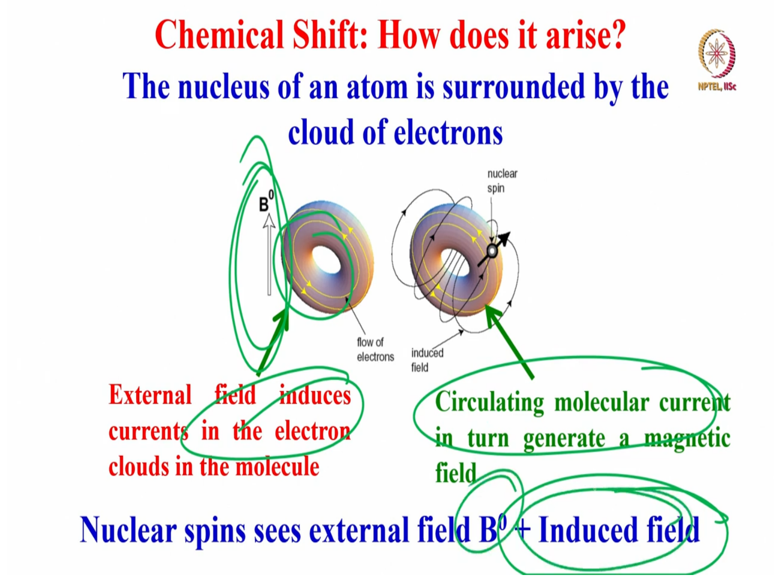

Chemical Shift: How does it arise?

The nucleus of an atom is surrounded by the cloud of electrons

External field induces currents in the electron clouds in the molecule

Circulating molecular current in turn generate a magnetic field

Nuclear spins sees external field B^0 + Induced field

Now chemical shift how does it arise? As I already told you the nucleus of an atom is surrounded with a cloud of electrons. As you know if you have a nucleus we have electrons surrounding it. Then what happens the electrons are not stationary electrons, and are in motion. When you put this in an external magnetic field it induces motion of electrons in the molecule. And then what is going to happen? The circulating molecular current in turn generates magnetic field. Please understand, the external field induces currents in the electron clouds in the molecule and this circulating electron current in turn generates a magnetic field. So, what? what will happen? how does it affect? it means the nuclear spin is not seeing just B_0, in addition to B_0 it is seeing some other field, called the induced field. This comes because of the electrons which are surrounding the nucleus. So that is going to induce the field. So, nuclear field sees in addition to B_0 magnetic field, plus the induced field together.

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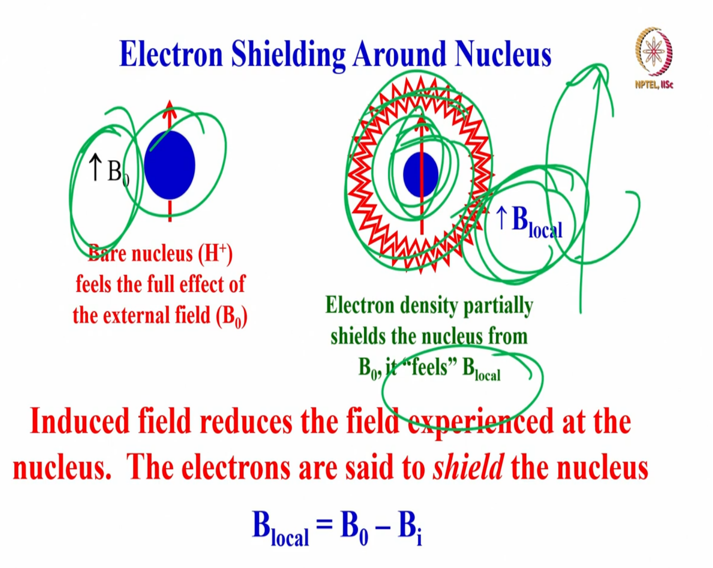

Electron Shielding Around Nucleus

NPTEL, IISc

↑ B_0

↑ B_{local}

Bare nucleus (H^+) feels the full effect of the external field (B_0)

Electron density partially shields the nucleus from B_0, it "feels" B_{local}

Induced field reduces the field experienced at the nucleus. The electrons are said to *shield* the nucleus

$$B_{local} = B_0 - B_i$$

So, the electron shielding surrounding the nucleus can be seen like this. If you have a bare nucleus; we call the electron it is like this; the spins sees the external magnetic field, the nuclear spin sees the full effect of the external magnetic field; the complete effects is seen. Whereas if you have electron density surrounding it, like this, then this electron density partially shields this magnetic field.

For example I have B_0 here, B_0 is not directly seen by this nucleus; it is shielded by something the local field, because of the electronic motion the electron density partially shields the nucleus so B_0 field shields. In addition to B naught, there is some B local field also. And the individual field here reduces field experienced by this nuclear spin; and we say the electrons are the ones which are going to shield the nucleus, or we say nucleus spins are shielded with this electron density.

So, we can calculate what is the B local field. The B local field is the main magnetic field minus the induced local field. That is the field which is generated locally because of this circulating electrons.

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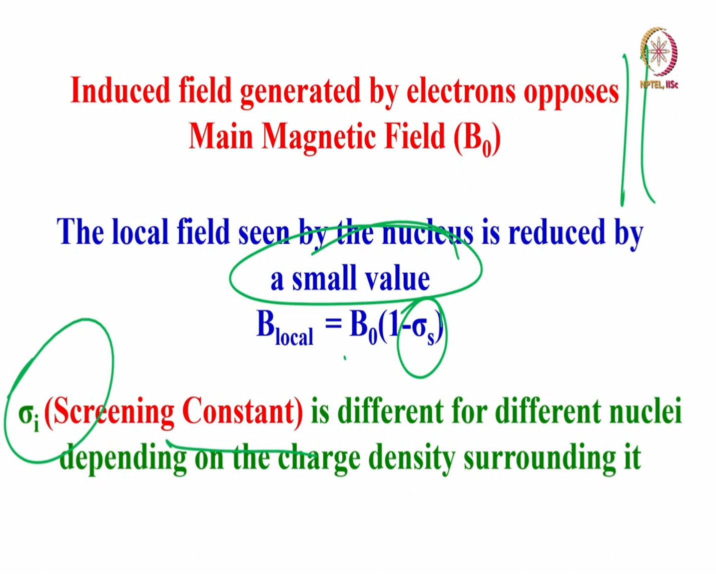

Induced field generated by electrons opposes Main Magnetic Field (B_0)

The local field seen by the nucleus is reduced by a small value

$B_{local} = B_0(1-\sigma_s)$

σ_i (Screening Constant) is different for different nuclei depending on the charge density surrounding it

The induced field generated by electrons always opposes the main magnetic field. This is the basic theorem in physics, which you all should know; in primary school high school you would have studied by Lenz law. So, the local field seen by the nucleus is reduced by a small value which is given by the equation B_0 into 1 - σs, σs is called a screening constant, or called the shielding constant; and it is different for different nuclei depending on the charge density surrounding it.

In a given molecule we may have a CH2 group CH group and NH2 group, no problem. But the charge density, because of the different functional groups, could be different because the sigma will be different. So, depending upon the charge density at the site of the given nucleus, the screening constant will be different. So, this is the important concept. This chemicals shift which comes because of the electronic charge distribution at site of the nucleus is different for different functional groups surrounding the nucleus.

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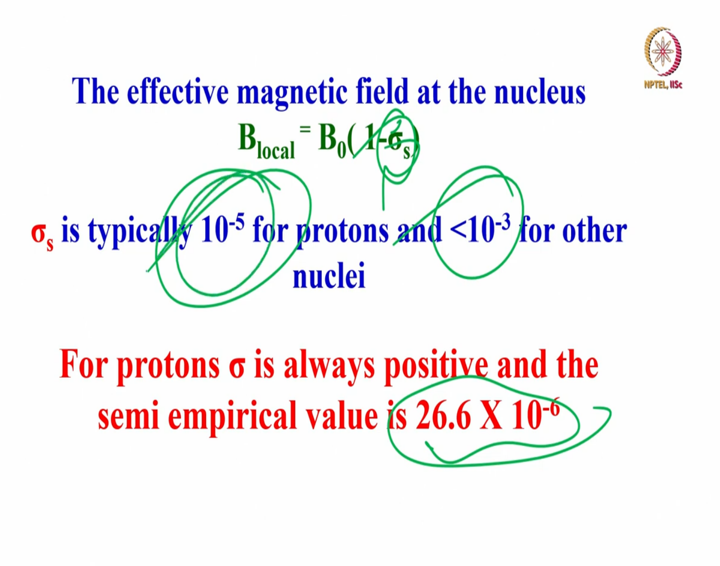

The effective magnetic field at the nucleus

$B_{local} = B_0(1-\sigma_s)$

σ_s is typically 10^{-5} for protons and $<10^{-3}$ for other nuclei

For protons σ is always positive and the semi empirical value is 26.6×10^{-6}

With this we will find out what is the value of this sigma. It is not too large, it is very small; typically the screening constant is of the order of 10 to the power of - 5 for protons, and for other nuclei it is 10 to power - 3. And we can even calculate what is the sigma, it has the semi empirical value, this is some value which can be calculated; and do not worry. In the previous course I discussed all these things in detail.

But just to understand the B local field is B naught - 1 over sigma s which is a screening content and typically the screening constant value is of the order of 10 to power of -5 for protons.

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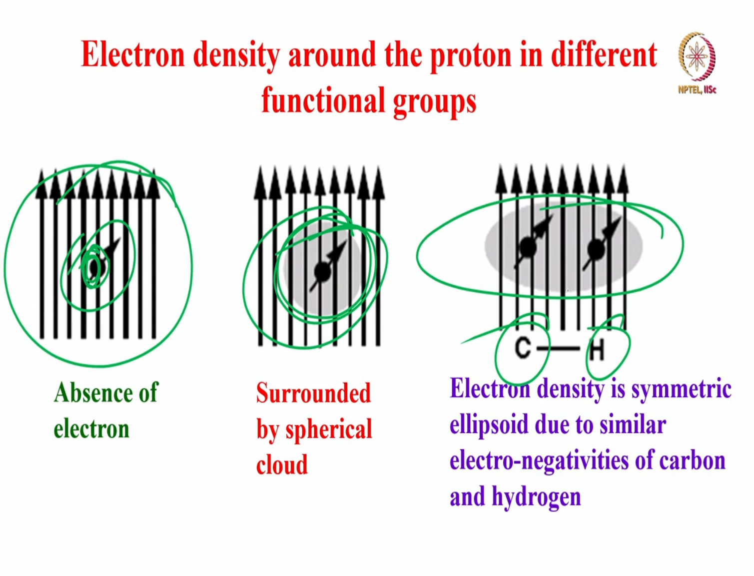

Electron density around the proton in different functional groups

Absence of electron

Surrounded by spherical cloud

Electron density is symmetric ellipsoid due to similar electro-negativities of carbon and hydrogen

So, now with this idea we will see some of these different functional groups. Consider a situation we have a bare nucleus here; this nucleus do not have any electrons at all; that is the bare nucleus I have taken. Then the electronic cloud charge distribution is spherical. You can see here that it is the spherical charge distribution, does not matter. Now I will take the bare nucleus put it in a spherical cloud of electronic charge, which is again, as I said spherical, the charge distribution; the nucleus is put inside this spherical charge distribution. Again in this spherical charge distribution, the charge distribution is easy to understand. It is all bare nucleus I am talking, put it in electronic cloud; it is in the absence of electronic cloud. Now consider CH bond the electron density is not symmetric; the charge density at the site of carbon and the site of protons are not same. Let us say you say, you know all the there is a bond polarity; you say C delta plus H delta minus when you are write about the bond polarity.

So, electron density is not same, the distribution not spherical; but it ellipsoid, like an ellipse. If you see the charge distribute distribution of CH bond, it comes because of the electronegativites of carbon and hydrogen which are not being same.

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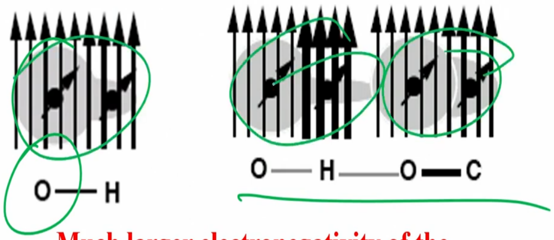

Much larger electronegativity of the oxygen results in asymmetric cloud

Similarly, if you have oxygen group, which is an electron withdrawing group; which is much more electro negative compared to carbon; and otherwise you can also take a lengthy bond like this OC, then this type of charge distribution you can calculate. For example you see here asymmetric distribution; here also asymmetric distribution; here they are not same they are different.

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What is the strength of field induced by surrounding electrons ??

400 MHz = 9.3949 T Magnetic Field (= 93949 G)

B_0

Field Induced due to electronic environment:
0.0000093949 G

Total Magnetic Field Experienced by the Nuclei :
93439.0000093949 G

Resonating frequency is not 400 MHz but
400 MHz + 400 Hz

So, this means you can understand now, with this idea, what is the strength of the field induce we can calculate. But remember one thing depending on the different functional groups present, the charge distribution of the site of different nucleus, then the field experienced by the nucleus in an external magnetic field, is different. That you should understand, but we will find out what is this induced field. You may say okay, how much is the induced field, you may ask the question. For 400 megahertz spectrometer we use 9.3949 Tesla magnetic field; as I said yesterday one Tesla is 10000 Gauss. So, 9.3949 Tesla is 93949 Gauss. What is the field induced? This is the external magnetic field B_0. Now the induce field is very, very small. Remember 0.0000093949; extremely small; not even 1 gauss. Such a small value of the magnetic field is being created at the site of the nucleus, because of the electronic charge distribution.

So, then what is the total magnetic field now in addition to B_0; this will be added up. So, this is the total magnetic field seen by the nucleus. That means the resonant frequency for this magnetic field would have been 400 megahertz; but now because of this it is not 400 megahertz, plus 400 hertz will be there. So, what you expect in a given magnetic field precisely 400 megahertz would have been the resonant frequency, instead because of the charge density distribution at the site of the nucleus, now the resonant frequency is different by 400 Hertz.

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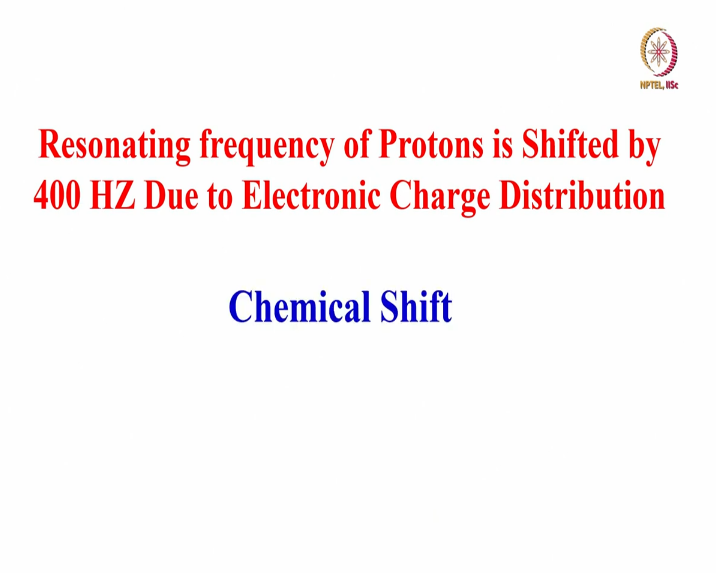

Resonating frequency of Protons is Shifted by
400 HZ Due to Electronic Charge Distribution

Chemical Shift

And we say the resonance frequency has shifted from 400 megahertz by a small amount called 400 hertz; this is what is called chemical shift. Please remember why the chemical shift is coming; this is the chemical shift.

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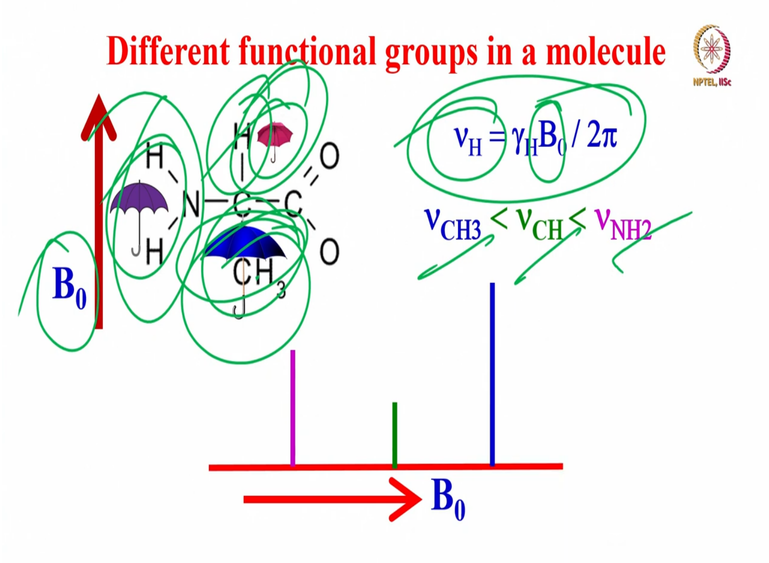

So, now with this we will come back with this knowledge; there is a charge density distribution which are different for different functional groups in a given molecule, because it is an internal interaction. Let us see this molecule again. Now as I said earlier when I put this in a magnetic field, using this equation I said we got a single peak. In principle it is theoretically correct, you must get a single peak.

But now we have understood also there is a charge density distribution which is different for different functional groups in the molecule. What does it mean? The shielding constant is different for CH3 group, it is different for CH group and different for a NH2 group. All these are different, because of that I am going to put different sizes umbrella here, umbrella being larger size means shielding is larger; then comes NH2, then comes CH.

There are 3 different shielding constants it means the fields experienced by each of these things with respect to B_0 are different; they are not same. This experiences more magnetic field than this, and then this. As a consequence we can say we get 3 different resonating frequencies; because now B_0 is not same; B_0 plus this induce field for this thing; B_0 for this, plus this and again for this; they are all different.

So, we get 3 resonating frequencies that is one for CH3 one for CH and one for NH2. So, you are going to get a spectrum like this. So, instead of one peak for this molecule, if we understand internal interaction I can say we are getting 3 peaks; fantastic. Now you can understand why NMR becomes very, very useful and very interesting.

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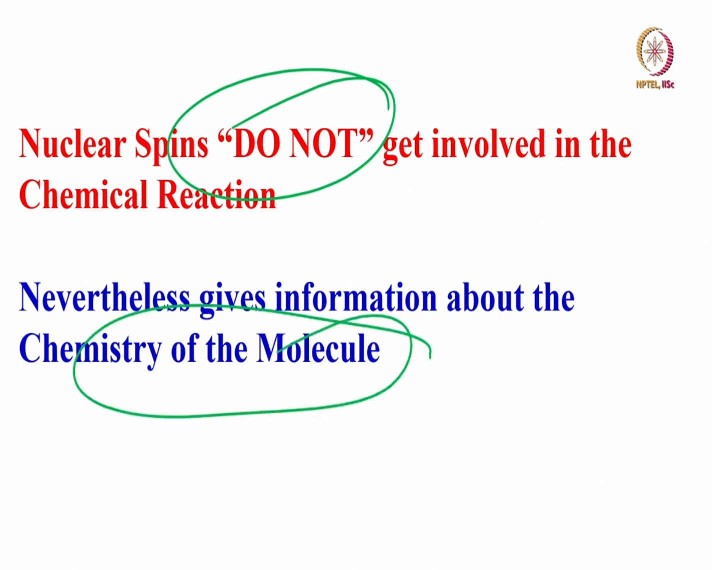

Nuclear Spins "DO NOT" get involved in the Chemical Reaction

Nevertheless gives information about the Chemistry of the Molecule

Because it is an internal interaction we can understand a lot of things. So, please understand one more important point, nuclear spins do not get involved in the chemical reaction. But just know we understood, it can give information about the chemistry of the molecule. About the charge distribution can understand. Once you know the charge distribution, you can understand the structure of the molecule, can get the conformation of the molecules. So, as a consequence you can get the chemistry of the molecule by using these things.

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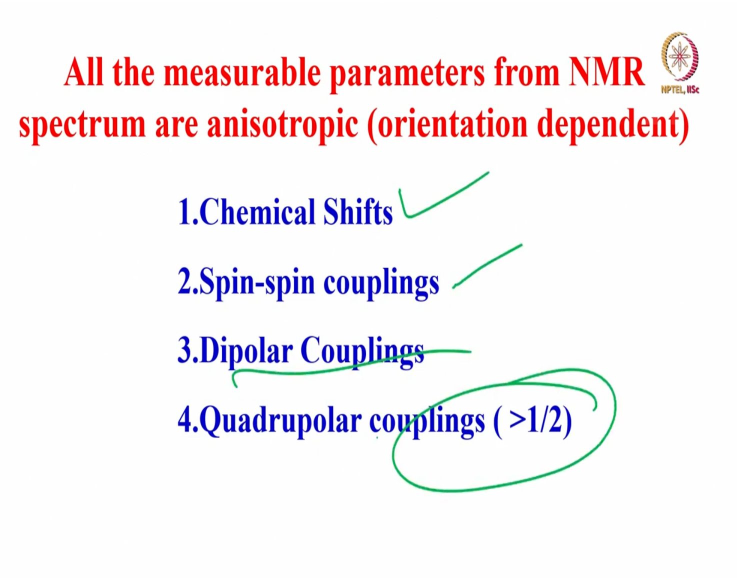

All the measurable parameters from NMR spectrum are anisotropic (orientation dependent)

1. Chemical Shifts
2. Spin-spin couplings
3. Dipolar Couplings
4. Quadrupolar couplings (>1/2)

So, now all the measurable parameters for NMR spectrum are anisotropic; for example I said chemical shift, spin - spin coupling, dipolar coupling and quadrupolar coupling are anisotropic; they are orientation dependent.

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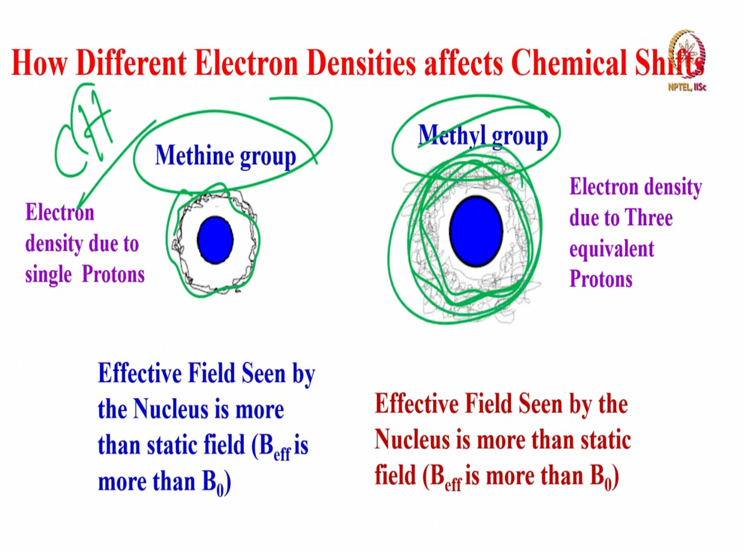

How Different Electron Densities affects Chemical Shifts

CH

Methine group

Electron density due to single Protons

Effective Field Seen by the Nucleus is more than static field (B_{eff} is more than B_0)

Methyl group

Electron density due to Three equivalent Protons

Effective Field Seen by the Nucleus is more than static field (B_{eff} is more than B_0)

So, then how different electron densities affect these chemical shifts we can find out. One more thing, consider this methine group; you know what the methine group, it is a CH group. Electron density due to single proton. There is only one proton, I will put some figure like this for charge density distribution. Now effective fields seen by this nucleus is different from B_0; that is clear; that is what we understood. We have been discussing about charge density distribution.

Now I go to a methyl group there are 3 protons the charge density distribution is much more here; much larger than the CH group. Again, the effective field seen by this nucleus is different than that of B_0; both are different. But remember charge density distribution is much more here ;electron density distribution is more here; than this one.

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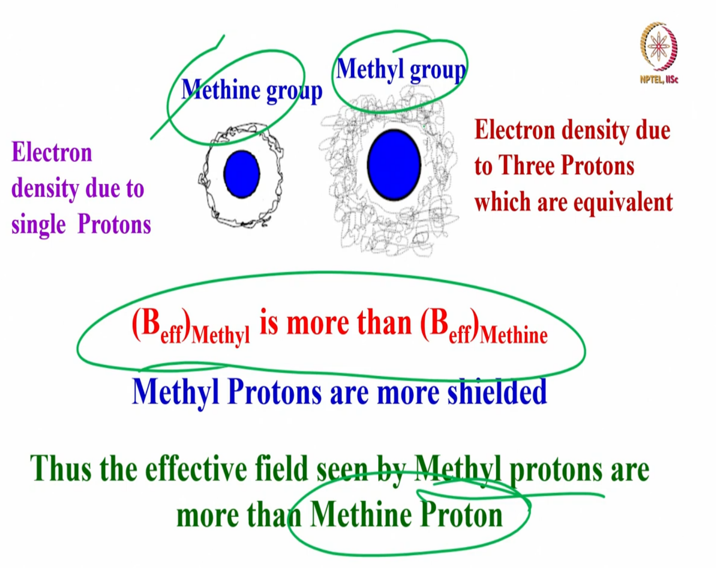

Methine group

Methyl group

Electron density due to single Protons

Electron density due to Three Protons which are equivalent

$(B_{eff})_{Methyl}$ is more than $(B_{eff})_{Methine}$

Methyl Protons are more shielded

Thus the effective field seen by Methyl protons are more than Methine Proton

So, as a consequence then what is going to happen is Bmethyl is more shielded than Bmethine proton. So, CH3 protons here are more shielded than CH protons. The effective field seen by the methyl group is more than that of the methyl proton, because there are 3 protons here; there is only a single proton in the methine group.

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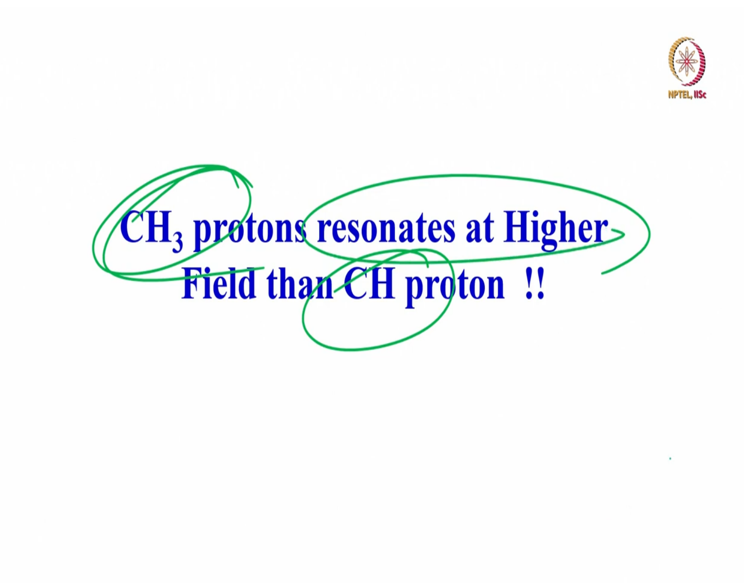

CH$_3$ protons resonates at Higher Field than CH proton !!

What does it tell you? CH3 protons experience a larger magnetic field than CH proton. It means CH3 protons resonating frequency is at higher field than CH proton. So that is what happens; the CH3 comes at higher field, resonates at higher field than CH proton.

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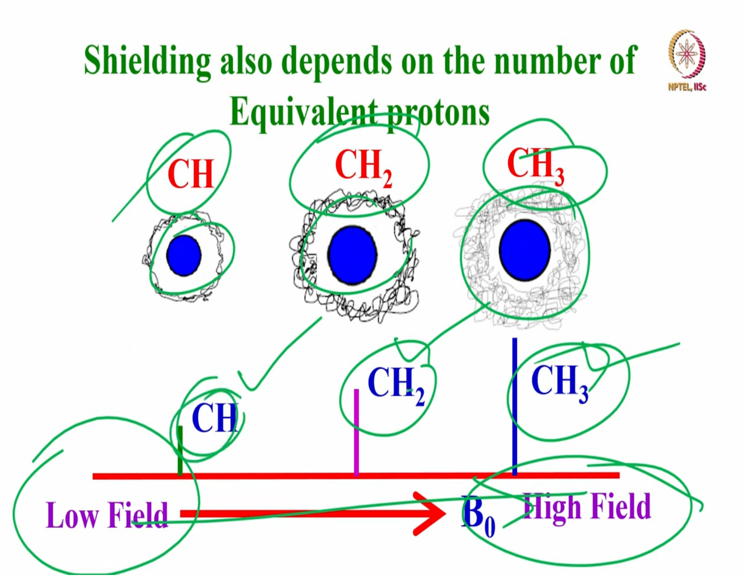

Shielding also depends on the number of Equivalent protons

The shielding also depends upon varieties of functional groups present. Now for example if I take CH proton I took the example of CH, CH3. What happens if I take CH2 now? 1 proton 2 protons 3 protons, exactly the electron charge density distribution here is much more, this is less than this, it is even less than this. We get 3 different peaks CH3 comes at high field, than CH2 than CH.

And remember this is always in the right side of my spectrum; from my side right side high field from my left side it is called low field. So, as you go from left to right, the magnetic field is increasing. So, CH3 comes at high field; CH2 comes less than this. But higher field than CH and CH comes lower than this CH2.

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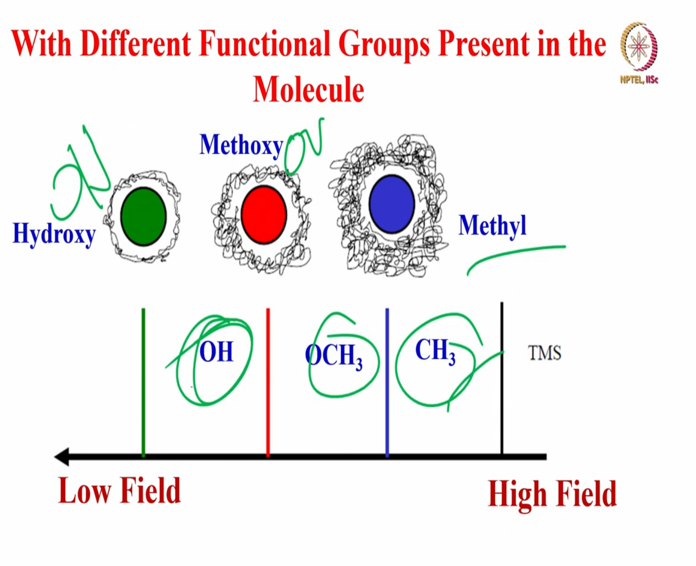

With Different Functional Groups Present in the Molecule

And it also depends upon varieties of functional groups; for example OH group hydroxyl, methoxy OCH3 and methyl. If you take 3 different groups, they all will come at different positions. Again CH3 comes at a high field than OH, CH3 comes at low field and then OCH3. So, what I am trying to say is, different functional groups of the molecule has different resonating frequencies, because of charge density distribution.

Now I will introduce a term called chemical equivalence; it is very, very important to understand the NMR spectrum. So, far I was talking about the chemical shift that also depends upon a term called chemical equivalence. And the number of peaks what you are going to see largely depends upon the symmetry of the molecule. So, with this we will understand what is chemical equivalence?

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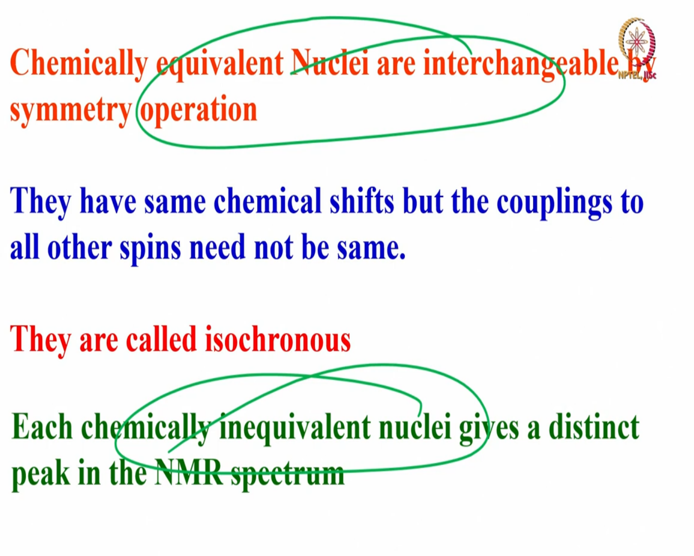

Chemically equivalent Nuclei are interchangeable by symmetry operation

They have same chemical shifts but the couplings to all other spins need not be same.

They are called isochronous

Each chemically inequivalent nuclei gives a distinct peak in the NMR spectrum

Consider a molecule like this; I mean we will come to that. Let us say the nuclei because of symmetry operation, they are interchangeable; that is a molecule as C2v symmetry. There are 2 protons which are equivalent. And then they have a same chemical shift, if they are interchangeable by symmetry operation they are called isochronous nuclei. They have identical chemical shift; they cannot be distinguished as different chemical shifts.

Now then question is how many peaks you are going to get in the NMR spectrum. If a molecule has 10 protons, or 10 different functional groups, let us say all these 10 functional groups are entirely different. Then you get 10 different groups of peaks; you understand; 10 different groups of peaks. What it means is, each chemically inequivalent nuclei or inequivalent group of nuclei gives distinct peaks in the NMR spectrum.

So, if I have 4 different functional groups, I get 4 different types of groups of peaks. If I have 3, I get 3 different groups of peaks. On the other end if they are chemically equivalent the number or peaks which are going to be seen the spectrum drastically reduces; we will see that now what happens to that.

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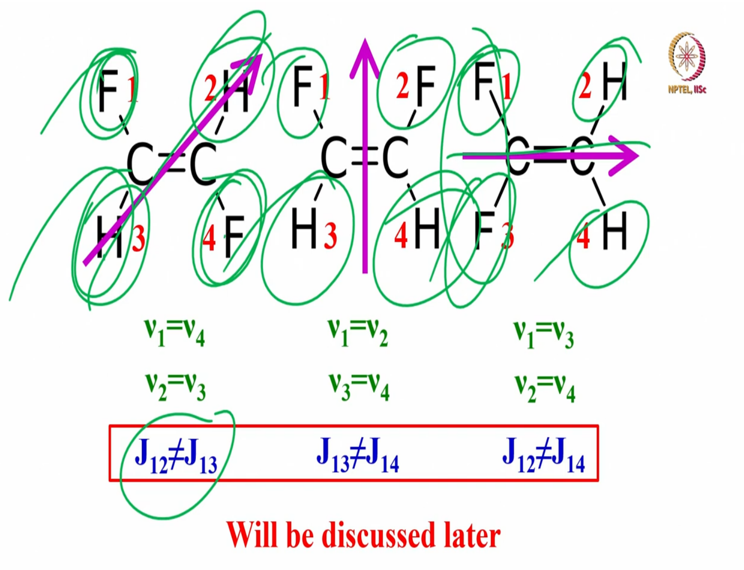

$\nu_1=\nu_4$ $\nu_1=\nu_2$ $\nu_1=\nu_3$

$\nu_2=\nu_3$ $\nu_3=\nu_4$ $\nu_2=\nu_4$

$J_{12}\neq J_{13}$ $J_{13}\neq J_{14}$ $J_{12}\neq J_{14}$

Will be discussed later

Consider a molecule like this; does this molecule has a symmetry? Yes, if I look at this direction of my arrow here this fluorine and this fluorine are symmetric; this proton and this proton are symmetric. In which case I would say the resonanting frequencies of 1 and 4 are same; 2 and 3 are same. If I take the proton resonance there is no difference between these 2. If I take the fluorine NMR, there is no difference between these 2.

And there is also an interaction we will talk to talk about it later. Now on the other hand instead of putting fluorine in a trans position I will put the fluorine in the cis position like this. Then what will happen? again there is a symmetry; again this fluorine is same as this fluorine, this proton is equal to this proton chemically. Again ν1 = ν2 and ν3 = ν4.

Now I will change the position of the fluorine here. Now I make them geminal, now what will happen? there is symmetry along this axis. Now what will happen? Again this 1 and 3 are same 2 and 4 are same. So, what does it mean? This part we will discuss later, if there is symmetry the resonant frequencies become equal. As a consequence, the number of peaks you are going to see in the spectrum drastically gets reduced. The symmetry plays a dominant role in the NMR spectrum.

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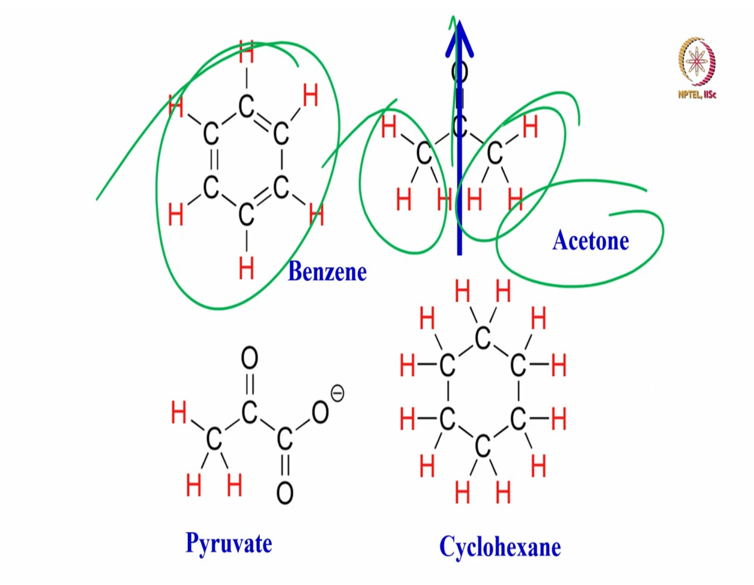

For example benzene; consider a molecule like benzene; all the 6 protons are chemically equivalent. In principle you get only a single peak. Look at acetone, I am go to put a symmetry axis here. That mean this CH3 and this CH3 are equivalent; you are going to get only one peak for CH3. And similarly, you can see here, there is no symmetry here, you can only for CH3 group; this is cyclohexane. All 12 protons here are chemically equivalent; they give rise to single peak.

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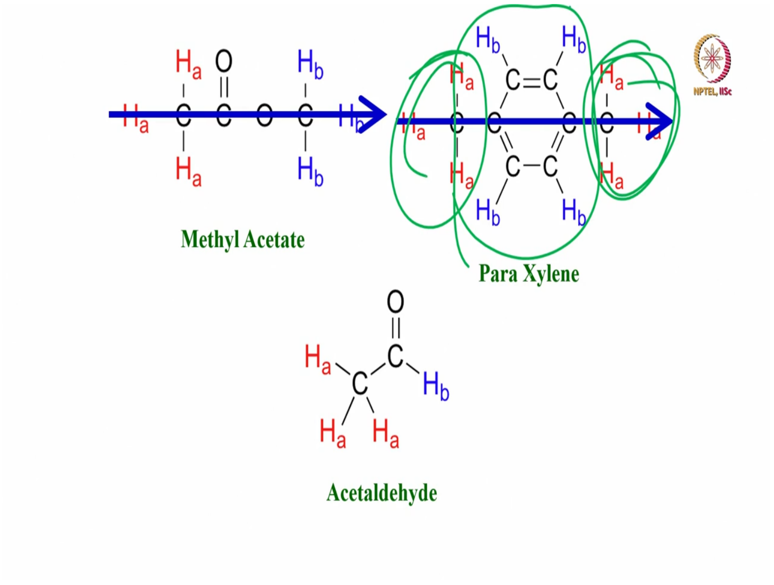

Like this you can talk more about symmetry. Look at this one there is symmetry axis along this. This CH3, this CH3 are same; all these 4 protons are identical. They are chemical equivalent, so you get 2 peaks; one for 2 CH3 groups and one for 4 proton groups.

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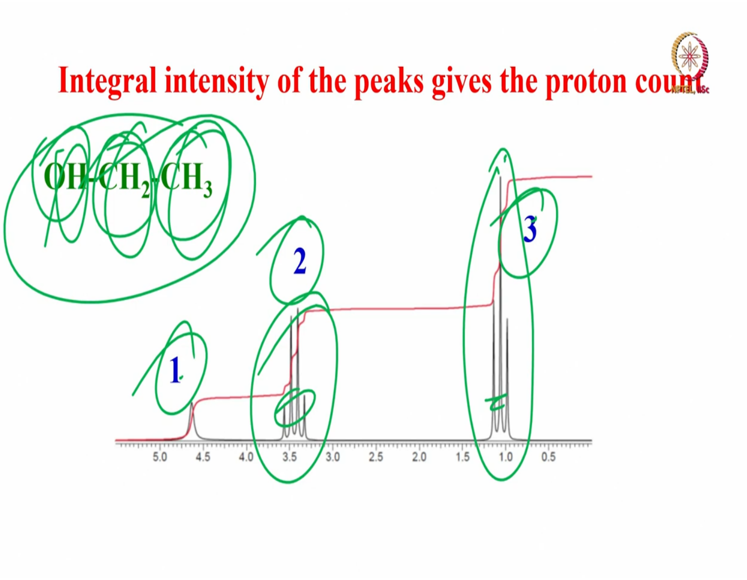

Integral intensity of the peaks gives the proton count.

So, we can talk about it like this. But now how do you know there is a symmetry or there is equivalent protons, but they are coming at the same frequency. Simple example, looks at this ethyl alcohol, this is CH3 this CH2 and OH. And you see there is a multiplicity here. Do not worry, I will discuss when we come to the scalar coupling. You can look at the three peaks here, this intensity together is 3 I will put.

These there are 4 peaks here intensity together I will put it as 2; and this is 1 the intensity ratio goes to 1 is to 2 is to 3; what does it mean? Remember there is only one proton here, there are 2 protons here; and 3 protons here. It means the intensity of the peak or the integral area of the peak tells you how many protons are present in that group. So, it is a proton count, internal integral proton count.

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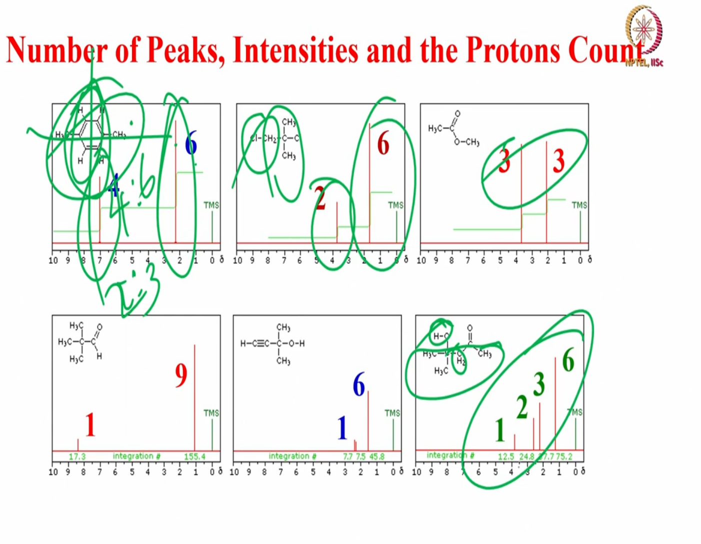

Number of Peaks, Intensities and the Protons Count

I can see like this. For example look at this molecule. For example, I get 2 peaks here in the aliphatic region; in this region what we are going to get is generally CH3 group. So, this is CH3 and all the 4 protons are equal and there is symmetry along this axis along this axis. That means intensity ratio if you consider it is 4 : 6 or 2 : 3. It means I can immediately say this peak corresponds to benzene protons and this peak corresponds to CH3 group.

Similarly you can talk about it, for a variety of molecules this intensity ratio is 2 is to 6; 2 correspond to the CH2 group and 6 intensity corresponding to 2 CH3 groups. Like this, 3 : 3 here 1 : 1 ratio 3 : 3 ratio. So, simply you remember the integral intensity of the peaks gives you the proton count in a different molecule. In each molecule if you take the NMR spectrum, look at this 1, 2, 3, 6 is the intensity ratio; there is 1 proton with the CH protons here, one OH proton here, then CH2 here and there are 3 different CH3s here.

But you take the NMR spectrum, take the integral intensity ratio, you will find out t it is 1 is to 2 is to 3 is to 6.

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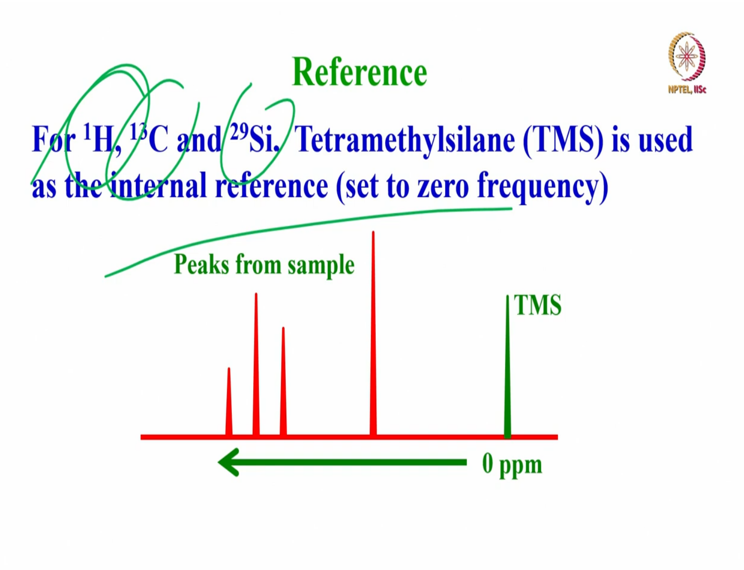

Reference

For ^{1}H, ^{13}C and ^{29}Si, Tetramethylsilane (TMS) is used as the internal reference (set to zero frequency)

So, this is how you understand this thing. And remember always when we measure the chemical shift for any spectrum, for any nuclei whether proton carbon or silicon or any nuclei you take, we always need a reference. And for proton carbon and silicon we use that Tetramethylslinane as the reference, because Tetramethylslinane has carbon, protons and silicon.

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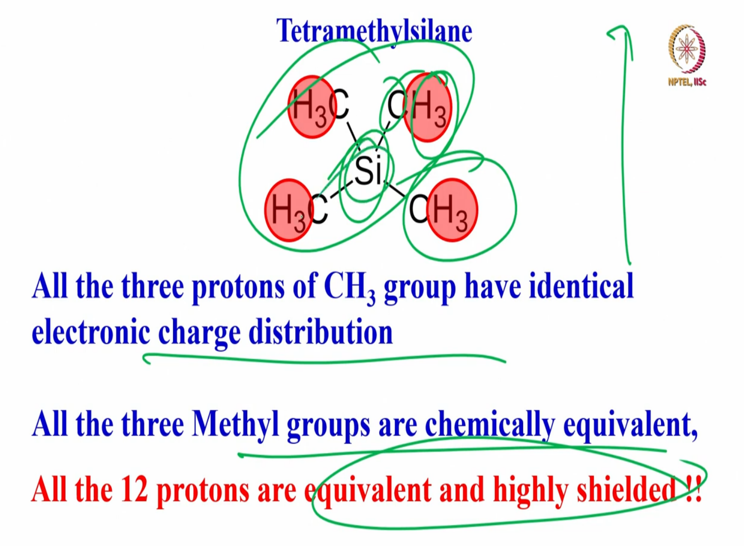

Tetramethylsilane

All the three protons of CH_3 group have identical electronic charge distribution

All the three Methyl groups are chemically equivalent,

All the 12 protons are equivalent and highly shielded !!

All the protons 4 photons of CH3 have identical charge distribution, all the 4 methyl are chemically equivalent, and now all the 12 protons are highly shielded, and gives it a single peak the high field region. And also it is inert and do not react with any of your molecules, and highly volatile. That is why Tetramethysilane is used as a reference for protons. Since it contains silica and carbon we also use this for silicon NMR and carbon NMR.

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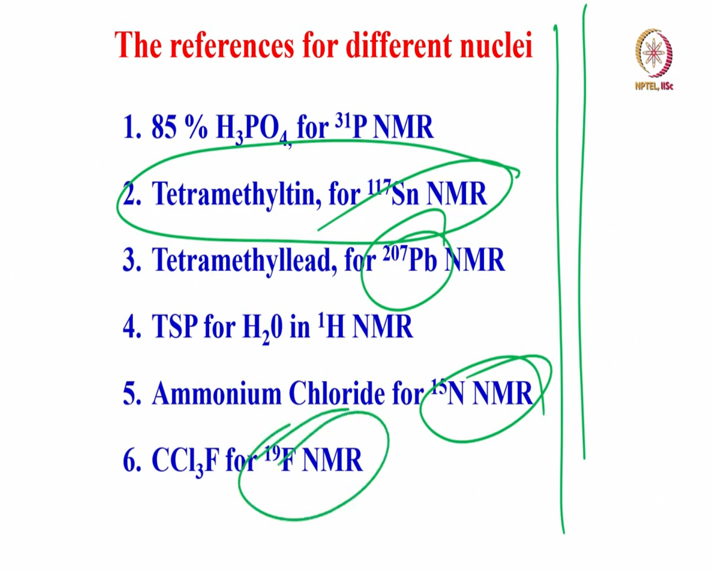

The references for different nuclei

1. 85 % H_3PO_4 for ^{31}P NMR
2. Tetramethyltin, for ^{117}Sn NMR
3. Tetramethyllead, for ^{207}Pb NMR
4. TSP for H_20 in ^{1}H NMR
5. Ammonium Chloride for ^{15}N NMR
6. CCl_3F for ^{19}F NMR

So, for different nuclei, we have different types of references, which you can find out from any of the books. And for example if I want to see Tin NMR, I can use Tetramethyltin Tetramethyllead for lead NMR; and ammonium chloride for nitrogen-15 and CCl3F for 19F NMR, like this.

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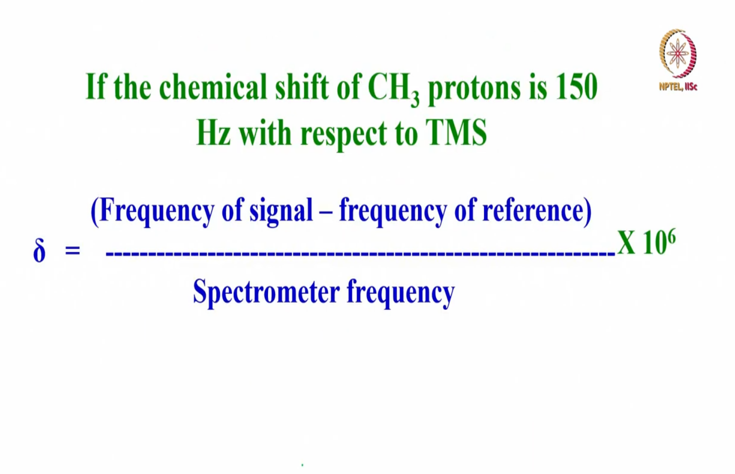

If the chemical shift of CH_3 protons is 150 Hz with respect to TMS

$$\delta = \frac{\text{(Frequency of signal – frequency of reference)}}{\text{Spectrometer frequency}} \times 10^6$$

So, we can talk more about these things here; now next part is we are going to talk about chemical shift; this is the reference, using this reference you measure the resonaning frequencies of different functional groups; or different protons present in the molecule. So, what you are going to understand? how do you measure it? This we will discuss; how do you measure the chemical shift, what is the reference, how you define these will come in the next class.

But today you have understood something about the basics of chemical shift, what is the chemical shift? why does it come and what will happen to chemical shift with the symmetry of the molecule, and what is the reference which we are using for different nuclei, and how different charge density distribution gives rise to different resonant frequencies. So, this is what we have understood, in the next class we will talk more about how do you measure this chemical shift; how different functional groups affect; and a lot about chemical shifts; we can discuss subsequently; I will stop today. Thank you.