Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture – 03

Nuclear Magnetic Resonance Spectroscopy
Principle and Application in Structure Elucidation

Hello. Welcome to module 3 of the course on application of spectroscopic methods in molecular structure and determination. In this particular module, we will consider the concept of chemical shift, the concept of spin-spin coupling and look at the parameters that affect the chemical shift and the coupling constant, which is coming, arising out of the spin-spin coupling.

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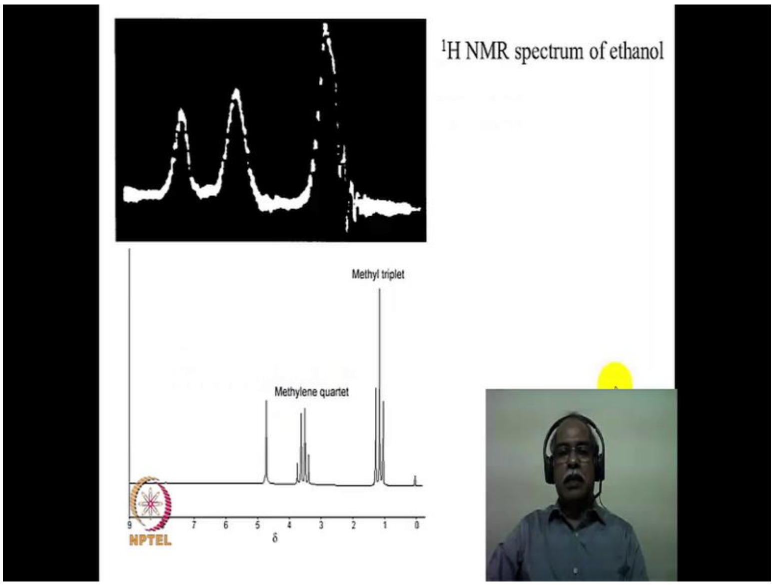

^{1}H NMR spectrum of ethanol

Now, in the last lecture, we ended the lecture with the presentation of the spectrum of ethyl alcohol, and we indicated that, ethyl alcohol has three different types of hydrogen, corresponding to the OH hydrogen, the CH 2 hydrogen and the CH 3 hydrogen which appear at different frequencies in the NMR spectrum.

We also discussed the possibility of having fine structures like this in a high resolution spectrum of the NMR of ethyl alcohol.

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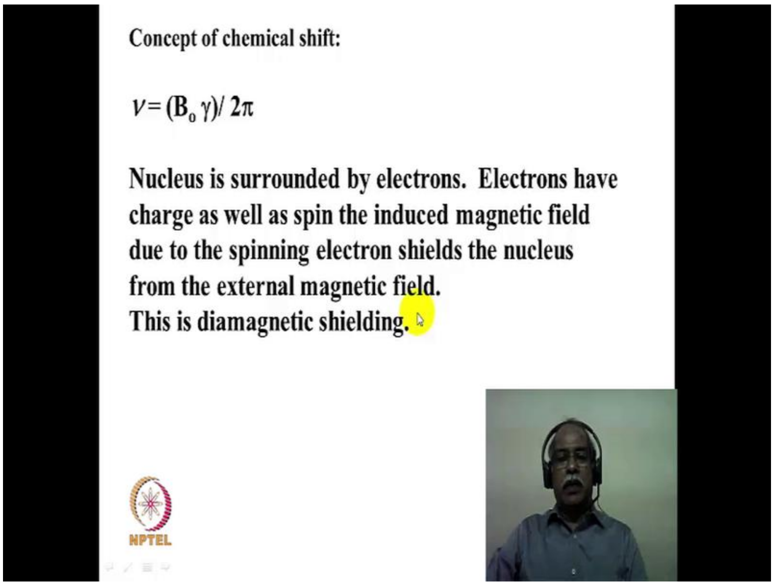

Concept of chemical shift:

$\nu = (B_o \gamma)/ 2\pi$

Nucleus is surrounded by electrons. Electrons have charge as well as spin the induced magnetic field due to the spinning electron shields the nucleus from the external magnetic field.
This is diamagnetic shielding.

Now, if the concept of chemical shift were to be introduced, one has to understand that, based on this particular equation, one would expect all the hydrogens to come at the same resonance frequency, because for a hydrogen atom, gamma is constant and B zero which is the applied a magnetic field for a given field strength, it would be a constant value; however, we seldom observe the same frequency for all the different types of hydrogens present in a molecule. So, there must be a reason that the different hydrogens show different frequency in the NMR spectrum, which makes the NMR a very valuable tool for structural ((Refer Time: 01:46) considerations.

Now, when we talk about this equation, we are considering a bare hydrogen without consideration of any electron density around the hydrogen. We seldom have hydrogen without any electron density in a molecule. In fact, we will have different electron density, depending upon the chemical nature of the hydrogen. If the hydrogen is highly acidic, it will be surrounded by less electron density; if the hydrogen is highly basic, it will be surrounded by high electron density. This is based on our chemical knowledge, we can say that, the different hydrogens come under the different electron crowd, depending upon the chemical environment of the hydrogen that is being present. Now, nucleus is surrounded by electrons, and electrons are charged particles; and, they also spin in the induced magnetic field. Due to the spinning electron, it shields a nucleus from the external magnetic field. In other words, a spinning electron produces its own induced magnetic field, and this induced to magnetic field is supposed to be opposing the external magnetic field. In other words, it will be shielding the hydrogen from a external magnetic field. This is called a diamagnetic shielding, because we are talking about diamagnetic material in most of the organic chemistry that we deal with.

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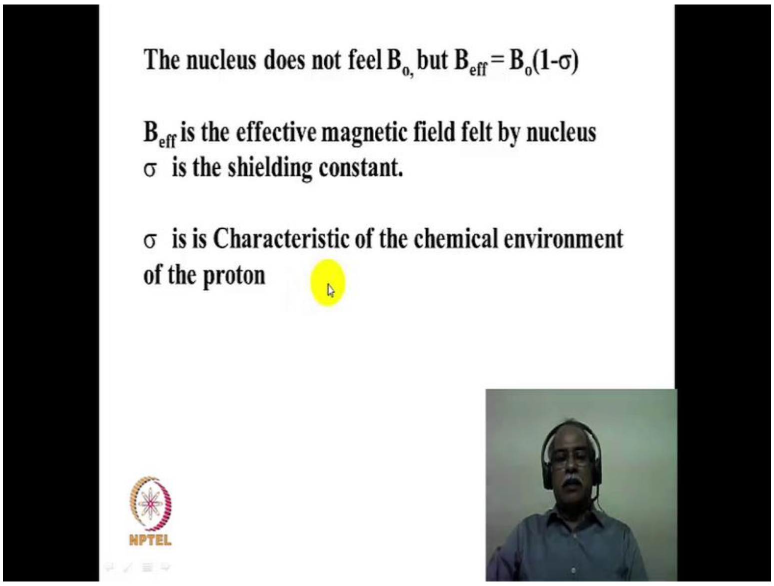

The nucleus does not feel $B_{o,}$ but $B_{eff} = B_o(1-\sigma)$

B_{eff} is the effective magnetic field felt by nucleus

σ is the shielding constant.

σ is is Characteristic of the chemical environment of the proton

So, the nucleus, actually, does not feel the applied magnetic field; it feels less magnetic field than the applied magnetic field to an extent of B zero 1 minus sigma, where sigma is the shielding constant. In fact, sigma is proportional to the applied magnetic field. So, B zero minus B zero sigma is the correct expression for the effective magnetic field that is felt by the nucleus. Now, sigma is a characteristic feature of the chemical environment of the proton. It depends on the electron density around the particular hydrogen that we are referring to; and hence, sigma will be different for different types of hydrogens.

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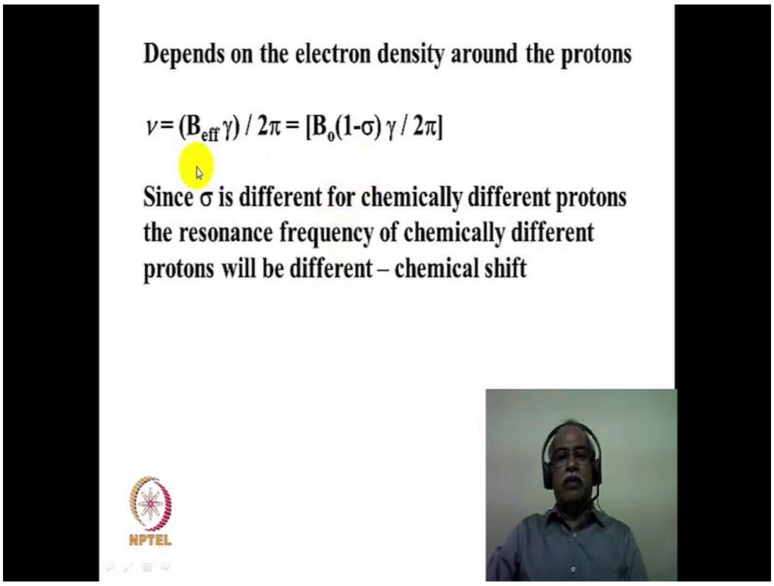

Depends on the electron density around the protons

$\nu = (B_{eff}\gamma) / 2\pi = [B_o(1-\sigma)\gamma / 2\pi]$

Since σ is different for chemically different protons the resonance frequency of chemically different protons will be different – chemical shift

Once you define the basic NMR equation in this particular format, incorporating the shielding constant also, then, we are able to recognize why different hydrogens come in different frequencies in the NMR experiment. Since sigma is going to be different for chemically different protons, the resonance frequencies of the chemically different hydrogens will also be different; hence the concept of chemical shift comes into picture.

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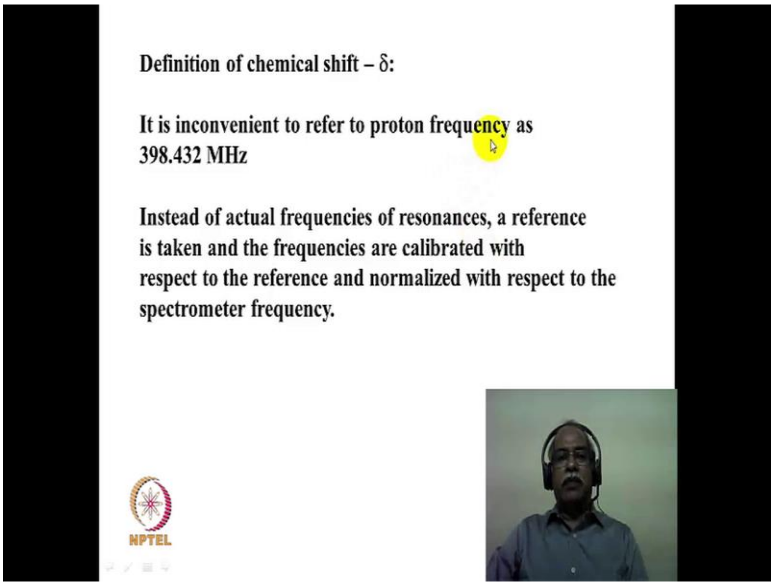

Definition of chemical shift – δ:

It is inconvenient to refer to proton frequency as 398.432 MHz

Instead of actual frequencies of resonances, a reference is taken and the frequencies are calibrated with respect to the reference and normalized with respect to the spectrometer frequency.

Now, the definition of chemical shift can be followed in the next couple of slides. For example, if one were to refer the proton frequency in the NMR experiment as 392.432, some such large number, and a fractional number, it will be extremely inconvenient to remember. Instead of doing that, instead of dealing with actual frequencies of the resonances, one can take a reference compound, and with respect to the reference compound, one can calibrate all the frequencies; and, in order to make the frequencies independent of the spectrometer frequency, one can normalize it with respect to the spectrometer frequency. And, this is precisely what is done, when you are defining the chemical shift values of the NMR spectrum.

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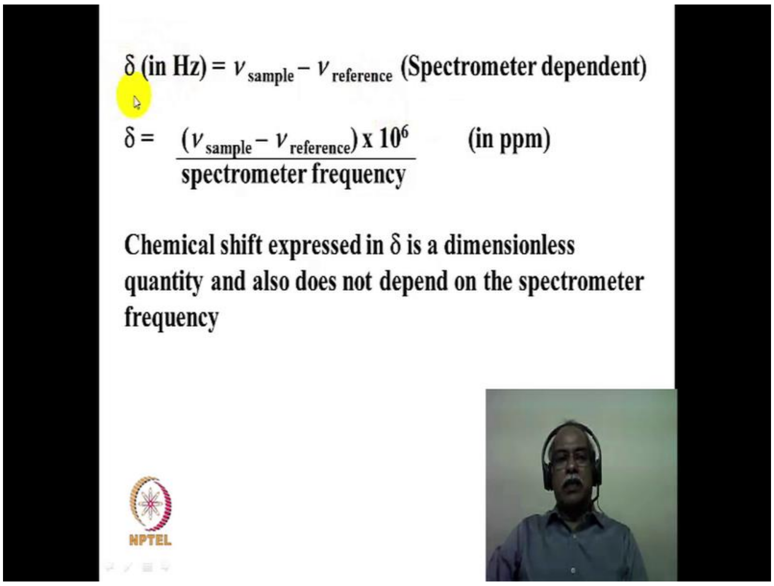

δ (in Hz) = $\nu_{\text{sample}} - \nu_{\text{reference}}$ (Spectrometer dependent)

$$\delta = \frac{(\nu_{\text{sample}} - \nu_{\text{reference}}) \times 10^6}{\text{spectrometer frequency}} \quad \text{(in ppm)}$$

Chemical shift expressed in δ is a dimensionless quantity and also does not depend on the spectrometer frequency

Now, the delta, which is the chemical shift expressed in hertz, is simply the difference between the sample frequency and the reference frequency. This will be highly dependent on the NMR spectrometer. The reason this is dependent on the NMR spectrometer is that, it is not normalized with respect to the spectrometer frequency. We already know that, the sample frequency and the reference frequencies are dependent on the NMR spectrometer. In other words, it is dependent on the B zero that is being applied. Different spectrometers will have different B zeros, and that is the reason, the delta expressed in hertz as a unit, in other words, in frequency units it is expressed, it is dependent on the spectrometer frequency. However, if we divide the difference between the sample frequency and the reference frequency by a spectrometer frequency, then it becomes independent, dimensionless feature of the delta comes into picture. Now, the spectrometer frequency is generally of the order of megahertz; that is, 10 to the power 6 hertz is what we are talking about.

On the other hand, the difference between the sample and the reference frequencies are of order of hertz. So, there is a factor of 10 to the power 6 comes into picture in this particular equation, and that is why, delta is represented in parts per million in the NMR experiments. The delta expressed in parts per million now is dimensionless quantity and it is independent of the spectrometer frequency. So, it does not matter whether one is recording the NMR spectrum in a 60 megahertz NMR spectrometer, or a 600 megahertz NMR spectrometer. When delta is expressed in parts per million, it is independent of the spectrometer. So, whatever is being measured in one spectrometer can be easily compared with what is measured in another spectrometer.

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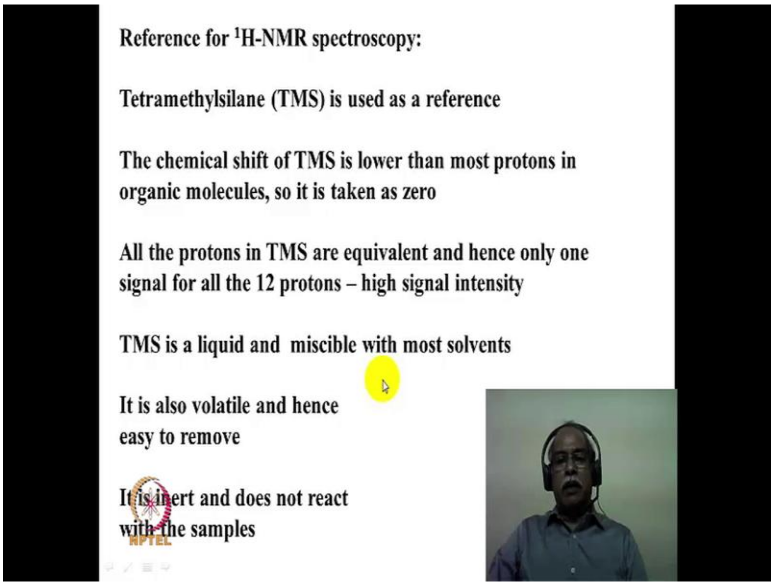

Reference for ^{1}H-NMR spectroscopy:

Tetramethylsilane (TMS) is used as a reference

The chemical shift of TMS is lower than most protons in organic molecules, so it is taken as zero

All the protons in TMS are equivalent and hence only one signal for all the 12 protons – high signal intensity

TMS is a liquid and miscible with most solvents

It is also volatile and hence easy to remove

It is inert and does not react with the samples

Now, the reference that is normally used for proton NMR spectroscopy is Tetramethylsilane. This compound is used as a reference for the following, for the following convenient reasons: the chemical shift of Tetramethylsilane is lower than most protons in organic molecules, because silicon is more electropositive than carbon. So, it is taken as zero, and it comes at the lowest delta value in the NMR spectrometer, in the NMR spectrum. All the protons in the Tetramethylsilane, there are 12 protons in the

Tetramethylsilane, and all of them are equivalent. We will come to the point of what is meant by equivalent a little later; for the time being, let us assume, they are all chemically equivalent. So, they give just 1 signal of high intensity for the 12 hydrogens in this compound. Tetramethylsilane is a liquid and it is miscible with most organic solvents; that is a very convenient feature, because, depending on the solvent that we use, we can always use the Tetramethylsilane as the internal reference without having to worry about the solubility properties. Tetramethylsilane is also highly volatile. So, one can also remove it very easily from the sample after the measurement is made. Finally, the most important of all the properties, Tetramethylsilane is a inert liquid, and it does not react with the sample itself. So, sample can be recovered intact after the measurement of the NMR spectrum.

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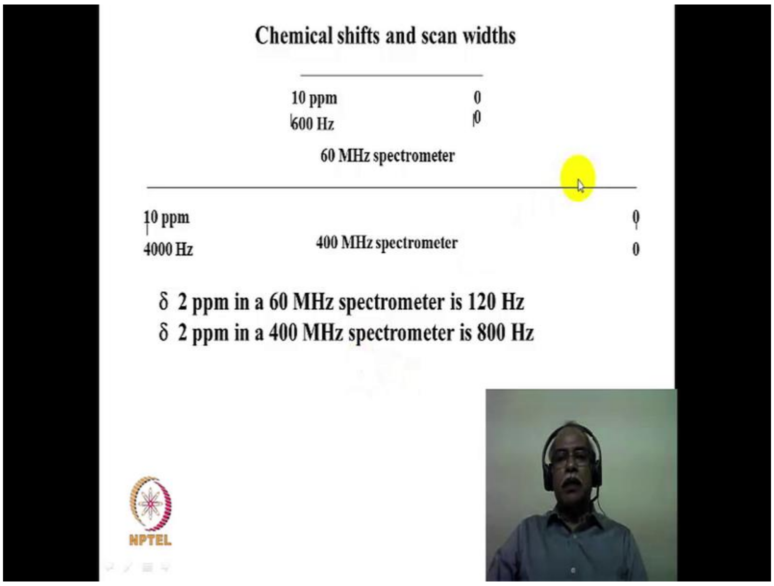

Chemical shifts and scan widths

10 ppm 0
600 Hz 0
60 MHz spectrometer

10 ppm 0
4000 Hz 0
400 MHz spectrometer

δ 2 ppm in a 60 MHz spectrometer is 120 Hz
δ 2 ppm in a 400 MHz spectrometer is 800 Hz

So, let us talk about the scan widths in the NMR spectrum. Suppose, for example, you have a 60 megahertz NMR spectrometer and a 400 megahertz NMR spectrometer. Normally, in the proton NMR spectrum, you scan from zero p p m, which corresponds to the Tetramethylsilane signal, to about 10 p p m. This is the normal scan width, of the order of about 10 p pm is what is normally measured in the NMR spectrometer. Now, for a 60 megahertz NMR spectrometer, the scan width of this 10 p p m would be zero to 600 hertz. In other words, one has to scan 600 hertz of scan width to cover the region of zero to 10 p p m. On the other hand, if we come to 400 megahertz NMR spectrometer, in order to cover the same scan width, scan width, in other words, the 10 p p m scan width, one has to scan about 4000 hertz as a scan width in the NMR spectrum. So, what is a 2 p p m value in a 60 megahertz spectrometer? This would be simply 120 hertz, whereas the 2 p p m in a 400 megahertz NMR spectrometer would be, NMR spectrum would be about 800 hertz. So, depending upon the frequency of the NMR spectrometer the scan width also keeps increasing for the zero to 10 p p m of the scan width of the spectrum. So, this essentially explains the higher resolution capability of the higher, high resolution capability of high frequency NMR instruments.

Suppose, if we consider a difference between 2 p p m and 2.1 p p m signal; let us say, there is a signal at 2 p p m and another signal is 2.1 p p m. The difference in the 60 megahertz NMR spectrum is, spectrometer is going to be smaller compared to the difference in the 400 megahertz NMR spectrometer. In the 60 megahertz NMR spectrometer, it is going to be roughly 6 hertz or so, the difference; whereas in a 600 megahertz NMR spectrometer, it is going to be something like 40 hertz or so. So, such a large difference is there in the frequency, difference is there in this 0.1 p p m, difference in the 2 signals, there will be a large difference in the hertz value of the corresponding signal. Hence, the high spectrometer frequency corresponds to a high resolution spectrometer.

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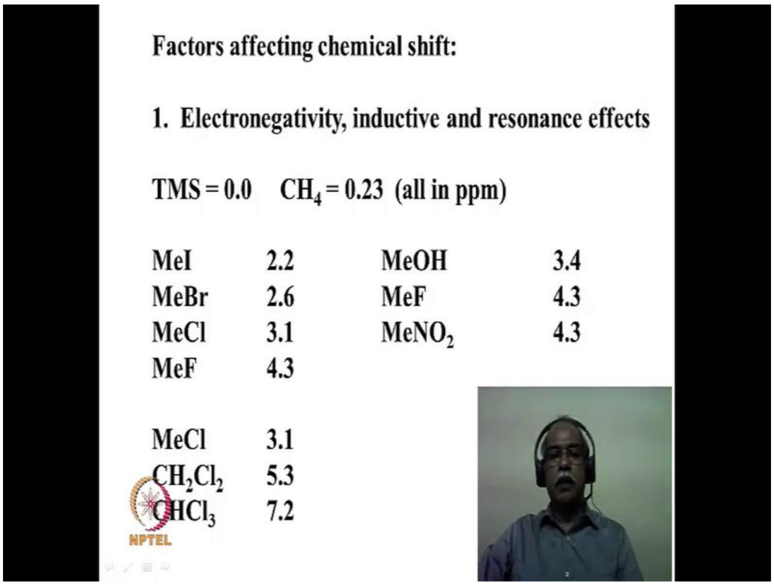

Factors affecting chemical shift:

1. Electronegativity, inductive and resonance effects

TMS = 0.0 CH_4 = 0.23 (all in ppm)

MeI	2.2	MeOH	3.4
MeBr	2.6	MeF	4.3
MeCl	3.1	$MeNO_2$	4.3
MeF	4.3		
MeCl	3.1		
CH_2Cl_2	5.3		
$CHCl_3$	7.2		

Let us now look into the factors that affect the chemical shift value. Electronegativity, inductive and resonance effects are essentially responsible for the changes in the electron density that one observes in the compounds, in the substances, and hence, these are the parameters which essentially also affect the chemical shift value of a given hydrogen. Tetramethylsilane is taken as zero p p m, as a reference standard. With respect to Tetramethylsilane, all the other samples, or all the other compounds chemical shift values are given. The chemical shift value of only the methyl hydrogens are given in this particular table. Now, with respect to the Tetramethylsilane, methane is about 0.23 p p m.

Now, we can see here, the variation is the halogen; you have the most electronegative fluorine here, and the least electronegative iodine and methyl iodide. As we increase the electronegativity of the atom that is attached to carbon, the chemical shift value of the hydrogen which are attached to that particular carbon keeps on increasing. In other words, the electron density around the hydrogens of the methyl fluoride is much lower than the electron density around the hydrogens of the methyl iodide, because iodine has a lesser electronegativity compared to fluorine. Now, the effect is also cumulative; as you go with increasing number of halogen atoms, as in this particular case, from methyl chloride to methylene chloride to chloroform, the chemical shift keep increasing from 3 point 1 to 5.32 to 7.2 p p m.

If you compare different functional group, for example, methyl alcohol, methyl fluoride and nitromethane, there also, there is an effect of the corresponding electronegativity of this particular atom that is attached to the carbon that plays the role. Methanol comes at 3.4 p p m; methyl fluoride and nitromethane, both of them come around 4.3 p p m. From this we can conclude that, the electronegativity, or the electron withdrawing effect, inductive effect of the fluorine is nearly same as the electron withdrawing inductive effect of the nitro group, because they come at the similar chemical shift values with respect to each other.

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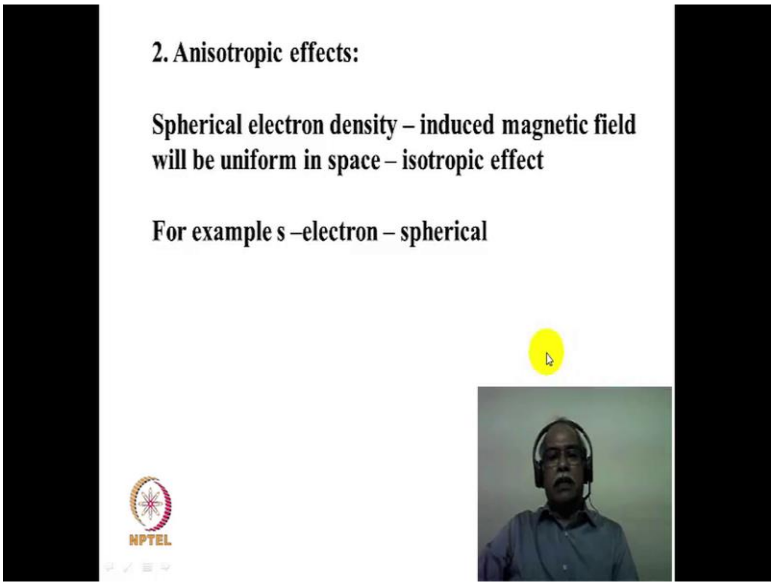

2. Anisotropic effects:

Spherical electron density – induced magnetic field will be uniform in space – isotropic effect

For example s –electron – spherical

Now, the second aspect which is responsible, or the second parameter which is responsible, is the anisotropic effect. Anisotropy is the non-uniform nature of any property. The second parameter is the anisotropic effect, which is responsible for affecting the chemical shift value.

Suppose, you consider spherical electron density around an atom. The induced magnetic field will be uniform in space; in other words, the induced magnetic field has a property will be isotropic with respect to the spherical electron density around the atom, but we seldom have spherical electron density, except in the case of s electron.

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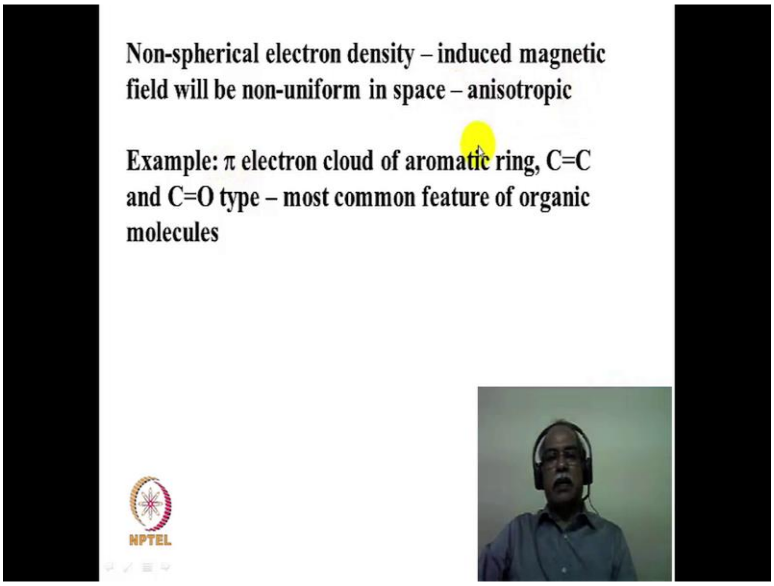

Non-spherical electron density – induced magnetic field will be non-uniform in space – anisotropic

Example: π electron cloud of aromatic ring, C=C and C=O type – most common feature of organic molecules

The hydrogens that are attached to various carbons, for example, are unlikely to have spherical electron density. So, therefore, the induced magnetic field will be non-uniform in space. Hence, the anisotropic effect plays a major role in defining the chemical shift value of hydrogen. Typically, for example, pi electron cloud of the aromatic, or carbon-carbon bond, or carbonyl, carbonyl bond, for example, they do not have a spherical electron density. They have very specific shapes and size, and these are the most common features in most organic molecules, and hence, the electron density cloud which is non-spherical in nature in these system, will lead to anisotropic effect, and we will discuss the anisotropic effect in the next 2 slides.

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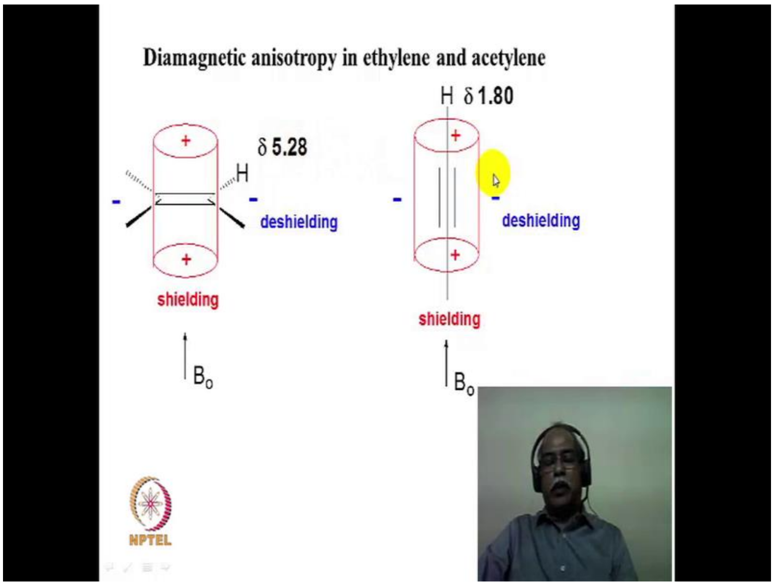

Diamagnetic anisotropy in ethylene and acetylene

Now, let us consider a small experiment of taking a double bond, and, this is the externally applied magnetic field. In other words, the plane of the ethylene molecule in this particular case is perpendicular to the externally applied magnetic field. Under these circumstances, the induced magnetic field because of the pi electron will have anisotropic effect, such that, the cylinder that is shown here, the area under the cylinder here, for example, will be a shielding zone, whereas, the area which is away from the cylinder, which is indicated in the blue here, will be deshielding zone. In other words, the hydrogens which are occupied in this area, the red area, will be highly shielded, whereas, the hydrogens which are away from the red shielded area will be highly deshielded. So, the ethylene hydrogen comes typically around 5 to 6 p p m, around 5 point 28 p p m is the actual chemical shift value of the hydrogens in ethylene molecule.

On the other hand, if you consider acetylene molecule, it has a spherical electron density to start with, unlike the, kind of banana bend shaped pi electron density of the ethylene. The cylindrical electron density of acetylene itself causes an anisotropic effect in such a way that, if this is the applied magnetic field, which is aligning with the axis of the acetylene molecule, then, the red shield, the red zone that is shown here, is the shielding zone and the area around it, or away from it, is going to be the deshielding zone. The acetylene hydrogen itself falls along the axis, or along the direction of the B zero. Therefore, this will be highly shielded in comparison to, for example, the olefinic hydrogen which is coming around 5.28 p p m, whereas the acetylene hydrogen comes around 1.8 p p m or so.

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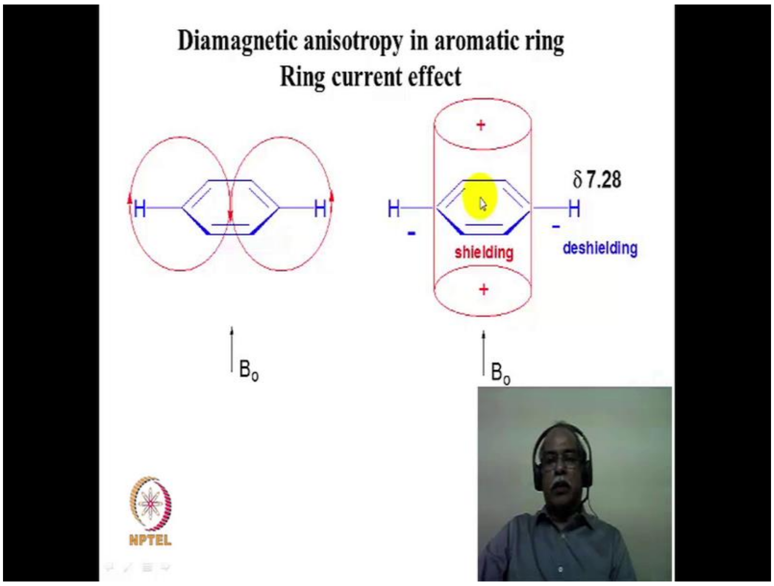

Diamagnetic anisotropy in aromatic ring

Ring current effect

In the case of aromaticity, aromatic rings, for example, we have pi electron cloud in the form of a doughnut shaped form, doughnut shaped pi electron density is present in the aromatic system. When the aromatic plane is perpendicular to the externally applied magnetic field, which is B zero here, the aromatic electrons undergo a circular motion which is called the ring current effect. As a result of the ring current effect, we have a induced magnetic field, and this induced magnetic field is what is being represented by the lines of forces which are shown by the red circles here. So, you consider a doughnut shaped lines of forces around the periphery of the aromatic ring in such a manner that, in the center of the aromatic ring, the lines of forces of the induced magnetic field is opposing the external magnetic field.

So, this is going to be highly shielding in nature, whereas, in the periphery, where the hydrogens of the aromatic nucleus lies, the lines of forces of the induced magnetic field is going to be aligning with the external magnetic field. So, this is going to be shielding, deshielding in nature, in terms of the nature of the lines of forces for this particular hydrogen. So, this is represented by means of a cylinder, representing the shielding zone in the red and the deshielding zone in the blue. So, the hydrogens of an aromatic ring always lies in the deshielding zone of the anisotropic effect, of the ring current effect of the aromatic ring. It is for this reason benzene comes around 7.28 p p m, which is the highly deshielded hydrogen in the NMR spectrum, from zero to 10 p p m, it comes around 7.28 p p m or so. Now, if there is a hydrogen which is placed right above the benzene ring, then, that should be highly shielded in nature, and this hypothesis has been in fact tested. We will see some examples later.

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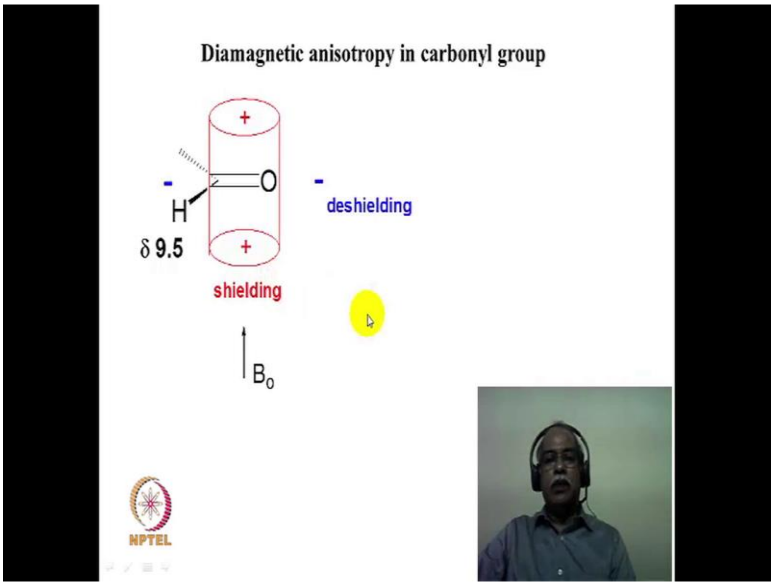

Diamagnetic anisotropy in carbonyl group

Now, in the case of carbonyl compounds, the carbonyl pi electron also shows anisotropic effect. Anisotropic effect is such that, you have a shielding zone which is shown by this cone, sorry, shown by the cylinder, as a red cylinder. So, anything that falls in this particular region is going to be shielded; whereas, the aldehyde hydrogen falls in the deshielding zone, and that is one of the reasons why the aldehyde hydrogen is coming at a very high delta value. There are 2 effects; one is the electron withdrawing effect of the carbonyl functional group, which decreases the electron density around the carbon hydrogen bond; and secondly, the anisotropic effect also adds to this particular effect leading to a highly deshielded hydrogen of the aldehydic systems.

Now, in all these cases, one must remember that, we are talking about a very specific geometry. We are talking about the plane of the benzene to be perpendicular to the B zero in order to observe this anisotropy effect. But, in solution, the benzene ring is going to be randomly oriented with respect to the applied magnetic field direction. So, what we are observing in solution is only an average effect of the anisotropic effect. The maximum anisotropic effect will be felt in this particular geometry. Any other geometry where the benzene is at an angle, or perpendicular to the externally applied magnetic field for example, will be averaged out in a solution phase spectrum.

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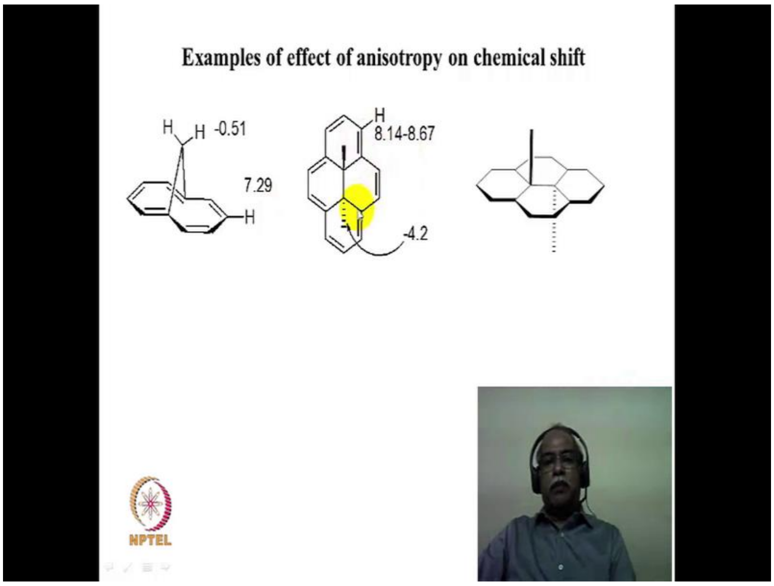

Examples of effect of anisotropy on chemical shift

So, what we are observing in a solution phase spectrum is only an average anisotropic effect of the various possible orientations of a molecule with respect to the externally applied magnetic field. Now, remember, we said that, if the hydrogens are just above the plane of the aromatic ring, that should be highly shielded. These are 2 beautiful examples to illustrate the point, that you have a ring current effect, and the ring current effect produces an anisotropy in aromatic system, and this anisotropic effect is what is responsible for the shielding of the hydrogens which are placed above the aromatic ring, and the deshielding of the hydrogens which are on the periphery of the aromatic ring.

Now, this is 10-annulene; this is a bridged 10-annulene; it is a methano-10-annulene. The compound was specifically synthesized to test the concept of aromaticity. This compound is aromatic in nature because of the planarity of this particular ring, and the 10 electron system which corresponds to the Huckel’s 4n plus 2 rule. Huckel’s 4n plus 2rule is obeyed. So, this is an aromatic ring, and this methylene hydrogens just fall about the plane of the aromatic ring; and therefore, they are appearing in the highly shielding zone of the ring current effect, anisotopic effect. So, the 2 hydrogens which are indicated here, on the bridge, actually comes at a negative delta value, less than Tetramethylsilane’s signal. It comes around minus 0.51 p p m or so; whereas the peripheral hydrogens, which are the aromatic hydrogen, typically come in the aromatic region, which is around 7.29 p p m.

Even more dramatic example is this particular molecule; this is dimethyl dihydro pyrene. If you look at the peripheral number of electrons that are present in this particular system, this is a 14 electron system, corresponding to the 4n plus 2Huckel system. This molecule is planar; you can visualize the molecule in this way. This is a planer molecule, and the 2 methyl group, 1 methyl group is above the plane; the other methyl group is below the plane, such that, the hydrogens of the methyl group, both the methyl groups are actually lying above and below the plane of the aromatic ring. As a result of the anisotropic effect, which is a highly shielding zone above and below the plane of the aromatic ring, these hydrogens appear at minus 4.2 delta p p m. And, this is the, one of the lowest values that is reported for an aromatic system. And, if you look at the peripheral hydrogen, they appear in the normal region of the aromaticity, around 8 p p m or so, is the chemical shift value of the various hydrogen in this one.

As you increase the number of pi electrons, the ring current effect also increases; as a result of that, anisotropic effect also increases; that is the reason, compared to benzene, which comes around 7.28 p p m, this is a 14-annulene system which comes around 8.4 p p m or so.

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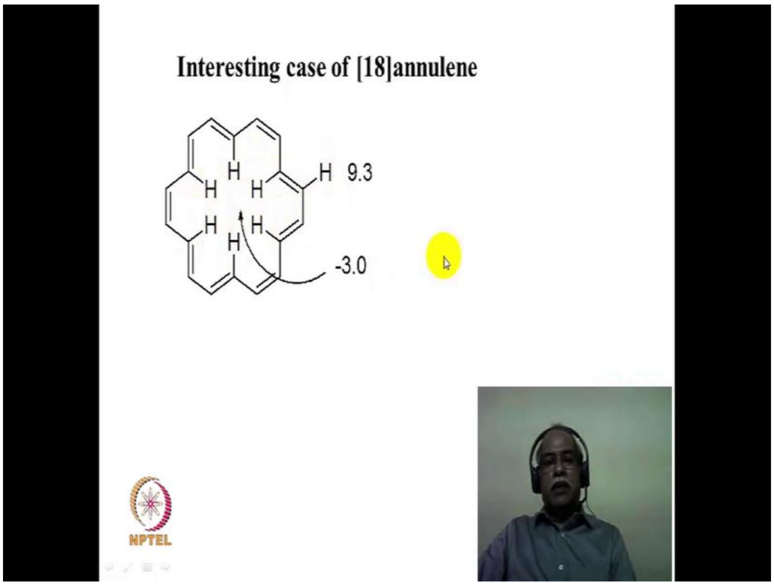

Interesting case of [18]annulene

This is a very interesting example of 18-annulene. There are 6 hydrogens which are in the interior of the aromatic core, and there are 12 hydrogens on the exterior of the aromatic core, for example. This is an aromatic system because this is a 18-annulene system. It is a 4n plus 2 system. And, in this particular molecule, the peripheral hydrogens come at plus 9.3 p p m delta, whereas the core hydrogens, which are highly shielded, comes at minus 3.0 p p m delta value. So, this is a beautiful illustration of the ring current effect, and the associated anisotropic effect, and the effect of the anisotropic effect on the various types of hydrogens in an aromatic system.

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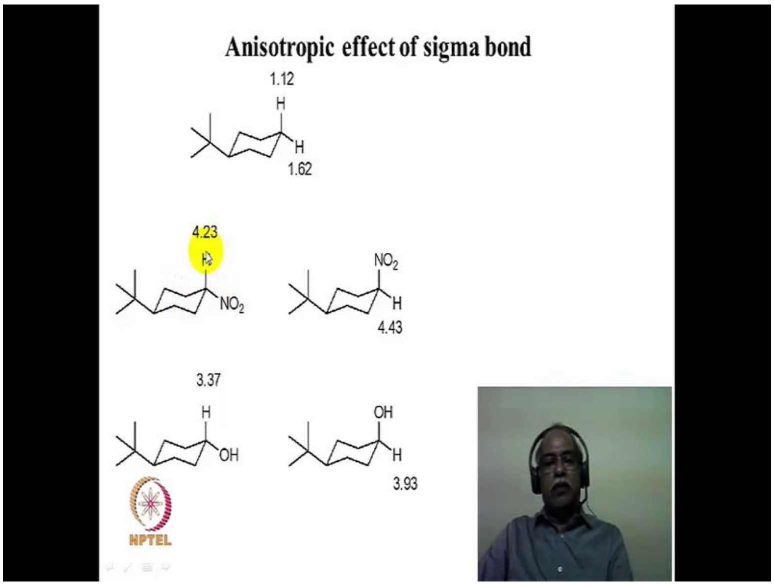

Anisotropic effect of sigma bond

Now, in saturated compounds also, you have a sigma bond anisotropic effect. Let us take the example, the familiar examples of cyclohexane, for example. Cyclohexane has the chair type of a conformation. So, if you are considering the axial and the equatorial hydrogens of the cyclohexane, this particular bond which is away from the hydrogens which are indicated, in other words, if you consider this to be alpha, this is beta-delta bond is what we are refereeing to. This beta-delta bond has an anisotropic effect that causes deshielding of the equatorial hydrogen in comparison to the axial hydrogen. So, the axial hydrogen is more shielded compared with the equatorial hydrogen. Therefore, the axial hydrogen comes at a lower delta value always, compared to the equatorial hydrogen. In the case of the 4-tert-Butylcyclohexane itself, if you consider the axial hydrogen, this comes around 1.12 p p m, whereas, the equatorial hydrogen comes around 1.62 p p m.

Now, the case of 4-tertiary Butylcyclohexane is taken because, there is no chair to chair inter-conversion in this system. So, one can easily define the axial and the equatorial hydrogen of this system, because there is no flipping of the ring from one chair from to another chair form; because, you have attached an anchoring group, which is a bulky group, namely the tertiary butyl group. Now, let us consider the nitro derivative of the 4-tertiary Butylcyclohexane. This is the equatorial nitro functional group, substituted; equatorial is substituted nitro cyclohexane. This is axially substituted nitro cyclohexane.

Now, this hydrogen is an axial hydrogen and this is an equatorial hydrogen. These 2 compounds are dia-stereoisomers. This is the trans isomer of the nitro tertiary butyl cyclohexane, whereas, this is a sis isomer of the of the nitro tertiary butyl cyclohexane. Now, you can see here, the axial hydrogen comes at a lower delta value compared to the equatorial hydrogen, which is coming at a higher delta value by about 0.2 p p m or so.

If you take the tertiary butyl cyclohexanol, here also, the axial hydrogen comes around 3.7 p p m, whereas the equatorial comes around 0.2 p p m more than the axial hydrogen, around 3.93 p p m or so. So, this kind of a difference in the axial and the equatorial hydrogen allows one to determine the stereochemistry aspects of this kind of compounds, where you have the axial and equatorial differences and the sigma bond anisotropy that is responsible for the differences in the chemical shift values of the axial and the equatorial hydrogens.

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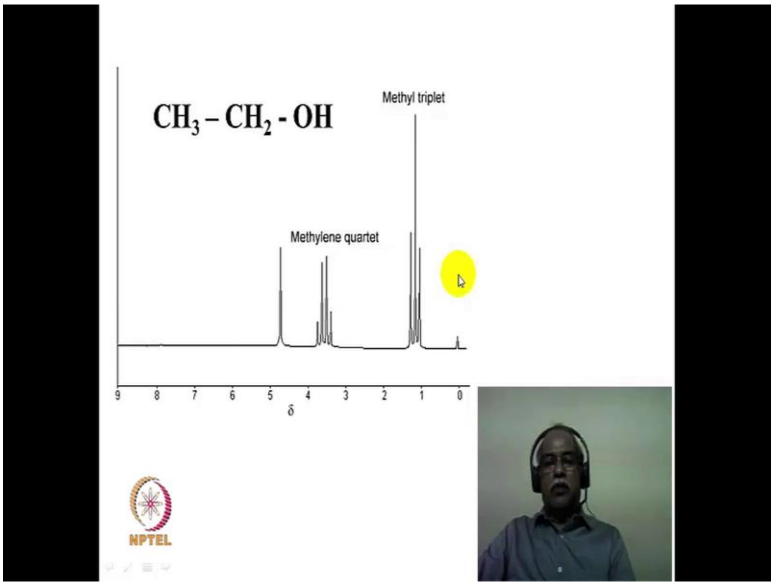

$CH_3 - CH_2 - OH$

Now, let us come back to the spectrum of ethyl alcohol. Ethyl alcohol shows 3 signals, 3 frequencies; that is ok because, we have 3 different types of hydrogen in the molecule. But then, why is that the OH hydrogen comes as singlet, whereas the CH2 hydrogen has 4-line pattern which is known as quartet, and the CH3 hydrogens have 3-line pattern which is known as the triplet? In other words, the spectrum of ethyl alcohol shows multiplicity in the case of the CH2 and the CH3 signals; and what is the reason for this, is what we are going to discuss in the next few minutes.

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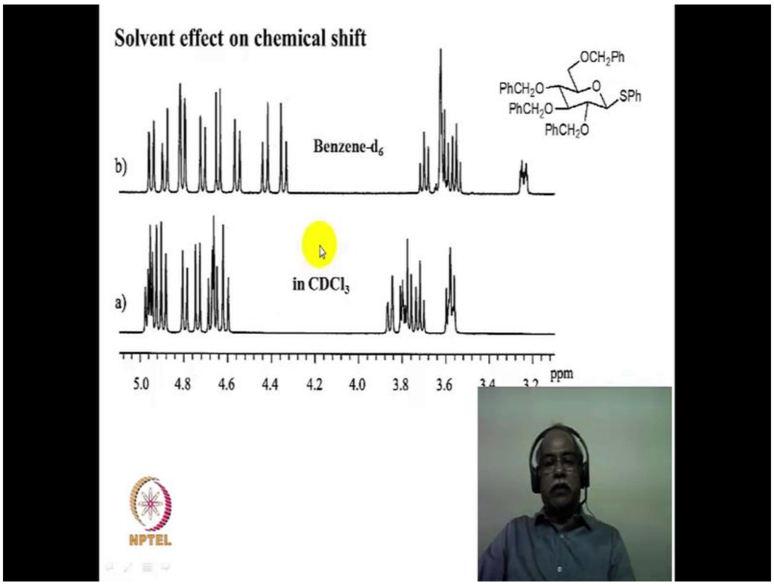

Solvent effect on chemical shift

Before we go into that, let me also say that, the solvent has also a major role to play in terms of the chemical shift values. This is a solvent effect. The spectrum of this particular compound which is a sugar derivative is measured in CDCl 3, in other words, deuterated chloroform, or in deuterated benzene. You can see, visually you can see the difference in the spectral resolution in the benzene d 6 and the CDCl 3 spectrum, for example. So, solvation can also affect the chemical shift values of various hydrogens. So, in addition to the inductive effect, electromeric effect and the anisotropic effect, you can also have solvent effect, which affects the chemical shift values of various hydrogens.

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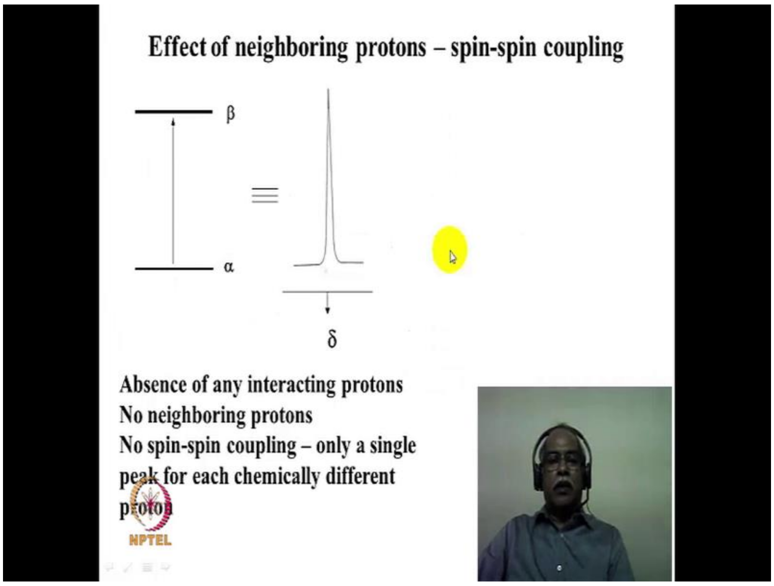

Effect of neighboring protons – spin-spin coupling

Absence of any interacting protons
No neighboring protons
No spin-spin coupling – only a single peak for each chemically different proton

Now, coming back to the multiplicities that we saw in the case of the ethyl alcohol spectrum, let us consider an isolated hydrogen atom. If you consider an isolated hydrogen atom, it can either exist in the alpha state, or in the beta state, or the minus half state, or in the plus half state. The nuclear spin can exist in these 2 states. So, therefore, when radio frequency of an appropriate frequency is applied, when the resonance condition is met, there will be an absorption, and that absorption is shown in the form of a signal in NMR spectrum. So, what you see is, just 1 sharp peek for the hydrogen that is present in the molecule. In the absence of any other interacting protons, there are no neighboring protons. So, there is no coupling of any kind; only a single peak for chemically equivalent hydrogen will be seen.

Suppose, you take benzene. There are 6 hydrogens in benzene, but all the 6 hydrogens are identical in nature in terms of their chemical environment. As a result of that, there will be 1 transition that is taking place. So, all the 6 hydrogens of benzene will come exactly at the same place as a single line. You take the example of methane; again, all the 4 hydrogens of methane are identically arranged in a tetrahedral fashion; that will also lead to only one kind of a chemical shift value. So, methane will also give only 1 signal without any kind of a spin-spin coupling.

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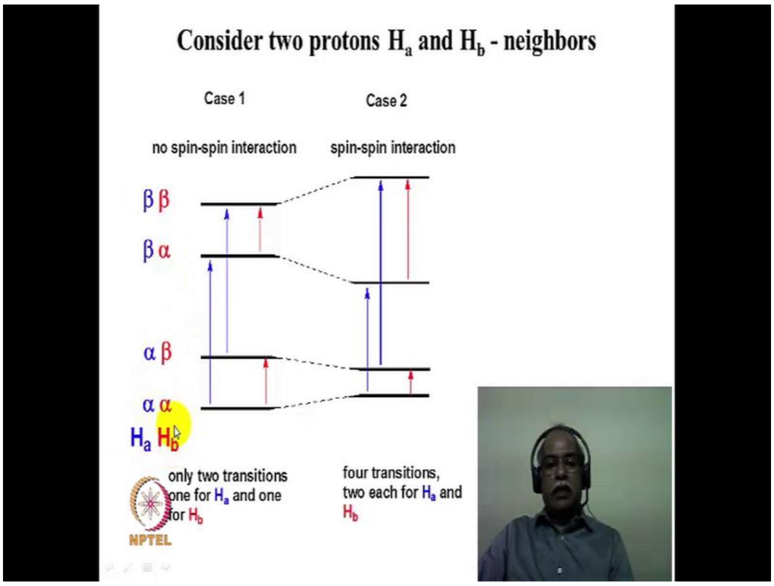

Consider two protons H_a and H_b - neighbors

Case 1

no spin-spin interaction

Case 2

spin-spin interaction

only two transitions one for H_a and one for H_b

four transitions, two each for H_a and H_b

Now, there are 2 cases, case scenarios that are presented here. The first case is, there are 2 spins, but there is no interaction between these 2 spins. What is meant by interaction is, the magnetic field, induced magnetic field of the first hydrogen is not felt by the second one, and vice versa. So, that means, these 2 spins are acting independently. Therefore, there are 2 transitions possible; the blue hydrogen that is shown here, has a transition going from alpha to beta, when the red is in the alpha state, for example; it is also possible that, the blue hydrogen is going from alpha state to beta state, when the red is in the beta state. So, there are 2 possibilities, but these 2 possibilities are isoenergetic in nature. In other words, this will have the same frequency in terms of the transition. So, that will appear as 1 signal. Similarly, for the red hydrogen also, it goes from the alpha to beta state when the blue hydrogen is in the alpha state, or blue hydrogen is in the beta state. These 2 states are also isoenergetic in nature. So, you will just see 1 signal for the H alpha and 1 signal for the H beta.

Suppose, if these two hydrogens are interacting in terms of spin-spin interaction, in other words, the induced magnetic field that is created by one hydrogen is felt by the other hydrogen, then it is possible that, you have differences in the energy between alpha and beta states. For example, the alpha-alpha and the beta-beta states go up in energy; alpha-beta and the beta-alpha states come down in energy, making these 2 blue transitions unequal, and similarly, the 2 red translations also unequal. So, what was originally an equal transition, equal energy transition of the blue, and equal energy transition of the red, which gave rise to only 2 signals, now, there are 4 signals possible, corresponding first transitions of this kind; the second transitions, which is this one; the third transition, which is this one; and, the fourth transition, which is this one. So, there are 4 lines that are possible. In other words, the H a goes from alpha state to beta state, when H b is in the alpha state; similarly, when H a goes from alpha to beta state, when H b is in the beta state. These are the 2 possibilities that you can have for H a. Similarly, for H b also, it can go from the alpha state to beta state, when H a is in the alpha state; when H a is in the beta state also, it can go from the alpha state to beta state, corresponding to 2 transitions.

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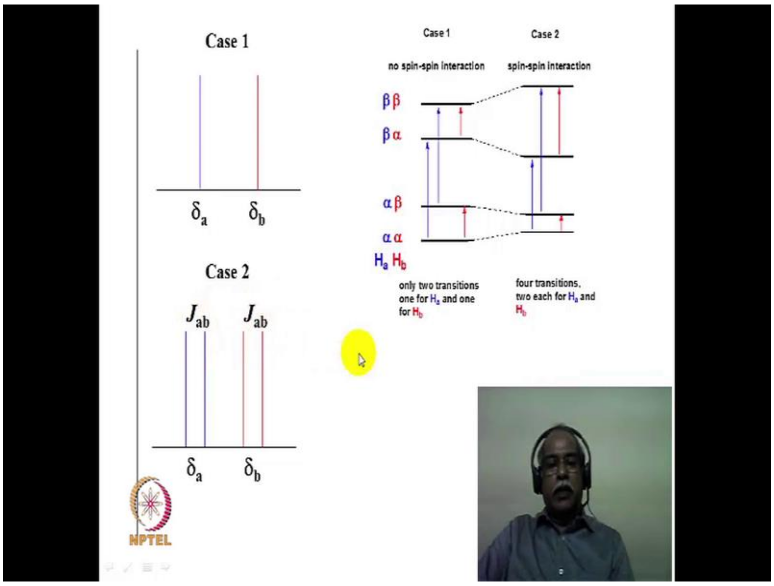

So, a system, 2-spin system which are not interacting with each other, essentially, will act independently, and give respective signals as a single line; when they are spin-spin coupled, or if they are interacting with respect to each other, then, there will be a coupling between this two. They are mutually coupled to each other. a will be split into 2 lines. Similarly, b will also be split into 2 lines. This is because of the fact that, H a influences the magnetic field strength that is perceived by H b and vice versa. And, they are mutually coupled, therefore, the gap between the 2 lines that you see for H a, will be identical to the gap that you see for the 2 lines of the H b. These mid portions of the 2 blue lines is the chemical shift value of the hydrogen a, and the mid portion, or the mid value of the 2 lines of the H b is corresponding to the chemical shift value of the hydrogen b.

Now, J is the coupling constant which is measured by taking the difference between the 2 blue lines, or the 2 red lines. In fact, it does not matter whether you are measuring it between, difference between the 2 red lines or 2 blue lines, because they are mutually coupled; this gap will be identical to this particular gap. And, this is what is known as the coupling constant, J, coupling constant.

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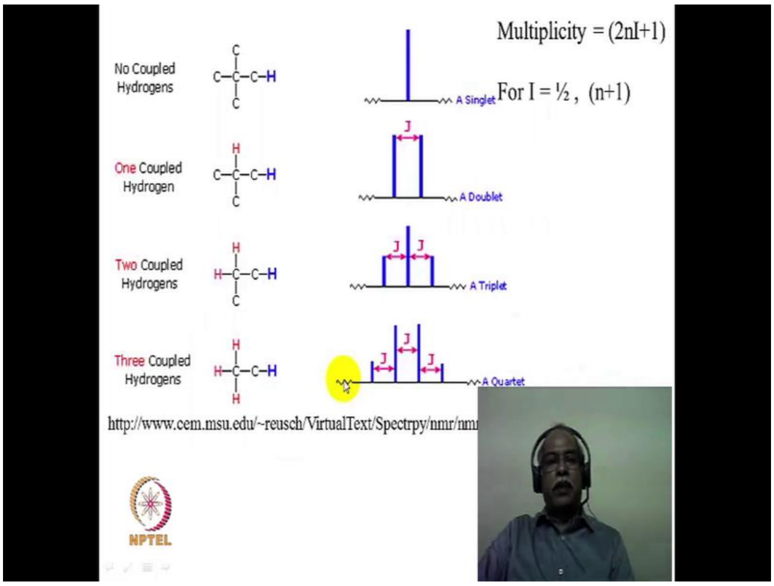

Multiplicity = (2nI+1)

For I = ½ , (n+1)

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nm

Now, having said what is responsible for the multiplicities that one observes in the case of 2-spin system, let us generalize it for many spin systems now. Initially, we are talking about, in all these cases, we are talking about the resonance of the hydrogen which is indicated by the blue color. Suppose, if there are no another coupling partners, it just appears as a singlet. If it has an adjacent coupling partner, then, it would give a doublet, because hydrogen, which is in the red, is going to influence the magnetic field, induced magnetic field of this particular hydrogen is going to affect the, affect the blue hydrogen, in terms of the magnetic field that is felt by the blue hydrogen. So, it will appear as a doublet. When you have 2 equivalent hydrogens in the adjacent position, this will be splitting into 2, and then, further splitting it into 2; 2 times 2 would be 4; but then, the coupling constants are same. So, as a result, you see a multiplicity, which is a triplet multiplicity. If you have 3 hydrogens, equivalent hydrogens, then, the multiplicity will be 4. The multiplicity can be easily calculated using the formula 2 n I plus 1, where n is the number of equivalent hydrogens which are in the adjacent position, or the coupling partner for example, which are identical in nature in terms of their chemical environment, and I is the spin value of that particular nuclei. If you have a spin half nucleus, then it reduces down to n plus 1 value, in terms of the multiplicity. So, if you have 3 adjacent hydrogen, you will have 4; if we have 2 adjacent hydrogen, you will have 3.

This is called a quartet and this is called a triplet. This is called a doublet and this is called a singlet. So, we can now realize that, the multiplicity actually tells you a lot about the structural fragment that is being present, and that is the reason the spin-spin coupling is a invaluable tool, if you can identify it properly and correlate it to a structural feature of the molecule, and that solves the problem of the structure solving problem of this particular system.

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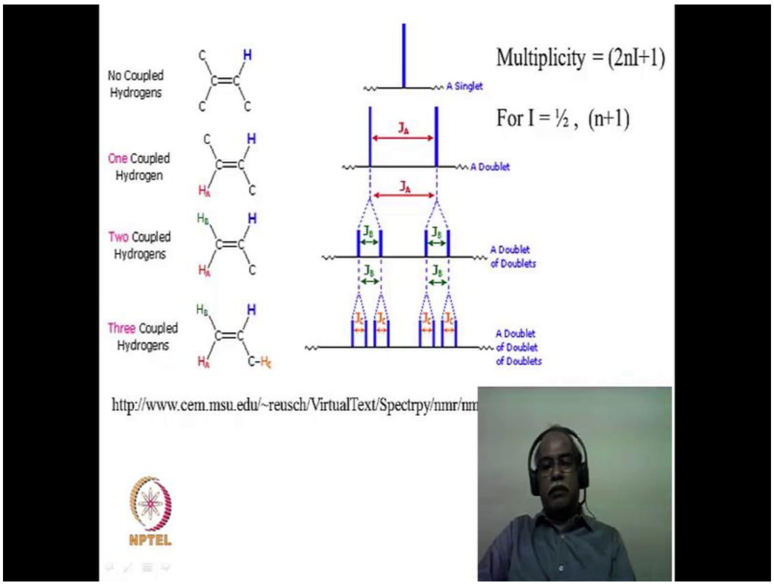

Multiplicity = (2nI+1)

For I = ½ , (n+1)

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nm

Let us take the olefinic system. In the olefinic system, the first example, there is only 1 hydrogen. So, you see only 1 transition. Suppose, you have a trans hydrogen associated with this molecule; in other words, this is a trans isomer of a olefinic system. This trans hydrogen will couple with the H a, and the H a will in turn couple with the H b, which is the blue hydrogen. So, the blue will have a transition. There are 2 possible transitions the blue can have, because of spin-spin coupling it will appear as a doublet. Suppose, if there are two different types of hydrogens, one is a cis hydrogen and another one is a trans hydrogen. The trans hydrogen can couple with this to make it into a doublet, and the cis hydrogen, which is geometrically different from the trans hydrogen, will also couple with this, but the coupling constant will be different. We will look into the parameter that affects coupling constant in a minute. For the time being, assume that, this coupling is different from this coupling.

So, originally, the line is split into a two, and it is further split into… Initially, you have a singlet with no coupling; with only 1 coupling partner, you have a doublet; and, with 2 coupling partner, you have a doublet of a doublet. Suppose, if we have 3 coupling partners, that is 1 cis coupler, and 1 trans coupling partner and 1 geminal coupling, sorry, vicinal coupling partner which is in this position, for example. So, the trans coupling can be making, the trans coupling can make the hydrogen into a doublet; the cis coupling can make it into a doublet of a doublet; and this vicinal coupling can make it into a doublet of a doublet of a doublet. A doublet of a doublet of a doublet should have 8 lines. So, you can see here the 8 lines, which is the doublet of a doublet of a doublet.

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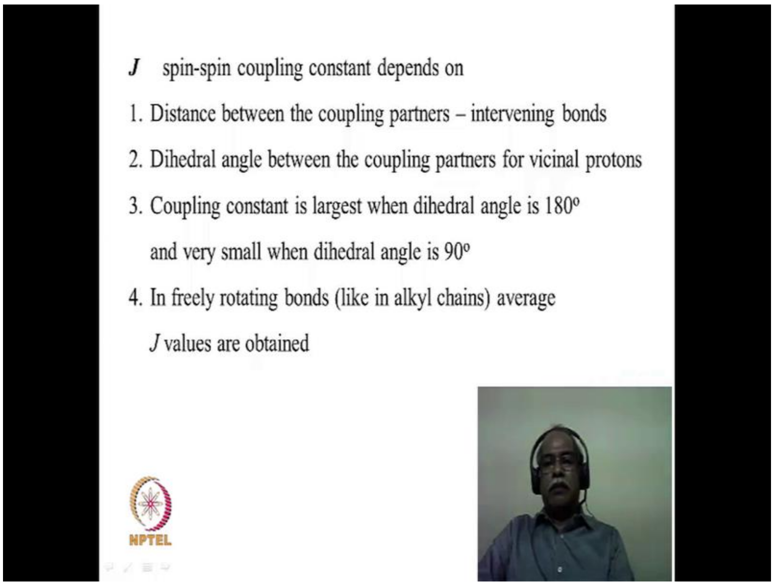

J spin-spin coupling constant depends on

1. Distance between the coupling partners – intervening bonds
2. Dihedral angle between the coupling partners for vicinal protons
3. Coupling constant is largest when dihedral angle is 180°
   and very small when dihedral angle is 90°
4. In freely rotating bonds (like in alkyl chains) average
   J values are obtained

Now, the parameters on which the J, sorry, the spin-spin coupling depends on are as follows: it depends on the distance between the coupling partners and the intervening number of bonds; the more number of bonds that you have at the intervening between 2 atoms, or the 2 hydrogens, smaller will be the coupling. More importantly, the dihedral angle plays a major role in the coupling partners of vicinal hydrogen. We will see the relationship in a minute. The coupling constant is largest when the dihedral angle is about 180 degree, and it is very small when the dihedral angle is about 90 degree. In freely rotating bonds, like in the alkyl chain, average J values are obtained; in other words, this is an illustration that we will give at later stage.

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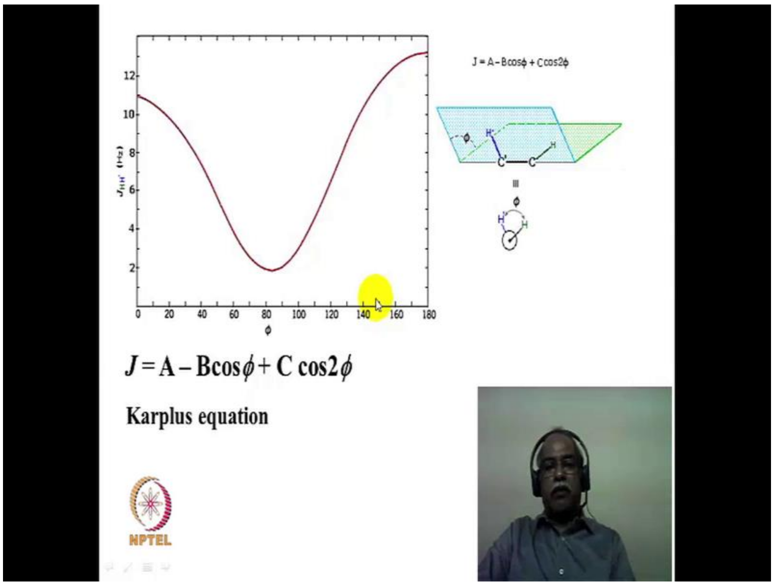

$J = A - B\cos\phi + C\cos 2\phi$

Karplus equation

Now, this is a diagrammatic representation of Karplus equation which is relating the J value to dihedral angle in a cos type of a relationship. What is dihedral angle? Dihedral angle is the angle which is obtained by the 2 hydrogens which are in adjacent hydrogen atoms; in other words, if you look at this picture, this is like a open book kind of a confirmation that you have. The dihedral angle is this particular angle, denoted by phi here; and between this hydrogen and this hydrogen, that is a dihedral angle. In a Newman projection, this is represented, the dihedral angle is represented like this.

Now, as the carbon-carbon bond rotates, the dihedral angle can vary, and depending upon the average dihedral angle of that particular molecule, it can have value anywhere from zero, which is in eclipsed conformation, to 180, which is an anti-conformation of the 2 hydrogen. In the anti-conformation, you have the maximum J value, which is roughly about 14 hertz or so, whereas, when it is at 90 degrees, for example, it has the minimum coupling constant, which is about 1 or 2 hertz or so; when it is zero dihedral angle, this has a value of about 10 to 12 hertz or so, in terms of the J value that we are talking about. This is applicable to all vicinal coupling, freely rotating vicinal coupling, as well as not really rotating vicinal coupling.

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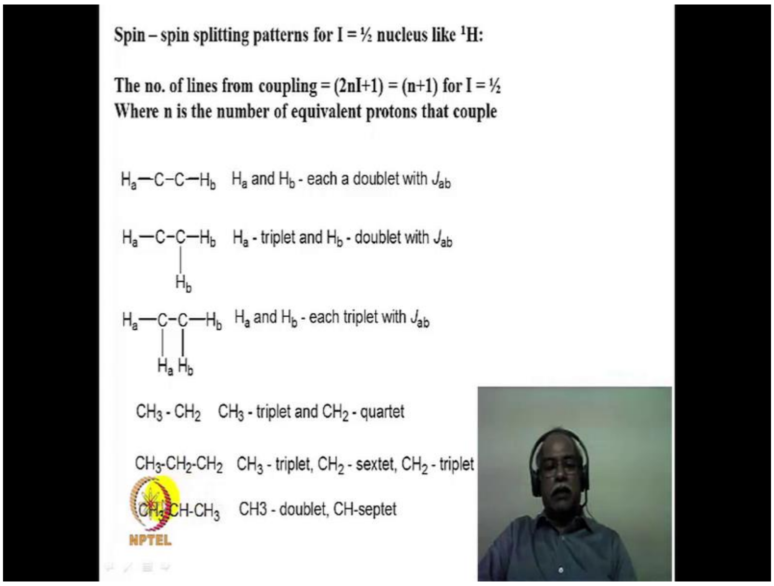

Spin – spin splitting patterns for I = ½ nucleus like ^1H:

The no. of lines from coupling = (2nI+1) = (n+1) for I = ½
Where n is the number of equivalent protons that couple

$H_a-C-C-H_b$ H_a and H_b - each a doublet with J_{ab}

$H_a-C-\underset{\displaystyle H_b}{\underset{|}{C}}-H_b$ H_a - triplet and H_b - doublet with J_{ab}

$H_a-\underset{\displaystyle H_a}{\underset{|}{C}}-\underset{\displaystyle H_b}{\underset{|}{C}}-H_b$ H_a and H_b - each triplet with J_{ab}

CH_3-CH_2 CH_3 - triplet and CH_2 - quartet

CH_3-CH_2-CH_2 CH_3 - triplet, CH_2 - sextet, CH_2 - triplet

CH_3-CH-CH_3 CH3 - doublet, CH-septet

Now, let us summarize what we said in the previous 2 slides. The spin-spin splitting pattern can be for a spin half nucleus as follows: the number of lines that one expects is 2 n I plus 1; otherwise, it is n plus 1 for a spin of half, because I is equal to half, where n is the number of equivalent protons that couple. This is extremely important, the protons are to be equivalent; then only the coupling constants will be same, so that, you can interpret it with this n I plus rule, n plus 1 rule. So, when you have an adjacent hydrogen, each of the H a and H b is going to be doublet with 1 single coupling constant of J a b. When you have 2 coupling partners, which are chemically equivalent partners, then H a will be a triplet, because n plus 1 will be a triplet for this hydrogen; and, this will be a doublet, because there is an adjacent hydrogen which leads to a doublet.

Suppose, if you have a CH 2, CH 2, each would be a triplet; H a will couple with H b and in turn, H b will also couple with H a; each of them will appear as a triplet. So, if you have an ethyl group, it will be, CH 3 will be a triplet, and CH 2 will be a quartet. So, now, you can understand why ethyl alcohol spectrum showed 1 triplet and 1 quartet, because there is a CH 2, CH 3 group there.

In other words, looking at the spectrum, if you see a triplet and the quartet which are mutually coupled in terms of being a same J value, one can come to the conclusion that, there is an ethyl group present in the system. Similarly, if you have a doublet and a septet, septet is a 7 line pattern, you come to the conclusion that, there is a structural element which corresponds to an isopropyl group; only isopropyl group will give you a doublet and a septet; doublet for this methyl group, because it is split by the CH, and septet is for this hydrogen, because it is split by 6 equivalent hydrogens of the methyl group in the system.

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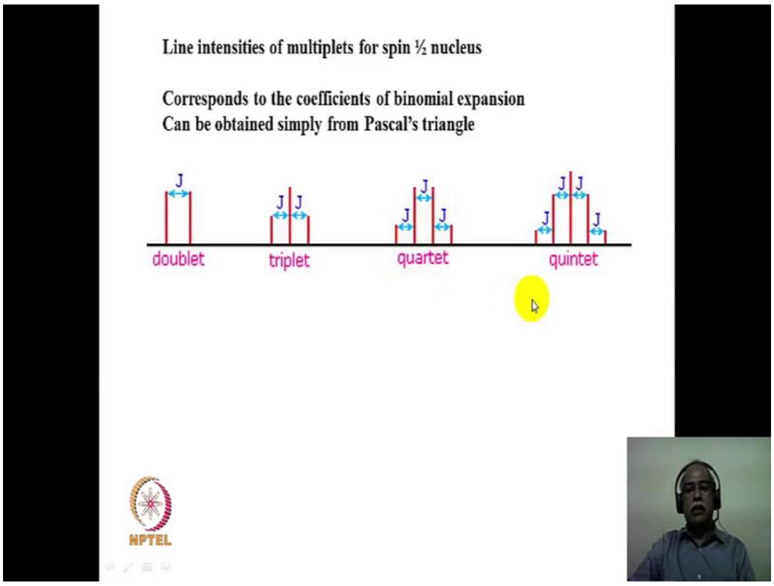

Line intensities of multiplets for spin ½ nucleus

Corresponds to the coefficients of binomial expansion
Can be obtained simply from Pascal's triangle

In the case of spin half nucleus, the line intensities of multiplets can be easily calculated, or predicted from Pascal triangle. The line intensities are corresponding to the coefficients of the binomial expansion. For example, if it is a doublet, it will be a 1 is to 1 intensity ratio; if it is a triplet, it will be a 1 is to 2 is to 1 intensity ratio; if it is a quartet, it will be the 1 is to 3 is to 3 is to 1 intensity ratio and so on.

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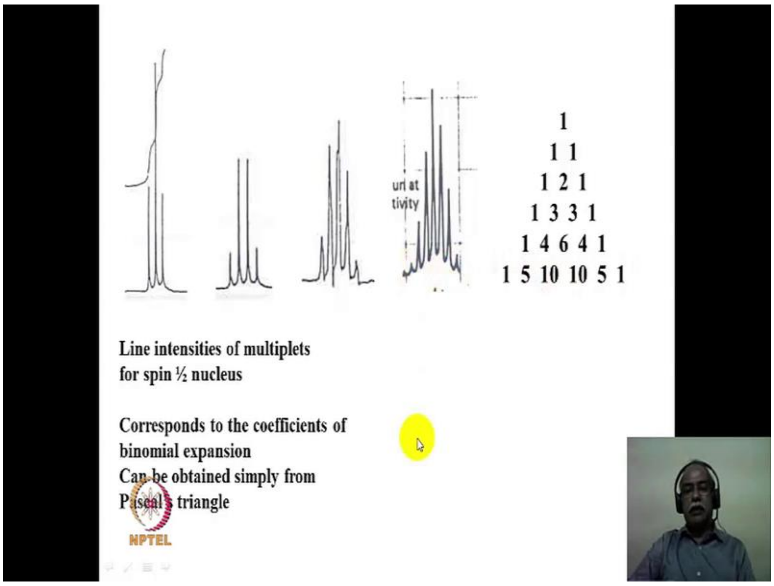

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1

Line intensities of multiplets
for spin ½ nucleus

Corresponds to the coefficients of
binomial expansion
Can be obtained simply from
Pascal's triangle

These are the actual multiplets seen in the actual spectrum; for example, this is a triplet, quartet, quintet, and a septet are the multiplets that are shown here. And, this is the Pascal triangle which can be easily constructed by adding 2 numbers and bringing out the central number by adding the adjacent numbers, for example. And, you can see here, when you come to large multiplicities, the end lines are much less intense in comparison to the central line. So, it is possible to easily miss these multiplets that are seen in the septet, or heptet kind of a multiplicity. So, one needs to be careful in expanding, or zooming the spectrum in the y axis, so that the intensities can be very clearly seen, because of the fact that, the central intensity relative to the end intensities are much higher. So, you may miss out the end lines all the way in the spectrum.

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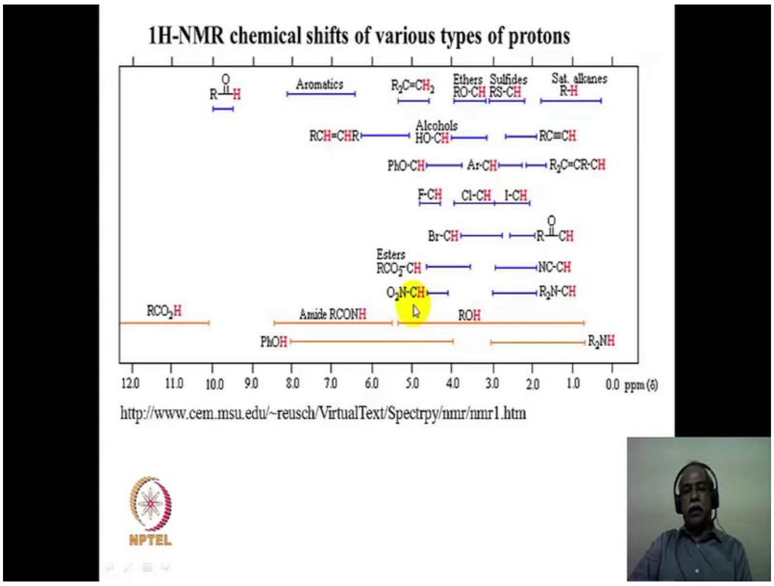

1H-NMR chemical shifts of various types of protons

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm

This is a correlation chart of chemical shift of various protons in the aromatic molecule. Typically, the proton NMR spectrum is scanned between zero to 12 p p m or so. And, the most acidic hydrogen, which are the carboxylic acid hydrogens, or hydrogen bonded enolic hydrogens, they come in the region between 10.5 to about 12 p p m or so. The aldehyde hydrogen typically come between 9 p p m to 10 to 10.5 p p m; sometime even all the way up to 11 p p m it can come. The aromatic hydrogens typically come in the region between 6.5 to about 8.5 p p m. The ones that are electron rich in nature, that is, end out with electron donating substituents, will have a shielding effect.

So, as a result of that, it will come in the region of 6.5 to 7.5; whereas those aromatics, which are electron deficient, or endowed with electron withdrawing functional group, like the nitro group, they will come, appear in the region between 7.5 to 8.5 p p m. So, one can tell from the NMR chemical shift value, whether the aromatic system is electronically endowed system, or electronically depleted system, in terms of the electron withdrawing substituents, or the electron donating substituent being present, because it is reflected in the chemical shift value in this narrow region. Olefinic hydrogen typically come in the region between 5 p p m to 7 p p m. It can come all the way up to 7.5 p p m also, depending upon the electron withdrawing substituent that is attached to it.

Mono substituted derivatives, as we have seen in the earlier cases, depends on the electronegativity of the group that is being attached; that can come anywhere between 2.5 p p m to about 5 p p m or so. Di-substituted derivatives can come between 4 p p m to about 6.5 p p m or so. Hydrogens which are exchangeable hydrogens, like, for example, the acidic hydrogen of phenol, or alcohol, they constantly undergo exchange from 1 molecule to another molecule; they can appear anywhere in the spectral region between zero to 10 p p m, and usually, they are broad signals, which are easily recognizable in the NMR spectrum. The easiest way to identify them, is to do a deuterium exchange. In other words, you take the sample and record the NMR spectrum, and see if there is a broad signal corresponding to a OH of an alcohol, or a phenol, and then, add a drop of D 2 O, and measure the spectrum again. This broad feature should disappear, because of the exchange of the hydrogen with the deuterium, because they are fairly acidic hydrogen. They have the capacity to exchange with the deuterium, and the signal corresponding to that particular OH peak will be disappearing in the NMR spectrum. This is called the Deuterium Exchange Studies.

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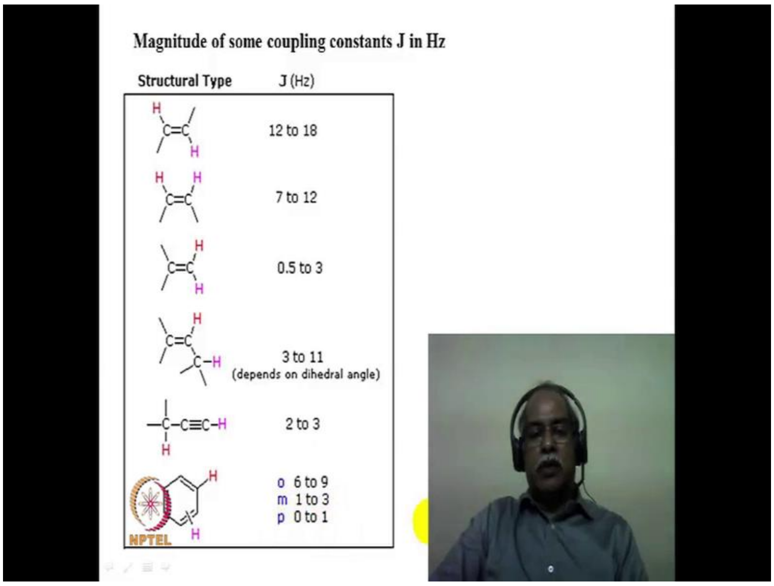

Magnitude of some coupling constants J in Hz

Structural Type	J (Hz)
	12 to 18
	7 to 12
	0.5 to 3
	3 to 11 (depends on dihedral angle)
	2 to 3
	o 6 to 9 m 1 to 3 p 0 to 1

This is a table correlating the structural feature to the J value, or the coupling constant values. The coupling constant depends on the number of intervening bond between the 2 hydrogen. If it is more than 4 or 5, the coupling is close to zero; unless, for example, there are some rigid orientation, ideal conditions are met by these 2 hydrogens to couple with each other; otherwise, typically, the vicinal couplings come in the region between 6 to 8 p p m in freely rotating system, or between 5 to 7 p p m in a more substituted, bulky kind of a system like this. The vicinal coupling can be highly dihedral angle dependent, if there is a restricted rotation, or some rigid geometry that is present, and this is essentially governed by the Karplus equation, which was, which we saw earlier, in terms of the equation, as well as the diagram representing the Karplus plot.

Vicinal coupling between aldehyde hydrogen and the adjacent hydrogen is generally very small. Sometime, you do not even see this coupling. And, geminal coupling between two hydrogens, provided they are diastereotopic in nature, they are chemically non–equivalent, as well as magnetically non-equivalent in nature; they can come, fairly large values of coupling constants are reported; between 12 to 15 p p m is the coupling value that one sees for geminal coupling of this kind. Now, in the case of olefinic system, you can have a trans coupling, or you can have a cis coupling; you can have geminal coupling, or you can have vicinal coupling of this type, where the hydrogen is in the adjacent carbon, not part of the olefinic system. Now, the trans coupling is a fairly large coupling.

Typically, it comes around 16 hertz or so. The cis coupling is smaller compared to the trans one; comes around 10 hertz or so. The geminal coupling is of an s p 2 carbon, is really very small; often, one can miss it, for example. It is typically of the order of 0.5 to about 3 hertz or so. This kind of a vicinal coupling is of the order of 3 to 11. It depends on dihedral angle. If it is not a freely rotating system, it will heavily dependent on the dihedral angle. Propargylic coupling of this type is very small; typically, 2 to 3 hertz is what is measured. In the case of aromatic systems, one can have ortho coupling, meta coupling, as well as para coupling. Ortho coupling is the largest coupling, typically, of the order of 7 to 8 hertz is what normally one sees. Meta coupling of the order of 1 to 3 hertz is what is normally seen. One can miss the para coupling completely in the NMR spectrum, because it is a very small coupling, typically of the order of zero to 1. So, often times, you do not see the para coupling at all.

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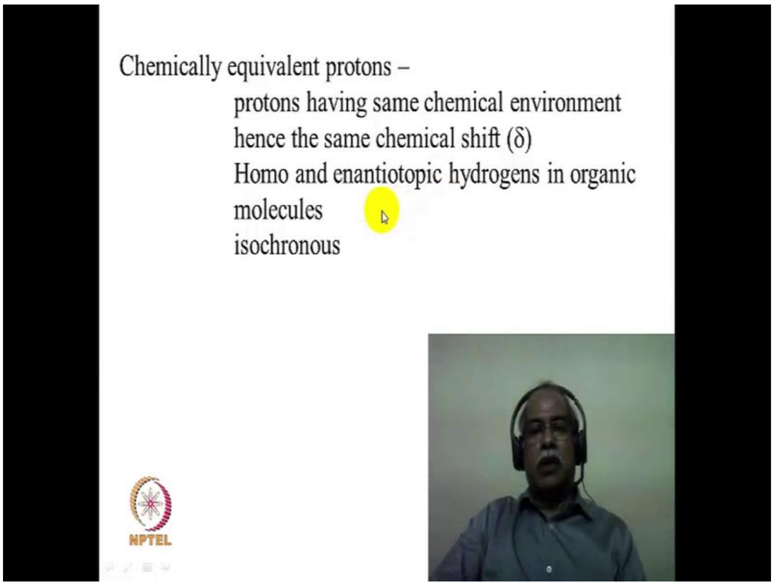

Chemically equivalent protons –

protons having same chemical environment

hence the same chemical shift (δ)

Homo and enantiotopic hydrogens in organic molecules

isochronous

Let us look into some definitions in terms of chemical and magnetic equivalence. When we say 2 protons are chemically equivalent, that means, they have identical chemical environment, which means, they will have identical chemical shifts. They are called isochronous nuclei, because they come in the same frequency; typically, homotopic and enantiotopic hydrogens in organic molecules are chemically …

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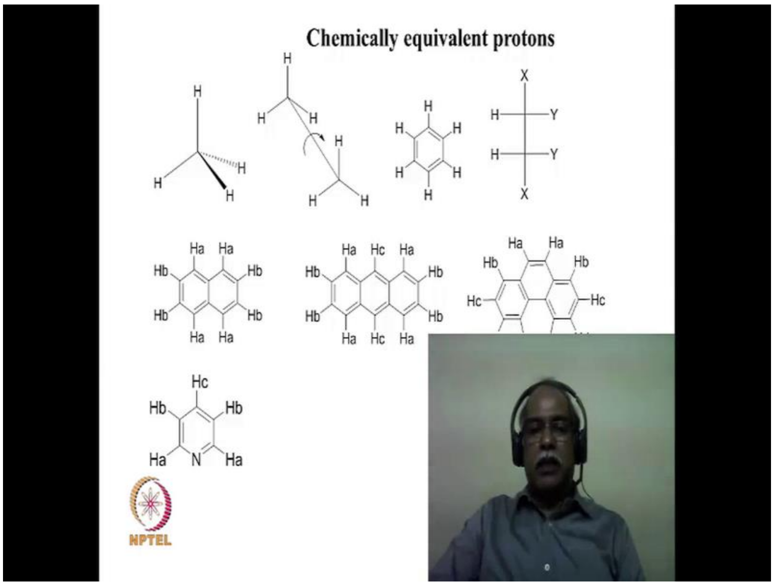

Chemically equivalent protons

Now, if you take the example of methane, all the 4 hydrogens are arranged in a tetrahedral fashion. It is highly symmetrical; T d symmetry is what is present. So, as a result of that, the chemical environment of each of these hydrogens is identical. So, all the 4 hydrogens will appear as a singlet in the NMR spectrum of methane. In the case of ethane, as long as this carbon-carbon bond is freely rotating, which is the case normally, in the case of ethane, all the 6 hydrogens will appear as a singlet only.

Benzene, for example, is a d 6 h symmetrical molecule. You can do either the symmetric criterion, or substitution criterion also. If you do a mono substitution of benzene, you will get only 1 isomer of nitrobenzene, or 1 isomer of chlorobenzene, which means all the 6 hydrogens are equivalent in terms of chemical equivalence. So, in the case of benzene, all the 6 hydrogens come as a single peak in the NMR spectrum of benzene. You take a meso isomer of this kind; this is a meso isomer; it has a plane of symmetry. So, these 2 hydrogens are related by the plane of symmetry; that means, they are enantiotopic in nature, and such enantiotopic hydrogens are also chemically identical in nature, or chemically equivalent in nature.

You take less symmetrical molecule like, for example, in the case of naphthalene, and in the case of, for example, anthracene and so on. In the case of naphthalene, if you take, there are 2 types of hydrogen; the H a hydrogens, which are the alpha hydrogens, and the H b hydrogens, which are the beta hydrogens. So, there are 2 types, sets of chemically equivalent hydrogen, namely H a and H b. Similarly, in the case of anthracene, there are 4 H a type of hydrogens, which are chemically equivalent, 4 H b type of hydrogens, which are chemically equivalent, and the hydrogen in the 9 and 10 positions are chemically equivalent, and they are chemically distinct from H a and H b very clearly.

Phenanthrene, if you take, it has only one plane of symmetry. So, on either side of the plane of symmetry, the hydrogens that appear are chemically equivalent. So, there are 5 sets of chemically equivalent hydrogens in the case of phenanthrene. You take either a mono-substituted aromatic derivative, or a pyridine derivative, it does not matter which kind of examples you take, the ortho hydrogens, or the 2, 6 hydrogens are chemically identical; the 3, 5 hydrogens are chemically equivalent, and the fourth hydrogen is chemically distinct from the 3, 5 and the 2, 6 hydrogen. So, H a, H b, H c are the symbols that are given for the chemically distinct hydrogens in this case. So, in order to define a chemically nonequivalent hydrogen, you give different alphabets as subscript; in order to define chemically equivalent hydrogen, you give the same alphabet as the subscript, and this is called purple notation.

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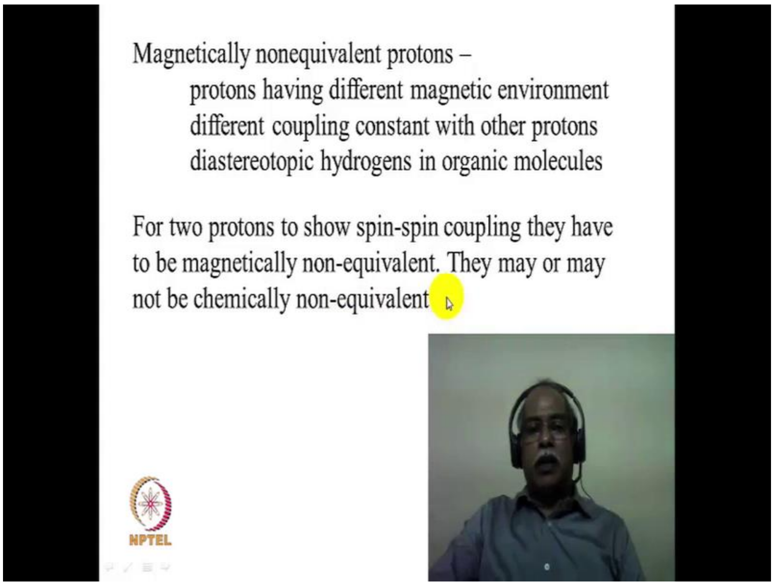

Magnetically nonequivalent protons –

protons having different magnetic environment
different coupling constant with other protons
diastereotopic hydrogens in organic molecules

For two protons to show spin-spin coupling they have to be magnetically non-equivalent. They may or may not be chemically non-equivalent

Now, magnetic nonequivalence can be defined, for 2 protons are said to be magnetically nonequivalent, if they have different magnetic environment. What is meant by different magnetic environment means, you compare, let us say, a set of chemically equivalent hydrogen; you want to find out whether they are also magnetically equivalent; if there is another hydrogen in the molecule, look for the geometric relationship between the set of hydrogen which you are comparing, to the hydrogen which is away from this 2 sets.

Suppose, if they have identical geometrical relationship with the other hydrogen, then, this 2 hydrogens are said to be magnetically equivalent. If they do not have same geometrical relationship, then, they are magnetically non-equivalent in nature. Typically, in organic compound, diastereotopic hydrogens are nonequivalent in nature. They are both chemically, as well as magnetically nonequivalent. For 2 protons to show a spin-spin coupling, they have to be, they must be magnetically nonequivalent; otherwise, they will not couple with each other; they may, or may not be chemically nonequivalent. This is something we will define in a, in the next slide, or so.

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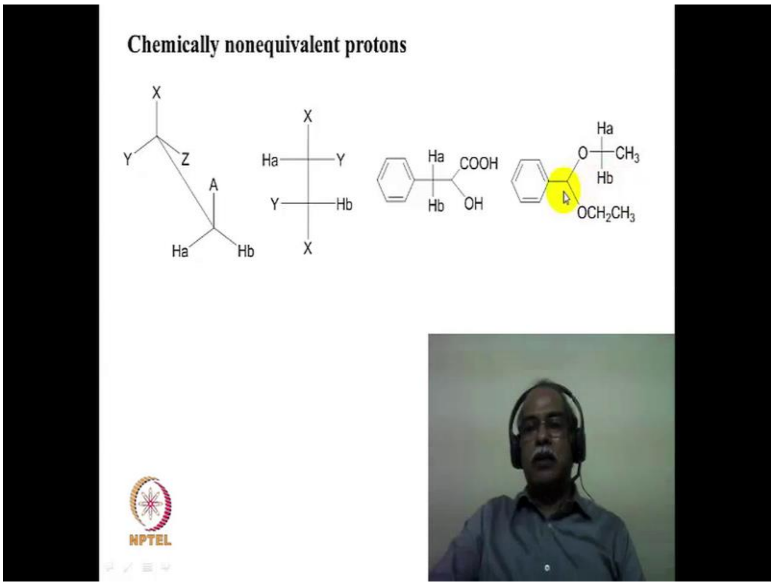

Chemically nonequivalent protons

Let us take this example; there is a chiral centre in this molecule. So, we are talking about chemically nonequivalent protons in molecules in this particular slide. This, because of the chiral centre, these 2 hydrogens are diastereotopic in nature. Because, if you substitute this hydrogen with a substituent, you will get a different isomer, compared to substituting this hydrogen with another substituent, a different isomer. So, they are truly diastereotopic, because they are adjacent to hydrogen. Diastereotopic hydrogens are chemically non-equivalent in nature.

You take a d l isomer; earlier, we considered a meso isomer with a plane of symmetry. The d l isomer does not have a plane of symmetry; it has a C 2 axis of rotation. These 2 hydrogens are related by C2 axes of rotation; as a result of that, they are diastereotopic in nature. This is an example of the same type, like here, what we had a chiral center here; this is also a chiral center; the adjacent methylene group is a diastereotopic methylene hydrogen.

Now, this molecule is not a chiral molecule. This center is not a chiral center, but it is a pro-chiral center, for the reason that, these 2 hydrogens are pro-diastereotopic in nature. Suppose, if I substitute this hydrogen with a substituent, that makes this a chiral center automatically, which in turn makes this chiral center, this center to be a chiral center, automatically. So, these 2 hydrogens, although there is no chiral center present, they are still considered to be diastereotopic, or pro-diastereotopic, for example, for the reason that, it generates a chiral center by means of a substitution criteria.

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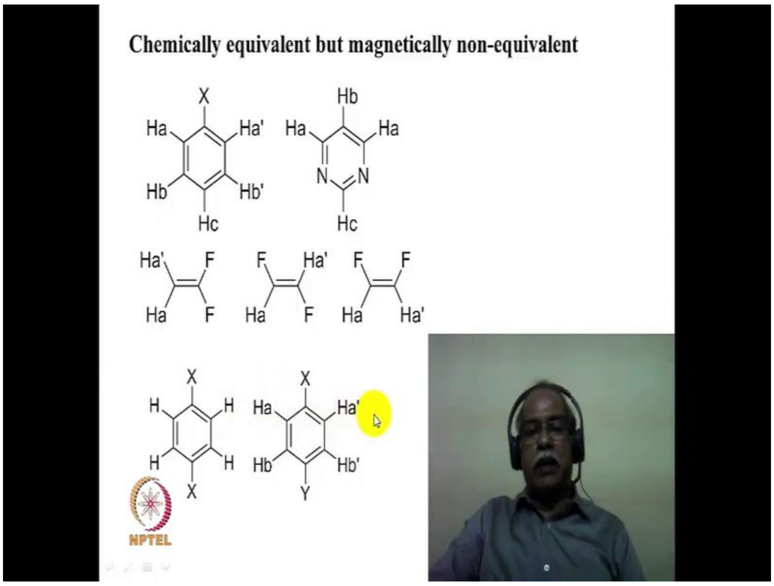

Chemically equivalent but magnetically non-equivalent

Now, let us define what is chemically equivalent but magnetically nonequivalent. Let us say, for example, a mono-substituted derivative is what we are talking about. We want to assign, whether these 2 hydrogens which are chemically equivalent, that is, the 2 ortho hydrogens are chemically equivalent; whether they are also magnetic equivalent or not. In order to define the magnetic equivalence, you compare it with another, magnetically active nuclei.

Let us take, for example, this hydrogen as a reference hydrogen. With reference to this particular hydrogen, these 2 hydrogens are not geometrically related in the same way; this is ortho, whereas this is para. So, they will not have the same coupling constant, in terms of the magnetic environment of this hydrogen to this hydrogen, and this hydrogen to this hydrogen will not be identical. So, although they are chemically equivalent, they are now magnetically nonequivalent. The same logic holds good for the H b hydrogens also; you compare it with, for example, H a hydrogen. This particular H a hydrogen you take as a reference point; this has a para relationship, whereas this has an ortho relationship. So, one can define the magnetic nonequivalence and chemical equivalence in this way. Chemically equivalent hydrogens need not be magnetically equivalent, and chemically nonequivalent hydrogens are by definition magnetically nonequivalent. Now, these are 3 isomers of difluoroethylene, for example. The geminal difluoro, the trans difluoro and the cis difluoro.

In each of this case, these two hydrogens are magnetically, chemically equivalent, but magnetically nonequivalent, for the reason, fluorine is a, F 19, fluorine is a magnetically active nucleus. So, that makes these 2 hydrogens magnetically nonequivalent, because, one has a trans relationship, and the other one has a cis relationship; geometrically they have 2 different relationship. So, they cannot be existing in the same magnetic environment, with respect to this fluorine, here.

Take this example, where you have 2 identical substituents situated in the para position in a aromatic ring; there is a plane of symmetry, the vertical plane of symmetry and a horizontal plane of symmetry, that makes all these 4 hydrogens identical. They are chemically, as well as magnetically identical. On the other hand, you remove one of the planes of symmetry along this direction by putting x and y substituent, instead of 2 x substituents here. Then, if you consider the pair of chemically equivalent hydrogen, they are magnetically nonequivalent for the same reason that we defined in the case of the mono-substituted derivative.

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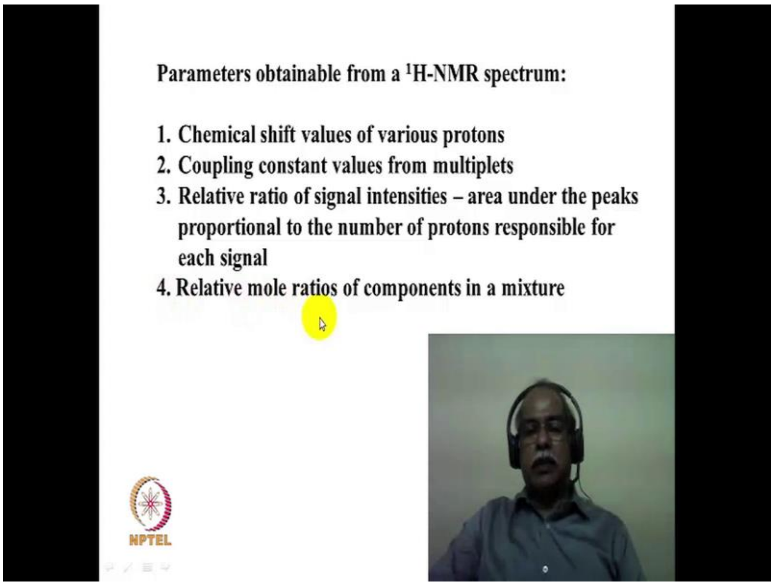

Parameters obtainable from a ^{1}H-NMR spectrum:

1. Chemical shift values of various protons
2. Coupling constant values from multiplets
3. Relative ratio of signal intensities – area under the peaks proportional to the number of protons responsible for each signal
4. Relative mole ratios of components in a mixture

Now, the parameters that one can obtain from the NMR are the chemical shift values of various protons, the coupling constants values of various multiplets, and the relative ratios of signal intensity, or the areas under the peaks are proportional to the number of protons responsible for each signal.

For example, in the case of ethyl alcohol spectrum, we saw 3 signals with the intensity ratio of 3 is to 2 is to 1. The 3 is to 2 is to 1 comes from the fact that you have a CH 3 and a CH 2 and a OH group. So, then, signal intensity, or the area under the peaks are actually proportional to the number of protons responsible for each of the signal.

Suppose, if we have a mixture of compounds, like ortho nitro toluene and para nitro toluene, if you integrate the methyl signal, there will be 2 different methyl signals for these 2 compounds, ortho and para. They are distinctly different compounds. There will be 2 signals. If you integrate the 2 signals, and take the ratio, that will correspond to the molar ratio, mole ratio of these two compounds in this mixture. So, this is very useful information, because it allows you to quantify using NMR spectroscopy, using a suitable internal standard, what are the mole ratios, or what is the absolute molar amount that is present in the mixture.

Now, in this particular, in this particular presentation, so far, we have seen the chemical shift, concept of chemical shift, the concept of coupling constant, and the concept of J values and delta values, and the parameters that are responsible for affecting the J values and delta values. We also defined what is the chemically equivalent hydrogen, what are chemically equivalent hydrogen and what are magnetically equivalent, or nonequivalent hydrogens. I hope you understand the concepts very clearly. Let us move on to the next lecture.

Thank you.