Modern Instrumental Methods of Analysis
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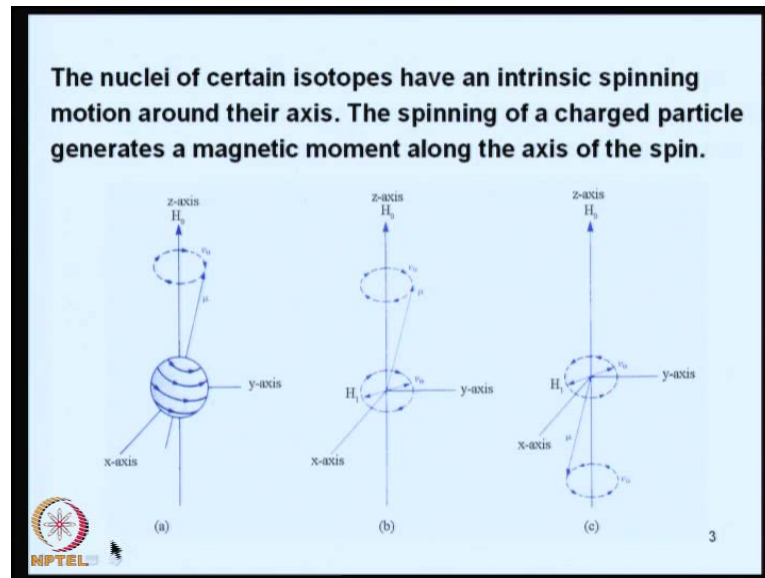**Indian Institute of Science, Bangalore**

Lecture No. # 34

Introduction to Mass Spectrometry

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Today, we will discuss about nuclear magnetic resonance spectrometry; like, what I was telling about the mass spectrometry? Same consideration hold good, with respect to nuclear magnetic resonance spectrometry also; the basic requirement is for the organic chemistry people. And we will take a quick look at the theoretical aspects and a slight inquiry into the instrumentation aspects, but more or less it is the domain of the organic chemist either for techno spectra interpretation and utilization of this spectrum.

However for brevities sake, we will discuss about the nuclear magnetic resonance spectroscopy and quickly we will run through and then we will go to electro chemical methods of analysis. So, in nuclear magnetic spectroscopy is a technique for determining this structure of the molecules and ions; and for their quantization based on the transitions between the energy levels of the atomic nucleus, not the electrons nucleus under certain conditions.
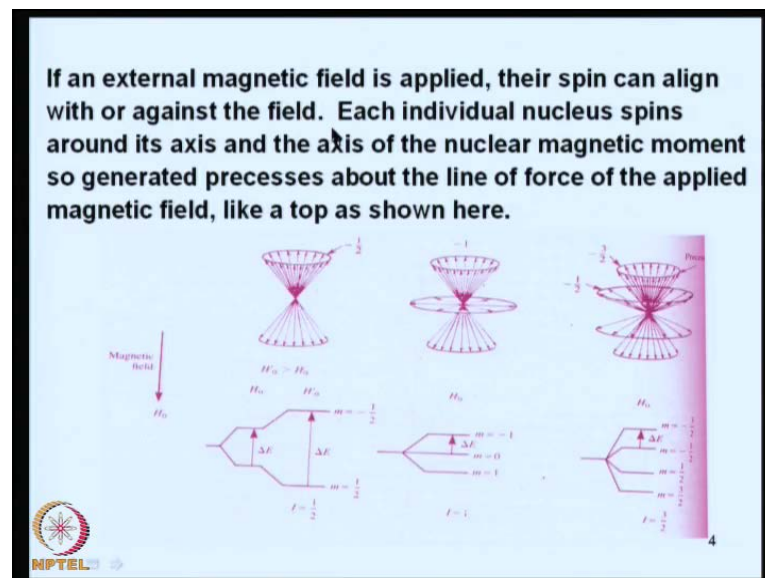
The energy involved is in the radio frequency range; only those nuclei which have got spin, which spin on their own axis can give rise to signal in NMR even. So, NMR is extremely useful, because the signal given by a nucleus is influenced by its environment; that is number of protons present, number of other functional group atoms, electronic distribution etcetera. In other words, the signal from nucleus gives information about its neighboring atoms, charge status, etcetera. This often leads to the determination of complete molecular structure; that is, where the value of NMR lies.

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The nuclei of certain isotopes have an intrinsic spinning motion around their axis. The spinning of a charged particle generates a magnetic moment along the axis of the spin.

We can take a look at this figure, and the nuclei of certain isotopes have an intrinsic spinning action; around their own axis. The spinning of a charged particle generates a magnetic moment as we all know along the axis of the spin. For example, in this figure we can see that; this is the nucleus and this is the x axis and this is the z axis, and this is the y axis. So, a spinning nucleus generates a magnetic momentum mu along the z axis, in the with a magnetic motion like this and these 2 I will explain to you later.

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If an external magnetic field is applied, their spin can align with or against the field. Each individual nucleus spins around its axis and the axis of the nuclear magnetic moment so generated precesses about the line of force of the applied magnetic field, like a top as shown here.

If an external magnetic field is applied now, their spin can align with or against the field and each individual nucleus spins around its axis, and the axis of the nuclear magnetic moment also processes around the line of the force of the applied magnetic field; like a top shown here in this case. Here, I am applying the magnetic field and this is the nucleus; this is the magnetic field generated here. It is H 0 and this is here, it is the magnetic moment generated here; this is exactly equal to H 0, is its H 0 greater H 0 dash is greater than H 0, and here it will be less than that.

So, you can see that the energy levels are split into state different states; that is minus half, plus half within a moment magnetic moment like this, and here also the lines are split and if it is magnetic moment is 1 by 2 you get plus or minus half, and if it is 3 by 2 you would end up with fine lines 2 I plus 1.

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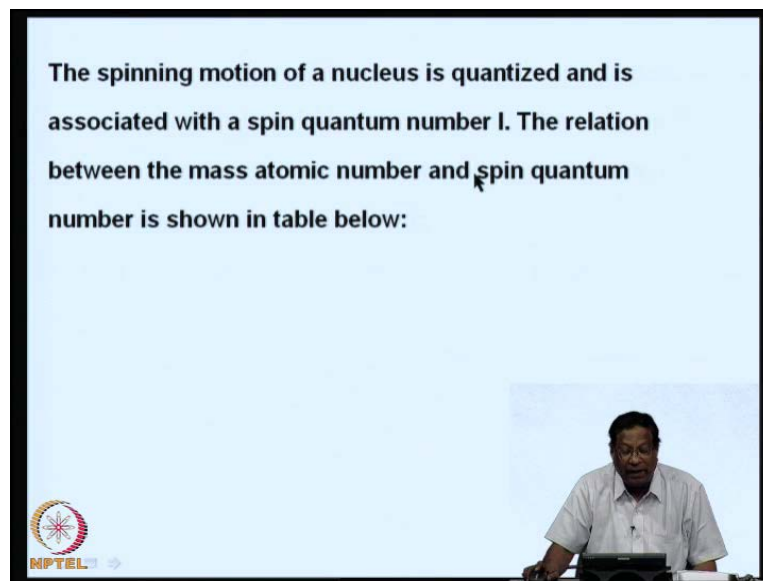
So, the spinning motion of the nucleus is quantized; and it is associated with a spin quantum number I .The relation between the mass atomic number and the spin quantum number is shown in the next table; that is we have some atoms with mass number even, and number of protons also even.
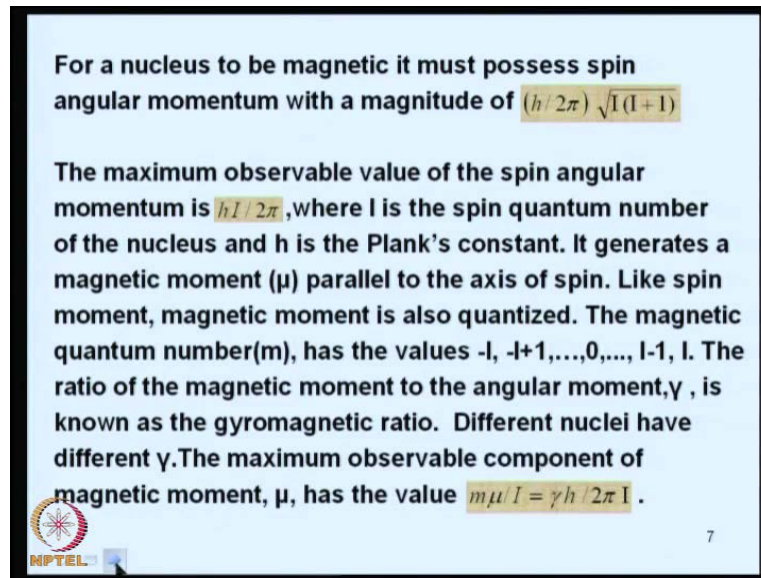
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Mass number, (Protons + Neutrons)	Atomic number (no of Protons) Z	No of Neutrons	Spin Quantum no I	Examples
Even	Even	Even	0	^{12}C, ^{16}O, ^{32}S
Odd	Odd	Even	1/2 3/2	^{1}H, ^{19}F, ^{31}P ^{11}B, ^{79}Br
Odd	Even	Odd	1/2 3/2	^{13}C ^{127}I
Even	Odd	Odd	1	$^{}N$

Nuclei with both A and Z even have I = 0 and they do n̶ als.

So, the number of neutron and neutrons must be even, such such elements will have 0 spin quantum number. Examples include 12 carbons, 16 oxygen, and 32 sulfur like that; all are even even. And we can have odd; mass number and atomic number could be odd and number of neutrons could be even; such elements will show spin quantum number either 1 by 2 or 3 by 2. Examples include 1 H, 19 F, 30 1 phosphorous, 11 boron and 79 boron.

Other examples are odd mass number and instead of odd; it is even number of protons and odd neutrons these are also NMR wise, they are active elements like 13 C and 127 iodine and then we can have even and odd in this range and then this also could be odd; that means, both protons and neutrons if they are odd, it gives you even mass number and these are the examples 2 hydrogen and 14.

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For a nucleus to be magnetic it must possess spin angular momentum with a magnitude of $(h/2\pi)\sqrt{I(I+1)}$

The maximum observable value of the spin angular momentum is $hI/2\pi$, where I is the spin quantum number of the nucleus and h is the Plank's constant. It generates a magnetic moment (μ) parallel to the axis of spin. Like spin moment, magnetic moment is also quantized. The magnetic quantum number(m), has the values -I, -I+1,...,0,..., I-1, I. The ratio of the magnetic moment to the angular moment,γ , is known as the gyromagnetic ratio. Different nuclei have different γ.The maximum observable component of magnetic moment, μ, has the value $m\mu/I = \gamma h/2\pi I$.

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So, nuclei with both a and z have I is equal to 0 and they do not give NMR signals. So, for a nucleus to be magnetic; it must possess spin angular momentum with a magnitude of H by 2 I, 2 pi square root of I into I plus1. So, the maximum observable value of the spin angular momentum is given by H I by 2 pi, where I is the spin quantum number of the nucleus, and H is the plank's constant; it generates a magnetic moment mu parallel to the axis of the spin like spin moment, magnetic moment is also quantized the magnetic quantum number m has the values of minus I, minus a plus 1, 0 and I minus1 and I. So, total is 2 I plus 1.

The ratio of the magnetic moment to the angular moment y is known as gyro magnetic ratio. Different nuclei have different gyro magnetic ratios, the maximum observable component of the magnetic moment mu, has a value of mu ,m mu divided by I is equal to frequency into H is equal to 2 pi into I.

So, the nuclei with I is equal to half behave like charged, spinning spheres and give well resolved spectra. such nuclei include 1 H, 13 C, 19 F and 31 phosphorous among the nuclei, with I is equal to 3 by 2, 7 lithium, 11 boron, 35 chloride chlorine are important nuclei with integral spins of I is equal to 1; include 2 H and 14 N, that we have seen in the table. Nuclei with spins greater than 1 by 2 behave like no spherical charged rotating bodies and show line broadening in NMR spectra.

Several organic compounds contain only carbon, hydrogen and oxygen. Since, 12 C and 16 Oxygen do not have nuclear magnetic moments, only the protons spectra are usually observed. 13 C has a low natural abundance of 1.1 percent only; that means, it is not observed in ordinary NMR.

The magnetic moment of a spinning nucleus can assume $2I + 1$ orientations with respect to the external magnetic field leading to $2I+1$ discrete energy levels. The energy levels can be calculated using the equation,

$$E = -m \, \mu / \, I \, H_0$$

where I = spin quantum number, m is the magnetic quantum number, μ is the magnetic moment of the nucleus, H_0 is the external (i.e., applied) magnetic field strength in gauss (G) and E is the energy corresponding to that orientation (in value).

The allowed values of m are I, (I-1), ..., 0, ...(-I+1), -I. Thus a nucleus with spin 1/2 has 2 orientations, with spin as 3 orientations; and so on.

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So, the most of the NMR work is related to the proton NMR. Now, a days C 13 NMR is also gaining lot of prominence and people are using C 30 instruments are commercial instruments are available C 13 NMR spectrometers. So, the magnetic moment of a spinning nucleus can assume 2 I plus 1 orientation, as I was telling you with respect to the external magnetic field leading to 2 I plus 1 discrete energy levels.

So, the energy levels can be calculated using this equation. This I have already told you, where I is the spin quantum number, m is the magnetic quantum number, mu is the magnetic moment of the nucleus, and H 0 is the external magnetic field; that is applied. Magnetic field having strength of gauss having the strength in gauss and E is the energy corresponding to that orientation. So, the allowed values are like this 2 I plus 1 and spin with half has got 2 orientation spin with 3 by 2 has 1 has 3 orientations etcetera.

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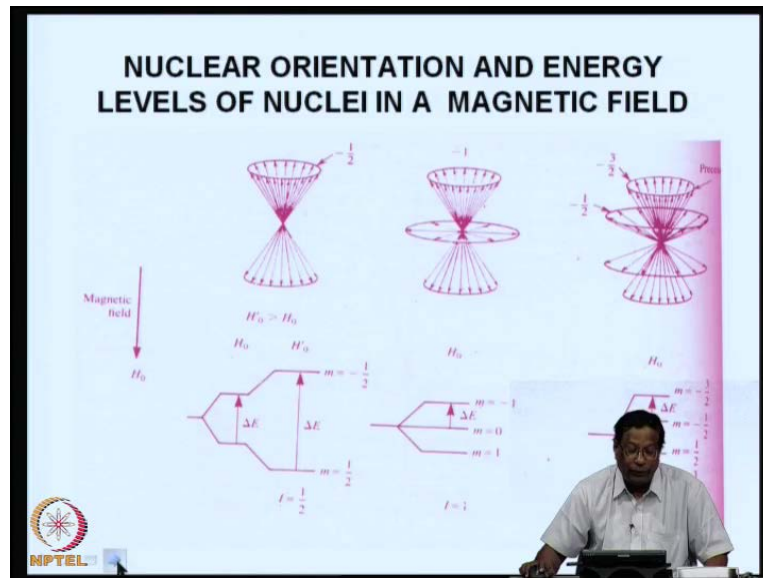
So, this is the figure, what I was showing you earlier? And the moment you see spin orientation and energy levels of nuclei in a magnetic field, you will be seeing this splitting of the magnetic energy levels; this figure, I have shown you earlier.

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So, the transitions between the energy levels produced by the application of the magnetic field can occur; according to the selection rule, delta m should be changing only by whole numbers; that is plus or minus 1.

So, the resonance frequency corresponding to this makes the transitions possible and it is given by delta E is equal to h v 0; which which is also equal to mu into H 0 upon I. So, keeping the magnetic filed H 0 constant, if an increasing radio frequency constant is passed through a coil in the Y Z plane and r f frequency creates an alternating field in the x direction. So, when H 1 equals the resonance frequency mu 0, the energy is absorbed by the spinning nucleus flipping the spin direction spin direction such that its magnetic moment processes against the applied fields; this is known as lamer frequency this I have shown you in the first slide.

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The nuclei of certain isotopes have an intrinsic spinning motion around their axis. The spinning of a charged particle generates a magnetic moment along the axis of the spin.
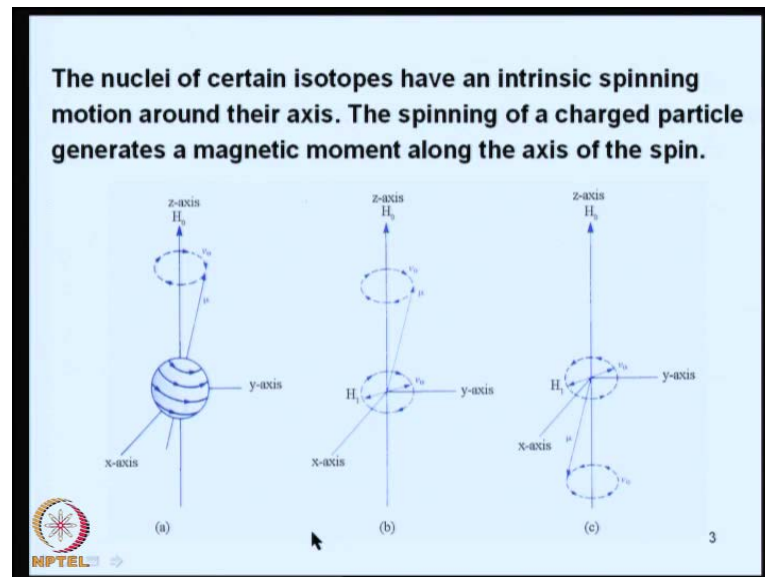
That is this, here I have the applied field here and the moment the magnetic frequency is matched by the applied field, the spin will be changed in the opposite direction like this; first it was on the top, now it is on the at the bottom. So, this is known as the frequency at which this happens is known as lamer frequency.

There is a linear relationship between the resonance frequency and the applied magnetic field H_0. Therefore, either H_0 can be kept constant and sweep radio frequency (rf) or keep a constant rf and vary the applied magnetic field H_0.

Magnetic field strength can be expressed in units of Gauss (G) or Tesla (T). 1T = 10,000 G

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So, there is a linear relationship between the resonance frequencies of the applied magnetic field H 0. Therefore, we can either keep H 0 as constant and sweep the radio frequency or keep the radio frequency constant and vary the applied magnetic field H 0. Therefore, this gives us two ways of running a and NMR spectrometry. So, magnetic field strength usually is expressed in terms of gauss or tesla; and one tesla corresponds to about 10000 gauss.

For a proton μ = 1.41 x 10^{-30} JG^{-1} or 2.7927 nuclear magnetons. If a magnetic field of 14092 G is applied,

$$\nu_0 = \frac{\Delta E}{h} = \frac{(1.41 \times 10^{-30} \, J \, G^{-1})(14,092 \, G)}{(6.626 \times 10^{-34} \, J \, sec)\,(0.5)} \quad sec^{-1} = 60 \times 10^{6} \, sec^{-1}$$

Thus, the resonance frequency of a proton in a magnetic field of 14,092 G would be 60 MHz.

In NMR the strength of the signal is approximately equal to the square of the magnetic field applied. Strong magnetic fields can be produced using ....er conductors.

So, for a proton we have the momentum corresponding to 1.41 into 10 raise to minus 30 joules per gauss inverse or 2.7927 nuclear magnetrons. So, if a magnetic field of 14,092 gauss is applied, then we can ==we can== calculate the frequency corresponding to the change and you would end up with 60 into 10 raise to 6 seconds inverse.

Thus, the resonance frequency of a proton in a magnetic field of 14,092 gauss would be around 60 megahertz; that is all it means. So, you can have a magnet of 60, 14092 gauss and you should operate it at 60 mega hertz to see the NMR spectrum. So, in NMR the strength of the signal are approximately equal to the square of the magnetic field; strong magnetic fields can be produced using super conductors.

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MAGNETIC RESONANCE PROPERTIES OF SELECTED NUCLEI

Isotope	Magnetic moment, μ/μ_N*	Relative sensitivity at constant H_0†	NMR frequency (MHz)		
			At 14.09 kG	At 21.14 kG	At 23.49 kG
^{1}H	2.7927	100	60.000	90.000	100.000
^{2}H	0.8574	0.96	9.210	13.815	15.352
^{13}C	0.7024	1.59	15.086	22.629	25.147
^{19}F	2.6288	83.4	56.444	84.666	94.087
^{31}P	1.1317	6.64	24.288	36.432	40.485

* In multiples of the nuclear magneton, $eh/4\pi\ Mc$.
† Sensitivity relative to the proton, assuming equal numbers of nuclei and the same relaxation time ratio, T_2/T_1.

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So, this is what? Has (()) the development of NMR, because very strong good magnetic magnets have become available.

So, the magnetic resonance properties of selected nuclei, I have put them here this is 1 H, 2 H, 13 C, 19 F etcetera; their magnetic moments are here, and relative sensitivity at constant H 0 is these are all in the multiples of the nuclear magneton; that is e h by 4 pi M c, and NMR frequency corresponding to that is 60; this is at 14.09 kilo joules that is 14,960 kilometer kilo joules, and this is at 921.14 kilo joule, kilo gauss if you apply a magnetic field, the frequency would be ==would be== getting is around 90 megahertz.
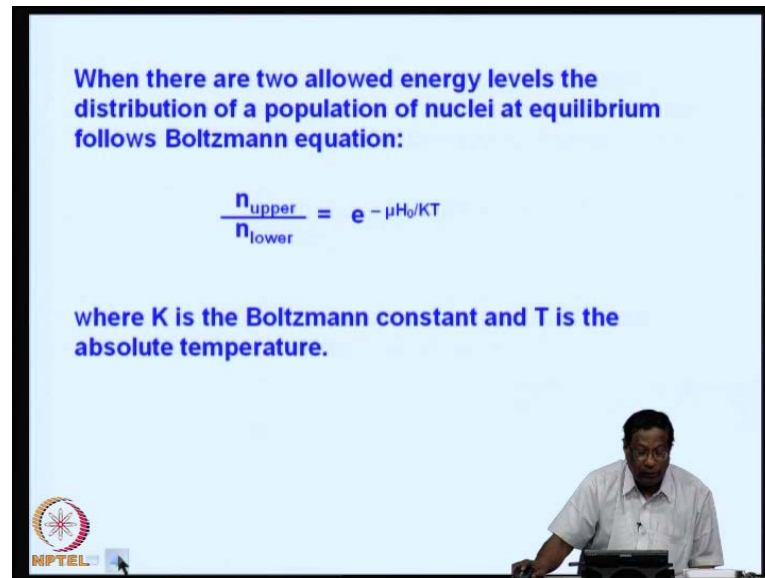
Similarly, at this 23.49 you would get a frequency of about 100. Similarly, you can see that 1 H, 2 H, 13 C, etcetera. Here, you can see that, with respect to 1 H relative sensitivity is 100. Whereas, for 2 H it is only 0.96, similarly for 13 C it is 1.59, because of the presence of the magnetic the isotope, but the intensity is only about 1.59 compare to 100.

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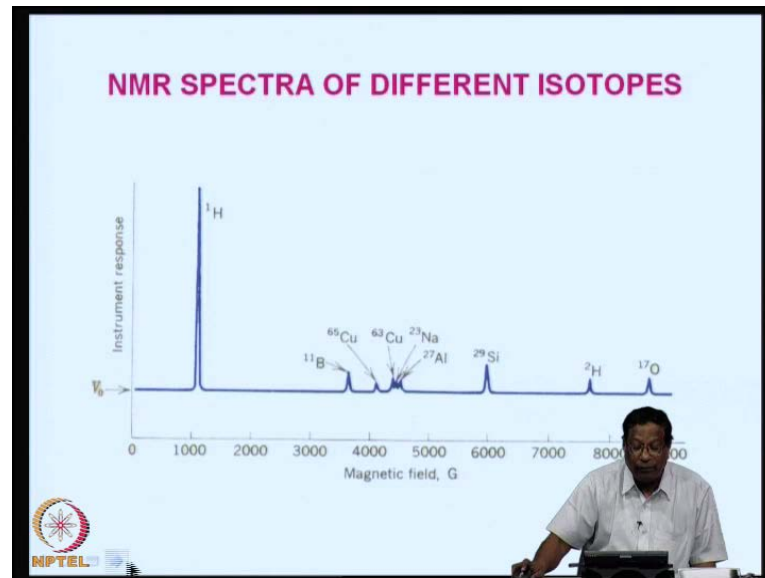
So, like that one can calculate, what are the different numbers involved? this is the NMR spectrum of different isotopes, here you can see 1 H assuming that this is around 100, we can see that intensities of the peaks or instrument response is for boron, copper and then sodium, etcetera they are all very small compare to protons and silicon is slightly better 2 H is very less, and this is the x axis is the magnetic field.

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So, when there are two allowed energy levels the distribution of a population of nuclei at equilibrium follows the Boltzmann distribution, what is Boltzmann distribution? It is this part of e to the power minus mu H 0 upon K T. where, K is the Boltzmann constant and T is the absolute temperature. So, the distribution in the upper energy state to compare to the lower energy state; that is the ratio is governed by the Boltzmann equation.
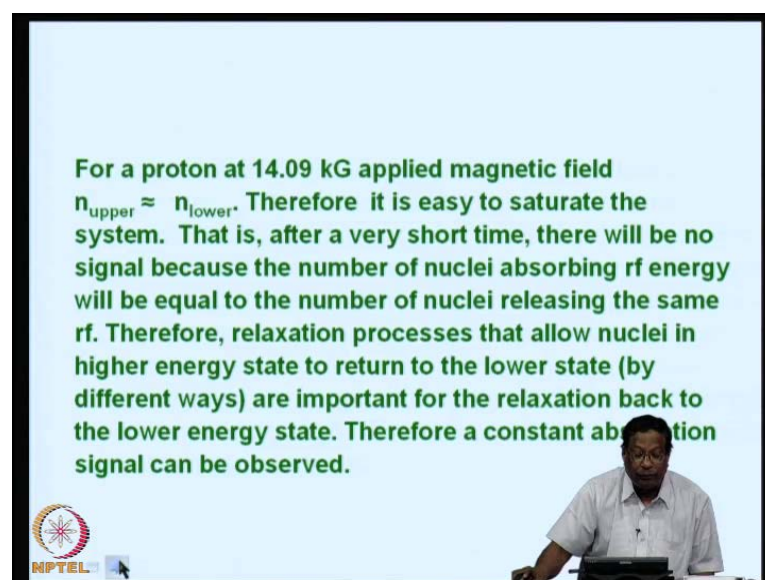
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So, for a proton at 14.09 gauss the applied magnetic field should be approximately equal to lower and higher population; populations of the nucleus at lower and higher energy
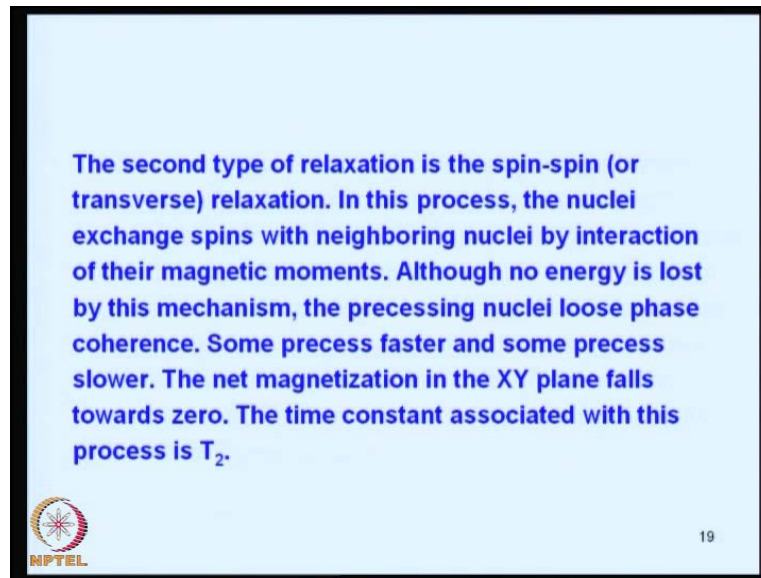
levels therefore, it is easy to saturate the whole system; that means, after a very short time there will be no signal. Because, the number of nuclei absorbing r f energy and flipping over from one to another would become equal and therefore, the relaxation process that allow nuclei at higher energy state to the lower energy state.

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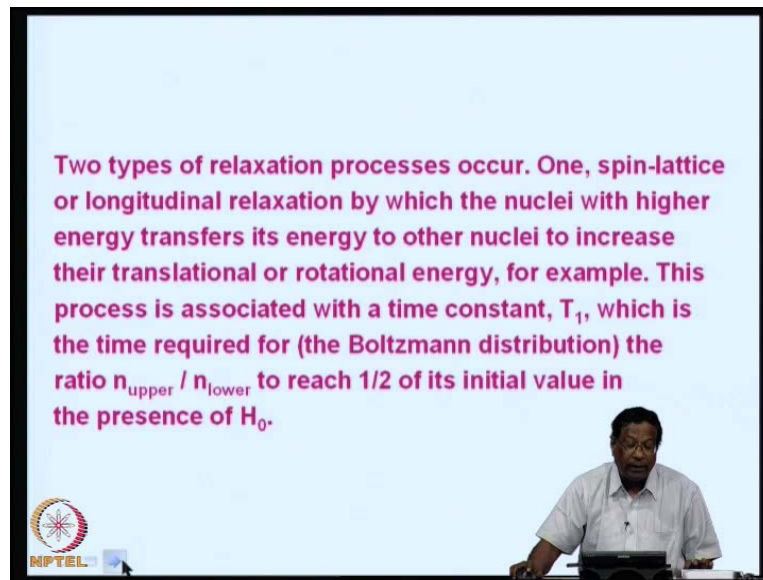
Why different ways are important? For the relaxation back to the lower energy states therefore, we can see only a constant absorption peak. So, there are two types of relaxation processes; one is spin-lattice or longitudinal relaxation by which the nuclei with higher energy transfers; its energy to the lower other nuclei to increase their translational and rotational energy; that means, the one with higher energy can translate its energy to other nuclei and other nuclei will gain translational or rotational energy, For example. This process is associated with a time it takes some time for the excited nuclei to transfer part of its energy this is denoted by, T 1, which is the time required for the ratio n upper to n lower; that is population of the atoms to reach 50 percents of its actual value, in presence of it is the applied magnetic field H 0.
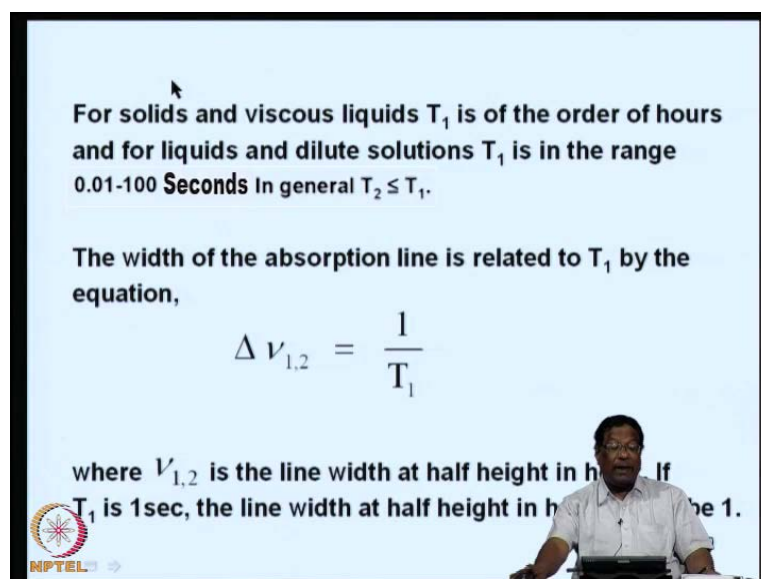
The second type of relaxation is the spin-spin (or transverse) relaxation. In this process, the nuclei exchange spins with neighboring nuclei by interaction of their magnetic moments. Although no energy is lost by this mechanism, the precessing nuclei loose phase coherence. Some precess faster and some precess slower. The net magnetization in the XY plane falls towards zero. The time constant associated with this process is T_2.

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The second type of relaxation is the spin-spin transverse relaxation. In this process, the nuclei exchange the spins with neighboring nuclei by interaction of their magnetic moments. So, in this process the nuclei exchange the spins with the neighboring nuclei by interaction of their magnetic moments. Although no energy is lost by this mechanism the processing nuclei loose phase ==phase== coherence. Some processes faster and some process slower. So, the net magnetization in the X Y plain falls towards zero. The time constant for this type of relaxation is associated with this process is T 2.

For solids and viscous liquids T_1 is of the order of hours and for liquids and dilute solutions T_1 is in the range 0.01-100 **Seconds** In general $T_2 \leq T_1$.

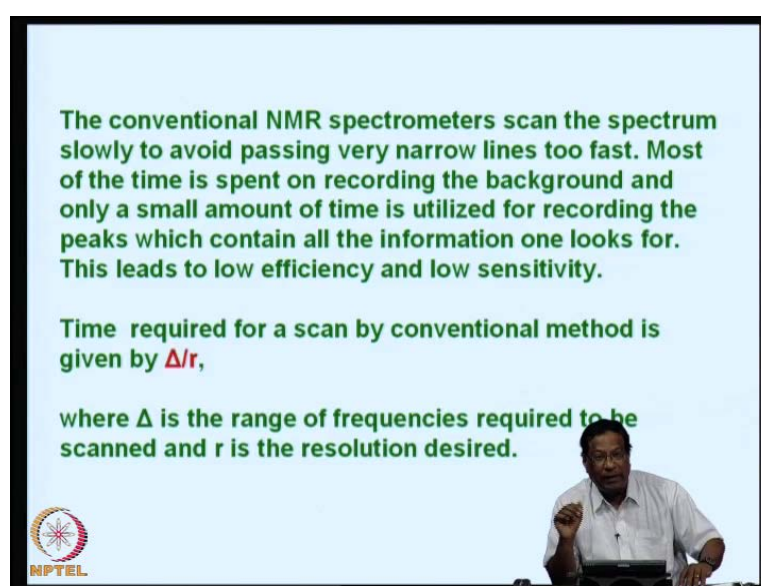The width of the absorption line is related to T_1 by the equation,

$$\Delta \nu_{1,2} = \frac{1}{T_1}$$

where $\nu_{1,2}$ is the line width at half height in h   If T_1 is 1sec, the line width at half height in h   be 1.

We will discuss in later, the thing is for solids and viscous liquids the first type that is T 1 is of the order of hours and for liquids and dilute solutions T 1 is in the range of 0.01 to 100 seconds; that is hardly about 1 and half to 2 minutes. In general, T 2 is less than or equal to T 1; that is translational and rotational energy transfer is always higher than the spin translation the width of the absorption line therefore, it is related to T 1, because that is the fastest occurring relaxation it is related to this by the equation delta v 1, 2 is equal to 1 over T 1, where delta v; where v 1, 2 is the line width at half height in hertz. If, T 1 is one second, the line width at half the height in hertz would be 1.

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So, the conventional NMR spectrometers scan the spectrum slowly to avoid passing very narrow lines too fast. If, you scan it very fast you would miss. So, many narrow lines which are having very low intensity. So, most of the time is spent on recording the background and only a small amount of time is utilized for recording the peaks which contain all the information one looks for. Basically, this leads to low efficiency and low sensitivity. The time required for a scan by the conventional method is given by delta by r; that is where, delta is the range of frequencies required to be scanned and r is the resolution desired.

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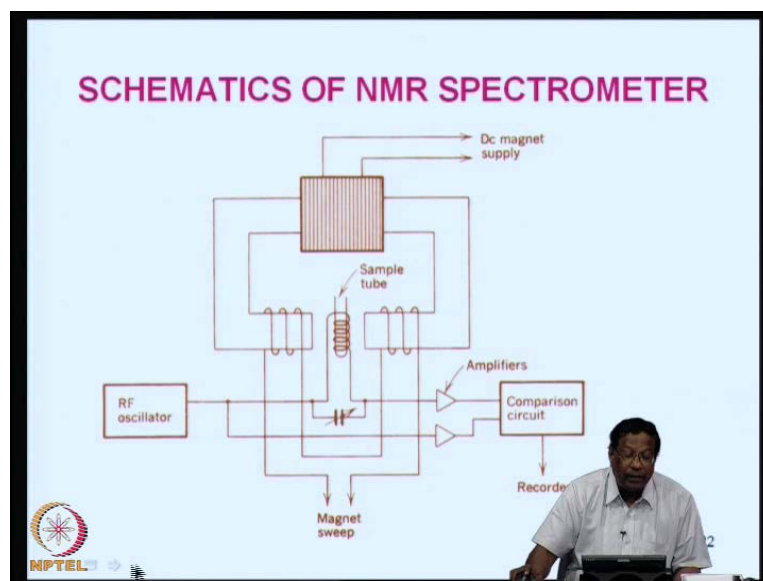
So, if you take a look at the magnetic schematic diagram of NMR spectrum, you would see that there is a DC magnet and a supply is there power supply and the sample is and… in a coil again. And this is an R F oscillator and then there are at least 2 or 3 R F oscillators in a given NMR; and all these R F oscillators are tuned to magnets, magnetic sweeps and sample around that and then we have routine amplifiers and comparison circuits and recorder. And this is the NMR sweep that is one of the R F coil is use for sweeping the NMR from 0 to 60 hertz or something like that.

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And for a 13 C NMR at 25 megahertz and a typical delta of 5 kilo hertz and the line widths of about 1 hertz, the scan rate has to be 1 hertz per second and the total time required would be 1 hour 23 minutes. If this spectrum is divided into a number of small frequency intervals and if all these frequencies are applied simultaneously the spectrum can be obtained much more quickly. That is, if N is the number of the bandwidths of the signal, and S by N ratio improves by a factor of N raise to half, this is known as felgett's advantage. We have discussed about, felgett's advantage and other things in F T I R.

Now, the same thing can be applied in the case of magnets NMR and to obtain the felgett's advantage, this is achieved by Fourier transform NMR. So, for felgett's advantage for a proton is about 30 and for 13 C atoms; C 13, it is about 100 protons is 30 and C 13 is 100.

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In FTNMR a strong rf pulse is applied to the sample in a short time of 1-100 μ seconds. This is applied by means of a coil placed parallel to X-axis of the spectrometer. The pulse contains a wide band of frequencies on either side of the center. Due to this all the magnetic nuclei are excited simultaneously. After the pulse, the precessing magnets revert back to their original state inducing a sinusoidal voltage in a coil surrounding the sample. This is the sum of all signals. After Fourier transformation, the spectrum appears similar to conventional spectrum.

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So, in FTNMR, what do we do exactly? Is we take a strong r f pulse and apply it to the sample in very short time duration of 1 to 100 mu seconds. This is applied by means of a coil placed parallel to X axis of the spectrometer. The pulse contains a wide band of frequencies on either side of the center. Due to this all the magnetic nuclei are excited simultaneously. So, after the pulse, the processing magnets revert back to their original state inducing a sinusoidal wave that we have discussed in F T? Will discuss in F T I R and a sinusoidal voltage is also obtained a corresponding corresponding ONE and it

obtains in a coil surrounding the sample. So, this is the sum of all the NMR signals. And after Fourier transformation, the spectrum appears similar to conventional spectrum.

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Nuclear magnetic resonance frequencies are to a small degree dependent on the molecular environment of the nucleus. Since surrounding electrons shield the nucleus, the effective magnetic field experienced by the nucleus is slightly different from the applied field. Electronic shielding results from an induced circulation of electrons about the nucleus. These circulations are induced by the applied field and are in a direction perpendicular to the applied field. They produce a magnetic field opposing the applied field and proportional to the magnitude of the applied field.

The effective magnetic field, $H_{eff} = H_0 - \sigma H_0$.
where σH_0 is the induced magnetic field. The separations of resonance frequencies of nuclei in different structural environments from some arbitrary standard is known as chemical shift.

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So, the NMR spectrum can also be operated using F T Fourier transform method. So, nuclear magnetic resonance frequencies are to a small degree dependent upon the molecular environment of the nucleus. This point we have to understand very clearly, because it is the protons that we are handling the signal, but the frequency of each proton is dependent on the molecular environment of that proton particular proton.

Since the surrounding electrons shield the nucleus, the effective magnetic field experienced by the nucleus is lightly different from the applied field. Therefore, electronic shielding results in induced circulation of the electrons about the nucleus. These circulations are induced further by the applied field and are in a direction perpendicular to the applied field; that means, you have apply the field, but the variation will be in the direction perpendicular to the field.

They produce a magnetic field in turn opposing the applied filed and the proportional to the magnitude of the applied field. The first is, they produce a magnetic field, opposing the magnetic field another is it is the signal is proportional to the magnitude of the applied field. So, the effective magnetic field is given by H 0 that is original applied filed minus that shielding affect that is given by sigma into H 0. So, where sigma is a small fraction and sigma H 0 is the induced magnetic field.

The separations of resonance frequencies of nuclei in different structural environments from some arbitrary standard. We have to know, because every electron, every proton experiences different electric electromagnetic field depending upon the sigma into H 0. Therefore, how do you rate the frequencies? How much each proton is feeling the effect of other protons?
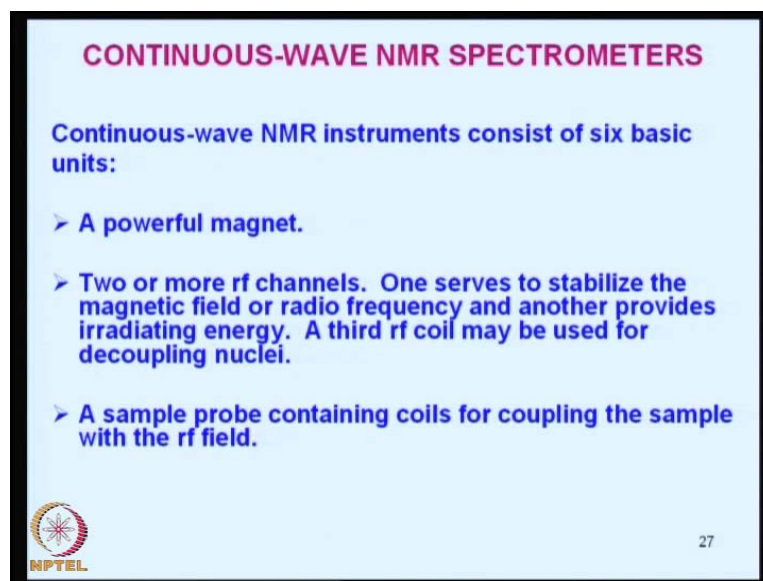
So, you need to have a standard; and this is known as arbitrary standard that is known as chemical shift. So, you take an arbitrary standard and from the standard you shift make the measure the distance where the peak appears. So, the NMR spectra in which the width of the resonance line is as large as or larger than the resonance shifts caused by different chemical environments are known as wide line NMR spectra.

This can give information wide line NMR spectra's can give information regarding the concentration and physical environment of the nuclei, but not their chemical environment. So, wide line NMR spectra provide a rapid non destructive method of quantitative analysis. For example, proton contents of the facts and oils can be measured it you can just calculate, how many hydrogen and ions are there? You may give a fact sample or oil sample.

Moisture content in a variety of samples can be determined by wide line NMR spectra, because it is a question of determining, how many hydrogen atoms are there? So, fluorine mean fluorocarbons that can be determined the width of the absorption line is related to the motional freedom of the nucleolus in the lattice.

This gives valuable information also to polymer chemist and solid state physicist also. So, the applications are usually interesting to the chemistry people, medicine people as well as oil technologies and physicist and polymer chemist. So, we can let us discuss a little bit about the NMR spectra meters.

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So, continuous-wave NMR spectra meters consist of six basic units: one is you need A powerful magnet and you need two or more r f channels. I had explained to you this earlier, one serves to stabilize the magnetic field or radio frequency and another provides irradiating energy. A third r f coil may be used for decoupling the nuclei.
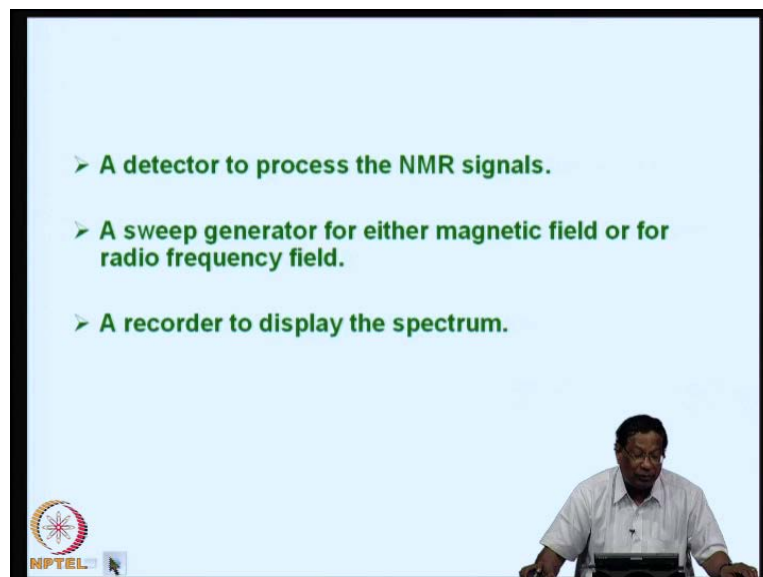
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A then you need a sample probe containing coils for coupling the sample with the r f field. That is also important; that means, the sample also must be having some short of a coil, which can couple with the applied r f field. And a detector you need to process the

NMR signals. A sweep generator for either magnetic field or for radio frequency field. You need to sweep the magnetic field or the radio frequency field, and then you need a recorder to display the spectrum. So, these are the basic fundamental machine parts NMR.

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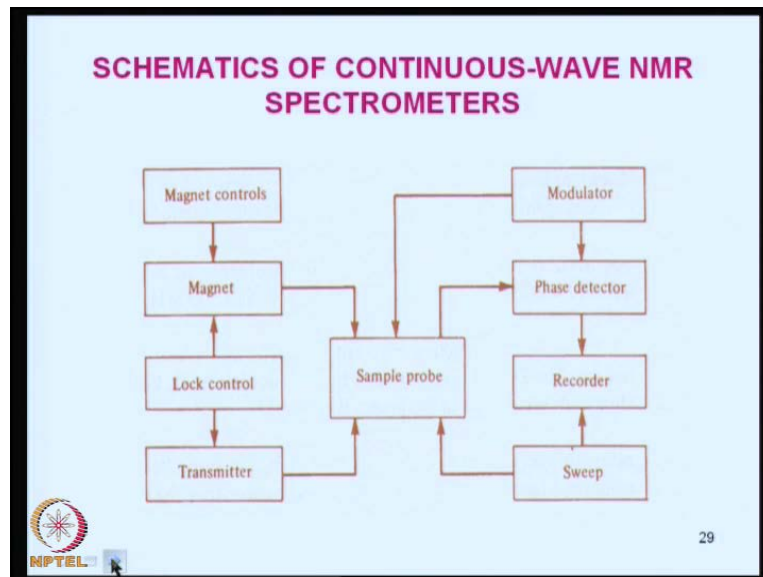
Schematics of the continuous-wave NMR include; a magnetic control, a magnet a lock control, transmitter, sample probe on the magnetic have magnetic have to be applied are on the sample and you need a modulator phase, detector and then recorder and a sweep mechanism for the sample.

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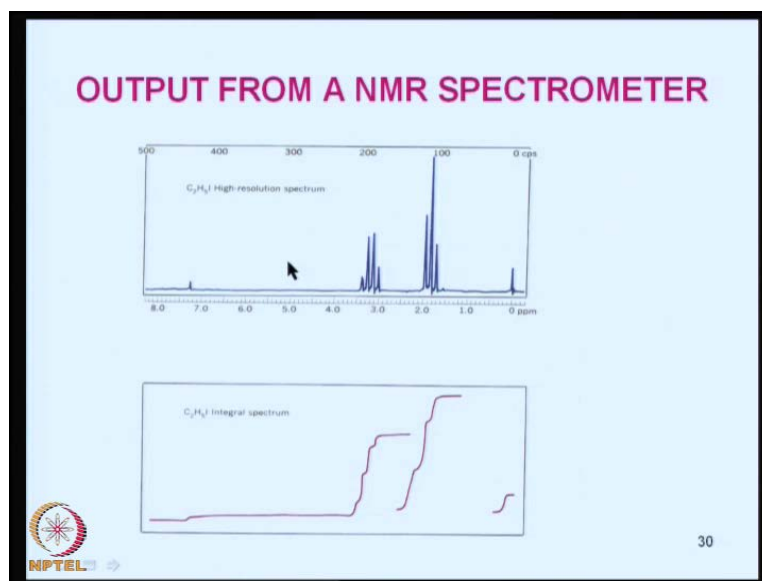
So, what type of output you get from NMR? Is the question. So, here is the C 2, H phi I that is methyl iodide, high resolution spectrum you would get something like this; a single peak and this is a multiple, and these are the other peaks you would get and this is the integral spectrum; that is the total height of the peaks. For example, the integral in this range corresponds to this peak in general integral in this range will correspond to this and integral here this corresponds to this. So, we this integration data you can calculate, how much hydrogen are there with respect to each other or each carbonator and this is the reference signal.

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So, this is how? You would see a NMR spectrum and the magnet should give a very high field strength which is homogenous and stable. The stronger the magnetic field the better is the separation of the absorption lines. Also, multiple overlapping decreases with increasing field strength.

In a stronger field is applied the separation of the energy levels of the nuclei would be greater and the Boltzmann distribution favors the lower energy level. Therefore sensitivity also increases. Because, more number of nucleus are there at the lower energy level to ensure homogeneity of the magnetic field two large pole pieces made of the homogenous material must be put together in between the sample must be inserted. So, that the sample should experience the magnetic field.

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The pole faces are polished. The gap between the poles is kept narrow. Slim coils are used for correcting any inhomogeneity. Permanent magnets are cheaper than electromagnets but require elaborate shielding and should be thermostated to $\pm 0.001^0$ C. Electromagnets require elaborate power supply and cooling systems but they can be operated at different field strengths. Commercial NMR spectrometers operate at 14.09, 21.14 or 23.49 kG. Using super conductivity technology 51.7, 70.5, 93.5 or 117.4 kG fields can be produced providing high resolution NMR.

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So, the pole faces are usually polished. The gap between the poles is kept narrow. Slim coils are used for correcting any in homogeneity and usually permanent magnets are cheaper than the electromagnets. Because, permanent magnets are easy to maintain but they require elaborate shielding and should be thermo stated to plus or minus 0.001 degree centigrade. Electromagnets usually require elaborate power supply and cooling system also, but they can be operated at different field strengths, just by changing the input.

So, commercial NMR spectrometers operate at a 14.09, 21.14 or 23.49 kilogauss. Using upper super conductivity technology we can even operate them like 51.7, 70.5,93.5 or

117.4 kilogauss fields can be produced providing which can provide provide very high resolution NMR.
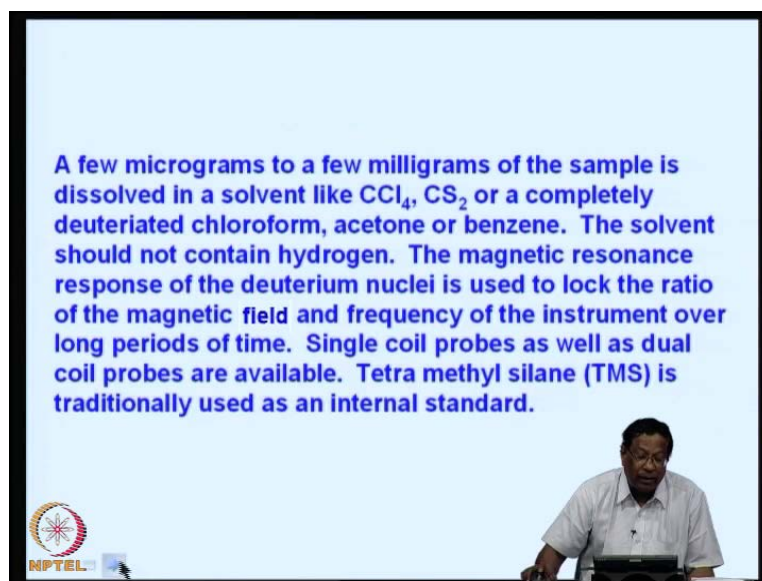
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THE PROBE UNIT

The probe unit is the sensing element of the spectrometer. It is inserted between the magnetic poles by an adjustable probe holder. The probe holder houses the sample holder, the rf transmitters, output attenuator, receiver and a phase-sensitive detector. The sample holder is a thin walled glass tube of 5mm outer diameter. To average minute inhomogeneities the sample holder is rotated at 1200 to 2400 rpm. The sample is filled to get a length / diameter ratio of 5.
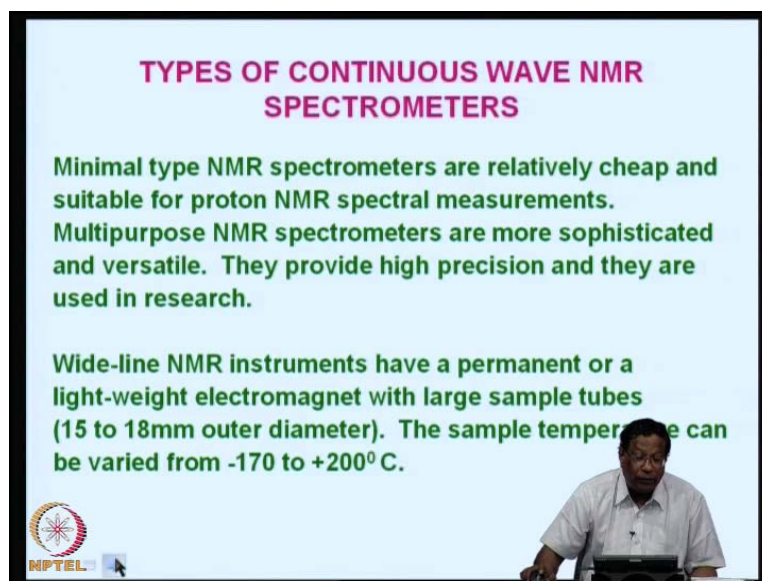
So, the probe unit let us discuss the probe unit; the probe unit it is basically a sensing element of the spectrometer. It is inserted between the magnetic poles by an adjustable probe holder. It is just a sample holder in which you can insert the sample. So, the probe holder houses the sample holder, r f transmitters, output attenuator, receiver and a phase-sensitive detector. The sample holder is basically a thin walled glass tube of about a 5 mm outer diameter. And to average minute inhomogenities the sample holder also must be rotated during the operation of a NMR at around 1200 to 2400 r p m. The sample is filled to get a length to diameter ratio of about 5; that means, you can have either the liquid sample or the solid sample.

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And there usually a mark is provided in the sample up to which the sample must be filled. So, if you micrograms to a few milligrams of the sample can be dissolved in a solvent like carbon tetrachloride, carbon disulphide or a completely deuteriated chloroform, acetone or benzene; that means, there should not be any hydrogen in the given sample except your sample. The solvent should not have any hydrogen item that is, why which is carbon tetrachloride, carbon disulphide or completely deuteriated chloroform, acetone or benzene the solvent should not contain hydrogen. The magnetic resonance responds of the deuteriated nuclei is used to lock the ratio of the magnetic field and frequency of the instrument over long periods of time. So, single coil probes as well as dual coil probes are available. Tetra methyl silane; that is, this very standard internal standard is traditionally used as internal standard, but there is other material also available nowadays.

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So, minimal types of NMR; minimal type of NMR spectrometers are relatively cheap and suitable for proton NMR measurements. Multipurpose NMR spectrometers are more sophisticated line and they are versatile. They provide high precision and they are used in research. Wide-line NMR spectra instruments spectrometers have a permanent or a light-weight electromagnet with large sample tubes. And the sample temperature can be varied from minus 170 to 200 degree centigrade.
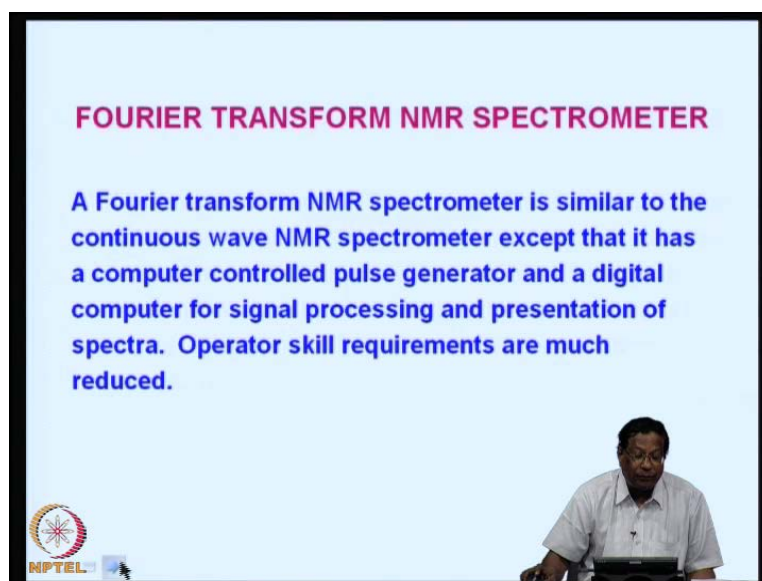
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So, FTNMR spectrometer is similar to the continuous wave NMR except that it has a computer controlled pulse generator and a digital computer for signal processing and presentation of the spectra. So, operator skill requirements are much reduced in FTNMR.

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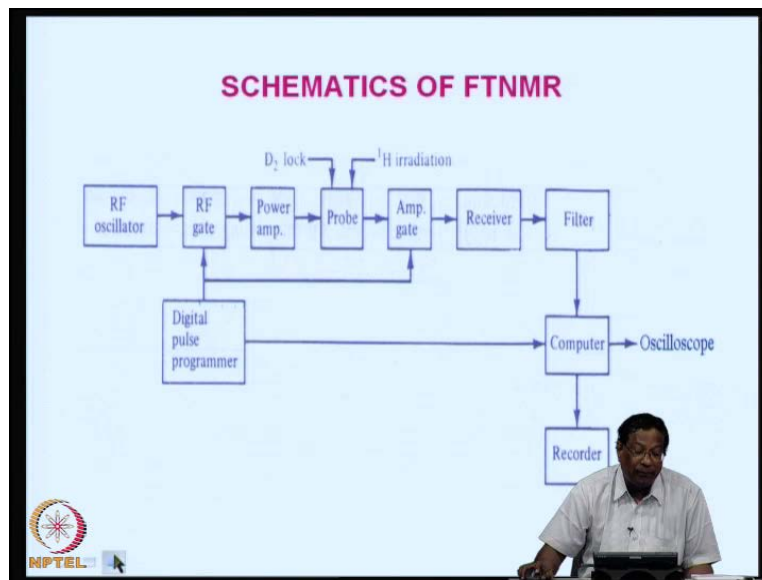
So, this is the schematics of the FTNMR and you can see that, R F oscillator is there and this is the R F gate; which can be opened on and off depending upon the requirement and it will only when the gate is on. The power amplifier it is fact to the power amplifier and it goes to the probe and this will then there is a D2 lock and then amplifier gate this two must open simultaneously. And then it goes to a receiver filter and whole operation is controlled by the computer at which the spectrum can be displayed on the oscilloscope you can have a recorder also automatically.
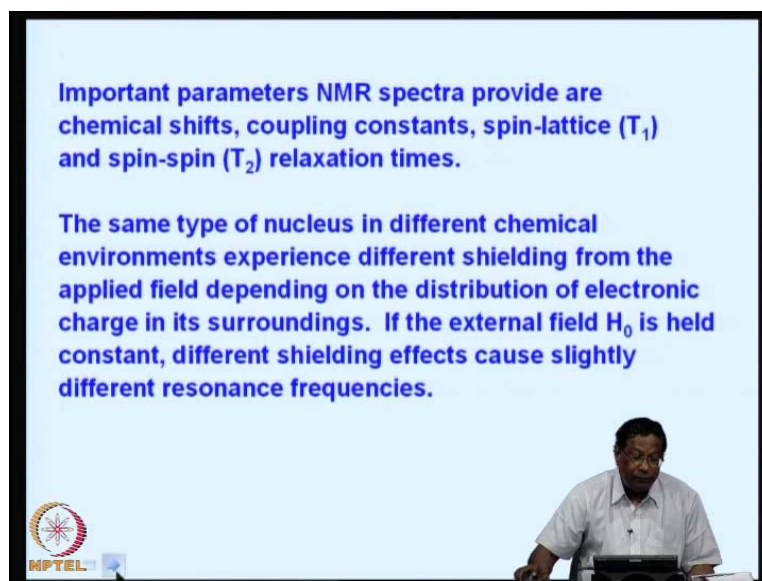
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So, in powdered solid samples, molecules are oriented in all possible directions. This results in broadening of the NMRS lines. The shielding of any particular nucleus depends upon the electronic environment and the orientation of the molecules in which it is present. This is known as Chemical Shift Anisotropy.

The this kind of broadening of NMR spectrum can be overcome to a large extent by rotating the sample very speed rapidly of the order of about more than 2 kilohertz about an axis oriented at an angle of 54.7 degrees; this is known as the magic angle, with respect to the applied field. The averaging that occurs is similar to tumbling in liquids, and the angle is a property of the local fields that electrons exert on the nuclei.

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Important parameters NMR spectra provide are chemical shifts, coupling constants, spin-lattice (T_1) and spin-spin (T_2) relaxation times.
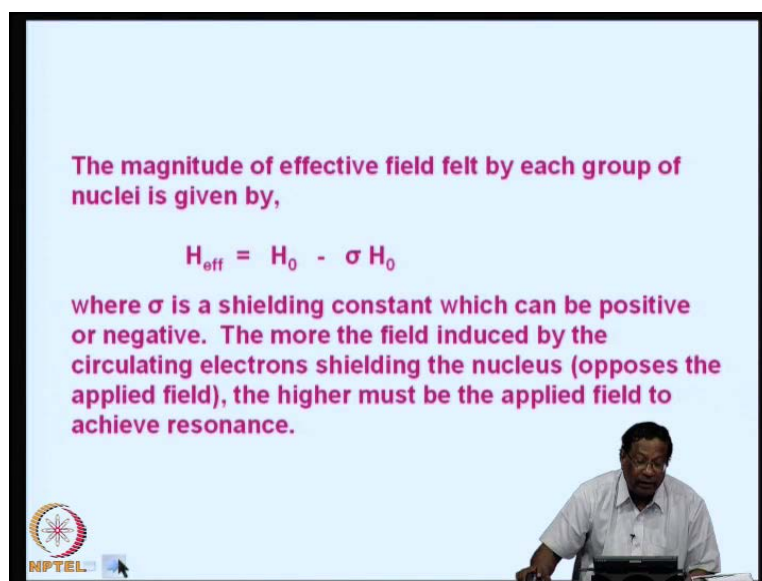
The same type of nucleus in different chemical environments experience different shielding from the applied field depending on the distribution of electronic charge in its surroundings. If the external field H_0 is held constant, different shielding effects cause slightly different resonance frequencies.

Another important parameter that NMR spectra provide is chemical shifts, coupling constants, and spin-lattice and spin-spin relaxation times. The same type of nucleus in different chemical environments experience different kinds of shielding from the applied field depending upon the distribution of the electronic charge in its surroundings; every proton must experience different electromagnetic field. And if the external field H 0 is held constant different shielding effects can cause slightly different resonance frequencies this is the fundamental principle.

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The magnitude of effective field felt by each group of nuclei is given by,
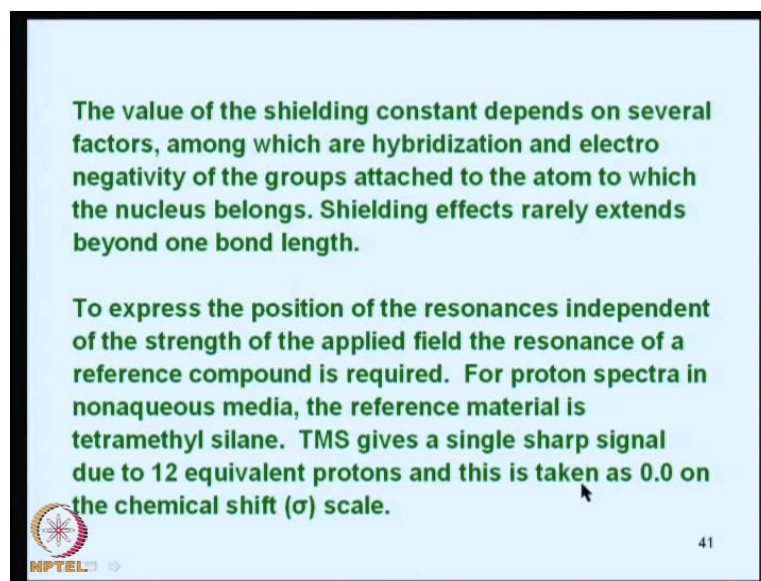
$$H_{eff} = H_0 - \sigma H_0$$

where σ is a shielding constant which can be positive or negative. The more the field induced by the circulating electrons shielding the nucleus (opposes the applied field), the higher must be the applied field to achieve resonance.

So, you would get different kinds of spectra defined by the shielding constant given by, H 0 minus sigma H 0; this we have already discussed. But, what is more important is? The more the field is induced by the circulating electrons shielding the nucleus, the higher must be the applied field to achieve resonance. The field is more; field applied field also should be more to obtain the resonance.

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The value of the shielding constant depends on several factors, among which are hybridization and electro negativity of the groups attached to the atom to which the nucleus belongs. Shielding effects rarely extends beyond one bond length.

To express the position of the resonances independent of the strength of the applied field the resonance of a reference compound is required. For proton spectra in nonaqueous media, the reference material is tetramethyl silane. TMS gives a single sharp signal due to 12 equivalent protons and this is taken as 0.0 on the chemical shift (σ) scale.

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So, the value of the shielding constant depends on several factors, among which are hybridization and electro negativity of the groups attached to the atom to which the nucleus belongs. The shielding effects rarely extends beyond one bond length; that means, if you have a long molecule the shielding effect a particular proton experiences. Does not it will experience only from the carbon atoms and the environment to the next carbon atoms and not next to next or something like that.

So, to express the position of the resonances independent of the strength of the applied field the resonance of a reference compound is required. For proton spectra in no aqueous media, the reference is tetramethyl silane, so, this does not have any hydrogen groups. TMS gives a single sharp signal due to 12 equivalent protons and this is taken as 0.0 on the chemical shifts scale; that means, you take the spectra of tetramethyl silane applied say this is the zero; from this is the reference material, from which we measure the different chemical shifts.

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The magnitude of the chemical shift is expressed as parts per million:

$$\delta = \frac{H_{ref} - H_{sample}}{H_{reference}} \times 10^{-6} = \frac{V_{sample} - V_{reference}}{V_{reference}} \times 10^{6}$$

where H_{ref} and H_{sample} are the positions of the absorption lines for the reference and the sample, respectively expressed in Gauss and V ref and V sample are the corresponding frequencies expressed in hertz. A positive σ represents a greater degree of shielding than in the reference.

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So, the magnitude of the chemical shift is expressed as simple equation like this; that is delta is equal to H reference minus H sample by H reference multiplied by 10 raise to minus 6 that is for the applied field; and which can be converted which is almost equal into v reference v sample and multiplied by 10 raise to 6. So, positive delta shift represents greater degree of shielding than the reference.

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For other nuclei, recommended reference materials are:

CS_2 or TMS for ^{13}C
CCl_3F for ^{19}F
NH_3 liquid for ^{14}N and ^{15}N
TMS for ^{29}Si
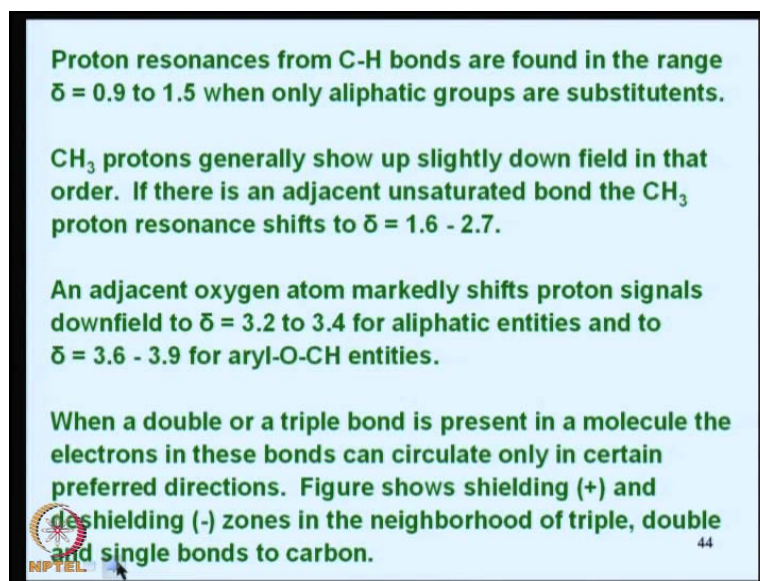85% Orthophosphoric acid for ^{31}P

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If it comes on the right side, then we know that; it is a longer the positive shift. So far, other nuclei the recommended reference materials are: carbon disulphide for C 13, carbo

CCL 3 F for 19 F, and ammonia you can use it for 14 N and 15 nitrogen, TMS is for 29 silicon and 85 percent orthophosphoric acid for phosphorous, you can see that most of the reference materials contained florid of 19; of it is there has to be one florin for nitrogen there has to be nitrogen, silicon is silicon and for phosphorous it has to be orthophosphoric acid these are the reference materials.

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Proton resonances from C-H bonds are found in the range δ = 0.9 to 1.5 when only aliphatic groups are substitutents.

CH_3 protons generally show up slightly down field in that order. If there is an adjacent unsaturated bond the CH_3 proton resonance shifts to δ = 1.6 - 2.7.

An adjacent oxygen atom markedly shifts proton signals downfield to δ = 3.2 to 3.4 for aliphatic entities and to δ = 3.6 - 3.9 for aryl-O-CH entities.

When a double or a triple bond is present in a molecule the electrons in these bonds can circulate only in certain preferred directions. Figure shows shielding (+) and deshielding (-) zones in the neighborhood of triple, double and single bonds to carbon.

So, proton references from C- H bonds are found in the range delta is equal to 0.9 to 1.5 when aliphatic groups are the substituents. So, now, we are talking about the chemical shifts, where the peaks may appear. So, from tetrarmythl silane the shift should be 0.9 to 1.5.

For methyl protons they generally show ups slightly down the field in that order. If there is an adjacent unsaturated bond the proton shifts will you will be observing slightly higher than this 1.5, but in the range of 1.6 to 2.7 ranges. So, supposed there is an adjacent oxygen atom like O, H group then this shifts the proton signal down field almost 3.2 to 3.4 for aryl groups or aryl-O-CH entities. And for 3.6 to 3.9 for aryl groups that is aryl oxygen and C H entities, C 6, H 5, O C H 3 something like that you would be seeing the chemical shifts of the order of what 3 .6 to 3.9.

Suppose there is a double bond or triple bond present in the molecule the electrons in these bonds can circulate only in particular directions double bond is always parallel to be main axis so, but the actual electronic orientation is perpendicular to that. So, this

figure shows shielding and deshielding zones in the neighborhood of triple bond ,double bond and single bonds to carbon, just look at this figure.

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So, here you can see this is the triple bond, and this is the double bond; this shielding effect is like this and the this is minus, this is plus and this is plus and this is for aromatic compounds induced magnetic fields have got to be above the basic ring structure and below the basic ring structure. So, the electrons are got to be moving around it like this similarly on the other side also.
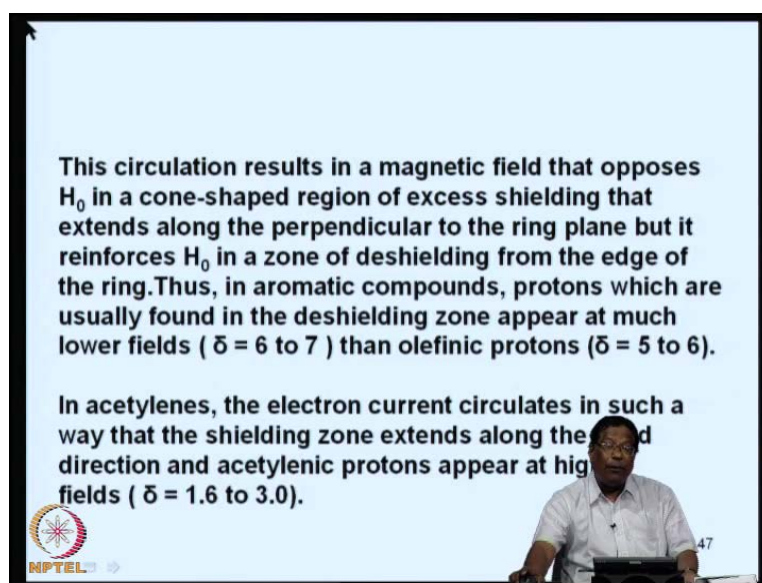
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So, in carbon carbon double bond and carbon oxygen double bond suppose there are you are handling different compounds, the deschielding zone extends along the bond direction. The carbon carbon bonds also show this some amount of deshielding in this direction; that is single bonds. The deshielding of a proton depends upon the latter's distance from the bond and also on its orientation with respect to that bond, alternative or aromatic ring structures have a strong anisotropic field effect. And the delocalized pi electrons of an aromatic ring circulate in a two doughnut-shaped orbits on each side of the ring, just just now; I have shown you this doughnut-shaped ring.

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This circulation results in a magnetic field that opposes H_0 in a cone-shaped region of excess shielding that extends along the perpendicular to the ring plane but it reinforces H_0 in a zone of deshielding from the edge of the ring. Thus, in aromatic compounds, protons which are usually found in the deshielding zone appear at much lower fields (δ = 6 to 7) than olefinic protons (δ = 5 to 6).

In acetylenes, the electron current circulates in such a way that the shielding zone extends along the bond direction and acetylenic protons appear at high fields (δ = 1.6 to 3.0).

So, the circulation results in a magnetic field that opposes the applied magnetic field H 0 in a cone-shaped region of excess shielding that extends along the particular that extends of along the perpendicular to the ring plane, but reinforces H 0 in a zone of deshielding from the age of the ring. Thus, in aromatic compound protons which are usually found in the deshielding zone appear at much lower fields approximately delta shift should be between 6 and 7.

Then the olefinic electrons where an olefin electrons will show you the shift between 5 and 6. So, in acetylenes it has to be still less, the electron current circulates in such a way that the shielding zone extends along the bond direction, and acetylene protons appear at still higher fields approximately 1.6 to 3.0.

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CHEMICAL SHIFT OF SOME COMPOUNDS

Substituent group	Methyl protons (δ)	Methylene protons (δ)	Methine proton (δ)
HC—Cl	3.05	3.45	4.05
HC—OH and —OR	3.20	3.40	3.60
HC—NH$_2$	3.50	3.75	4.05
HC—O(C=O)R	3.65	4.10	4.95
HC—OAr	3.80	4.00	4.60
HC—O(C=O)Ar	3.80	4.20	5.05
HC—F	4.25	4.50	4.80
HC—NO$_2$	4.30	4.35	4.60
Cyclopropane		0.20	0.40
Cyclobutane		2.45	
Cyclopentane		1.65	
Cyclohexane		1.50	1.80
Cycloheptane		1.25	

Substituent group	Proton shift (δ)	Substituent group	Proton shift (δ)
HC≡CH	2.35	HO—C=O	10–12
HC≡CAr	2.90	HO—SO$_2$	11–12
HC≡C—C=C	2.75	HO—Ar	4.5–6.5
HAr	7.20	HO—R	0.5–4.5
HCO—O	8.1	HS—Ar	2.8–3.6
HCO—R	9.4–10.0	HS—R	1–2
HCO—Ar	9.7–10.5	HN—Ar	3–6
HO—N=C(oxime)	9–12	HN—R	0.5–5

SOURCE: J. A. Dean, ed., *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, 1985, in which additional proton chemical shifts may be found. *NOTE:* Values are given on the officially approved δ scale. R = alkyl group; Ar = aryl group.

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Now, you would see that, I have listed here some of the chemical shift of some compounds that is H C- C l; that is carbon chlorine and this hydrogen where you would see, if it is methyl you would see 3.05 and if it is methylene protons; it is around 3.45, if it is methane, protons like in acetylene groups they shift would be around 4 .05.

Similarly, data bases are available for different types of compounds for example, the second one is H C- O H instead of chlorine or here you would see the numbers like 3.20 for methyl 3.40 for methylene and 3.60 for methane groups. So, suppose you have a cyclopropane group all of them are approximately equivalent, but if the substituents are methylene, protons then the chemical shift would be hardly 0.20 and this would be around 0.40, I suggest you study all these chemical shifts to get an idea of about, how these chemical shifts are manipulated? And then interpreted this, I had taken it from J A D, Lange's handbook of chemistry 13 edition it is available.

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Similarly, I put the data of our chemical shifts of some compounds like alkenes and then halides, alkynes, alkenes, etcetera. Here, in this case; it is primary carbon, secondary carbon, tertiary carbon and quaternary carbon. And substituent groups will show the delta chemical shifts in this range and it is a good idea to study the effect of functional groups and the shifts.

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Now, let us discuss about the spin-spin coupling. Nuclei in proximity with each other causing a splitting of resonance lines into multiples. So, this I have shown you a figure of

C 2, H phi I; this is called a spin-spin coupling or J coupling. This is due to the interaction of magnetic moments of the nuclei through the magnetic properties of the electrons in the intervening bonds. The strength of the coupling is denoted by J which is equal to the spacing of the multiples in hertz. So, the proton-proton couplings in aliphatic organic compounds are normally transmitted through only two or three bonds.

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So, the proton spin coupling also I have put it in in this small table, we can go through this and study the proton-proton spin coupling.

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In the double bond spectrums double bond straight chain systems coupling can be observed over several bond lengths. In aromatic rings coupling of protons in ortho positions you can calculate from the table, you can see that there are around 7 to 9 hertz and for meta it is 2 to 3 and for Para positions it is 0.5 to 1; that means, depending upon the chemical shifts you can find out whether particular substituent is in Roth meta or Para.

So, coupling also depends further on the geometry. So, axial-axial protons are strongly coupled, but axial-equatorial and equatorial-equatorial protons are coupled moderately. It has been shown that the J translation and J eis is approximately 2. The number of lines in a multi plate is always given by 2 and plus 1 lines.

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So, in a multi plate, the total intensity also varies according to the proportional to the number of nuclei involved and the individual peaks follow the coefficients of binomial expansion. For example, one neighboring proton splits the observed resonance into a double and two will produce a triplet of 1 is to 2 is to 1, ratio three would be a quartet with 1 is to 3 is to 3 is to 1 and four would be a quintet with 1 is to 4 is to 6 is to 4 is to 1 etcetera.

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> **The magnitude of J is independent of the field strength.**
> **Other nuclei with spin 1/2., i.e., ^{19}F and ^{31}P interact**
> **with protons and cause spin-spin splitting. J is usually**
> **larger than for proton-proton coupling. ^{13}C proton**
> **coupling can be noticed.**
>
> **When a proton is coupled to a nucleus that has a**
> **quadrupole moment, spin-lattice relaxation becomes so**
> **efficient (T_1 is reduced) that the spin-spin interaction**
> **with proton is greatly or completely decoupled.**
> **Coupling of protons with chlorine, bromine or iodine is**
> **thus not observed. In case of ^{14}N, the decoupling is**
> **partial, so ^{14}N-^{1}H protons give a broad peak.**
>
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So, the magnitude of the J is independent of the field strength, but other nuclei with spin half etcetera; that is 19 F and 31 P interact with protons and cause spin-spin splitting. So, when a proton is coupled to a nucleus that has a quadruple moment spin-lattice relaxation becomes. So, efficient that the spin-spin interaction becomes proton is greatly or completely decoupled coupling of protons with chlorine bromine iodine is etcetera is therefore, not observed.

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> **NUCLEAR OVERHAUSER EFFECT (NOE)**
>
> The nuclear overhauser effect is observed when the
> signal of one nucleus (^{1}H) is saturated and that of
> another nucleus (^{13}C) is not spin coupled. Decoupling
> takes place due to intra-molecular dipole-dipole
> relaxation. The intensity of the signal (^{13}C) will be more
> than the total intensities of the multiplets that would have
> shown up if there was no decoupling. This additional gain
> in intensity is the overhauser effect. This arises because
> saturation of one nucleus (^{1}H) causes a change in the
> population of the nuclear energy levels of the other
> nucleus (^{13}C).
>
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So, what I we will continue our discussion and there are hardly about three or four figures slides in which I want to convey the remaining information and then we will move on to the electrometric techniques. .