Advance Analytical Course

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Lecture No. # 35

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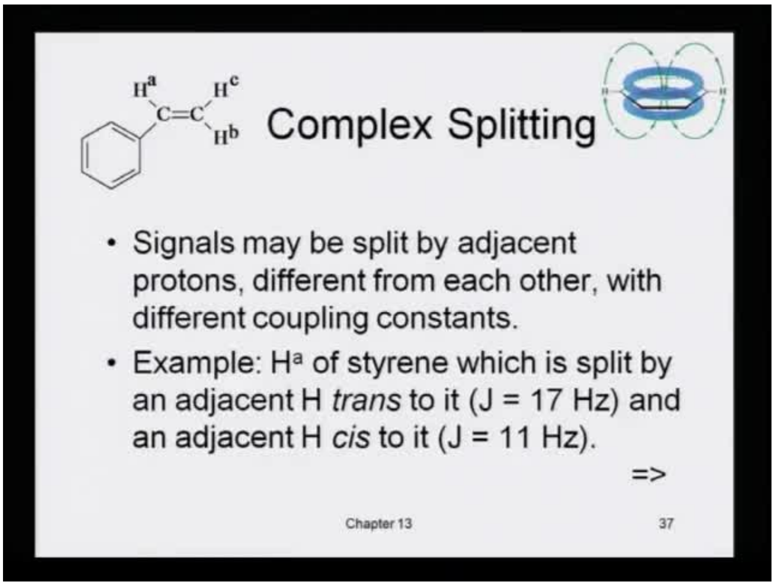

Complex Splitting

- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- Example: H^a of styrene which is split by an adjacent H *trans* to it (J = 17 Hz) and an adjacent H *cis* to it (J = 11 Hz).

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We were trying to look at a little more complicated splitting system, and in the case of styrene, the signals may be split by adjacent proton, different from each other, with different coupling constants.

So, we were looking at the coupling constant or the J values, and how these J values can differ - because the environment of these protons is quite different. If one tries to look at the H a, H b, H c, all 3 are ethylenic bond protons, but they have a different environment. As a result, they show a little complicated splitting pattern.

For example, the H a of styrene, which is split by an adjacent H trans to it, which is H b. If the coupling constant will be 17 hertz and with its own adjacent hydrogen, which is cis to it, the coupling constant will be 11 hertz.

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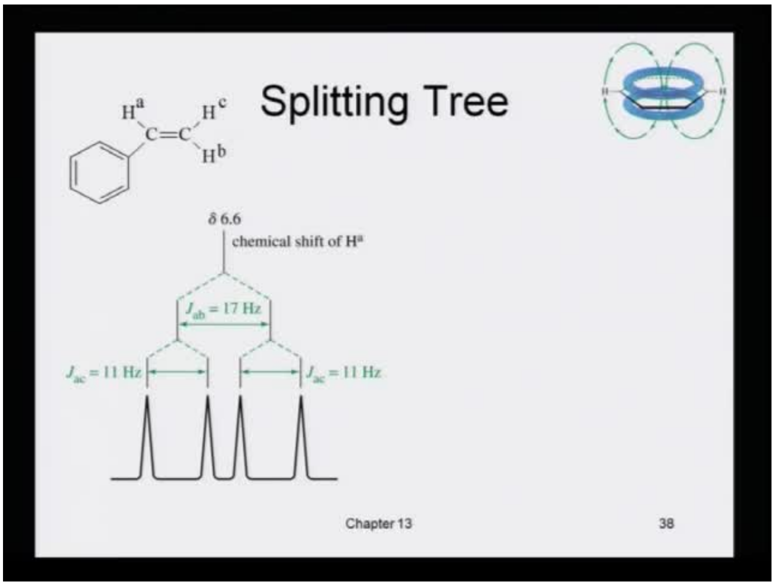
Splitting Tree

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So, that is the kind of splitting pattern or splitting tree that one shows, because all these protons appear at delta value, of ppm value 6.6, that is, the chemical shift. But the splitting patterns are showing the a b and the a c, have a different kind of splitting pattern altogether.

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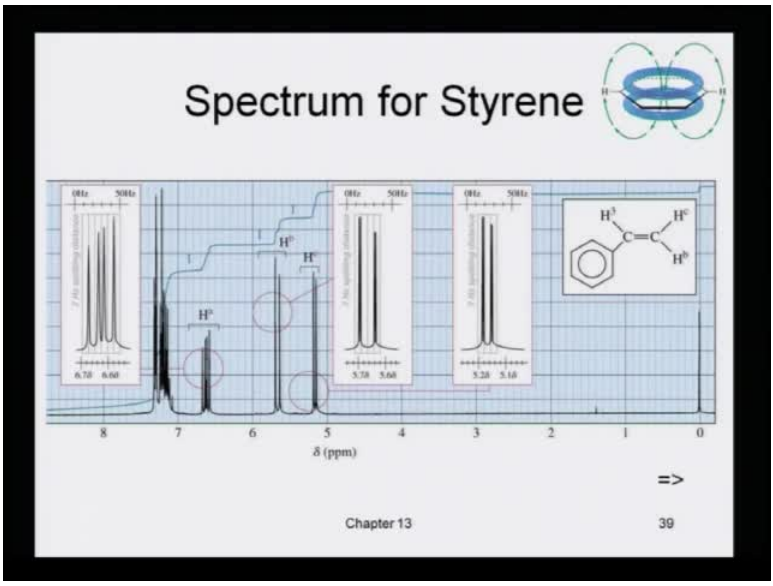
Spectrum for Styrene

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Now, coming to yet another complicated…, So, this is how the NMR spectrum of styrene looks like, it is a jumble of protons between 7 to 8. Then, there are several protons, which is representing the H a, then there are doublet at H b and at H c. So, this is a very, very typical splitting pattern of styrene molecule.

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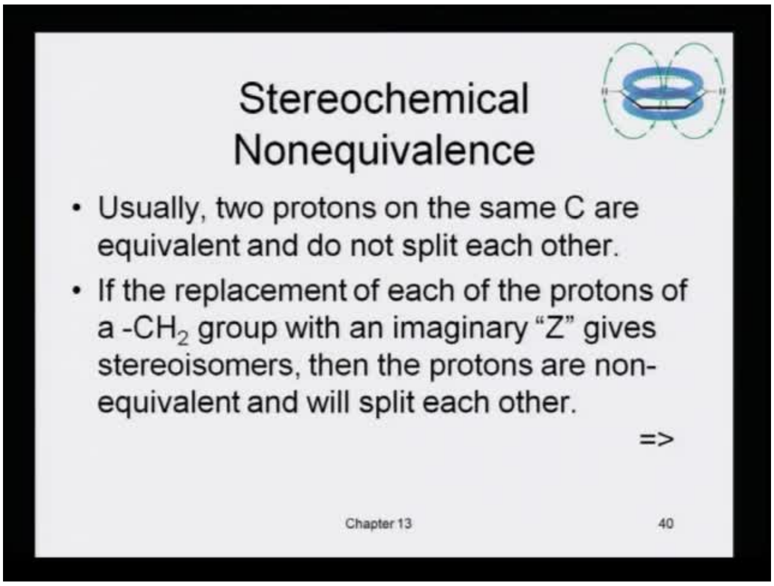

Stereochemical Nonequivalence

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

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When the protons are stereo chemically non-equivalent, then what happens? Usually 2 protons on the same carbon are equivalent and do not split each other. Therefore, you know, if the replacements of each of the protons of the CH 2 group with an imaginary X gives a stereoisomer, then the protons are non-equivalent and will split each other. So, this is a special type of situation.

When there are 2 protons on the same carbon and if the protons are replaced by say, another group, then what happens? Then, they become non-equivalent and therefore, they will show splitting pattern.

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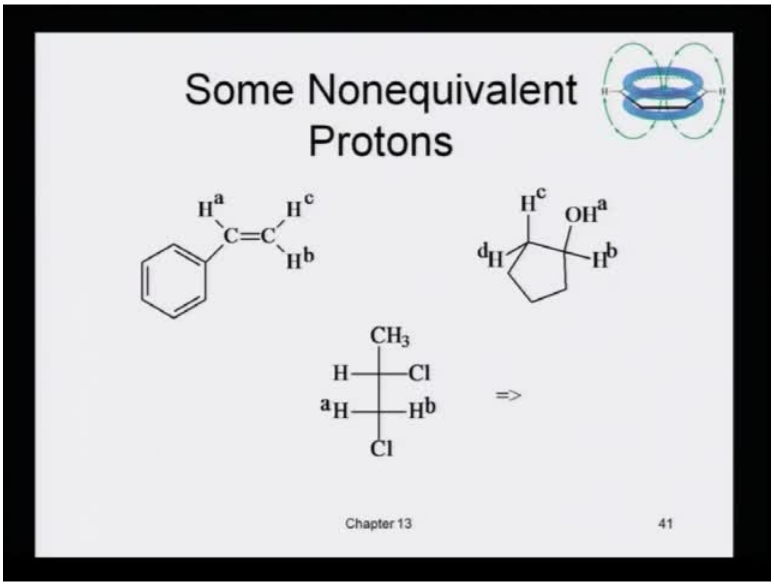

Some Nonequivalent Protons

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Some examples of non-equivalent protons would be the example of styrene or in this case, the cyclo pentene or pentol. And in this case, where we have methyl H Cl and H, the Cl is at a different place. So, these are different types of molecules where the protons are non-equivalent.

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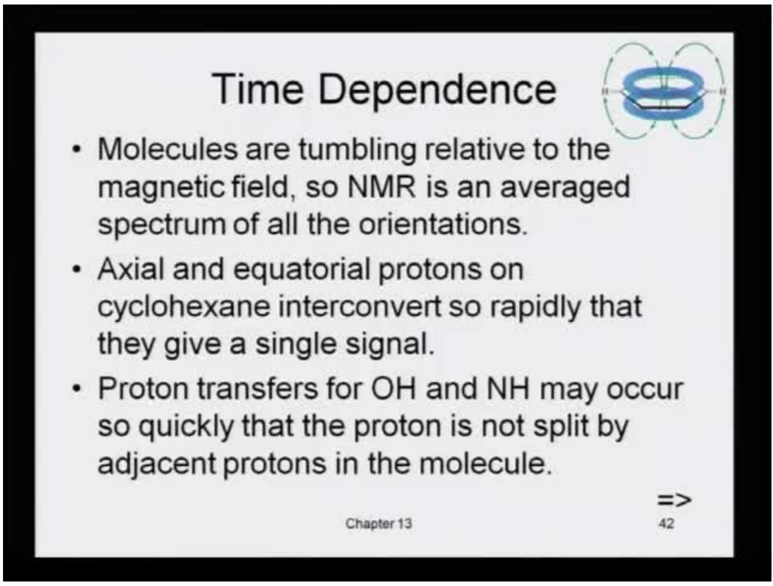

Time Dependence

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

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Now, time dependence - molecules are tumbling relative to the magnetic field, all the time. So, NMR is an averaged spectrum of the orientation.

The molecule, because of the radio frequency being shown on it, is all the time in the state of tumbling or rotatory motion and so it is averaged out, that when the spectrum is taken, all these different orientations are averaged out.

Axial and equatorial protons on cyclo hexane interconvert so rapidly, that they give a single signal. Now, as you all know, that cyclo hexane can exist as chair form or as board form and between the chair form and the board form, the protons actually change from axial to equatorial and equatorial to axial. So, now, because if they are in a state of rotation, it is possible, that they interchange very rapidly and therefore, they do not exist either as axial or as equatorial, in an isolated case. But they are all the time flipping from axial to equatorial and therefore, they will give only 1 type of signal.

Proton transfers for OH and NH may occur so quickly, that proton is not split by the adjacent proton in the molecule. So, that is also possible, particularly when it is, the proton is attached to a heteroatom like oxygen or nitrogen. The proton transfer can take place so quickly, that the proton does not show any kind of splitting with the adjacent proton.

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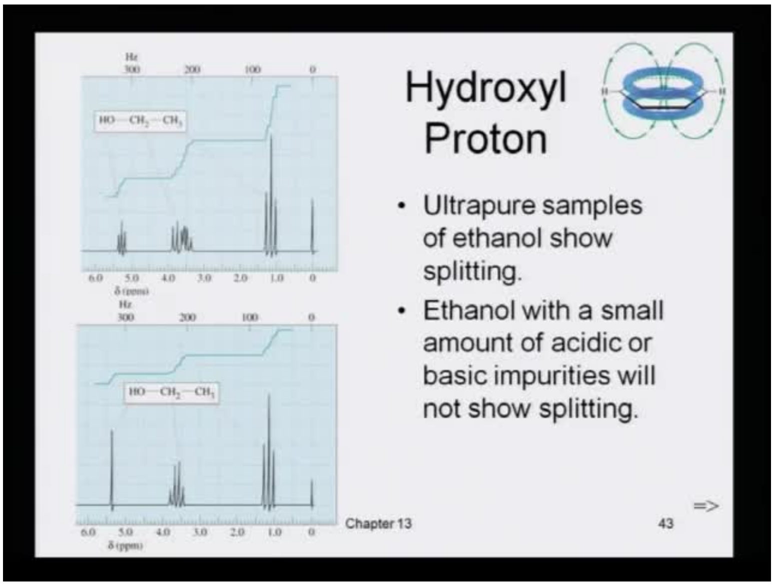

Hydroxyl Proton

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

Therefore, if one tries to look at the hydroxyl proton of a simple ethanol, one can see that the splitting pattern would show a triplet, a multiplet and a triplet, but that is how it should ideally be. Ultrapure samples of ethanol show splitting of this kind and ethanol with a small amount of acidic or basic impurities will not show splitting, why? Because this change does not take place.

So, just now I said, that protonated OH and NH will not show splitting, so that is the reason why, in, when ultrapure sample of ethanol is taken, this is the usual splitting pattern. But when the ethanol is having small amount of acid or base, then the splitting pattern completely changes to a triplet and a quartet and a singlet. So, you see, that there is a difference between the same molecule, if it is in this purest form and if there are some acidic or basic impurities.

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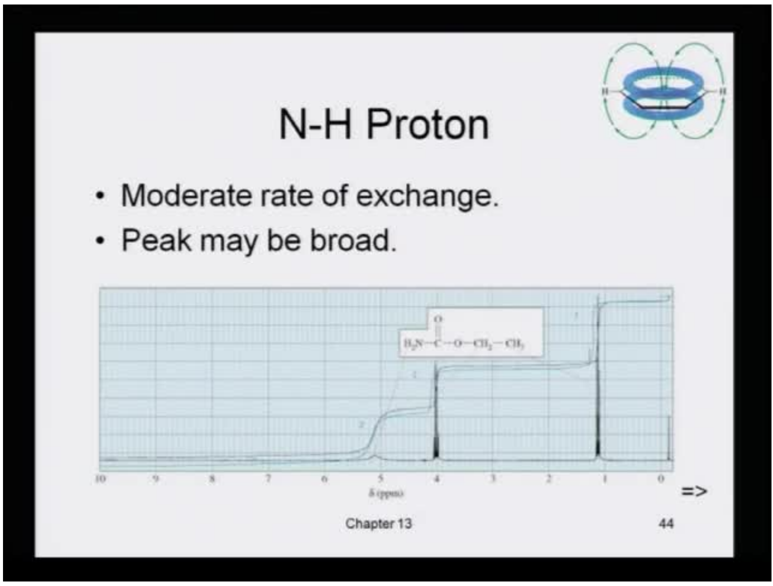

N-H Proton

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

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Now, NH protons - moderate rate of exchange can occur, peak may be broad and therefore, one tries to see, that this kind of substance, which is an amide, can show very broad peaks of the NMR.

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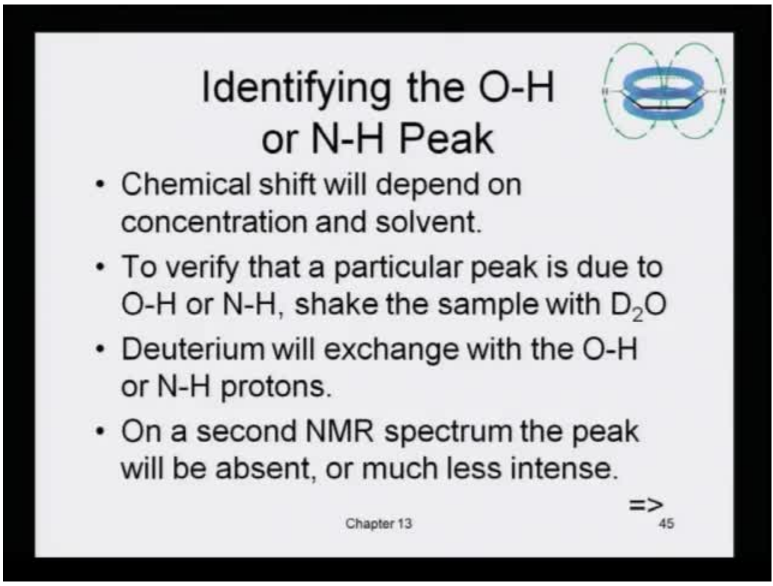

Identifying the O-H or N-H Peak

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

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Identifying whether, how to identify, whether it is belonging to O-H proton or an N-H peak, the best way to do is to look at, the chemical shift will depend on the concentration and solvent; to verify, that a particular peak is due to O-H or N-H, just the sample is shaken with D 2 O, that is deuterated water and this deuterated water can then replace the O-H, the H of the O-H or the N-H and that will be identified. Deuterium will exchange with the O-H, the H of the O-H or N-H protons very readily, and on the 2nd NMR spectrum, the peak will be absent, so much less intense, that it can be identified, that this represents either the O-H peak or the N-H peak.

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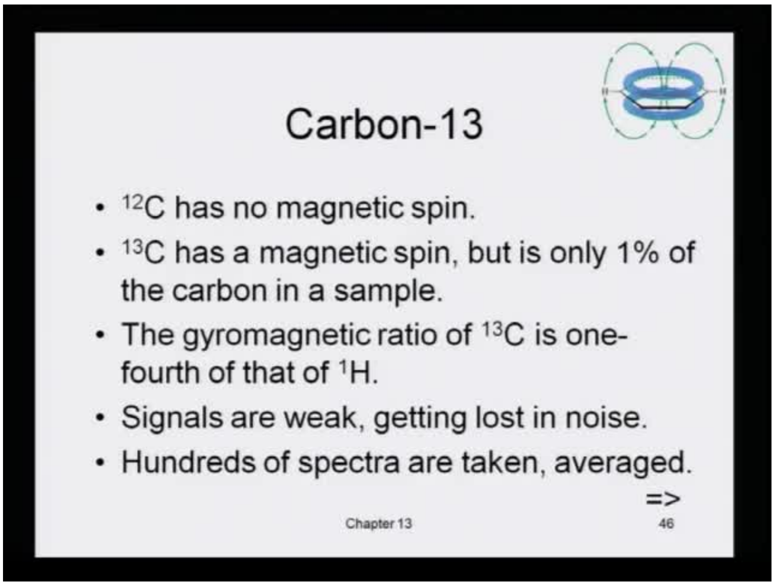

Carbon-13

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

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Now, coming to carbon-13 NMR. It is very interesting, that I had time and again told you, that the backbone of the organic molecule consists of carbon and it is the isotope of carbon, which is 13, which has this nucleus, which is spinning and therefore, only carbon-13 is suitable for NMR analysis and not carbon-12, which is more abundantly present.

Carbon-12 has no magnetic spin, carbon-13 has a magnetic spin but, is only 1 percent of the carbon in the sample, therefore the sample should be taken in large quantities. The gyromagnetic ratio of C-13 is 1-4th of that of the proton. So, you see, that more sample will be required in order to analyze the carbon-13 NMR.

Signals are weak, getting lost in the noise. Sometimes, that is what is happening, because the percentage of carbon-13 in the sample, which contains carbon-12 in 99 percent and 1 percent only carbon-13, shows very poor signals. So, 100 of spectra are taken and then it is averaged out.

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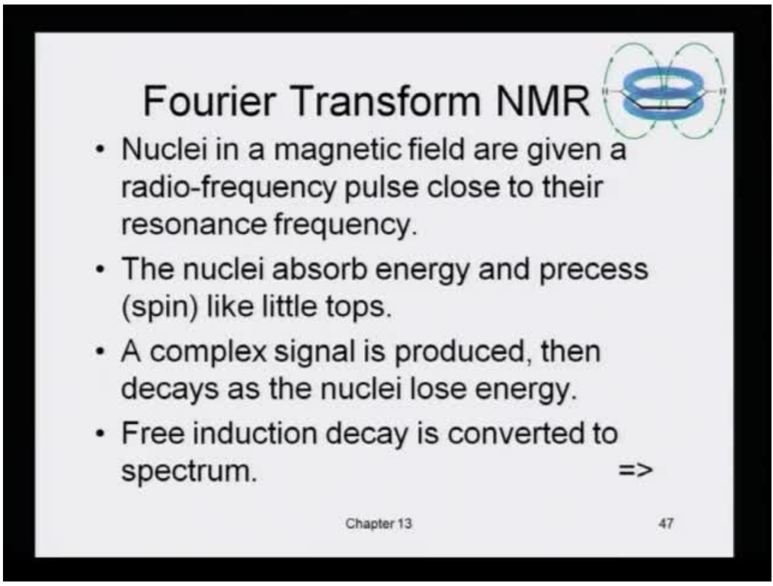

Fourier Transform NMR

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

So, a Fourier transform NMR - just the way we had Fourier transform IR, there we took several spectrum and superimposed it, similarly here also, in NMR, the Fourier transform idea is applied. Nuclei is magnetic, in a magnetic field, are given a radio frequency pulse close to the resonance frequency. Only the ones, which are matching with the frequency, will show resonance, so that has to be borne in mind. Any kind of radio waves will not create any resonance.

The nuclei absorb energy and precess or spins like small tops. A complex signal is produced, then decays as the nuclei lose energy. Free induction decay is converted to spectrum, so this is what is actually, then amplified and recorded as a spectrum. Hydrogen and carbon chemical shifts are quite different because in the hydrogen it is a scale from 0 to 10 and different types of protons, be it acidic proton, aldehydic proton, aromatic proton, acetenelic, ethenylic proton, carbon containing a halogen or carbon, which is adjacent to a carbonyl, they will all fall in the category from 0 to 10.

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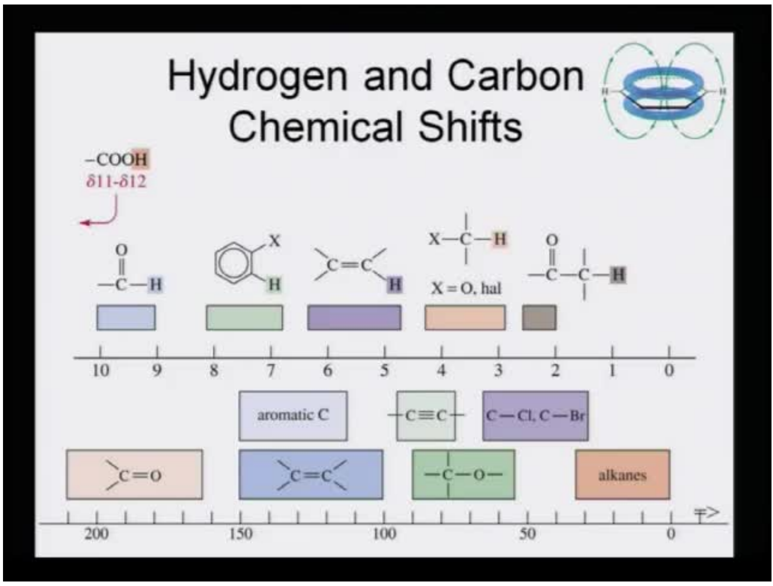

Hydrogen and Carbon Chemical Shifts

However, in the case of carbon chemical shifts, the range is from 0 to 200 and primarily, it is ranging from the alkanes and near 0 to 50, then from 50 to 100 are the ethers or the acetylenes, from 100 to 150 is the range for ethene and aromatic and the carbonyls are in the range of 200, and so on.

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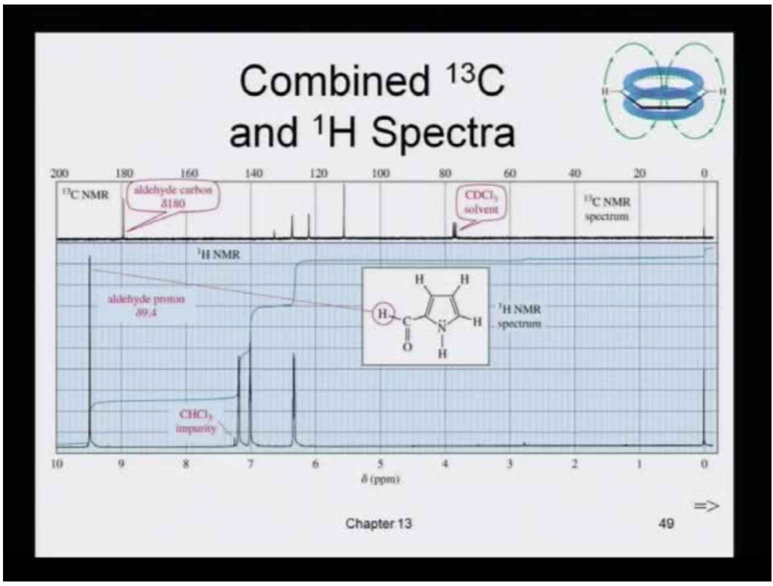

Combined ^{13}C and ^{1}H Spectra

Combined carbon-13 and proton spectra - when we try to look at it, we can have 2 scales, carbon scale on the top and the proton scale at the bottom and both can show different values for different compounds, depicting the positioning. But in the case of carbon-13, it is more like line spectra rather than peak spectra. Whereas, in the case of proton, it is more pronounced, so it looks like a peak, so that is where the difference lies.

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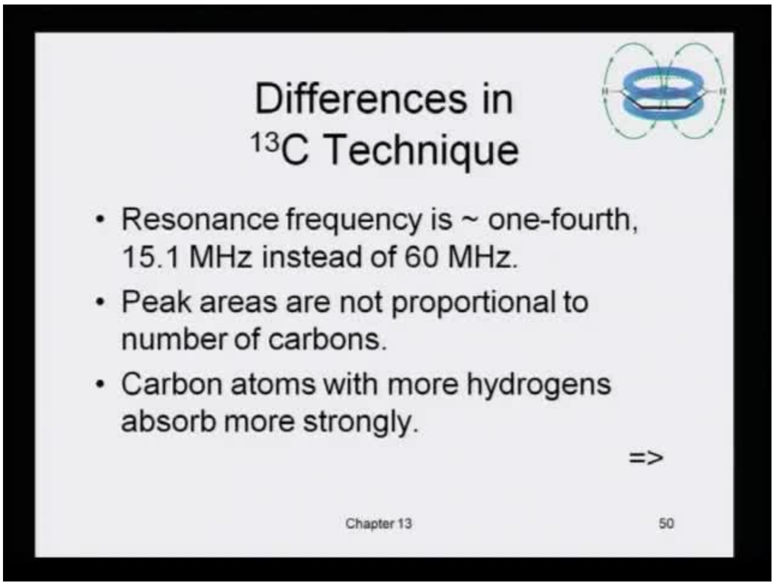

Differences in ^{13}C Technique

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

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Differences in C-13 techniques - because they are much smaller in quantity, the C-13 isotope is much more smaller in quantity, certain adaptations have to be brought about, so that the C 13 content can be recorded. Resonance frequency is 1-4th, that is, 15.1 megahertz instead of 60 megahertz, which was used actually in the case of proton NMR recording. So, it is just 1-4th of that and that is 15.1 megahertz.

Peak areas are not proportional to the number of carbons. So, here, the sign of proportionality does not hold good; the peak areas are not truly proportional. The way we were able to integrate the peak and find out a correlation between the peak height and the number of protons that is not truly applicable in the case of C-13.

Carbon atoms with more hydrogen absorb more strongly. So, it is on the contrary, it is not more number of carbons, but more number of hydrogens on the carbon will absorb. So, those peaks will be more taller as compared, but here also, there is a spin-spin splitting.

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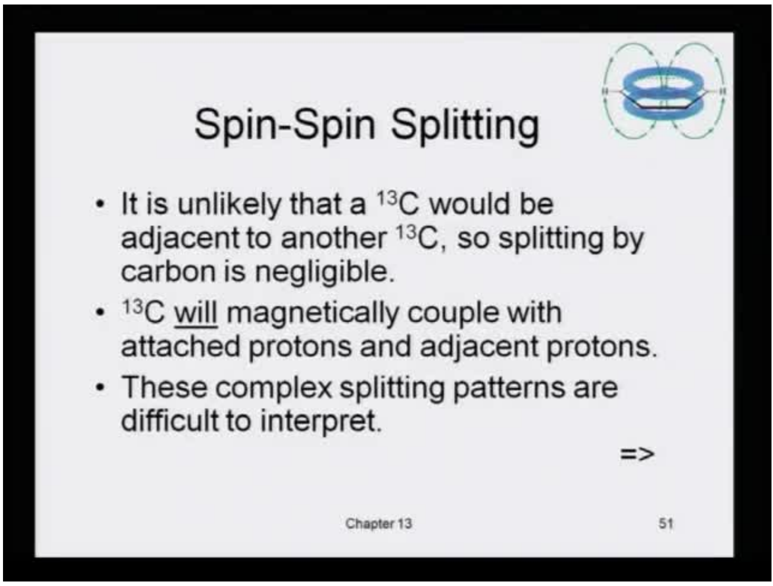

Spin-Spin Splitting

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

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It is unlikely, that the C-13 would be adjacent to another C-13, so splitting by carbon is almost negligible and they do not cause, because as it is the quantity is very small. C-13 will magnetically couple with, adjust, the attached proton and adjacent protons. So, that is why, the proton plays a role with C-13, but C-13 with its C-13 does not play much role in influencing each other. These complex splitting patterns are difficult to interpret. So, because of the proton interfering with the C-13 and splitting occurring because of that, the whole spectrum or the splitting pattern becomes very complicated.

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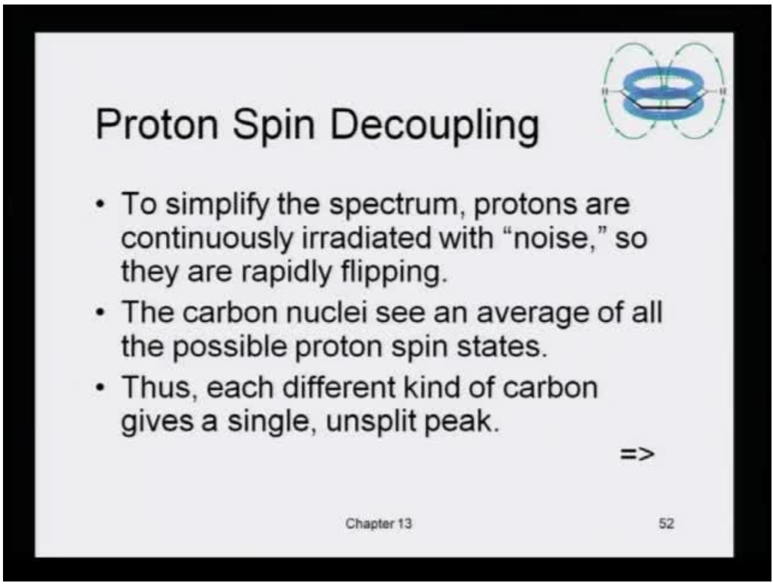

Proton Spin Decoupling

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

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Proton spin decoupling is therefore applied. To simplify the spectrum, the protons are continuously irradiated with noise, so they are rapidly flipping. The carbon nuclei see an average of all the possible protons split states.

So, they, then look at the nuclei and they, kind of, carbon nuclei will see an average of all the possible protons split states, which can influence the carbon. Thus, each different kind of carbon gives a single un-split peak; so, one finds only the line, not a real peak, as what we were seeing in the case of proton.

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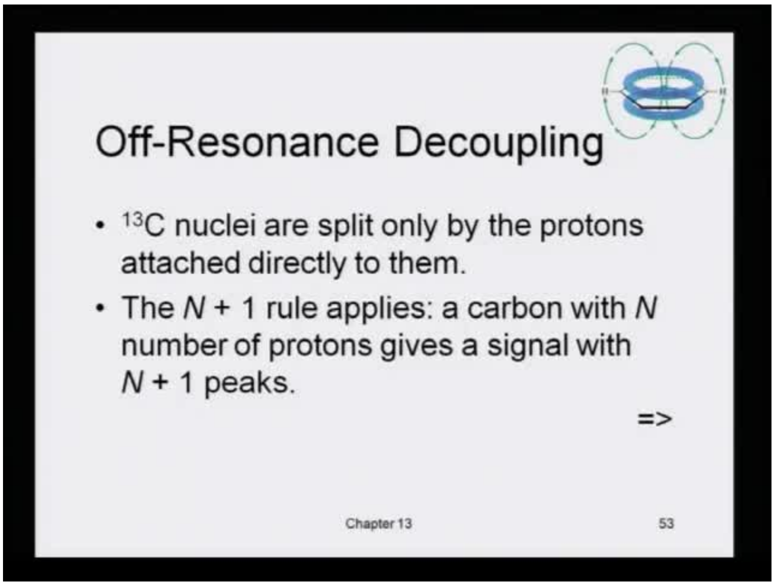

Off-Resonance Decoupling

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

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Off-resonance decoupling is also possible. C-13 nuclei are split only by the protons attached directly to them. So, it is only the protons, which are connected to that carbon will cause the splitting and not the neighboring protons. N plus 1 rule applies; a carbon with N number of proton gives a signal with N plus 1 peaks. So, that rule still holds good.

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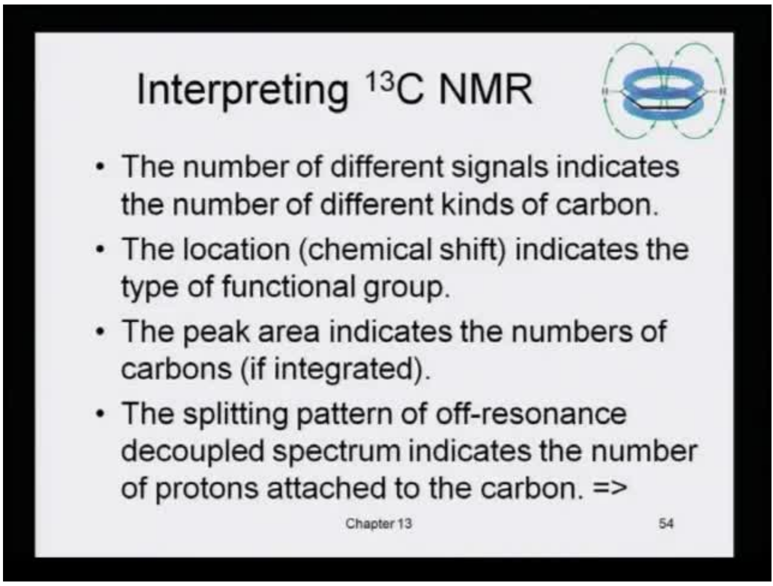

Interpreting ^{13}C NMR

- The number of different signals indicates the number of different kinds of carbon.
- The location (chemical shift) indicates the type of functional group.
- The peak area indicates the numbers of carbons (if integrated).
- The splitting pattern of off-resonance decoupled spectrum indicates the number of protons attached to the carbon. =>

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Interpreting C-13 NMR is a big challenge. The number of different signals indicates the number of different kinds of carbon. So, this should be understood very clearly, that suppose, if you find, that there are 2 or 3 or 4 lines, that means, that there are 2 or 3 or 4 different types of carbon in the molecule. It is not that 3 methyl will give 3 different lines, 3 methyl in the molecule will give only 1 line. So, one type of carbon, one line represented.

The location, that is, the chemical shift indicates the type of functional group. 2nd important point that should be remembered is that the location, where they are ranging from 0 to 200, will be the representing the chemical shift and it is actually, responsible for the functional group that is attached to it. And therefore, if there is a carbonyl or if there is an aldehyde or if there is a double bond, carbon-carbon double bond, it will, all show up very correctly. The peak area indicates the numbers of carbons, if integrated. And the splitting pattern of the off-resonance decoupled spectrum indicates the number of protons attached to the carbon.

So, this I have already said, that because the proton, then tries to interfere the splitting pattern, has to go through an off-resonance decoupled spectrum recording and therefore, if that would indicate, how many protons are attached to the carbon.

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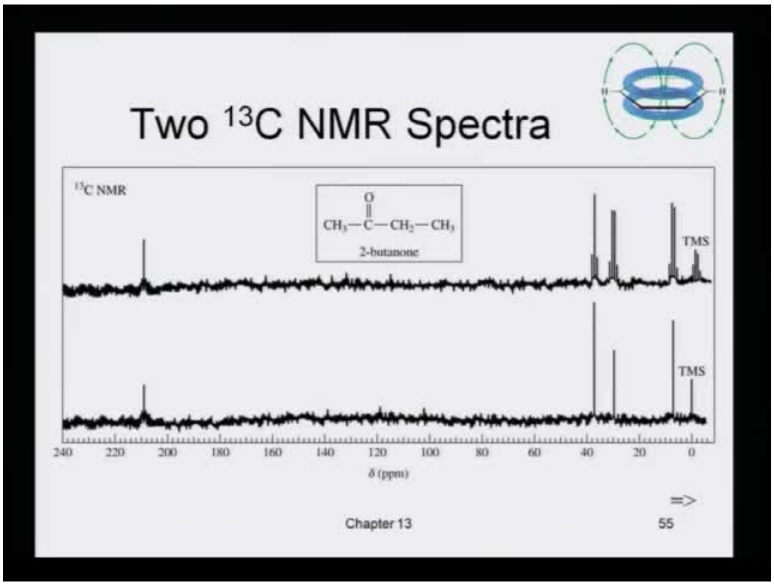

Two ^{13}C NMR Spectra

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A typical, you know, 2 butanone will show C-13 of this kind. So, you see that the peaks are not very clear, but they are truly decoupled in the 2nd one and therefore, they are showing line spectrum, instead of the splitted spectrum.

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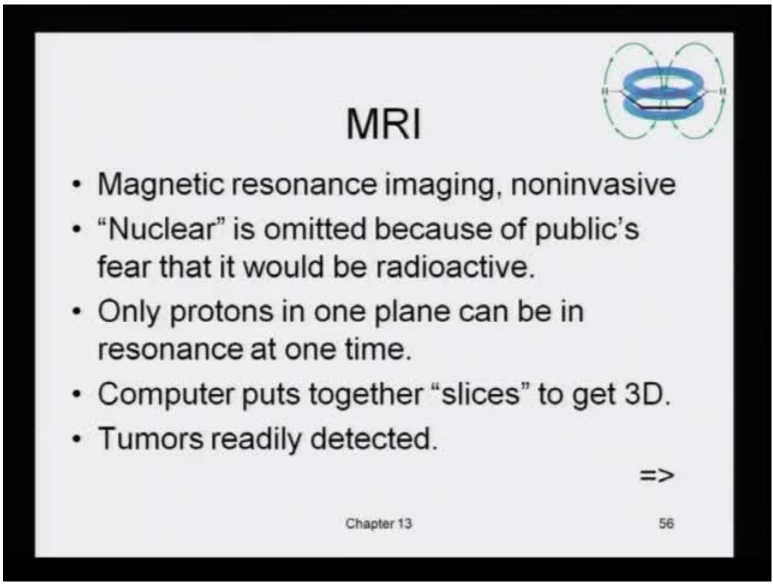

MRI

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

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How is this used for medical sciences? Magnetic resonance imaging is a nonivasive method and it is also used for medical examination. The nuclear is omitted because of the public, that it would be radioactive. Only protons in one plane can be in resonance at one time and computers put together slices to get 3-D, so that a more imaged picture can be obtained. Tumors can be readily detected by this MRI.

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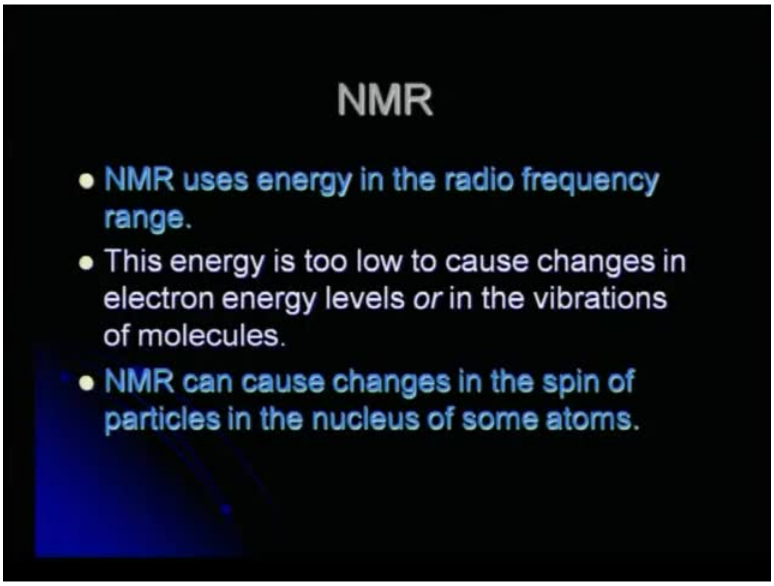

NMR

- NMR uses energy in the radio frequency range.
- This energy is too low to cause changes in electron energy levels *or* in the vibrations of molecules.
- NMR can cause changes in the spin of particles in the nucleus of some atoms.

So, with this, we have come to an end of understanding the NMR phenomenon. I would also try to take you to another experience of understanding or taking a recap of the NMR. It is a slideshow, which will probably be a more like a recap and understanding.

NMR uses energy in the radio frequency range. This energy is too low to cause changes in electronic energy levels or in the vibrations of the molecules. NMR can also cause changes in the spin of particles in the nucleus of some atoms.

So, first thing, that has to be kept in mind very clearly, that NMR uses radiofrequency and these, the energy of radiofrequency is very low. So, it cannot cause any electronic transition, as what we saw, in the case of UV spectroscopy. It cannot even cause a vibration in the molecules, in the bonds of the molecules because there also, the energy content required is in kilo joules. So, here, there is only the excitation or the spinning of the protons or C-13 that can get altered by the radio frequency.

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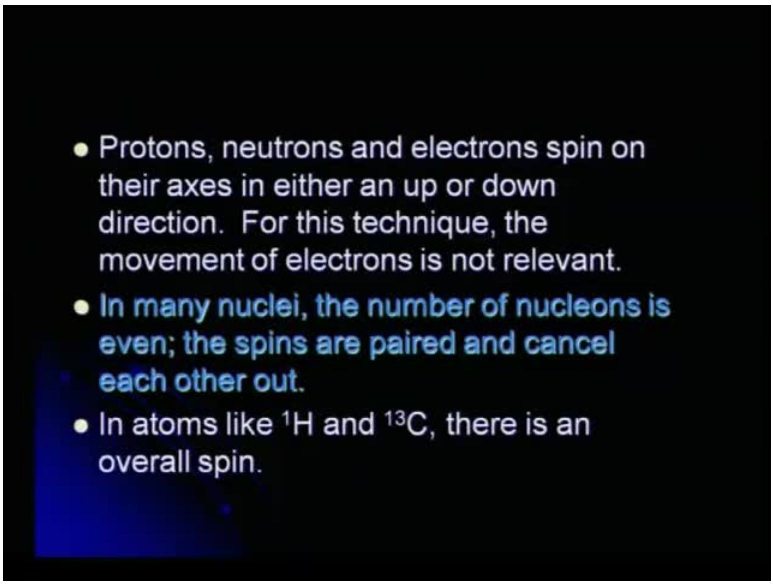

- Protons, neutrons and electrons spin on their axes in either an up or down direction. For this technique, the movement of electrons is not relevant.
- In many nuclei, the number of nucleons is even; the spins are paired and cancel each other out.
- In atoms like ^1H and ^{13}C, there is an overall spin.

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Protons, neutrons and electrons spin on their axes in either and up or down direction. For this technique, the movement of electron is not relevant, why? Because we are talking about proton NMR and electrons are very small entities. In many nuclei, the number of nucleons is even; the spins are paired and canceled out.

So, that is why, only the odd numbered, I had said, that the, an odd numbered atomic number having an odd mass number only are the atoms, which can show or which respond to NMR resonance.

In atoms like proton H-1 and C-13, there is an overall spin because there is an odd electron as well as odd proton.

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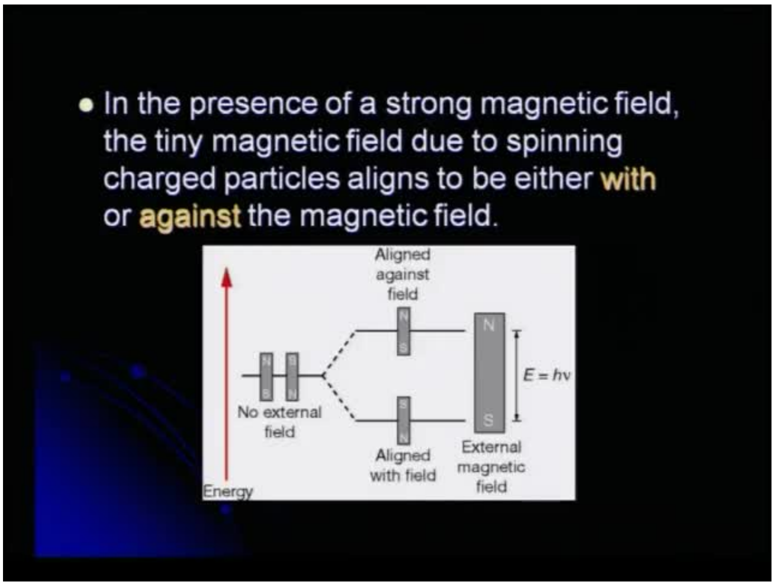

- In the presence of a strong magnetic field, the tiny magnetic field due to spinning charged particles aligns to be either with or against the magnetic field.

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In the presence of a strong magnetic field, the tiny magnet field, due to spinning charged particles aligns to be either with it or against the magnetic field.

So, we, just a while ago, we were discussing, that this small, you know, magnet of the compound can actually align and have lower energy or can align against the field, which will have higher energy as compared to the initial situation when kept in an external magnetic field.

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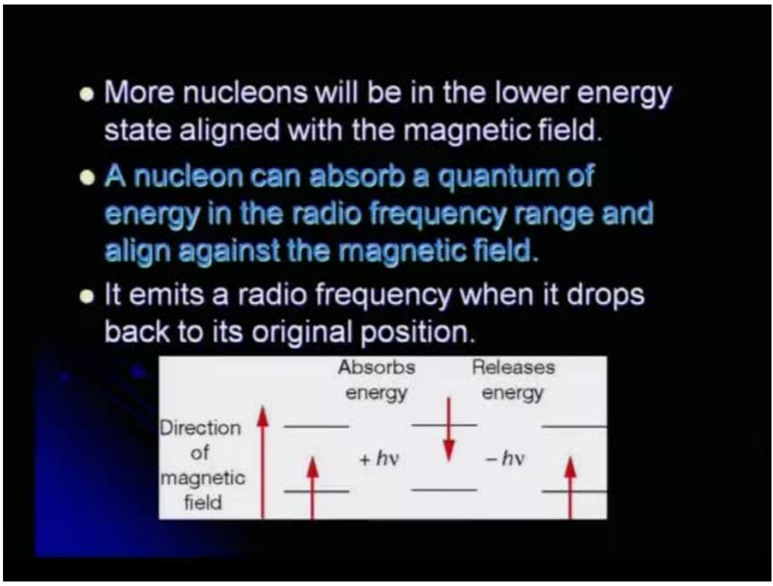

- More nucleons will be in the lower energy state aligned with the magnetic field.
- A nucleon can absorb a quantum of energy in the radio frequency range and align against the magnetic field.
- It emits a radio frequency when it drops back to its original position.

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Therefore, more nucleons will be in lower energy state aligned with the magnetic field. A nucleon can absorb a quantum of energy in the radio frequency range and align against the magnetic field. It emits the radio frequency when it drops back to its original position.

So, as what we very clearly know, that any system cannot remain in the energized situation for too long, it has to revert back. So, if it absorbs energy to get excited, it releases energy h nu to get back to its original state.

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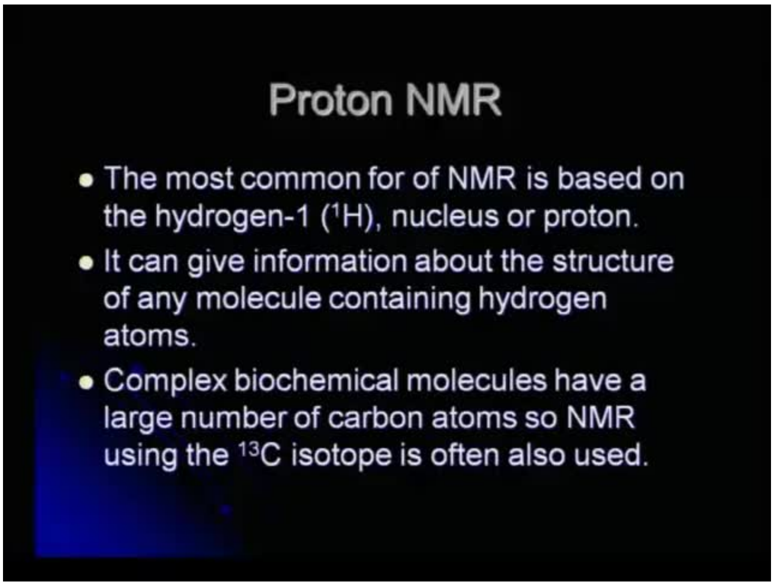

Proton NMR

- The most common for of NMR is based on the hydrogen-1 (^1H), nucleus or proton.
- It can give information about the structure of any molecule containing hydrogen atoms.
- Complex biochemical molecules have a large number of carbon atoms so NMR using the ^{13}C isotope is often also used.

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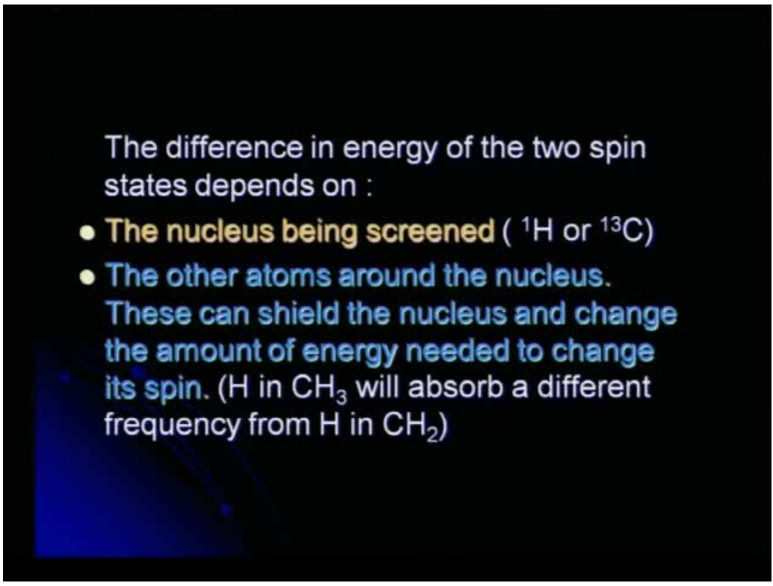

The difference in energy of the two spin states depends on :

- The nucleus being screened (^1H or ^{13}C)
- The other atoms around the nucleus. These can shield the nucleus and change the amount of energy needed to change its spin. (H in CH_3 will absorb a different frequency from H in CH_2)

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Proton NMR therefore, is very importantly understood and it is applied. The most common of the NMR is based on hydrogen or proton nucleus. It can give information about the structure of the molecule containing hydrogen atom. That means, that if we have a carbon chain and the carbon chain obviously has either hydrogen or halogens or oxygen or nitrogen, then what is the kind of arrangement of these hydrogens on the adjacent carbons? Complex biochemical molecules have a large number of carbon atoms, so NMR using C-13 isotope is often used.

The difference in energy of the 2 spin state depends on the nucleus being screened. Whether we are trying to look at the proton NMR or the C-13 NMR, we will get part of the information about the molecule. And when all the information is correlated, that means, information from UV information, from IR spectrum, information from proton NMR, information from C-13, then some idea of the structure of the molecule can be obtained. The other atoms around the nucleus, these can shield the nucleus and change the amount of energy needed to change its spin. So, H in CH 3 will absorb differently at a different frequency as H of the CH 2 and that is why, they appear as 2 different peaks in…, When we saw the example of ethanol, they were 3 different types of protons - one was the proton of OH, one was the protons or 2 protons of CH 2 and the 3rd one was the different variety, which was belonging to the methyl protons. So, those, all the 3, since they had different, you know, spins, that is why, they were diagnosed as different peaks in the spectrum.

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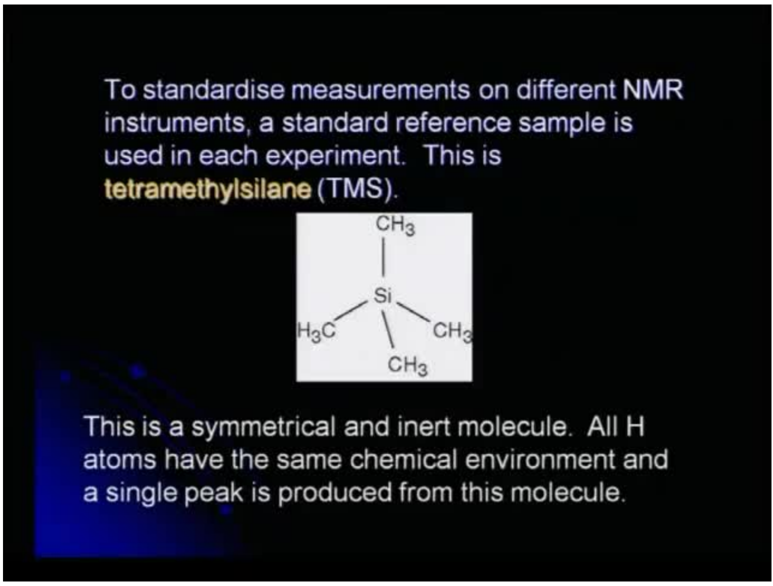

To standardise measurements on different NMR instruments, a standard reference sample is used in each experiment. This is **tetramethylsilane** (TMS).

This is a symmetrical and inert molecule. All H atoms have the same chemical environment and a single peak is produced from this molecule.

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To standardize the measurements on different NMR instrument, a standard reference is required and that is called the tetramethylsilane or the TMS. The beauty of this TMS is that all the 12 protons are equivalent and therefore, it is an inert molecule and all the proton atom or the hydrogen atom have the same chemical environment and shows a single peak, which is taken as a standard or 0.

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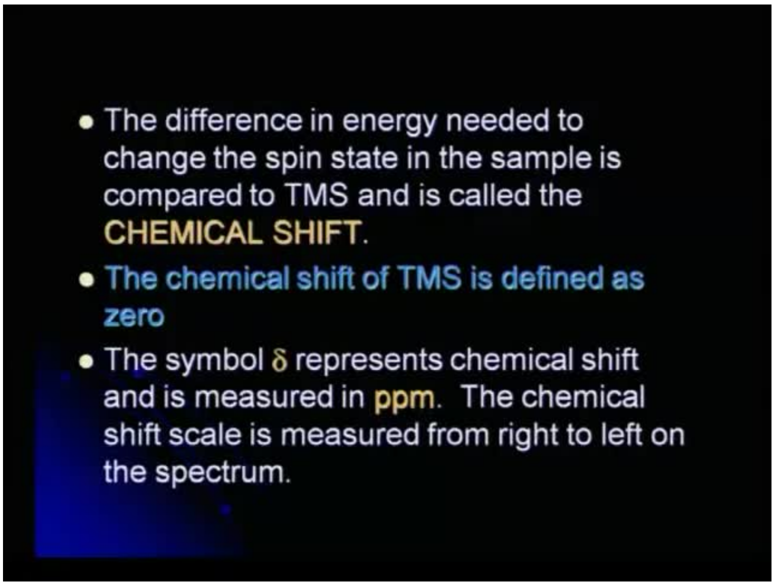

- The difference in energy needed to change the spin state in the sample is compared to TMS and is called the CHEMICAL SHIFT.
- The chemical shift of TMS is defined as zero
- The symbol δ represents chemical shift and is measured in ppm. The chemical shift scale is measured from right to left on the spectrum.

The difference in energy needed to change the spin state in the sample is compared to TMS and is called the chemical shift. The chemical shift of TMS is identified as 0. The symbol delta represents the chemical shift and is measured in ppm. The chemical shift scale is measured from right to left on the spectrum.

So, these things we have already covered, but it is like a recap, that I want you to understand what are the salient features of NMR. What does the words chemical shift mean? That chemical shift word means a particular proton attached to a particular type of carbon, will appear at a particular position in the scale of 0 to 10.

And we took an overview of different types of protons, which were attached to different types of carbons and we found, that the value for these different carbon containing protons show different values and that value is what is referred as chemical shift. So, these jargons, this particular nomenclature, these naming methods, must be very clear. Delta or ppm are equivalent and that is the scale 0 to 10 delta, you can say, or 0 to 10 ppm and we move from, this is the right side, from right to left we start moving because the rightest corner is the 0 of the TMS.

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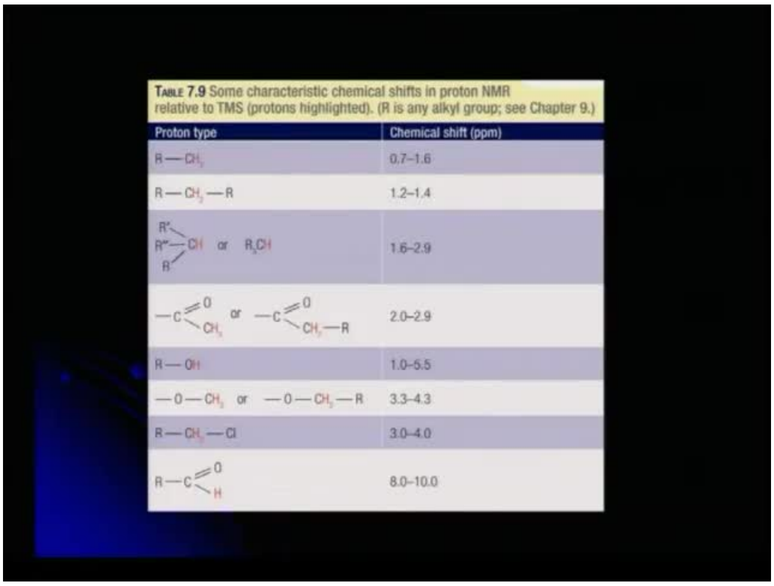

TABLE 7.9 Some characteristic chemical shifts in proton NMR relative to TMS (protons highlighted). (R is any alkyl group; see Chapter 9.)

Proton type	Chemical shift (ppm)
$R-CH_3$	0.7–1.6
$R-CH_2-R$	1.2–1.4
$R'R''R-CH$ or R_3CH	1.6–2.9
$-C(=O)-CH_3$ or $-C(=O)-CH_2-R$	2.0–2.9
$R-OH$	1.0–5.5
$-O-CH_3$ or $-O-CH_2-R$	3.3–4.3
$R-CH_2-Cl$	3.0–4.0
$R-C(=O)-H$	8.0–10.0

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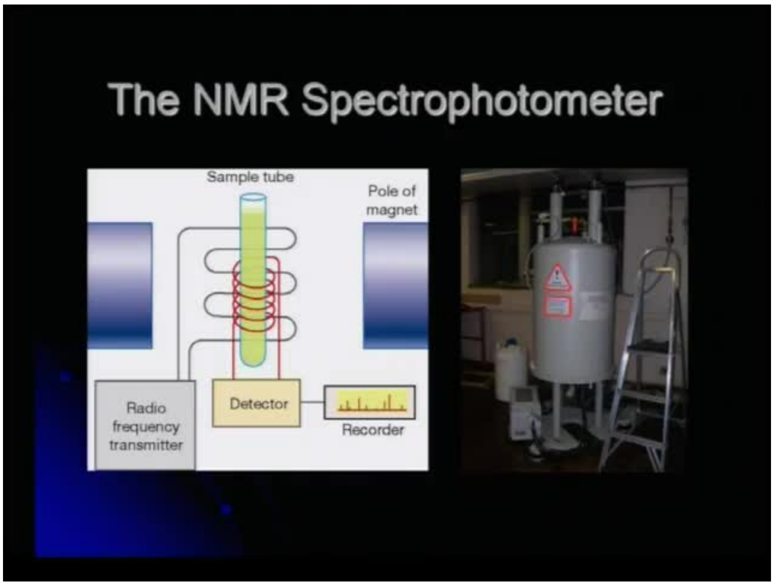

The NMR Spectrophotometer

So, when we try to look at various NMR values, we have already taken a look; this is what the spectrum looks like.

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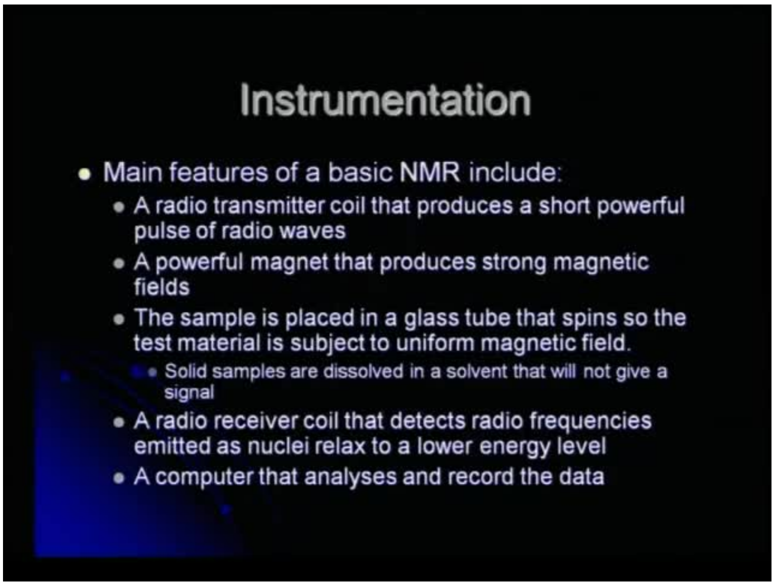

Instrumentation

- Main features of a basic NMR include:
  - A radio transmitter coil that produces a short powerful pulse of radio waves
  - A powerful magnet that produces strong magnetic fields
  - The sample is placed in a glass tube that spins so the test material is subject to uniform magnetic field.
    - Solid samples are dissolved in a solvent that will not give a signal
  - A radio receiver coil that detects radio frequencies emitted as nuclei relax to a lower energy level
  - A computer that analyses and record the data

.

The main instrumentation, main feature of the basic NMR includes, that it should have a radio transmitter coil that produces a short powerful pulse of radio waves; a powerful magnet that produces strong magnetic fields. The sample is placed in a glass tube that spins, so that the test material is subjected to uniform magnetic field. Solid samples are dissolved in a solvent that will not give any signal of its own; so, that has to be kept in mind, that we should not have any kind of contribution of protons from the solvent.

The radio receiver coil, that detects the radio frequency emitted as nuclei relax to a lower energy level, and there should be a computer, that analyzes and records the data.

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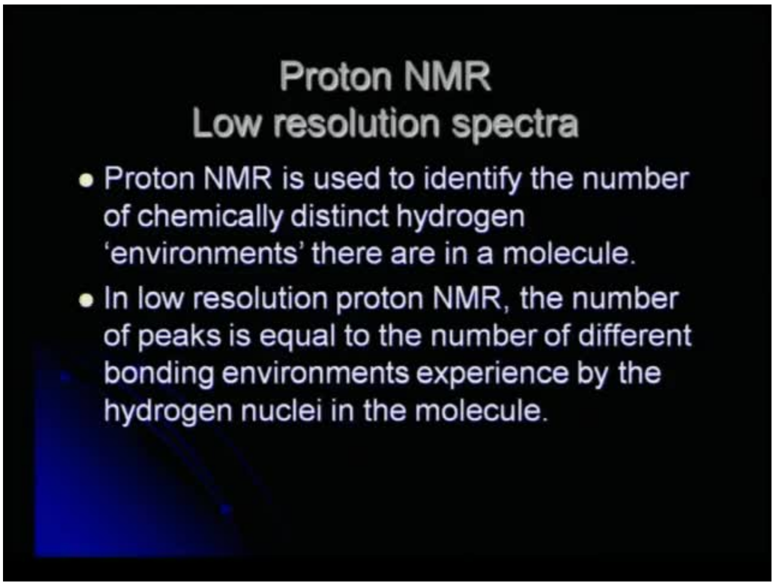

Proton NMR
Low resolution spectra

- Proton NMR is used to identify the number of chemically distinct hydrogen 'environments' there are in a molecule.
- In low resolution proton NMR, the number of peaks is equal to the number of different bonding environments experience by the hydrogen nuclei in the molecule.

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So, proton NMR low resolutions spectra - proton NMR is used to identify the number of chemically distinct hydrogen, which are environmentally, you know, in a different kind of situation there, in the molecule. So, if we have like, I again take the example of ethanol, CH 3 CH 2 OH. The CH 3 also has H, the CH 2 also has 2 H and OH of course, has 1 H; so, these 3 different types of protons are in a different environment.

In low-resolution proton NMR, the number of peaks is equal to the number of different bonding environments experienced by the hydrogen nuclei in the molecule and therefore, they can be identified separately.

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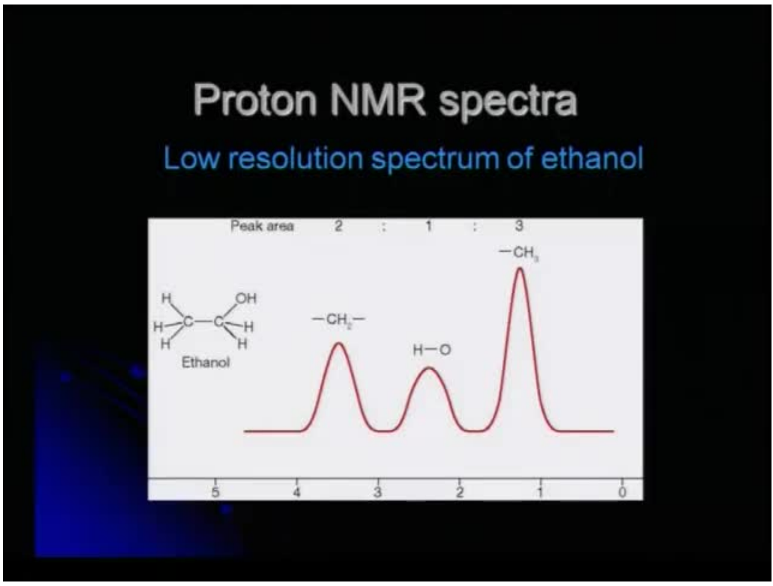

Proton NMR spectra

Low resolution spectrum of ethanol

Now, this is a very typical example of ethanol, which I have been time and again talking about, and this shows a typical peak of with, this is now low resolution. So, there is no splitting, that can be seen. There is a hump of CH 3, there is a hump of OH and there is a hump of CH 2.

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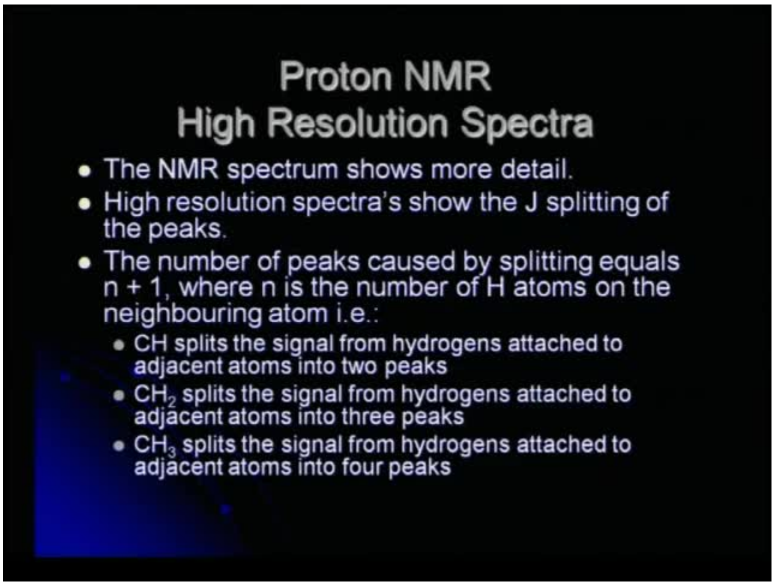

Proton NMR
High Resolution Spectra

- The NMR spectrum shows more detail.
- High resolution spectra's show the J splitting of the peaks.
- The number of peaks caused by splitting equals n + 1, where n is the number of H atoms on the neighbouring atom i.e.:
  - CH splits the signal from hydrogens attached to adjacent atoms into two peaks
  - CH_2 splits the signal from hydrogens attached to adjacent atoms into three peaks
  - CH_3 splits the signal from hydrogens attached to adjacent atoms into four peaks

Now, the same, when it goes to high resolution, will be split and this splitting is because of the J values, which are very typical of these protons. The NMR spectrum shows more details in high resolution spectra. High resolution spectra show the J's splitting of the peaks. The number of peak cause by the splitting equals to n plus 1 rule; that, you cannot afford to forget.

How many peaks will be arising will be determined by the simple N plus 1 rule, where N is the number of H atoms on the neighboring atom. CH splits the signal from hydrogen attached to the adjacent atoms into 2 peaks; CH 2 splits the signal from hydrogen attached to the adjacent atoms into 3 peaks. So, it is all the time increasing by a factor of 1. So, that is why the rule, N plus 1.

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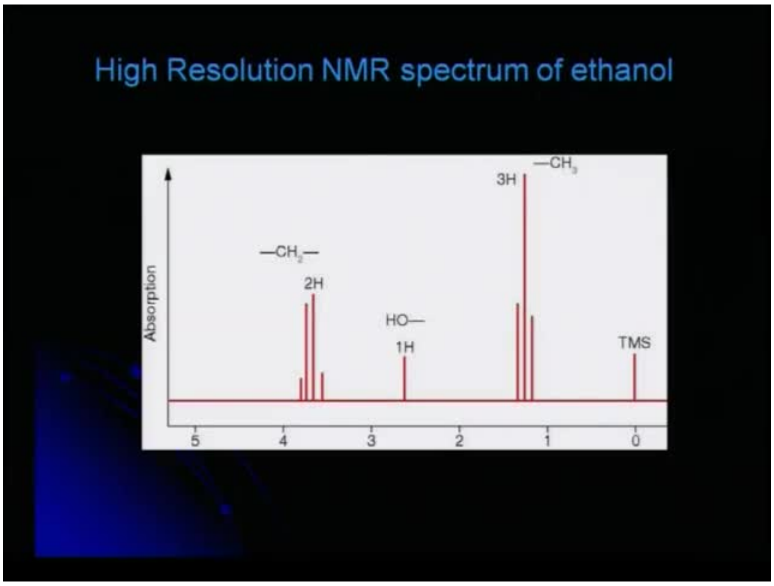

High Resolution NMR spectrum of ethanol

So, the same spectrum, which you saw, the humpies spectrum of ethanol, now has beautifully split into triplet, singlet and quartet in the high resolution NMR.

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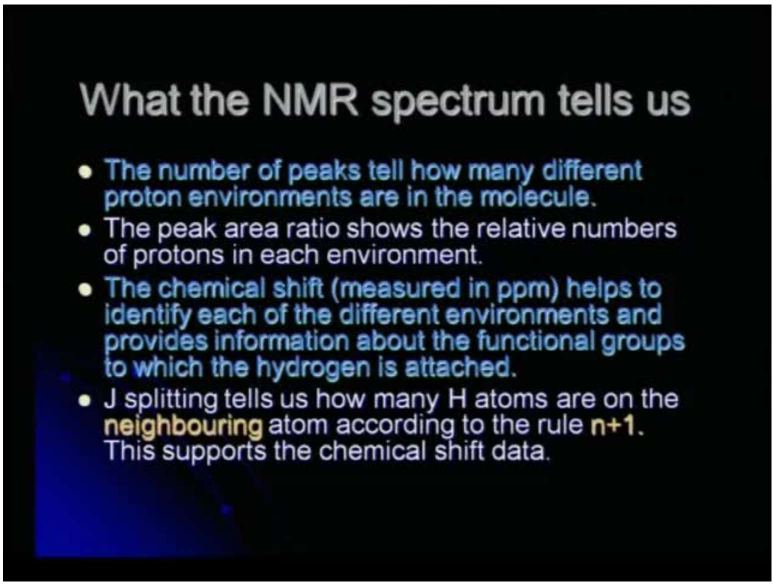

What the NMR spectrum tells us

- The number of peaks tell how many different proton environments are in the molecule.
- The peak area ratio shows the relative numbers of protons in each environment.
- The chemical shift (measured in ppm) helps to identify each of the different environments and provides information about the functional groups to which the hydrogen is attached.
- J splitting tells us how many H atoms are on the neighbouring atom according to the rule n+1. This supports the chemical shift data.

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What the NMR spectrum tells us? The number of peak tell us how many different proton environments are in their in the molecule. The peak area ratio shows the relative numbers of protons in each environment. The chemical shift, measured in ppm, helps to identify each of the different environments and provides information about the functional groups to which the hydrogen is attached. J splitting tells us how many H protons are on the neighboring atom according to the rule N plus 1. This supports the chemical shift data.

So, first and the foremost thing is that you should know, what type of proton it is, from the chemical shift value. Then the splitting will occur because of the n plus 1 rule and the chemical shift value in the ppm scale or the delta scale will actually identify, what type of carbon, what type of proton is attached to which type of carbon.

So, all this is very, very well understood and it can give information about molecules to a very large extent, very accurately. And this is one of the tools, which is extensively used in understanding the structure of a compound. What C-13 gives us? The carbon backbone information and the proton NMR gives us the information related to how many protons are present on each of these carbons of the backbone.

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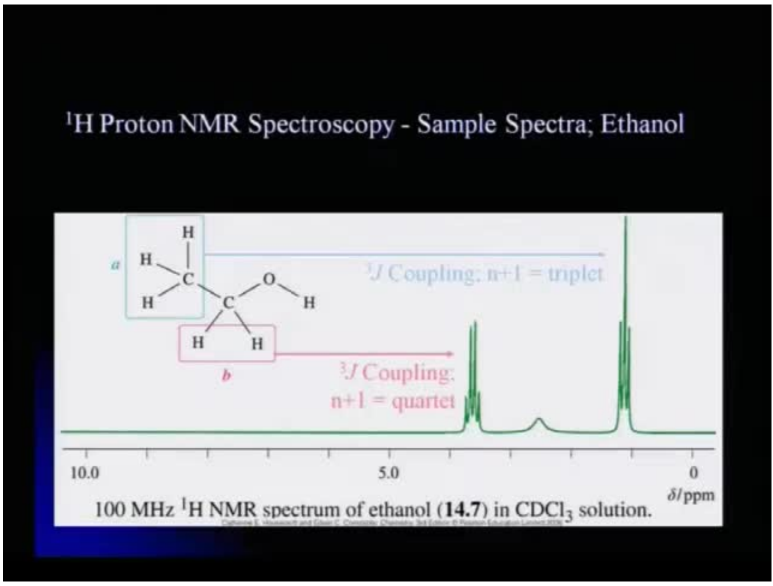

^{1}H Proton NMR Spectroscopy - Sample Spectra; Ethanol

100 MHz ^{1}H NMR spectrum of ethanol (**14.7**) in $CDCl_3$ solution.

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If one tries to look at the proton NMR of a sample of ethanol, this is how the splitting pattern would look in a 100 megahertz NMR spectrum or ethanol.

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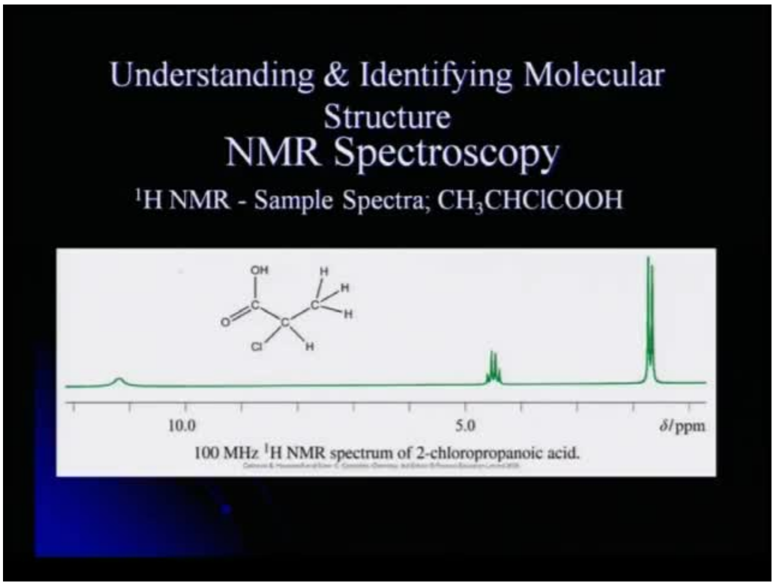

Understanding & Identifying Molecular Structure

NMR Spectroscopy

^{1}H NMR - Sample Spectra; $CH_3CHClCOOH$

100 MHz ^{1}H NMR spectrum of 2-chloropropanoic acid.

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Understanding and identifying molecular structures, then becomes very easy because the same ethanol can be understood or looked at; different types of molecules can be understood in this by the help of NMR spectrum.

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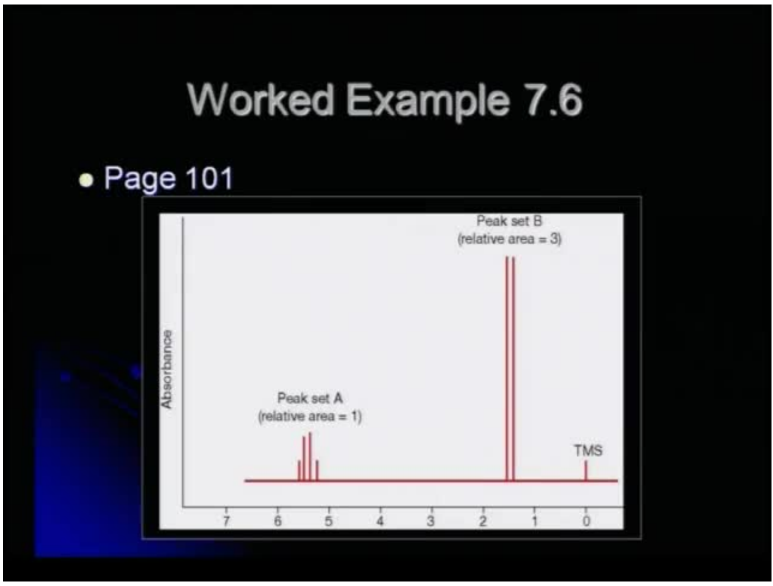

Worked Example 7.6

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Similarly, there are several examples and one can take an overview of this particular spectroscopic method to understand, how this NMR can help us to understand the structure.