Republic of Iraq
Ministry of Higher Education & Scientific research
Al-Mustaqbal University
Science College
Biochemistry Department

Analytical Chemistry Instrumental Analysis

For

Second Year Student/course 1

Lecture 6

By

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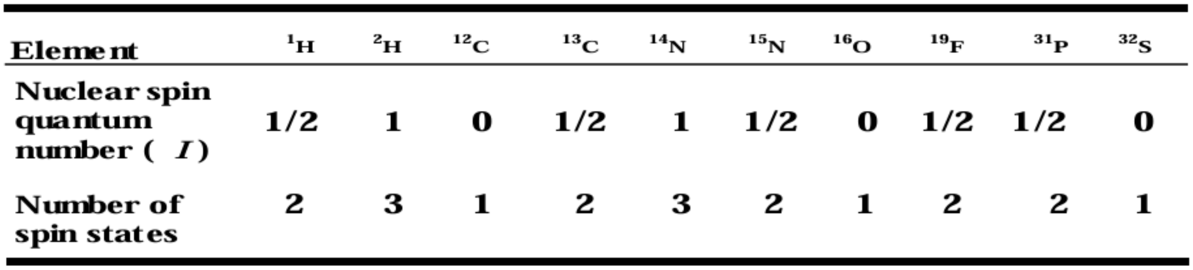
Nuclear Magnetic Resonance Spectroscopy(NMR)

Theory of NMR

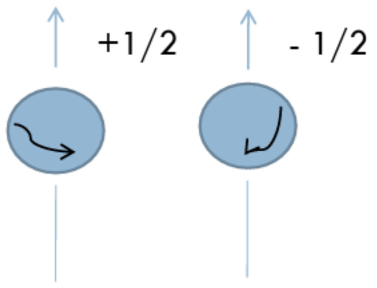
- A spectroscopic technique that gives us information about the number and types of atoms in a molecule.
- Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.
- Two common types of NMR spectroscopy are used to characterize organic structure: 1H NMR is used to determine the type and number of H atoms in a molecule; 13C NMR is used to determine the type and number of C atoms in the molecule.
- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.
- When low-energy radio waves interact with a molecule, they can change the nuclear spins of certain atoms in presence of strong magnetic fields, including ^{1}H and ^{13}C.
- Spin nuclei are those which contains either Odd atomic number or odd atomic mass number or both e.g. ^{1}H, ^{2}H, ^{13}C, ^{14}N, ^{17}O, ^{35}Cl etc are useful for NMR.
- Those nuclei contains Even number of atomic and mass number are not useful for NMR e.g. ^{12}C, ^{16}O etc.

- The nuclei posses spin, they spin on their nuclear axis leads to generate magnetic dipole ‘μ’ so the angular momentum of this spinning charge is quantified and described by Quantum Spin Number “ I ”.



Element	^{1}H	^{2}H	^{12}C	^{13}C	^{14}N	^{15}N	^{16}O	^{19}F	^{31}P	^{32}S
Nuclear spin quantum number (I)	1/2	1	0	1/2	1	1/2	0	1/2	1/2	0
Number of spin states	2	3	1	2	3	2	1	2	2	1

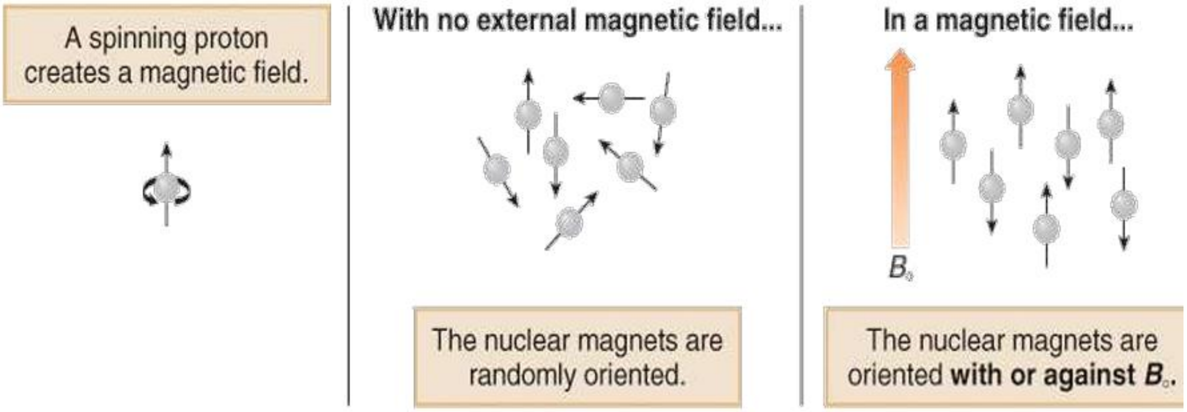
- The individual protons have spin quantum number +1/2 or-1/2.
- i.e. Hydrogen have spin quantum number (l) = +1/2 or-1/2.

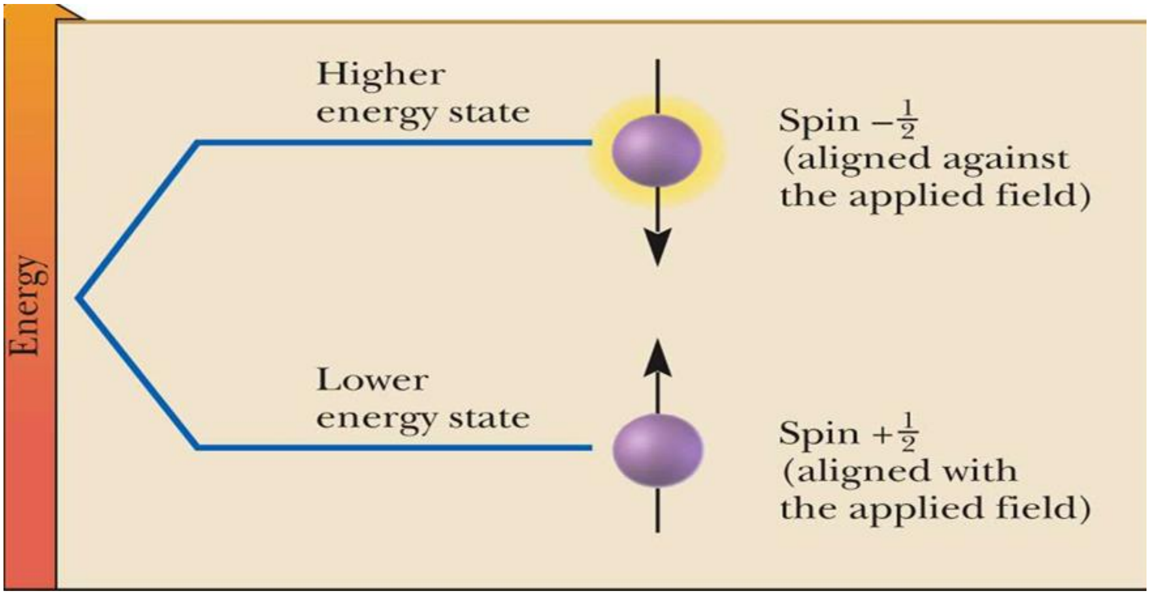


Two spin states allowed for proton (H)

- These spin states have equal amount of energy (degenerated) in the absence of magnetic field.
- When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.
- But when magnetic field is applied, the proton (H) posses spin & their own magnetic field align themselves either or opposite to magnetic field.

- For e.g. 1H has +1/2 &-1/2 spin state, the proton (H) have +1/2 spin state align themselves with field (Lower energy) and with-1/2 spin state align opposite to field (Higher energy).





Change in spin state energy separation with increase by applied magnetic field, B0

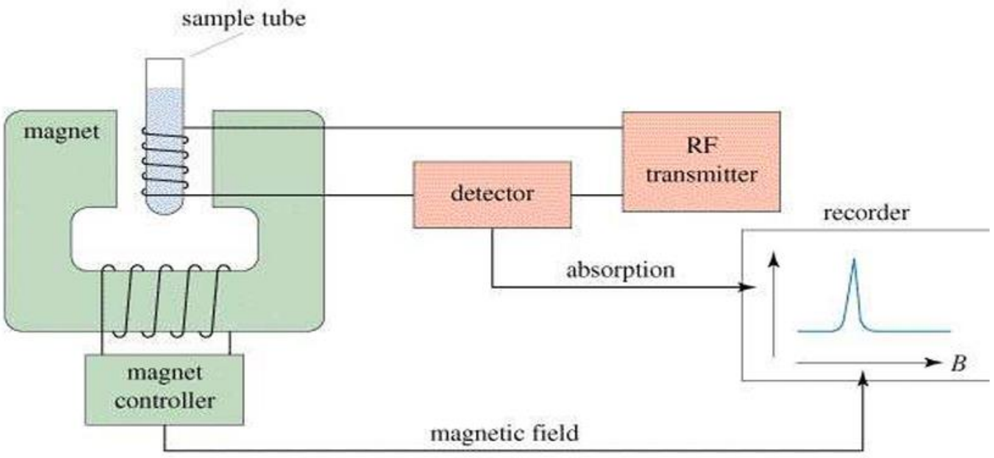
- The energy required to bring transition in NMR (ΔE = hv) or to flip proton depends upon the strength of external magnetic field.

Instrumentation

The NMR spectrophotometer consists of following components

- ✓ A magnet
- ✓ Sample and sample holder
- ✓ Radiofrequency generator
- ✓ Detector
- ✓ Recorder

- In NMR spectrophotometer, the sample is dissolved in $CDCl_3$ and placed in magnetic field. Then radiofrequency generator(RF) irradiates the sample with short pulse of radiation causing resonance. When nuclei fall back to their low energy state, detector measures the energy released and spectrum is recorded. The superconducting magnet in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with no resistance.
- A line diagram of NMR spectrophotometer along with its components are as follows;



Working of instrument

1. Sample placed in long cylindrical glass tube especially made for NMR.
2. Dissolved the sample in proton free solvent like $CDCl_3$ or CCl_4 and add small amount of TMS as internal reference.
3. Placed the sample in gap between two magnetic poles where coil is attached to a specific RF generator (e.g. 60 MHz).
4. This coil supply EMR energy required to change spin orientation of proton.
5. Then detector coil detects radiofrequency signal when resonance occurs.
6. As magnetic field strength increase, the precessional frequency of all protons increase and when this frequency proton reaches 60 MHz, the resonance occurs.
7. So, as magnetic field increase linearly the recorder pen travels from left to right, thus protons which achieve resonance faster i.e. (Deshielded) appears on left side (downfield), where as those protons (Shielded) appears on right side (up field) of chart in the form of peaks.
8. TMS is shown at a peak value of $\delta=0$ppm.

Solvents

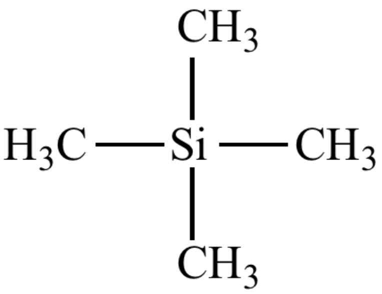
The solvent used for dissolving sample should have following properties;

- Should not contain proton,
- Inexpensive
- Low boiling point and non polar in nature.
- Generally deuterated chloroform CDCl3 is used as solvent.

- If sample is soluble in polar solvent, then deuterium oxide (D_2O), DMSO, CCl_4, CS_2, Cf_3, COOH are used as solvent.

Internal Standard

But TMS (Tetra methyl silane) is most commonly used as IS for measuring the position of ^1H, ^{13}C and ^{29}Si in NMR spectroscopy. Due to following reasons;



Tetramethylsilane (TMS)

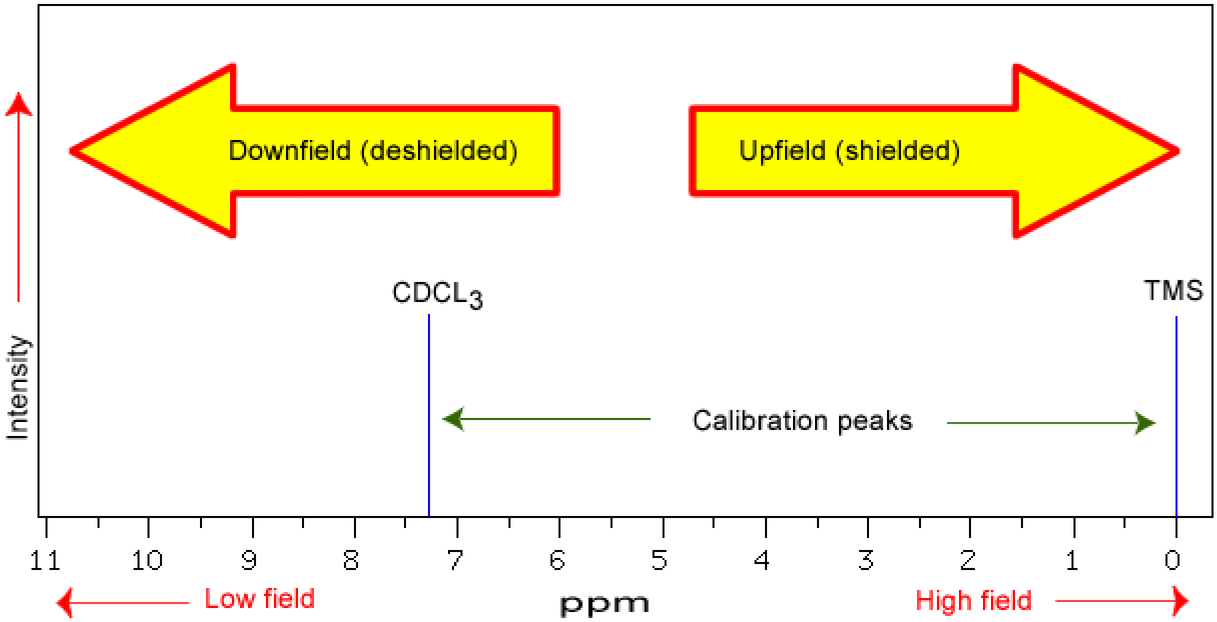
1. It is chemically inert and miscible with a large range of solvents.
2. Its twelve protons are all magnetically equivalent.
3. Its protons are highly shielded and gives a strong peak even small quantity.
4. It is less electronegative than carbon.
5. It is highly volatile and can be easily removed to get back sample.
6. It does not take part in intermolecular associations with sample.
7. Its resonance position is far away from absorptions due to protons in most organic molecules, thus signals of TMS = 0.

Chemical Shift (Position of Signals)

- Protons give signals at different frequencies because of their surroundings.
- Signal positions show the type of proton (aromatic, aliphatic, vinylic, etc.).
- Surrounding electrons reduce the magnetic field on the proton (shielded protons).

Shielding of protons: High electron density around a nucleus shields the nucleus from the external magnetic field, and the signals are upfield in the NMR spectrum.

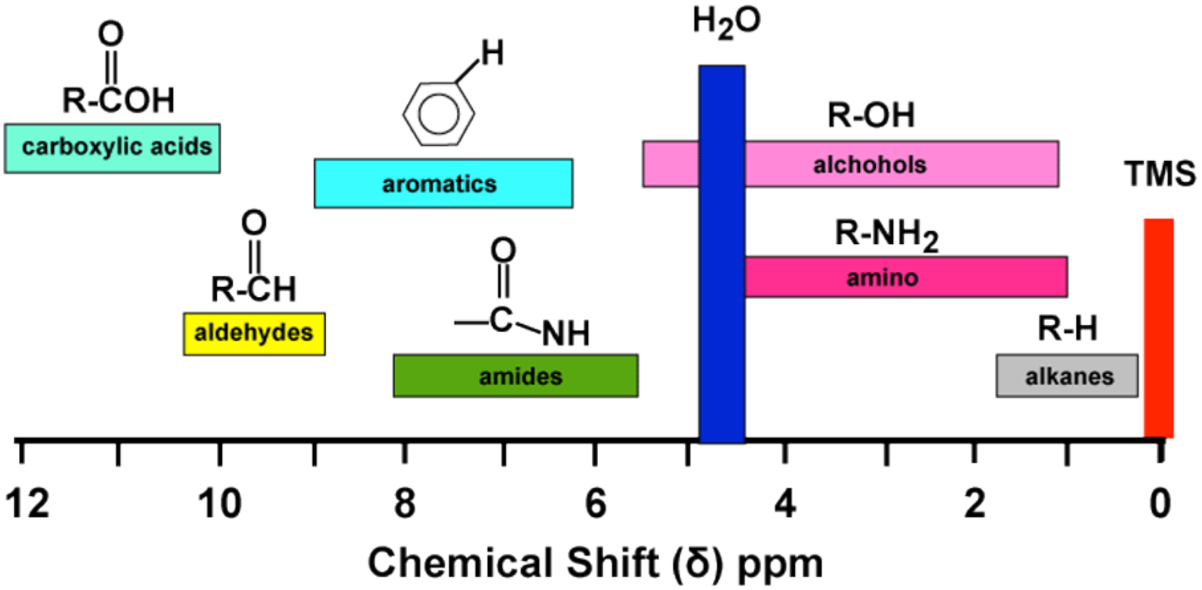
Deshielding of protons: Lower electron density around a nucleus deshields the nucleus from the external magnetic field, and the signals are downfield in the NMR spectrum.

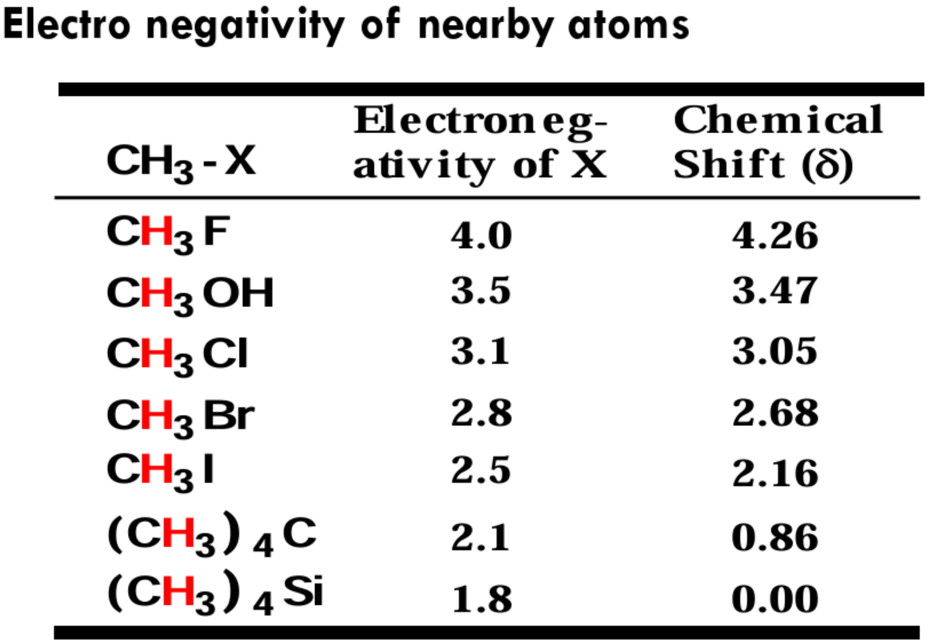


Chemical shift depends upon following parameters:

- Electro negativity of nearby atoms
- Hybridization of adjacent atoms

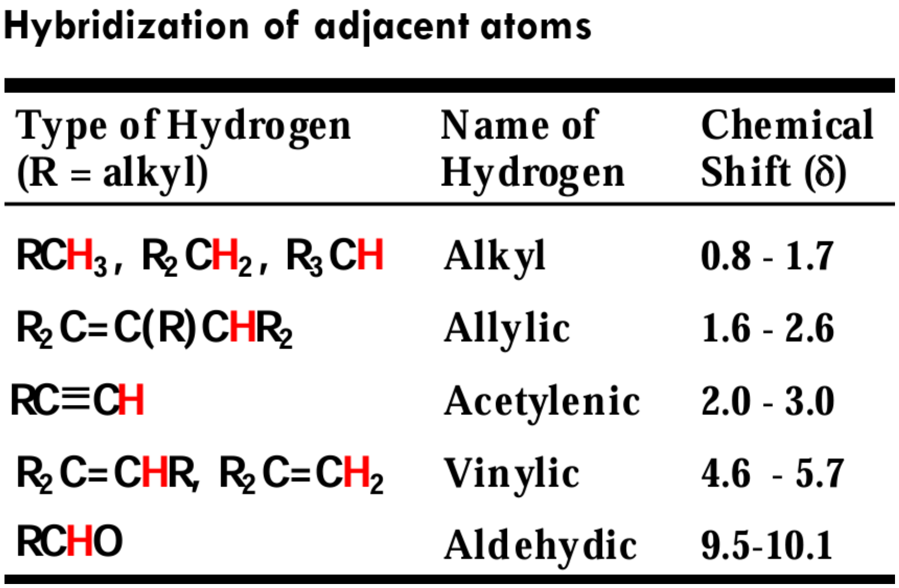
- Diamagnetic effects from adjacent pi bonds





Electro negativity of nearby atoms

CH_3 - X	Electroneg-ativity of X	Chemical Shift (δ)
CH_3F	4.0	4.26
CH_3OH	3.5	3.47
CH_3Cl	3.1	3.05
CH_3Br	2.8	2.68
CH_3I	2.5	2.16
$(CH_3)_4C$	2.1	0.86
$(CH_3)_4Si$	1.8	0.00

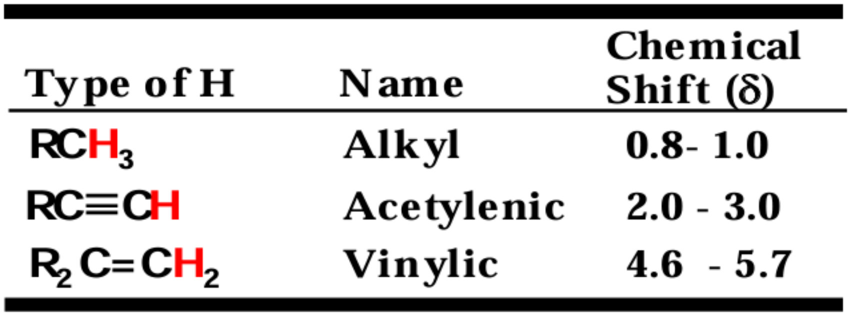


Hybridization of adjacent atoms

Type of Hydrogen (R = alkyl)	Name of Hydrogen	Chemical Shift (δ)
RCH_3, R_2CH_2, R_3CH	Alkyl	0.8 - 1.7
$R_2C{=}C(R)CHR_2$	Allylic	1.6 - 2.6
$RC{\equiv}CH$	Acetylenic	2.0 - 3.0
$R_2C{=}CHR$, $R_2C{=}CH_2$	Vinylic	4.6 - 5.7
$RCHO$	Aldehydic	9.5-10.1

Diamagnetic effects from adjacent pi bonds

- A carbon-carbon triple bond shields an acetylenic hydrogen and shifts its signal to lower frequency (to the right) to a smaller value.
- A carbon-carbon double bond deshields vinylic hydrogens and shifts their signal to higher frequency (to the left) to a larger value.



Type of H	Name	Chemical Shift (δ)
RCH_3	Alkyl	0.8- 1.0
$RC{\equiv}CH$	Acetylenic	2.0 - 3.0
$R_2C{=}CH_2$	Vinylic	4.6 - 5.7

Factors affecting chemical shift

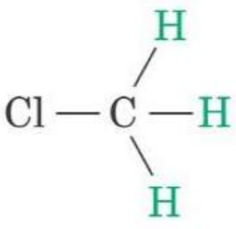
Following are the factors which influence the chemical shift;

1. Inductive effect
2. Van der Waal's deshielding
3. Anisotropic effect
4. Hydrogen bonding

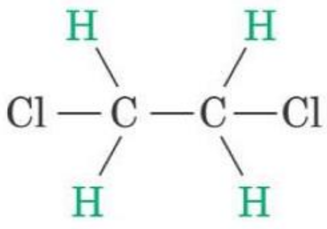
Spin-Spin Splitting in NMR Spectrum

- Peaks are often split into multiple peaks due to magnetic interactions between nonequivalent protons on adjacent carbons, The process is called Spin Spin-spin splitting
- spin - Splitting/Coupling . It occurs only between nonequivalent protons on the same carbon or adjacent carbons.
- Peak : The units into which an NMR signal is split; doublet, triplet, quartet, multiplet, etc.
- Signal splitting : Splitting of an NMR signal into a set of peaks by the influence of neighboring nonequivalent hydrogens.
- Signal coupling : An interaction in which the nuclear spins of adjacent atoms influence each other and lead to the splitting of NMR signals.

Equivalent protons are like this;

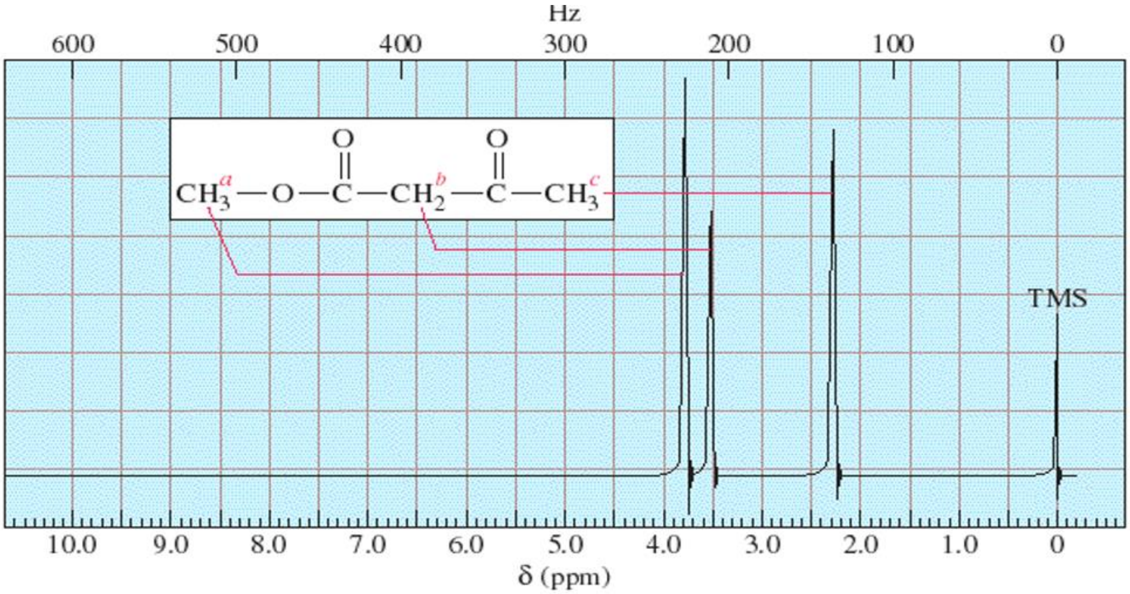


Three C–H protons are chemically equivalent; no splitting occurs.

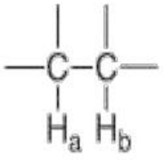


Four C–H protons are chemically equivalent; no splitting occurs.

Equivalent protons have same chemical shift without splitting occurs



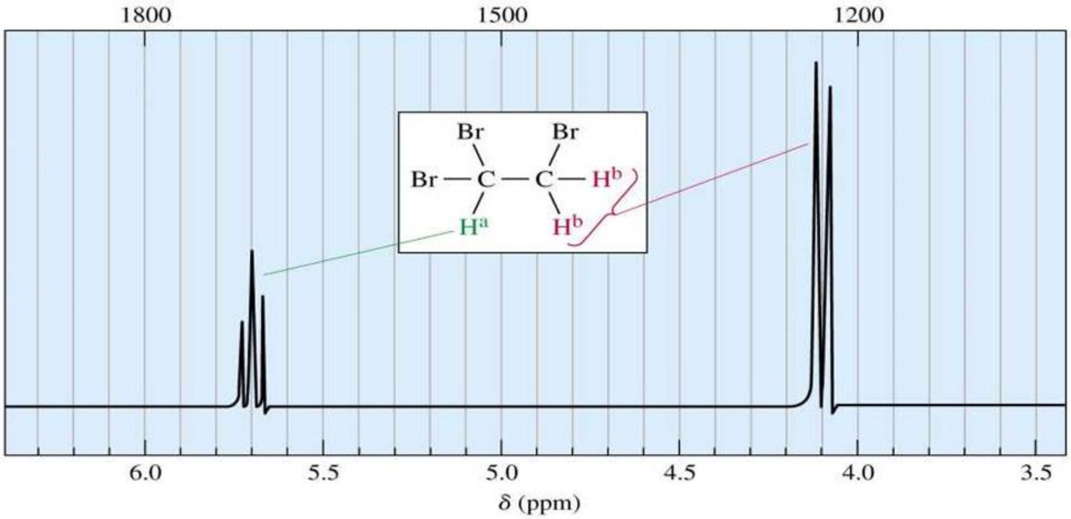
Nonequivalent protons are like this;



H_a and H_b are on the **same** carbon.

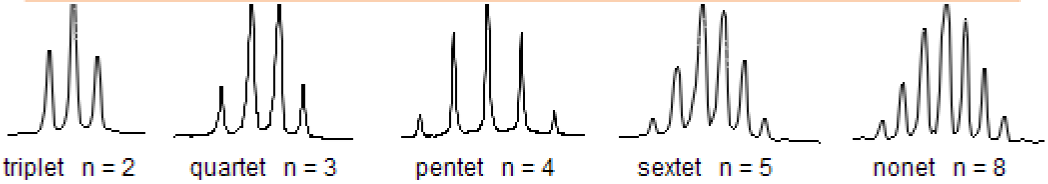
H_a and H_b are on **adjacent** carbons.

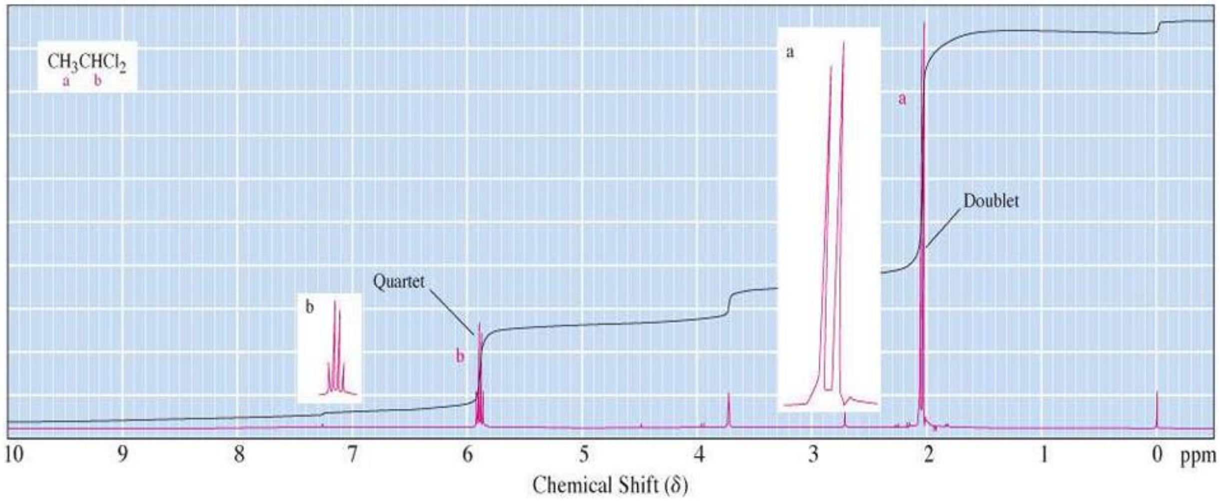
Nonequivalent protons have different chemical shift with splitting occurs



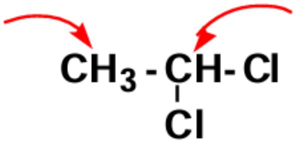
Signal Splitting: The (n + 1) Rule

Number of equivalent hydrogen atoms causing splitting	Multiplicity	Relative peak intensities
1	doublet	1 : 1
2	triplet	1 : 2 : 1
3	quartet	1 : 3 : 3 : 1
4	quintet	1 : 4 : 6 : 4 : 1
5	sextet	1 : 5 : 10 : 10 : 5 : 1
6	septet	1 : 6 : 15 : 20 : 15 : 6 : 1





For these hydrogens, n = 1; their signal is split into (1 + 1) = 2 peaks; a doublet



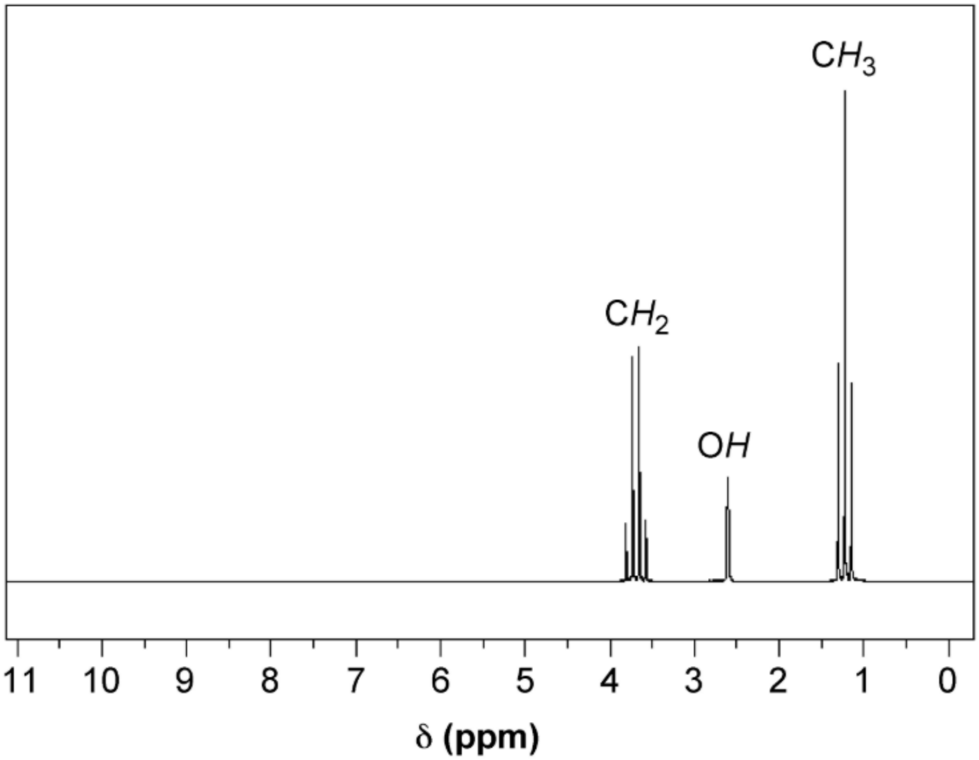
$CH_3-CH(Cl)-Cl$

For this hydrogen, n = 3; its signal is split into (3 + 1) = 4 peaks; a quartet

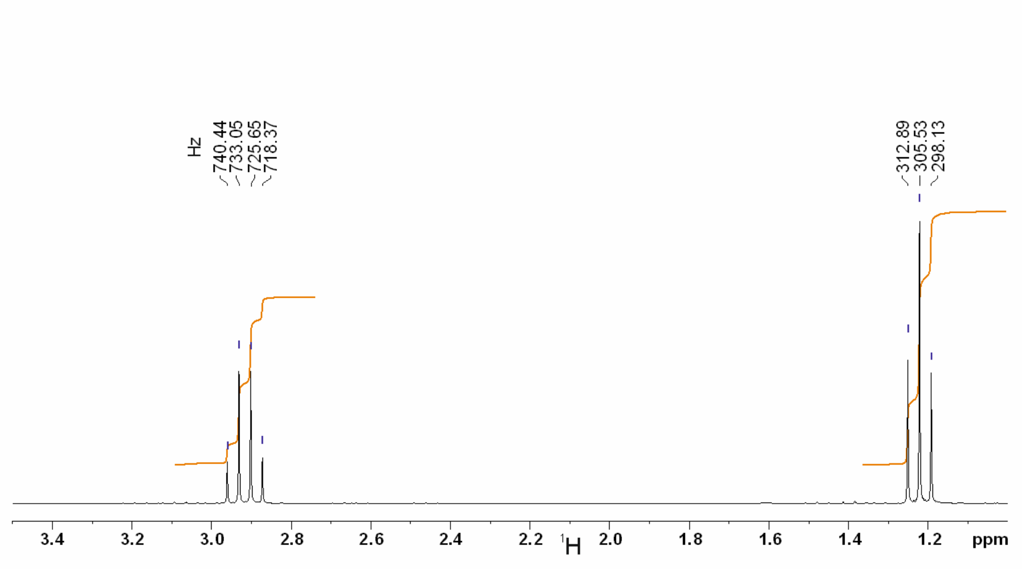
1H NMR—Structure Determination

Ex) an ^{1}H NMR spectra of ethanol, we can see a clear example of chemical shift. There are three sets of peaks that represent the six hydrogens of ethanol (C_2H_6O). The presence of three sets of peaks means that there are three different chemical environments that the hydrogens can be found in: the terminal methyl (CH_3) carbon's three hydrogens, the two hydrogens on the methylene (CH_2) carbon adjacent to the oxygen, and the single hydrogen on the oxygen of the alcohol group (OH). Once we cover spin-spin coupling, we will have the tools available to match these groups of hydrogens to their respective peaks.

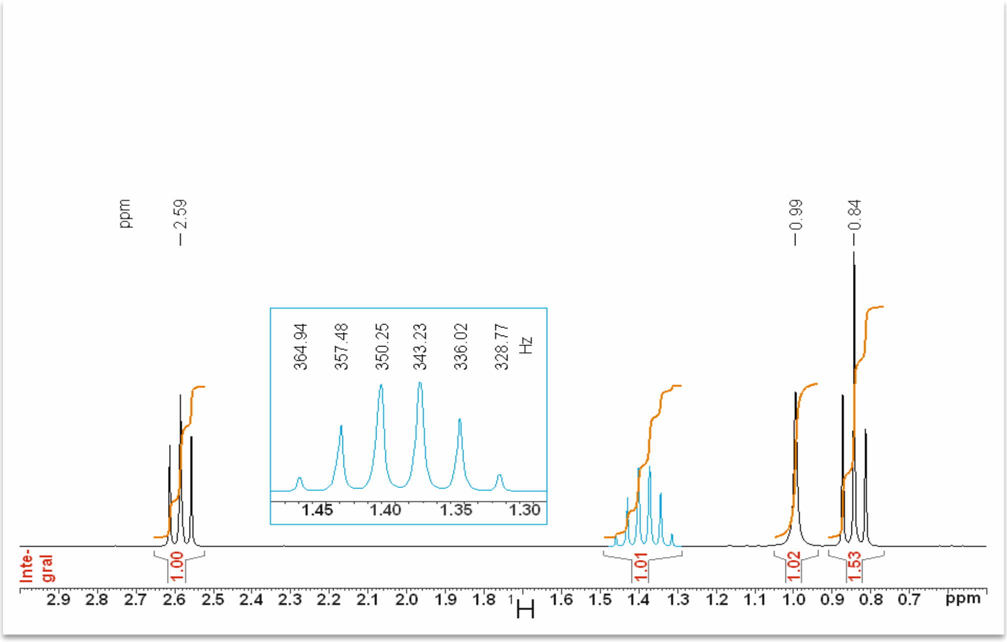
Unsaturated= 2C+2+N-H-X/2



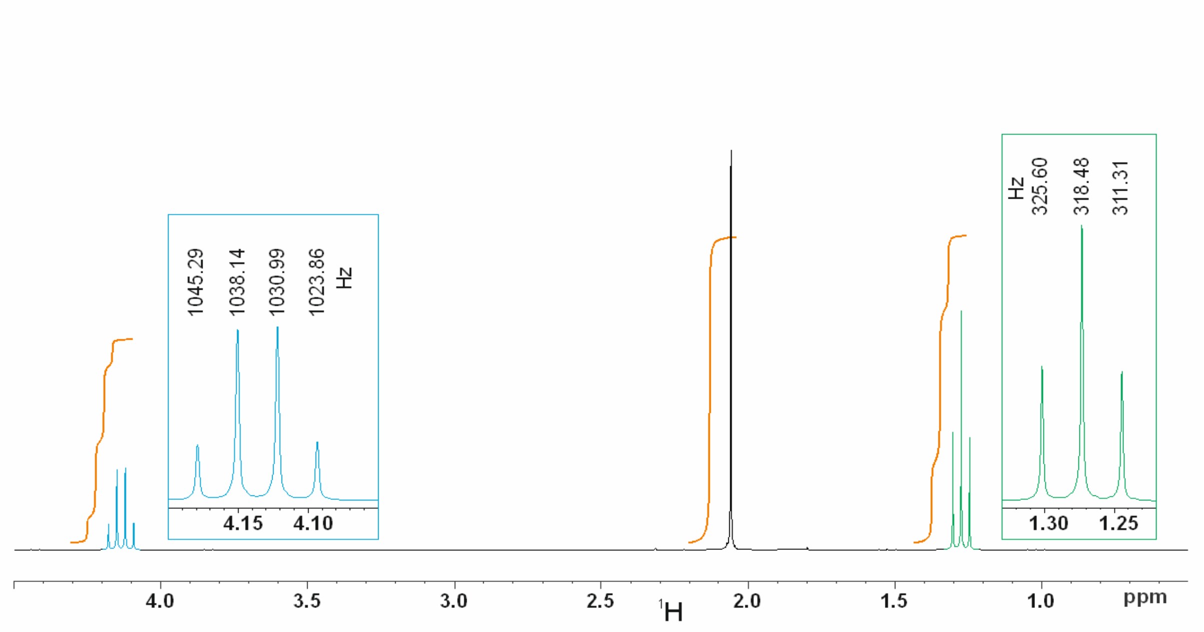
Predict the ^{1}H NMR spectrum of this compound by The structure of a compound is shown below (C_3H_5ClO)



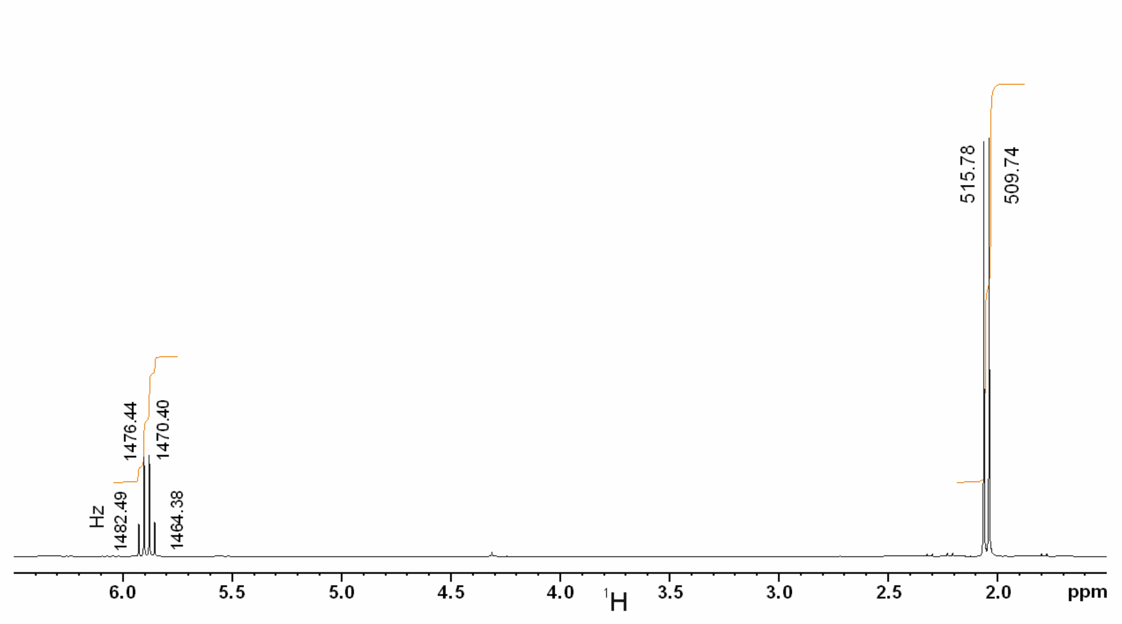
Predict the ^{1}H NMR spectrum of this compound by The structure of a compound is shown below (C_3H_8N)



Predict the ^{1}H NMR spectrum of this compound by The structure of a compound is shown below ($C_4H_8O_2$)



Predict the ^{1}H NMR spectrum of this compound by The structure of a compound is shown below ($C_2H_4Cl_2$)



Predict the ^{1}H NMR spectrum of this compound by The structure of a compound is shown below (C_8H_9BrO)