VIVEKANANDA COLLEGE OF ARTS AND SCIENCE (Women)

THENPATHI-SIRKALI
NAGAPATTINAM (Dt) - 609 111

Unit –V Chemical shift

S.Sandhiya
Asst professor
Department of Chemistry
Sub code: 16SCCCH8
Sub: Organic chemistry -ll

Chemical shift

- In nuclear magnetic resonance (NMR) spectroscopy, the **chemical shift** is the resonant frequency of a nucleus relative to a standard in a magnetic field.

- Often the position and number of chemical shifts are diagnostic of the structure of a molecule. Chemical shifts are also used to describe signals in other forms of spectroscopy such as photoemission spectroscopy.

- Some atomic nuclei possess a magnetic moment (nuclear spin), which gives rise to different energy levels and resonance frequencies in a magnetic field. The total magnetic field experienced by a nucleus includes local magnetic fields induced by currents of electrons in the molecular orbitals (note that electrons have a magnetic moment themselves).

- The electron distribution of the same type of nucleus (e.g. ^{1}H, ^{13}C, ^{15}N) usually varies according to the local geometry (binding partners, bond lengths, angles between bonds, and so on), and with it the local magnetic field at each nucleus.

- This is reflected in the spin energy levels (resonance frequencies). The variations of nuclear magnetic resonance frequencies of the same kind of nucleus, due to variations in the electron distribution, is called the chemical shift.

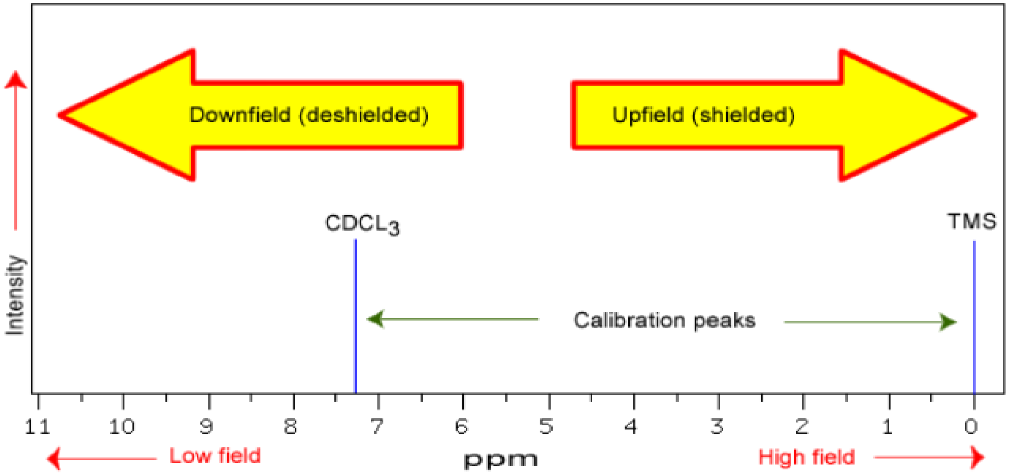
- The size of the chemical shift is given with respect to a reference frequency or reference sample (see also chemical shift referencing), usually a molecule with a barely distorted electron distribution.

- The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption. The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.
- Chemical shift δ is usually expressed in parts per million (ppm) by frequency, because it is calculated from:

$$\delta = \nu\text{sample} - \nu\text{ref} / \nu\text{res}$$

- ✓ The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption.

- ✓ The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.



^{1}H NMR Chemical Shifts

- Chemical shift is associated with the Larmor frequency of a nuclear spin to its chemical environment. Tetramethylsilan [TMS;$(CH_3)_4Si$] is generally used for standard to determine chemical shift of compounds: $\delta_{TMS}=0$ ppm. In other words, frequencies for chemicals are measured for a ^{1}H or ^{13}C nucleus of a sample from the ^{1}H or ^{13}C resonance of TMS. It is important to understand trend of chemical shift in terms of NMR interpretation.
- The proton NMR chemical shift is affect by nearness to electronegative atoms (O, N, halogen.) and unsaturated groups (C=C,C=O, aromatic). Electronegative groups move to the down field (left; increase in ppm). Unsaturated groups shift to downfield (left) when affecting nucleus is in the plane of the unsaturation, but reverse shift takes place in the regions above and below this plane.

- ^{1}H chemical shift play a role in identifying many functional groups. Figure 1. indicates important example to figure out the functional groups.

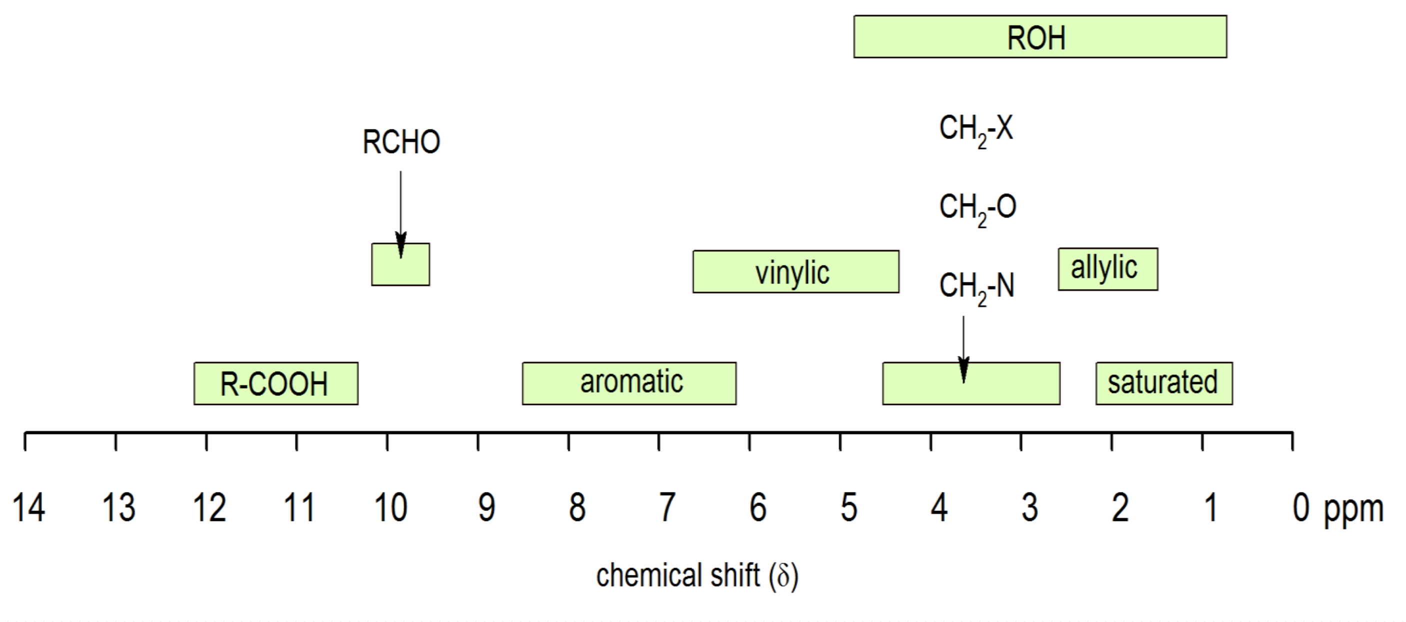


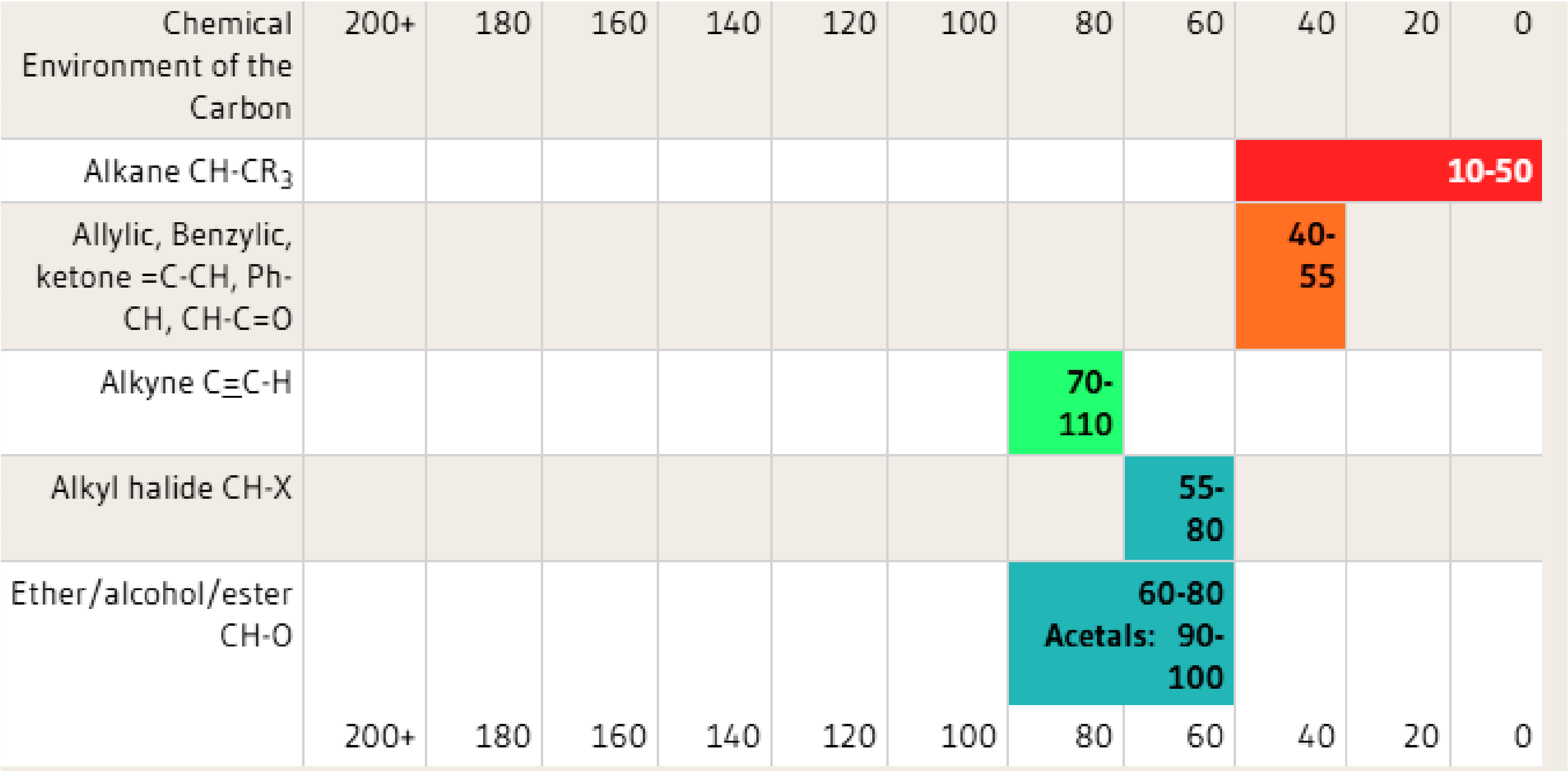
Figure 1. *^{1}H chemical shift ranges for organic compounds*

^{13}C NMR Chemical Shifts

- Carbon (^{13}C) has a much broader chemical shift range. One important difference is that the aromatic and alkene regions overlap to a significant extent. We now see all the carbons, though quaternary carbons (having no hydrogens) are usually quite weak; the proton decoupling process gives rise to an enhancement that quaternary carbons do not experience.

- The reference point (0 ppm) is also the chemical shift of carbon in tetramethylsilane, $(CH_3)_4Si$.

Here is a table of typical ^{13}C chemical shifts of important groups:



Chemical Environment of the Carbon	200+	180	160	140	120	100	80	60	40	20	0
Alkane CH-CR$_3$									**10-50**		
Allylic, Benzylic, ketone =C-CH, Ph-CH, CH-C=O									**40-55**		
Alkyne C≡C-H							**70-110**				
Alkyl halide CH-X								**55-80**			
Ether/alcohol/ester CH-O							**60-80 Acetals: 90-100**				
	200+	180	160	140	120	100	80	60	40	20	0

Influencing factors on chemical shifts

- **Electronegativity**
- Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus and result in a larger chemical shift. Compare the data in the table below.
- As can be seen from the data, as the electronegativity of X increases the chemical shift, δ increases. This is an effect of the halide atom pulling the electron density away from the methyl group. This exposes the nuclei of both the C and H atoms, "deshielding" the nuclei and shifting the peak downfield.

Compound, CH_3X	**CH_3F**	**CH_3OH**	**CH_3Cl**	**CH_3Br**	**CH_3I**	**CH_4**	**$(CH_3)_4Si$**
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ (ppm)	4.26	3.4	3.05	2.68	2.16	0.23	0

The effects are cumulative so the presence of more electron withdrawing groups will produce a greater deshielding and therefore a larger chemical shift. These inductive effects are not only felt by the immediately adjacent atoms, but the deshielding can occur further down the chain

NMR signal	**$-CH_2-CH_2-CH_2Br$**
δ (ppm)	1.25 1.69 3.30

- **Hydrogen bonding**

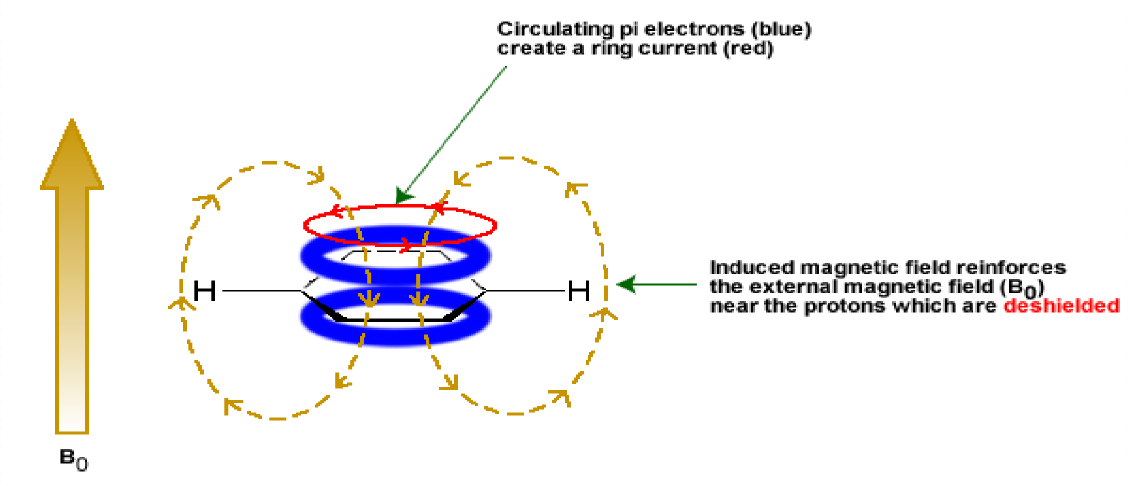
Hydrogen bonding results from the presence of electronegative atoms in neighbourhood of protons .The resulting deshielding leads to higher values of chemical shifts. This confirms the presence of hydrogen bonding in the molecules. Chemical shifts of NMR active protons and other nuclei serve to provide a wealth of structural information on molecules.

- Experimentally -OH and -NH can be identified by carrying out a simple D_2O exchange experiment since these protons are exchangeable.
  - ✓ run the normal H-NMR experiment on your sample
  - ✓ add a few drops of D_2O
  - ✓ re-run the H-NMR experiment
  - ✓ compare the two spectra and look for peaks that have "disappeared“
- **Anisotropy**

Anisotropy refers to the property of the molecule where a part of the molecule opposes the applied field and the other part reinforces the applied field. Chemical shifts are dependent on the orientation of neighbouring bonds in particular the π bonds. Examples of nucleus showing chemical shifts due to π bonds are aromatics, alkenes and alkynes. Such anisotropic shifts are useful in characterizing the presence of aromatics or other conjugated structures in molecules

Magnetic Anisotropy: π Electron Effects

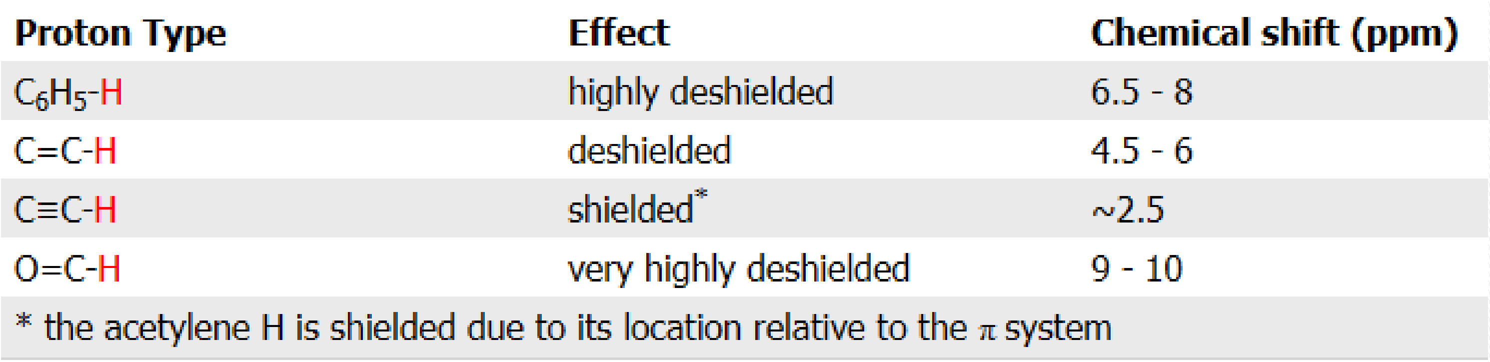
- The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field. The best example of this is benzene (see the figure below).



Circulating pi electrons (blue) create a ring current (red)

Induced magnetic field reinforces the external magnetic field (B_0) near the protons which are deshielded

This effect is common for any atoms near a π bond, *i.e.*

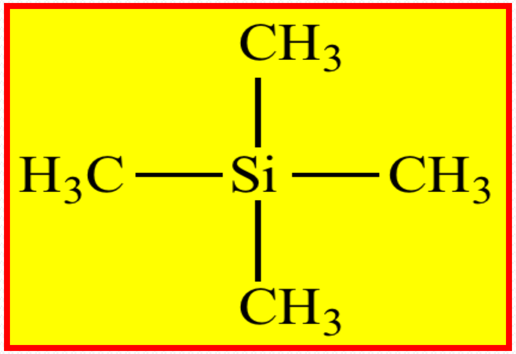


Proton Type	Effect	Chemical shift (ppm)
C_6H_5-H	highly deshielded	6.5 - 8
C=C-H	deshielded	4.5 - 6
C≡C-H	shielded*	~2.5
O=C-H	very highly deshielded	9 - 10

* the acetylene H is shielded due to its location relative to the π system

Why TMS is used as a reference standard in NMR spectroscopy?

- Because of its high volatility, **TMS** can easily be evaporated, which is convenient for recovery of samples analyzed by **NMR** spectroscopy. Because all twelve hydrogen atoms in a tetramethylsilane molecule are equivalent, its ^1H **NMR** spectrum consists of a singlet.



$$H_3C-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}-CH_3$$

TMS - Tetramethylsilane

- Tetramethylsilane became the established internal **reference** compound for ^1H **NMR** because it has a strong, sharp resonance line from its 12 protons, with a chemical shift at low resonance frequency relative to almost all other ^1H resonances. Thus, addition of **TMS** usually does not interfere with other resonances.