

NMR Spectroscopy



Dr. M. Ganapathi
Assistant Professor
Department of Chemistry
Government Arts College
Tiruvannamalai

Factors are affecting Chemical Shift



1. Shielding and deshielding

**2. Electronegativity (or)
& Inductive Effect**

**3. Anisotropic effect
(space effect)**

4. Vander Waals Deshielding

5. Hydrogen Bonding



1. Shielding and Deshielding



Shielding and Deshielding

- ❖ Rotation of electrons (π) to nearby nuclei generate field that can either oppose or strong the field on proton.
 - ❖ If magnetic field is oppose applied magnetic field on proton, that proton said **shielded** proton and if field is strong the applied field then, proton feels high magnetic field strength and such proton called as **Deshielded** proton.
- .

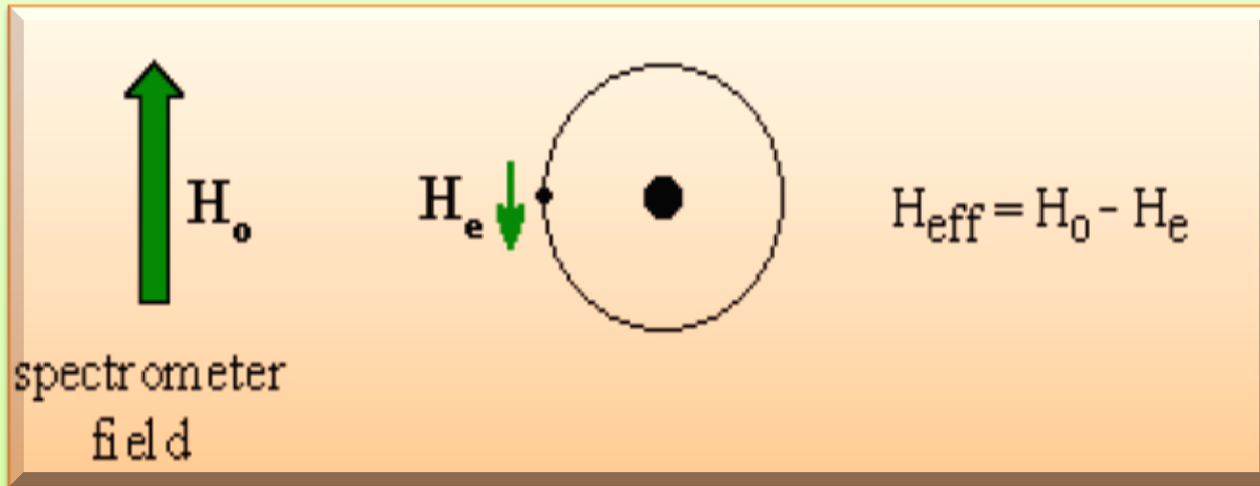


Shielding and Deshielding

- ❏ So, **shielded** proton shifts absorption signal to right side (upfield) and **deshielded** proton shifts absorption signal to left side (down field) of spectrum.
- ❏ So, electric environment surrounding proton tells us where proton shows absorption in spectrum.

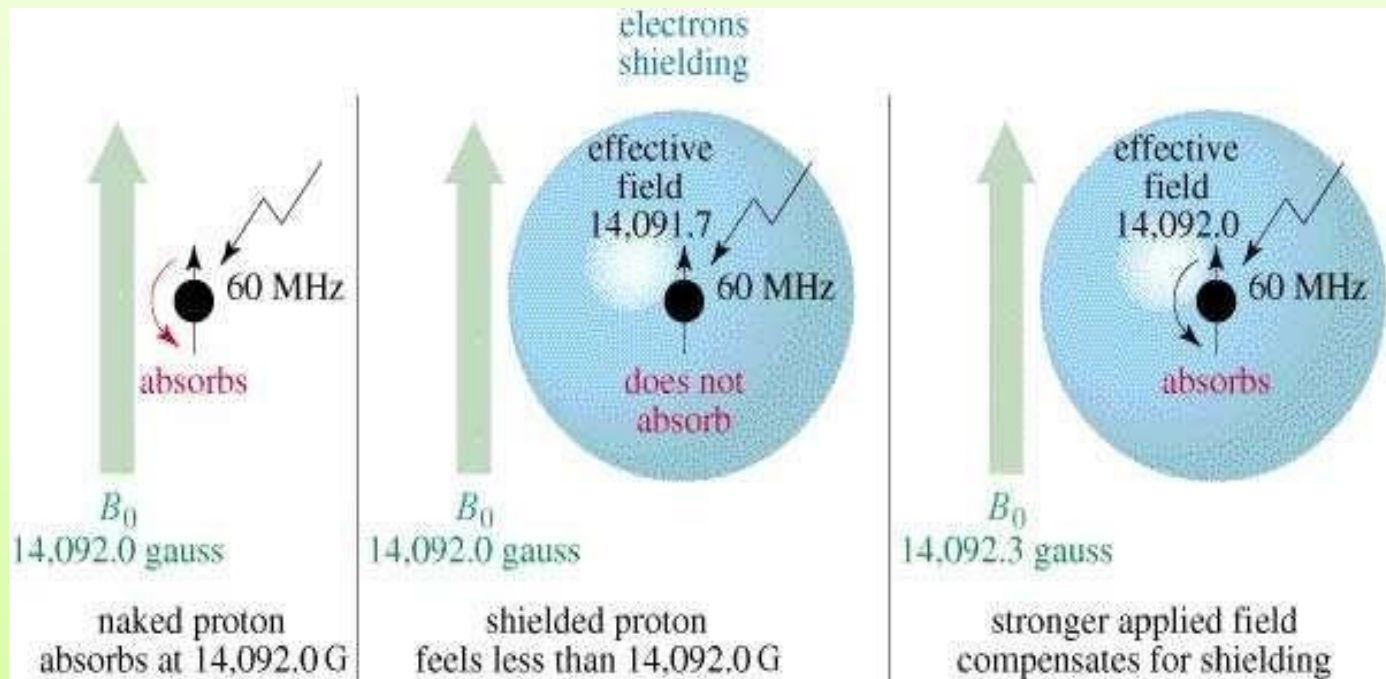
Shielding and Deshielding

- The electrons around the proton create a magnetic field that opposes the applied field. Since this reduces the field experienced at the nucleus, the electrons are said to **shield** the proton.



Shielding and Deshielding

- Shield Protons:** *Magnetic field strength must be increased for a shielded proton to flip at the same frequency.*





Shielding and Deshielding

- **The protons are shielded by the electrons that surround them. In an applied magnetic field, the valance electrons of the protons are caused to circulate.**
- **This circulation, called a local diamagnetic current, generates a counter magnetic field that opposes the applied magnetic field. This effect, which is called diamagnetic shielding or diamagnetic anisotropy.**



Shielding and Deshielding

- The counter field that shields a nucleus diminishes the net applied magnetic field that the nucleus experiences. As a result, the **nucleus processes at a lower frequency.**
- This means that it also **absorbs radiofrequency radiation at this lower frequency.**



Shielding and Deshielding

- When the secondary fields produced by the circulating electrons oppose the applied field at a particular nucleus in the molecule, it means that **effective field** experienced by the nucleus is **less than the applied field**.
- This is known as positive shielding and the resonance **position moves up field in NMR spectrum**.



Shielding and Deshielding

❖ If the secondary field produced by the circulating electrons reinforces the applied field, the position of resonance moves downfield. **This is known as negative shielding.**

■ **Shielded/upfield:**

higher electron density requires a stronger field for resonance

■ **Deshielded/downfield:**

lower electron density requires a weaker field for resonance

(using a constant radiofrequency)

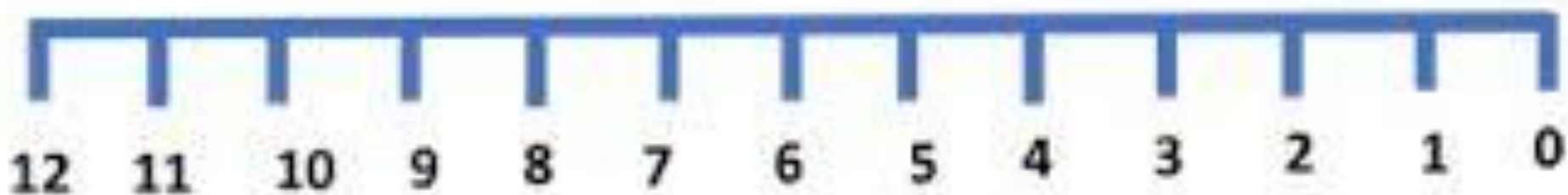


Shielding and Deshielding

De-shielded



Shielded



δ (ppm)



2. Inductive effect (Or) Electronegativity Effect

Inductive effect (Or) Electronegativity Effect

- The proton is said to be deshielded if its attached with an electronegative atom/group. Greater the electro negativity of atom greater is the Deshielding caused to proton. If the deshielding is more, then δ value also more.
- Electronegative atoms like Halogens, Oxygen and Nitrogen deshield the protons
- There for the absorption occurs downfield.

Inductive effect (Or) Electronegativity Effect

■ Two types of Inductive effects are,

i) + I Effect ii) - I Effect

An electron withdrawing group is able to reduce electron density around the proton and Deshields the proton.

An electron releasing group increase the electron density around the proton and give rise to its shielding.

ELECTRONEGATIVITY – CHEMICAL SHIFT

Dependence of the Chemical Shift of CH_3X on the Element X

Compound CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(\text{CH}_3)_4\text{Si}$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ	4.26	3.40	3.05	2.68	2.16	0.23	0

most
deshielded

← deshielding increases with the
Electronegativity of atom X

TMS



3. Anisotropic Effect

Due to the presence of pi bonds



3. Anisotropic Effect

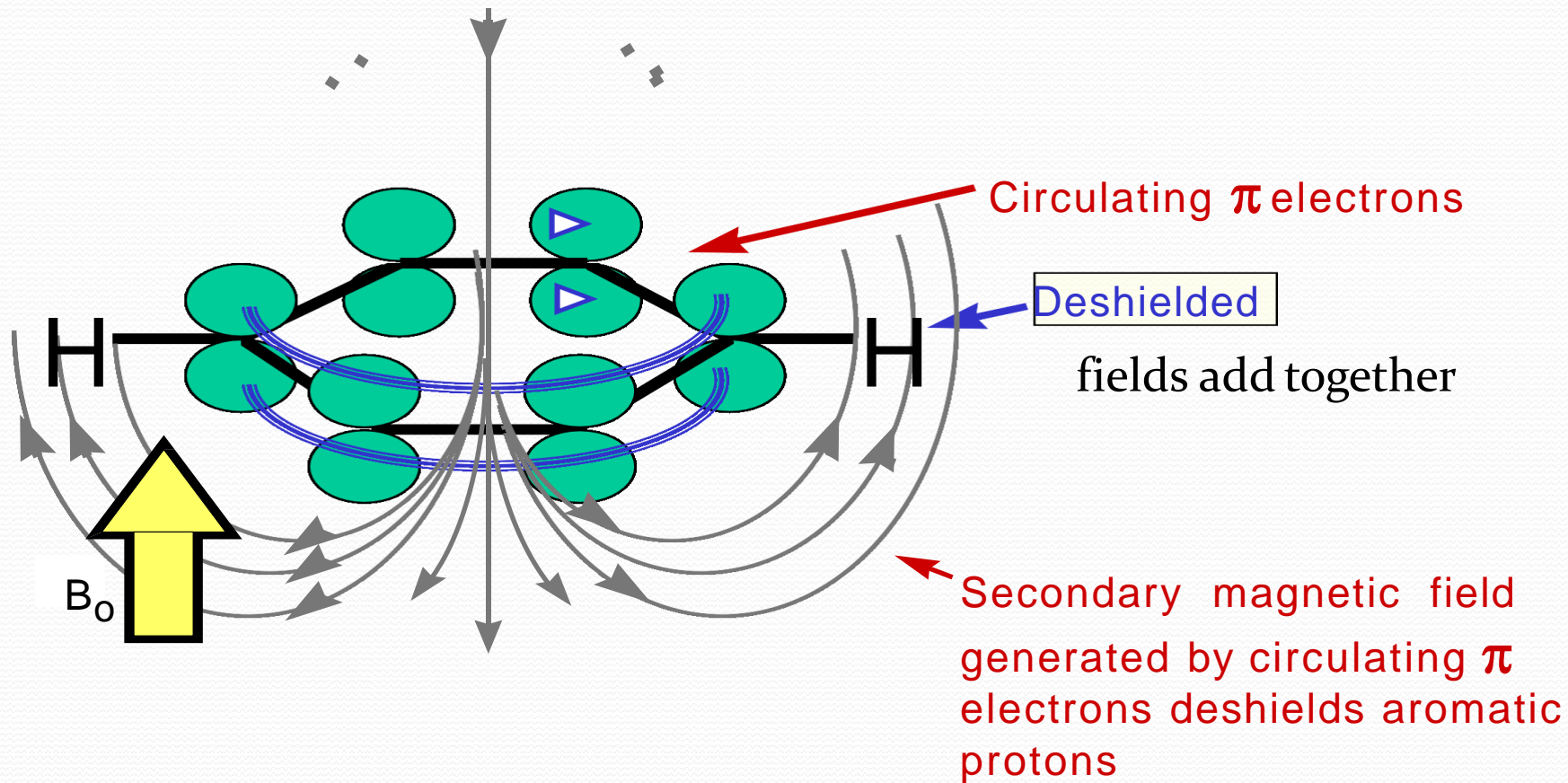
- Anisotropic effects constitute **shielding** and **deshielding** effects on the proton because of induced magnetic fields in other parts of the molecule which operate through space.
- For example if a magnetic field is applied to a molecule having π electrons, these electrons begin to circulate at right angles to the direction of the applied field thereby producing induced magnetic field.



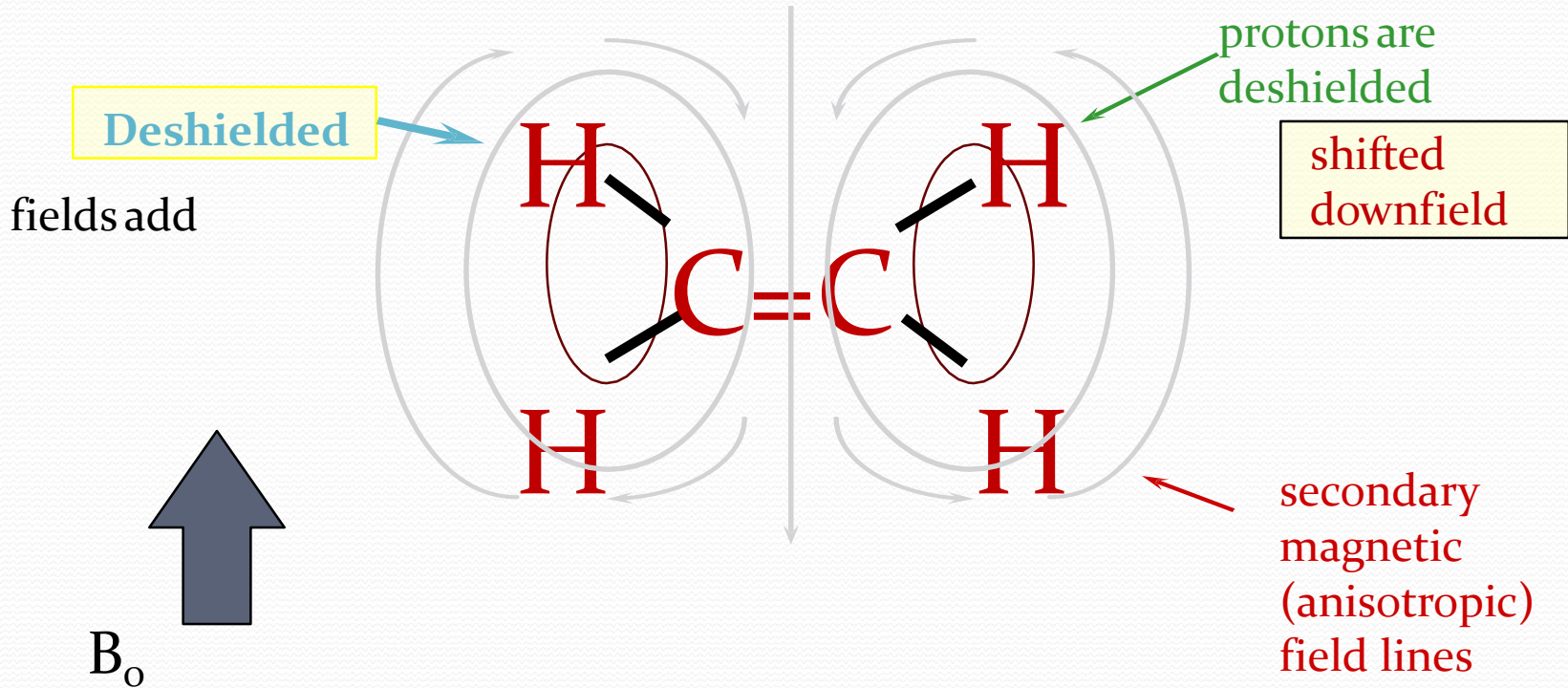
Anisotropic Effect

- ❖ The effect of this field on the nearby proton has been found to depend upon the orientation of the proton with respect to the Π bond producing the induced field.

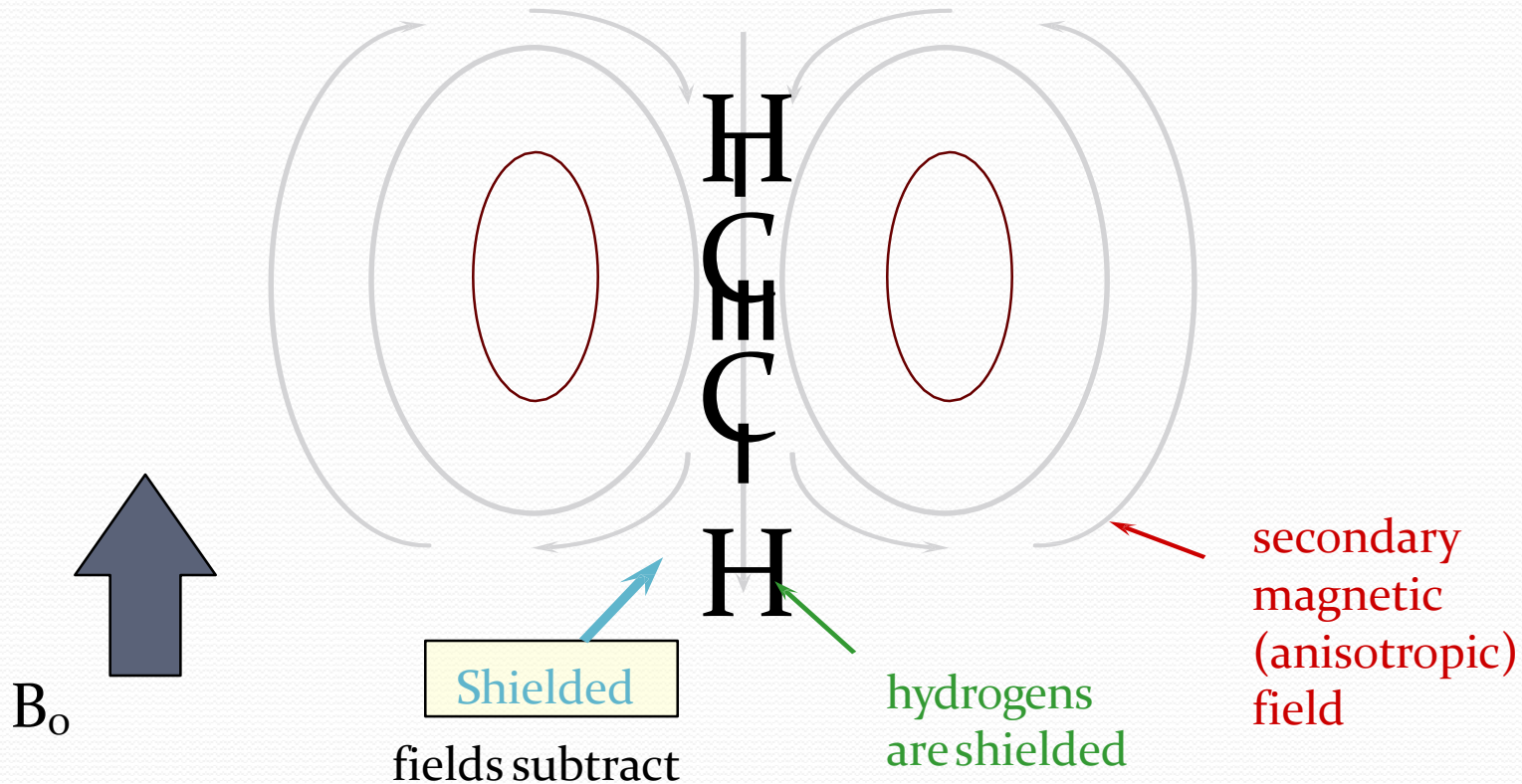
Ring Current in Benzene



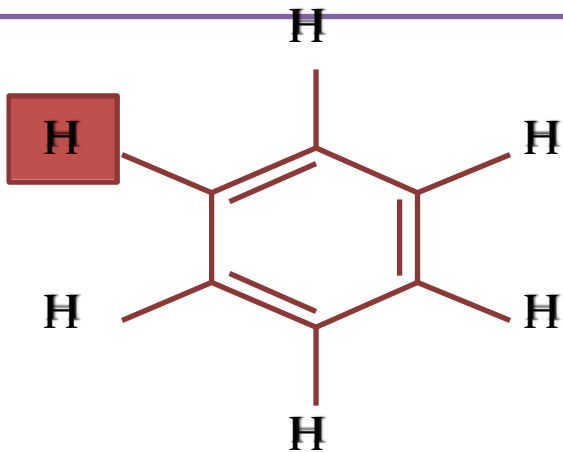
ANISOTROPIC FIELD IN AN ALKENE



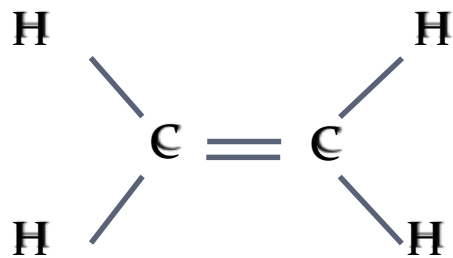
ANISOTROPIC FIELD FOR AN ALKYNE



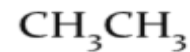
Protons attached to sp^2 hybridized carbon are less shielded than those attached to sp^3 hybridized carbon.



δ 7.3 ppm



$\delta = 5.3$ ppm



$\delta = 0.9$ ppm

3. Vander waal's deshielding

- In overcrowded molecules, it is possible that some proton may be occupying sterically hindered position.
- Electron cloud of a bulky group (hindering group) will tend to repel the electron surrounding the proton.
- Thus such a proton will be **deshielded**
- will resonate at slightly higher value of δ than expected in the absence of this effect

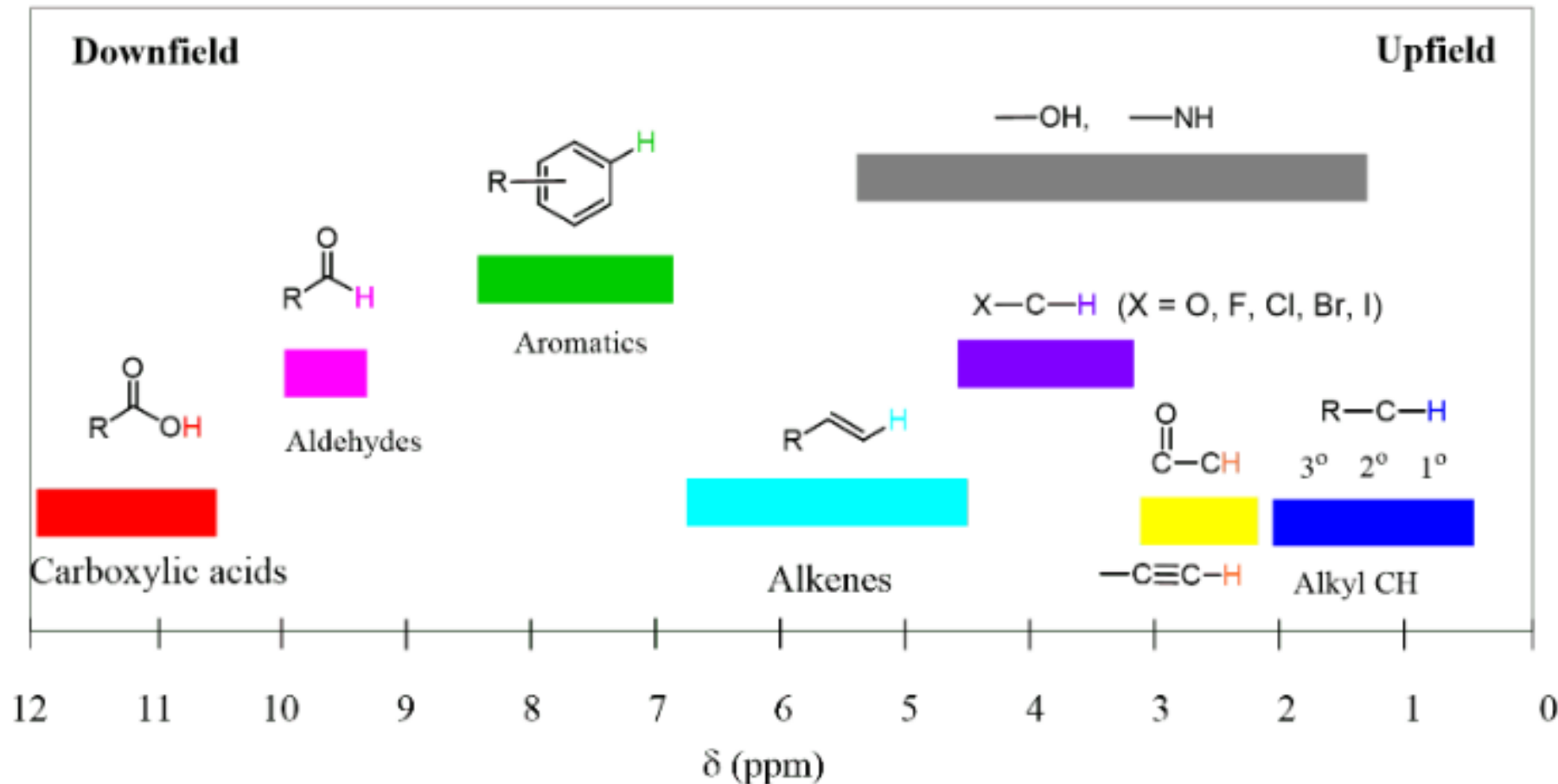


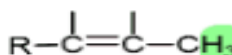
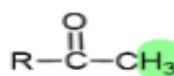
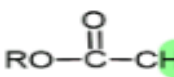
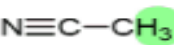
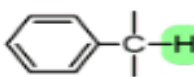
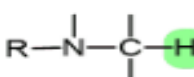
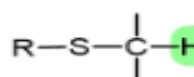
5. Hydrogen Bonding

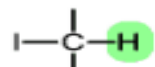
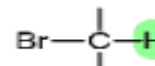
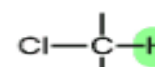
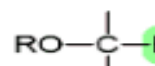
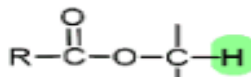
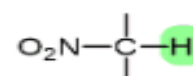
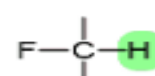
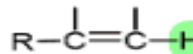
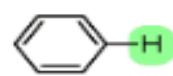
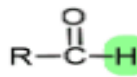
Hydrogen Bonding

- If an atom exhibits hydrogen bonding in a compound .
- It will **deshielded** due to the strongly electronegative atom attached to it.
- So absorption is shifted **downfield**.

Chemical Shifts of some protons in common environment

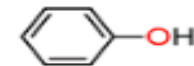
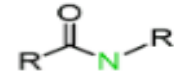
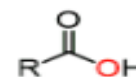


R-CH ₃	0.7 - 1.3
R-CH ₂ -R	1.2 - 1.4
R ₃ CH	1.4 - 1.7
	1.6 - 2.6
R = H or alkyl 	2.1 - 2.5
	2.1 - 2.6
	2.1 - 3.0
	2.3 - 2.7
R-C≡C-H	1.7 - 2.7
	2.2 - 2.9
	2.0 - 3.0

	2.0 - 4.0
	2.7 - 4.1
	3.1 - 4.1
	3.2 - 3.8
R = H or alkyl	
	3.5 - 4.8
	4.1 - 4.3
	4.2 - 4.8
	4.5 - 6.5
	6.5 - 8.0
	9.0 - 10

NH and OH peaks are most often broad or may as well be missing completely unless the sample is very dry.

This is also true for any proton capable of making hydrogen bonding:

R-SH	1.0 - 5.0
R = alkyl or aryl	
R-NH ₂	1.0 - 5.0
1°, 2°	
R-OH	1.0 - 5.0
1°, 2°, 3°	
	4.0 - 7.0
	5.0 - 9.0
1°, 2°	
	11 - 12

Downfield shifts more common



Thank You