

**CHEM202**

**Organic Chemistry**

Nick Green

nick.green@otago.ac.nz, 3n11

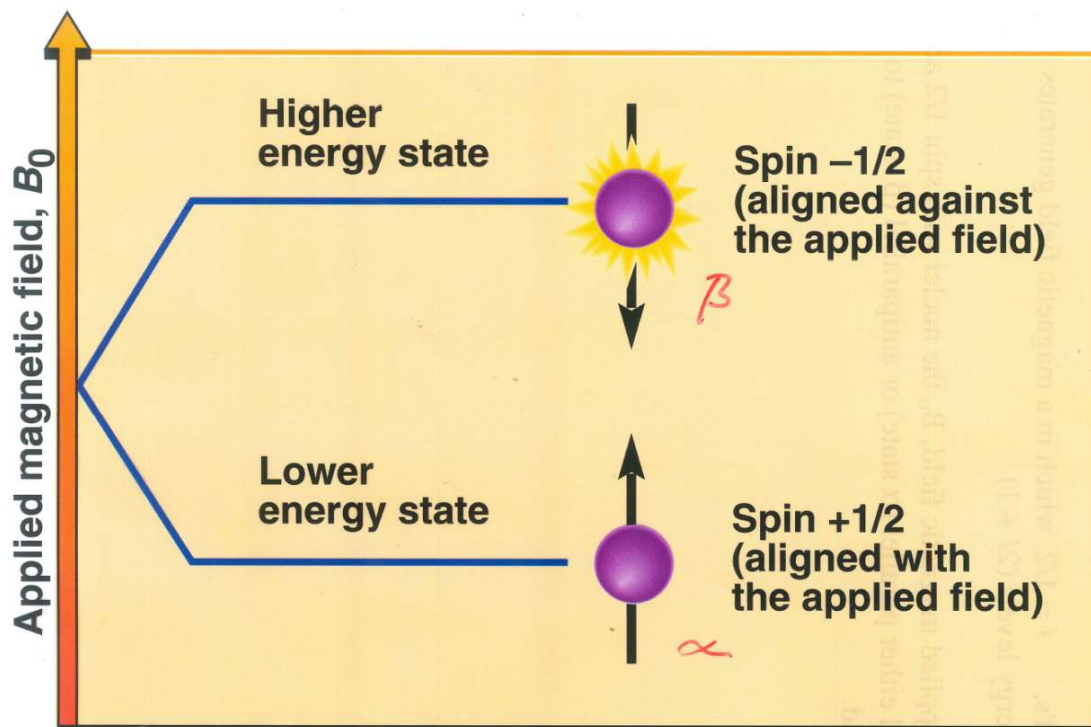
Module 1: Spectroscopy and Characterisation

***Lecture 3:  $^1\text{H}$  NMR Spectroscopy***

What molecule is being observed by NMR  
in a MRI scan?

# $^1\text{H}$ NMR Spectroscopy

- For  $^1\text{H}$ 's,  $I = 1/2$ , which in a magnetic field generates two energy levels ( $2I + 1$ )
- In an applied magnetic field,  $B_0$  the nuclei with spin  $1/2$  are aligned either parallel ( $\alpha$  state) or antiparallel ( $\beta$  state) to the field.



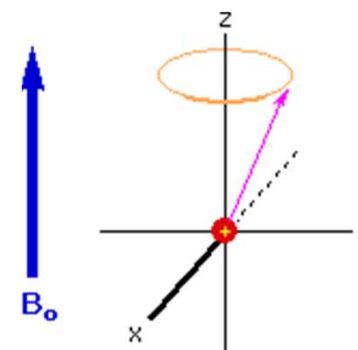
$$\nu = \gamma B_0 / 2 \pi$$

$$\Delta E = h \gamma B_0 / 2 \pi$$

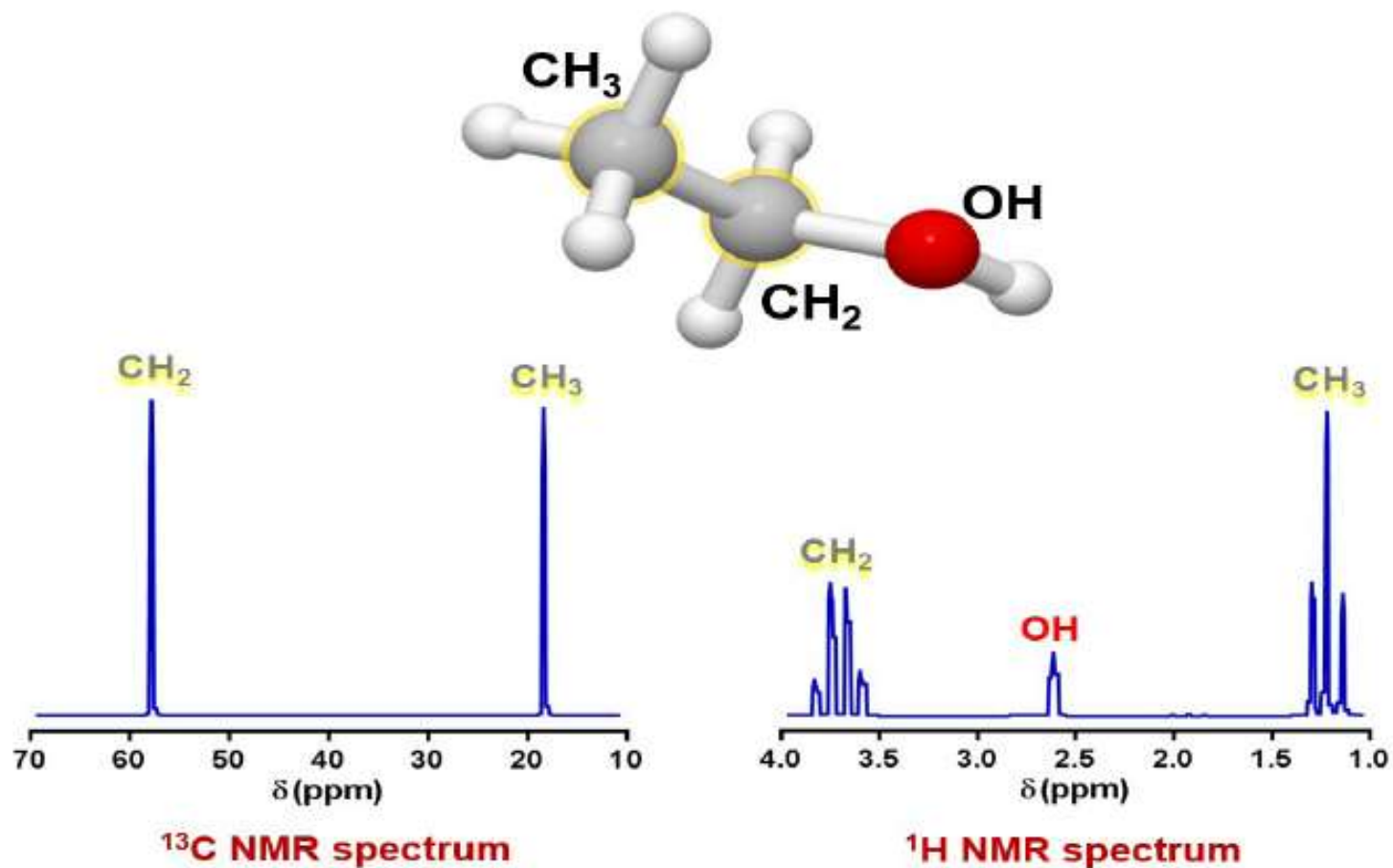
# NMR active nuclei

Properties of NMR active isotopes of commonly encountered nuclides. Resonance frequencies are for a field strength of 11.74 tesla and the relative sensitivity includes a term for the intrinsic sensitivity of a nuclide and its natural abundance.

Nucleus	Natural Abundance %	Nuclear Spin (I)	Magnetogyric ratio / $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$	Resonant frequency / MHz	Relative sensitivity
$^1\text{H}$	99.98	$\frac{1}{2}$	26.75	500.00	1.00
$^2\text{H}$	0.02	1	4.11	76.75	$1.45 \times 10^{-6}$
$^{13}\text{C}$	1.11	$\frac{1}{2}$	6.73	125.72	$1.76 \times 10^{-4}$
$^{14}\text{N}$	99.63	1	1.93	36.12	$1.01 \times 10^{-3}$
$^{15}\text{N}$	0.37	$\frac{1}{2}$	-2.71	50.66	$3.85 \times 10^{-6}$
$^{17}\text{O}$	0.04	$\frac{5}{2}$	-3.63	67.78	$1.08 \times 10^{-5}$
$^{19}\text{F}$	100.00	$\frac{1}{2}$	25.18	470.39	0.83
$^{31}\text{P}$	100.00	$\frac{1}{2}$	10.84	202.40	$6.63 \times 10^{-2}$



# NMR Spectra of Ethanol



# Shielding

The exact extent of the magnetic field that any nucleus experiences is a sum of:

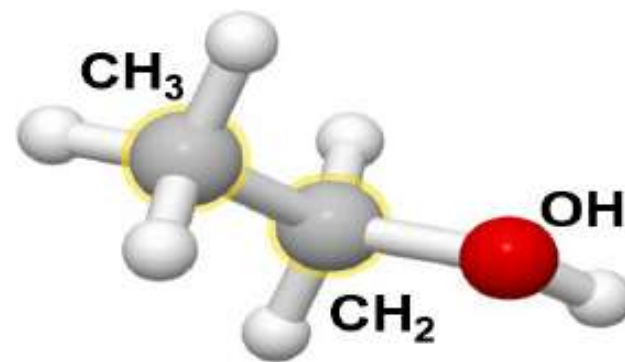
- The (large) external magnetic field
- Small local variations in the magnetic field

These small local variations arise from the movement of electrons, which generate their own tiny magnetic fields

Depending on the local environment, nuclei will experience a magnetic field slightly higher or lower than the external one  
**Shielding** reduces the strength of the magnetic field experienced.

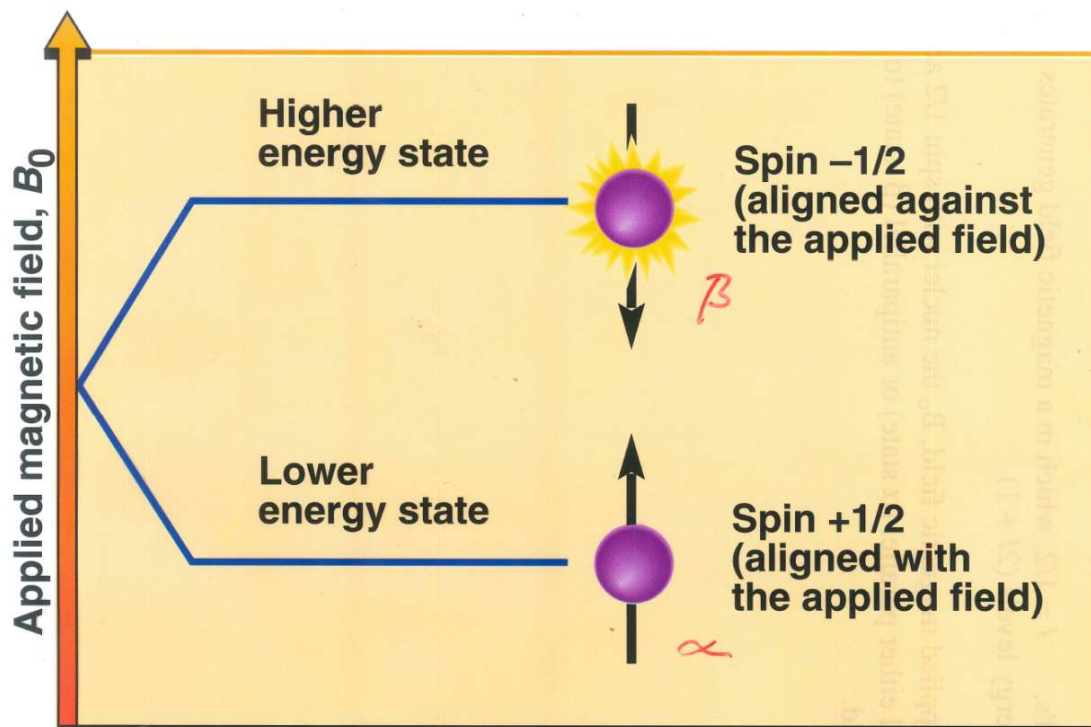
**Deshielding** increases it.

**These effects depend on structure.**



# $^1\text{H}$ NMR Spectroscopy

- For  $^1\text{H}$ 's,  $I = 1/2$ , which in a magnetic field generates two energy levels ( $2I + 1$ )
- In an applied magnetic field,  $B_0$  the nuclei with spin  $1/2$  are aligned either parallel ( $\alpha$  state) or antiparallel ( $\beta$  state) to the field.



$$\nu = \gamma B_0 / 2 \pi$$

$$\Delta E = h \gamma B_0 / 2 \pi$$

Given this energy difference the two spin states will be unequally populated (Boltzman distribution)

$$N_{\alpha}/N_{\beta} = e^{-\Delta E/RT}$$

The low frequency radiation required indicates that  $\Delta E$  is relative small, and correspondingly there will only be a small population difference between the  $\alpha$  and  $\beta$  states

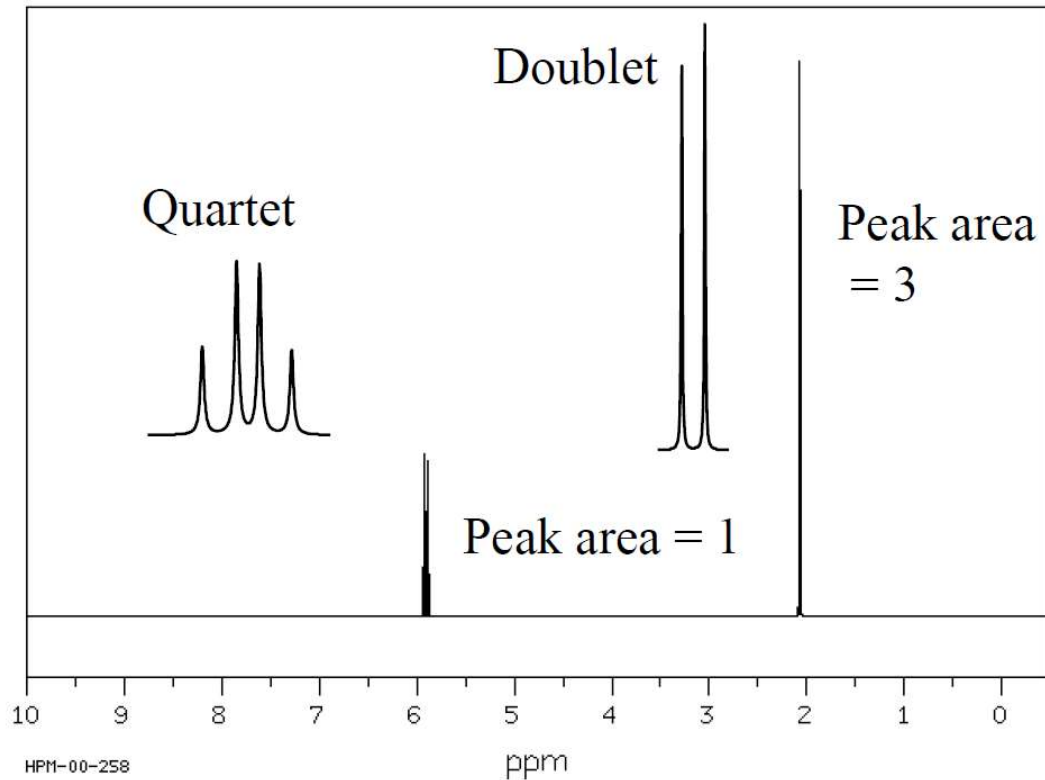
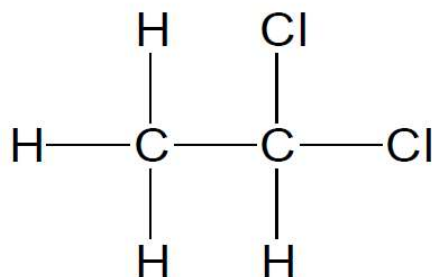
For protons at 200 MHz the population difference is remarkably small ( $\Delta E=6.6 \times 10^{-26} \text{J}$ )

$$\frac{10^5}{1 + 10^5} N_{\beta}$$
$$N_{\alpha}$$



## Features of the $^1\text{H}$ NMR Spectrum

$\Rightarrow$  a typical 1-D  $^1\text{H}$ -nmr spectrum is a plot of intensity vs chemical shift ( $\delta$ )



**Deshielded  
(higher freq)**

**Shielded  
(lower freq)**



## Information from data

Analysis yields detailed information regarding molecular structure and in particular a map of the C/H framework. Spatial information can also be ascertained *ie* analysis of a molecules conformation.

- number of different absorptions  $\Rightarrow$  how many different proton environments are present in the molecule
- the frequency of absorption, chemical shift ( $\delta$ )  $\Rightarrow$  the environment of the respective nuclei
- the intensities of the signals  $\Rightarrow$  relative number of nuclei of each type
- the splitting of the signals  $\Rightarrow$  information about neighboring nuclei, molecular geometry

## Chemical Shift

⇒ a typical 1-D  $^1\text{H}$ -nmr spectrum is a plot of intensity vs chemical shift ( $\delta$ )

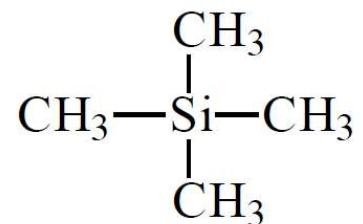
The chemical shift ( $\delta$ , ppm) is a universal, relative measure of frequency that is independent of  $B_0$

$$\delta = (\nu - \nu_{\text{ref}}) / \nu_0$$

$\nu_0$  = operating frequency of the spectrometer (MHz)

$\nu_{\text{ref}}$  = frequency of absorption for a reference compound (Hz)

The reference compound for both  $^1\text{H}$  and  $^{13}\text{C}$  nmr is tetramethylsilane (TMS) whose chemical shift is defined as 0.00 ppm



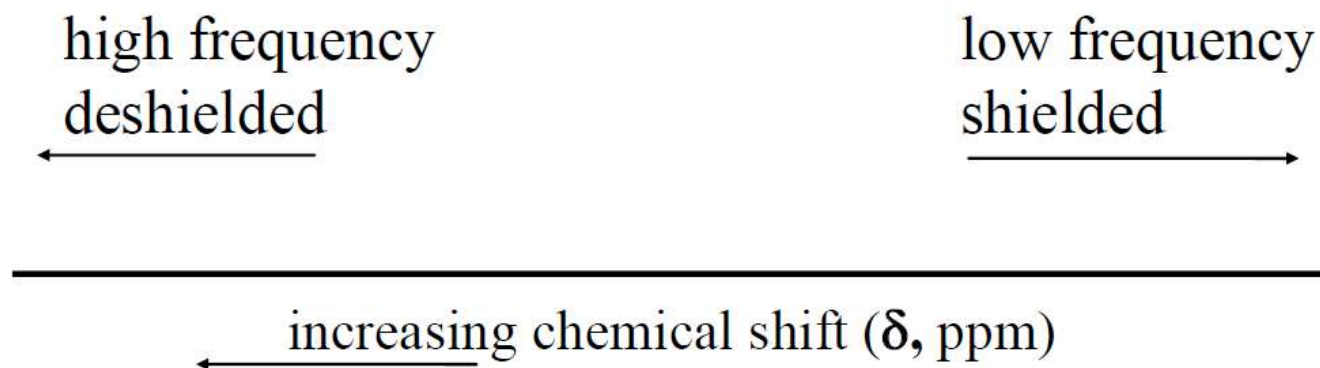
TMS, is volatile, inert, soluble in a majority of solvents, and displays a single resonance with a convenient  $\delta$ .

## Shielding and deshielding

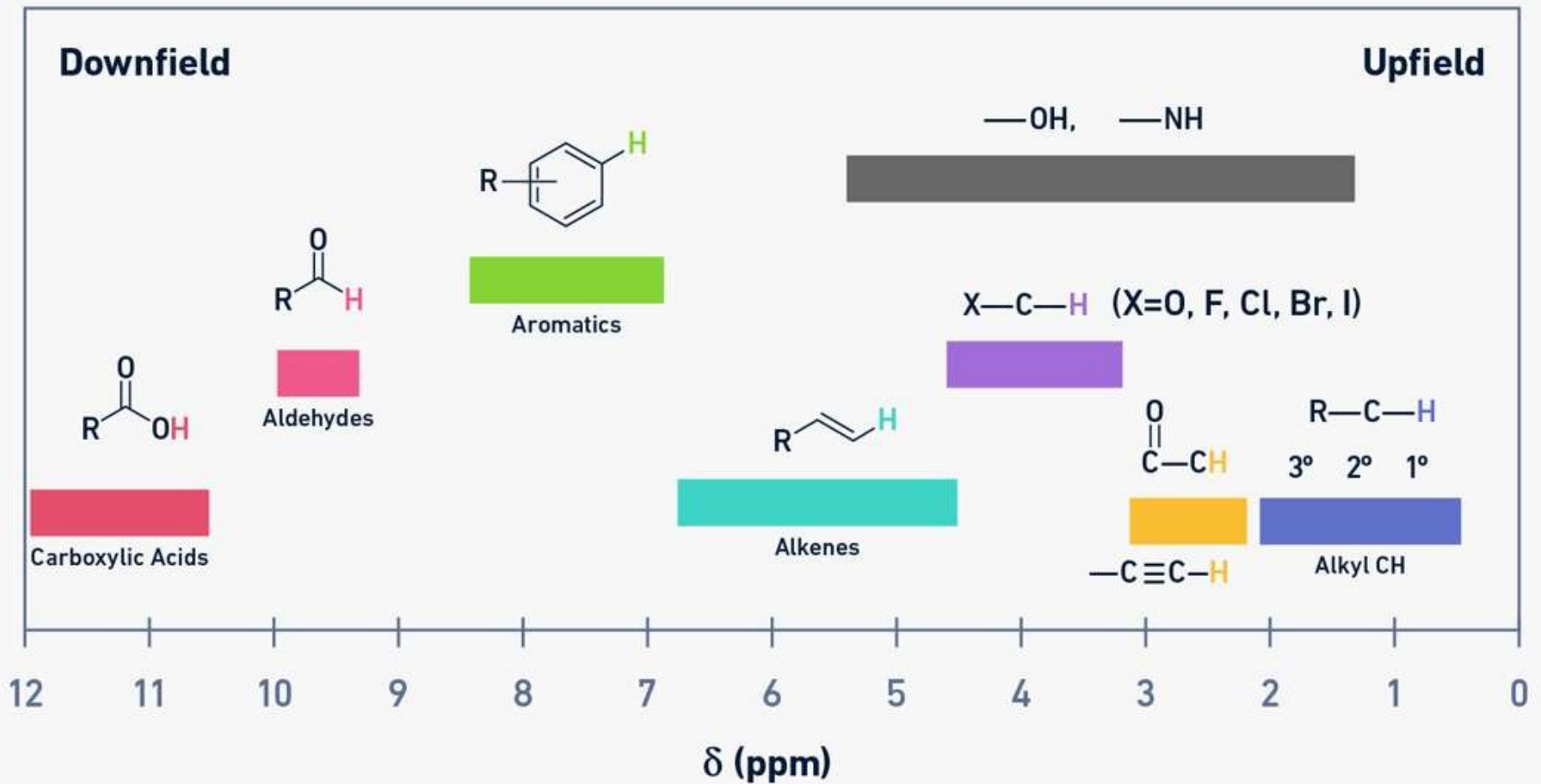
A nucleus is shielded or deshielded whenever it is influenced by the magnetic fields of nearby electrons. The applied magnetic field induces circulation of electrons in both the single and multiple bonds. Circulation of charge results in a magnetic field which opposes  $B_0$  thus shielding the nucleus from the applied magnetic field.

The larger the electron density  $\Rightarrow$  the greater the shielding, and the lower the frequency

### Nomenclature used when describing chemical shift



# Chemical shift is characteristic of structure





## What influences shielding?

Inductive effects

Anisotropic effects

Mesomeric effects

H-bonding

### Inductive Effects

- the degree of shielding about a nucleus is strongly influenced by the electron density surrounding it, which will be affected by electronegative and electropositive substituents in the immediate vicinity
- electron withdrawing groups will draw electron density away (- **I** effect) from the nucleus  
⇒ reduce the shielding effect and move the resonance frequency to higher values (higher ppm)
- electropositive groups have the opposite effect (+ **I** effect)
- the inductive effect is a short range effect      **(Through bond effect)**

# Inductive Effects

Proton Chemical Shifts of Methyl Derivatives

Compound	(CH <sub>3</sub> ) <sub>4</sub> C	(CH <sub>3</sub> ) <sub>3</sub> N	(CH <sub>3</sub> ) <sub>2</sub> O	CH <sub>3</sub> F
δ	0.9	2.1	3.2	4.1
Compound	(CH <sub>3</sub> ) <sub>4</sub> Si	(CH <sub>3</sub> ) <sub>3</sub> P	(CH <sub>3</sub> ) <sub>2</sub> S	CH <sub>3</sub> Cl
δ	0.0	0.9	2.1	3.0

Proton Chemical Shifts (ppm)

Cpd. / Sub.	X=Cl	X=Br	X=I	X=OR	X=SR
CH <sub>3</sub> X	3.0	2.7	2.1	3.1	2.1
CH <sub>2</sub> X <sub>2</sub>	5.3	5.0	3.9	4.4	3.7
CHX <sub>3</sub>	7.3	6.8	4.9	5.0	

# Inductive Effects

$$\text{XC}^1\text{H}_2\text{C}^2\text{H}_2\text{C}^3\text{H}_3$$

X	C <sup>1</sup> H <sub>2</sub>	C <sup>2</sup> H <sub>2</sub>	C <sup>3</sup> H <sub>3</sub>
Et	1.3	1.3	0.9
HOOC	2.3	1.7	1.0
SH	2.5	1.6	1.0
NH <sub>2</sub>	2.6	1.5	0.9
Ph	2.6	1.6	0.9
Br	3.4	1.9	1.0
Cl	3.5	1.8	1.0
OH	3.6	1.6	0.9
NO <sub>2</sub>	4.4	2.1	1.0

The influence of electronegative substituents on chemical shift (in ppm). The greater the electron withdrawing effect of the substituent, the greater the chemical shift of adjacent protons.



The hybridisation of a carbon atom has a substantial effect on the  $\delta$  for attached protons

$sp^3$	$\delta$ 0.8 - 2 ppm
$sp^2$	$\delta$ 4.5 - 6 ppm
$sp$	$\delta$ 2 - 3 ppm

This is partially a consequence of the increasing 'electron withdrawing nature' of the C on going from  $sp^3$  to  $sp$  hybridisation.

An  $sp$  carbon is the most electronegative, but there is an additional effect at play! (tbc...)