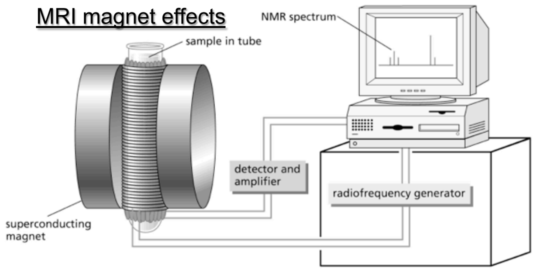
^{1}H NMR Spectroscopy:

Nuclear Magnetic Resonance

An NMR Spectrometer

MRI magnet effects



http://my.rsc.org/video/54

The nuclei that are most useful to organic chemists are:

^{1}H and ^{13}C

both have spin = ±1/2

^{1}H is 99% at natural abundance

^{13}C is 1.1% at natural abundance

NMR nuclei from isotopes of many other elements as well: ^{2}H, ^{10}B, ^{11}B, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{29}Si, ^{31}P, ^{35}Cl, ^{113}Cd, ^{195}Pt

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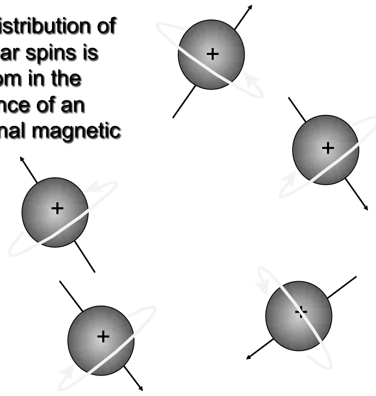
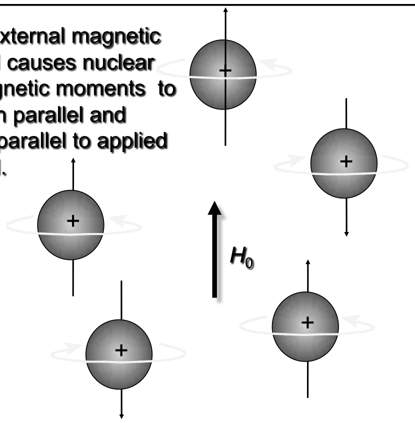
Nuclear Spin

A spinning charge, such as the nucleus of ^{1}H or ^{13}C, generates a magnetic field. The magnetic field generated by a nucleus of spin +1/2 is opposite in direction from that generated by a nucleus of spin –1/2.

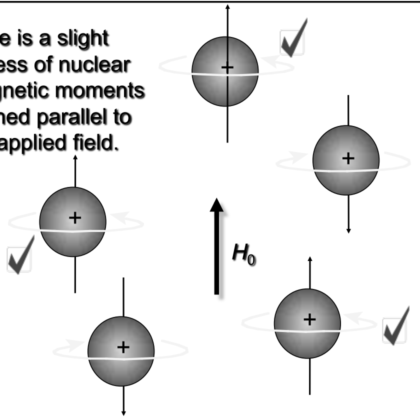
The distribution of nuclear spins is random in the absence of an external magnetic field.

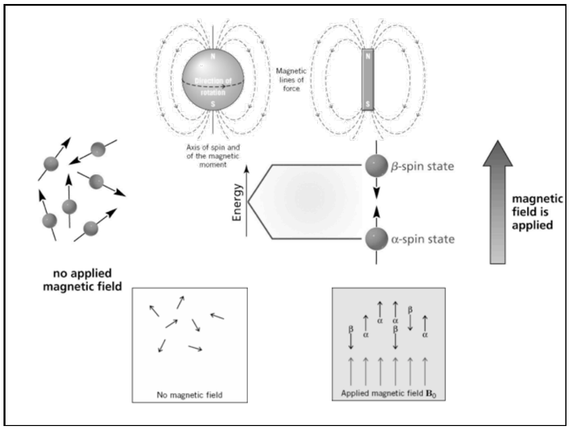


An external magnetic field causes nuclear magnetic moments to align parallel and antiparallel to applied field.

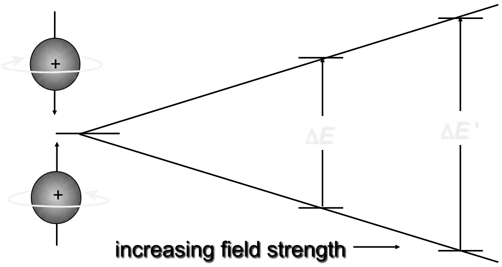


There is a slight excess of nuclear magnetic moments aligned parallel to the applied field.





Energy Differences Between Nuclear Spin States



increasing field strength →

no difference in absence of magnetic field
proportional to strength of external magnetic field

$$\alpha\text{-spin states} \underset{\text{release } \Delta E}{\overset{\text{absorb } \Delta E}{\rightleftharpoons}} \beta\text{-spin states}$$

↓

Signals detected by NMR

Some important relationships in NMR

The frequency of absorbed electromagnetic radiation is proportional to

the energy difference between two nuclear spin states which is proportional to

the applied magnetic field

Some important relationships in NMR

	Units
The frequency of absorbed electromagnetic radiation is proportional to	Hz
the energy difference between two nuclear spin states which is proportional to	kJ/mol (kcal/mol)
the applied magnetic field	tesla (T)

Some important relationships in NMR

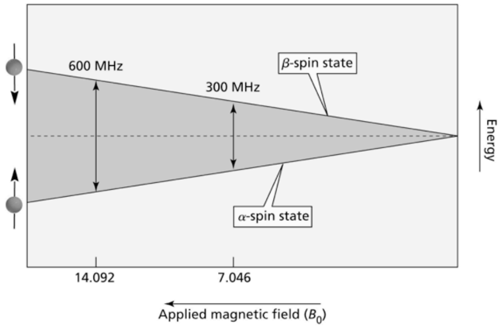
The frequency of absorbed electromagnetic radiation is different for different elements, and for different isotopes of the same element.

For a field strength of 4.7 T:

^{1}H absorbs radiation having a frequency of 200 MHz (200 x 10^6 s^{-1})

^{13}C absorbs radiation having a frequency of 50.4 MHz (50.4 x 10^6 s^{-1})

The energy difference between the two spin states depends on the strength of the magnetic field



900 MHz NMR Spectrometer

900MHz, 21.2 T NMR Magnet at HWB-NMR, Birmingham, UK being loaded with a sample

Some important relationships in NMR

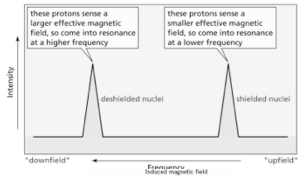
The frequency of absorbed electromagnetic radiation for a particular nucleus (such as ^{1}H) depends on its molecular environment.

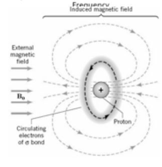
This is why NMR is such a useful tool for structure determination.

Nuclear Shielding
and
^{1}H Chemical Shifts

What do we mean by "shielding?"
What do we mean by "chemical shift?"

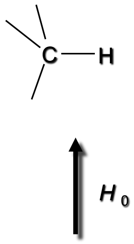
The electrons surrounding a nucleus affect the effective magnetic field sensed by the nucleus





Shielding

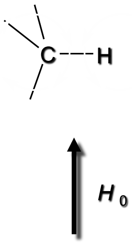
An external magnetic field affects the motion of the electrons in a molecule, inducing a magnetic field within the molecule.



Shielding

An external magnetic field affects the motion of the electrons in a molecule, inducing a magnetic field within the molecule.

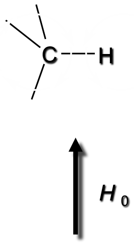
The direction of the induced magnetic field is opposite to that of the applied field.



Shielding

The induced field shields the nuclei (in this case, C and H) from the applied field.

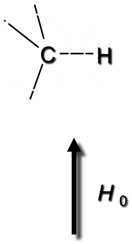
A stronger external field is needed in order for energy difference between spin states to match energy of rf radiation.



Chemical Shift

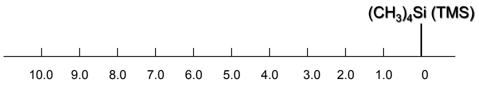
Chemical shift is a measure of the degree to which a nucleus in a molecule is shielded.

Protons in different environments are shielded to greater or lesser degrees; they have different chemical shifts.



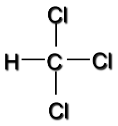
← Downfield
Decreased shielding

→ Upfield
Increased shielding



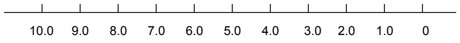
Chemical shift (δ, ppm)
measured relative to TMS

δ 7.28 ppm



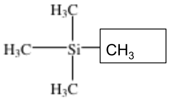
$HCCl_3$

The chemical shift, δ **ppm**, is a measure of how far the signal is from the TMS reference signal which is set to 0 **ppm**



Chemical shift (δ, ppm)

Chemical Shift:



The common scale for chemical shifts = δ (ppm)

$$\delta = \frac{\text{distance downfield from TMS (Hz)}}{\text{operating frequency of the spectrometer (MHz)}}$$

Chemical Shift

Example: The signal for the proton in chloroform ($HCCl_3$) appears 1456 Hz downfield from TMS at a spectrometer frequency of 200 MHz.

$$\delta = \frac{\text{position of signal - position of TMS peak}}{\text{spectrometer frequency}} \times 10^6$$

$$\delta = \frac{\text{1456 Hz - 0 Hz}}{200 \times 10^6 \text{ Hx}} \times 10^6$$

$$\delta = 7.28$$

Effects of Molecular Structure
on
^{1}H Chemical Shifts

protons in different environments experience different degrees of shielding and have different chemical shifts

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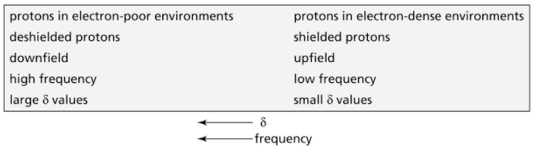

protons in electron-poor environments	protons in electron-dense environments
deshielded protons	shielded protons
downfield	upfield
high frequency	low frequency
large δ values	small δ values

The chemical shift is independent of the operating frequency of the spectrometer

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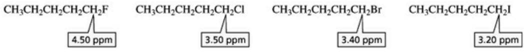
Electron withdrawal produces NMR signals downfield higher frequency (larger δ values)

F- = 4.50 ppm vs. I- = 3.20 ppm



Electronegative substituents decrease the shielding of methyl groups

CH_3F	**δ 4.3 ppm**
CH_3OCH_3	**δ 3.2 ppm**
$CH_3N(CH_3)_2$	**δ 2.2 ppm**
CH_3CH_3	**δ 0.9 ppm**
$CH_3Si(CH_3)_3$	**δ 0.0 ppm**

Electronegative substituents decrease the shielding of methyl groups

CH_3F	δ 4.3 ppm	*least shielded H*
CH_3OCH_3	δ 3.2 ppm	*downfield*
$CH_3N(CH_3)_2$	δ 2.2 ppm	
CH_3CH_3	δ 0.9 ppm	
$CH_3Si(CH_3)_3$	δ 0.0 ppm	*most shielded H*
		upfield

Effect is cumulative

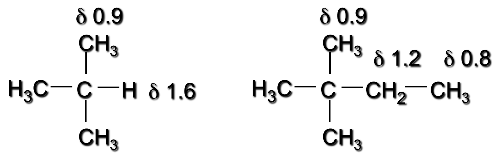
$CHCl_3$	δ 7.3 ppm
CH_2Cl_2	δ 5.3 ppm
CH_3Cl	δ 3.1 ppm

Question

- Which proton is most shielded?
- A) $CHCl_3$
- B) CH_2Cl_2
- C) $CHBr_3$
- D) CBr_4

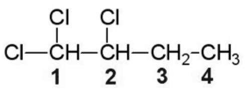
Methyl, Methylene, and Methine

CH_3 more shielded than CH_2 ;
CH_2 more shielded than CH



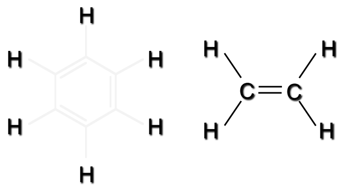
Question

- Select the most shielded proton in 1,1,2 -trichlorobutane.
- A) 1
- B) 2
- C) 3
- D) 4



$Cl{-}\overset{Cl}{\overset{|}{C}}H{-}\overset{Cl}{\overset{|}{C}}H{-}CH_2{-}CH_3$

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

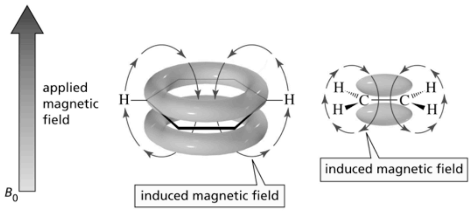


CH_3CH_3

δ 7.3 ppm δ 5.3 ppm δ 0.9 ppm

Diamagnetic Anisotropy

The π electrons are less tightly held by the nuclei than are σ electrons; they are more free to move in response to a magnetic field



Causes unusual chemical shifts for hydrogen bonded to carbons that form π bonds

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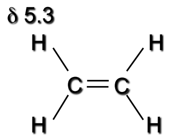
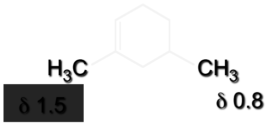
But Protons Attached to sp Hybridized Carbon are More Shielded than those Attached to sp^2 Hybridized Carbon



δ 2.4

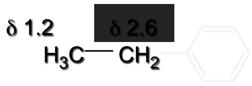
$H-C\equiv C-CH_2OCH_3$

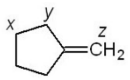
Protons Attached to Benzylic and Allylic Carbons are Somewhat Less Shielded than Usual



δ 0.9 δ 1.3 δ 0.9

$H_3C-CH_2-CH_3$

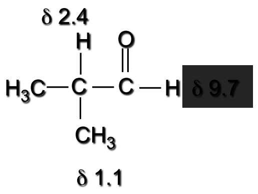


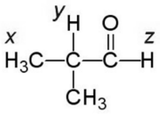


Question

- Assign the chemical shifts δ 1.6,
- δ 2.2, and δ 4.8 to the appropriate protons of methylene cyclopentane.
- A) x = 1.6; y = 2.2; z = 4.8
- B) x = 4.8; y = 1.6; z = 2.2
- C) x = 1.6; y = 4.8; z = 2.2
- D) x = 2.2; y = 1.6; z = 4.8

Proton Attached to C=O of Aldehyde is Most Deshielded C—H





Question

- Assign the chemical shifts δ1.1,
- δ2.4, and δ9.7 to the appropriate protons of propanal.
- A) x = 2.4; y = 1.1; z = 9.7
- B) x = 1.1; y = 9.7; z = 2.4
- C) x = 9.7; y = 2.4; z = 1.1
- D) x = 1.1; y = 2.4; z = 9.7

Chemical Shift Table

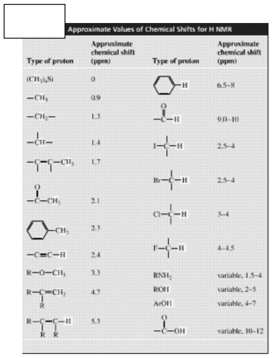
Type of proton	Chemical shift (δ), ppm	Type of proton	Chemical shift (δ), ppm
H—C—R	0.9-1.8	H—C—C≡C	2.5
H—C—C=C	1.6-2.6	H—C—Ar	2.3-2.8
H—C—C(=O)—	2.1-2.5	H(C=C)	4.5-6.5

Chemical Shift Table

Type of proton	Chemical shift (δ), ppm	Type of proton	Chemical shift (δ), ppm
H—Ar	6.5-8.5	H—C—Cl	3.1-4.1
H—C(=O)—	9-10	H—C—Br	2.7-4.1
H—C—NR	2.2-2.9	H—C—O	3.3-3.7

Chemical Shift Table

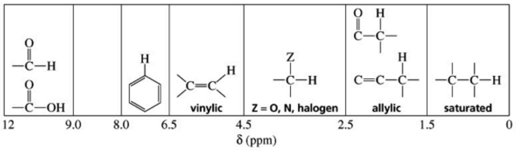
Type of proton	Chemical shift (δ), ppm
H—NR	1-3
H—OR	0.5-5
H—OAr	6-8
HO—C(=O)—	10-13



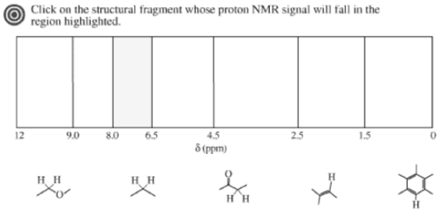
Approximate Values of Chemical Shifts for H NMR

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	C₆H₅—H	6.5–8
$—CH_3$	0.9	—C(=O)—H	9.0–10
$—CH_2—$	1.3	I—C—H	2.5–4
—CH—	1.4	Br—C—H	2.5–4
$—C=C—CH_3$	1.7	Cl—C—H	3–4
$—C(=O)—CH_3$	2.1	F—C—H	4–4.5
$C_6H_5—CH_3$	2.3	RNH_2	variable, 1.5–4
—C≡C—H	2.4	ROH	variable, 2–5
$R—O—CH_3$	3.3	ArOH	variable, 4–7
$R—C(R)=CH_2$	4.7	—C(=O)—OH	variable, 10–12
R—C(R)=C(R)—H	5.3		

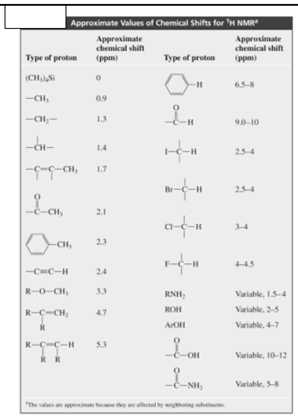
Characteristic Values of Chemical Shifts



http://chemconnections.org/organic/Movies%20Org%20Flash/nmr-shifts.swf



Click on the structural fragment whose proton NMR signal will fall in the region highlighted.



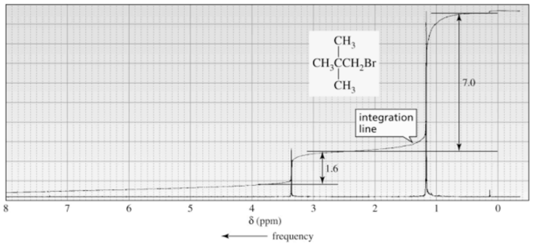
Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	⌬—H	6.5–8
$-CH_3$	0.9	$-\overset{O}{\overset{\Vert}{C}}-H$	9.0–10
$-CH_2-$	1.3	$I-\overset{\vert}{\underset{\vert}{C}}-H$	2.5–4
$-\overset{\vert}{C}H-$	1.4	$Br-\overset{\vert}{\underset{\vert}{C}}-H$	2.5–4
$-\underset{\vert}{C}=\underset{\vert}{C}-CH_3$	1.7	$Cl-\overset{\vert}{\underset{\vert}{C}}-H$	3–4
$-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.1	$F-\overset{\vert}{\underset{\vert}{C}}-H$	4–4.5
⌬—CH_3	2.3	RNH_2	Variable, 1.5–4
$-C\equiv C-H$	2.4	ROH	Variable, 2–5
$R-O-CH_3$	3.3	ArOH	Variable, 4–7
$R-\underset{\underset{R}{\vert}}{C}=CH_2$	4.7	$-\overset{O}{\overset{\Vert}{C}}-OH$	Variable, 10–12
$R-\underset{\underset{R}{\vert}}{C}=\underset{\underset{R}{\vert}}{C}-H$	5.3	$-\overset{O}{\overset{\Vert}{C}}-NH_2$	Variable, 5–8

[a] The values are approximate because they are affected by neighboring substituents.

^{1}H NMR spectrum / Integration

1-bromo-2,2-dimethylpropane



Integration

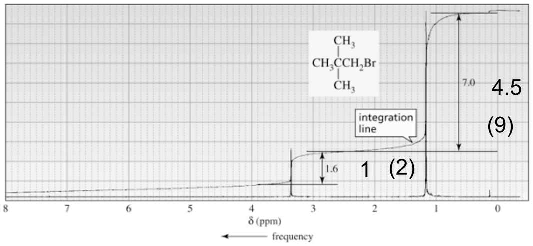
The area under each signal is proportional to the number of protons that give rise to that signal.

The height of each integration step is proportional to the area under a specific signal.

The integration tells us the relative number of protons that give rise to each signal, not absolute number.

^{1}H NMR spectrum / Integration

1-bromo-2,2-dimethylpropane



Question

A compound with the formula $C_6H_{14}O$ has the following signal integration for 3 signals: A, B, and C. How many protons are represented by each signal?

A. Signal at 0.9, integration of 6.3
B. Signal at 1.4, integration of 4.2
C. Signal at 3.5, integration of 4.2

A. A = 3; B = 4; C = 4
B. A = 3; B = 2; C = 2
C. A = 6; B = 2; C = 2
D. A = 6; B = 4; C = 4