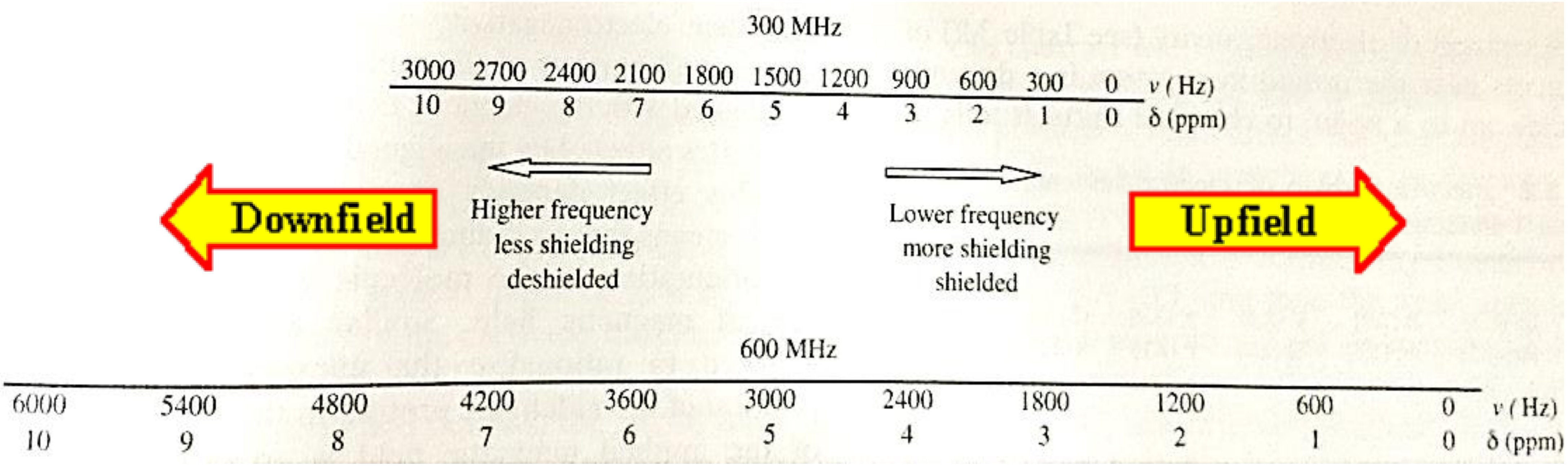
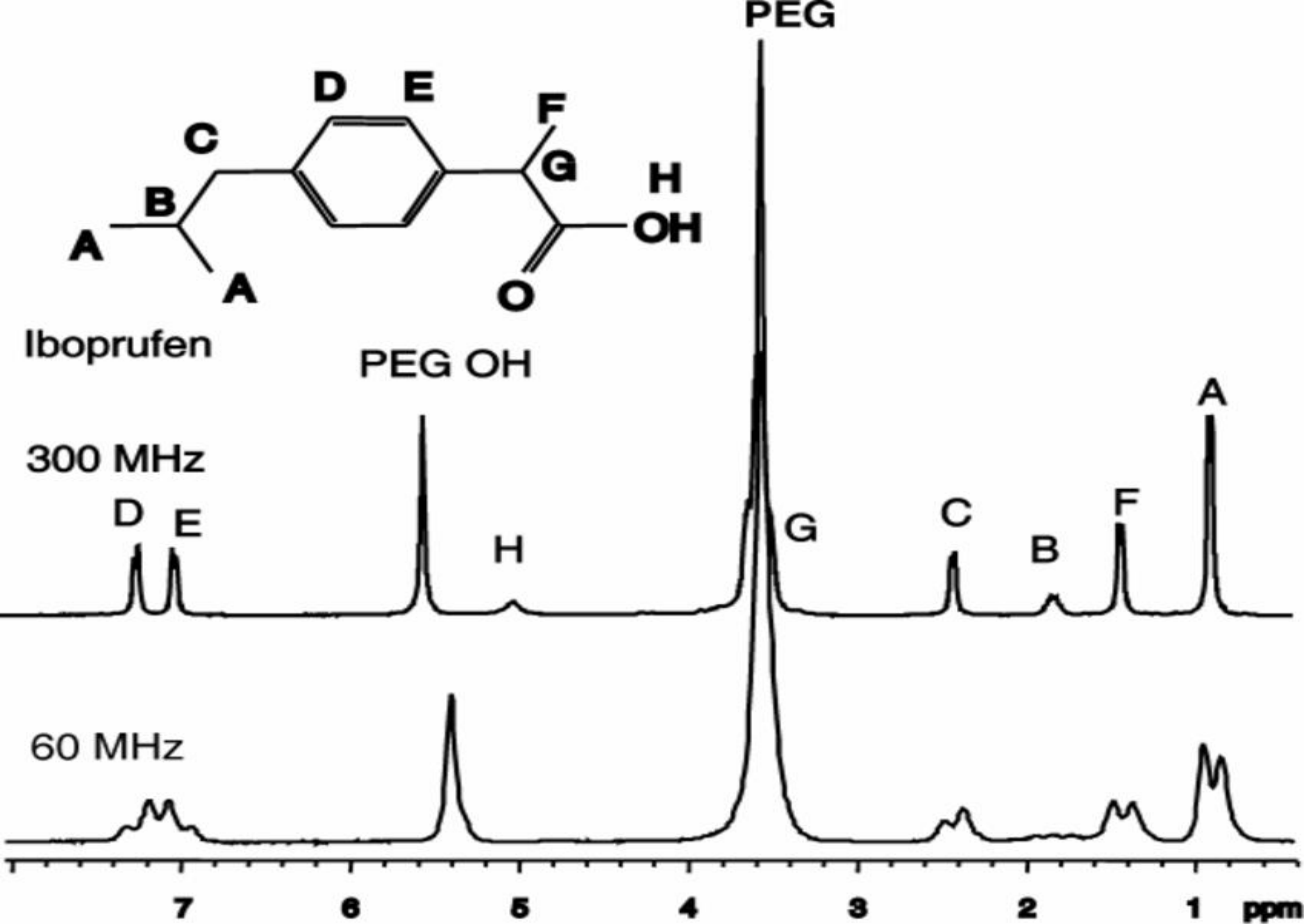
General notes about ^{1}H NMR spectrum:

- NMR absorptions generally appear as sharp peaks.
- Increasing chemical shift is plotted from left to right.
- Most protons absorb between 0-10 ppm.
- The terms "upfield" and "downfield" describe the relative location of peaks:
  - *Upfield means to the right.*
  - *Downfield means to the left.*

Instrumentation of NMR spectroscopy

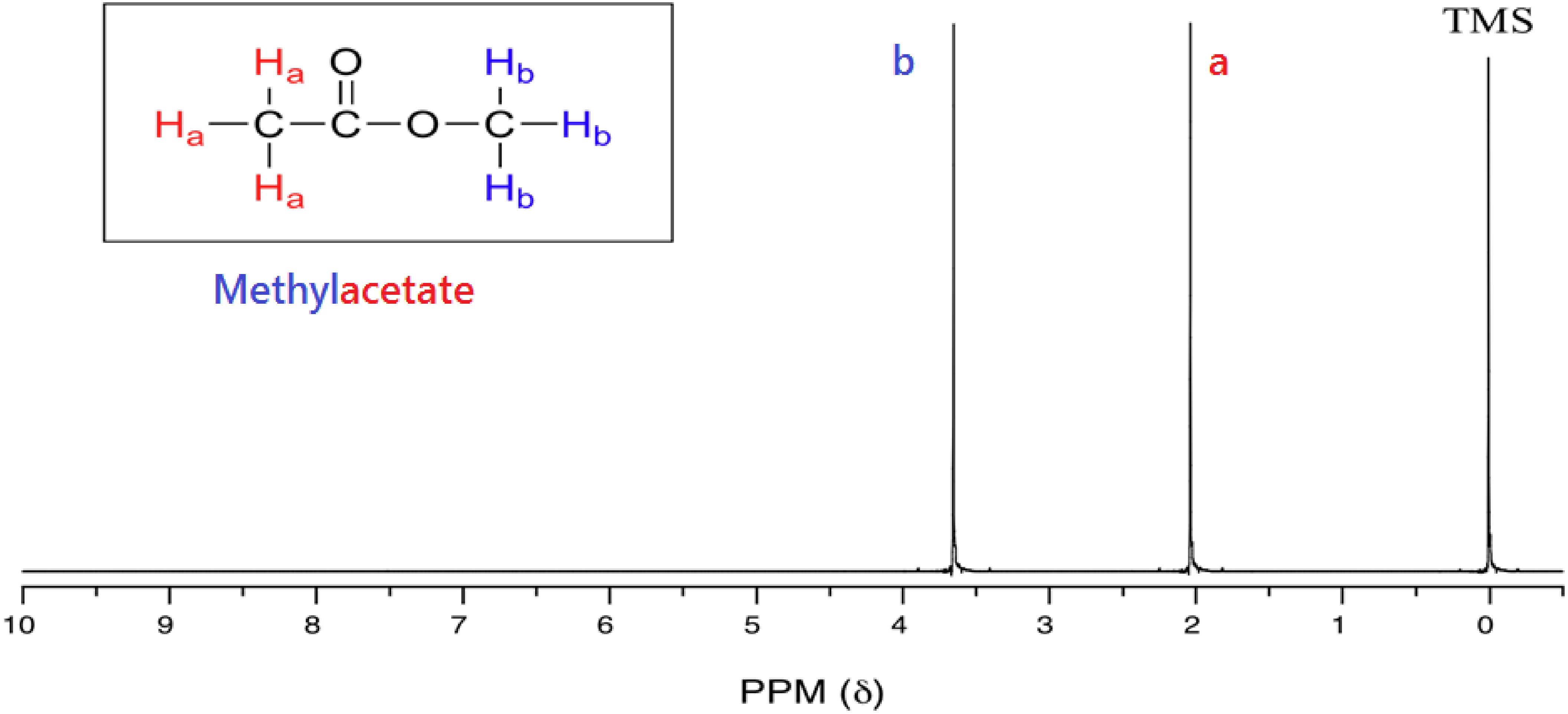
NMR spectrometers are referred to as 300 MHz instruments, 400 MHz instruments, 500 MHz instruments, 600 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance. (the higher the frequency, the better the resolution. Why?)




PEG
D
E
F
C
G
H
B
A
OH
A
O
Iboprufen
PEG OH
300 MHz
A
D
E
H
G
C
F
B
60 MHz
7
6
5
4
3
2
1
ppm

^{1}H NMR—The Spectrum

An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in parts per million (ppm).

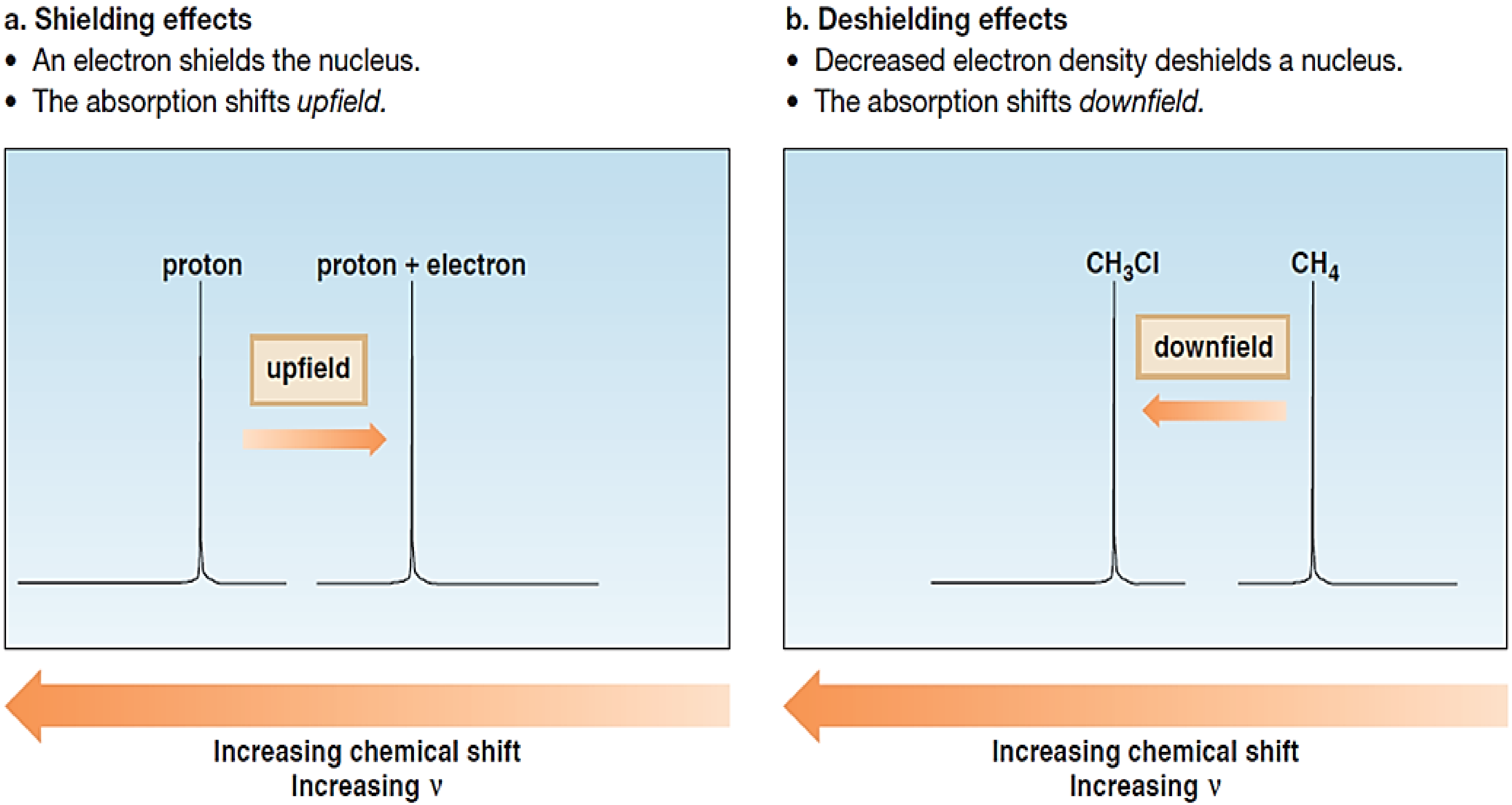


Methylacetate

Higher frequency is to the left in an NMR spectrum, toward higher chemical shift—so **deshielding shifts** an absorption downfield.

Protons near electronegative atoms are **deshielded**, so they absorb **downfield**.

How chemical shift is affected by electron density around a nucleus

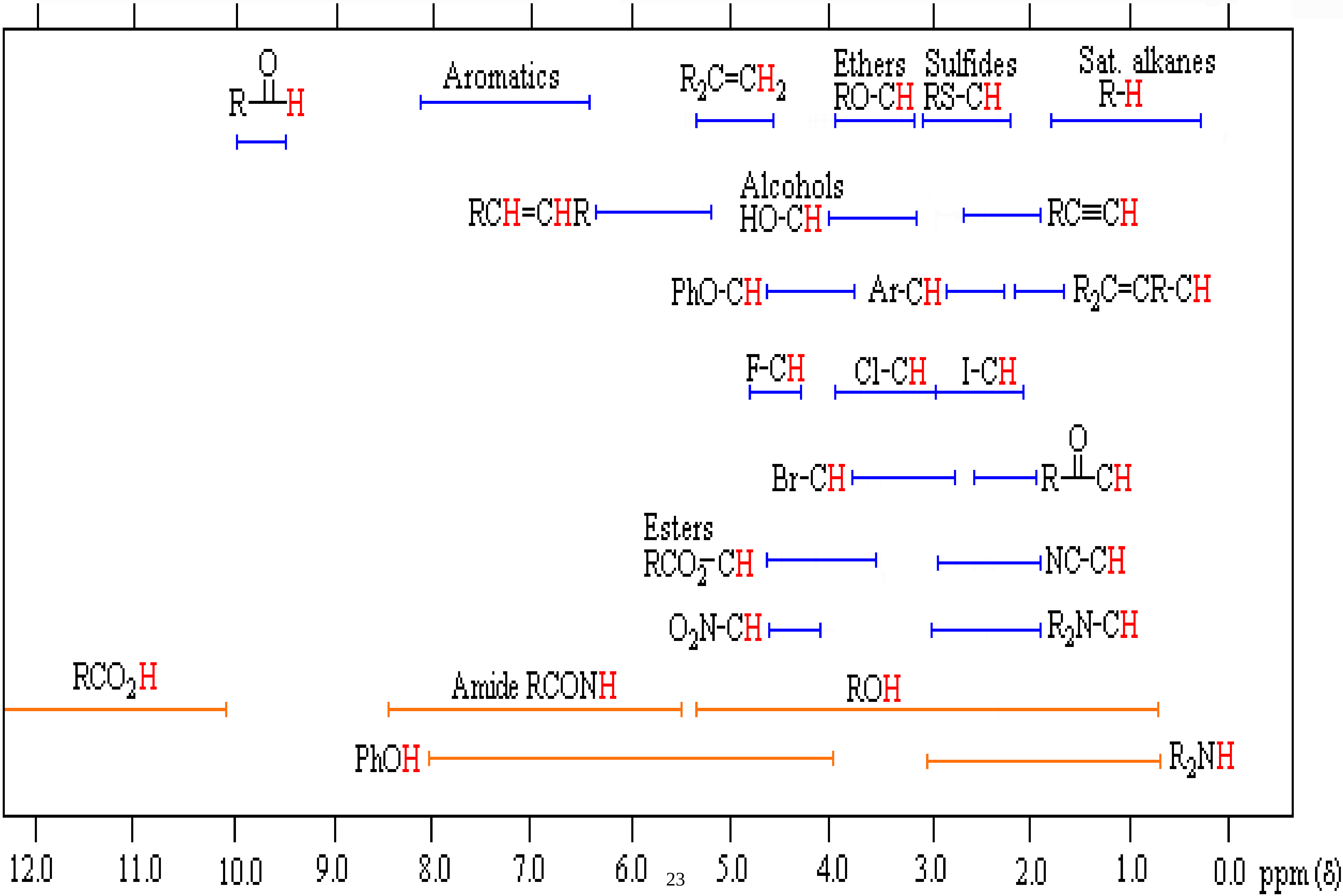


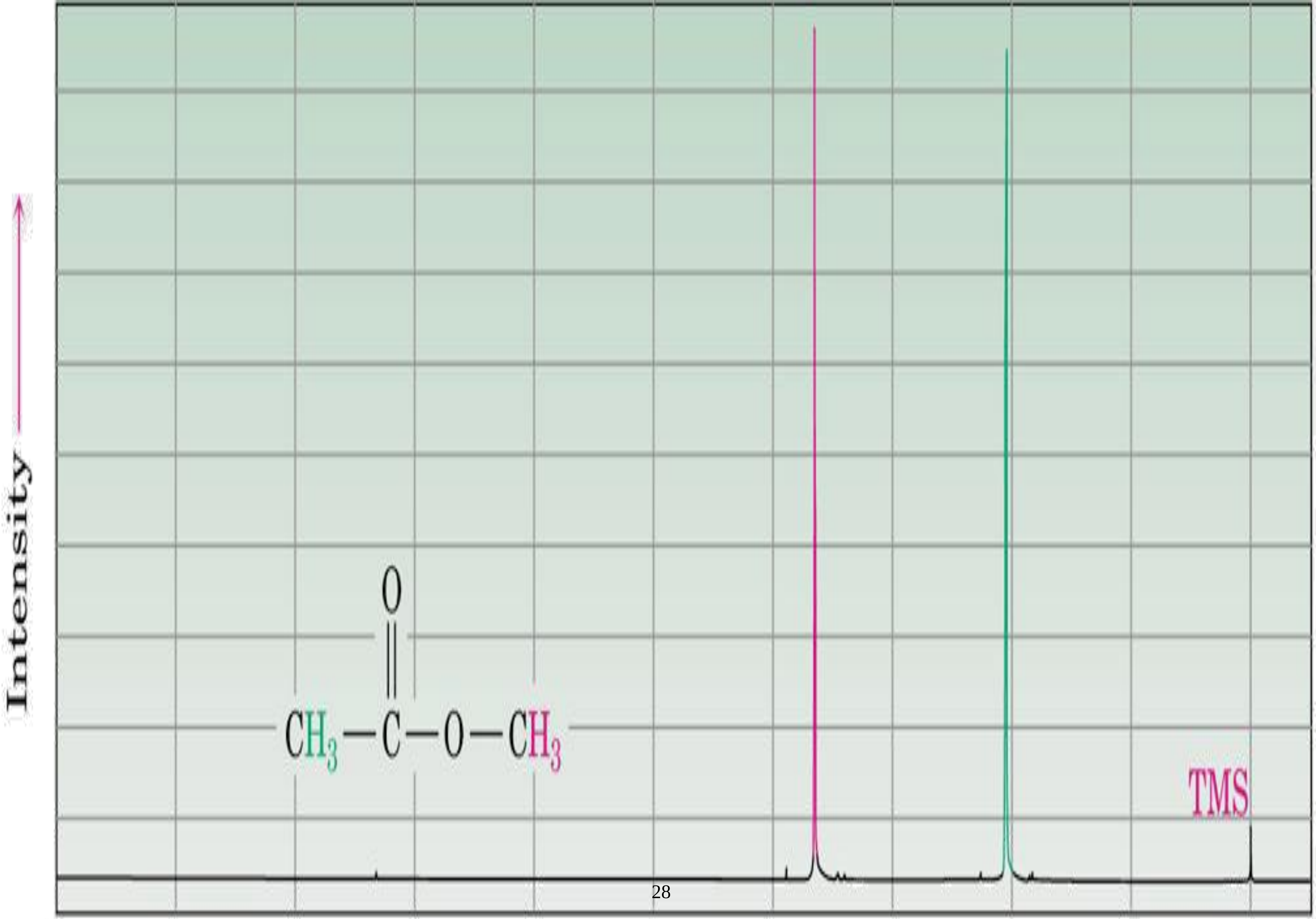
a. Shielding effects

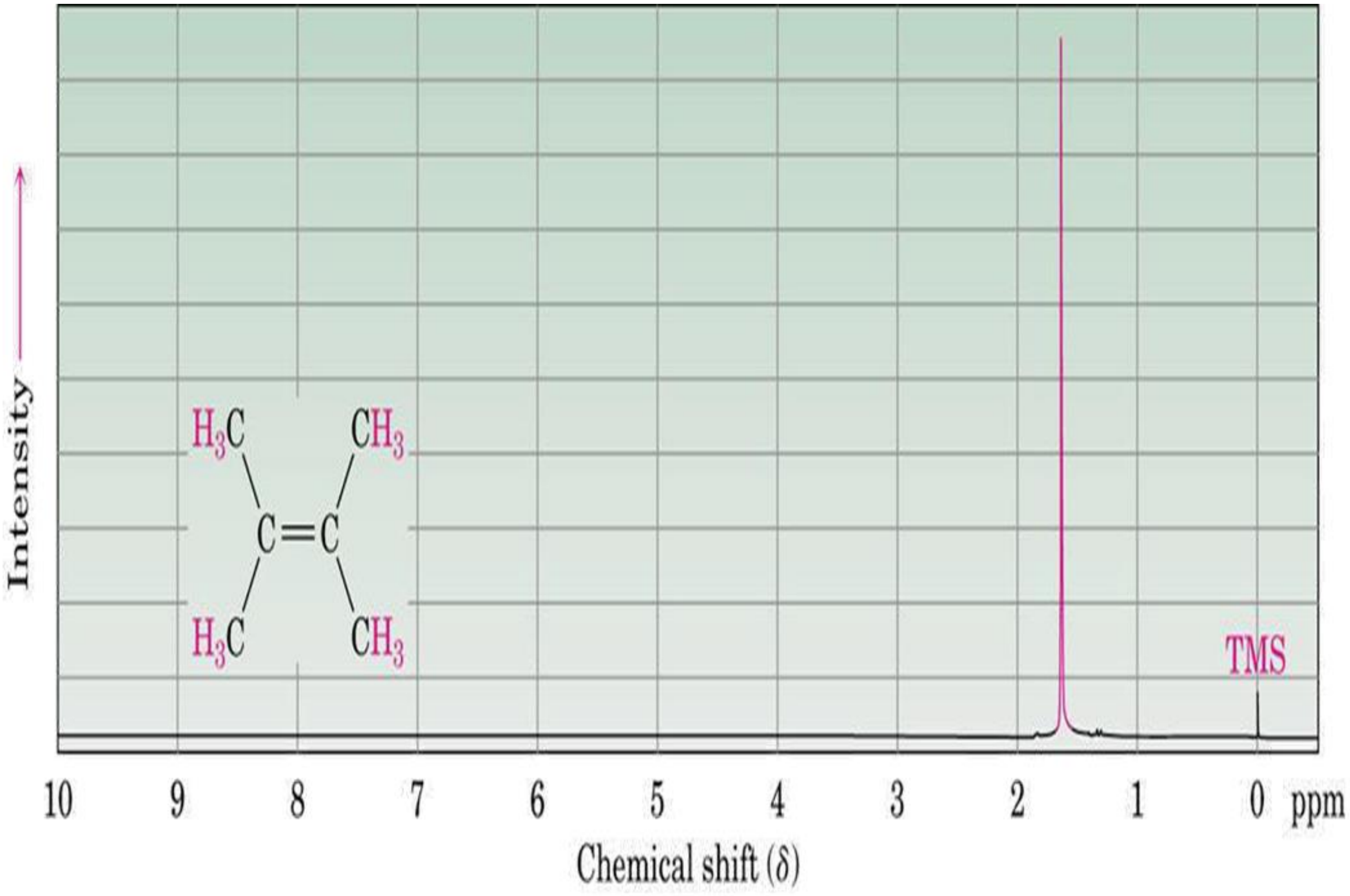
- An electron shields the nucleus.
- The absorption shifts *upfield*.

b. Deshielding effects

- Decreased electron density deshields a nucleus.
- The absorption shifts *downfield*.


$R-C(=O)-H$
Aromatics
$R_2C=CH_2$
Ethers RO-CH
Sulfides RS-CH
Sat. alkanes R-H
RCH=CHR
Alcohols HO-CH
RC≡CH
PhO-CH
Ar-CH
$R_2C=CR-CH$
F-CH
Cl-CH
I-CH
Br-CH
$R-C(=O)-CH$
Esters RCO_2-CH
NC-CH
O_2N-CH
R_2N-CH
RCO_2H
Amide RCONH
ROH
PhOH
R_2NH
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0 ppm (δ)


Intensity
O
CH3 — C — O — CH3
TMS



13/03/2018

Factors to Affect ^{1}H NMR Chemical Shift:

(1) Electronegativity of nearby atoms,
(2) Hybridization of adjacent atoms, and
(3) Diamagnetic effects

Electronegativity

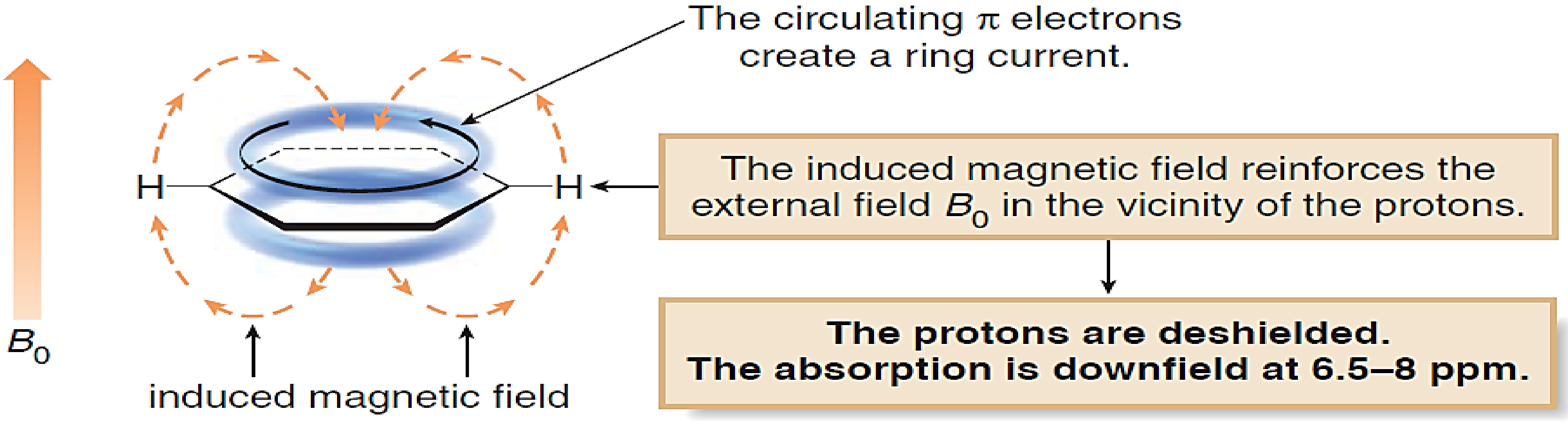
CH_3-X	Electronegativity of X	Chemical Shift (δ)
CH_3F	4.0	4.26
CH_3OH	3.5	3.47
CH_3Cl	3.1	3.05
CH_3Br	2.8	2.68
CH_3I	2.5	2.16
$(CH_3)_4C$	2.1	0.86
$(CH_3)_4Si$	1.8	0.00

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

Aromatic Effect

- In a magnetic field, the six π electrons in benzene circulate around the ring creating a ring current.
- The magnetic field induced by these moving electrons **reinforces** the applied magnetic field in the vicinity of the protons.
- The protons thus feel a stronger magnetic field and a higher frequency is needed for resonance. Thus they are deshielded and absorb downfield.



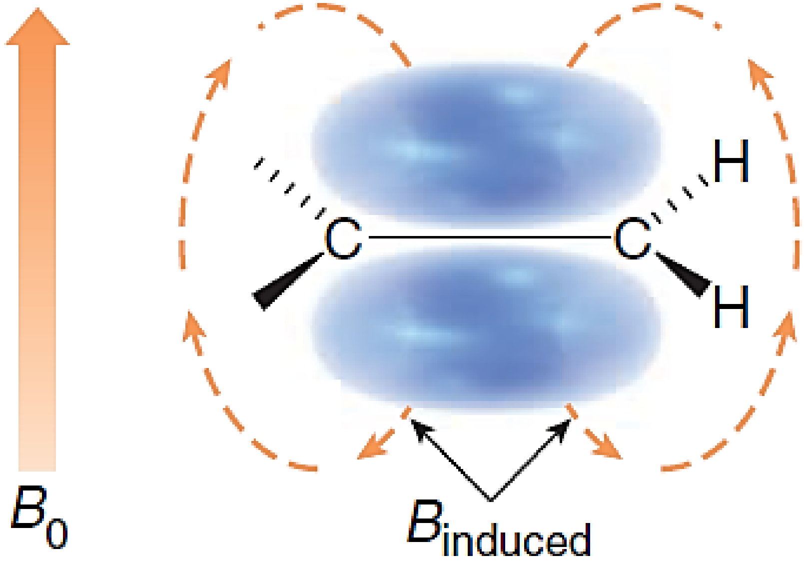
The circulating π electrons create a ring current.

The induced magnetic field reinforces the external field B_0 in the vicinity of the protons.

The protons are deshielded.
The absorption is downfield at 6.5–8 ppm.

Carbon-carbon double bond

- In a magnetic field, the loosely held π electrons of the double bond create a magnetic field that **reinforces** the applied field in the vicinity of the protons.
- The protons now feel a stronger magnetic field, and require a higher frequency for resonance. Thus the protons are deshielded and the absorption is downfield.

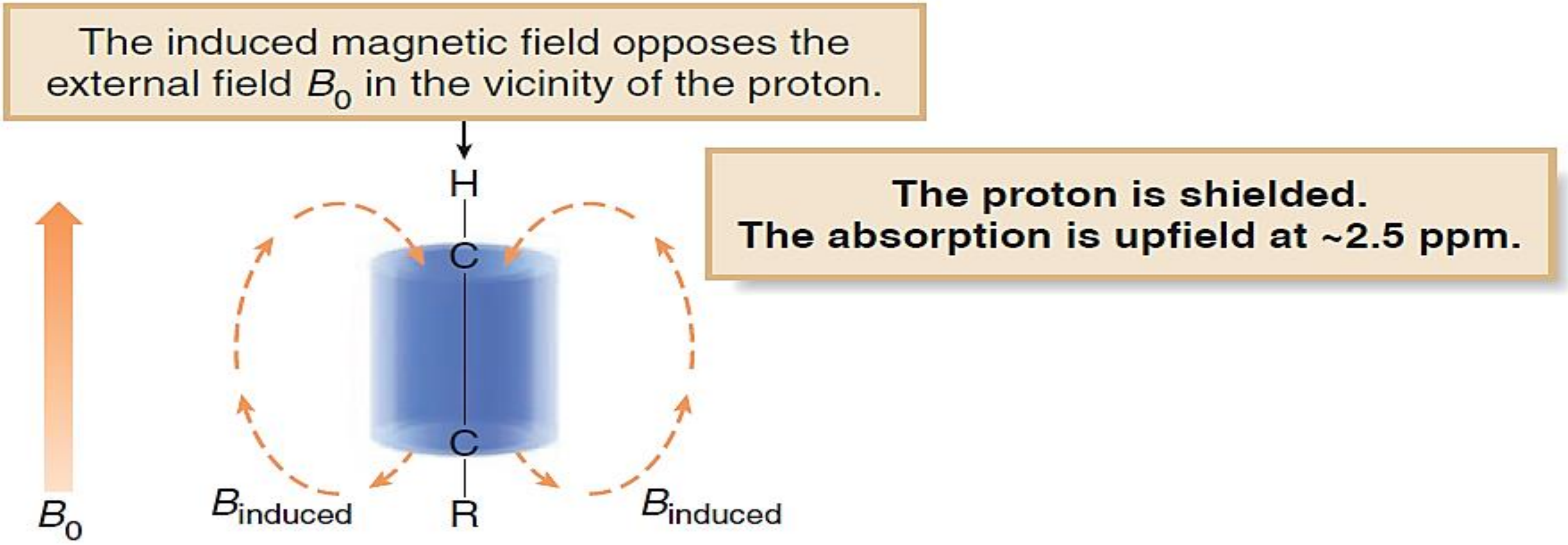


The induced magnetic field reinforces the external field B_0 in the vicinity of the protons.

The protons are deshielded.
The absorption is downfield at 4.5–6 ppm.

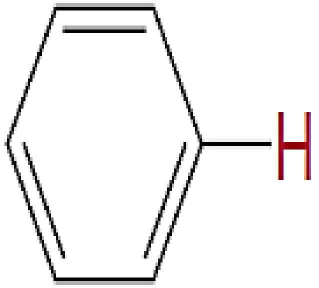
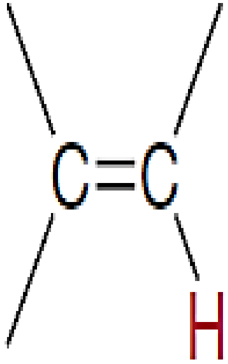
Carbon-carbon triple bonds

- In a magnetic field, the π electrons of a carbon-carbon triple bond are induced to circulate, but in this case the induced magnetic field **opposes** the applied magnetic field (B_0).
- Thus, the proton feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.


The induced magnetic field opposes the external field B_0 in the vicinity of the proton.

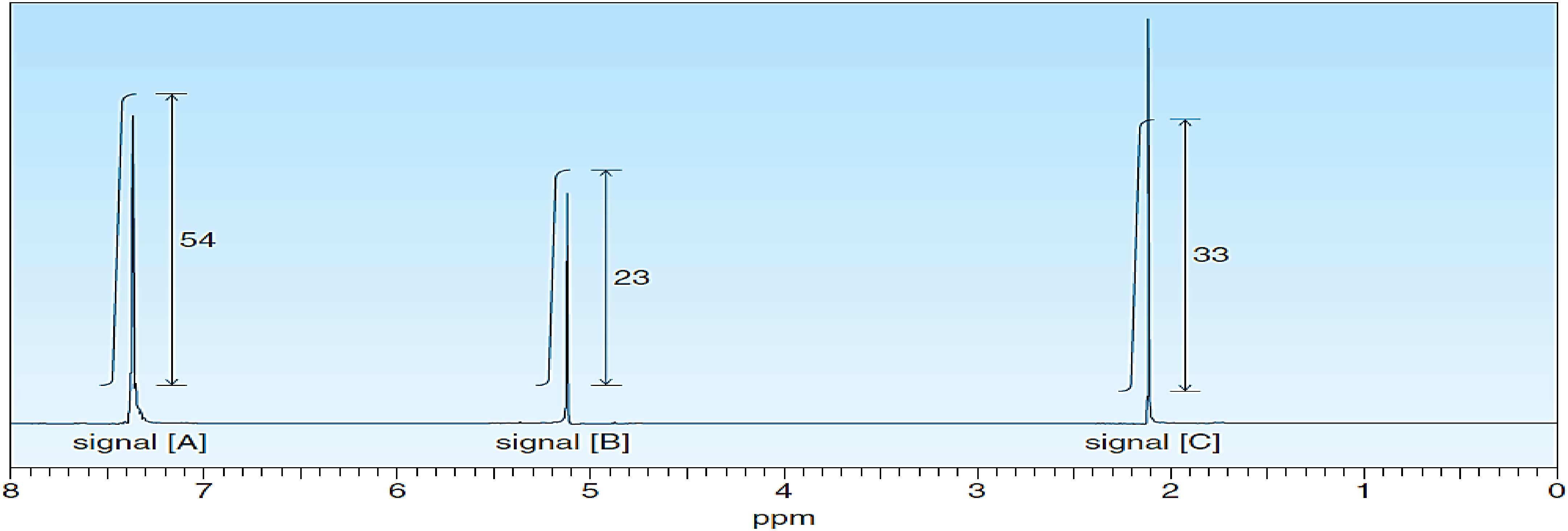
The proton is shielded. The absorption is upfield at ~2.5 ppm.

Effect of π Electrons on Chemical Shift Values

Proton type	Effect	Chemical shift (ppm)
	highly deshielded	6.5–8
	deshielded	4.5–6
$-C\equiv C-H$	shielded	~2.5

Determine the number of protons giving rise to an H NMR signal:

For instance, a compound with molecular formula of $C_9H_{10}O_2$ has the following spectrum. Calculate the number of protons for each signal.



Firstly: determine the total number of integration units then divide them on the total number of protons:

The total number of integration units = 33+23+54 = 110

The total number of protons = 10

Number of units per protons = 110/10 = 11

Secondly: determine the number of protons per each signal by dividing the integration units of each signal by the number of units per proton.

54/11 = 4.9 ≈ 5 H

23/11 = 2.1 ≈ 2 H

33/11 = 3 H

^{1}H NMR—Spin-Spin Splitting

Peak:

The units into which an NMR signal is split; doublet, triplet, quartet, multiplet, etc.

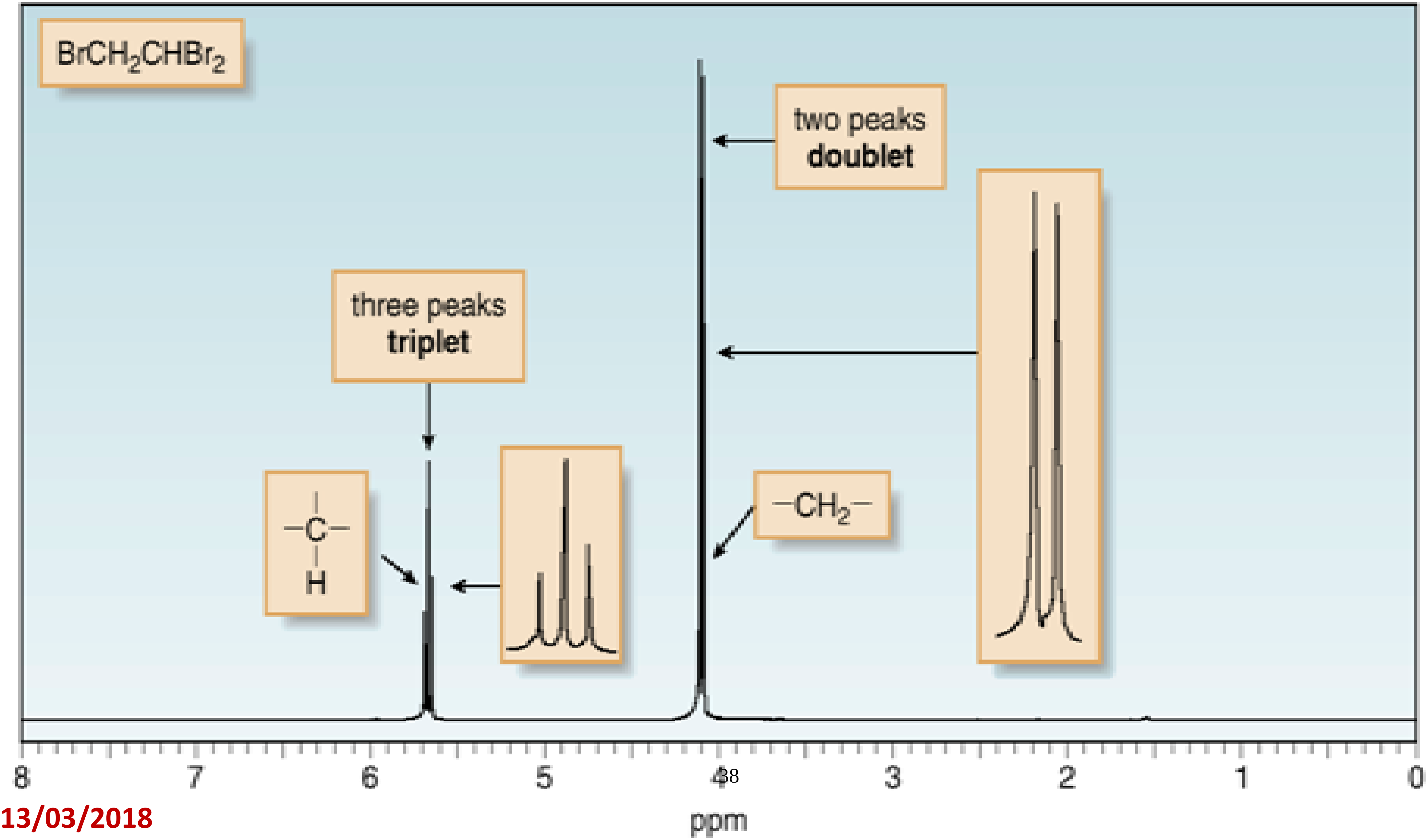
Signal splitting:

Splitting of an NMR signal into a set of peaks by the influence of neighboring nonequivalent hydrogens.

(n + 1) rule:

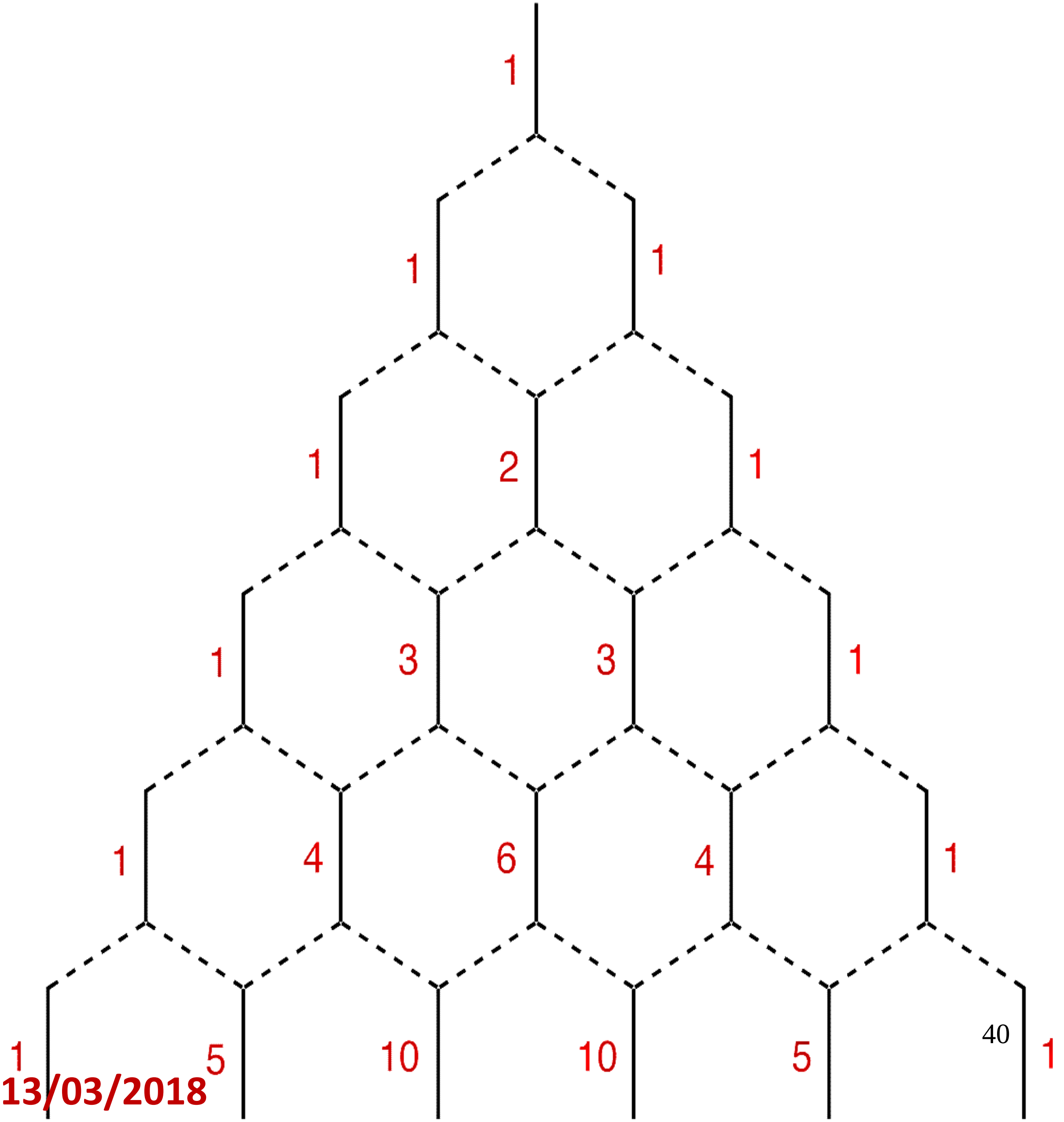
If a hydrogen has n hydrogens nonequivalent to it but equivalent among themselves on the same or adjacent atom(s), its ^{1}H-NMR signal is split into (n + 1) peaks.

Example of H^1-NMR (Spin-Spin splitting)



Peak Multiplicity:

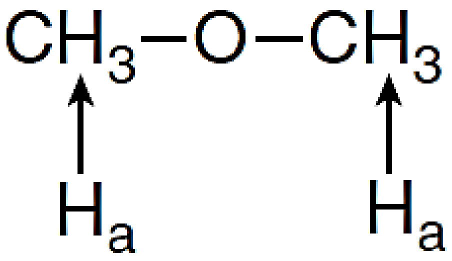
- Peaks are often split into multiple peaks due to ***magnetic interactions*** between nonequivalent protons on adjacent carbons, The process is called **spin-spin splitting**
- The splitting is into one more peak than the number of H's on the adjacent carbon(s), This is the **"n+1 rule"**
- The relative intensities are in proportion of a binomial distribution given by Pascal's Triangle
- The set of peaks is a **multiplet** (2 = doublet, 3 = triplet, 4 = quartet, 5=pentet, 6=hextet, 7=heptet…..)



splitting pattern	the ratio of heights of llines in the peak
singlet	1
doublet	1:1
triplet	1:2:1
quartet	1:3:3:1
quintet	1:4:6:4:1
sextet	1:5:10:10:5:1

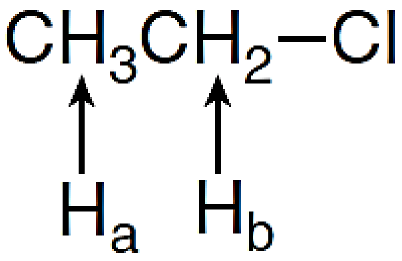
^{1}H NMR—Number of Signals

- The number of NMR signals equals the number of different types of protons in a compound.
- Protons in different environments give different NMR signals.
- Equivalent protons give the same NMR signal.



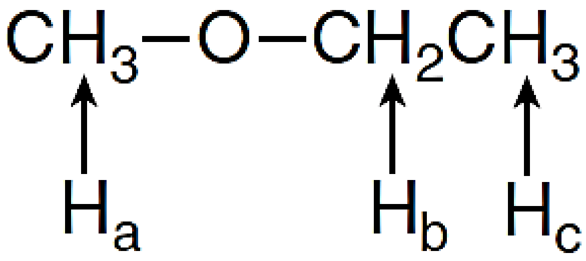
$CH_3{-}O{-}CH_3$

All equivalent H's
1 NMR signal



$CH_3CH_2{-}Cl$

2 types of H's
2 NMR signals

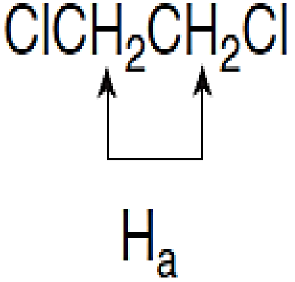


$CH_3{-}O{-}CH_2CH_3$

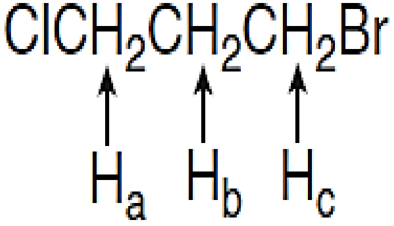
3 types of H's
3 NMR signals

^{1}H NMR—Number of Signals

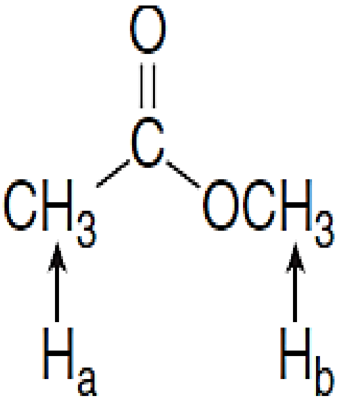
Always the number of NMR signals refers to the number of H, thus the equivalent H gives one signal for examples are shown below.



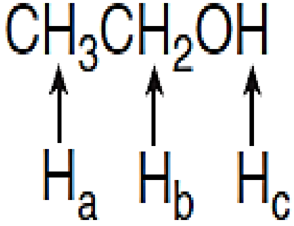
1 type of H
1 NMR signal



3 types of H's
3 NMR signals



2 types of H's
2 NMR signals

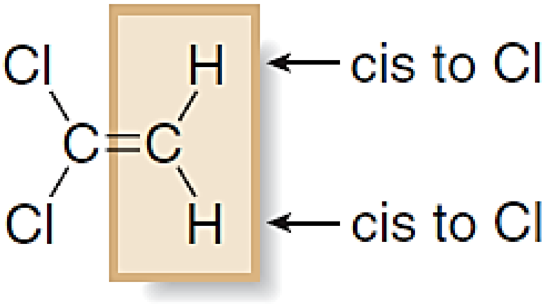


3 types of H's
3 NMR signals

^{1}H NMR—Number of Signals

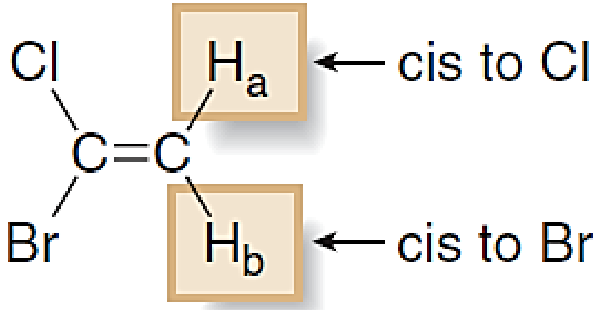
- To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen.

- In comparing two H atoms on a ring or double bond, two protons are equivalent only if they are cis (or trans) to the same groups.



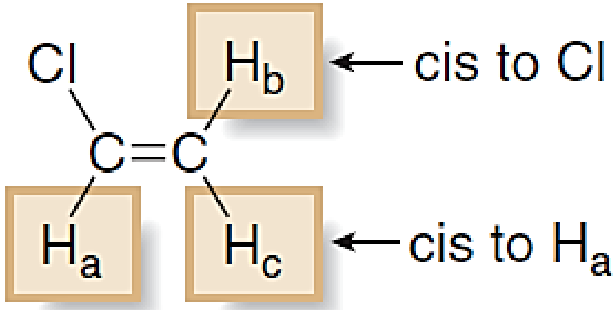
1,1-dichloroethylene

1 type of H
1 NMR signal



1-bromo-1-chloroethylene

2 types of H's
2 NMR signals

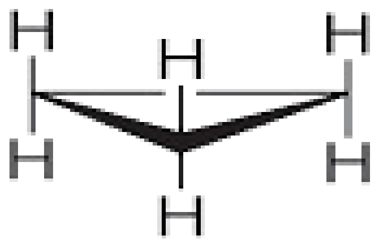


chloroethylene

3 types of H's
3 NMR signals

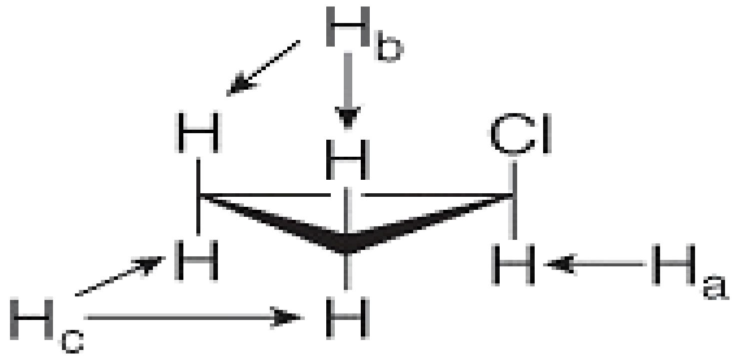
^{1}H NMR—Number of Signals

- Proton equivalency in cycloalkanes can be determined similarly.



cyclopropane

All H's are equivalent.
1 NMR signal

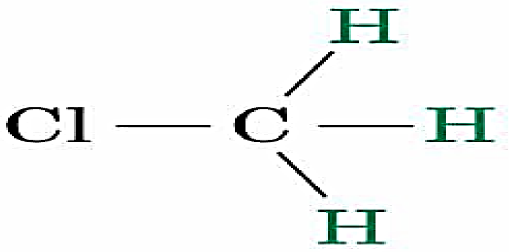


chlorocyclopropane

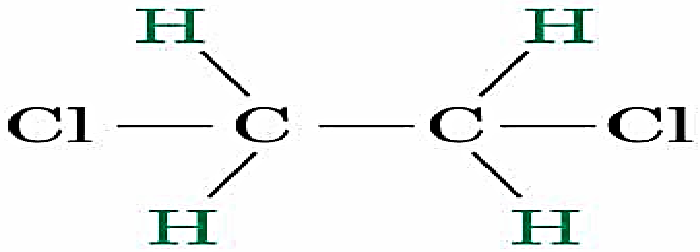
3 types of H's
3 NMR signals

Rules for Spin-Spin Splitting

- **Equivalent** protons **do not** split each other.

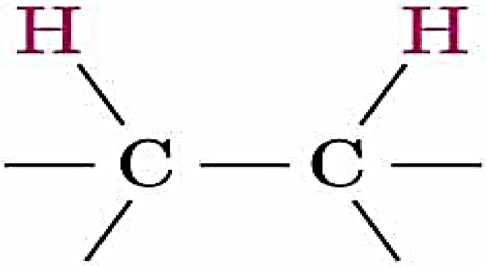


Three C—H protons are chemically equivalent; no splitting occurs.

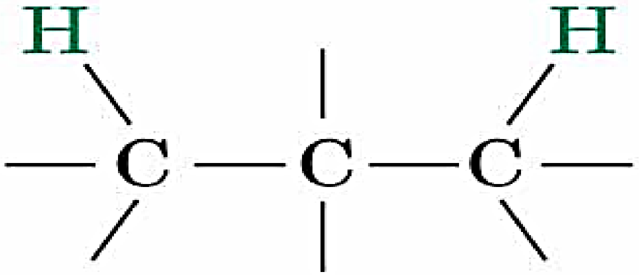


Four C—H protons are chemically equivalent; no splitting occurs.

- Protons that are **farther than two carbon atoms apart do not** split each other.

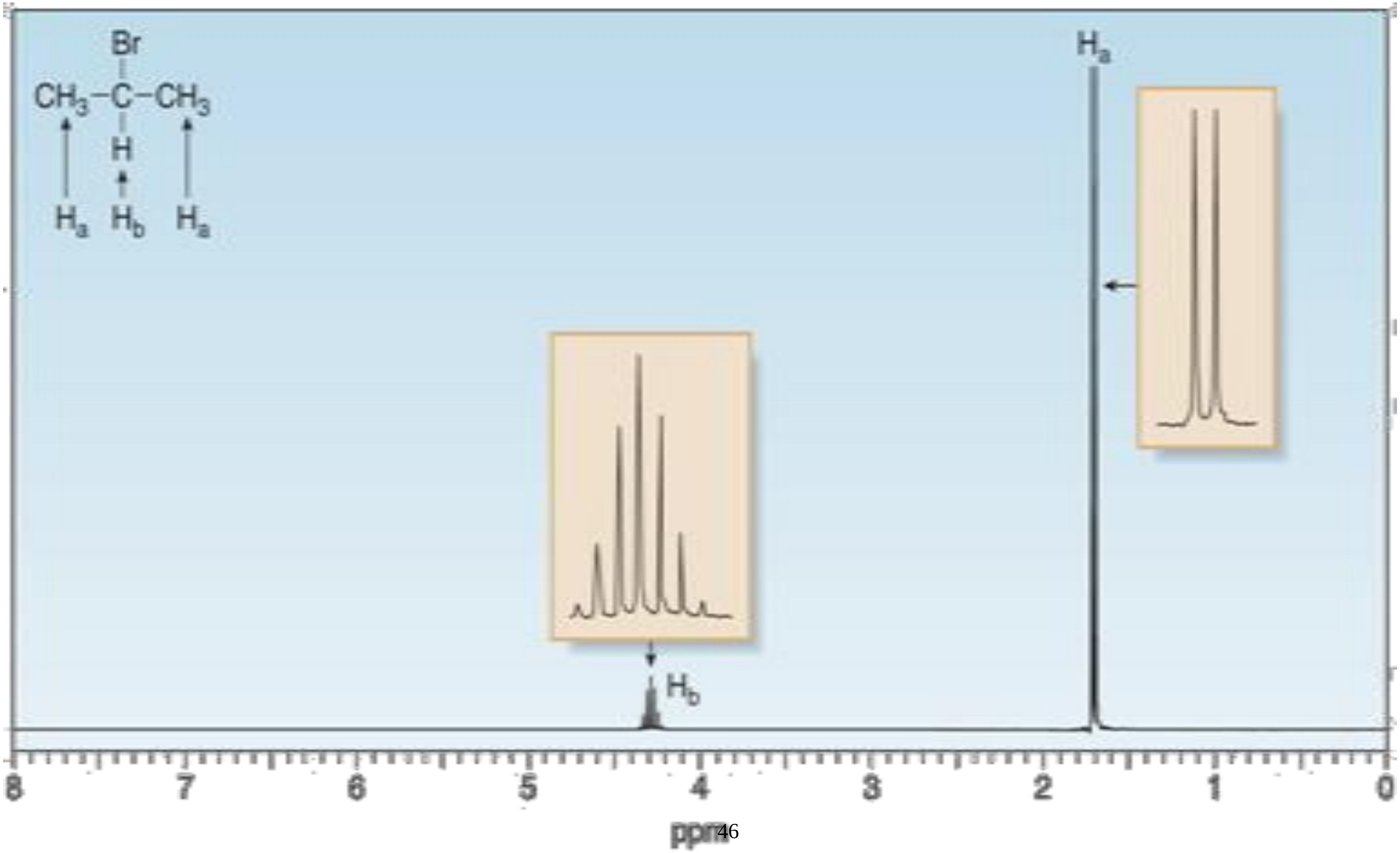


Splitting observed



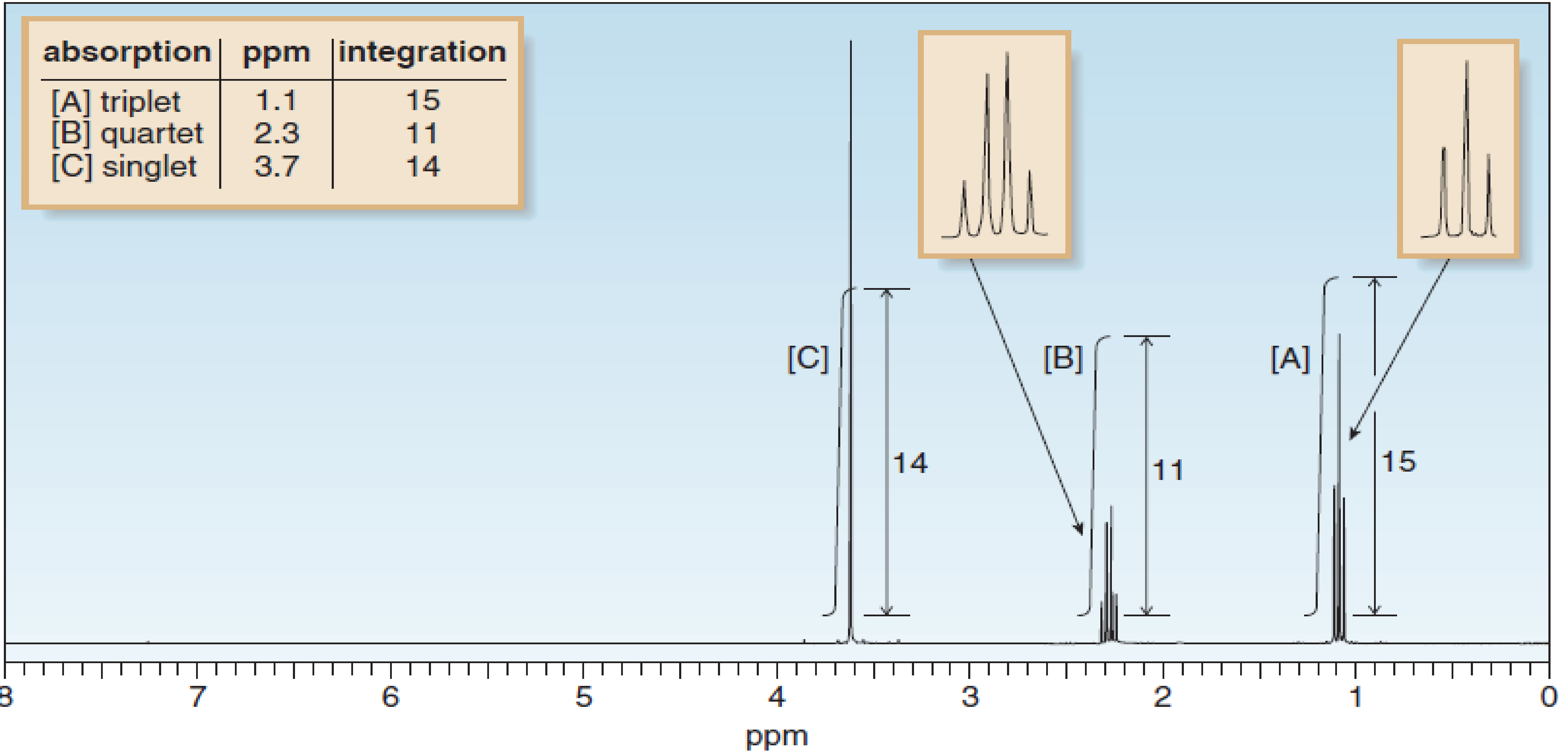
Splitting not usually observed

Examples of proton NMR spectra



Application of ^1H NMR to Determine a Structure

Example Using its ^1H NMR spectrum, determine the structure of an unknown compound X that has molecular formula $C_4H_8O_2$ and contains a C=O absorption in its IR spectrum.



absorption	ppm	integration
[A] triplet	1.1	15
[B] quartet	2.3	11
[C] singlet	3.7	14

Step [1] Determine the number of different kinds of protons.

The number of NMR signals equals the number of different types of protons.

This molecule has three NMR signals ([A], [B], and [C]) and therefore **three** types of protons (H_a, H_b, and H_c).

Step [2] Use the integration data to determine the number of H atoms giving rise to each signal.

Total number of integration units: 14 + 11 + 15 = 40 units

Total number of protons = 8

Divide: 40 units/8 protons = 5 units per proton. Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.

$\frac{15}{5} = 3$ H_a protons

signal [A]

Three equivalent H's usually means a **CH_3** group.

$\frac{11}{5} = 2.2 \approx 2$ H_b protons

signal [B]

Two equivalent H's usually means a **CH_2** group.

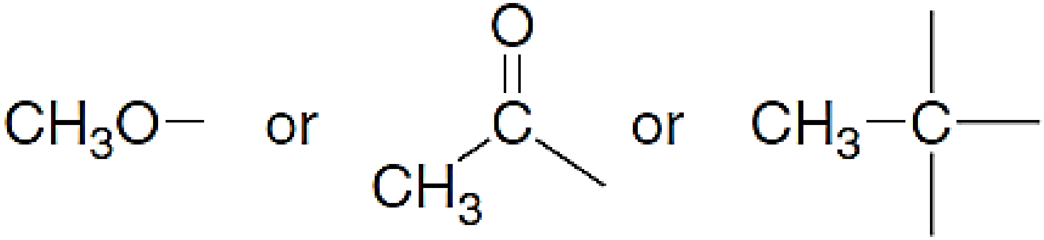
$\frac{14}{5} = 2.8 \approx 3$ H_c protons

signal [C]

Three equivalent H's usually means a **CH_3** group.

Step [3] Use individual splitting patterns to determine what carbon atoms are bonded to each other.

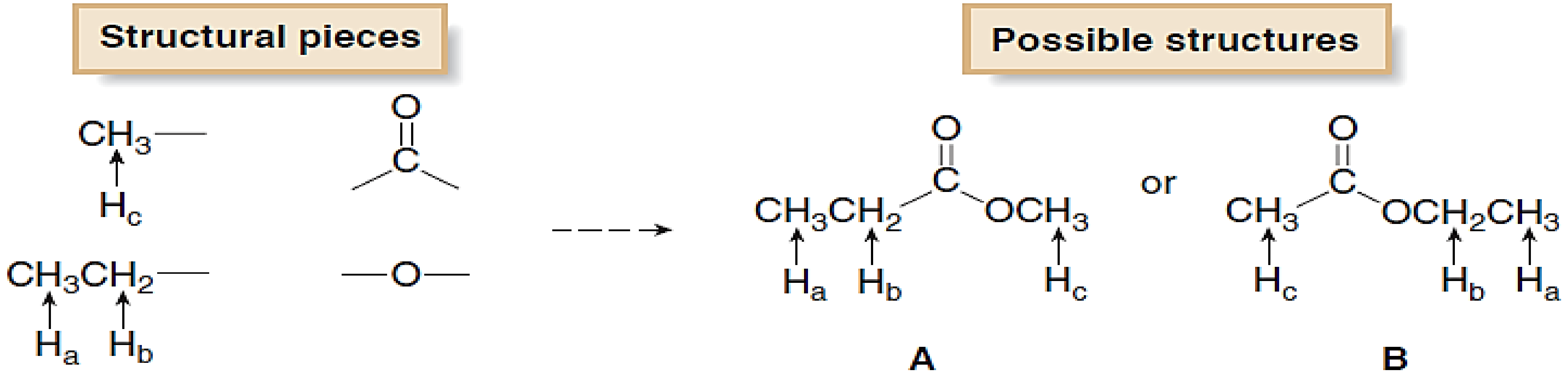
- Start with the singlets. Signal [C] is due to a CH_3 group with no adjacent nonequivalent H atoms. Possible structures include:



- Because signal [A] is a triplet, there must be 2 H’s (CH_2 group) on the adjacent carbon.
- Because signal [B] is a quartet, there must be 3 H’s (CH_3 group) on the adjacent carbon.
- This information suggests that X has an ethyl group CH_3CH_2- .

Step [4] Use chemical shift data to complete the structure.

- Put the structure together in a manner that preserves the splitting data and is consistent with the reported chemical shifts.
- In this example, two isomeric structures (A and B) are possible for X considering the splitting data only:



- Chemical shift information distinguishes the two possibilities. The electronegative O atom deshields adjacent H's, shifting them downfield between 3 and 4 ppm. If A is the correct structure, the singlet due to the CH_3 group (Hc) should occur downfield, whereas if B is the correct structure, the quartet due to the CH_2 group (Hb) should occur downfield.
- Because the NMR of X has a singlet (not a quartet) at 3.7, A is the correct structure.