Chapter 9

Nuclear Magnetic Resonance

Created by
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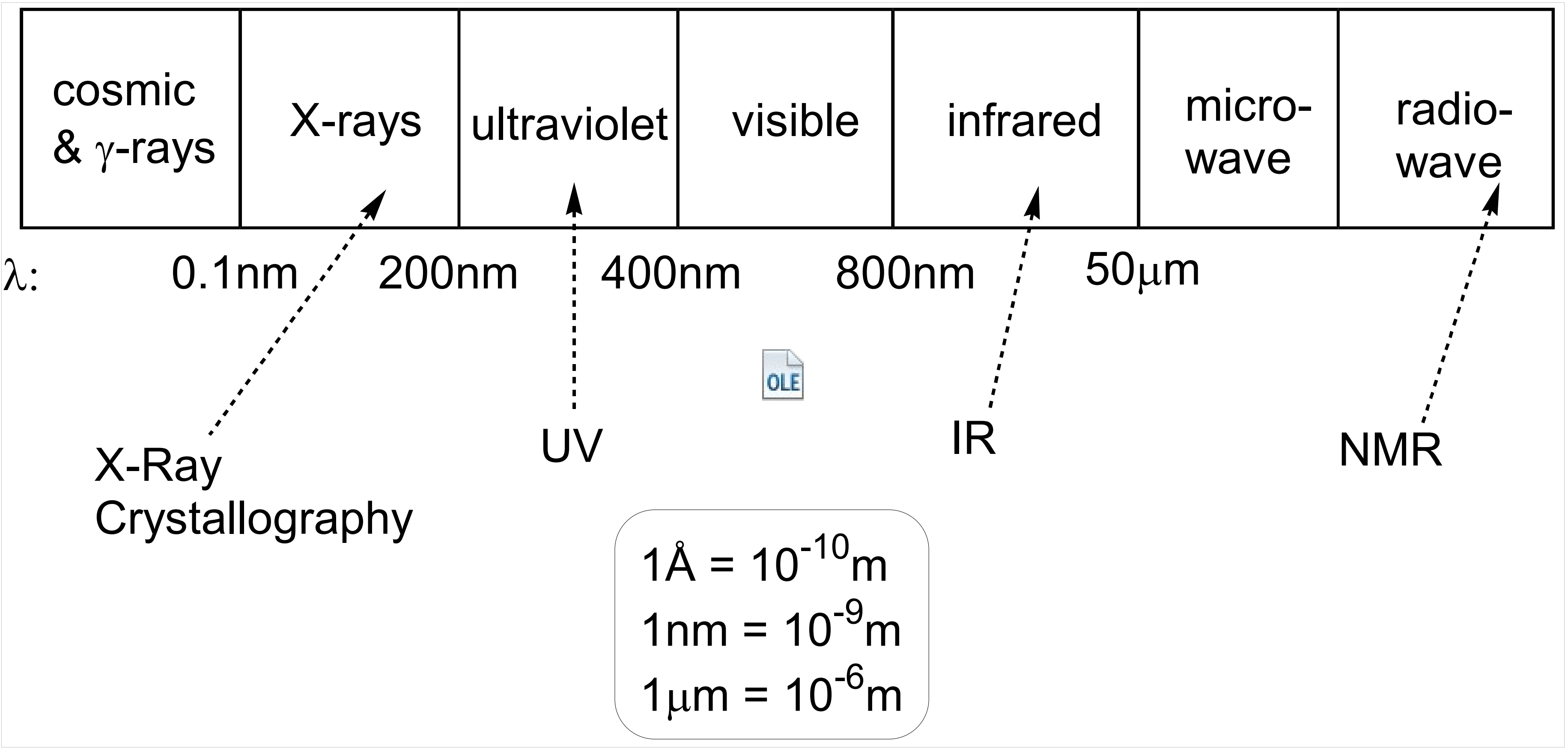
❖ Electromagnetic spectrum



cosmic & γ-rays

X-rays

ultraviolet

visible

infrared

micro-wave

radio-wave

λ: 0.1nm 200nm 400nm 800nm 50μm

X-Ray Crystallography

UV

IR

NMR

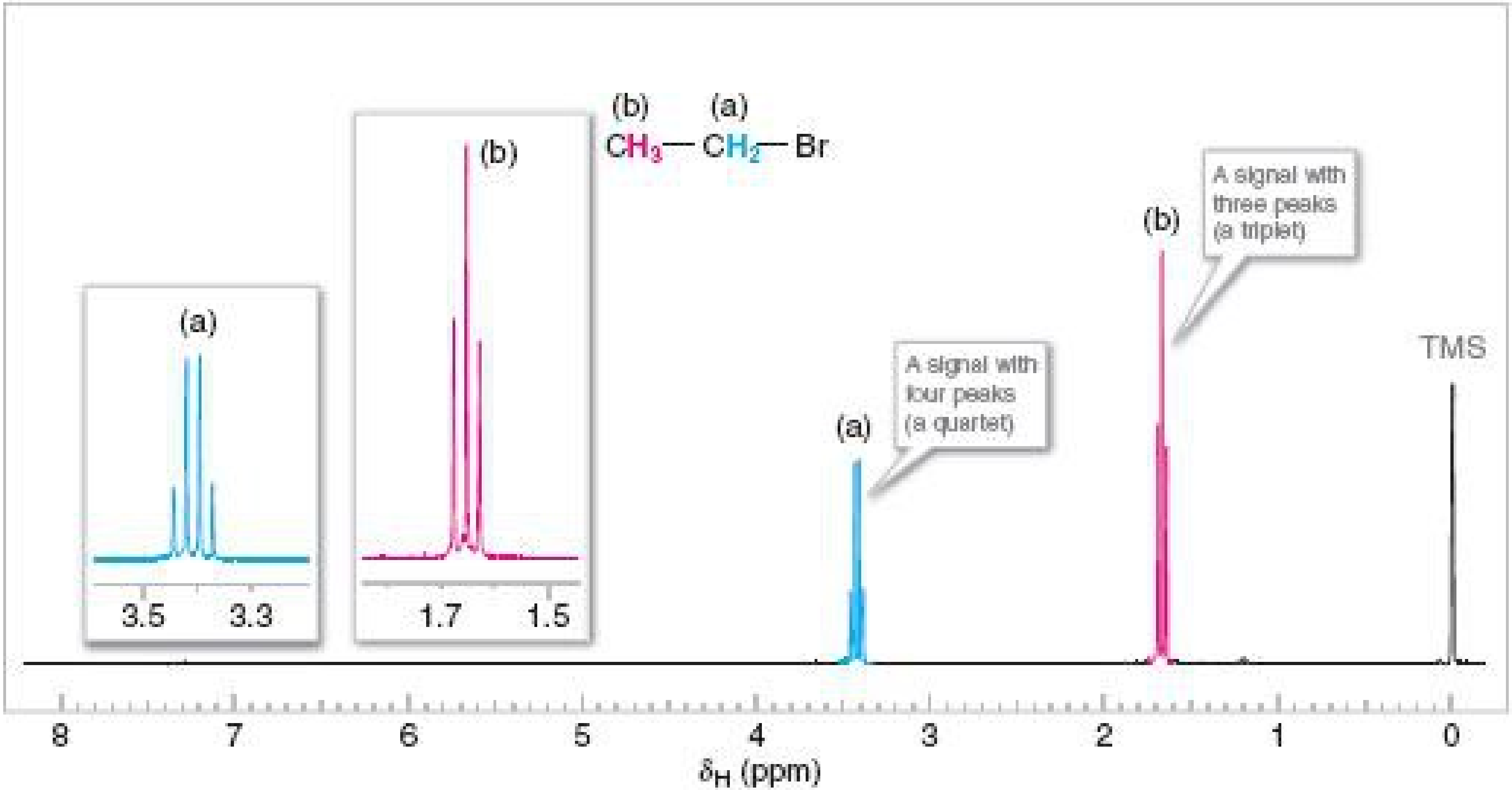
$1Å = 10^{-10}m$

$1nm = 10^{-9}m$

$1\mu m = 10^{-6}m$

2. Nuclear Magnetic Resonance (NMR) Spectroscopy

- A graph that shows the characteristic energy absorption frequencies and intensities for a sample in a magnetic field is called a **nuclear magnetic resonance (NMR) spectrum**


(b) (a)
CH3— CH2— Br
(a)
3.5
3.3
(b)
1.7
1.5
(a)
A signal with four peaks (a quartet)
(b)
A signal with three peaks (a triplet)
TMS
8
7
6
5
4
3
2
1
0
δH (ppm)

1. The number of signals in the spectrum tells us how many different sets of protons there are in the molecule

2. The position of the signals in the spectrum along the x-axis tells us about the magnetic environment of each set of protons arising largely from the electron density in their environment

3. The area under the signal tells us about how many protons there are in the set being measured

4. The multiplicity (or splitting pattern) of each signal tells us about the number of protons on atoms adjacent to the one whose signal is being measured

❖ Typical ^{1}H NMR spectrum

- Chemical Shift (δ)

- Integration (areas of peaks $\Rightarrow$ no. of H)

- Multiplicity (spin-spin splitting) and coupling constant

❖ Typical ^{1}H NMR spectrum

Record as: ^{1}H NMR (300 MHz, CDCl$_3$):

δ 4.35 (2H, t, J = 7.2 Hz, H^c)
2.05 (2H, sextet, J = 7.2 Hz, H^b)
1.02 (3H, t, J = 7.2 Hz, H^a)

chemical shift (δ) in ppm

no. of H (integration)

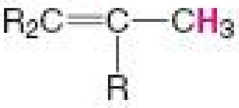
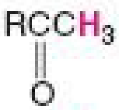
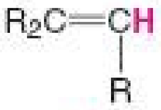
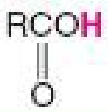
multiplicity

coupling constant in Hz

2A. Chemical Shift

- The position of a signal along the *x*-axis of an NMR spectrum is called its **chemical shift**
- The chemical shift of each signal gives information about the structural environment of the nuclei producing that signal
- Counting the number of signals in a ^{1}H NMR spectrum indicates, at a first approximation, the number of distinct proton environments in a molecule

TABLE 9.1 Approximate Proton Chemical Shifts

Type of Proton	Chemical Shift (δ, ppm)
1° Alkyl, RCH_3	0.8–1.2
2° Alkyl, RCH_2R	1.2–1.5
3° Alkyl, R_3CH	1.4–1.8
Allylic,  $R_2C{=}\underset{\displaystyle R}{\underset{\vert}{C}}{-}CH_3$	1.6–1.9
Ketone,  $R\underset{\displaystyle O}{\underset{\Vert}{C}}CH_3$	2.1–2.6
Benzylic, $ArCH_3$	2.2–2.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl chloride, RCH_2Cl	3.6–3.8
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic,  $R_2C{=}\underset{\displaystyle R}{\underset{\vert}{C}}H$	5.2–5.7
Aromatic, ArH	6.0–8.5
Aldehyde,  $R\underset{\displaystyle O}{\underset{\Vert}{C}}H$	9.5–10.5
Alcohol hydroxyl, ROH	0.5–6.0[a]
Amino, $R{-}NH_2$	1.0–5.0[a]
Phenolic, $ArOH$	4.5–7.7[a]
Carboxylic,  $R\underset{\displaystyle O}{\underset{\Vert}{C}}OH$	10–13[a]

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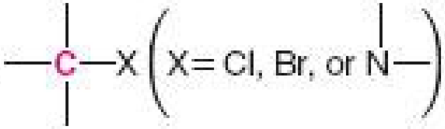
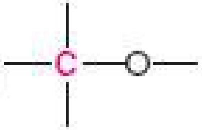
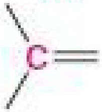
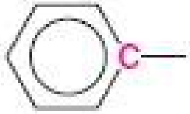
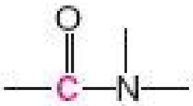
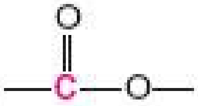
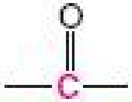
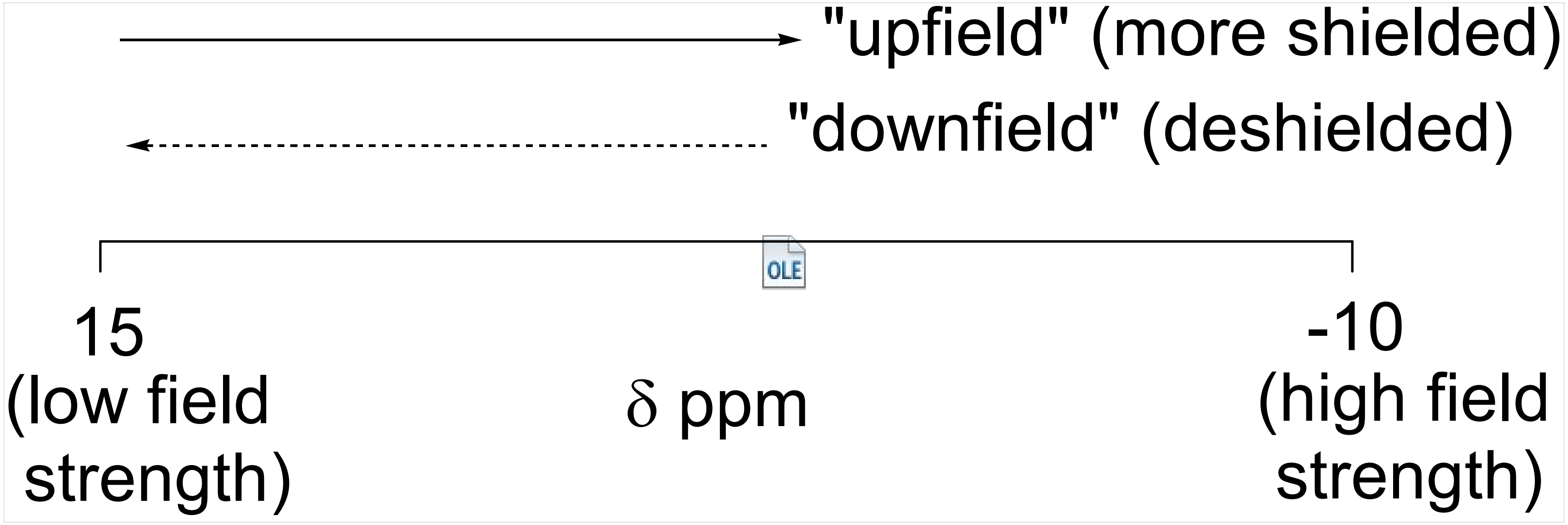
[a] The chemical shifts of these protons vary in different solvents and with temperature and concentration.

TABLE 9.2 Approximate Carbon-13 Chemical Shifts

Type of Carbon Atom	Chemical Shift (δ, ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine,  $-\overset{\vert}{\underset{\vert}{C}}-X \left(X= Cl, Br, \text{ or } \overset{\vert}{N}- \right)$	10–65
Alcohol or ether,  $-\overset{\vert}{\underset{\vert}{C}}-O-$	50–90
Alkyne, $-C\equiv$	60–90
Alkene, 	100–170
Aryl, 	100–170
Nitrile, $-C\equiv N$	120–130
Amide,  $-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{N}-$	150–180
Carboxylic acid or ester,  $-\overset{O}{\overset{\Vert}{C}}-O-$	160–185
Aldehyde or ketone,  $-\overset{O}{\overset{\Vert}{C}}-$	182–215

❖ Normal range of ^{1}H NMR



"upfield" (more shielded)

"downfield" (deshielded)

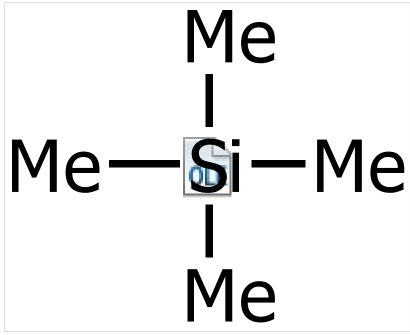
15
(low field
strength)

δ ppm

-10
(high field
strength)

❖ Reference compound

- TMS = tetramethylsilane



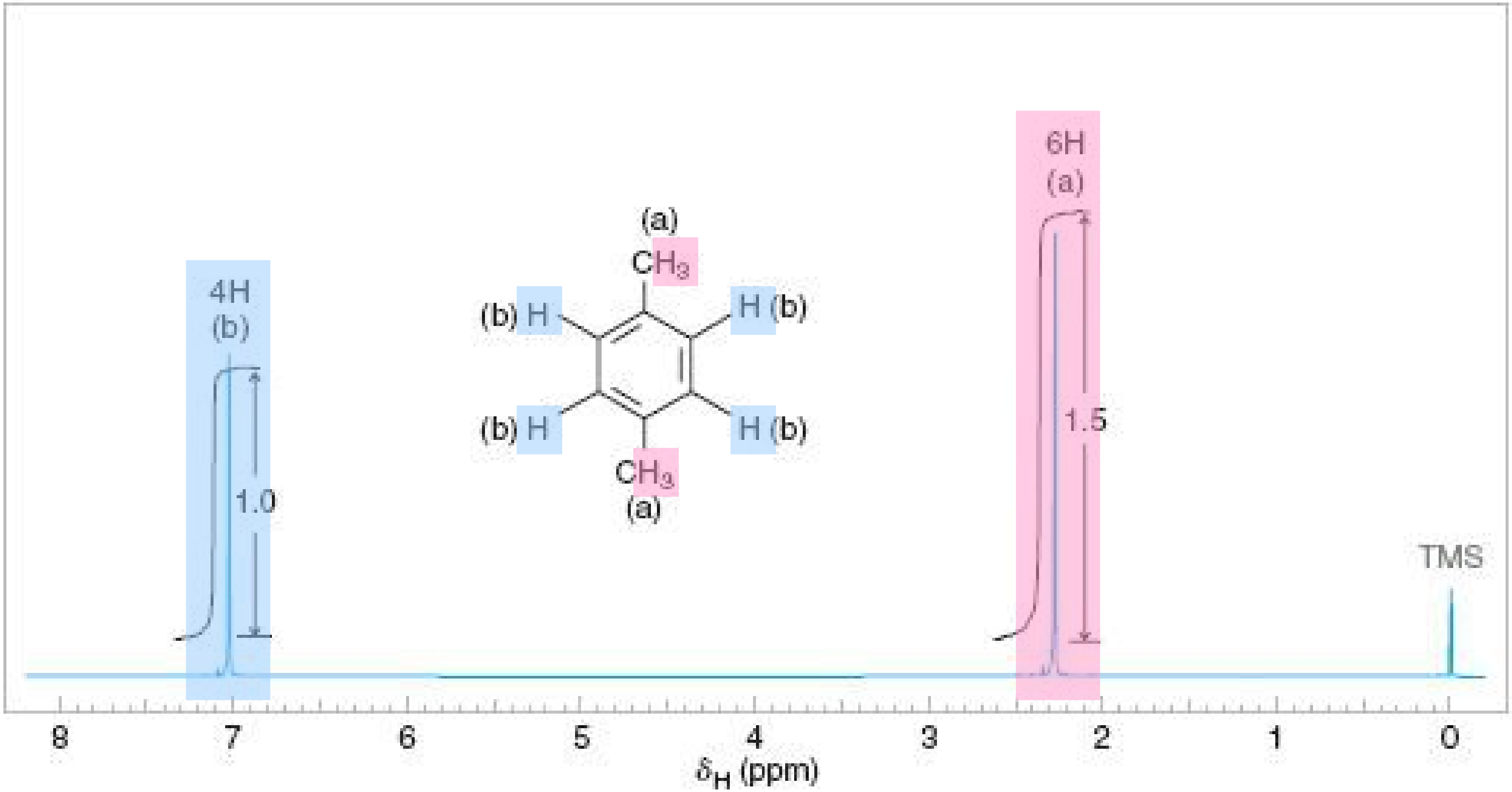
$$\mathrm{Me}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{Me}$$

  as a reference standard (0 ppm)

- Reasons for the choice of TMS as reference
  - ♦ Resonance position at higher field than other organic compounds
  - ♦ Unreactive and stable, not toxic
  - ♦ Volatile and easily removed (B.P. = 28°C)

- NMR solvent
  - Normal NMR solvents should not contain hydrogen
  - Common solvents
    - $CDCl_3$
    - C_6D_6
    - CD_3OD
    - CD_3COCD_3 (d_6-acetone)

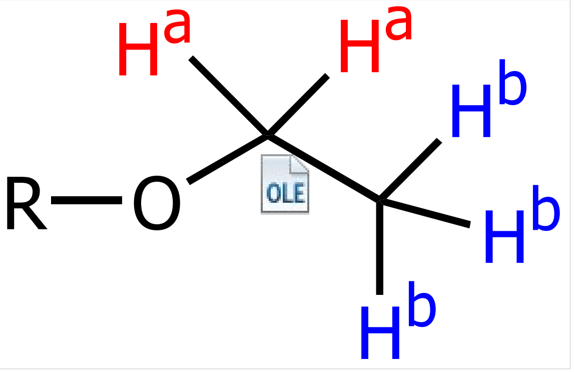
- The 300-MHz ^1H NMR spectrum of 1,4-dimethylbenzene

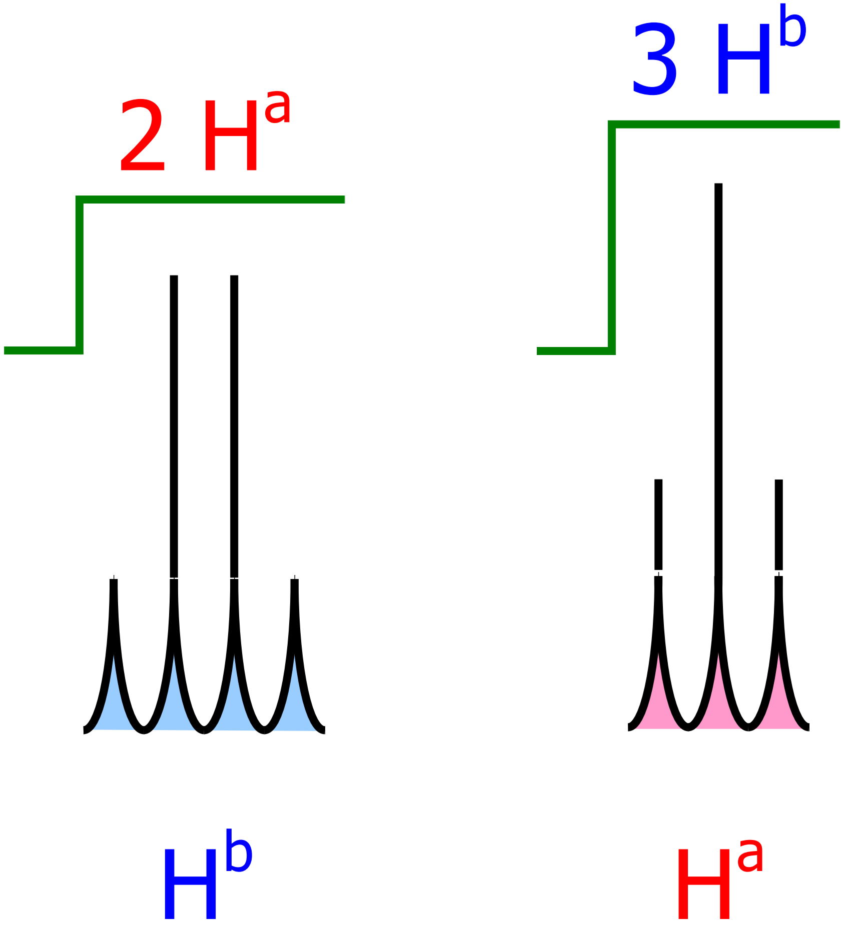


2B. Integration of Signal Areas

Integral Step Heights

- The area under each signal in a ^{1}H NMR spectrum is proportional to the number of hydrogen atoms producing that signal
- It is signal area (integration), not signal height, that gives information about the number of hydrogen atoms





3 H^b

2 H^a

H^b

H^a

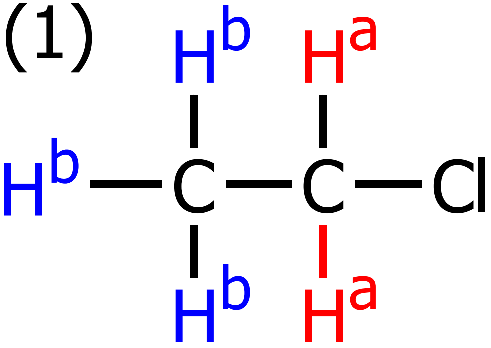
2C. Coupling (Signal Splitting)

- Coupling is caused by the magnetic effect of nonequivalent hydrogen atoms that are within 2 or 3 bonds of the hydrogens producing the signal
- The *n*+1 rule
  - Rule of Multiplicity:

    If a proton (or a set of magnetically equivalent nuclei) has *n* neighbors of magnetically equivalent protons. It's multiplicity is *n* + 1

❖ Examples

(1)

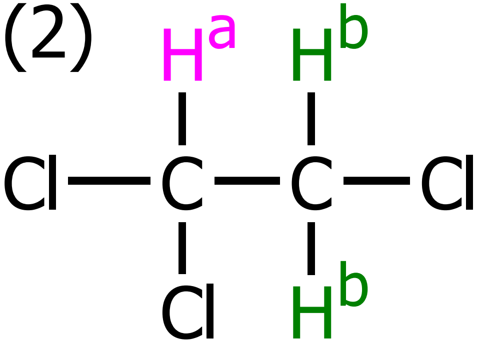


$$\begin{array}{cccc} & H^b & H^a & \\ & | & | & \\ H^b - & C - & C - & Cl \\ & | & | & \\ & H^b & H^a & \end{array}$$

H^a: multiplicity = 3 + 1 = 4 (a quartet)

H^b: multiplicity = 2 + 1 = 3 (a triplet)

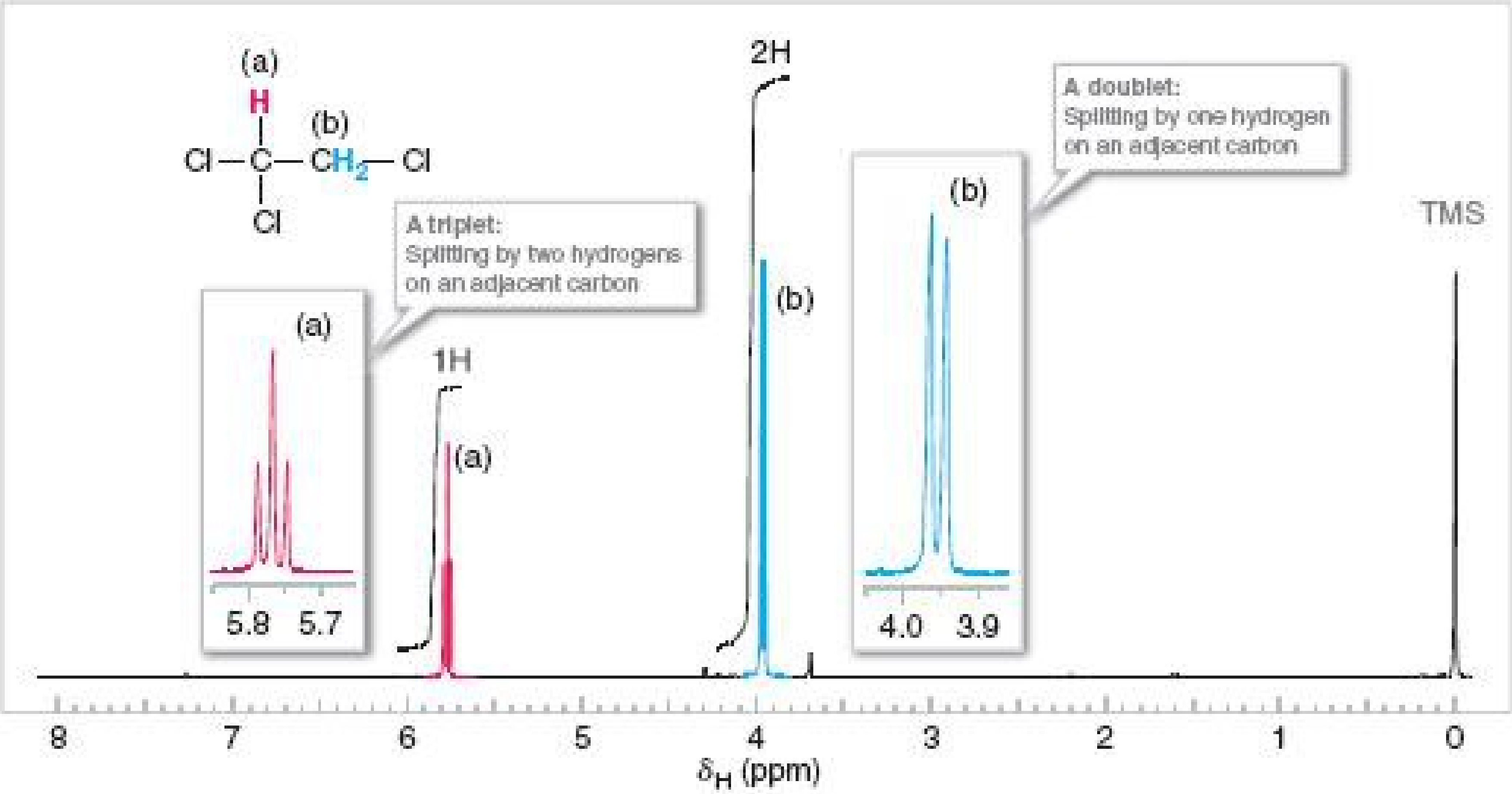
(2)



$$\begin{array}{cccc} & H^a & H^b & \\ & | & | & \\ Cl - & C - & C - & Cl \\ & | & | & \\ & Cl & H^b & \end{array}$$

H^a: multiplicity = 2 + 1 = 3 (a triplet)

H^b: multiplicity = 1 + 1 = 2 (a doublet)

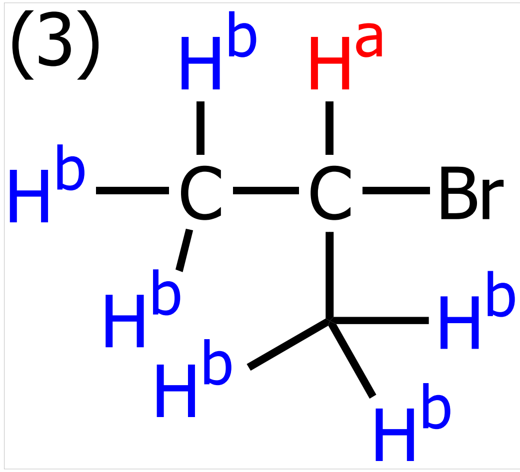


A triplet:
Splitting by two hydrogens on an adjacent carbon

A doublet:
Splitting by one hydrogen on an adjacent carbon

❖ Examples

(3)



H^a: multiplicity = 6 + 1 = 7 (a septet)

H^b: multiplicity = 1 + 1 = 2 (a doublet)

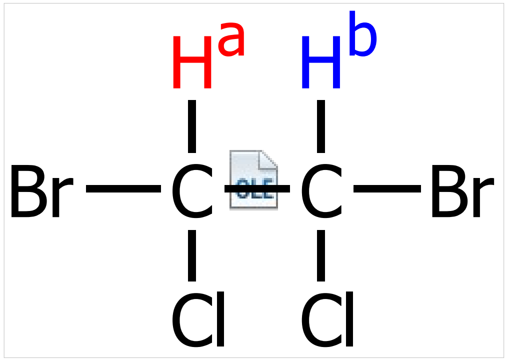
Note: All H^b's are <u>chemically</u> and <u>magnetically</u> equivalent.

- Pascal's Triangle
  - Use to predict relative intensity of various peaks in multiplet
  - Given by the coefficient of binomial expansion $(a + b)^n$

singlet (s)	1
doublet (d)	1 1
triplet (t)	1 2 1
quartet (q)	1 3 3 1
quintet	1 4 6 4 1
sextet	1 5 10 10 5 1

❖ Pascal’s Triangle

- For

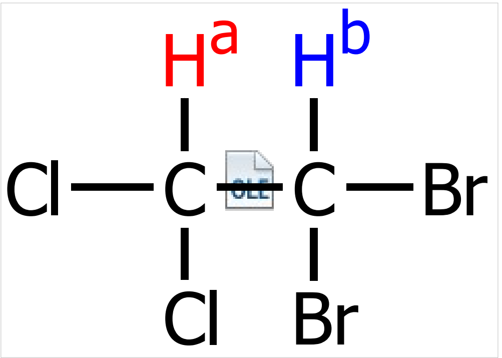


$$Br-\overset{H^a}{\underset{Cl}{C}}-\overset{H^b}{\underset{Cl}{C}}-Br$$

Due to symmetry, H^a and H^b are identical

⇒ a singlet

- For



$$Cl-\overset{H^a}{\underset{Cl}{C}}-\overset{H^b}{\underset{Br}{C}}-Br$$

$H^a \neq H^b$

⇒ two doublets

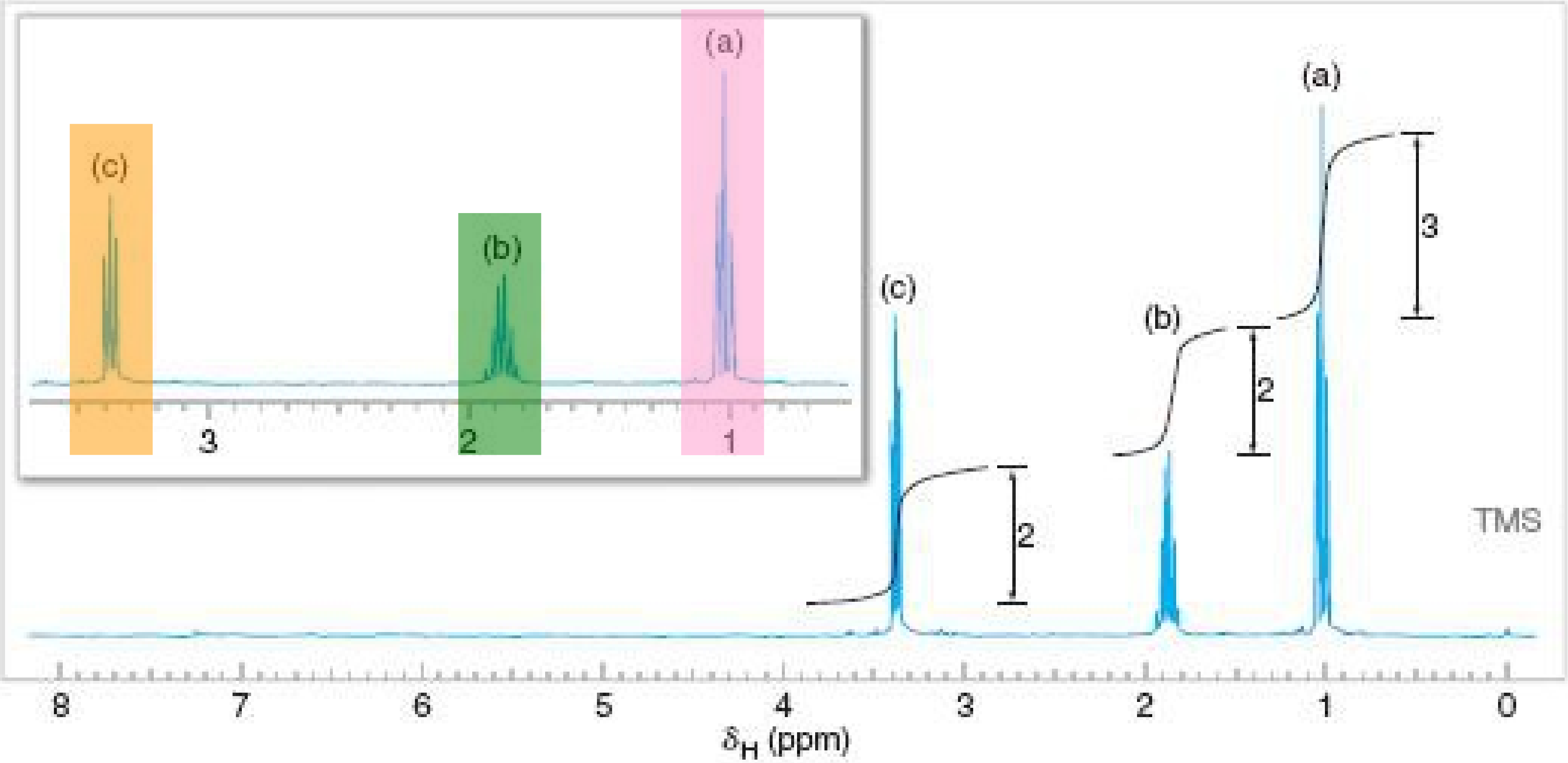
3. How to Interpret Proton NMR Spectra

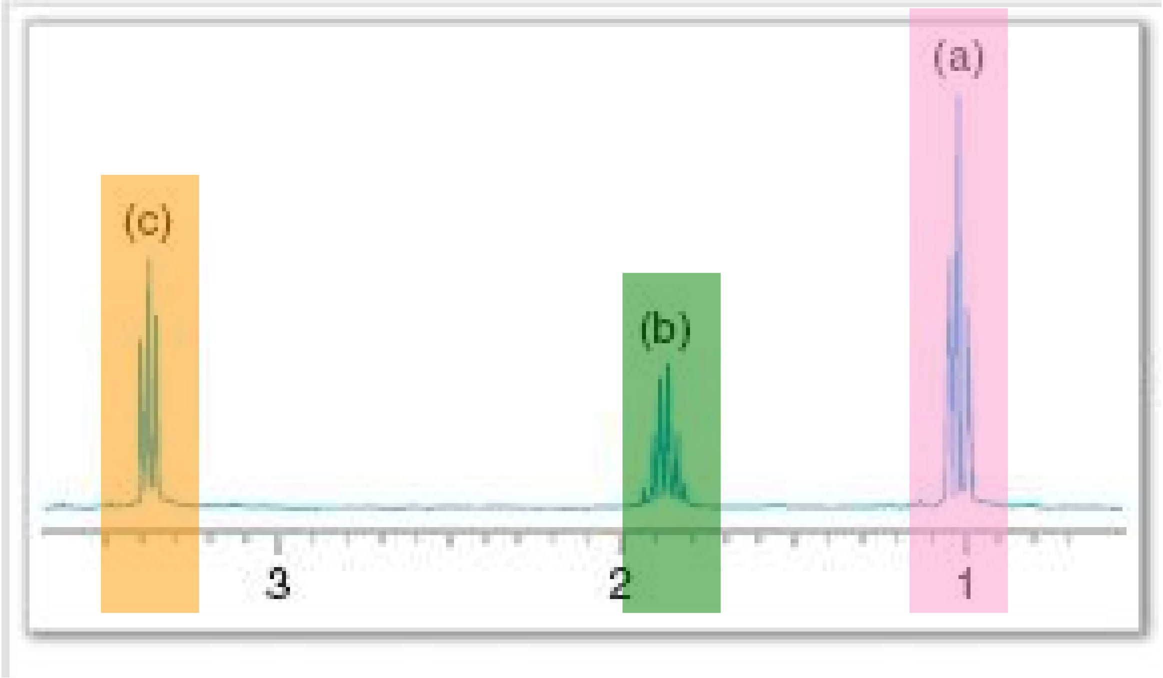
1. Count the number of signals to determine how many distinct proton environments are in the molecule (neglecting, for the time being, the possibility of overlapping signals)

2. Use chemical shift tables or charts to correlate chemical shifts with possible structural environments

3. Determine the relative area of each signal, as compared with the area of other signals, as an indication of the relative number of protons producing the signal
4. Interpret the splitting pattern for each signal to determine how many hydrogen atoms are present on carbon atoms adjacent to those producing the signal and sketch possible molecular fragments
5. Join the fragments to make a molecule in a fashion that is consistent with the data

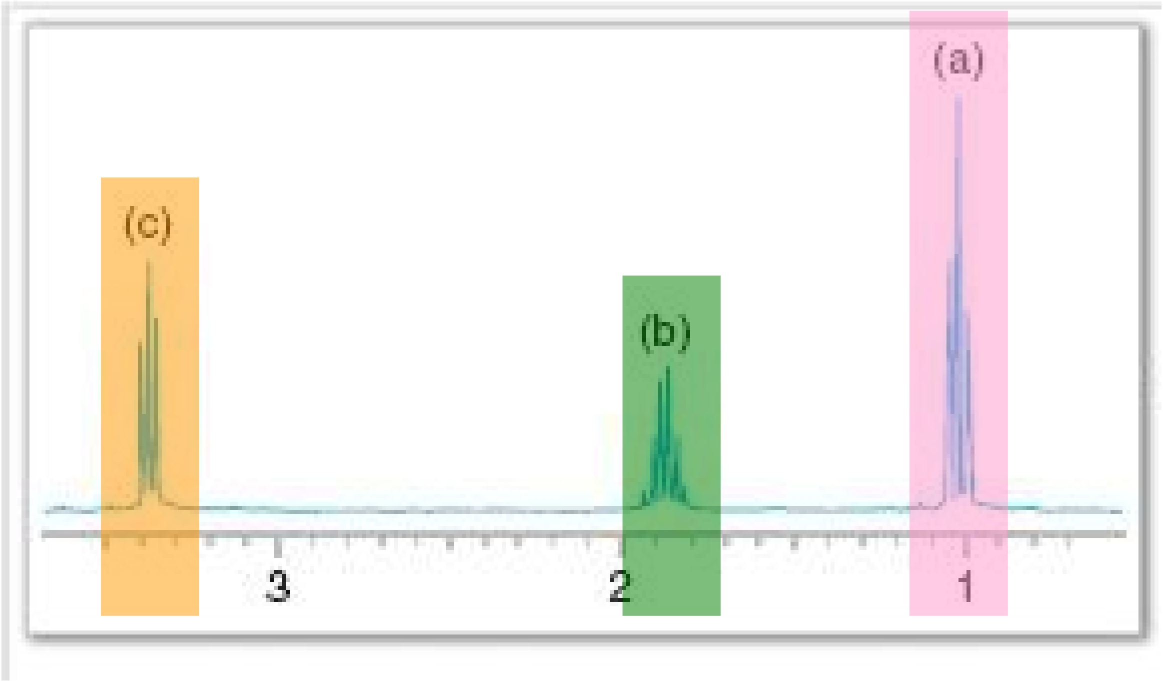
- Example: ^{1}H NMR (300 MHz) of an unknown compound with molecular formula C_3H_7Br



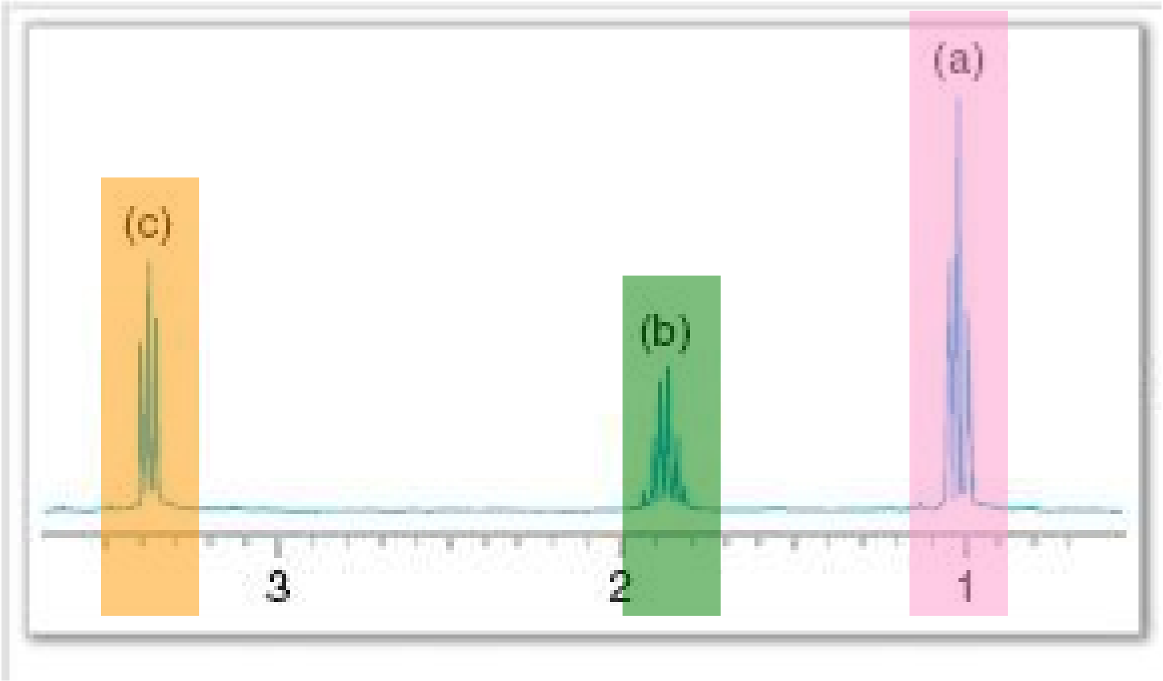


- Three distinct signals at ~ δ3.4, 1.8 and 1.1 ppm

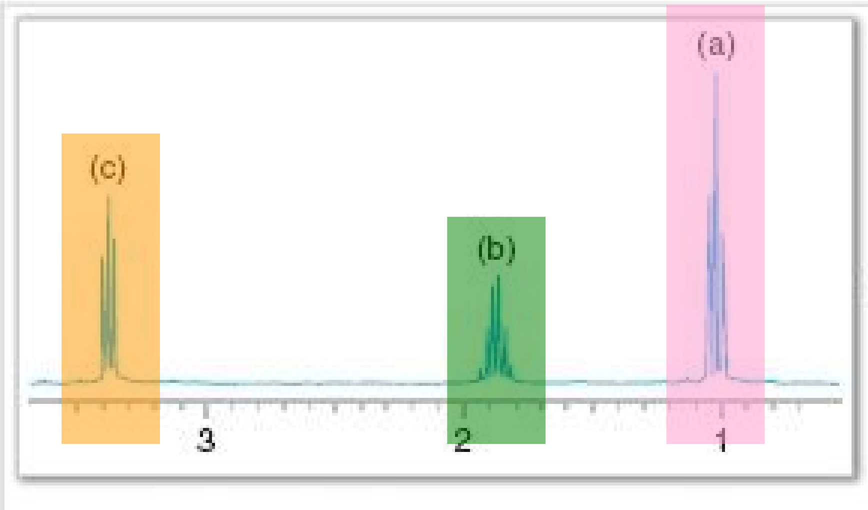
  ⇒ δ3.4 ppm: likely to be near an **electronegative** group (Br)



δ (ppm):	3.4	1.8	1.1
Integral:	2	2	3



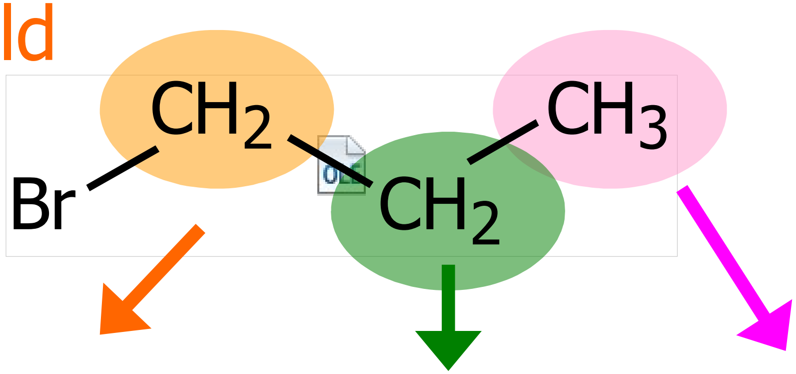
δ (ppm):	3.4	1.8	1.1
Multiplicity:	triplet	sextet	triplet
	↓	↓	↓
	2 H's on adjacent C	5 H's on adjacent C	2 H's on adjacent C



Complete structure:

most downfield signal

most upfield signal



- 2 H's from integration
- triplet

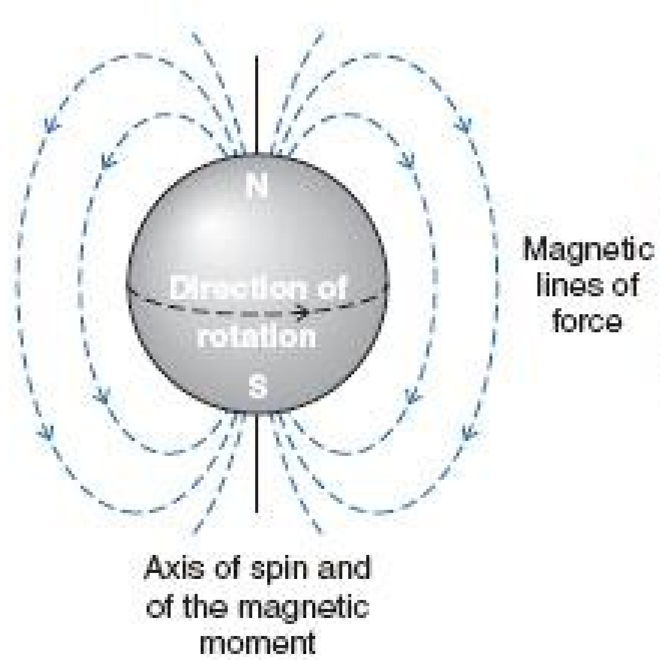
- 2 H's from integration
- sextet

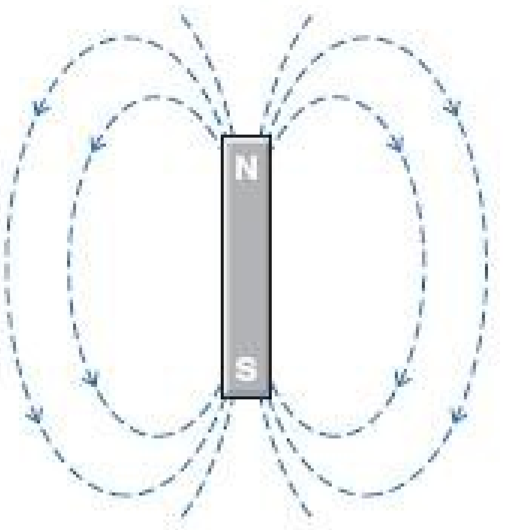
- 3 H's from integration
- triplet

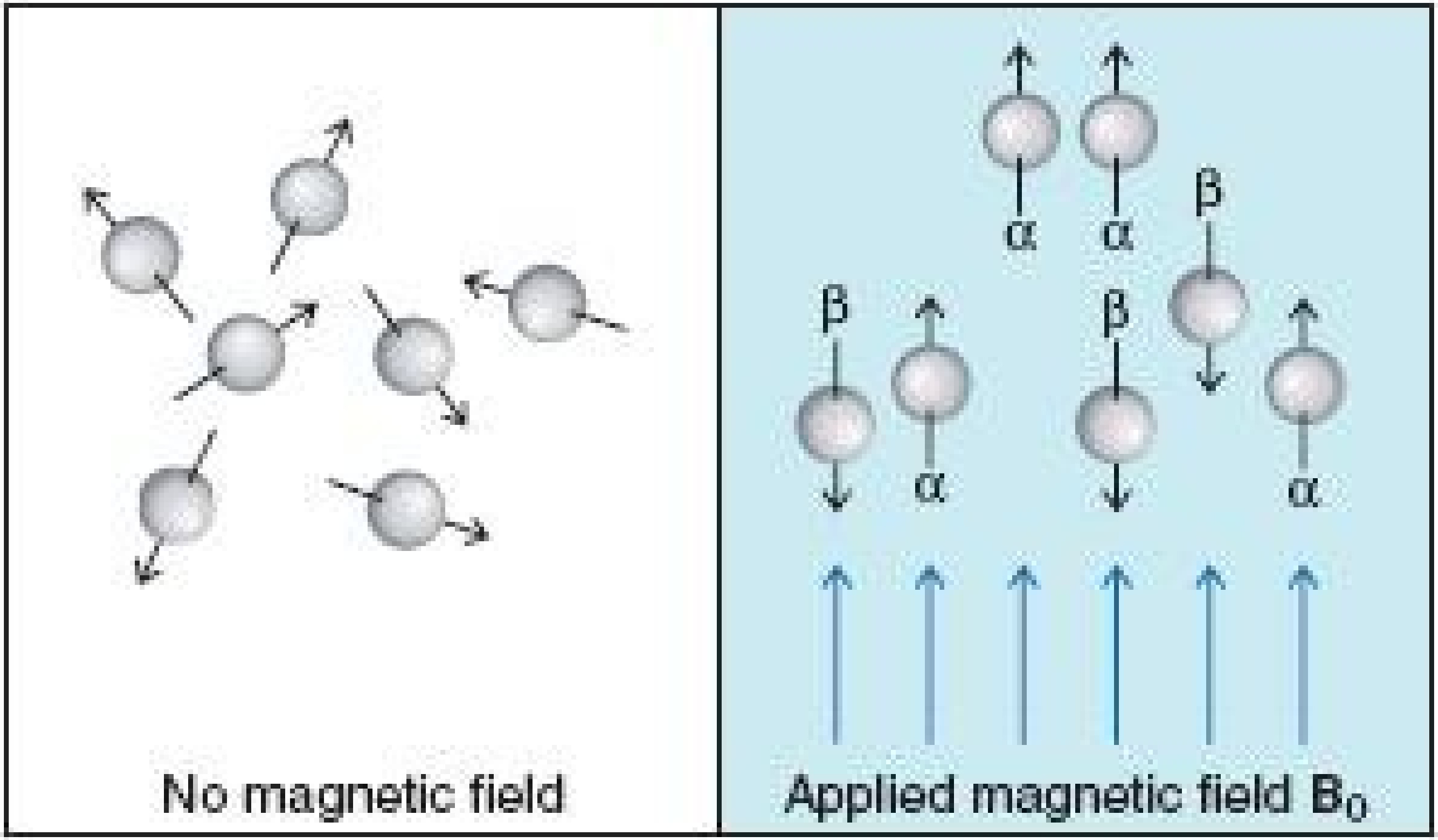
4. Nuclear Spin: The Origin of the Signal

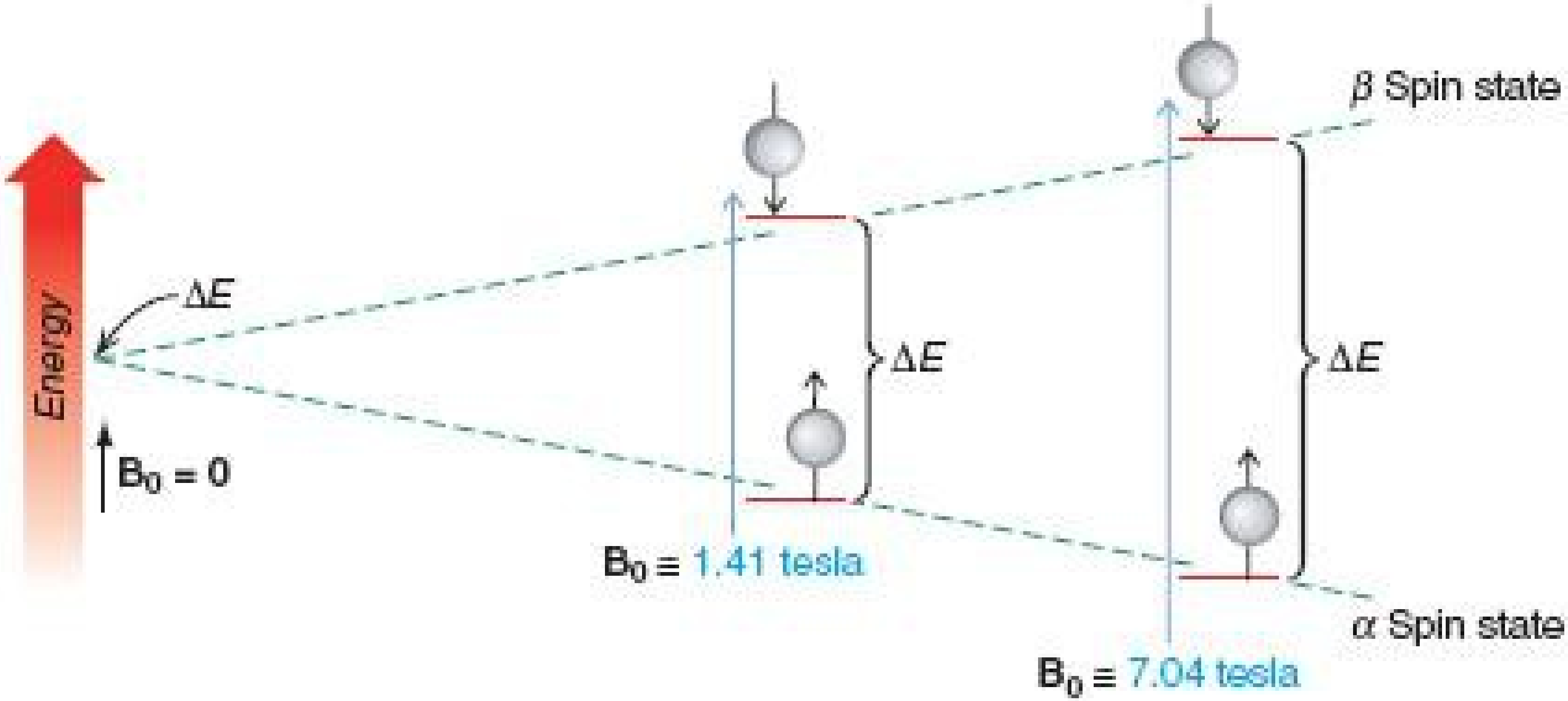
The magnetic field associated with a spinning proton

The spinning proton resembles a tiny bar magnet






α
α
β
β
α
β
α
No magnetic field
Applied magnetic field B_0


Energy
ΔE
$B_0 = 0$
ΔE
$B_0 \equiv 1.41$ tesla
ΔE
β Spin state
α Spin state
$B_0 \equiv 7.04$ tesla

❖ Spin quantum number (I)

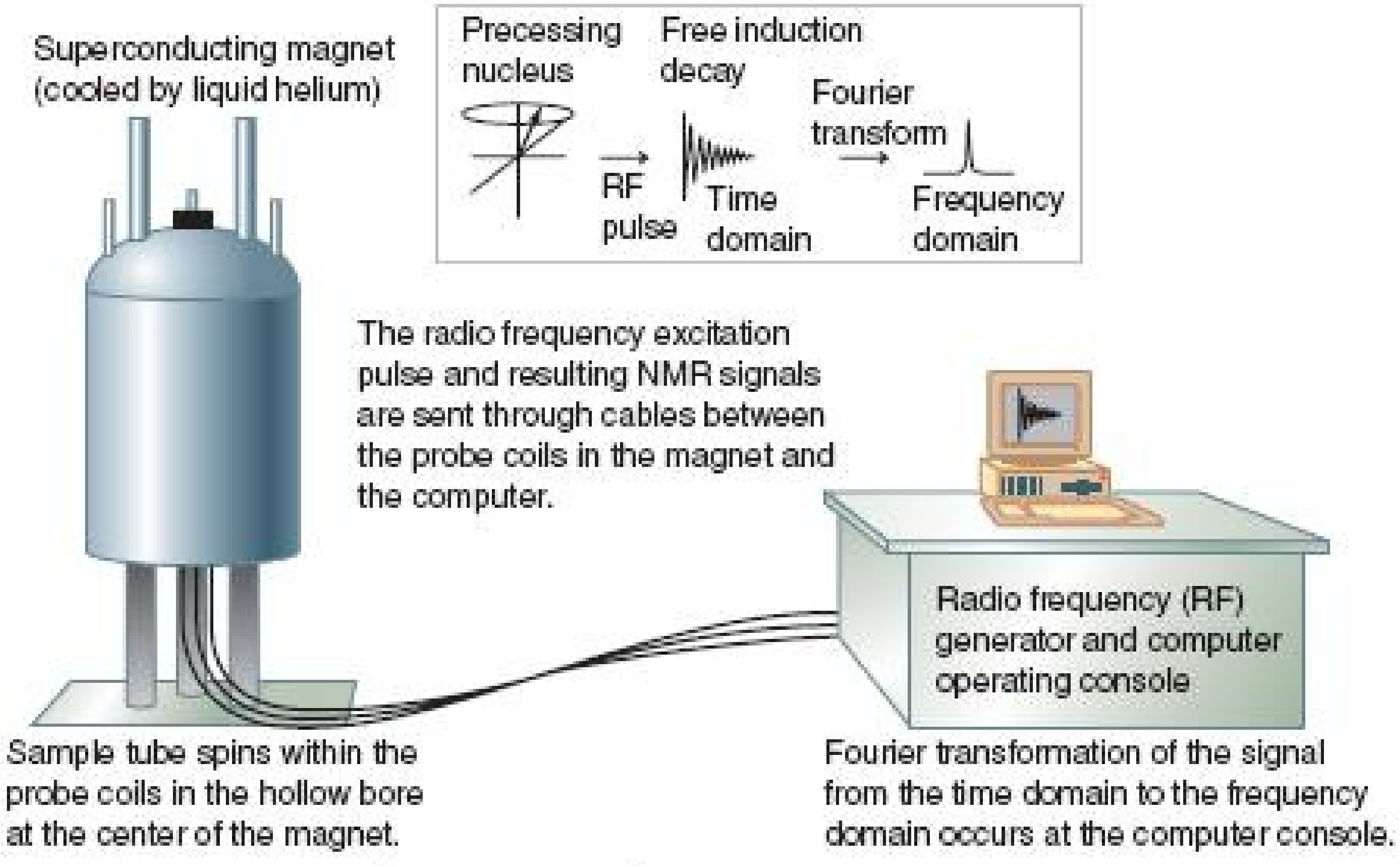
^1H: I = ½ (two spin states: +½ or -½)

⇒ (similar for ^{13}C, ^{19}F, ^{31}P)

^{12}C, ^{16}O, ^{32}S: I = 0

⇒ These nuclei do not give an NMR spectrum

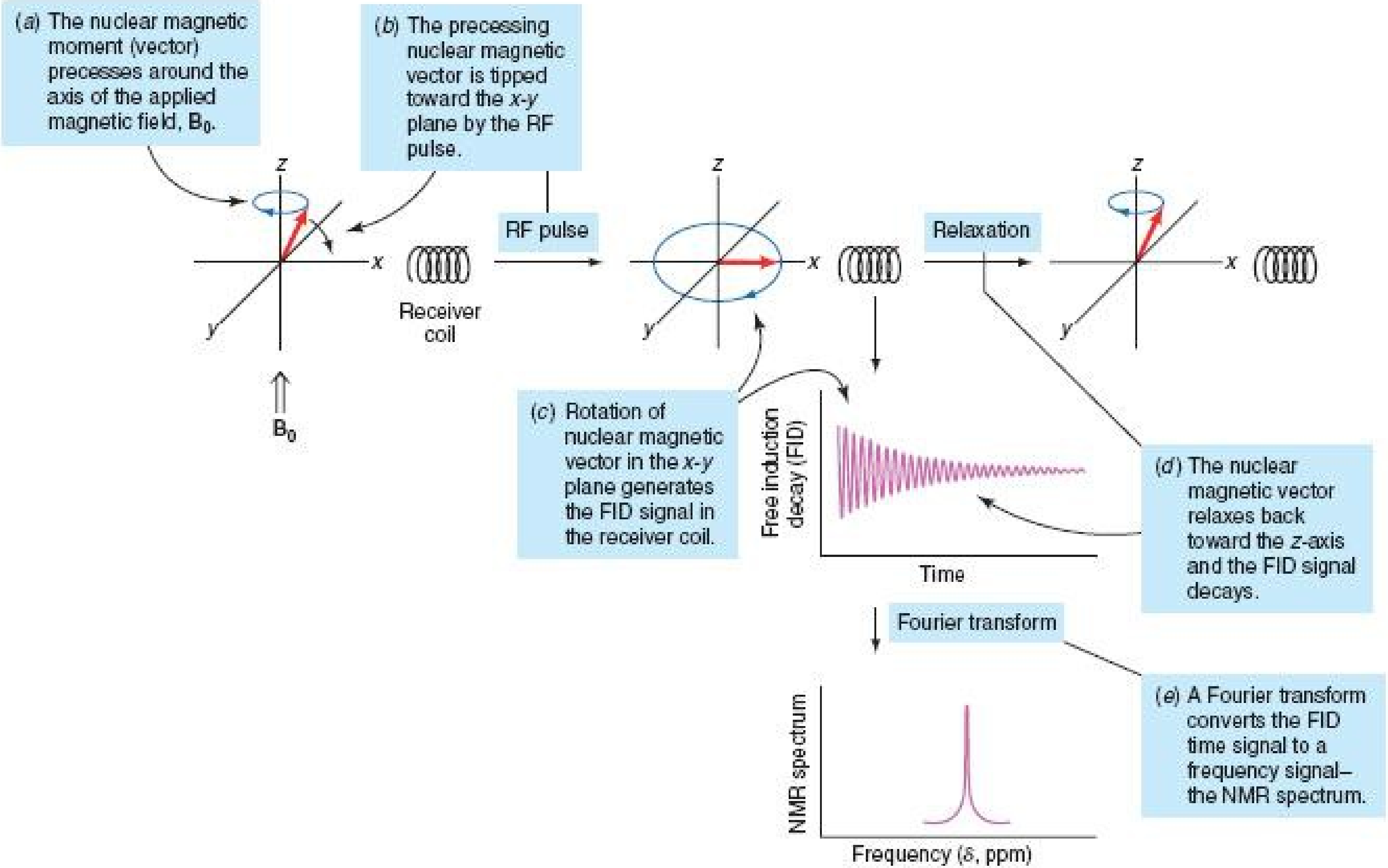
5. Detecting the Signal: Fourier Transform NMR Spectrometers



The radio frequency excitation pulse and resulting NMR signals are sent through cables between the probe coils in the magnet and the computer.

Sample tube spins within the probe coils in the hollow bore at the center of the magnet.

Fourier transformation of the signal from the time domain to the frequency domain occurs at the computer console.



(*a*) The nuclear magnetic moment (vector) precesses around the axis of the applied magnetic field, $\mathbf{B}_0$.

(*b*) The precessing nuclear magnetic vector is tipped toward the *x*-*y* plane by the RF pulse.

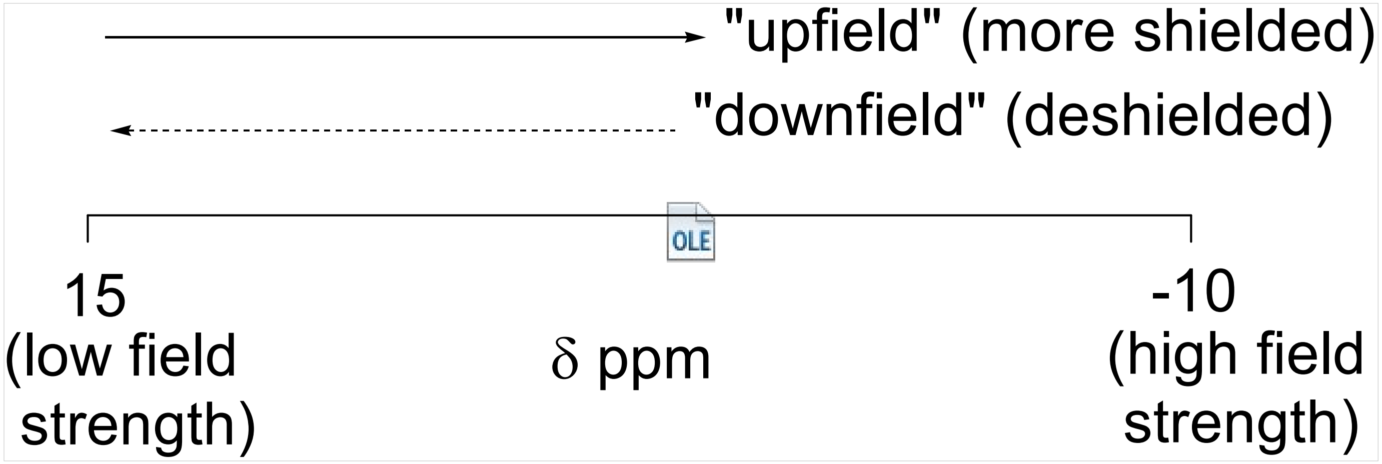
(*c*) Rotation of nuclear magnetic vector in the *x*-*y* plane generates the FID signal in the receiver coil.

(*d*) The nuclear magnetic vector relaxes back toward the *z*-axis and the FID signal decays.

(*e*) A Fourier transform converts the FID time signal to a frequency signal–the NMR spectrum.

6. Shielding & Deshielding of Protons

- All protons do not absorb energy at the same frequency in a given external magnetic field
- Lower chemical shift values correspond with lower frequency
- Higher chemical shift values correspond with higher frequency



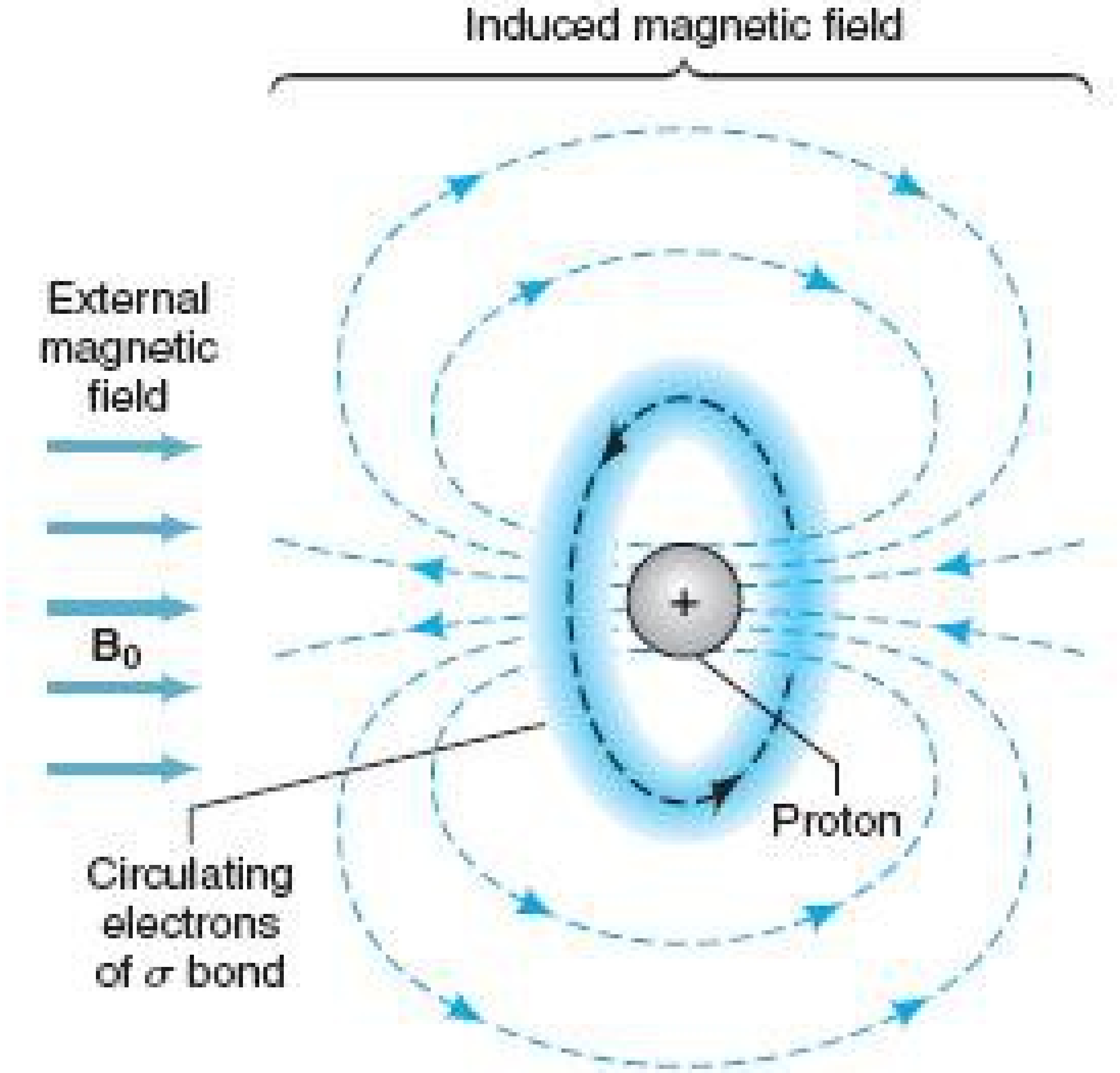
"upfield" (more shielded)

"downfield" (deshielded)

15
(low field strength)

δ ppm

-10
(high field strength)


Induced magnetic field
External magnetic field
B_0
Circulating electrons of σ bond
Proton
+

❖ Deshielding by electronegative groups

CH_3X						
X =	F	OH	Cl	Br	I	H
Electro-negativity	4.0	3.5	3.1	2.8	2.5	2.1
δ (ppm)	4.26	3.40	3.05	2.68	2.16	0.23

- Greater electronegativity
  - ♦ Deshielding of the proton
  - ♦ Larger δ

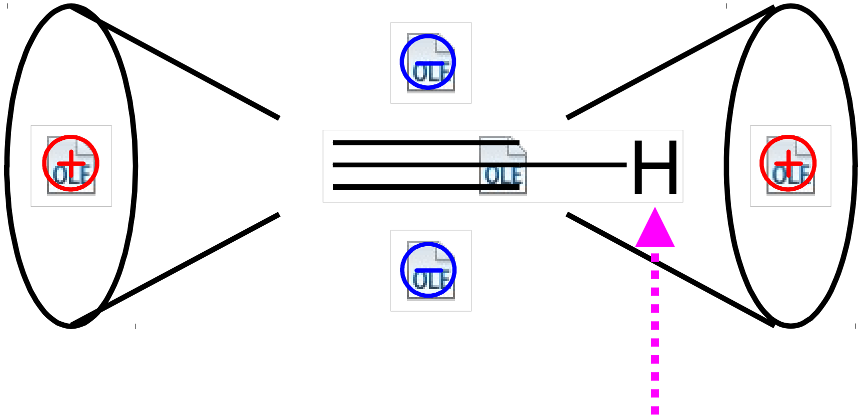
- Shielding and deshielding by circulation of π electrons
  - If we were to consider *only* the relative electronegativities of carbon in its three hybridization states, we might expect the following order of protons attached to each type of carbon:

(higher frequency) $sp < sp^2 < sp^3$ (lower frequency)

- In fact, protons of terminal alkynes absorb between δ 2.0 and δ 3.0, and the order is

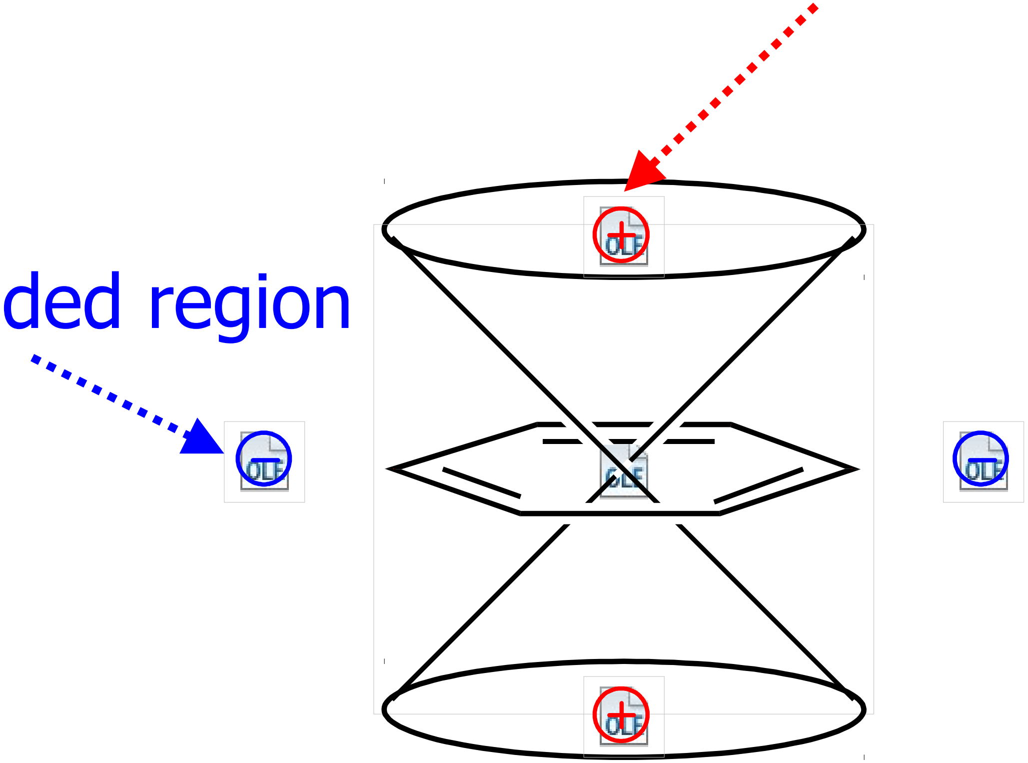
(higher frequency) $sp^2 < sp < sp^3$ (lower frequency)

- This upfield shift (lower frequency) of the absorption of protons of terminal alkynes is a result of shielding produced by the circulating π electrons of the triple bond



Shielded
(δ 2 – 3 ppm)

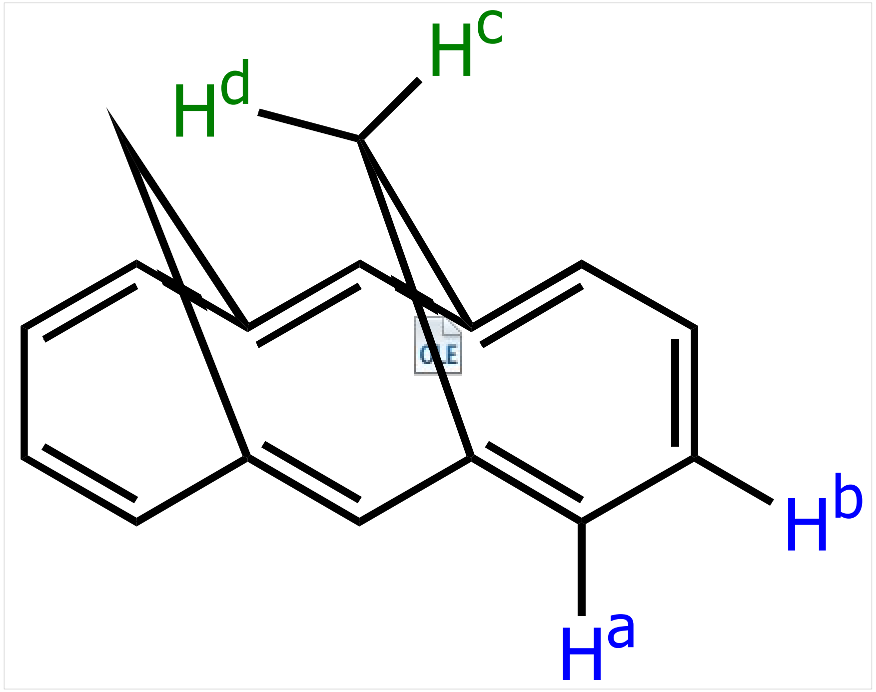
- Aromatic system



Shielded region

Deshielded region

- e.g.

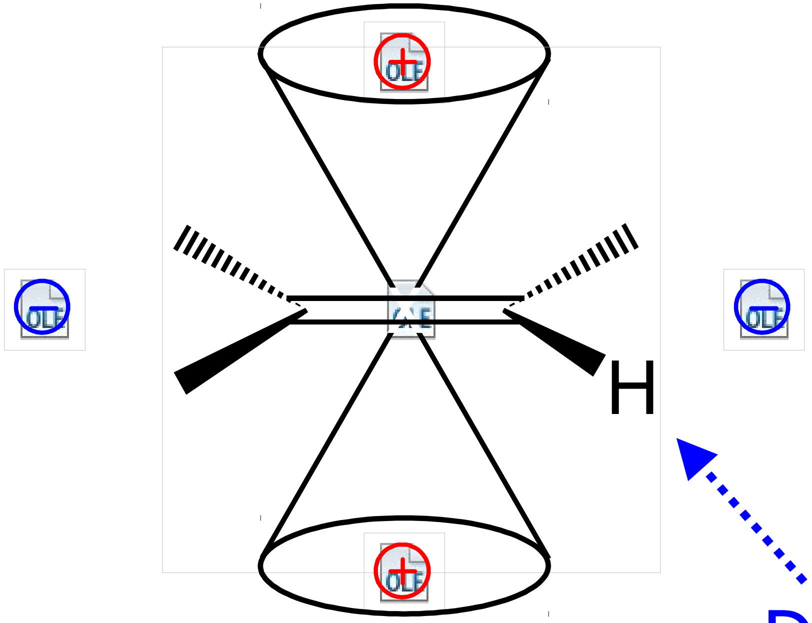


δ (ppm)

H^a & H^b: 7.9 & 7.4 (deshielded)

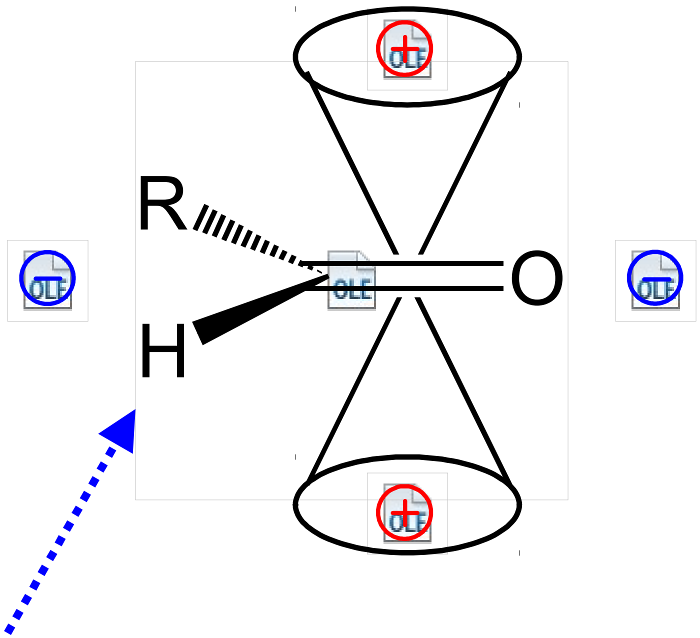
H^c & H^d: 0.91 – 1.2 (shielded)

- Alkenes



Deshielded
(δ 4.5 – 7 ppm)

- Aldehydes

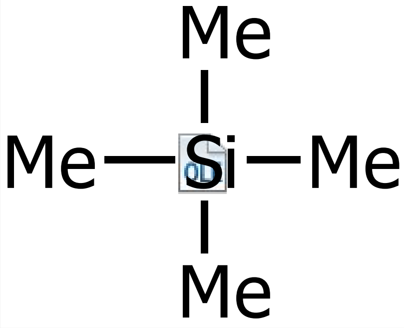


Electronegativity effect + Anisotropy effect

⇒ δ = 8.5 – 10 ppm (deshielded)

7. The Chemical Shift

- Reference compound
  - TMS = tetramethylsilane



    as a reference standard (0 ppm)
  - Reasons for the choice of TMS as reference
    - Resonance position at higher field than other organic compounds
    - Unreactive and stable, not toxic
    - Volatile and easily removed (B.P. = 28°C)

7A. PPM and the δ Scale

- The chemical shift of a proton, when expressed in **hertz (Hz)**, is proportional to the strength of the external magnetic field
- Since spectrometers with different magnetic field strengths are commonly used, it is desirable to express chemical shifts in a form that is independent of the strength of the external field

- Since chemical shifts are always very small (typically 5000 Hz) compared with the total field strength (commonly the equivalent of 60, 300, or 600 *million* hertz), it is convenient to express these fractions in units of *parts per million* (ppm)

- This is the origin of the delta scale for the expression of chemical shifts relative to TMS

$$\delta = \frac{(\text{observed shift from TMS in hertz}) \times 10^6}{(\text{operating frequency of the instrument in hertz})}$$

- For example, the chemical shift for benzene protons is 2181 Hz when the instrument is operating at 300 MHz. Therefore

$$\delta = \frac{2181\text{ Hz x }10^{6}}{300\text{ x }10^{6}\text{ Hz}} = 7.27\text{ ppm}$$

- The chemical shift of benzene protons in a 60 MHz instrument is 436 Hz:

$$\delta = \frac{436\text{ Hz x }10^{6}}{60\text{ x }10^{6}\text{ Hz}} = 7.27\text{ ppm}$$

- Thus, the chemical shift expressed in ppm is the same whether measured with an instrument operating at 300 or 60 MHz (or any other field strength)

8. Chemical Shift Equivalent and Nonequivalent Protons

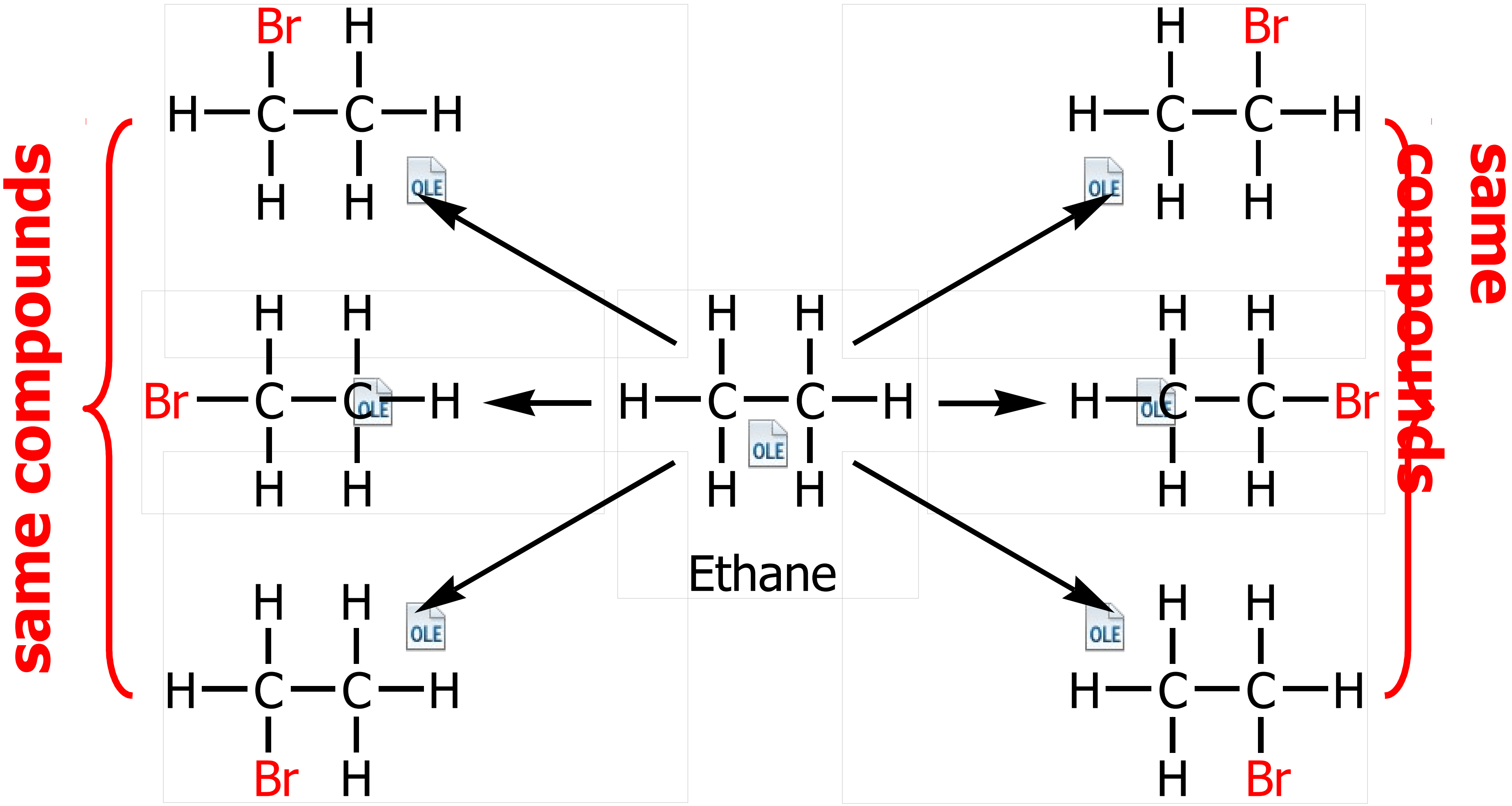
- Two or more protons that are in identical environments have the same chemical shift and, therefore, give only one ^{1}H NMR signal

- **Chemically equivalent** protons are **chemical shift equivalent** in ^{1}H NMR spectra

Homotopic and Heterotopic Atoms

- If replacing the hydrogens by a different atom gives the same compound, the hydrogens are said to be **homotopic**

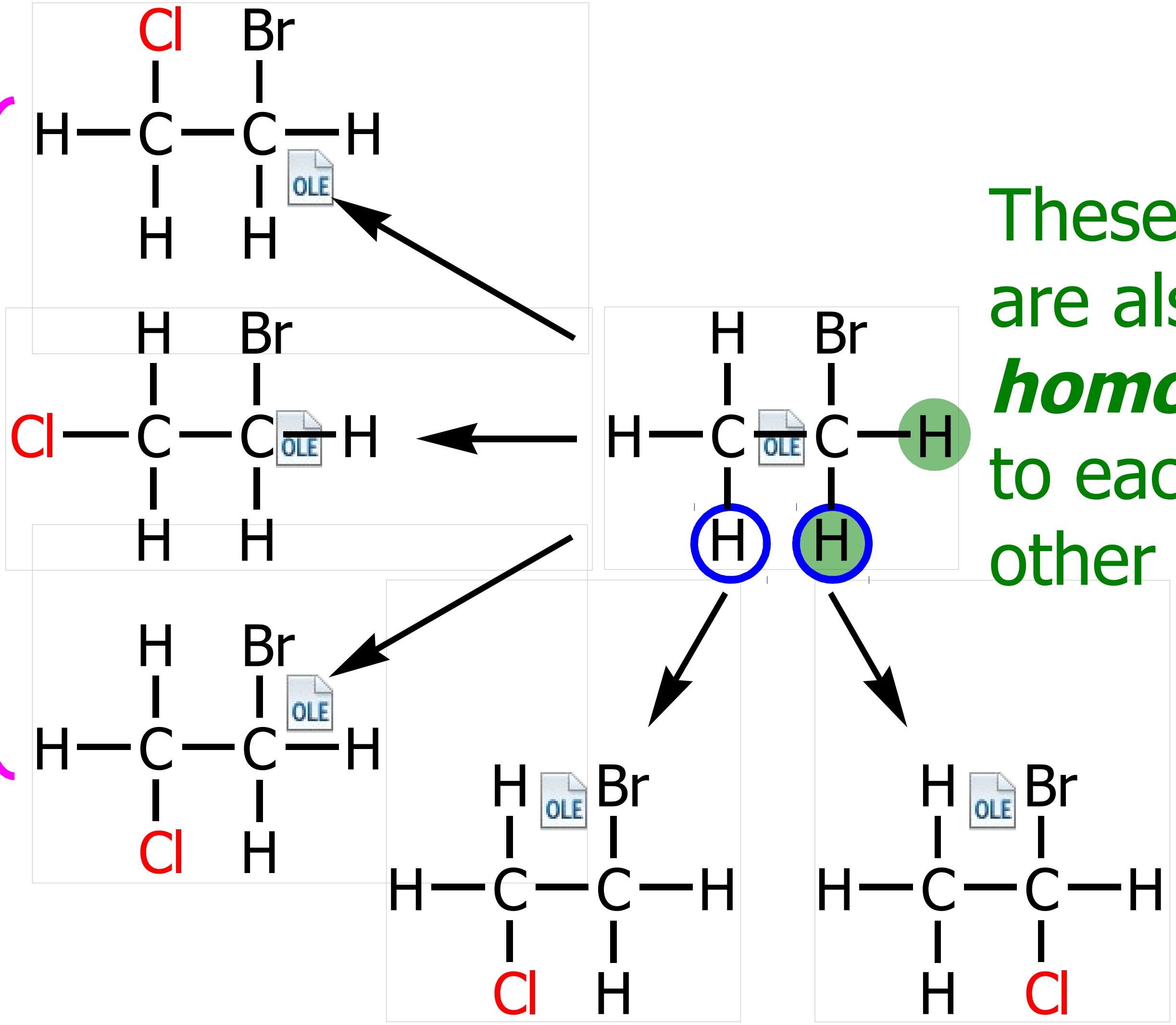
- Homotopic hydrogens have identical environments and will have the same chemical shift. They are said to be **chemical shift equivalent**



- The six hydrogens of ethane are *homotopic* and are, therefore, *chemical shift equivalent*
- **Ethane, consequently, gives only one signal in its ^1H NMR spectrum**

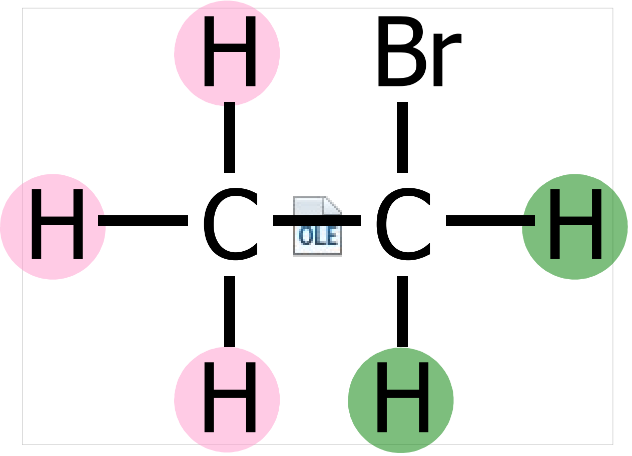
- If replacing hydrogens by a different atom gives **different compounds**, the hydrogens are said to be **heterotopic**

- Heterotopic atoms have **different chemical shifts** and are **not chemical shift equivalent** same compounds ⇒ these 3 H's of the CH_3 group are ***homotopic*** ⇒ the CH_3 group gives only one 1H NMR signal



These 2 H's are also ***homotopic*** to each other

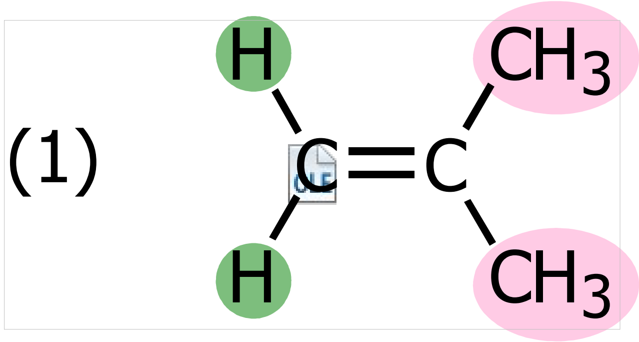
different compounds ⇒ ***heterotopic***



- CH_3CH_2Br
  - two sets of hydrogens that are heterotopic with respect to each other
  - two ^1H NMR signals

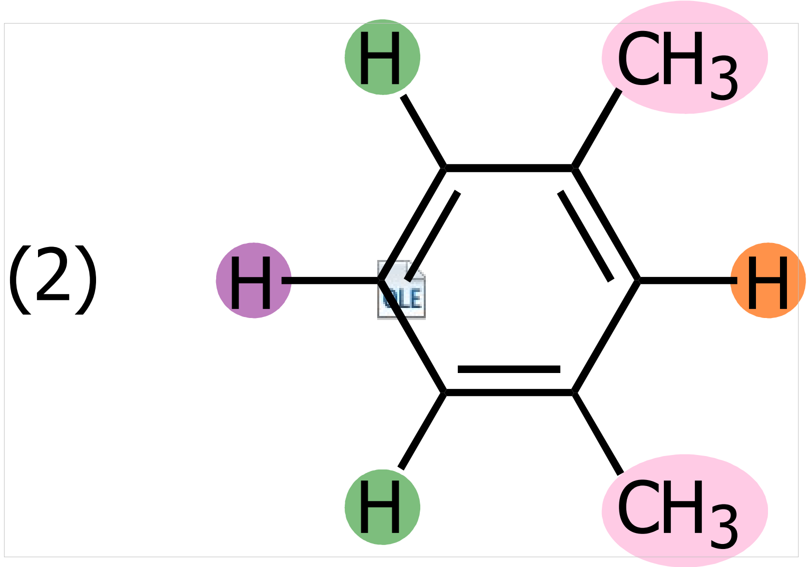
❖ Other examples

(1)



$\Rightarrow$ 2 ^{1}H NMR signals

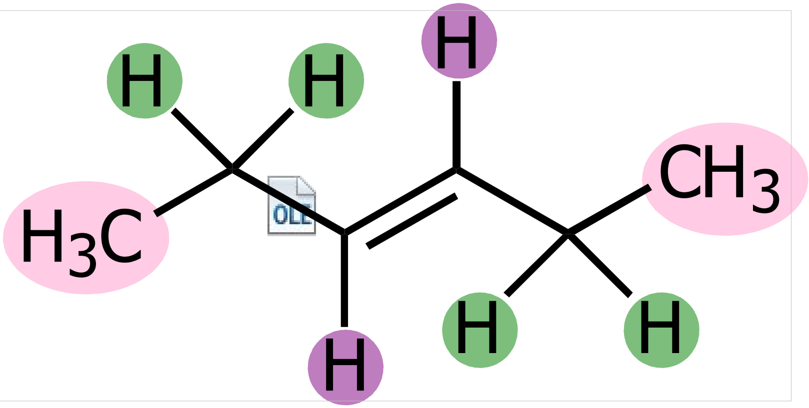
(2)



$\Rightarrow$ 4 ^{1}H NMR signals

❖ Other examples

(3)

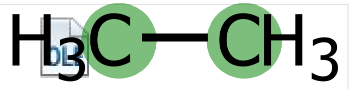


⇒ 3 ^{1}H NMR signals

❖ Application to ^{13}C NMR spectroscopy

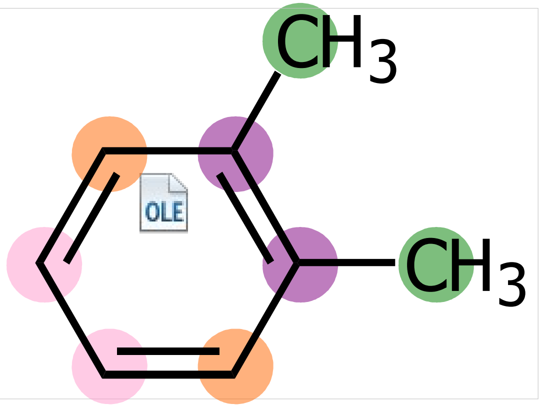
- Examples

(1)



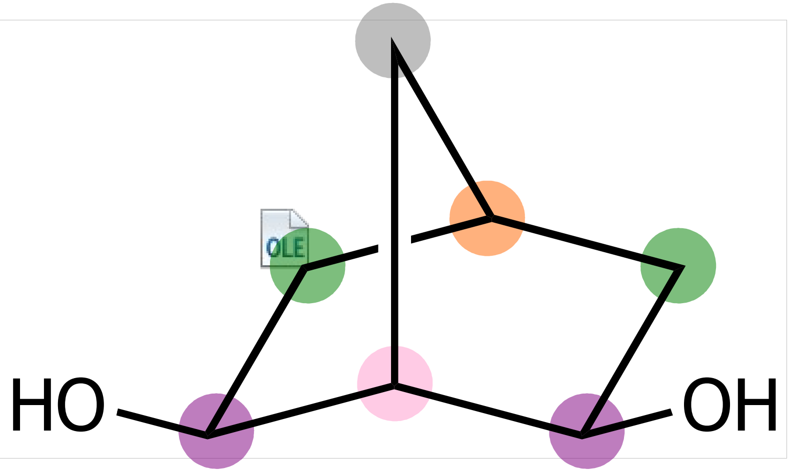
⇒ 1 ^{13}C NMR signal

(2)



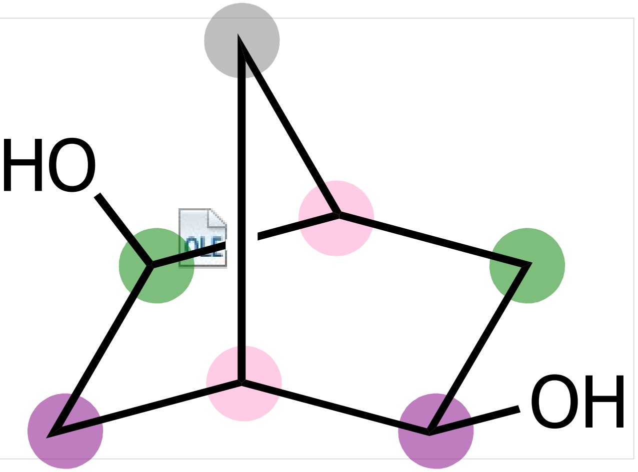
⇒ 4 ^{13}C NMR signals

(3)



⇒ 5 ^{13}C NMR signals

(4)

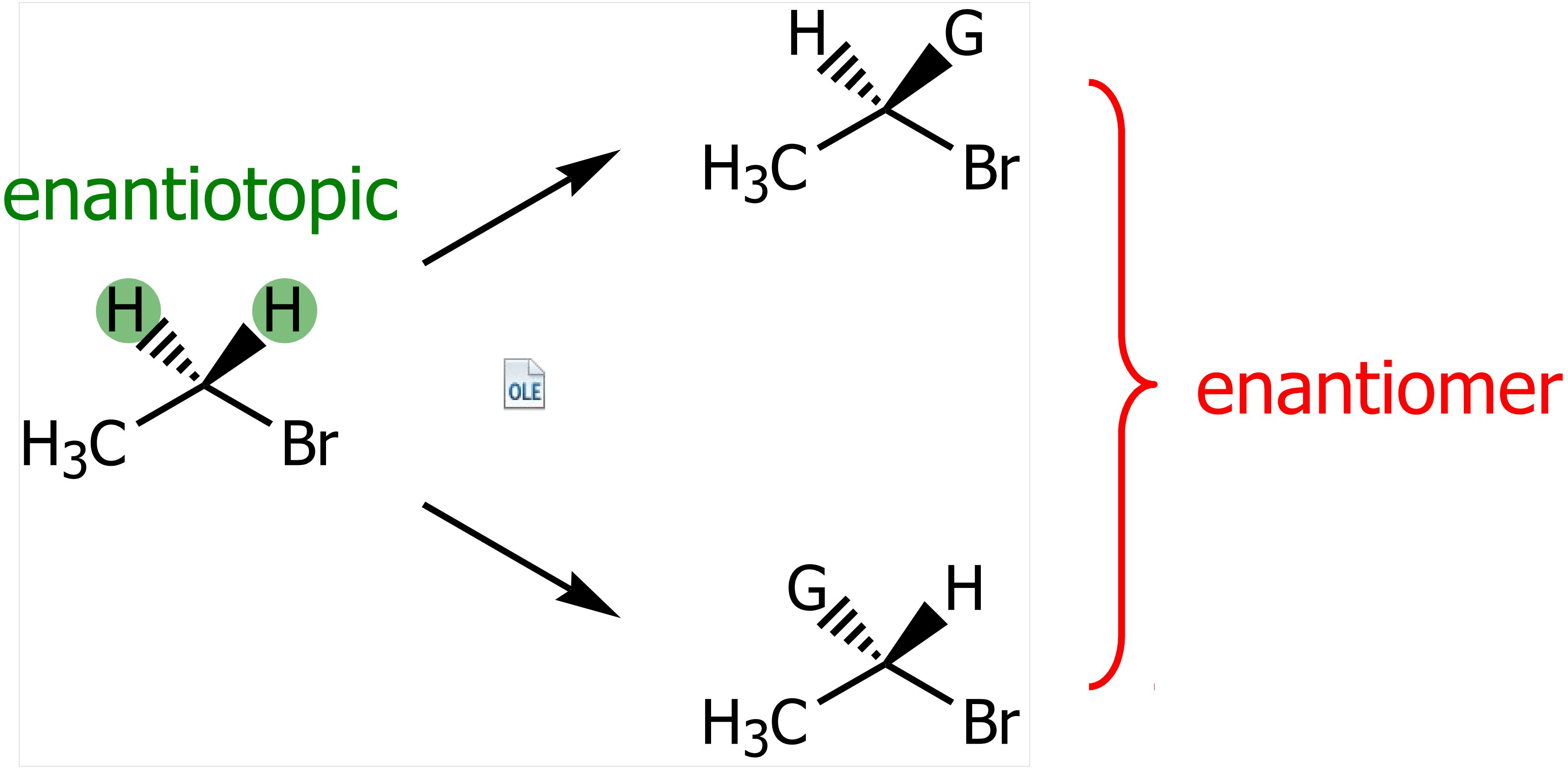


⇒ 4 ^{13}C NMR signals

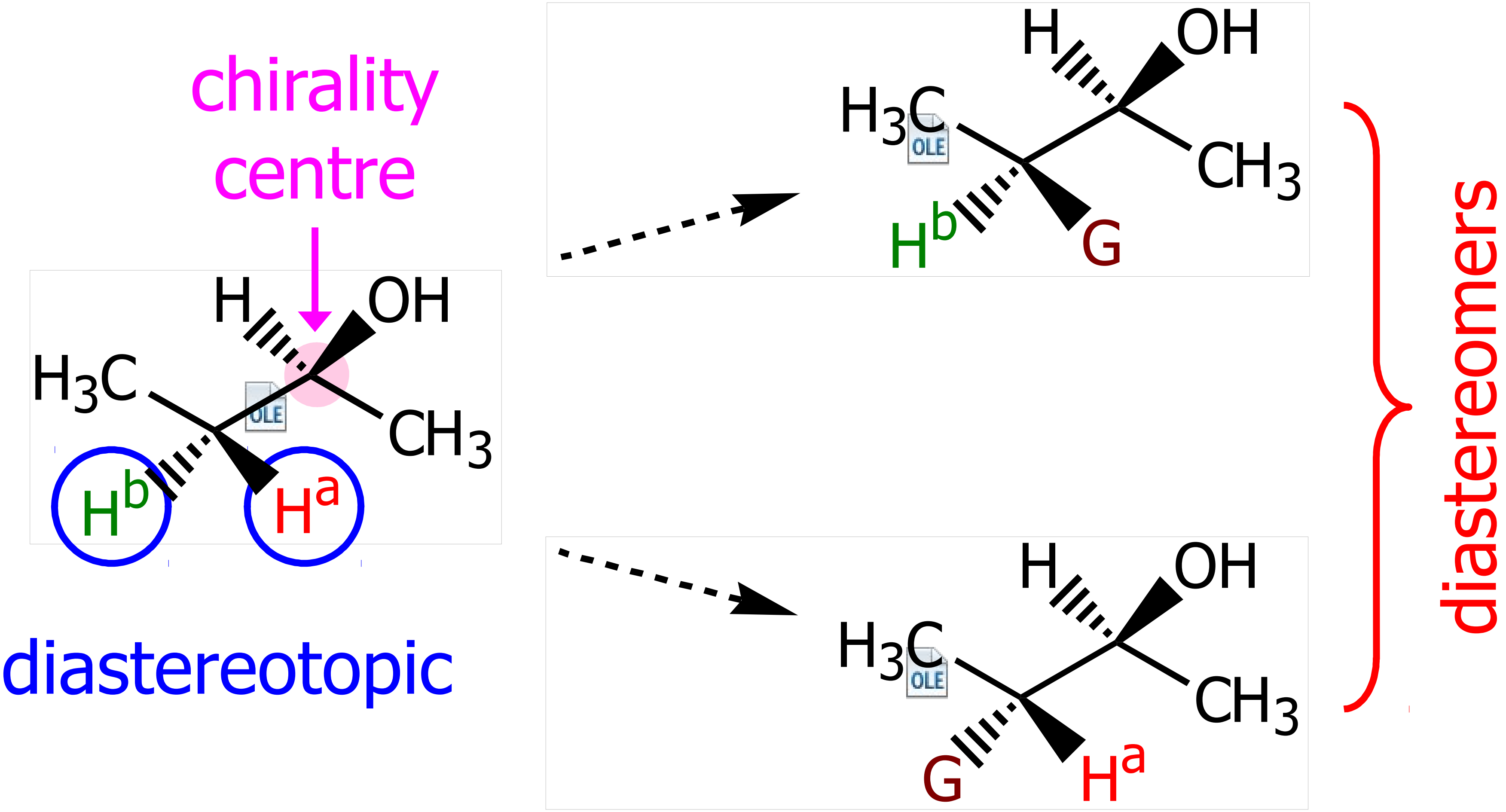
3. Enantiotopic and Diastereotopic Hydrogen Atoms

- If replacement of each of two hydrogen atoms by the same group yields compounds that are enantiomers, the two hydrogen atoms are said to be **enantiotopic**

- Enantiotopic hydrogen atoms have the same chemical shift and give only one ^1H NMR signal:


enantiotopic

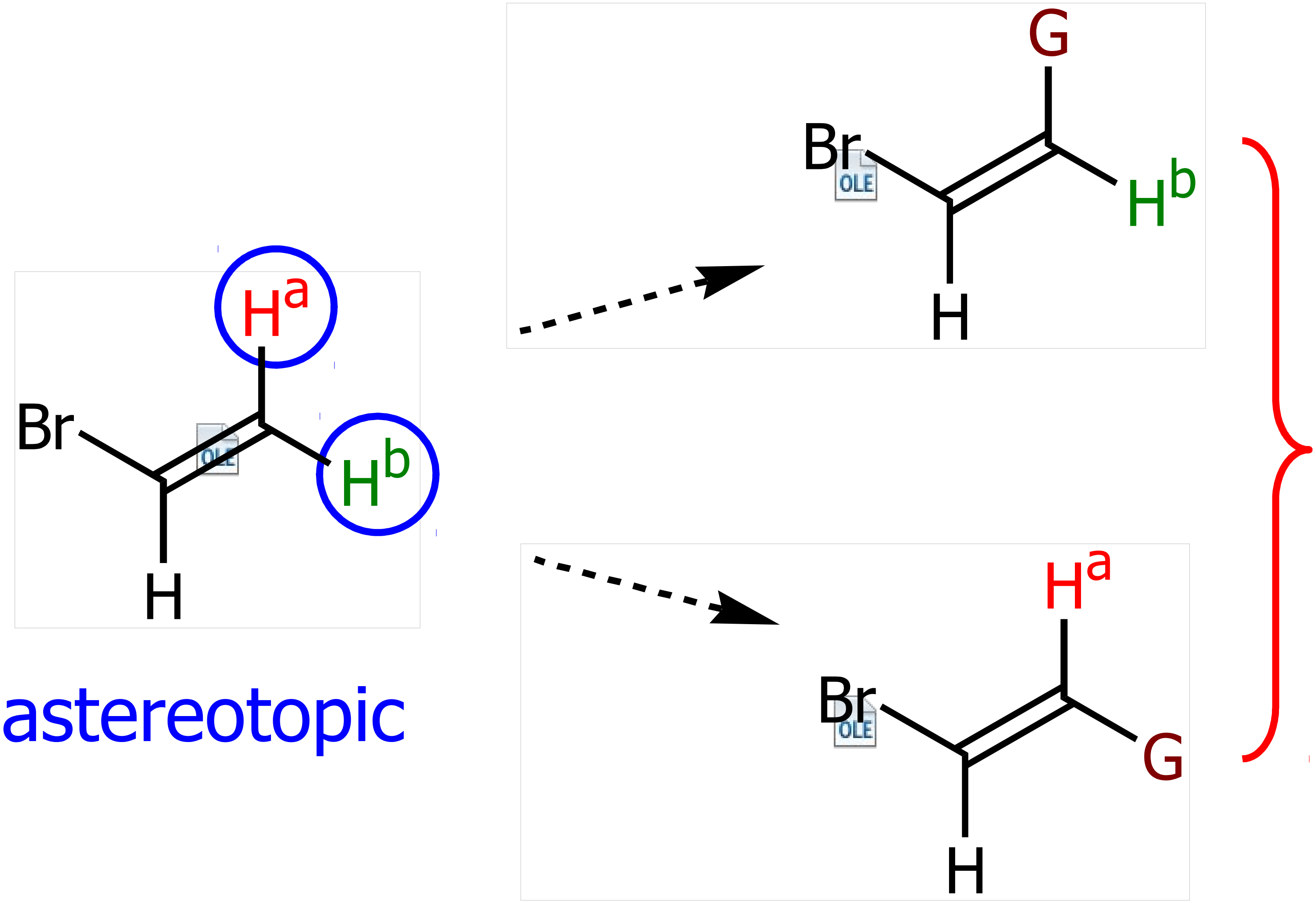
enantiomer



chirality centre

diastereotopic

diastereomers

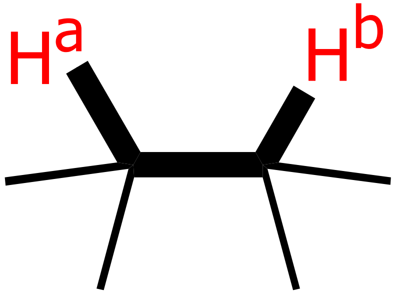


diastereotopic

diastereomers

9. Signal Splitting: Spin–Spin Coupling

- **Vicinal coupling** is coupling between hydrogen atoms on adjacent carbons (vicinal hydrogens), where separation between the hydrogens is by three σ bonds



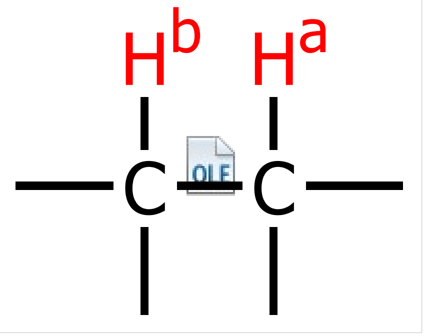
^3J or vicinal coupling

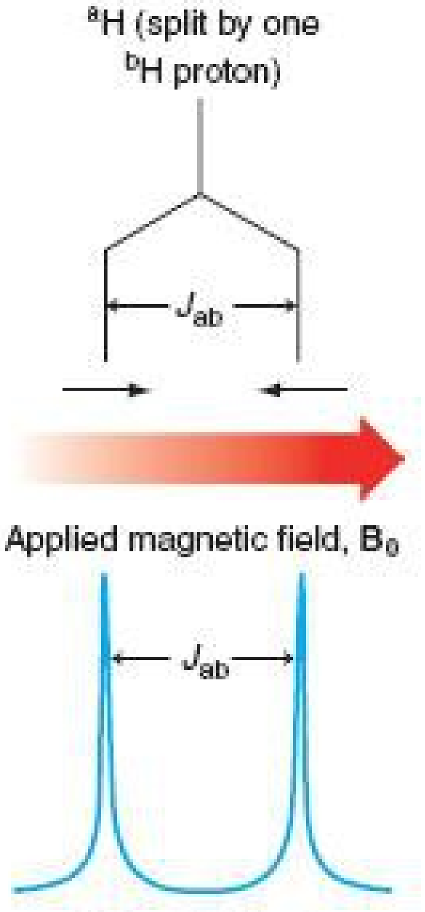
9A. Vicinal Coupling

- Vicinal coupling between heterotopic protons generally follows the *n* + 1 rule. Exceptions to the *n* + 1 rule can occur when diastereotopic hydrogens or conformationally restricted systems are involved
- **Signal splitting is not observed for protons that are homotopic (chemical shift equivalent) or enantiotopic**

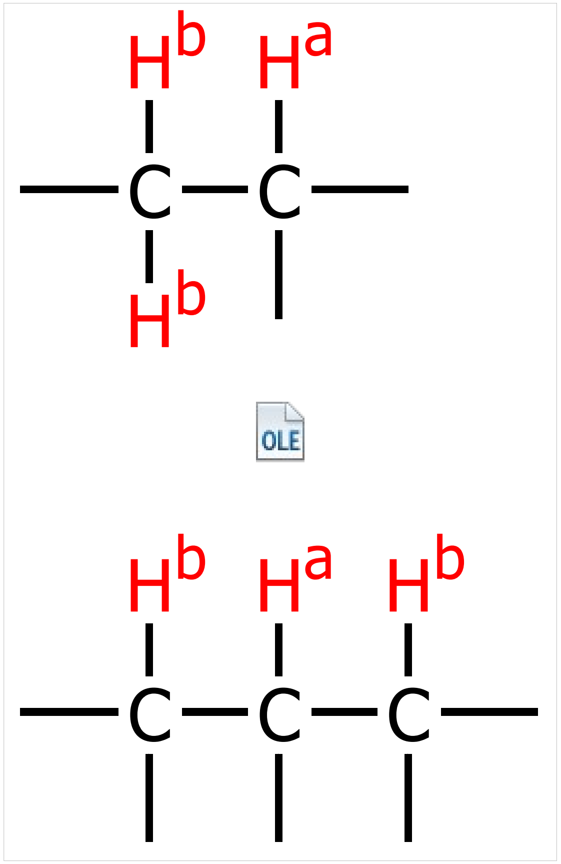
3. Splitting Tree Diagrams and the Origin of Signal Splitting

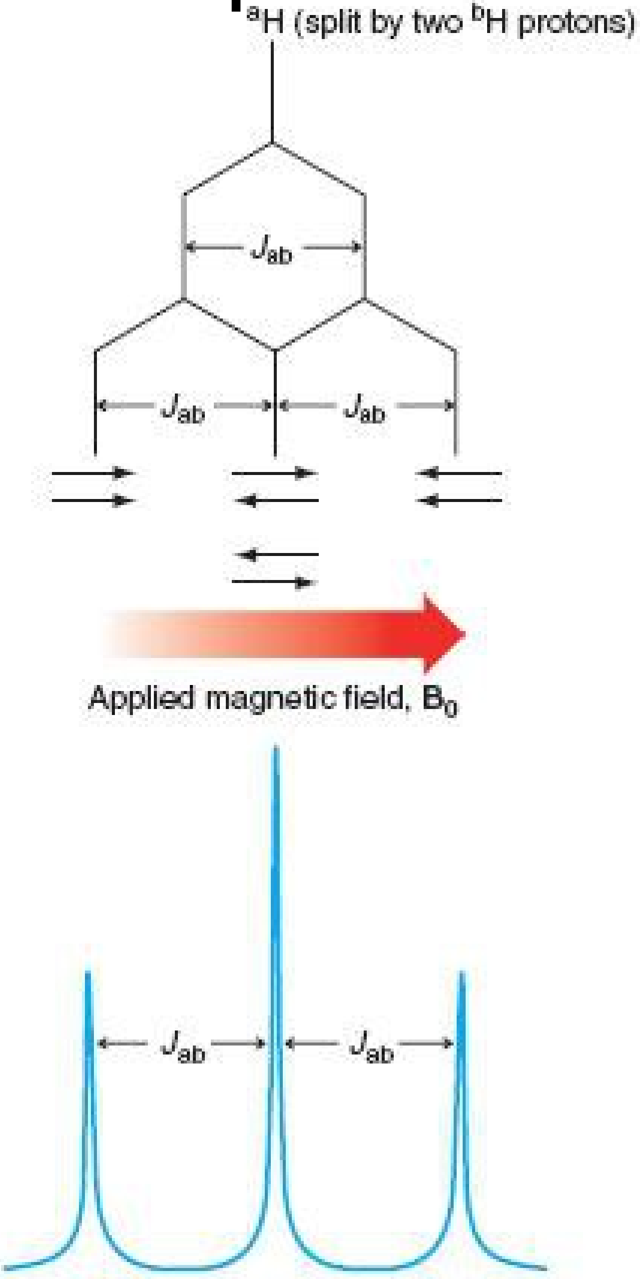
- ❖ Splitting analysis for a doublet



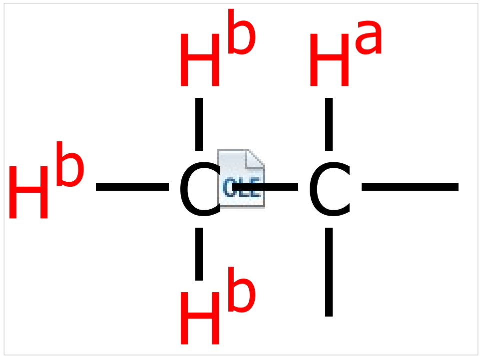


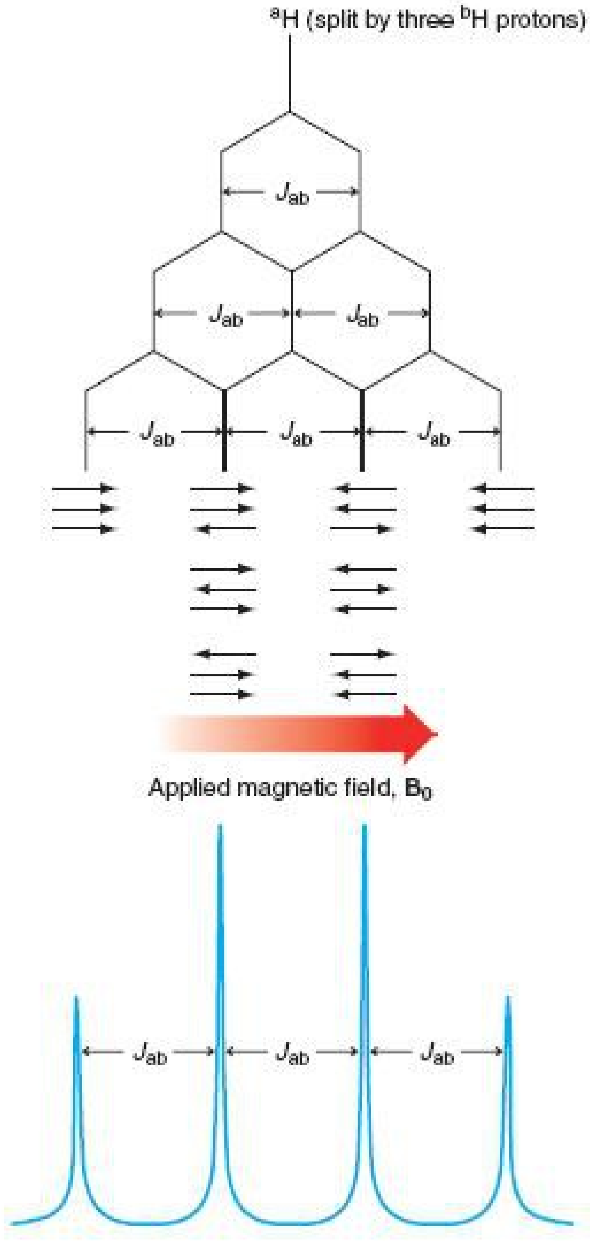
❖ Splitting analysis for a triplet





❖ Splitting analysis for a quartet

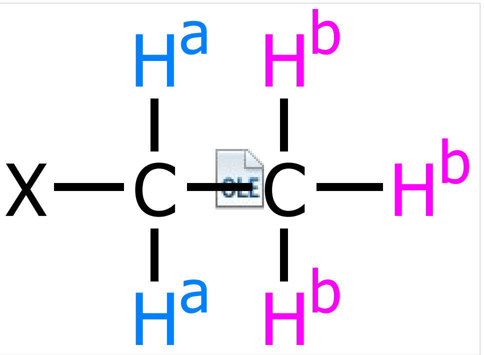


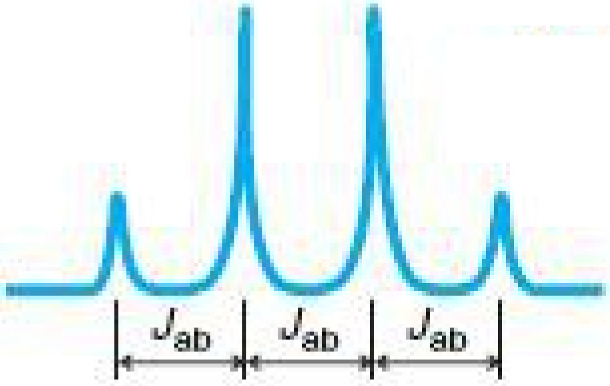


- Pascal’s Triangle
  - Use to predict relative intensity of various peaks in multiplet
  - Given by the coefficient of binomial expansion $(a + b)^n$

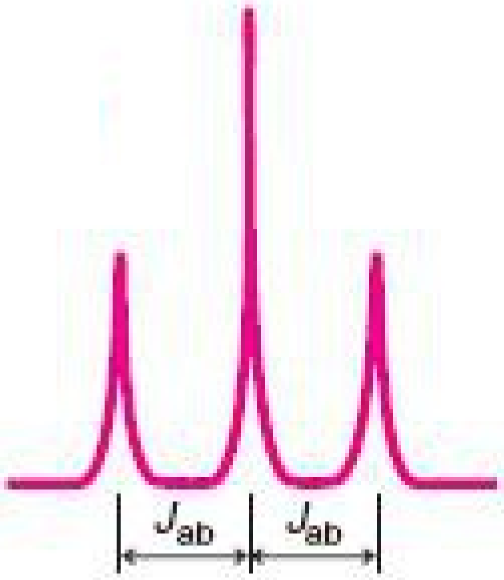
singlet (s)	1
doublet (d)	1 1
triplet (t)	1 2 1
quartet (q)	1 3 3 1
quintet	1 4 6 4 1
sextet	1 5 10 10 5 1

Coupling Constants – Recognizing Splitting Patterns





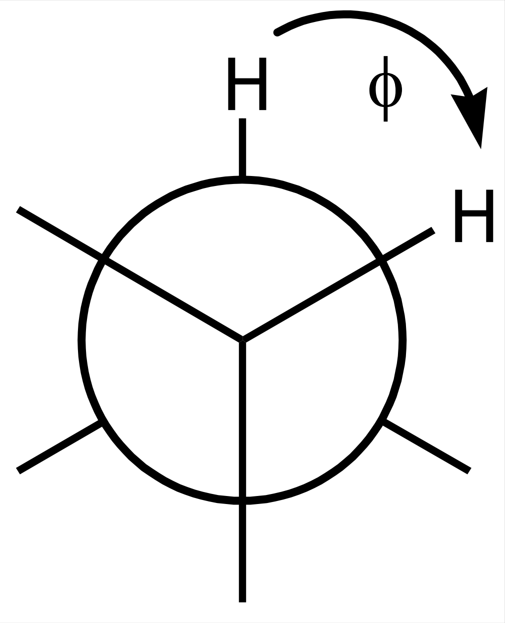
Signal for ^aH



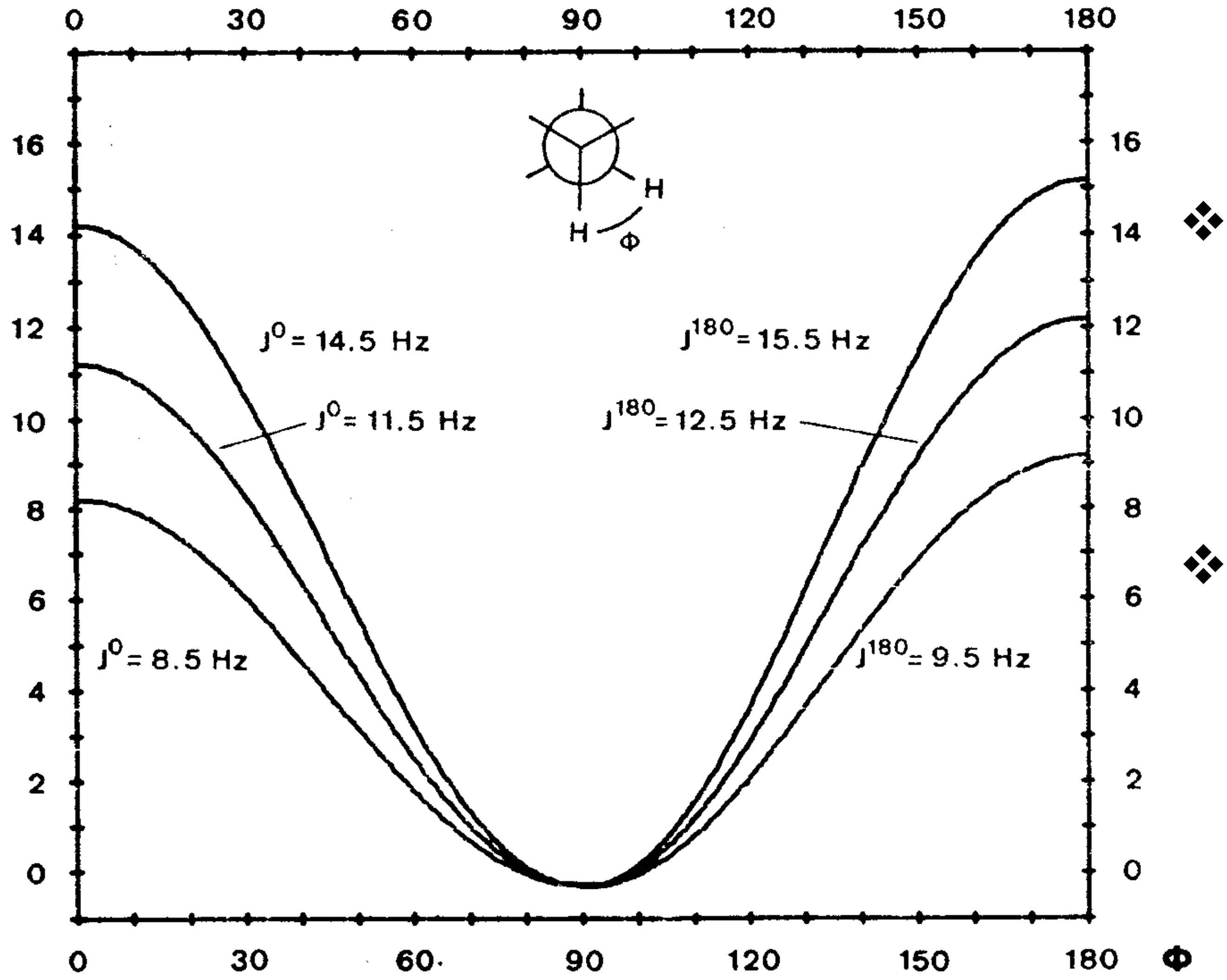
Signal for ^bH

D. The Dependence of Coupling Constants on Dihedral Angle

- ^3J values are related to the dihedral angle (ϕ)



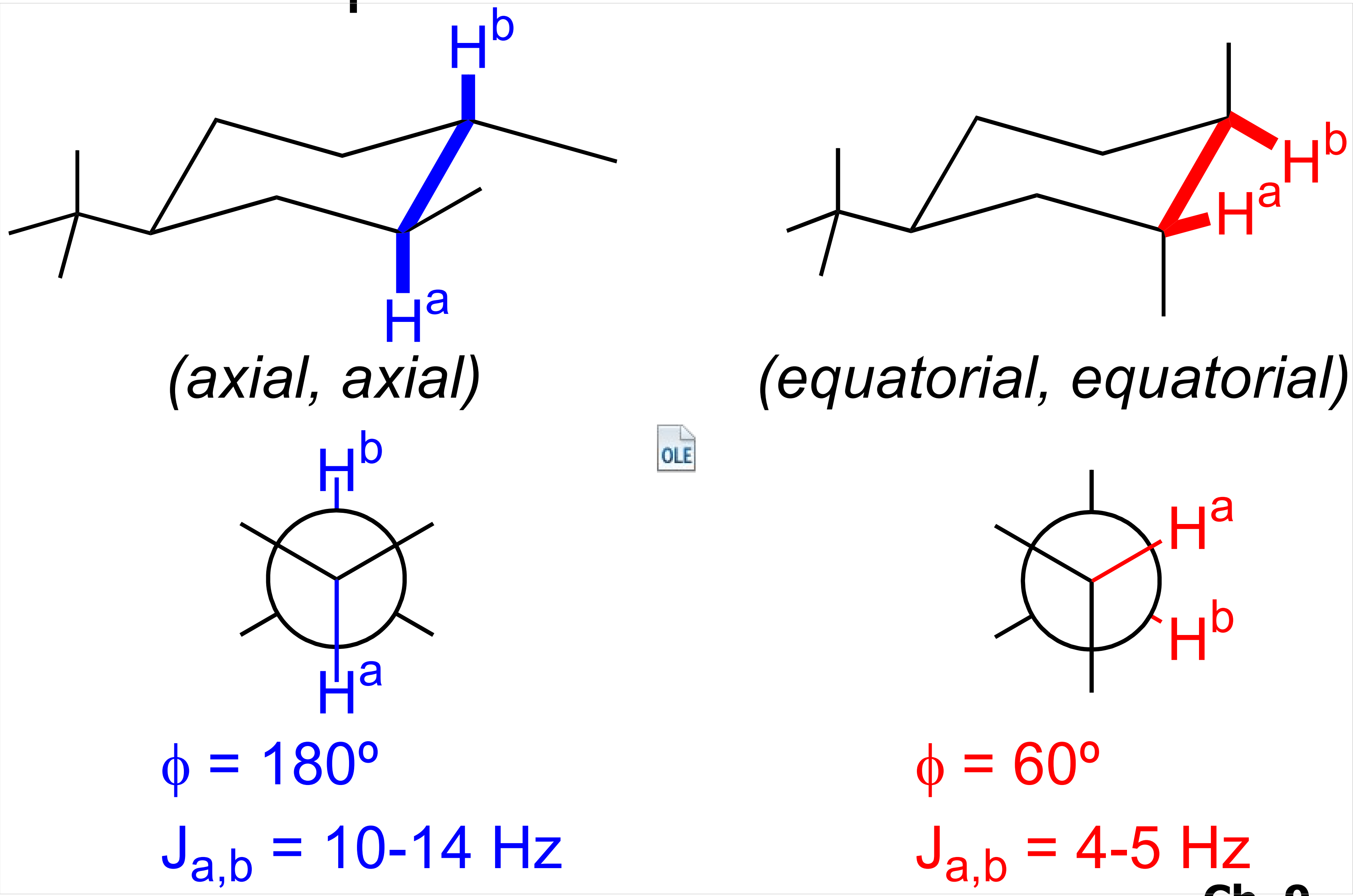
❖ Karplus curve



- ❖ ϕ ~0° or 180° ⇒ Maximum ^3J value

- ❖ ϕ ~90° ⇒ ^3J ~0 Hz

- Karplus curve
  - Examples



(axial, axial)

(equatorial, equatorial)

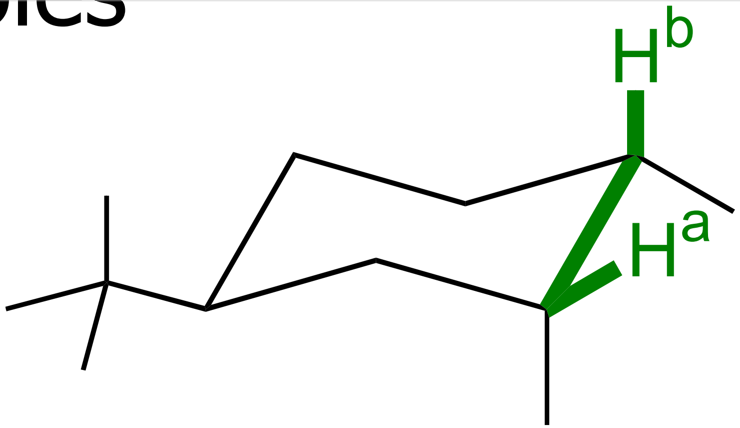
$\phi = 180°$

$J_{a,b} = 10\text{-}14$ Hz

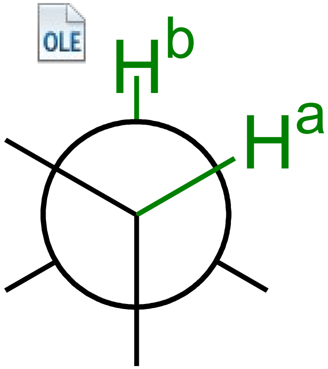
$\phi = 60°$

$J_{a,b} = 4\text{-}5$ Hz

- Karplus curve
  - Examples



(equatorial, axial)

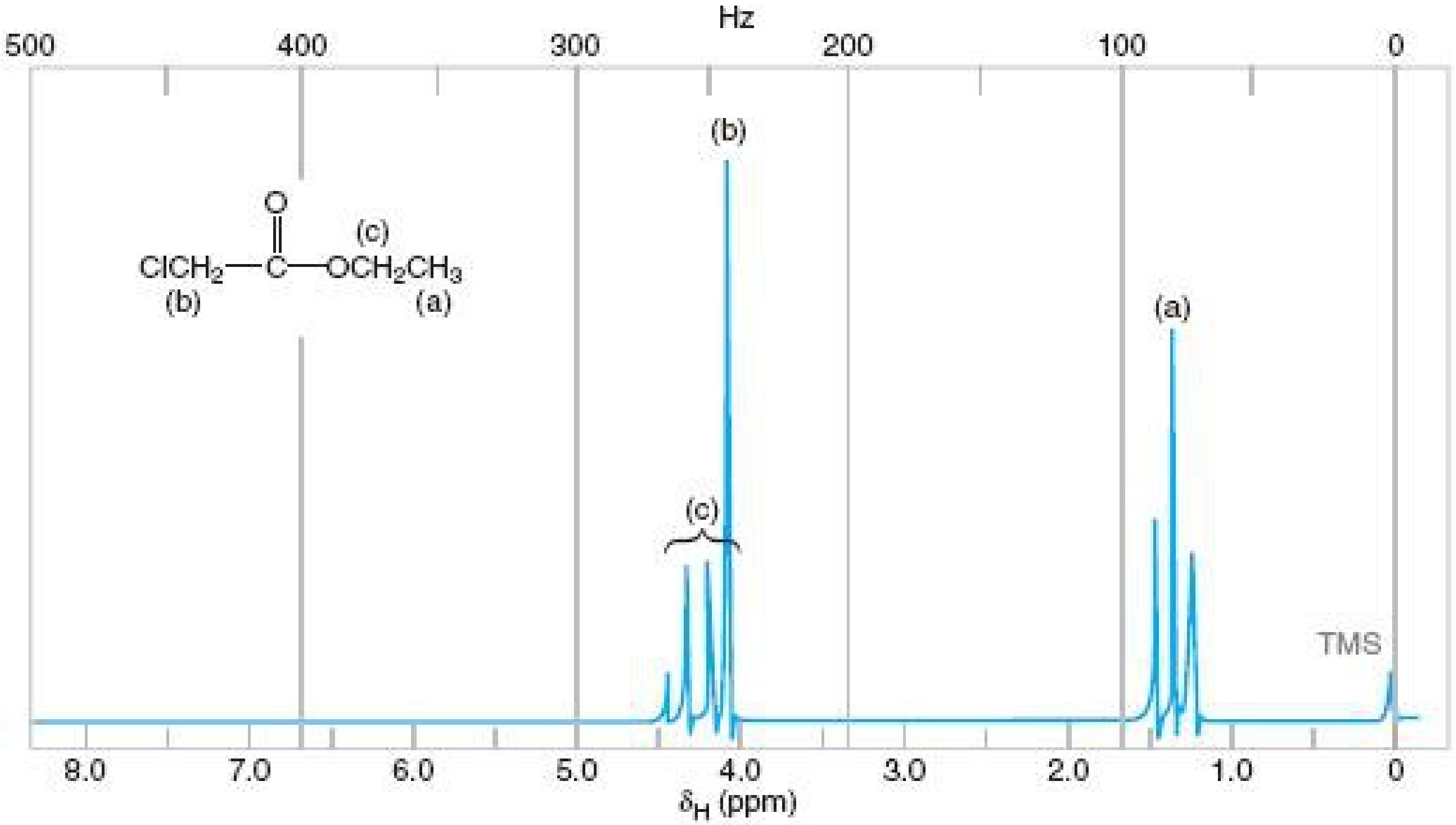


$\phi = 60°$

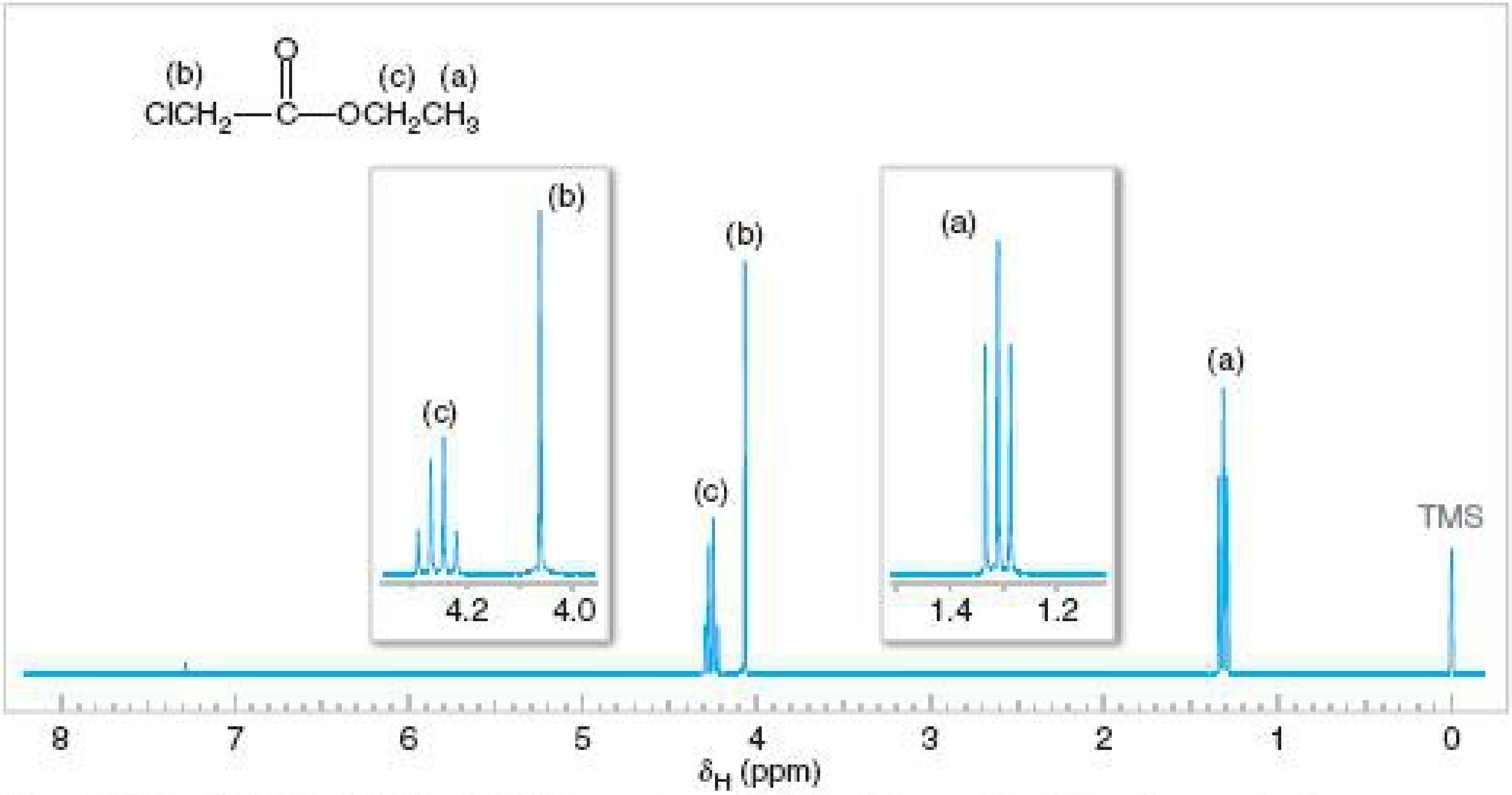
$J_{a,b} = 4\text{-}5\ \text{Hz}$

9E. Complicating Features

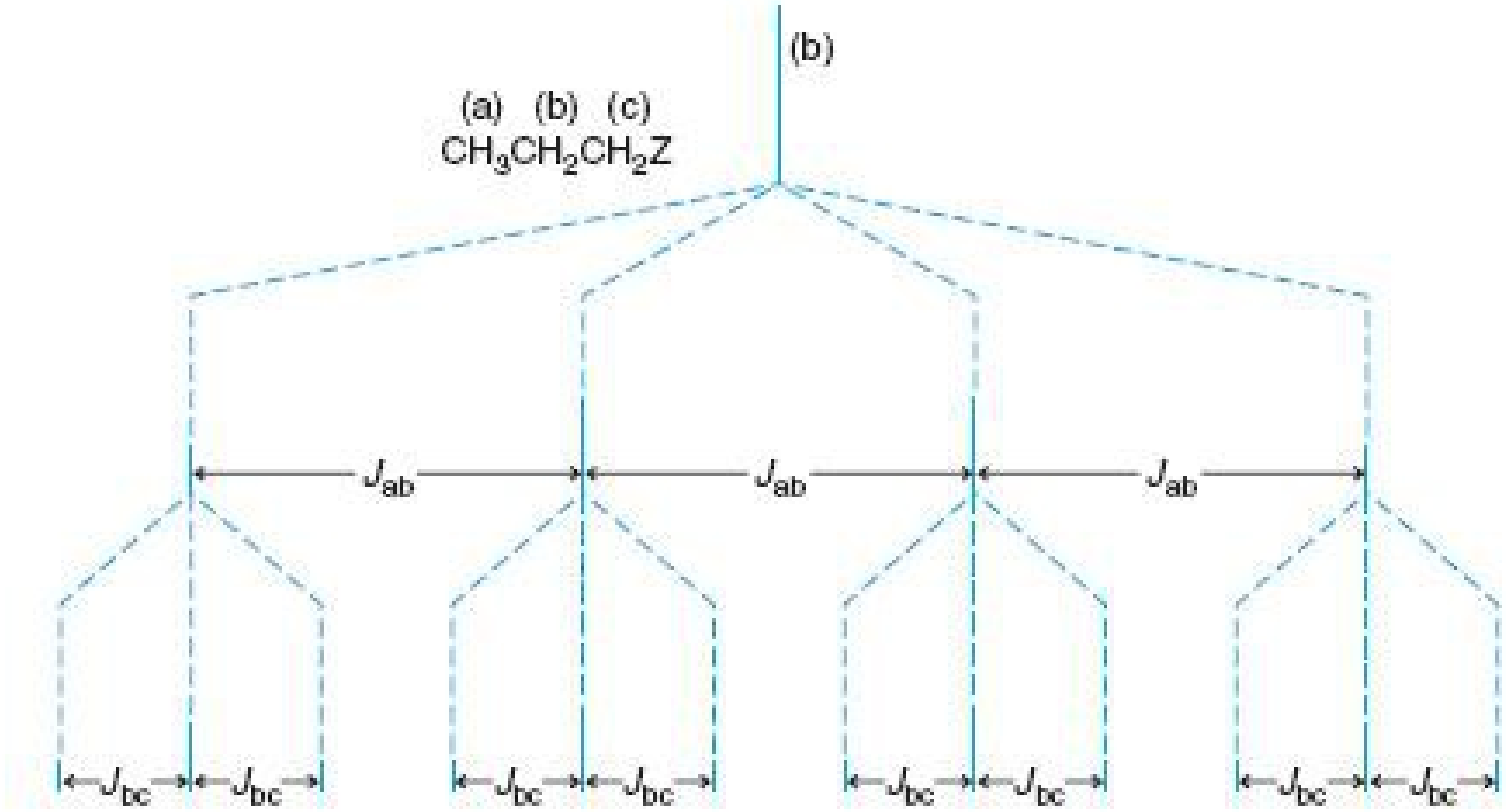
- The 60 MHz ^{1}H NMR spectrum of ethyl chloroacetate



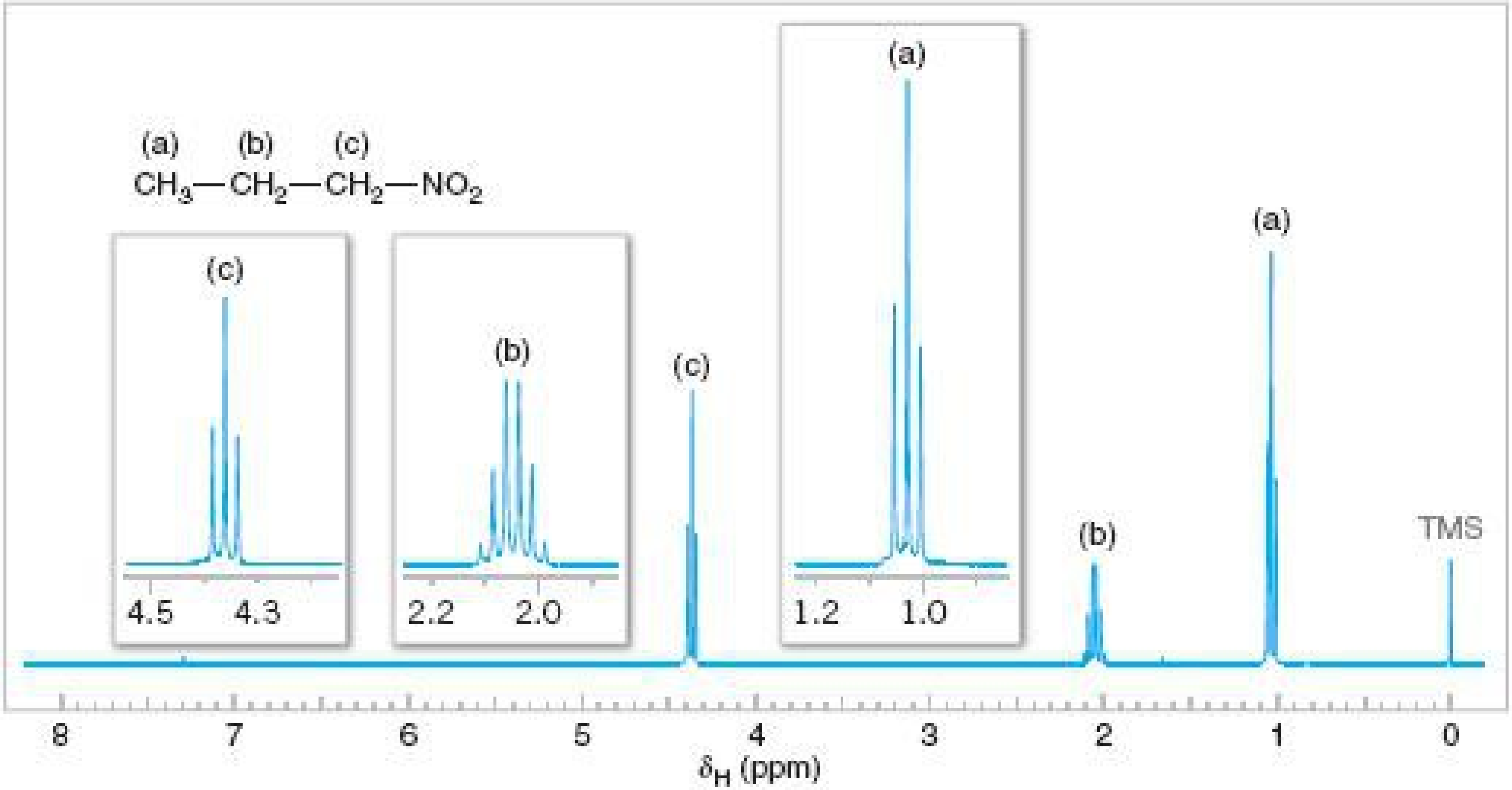
❖ The 300 MHz ^{1}H NMR spectrum of ethyl chloroacetate



. Analysis of Complex Interactions

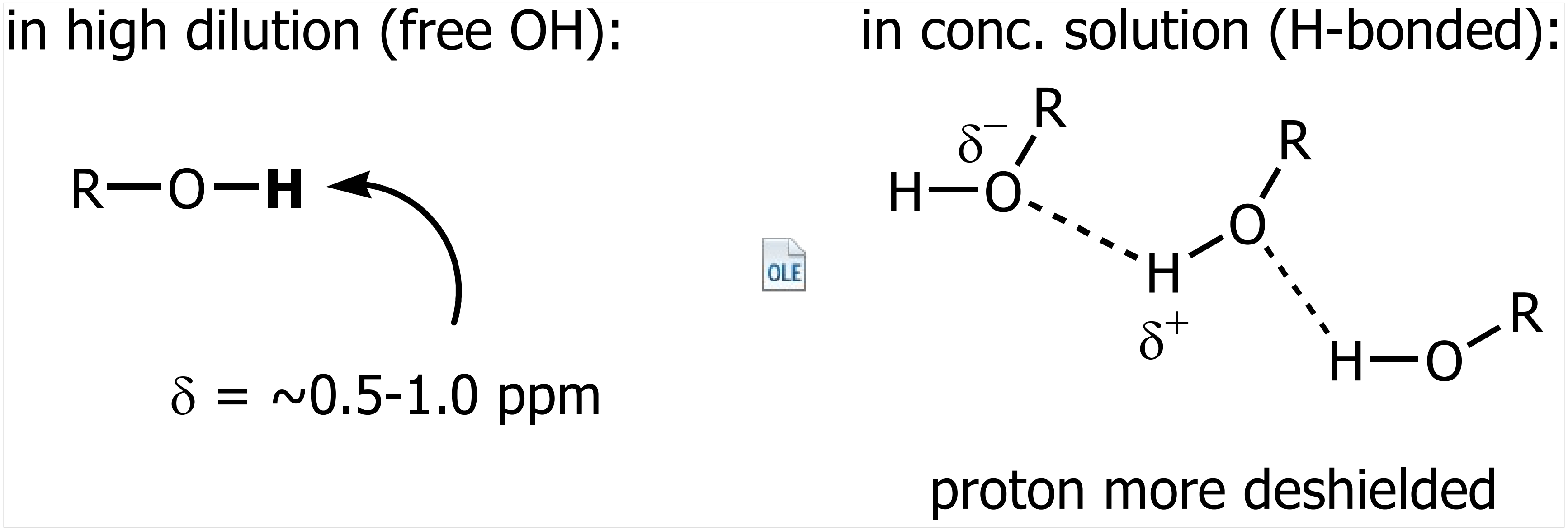


❖ The 300 MHz ^1H NMR spectrum of 1-nitropropane



10. Proton NMR Spectra and Rate Processes

- Protons of alcohols (ROH) and amines may appear over a wide range from 0.5 – 5.0 ppm
  - Hydrogen-bonding is the reason for this range



in high dilution (free OH):

δ = ~0.5-1.0 ppm

in conc. solution (H-bonded):

proton more deshielded

- Why don’t we see coupling with the O–H proton, e.g. $–CH_2–OH$ (triplet?)
  - Because the acidic protons are exchangeable about 10^5 protons per second (residence time 10^{-5} sec), but the NMR experiment requires a time of 10^{-2} – 10^{-3} sec. to “take” a spectrum, usually we just see an average (thus, OH protons are usually a broad singlet)

Trick:

- Run NMR in d_6-DMSO where H-bonding with DMSO’s oxygen prevents H’s from exchanging and we may be able to see the coupling

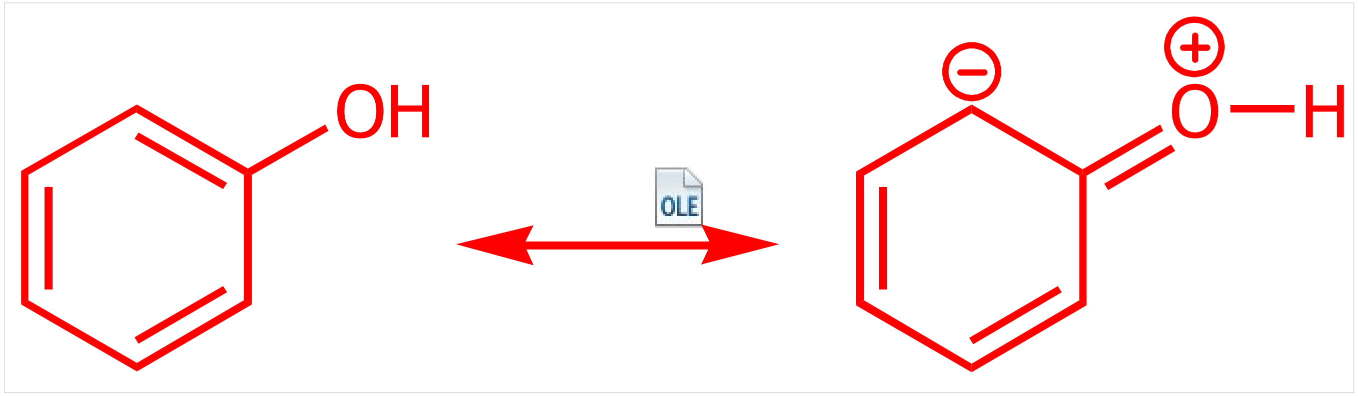
❖ Deuterium Exchange

- To determine which signal in the NMR spectrum is the OH proton, shake the NMR sample with a drop of D_2O and whichever peak disappears that is the OH peak (note: a new peak of HOD appears)

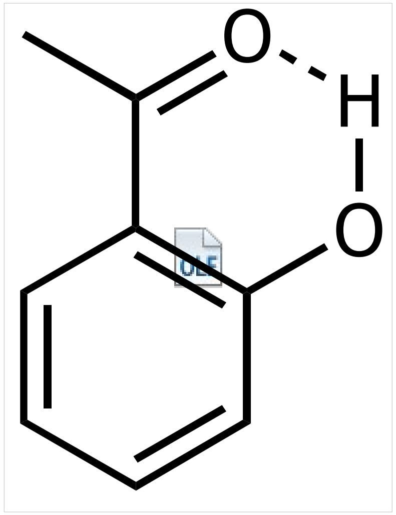
$$R\text{—}O\text{—}H \xrightarrow{D_2O} R\text{—}O\text{—}D \quad + \quad HOD$$

❖ Phenols

- Phenol protons appear downfield at 4-7 ppm
- They are more "acidic" - more H^+ character
- More dilute solutions - peak appears upfield: towards 4 ppm



- Phenols
  - Intramolecular H-bonding causes downfield shift



12.1 ppm

11. Carbon-13 NMR Spectroscopy

11A. Interpretation of ^{13}C NMR Spectra

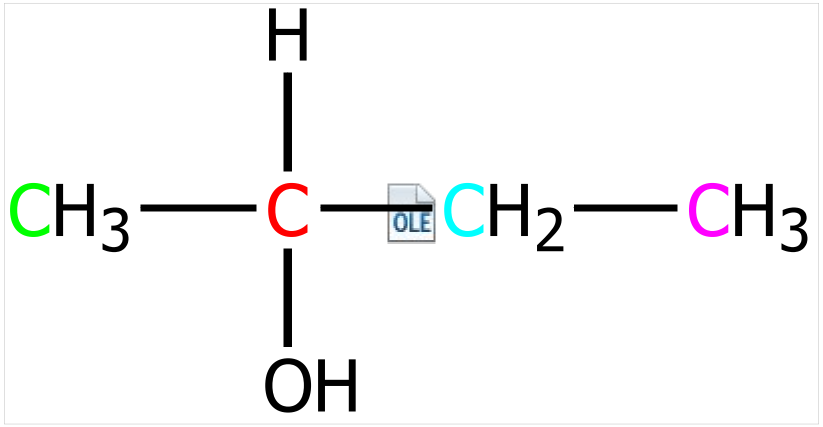
- Unlike ^{1}H with natural abundance ~99.98%, only 1.1% of carbon, namely ^{13}C, is NMR active

. One Peak for Each Magnetically Distinct Carbon Atom

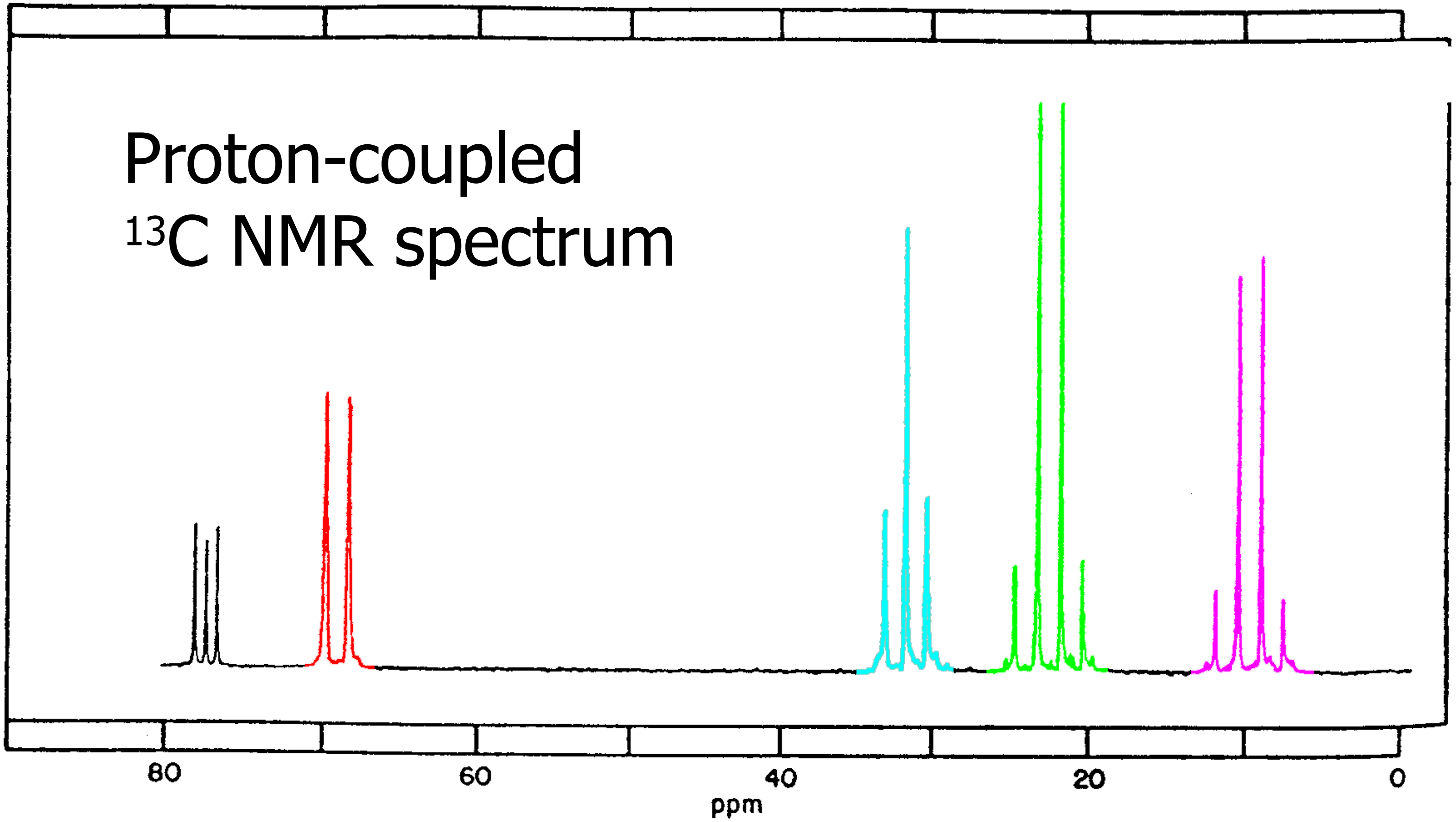
- ^{13}C NMR spectra have only become commonplace more recently with the introduction of the Fourier Transform (FT) technique, where averaging of many scans is possible (note ^{13}C spectra are 6000 times weaker than ^{1}H spectra, thus require a lot more scans for a good spectrum)

- Note for a 200 MHz NMR (field strength 4.70 Tesla)
  - ^{1}H NMR ⇒ Frequency = 200 MHz
  - ^{13}C NMR ⇒ Frequency = 50 MHz

- Example:
  - 2-Butanol

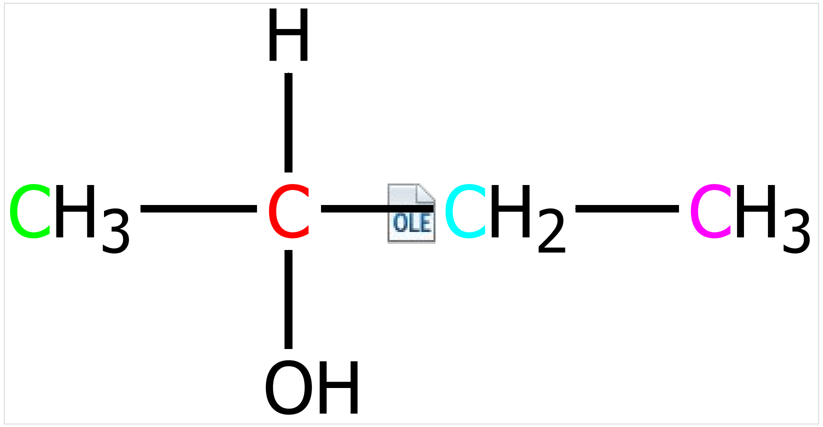


$$CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-CH_3$$

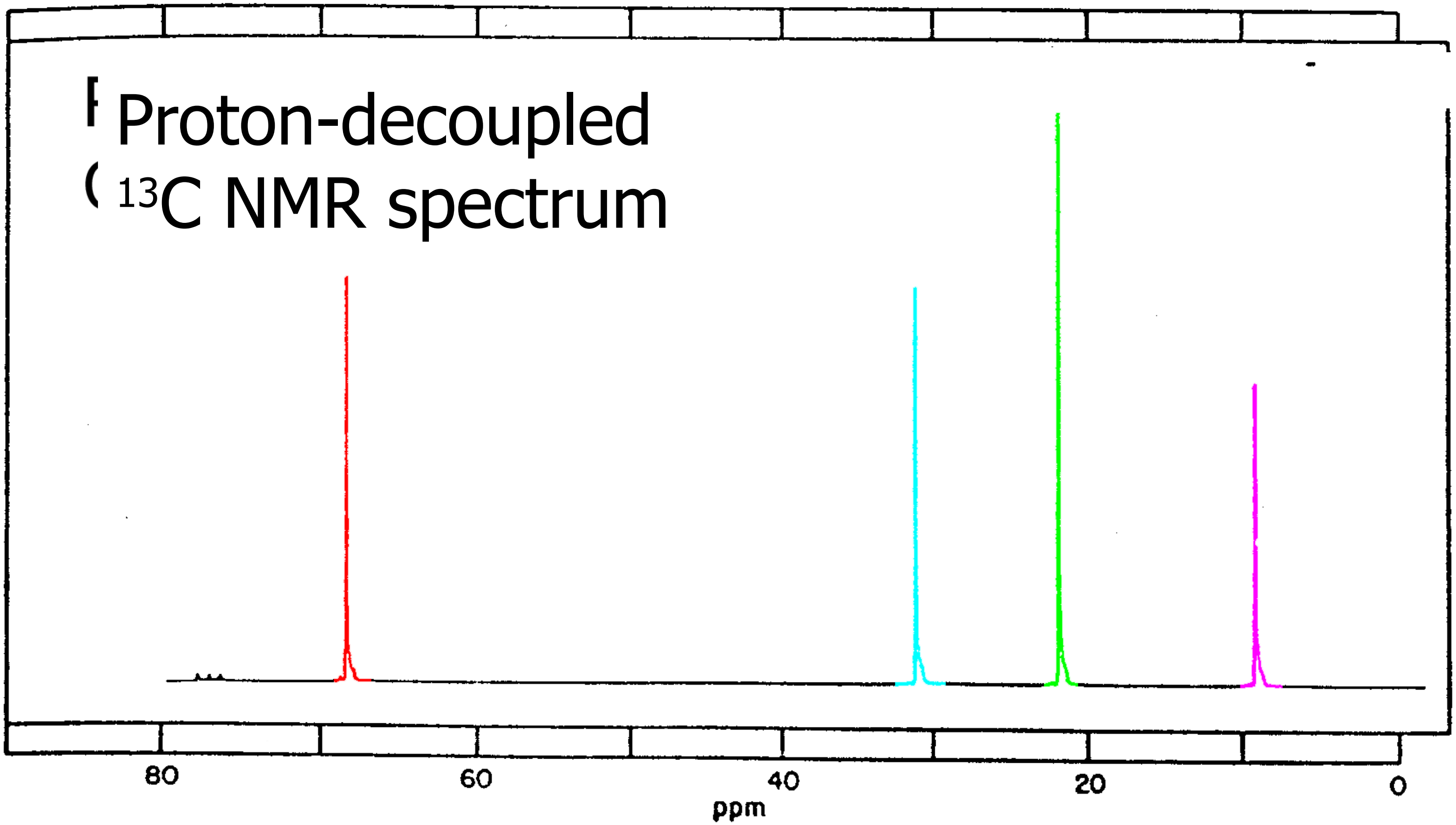


Proton-coupled
^{13}C NMR spectrum

- Example:
  - 2-Butanol



$$CH_3-\underset{OH}{\overset{H}{C}}-CH_2-CH_3$$



Proton-decoupled ^{13}C NMR spectrum

11C. ^{13}C Chemical Shifts

- Decreased electron density around an atom **deshields** the atom from the magnetic field and causes its signal to occur further **downfield** (higher ppm, to the left) in the NMR spectrum
- Relatively higher electron density around an atom **shields** the atom from the magnetic field and causes the signal to occur **upfield** (lower ppm, to the right) in the NMR spectrum

- Factors affecting chemical shift
  1. Diamagnetic shielding due to bonding electrons
  2. Paramagnetic shielding due to low-lying electronic excited state
  3. Magnetic Anisotropy – through space due to the near-by group (especially π electrons)

In ^{1}H NMR, (i) and (iii) most significant; in ^{13}C NMR, (ii) most significant (since chemical shift range >> ^{1}H NMR)

- Electronegative substituents cause downfield shift

- Increase in relative atomic mass of substituent causes upfield shift

X	Electronegativity	Atomic Mass	^{13}C NMR: **C**H_3X
Cl	2.8	35.5	23.9 ppm
Br	2.7	79.9	9.0 ppm
I	2.2	126.9	-21.7 ppm

Hybridization of carbon

- $sp^2 > sp > sp^3$

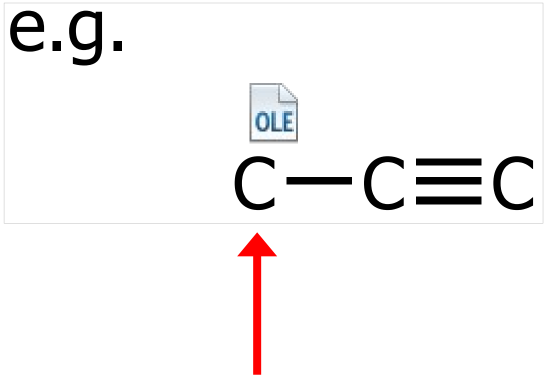
e.g.

$H_2C{=}CH_2$ $HC{\equiv}CH$ $H_3C{-}CH_3$

123.3 ppm 71.9 ppm 5.7 ppm

❖ Anisotropy effect

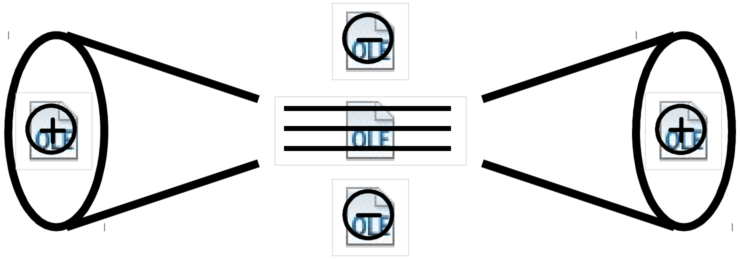
- Shows shifts similar to the effect in ^{1}H NMR



e.g.

$C-C\equiv C$

shows large upfield shift



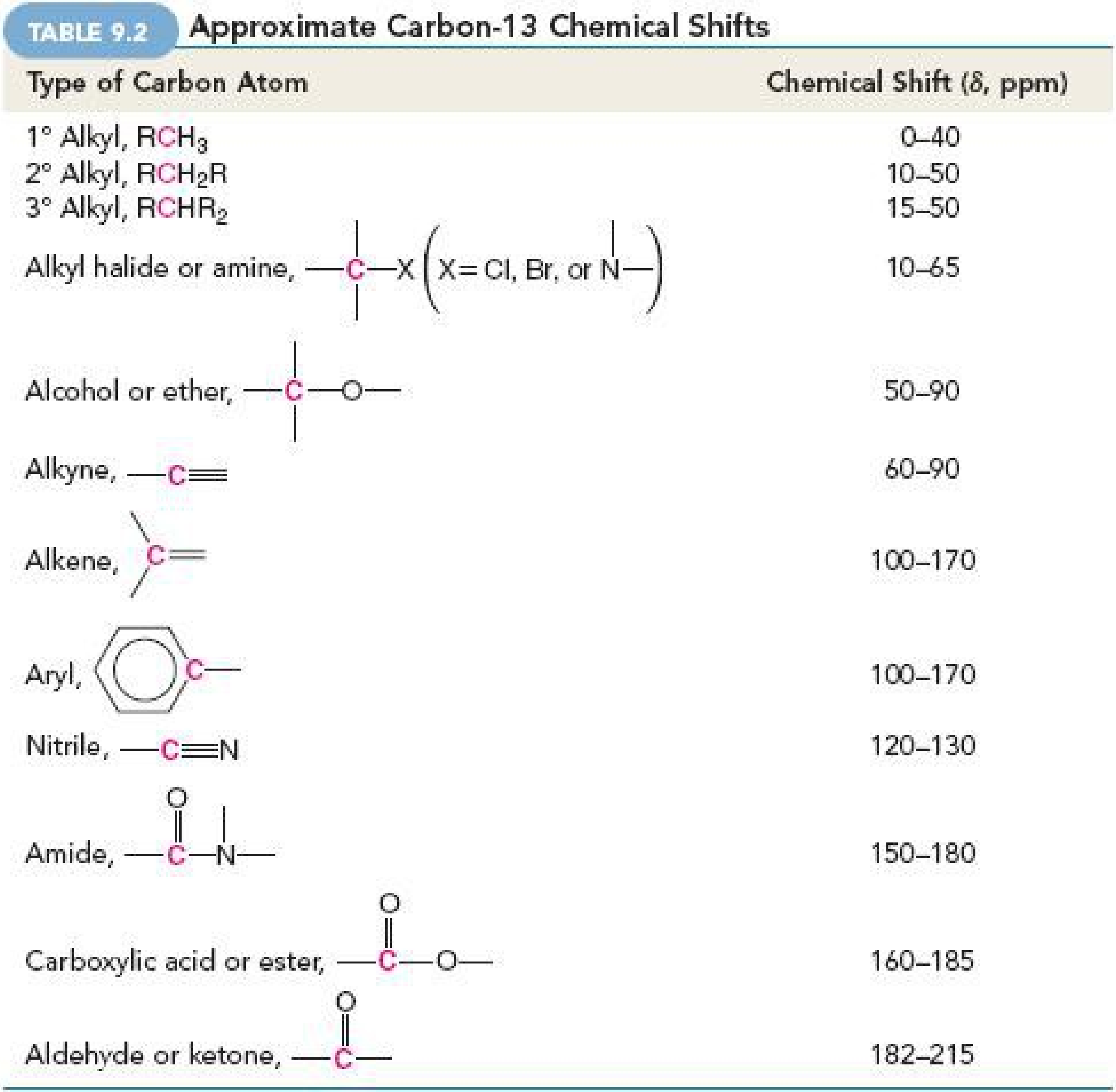
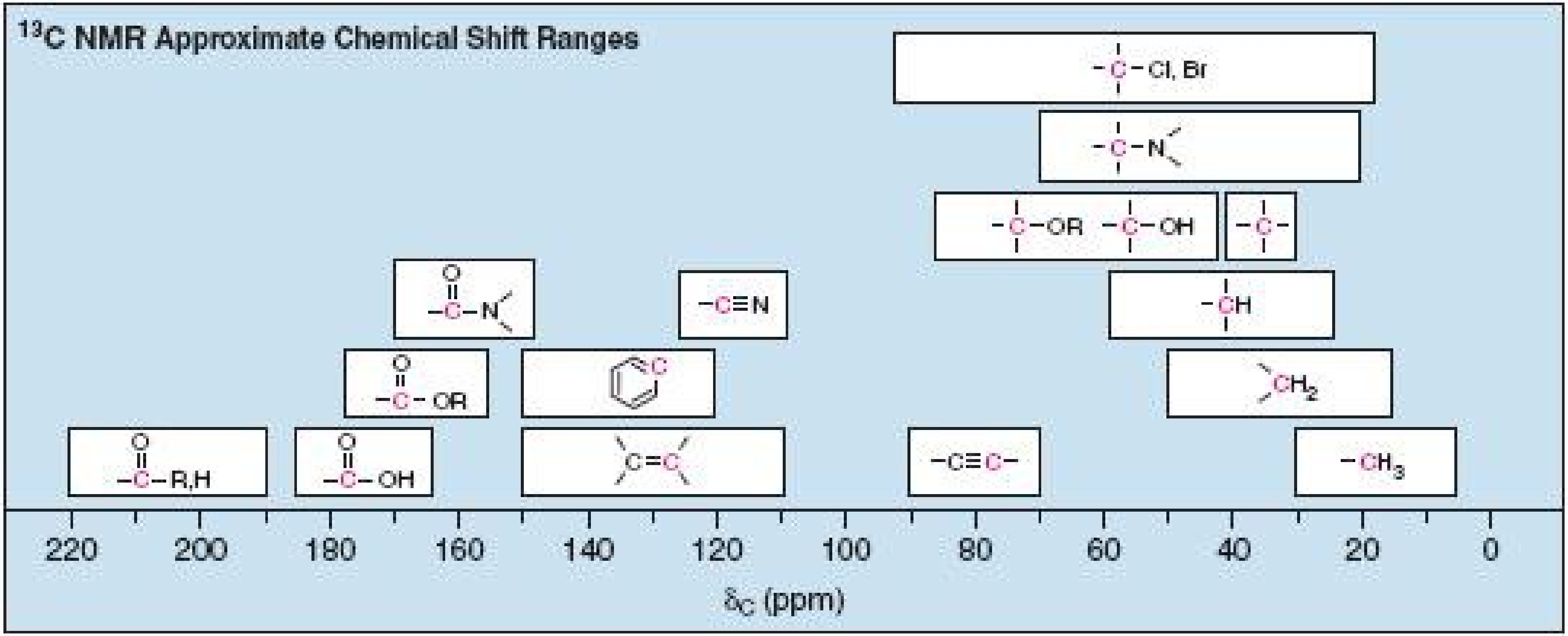
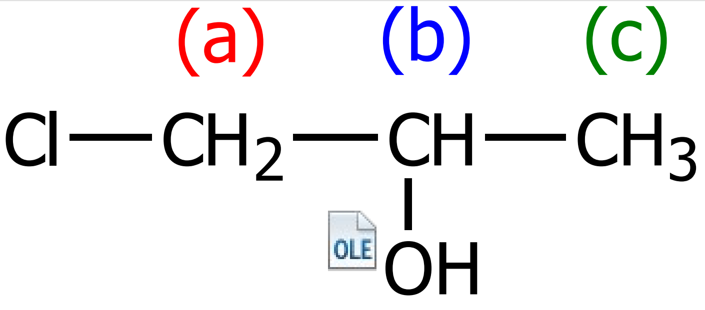


TABLE 9.2 Approximate Carbon-13 Chemical Shifts

Type of Carbon Atom	Chemical Shift (δ, ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, —C—X (X = Cl, Br, or N—)	10–65
Alcohol or ether, —C—O—	50–90
Alkyne, —C≡	60–90
Alkene, C=	100–170
Aryl, C—	100–170
Nitrile, —C≡N	120–130
Amide, —C(=O)—N—	150–180
Carboxylic acid or ester, —C(=O)—O—	160–185
Aldehyde or ketone, —C(=O)—	182–215


13C NMR Approximate Chemical Shift Ranges
–C–Cl, Br
–C–N
–C–OR
–C–OH
–C–
–CH
CH2
–CH3
–C≡N
–C≡C–
C=C
O ‖ –C–N
O ‖ –C–OR
O ‖ –C–R,H
O ‖ –C–OH
220
200
180
160
140
120
100
80
60
40
20
0
δC (ppm)



$$\mathrm{Cl-\overset{(a)}{CH_2}-\underset{OH}{\overset{(b)}{CH}}-\overset{(c)}{CH_3}}$$

1-Chloro-2-propanol