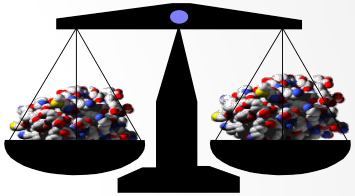
Mass Spectrometry

The main use of Mass in organic chemistry is:

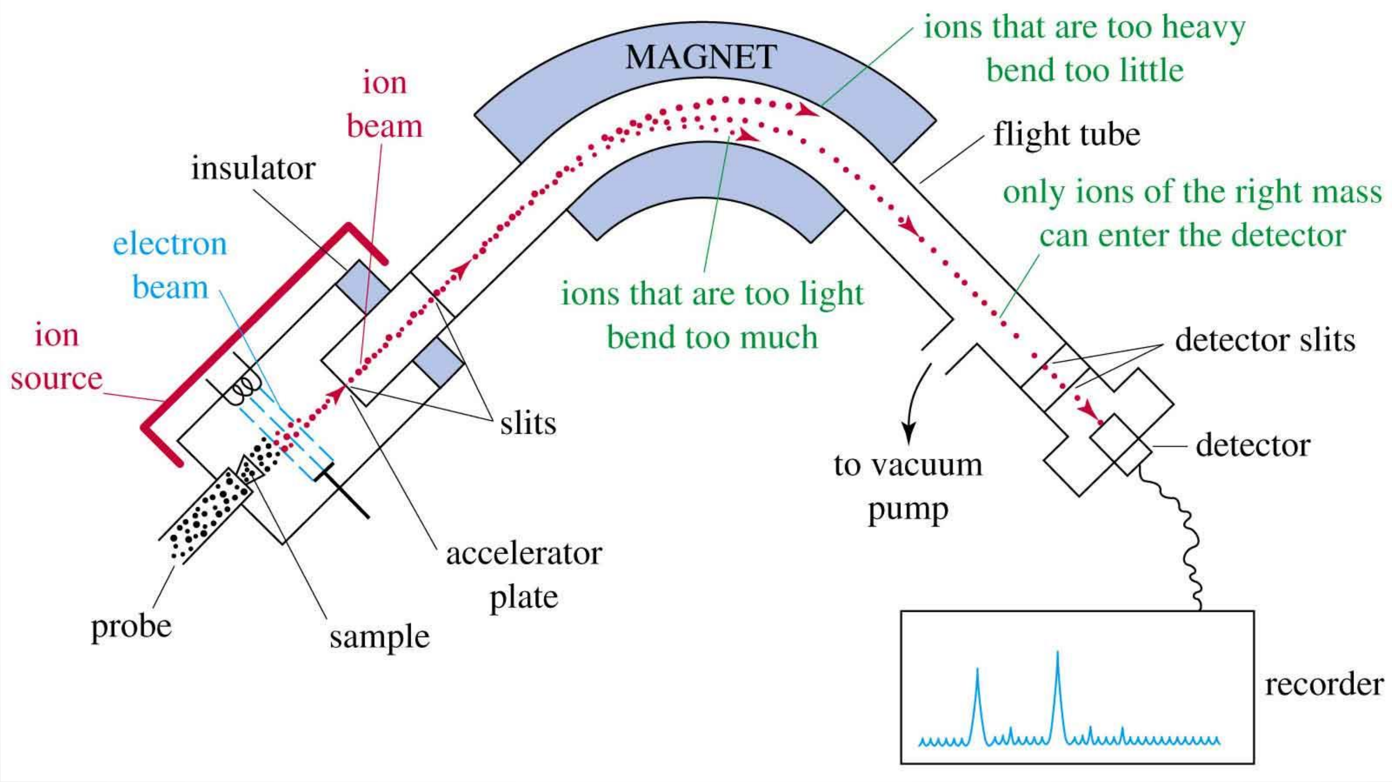


- Determine the Molecular Mass of organic compounds.
- Determine the Molecular Formula of organic compounds.
- Sometime identified the functional groups in organic compounds.

Mass Spectrometer

- Sample Inlet system
- Ionization Chamber
- Mass Analyzer
- Detector

$$M \xrightarrow{e^{\cdot}} M^{\dot{+}}$$



Mass Spectrum

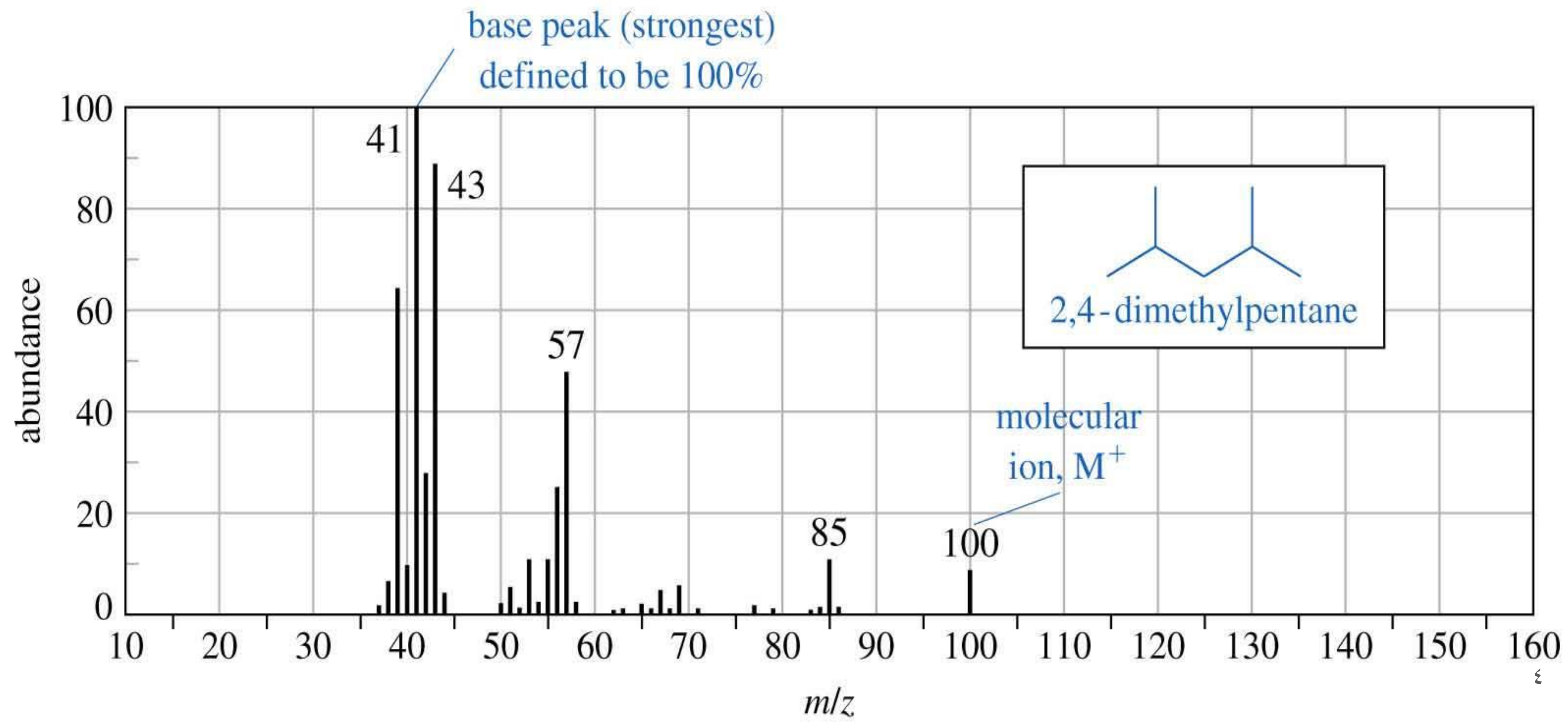
There are three kinds each of which we will consider each of these separately:

- Molecular ion
- Fragments
- Natural abundance of isotopes

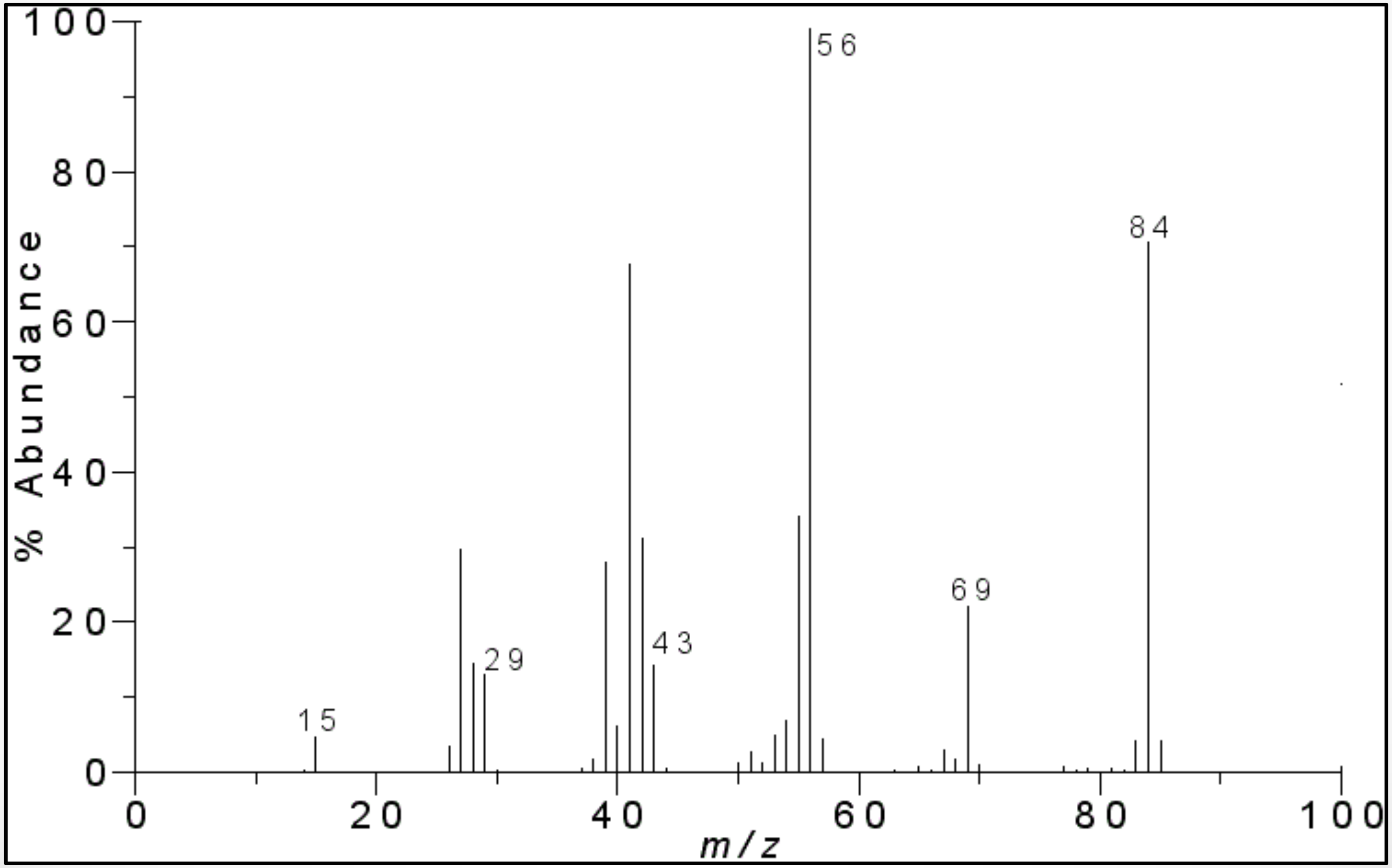
Molecular ion

$$M \xrightarrow{e^{\cdot}} M^{+\cdot}$$

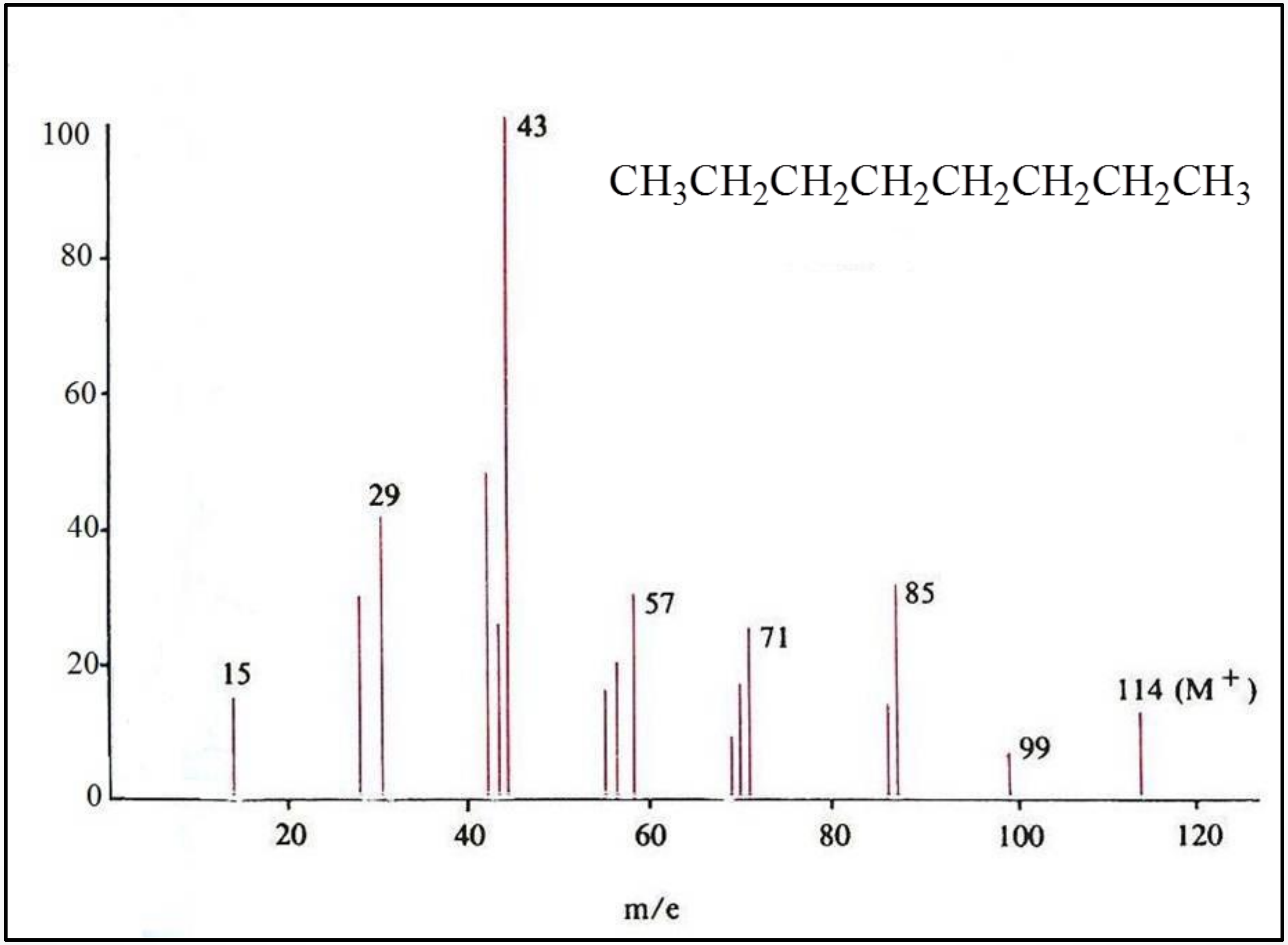
Separate the Ions according to their
Mass-to-Charge ratios (m/e)



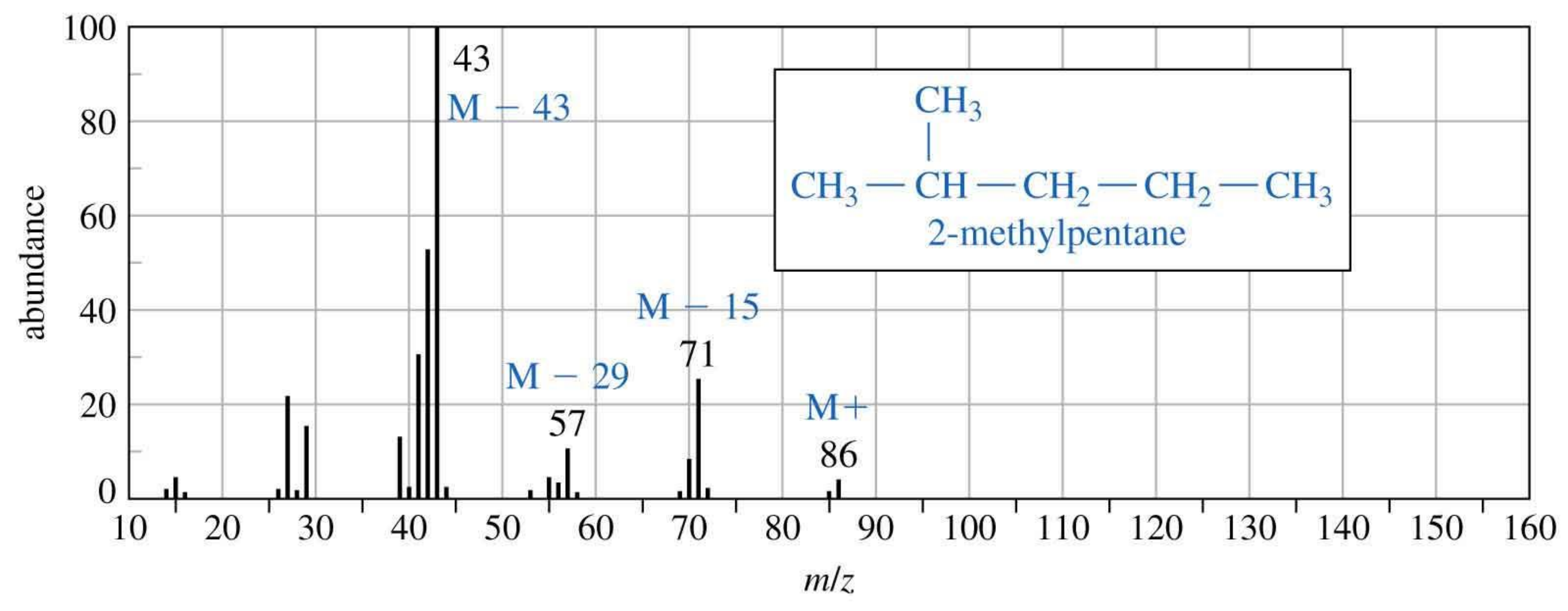
Cyclohexane



n-Octane


100
80
60
40
20
0
43
29
15
57
71
85
99
114 (M$^+$)
20
40
60
80
100
120
m/e
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

2-Methylpentane



Isotopic Abundance

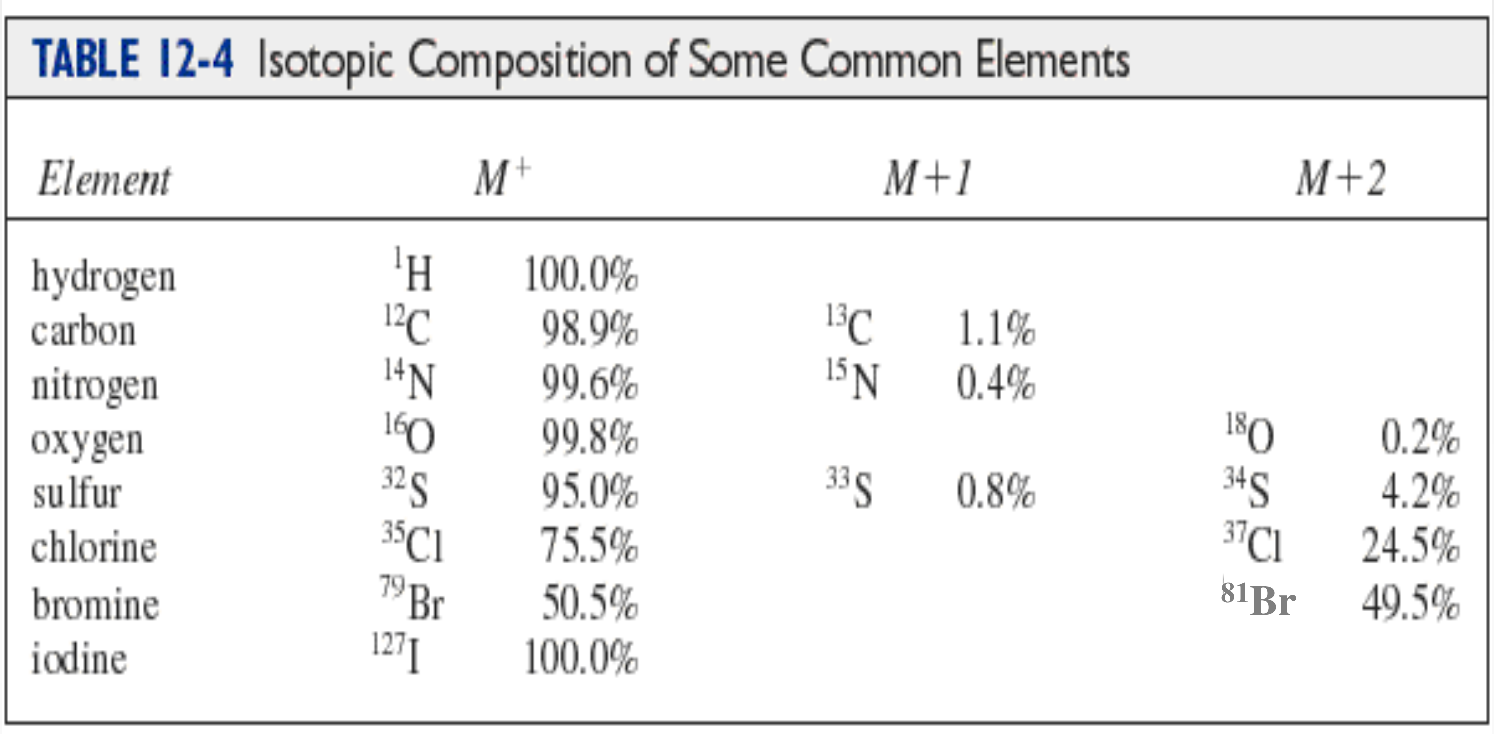
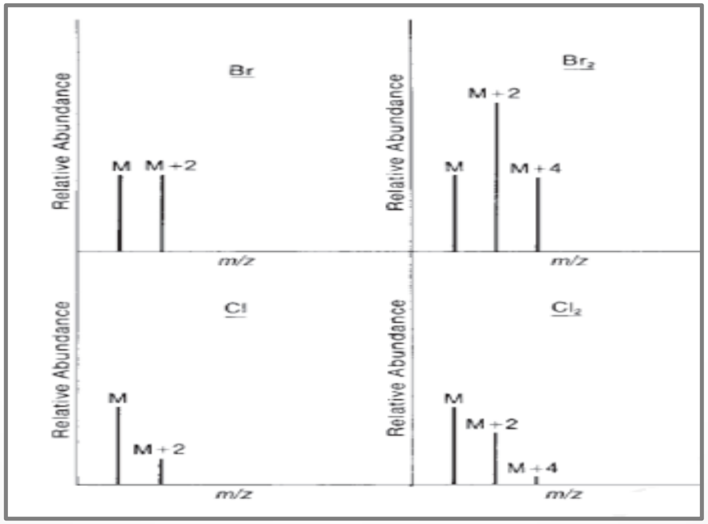
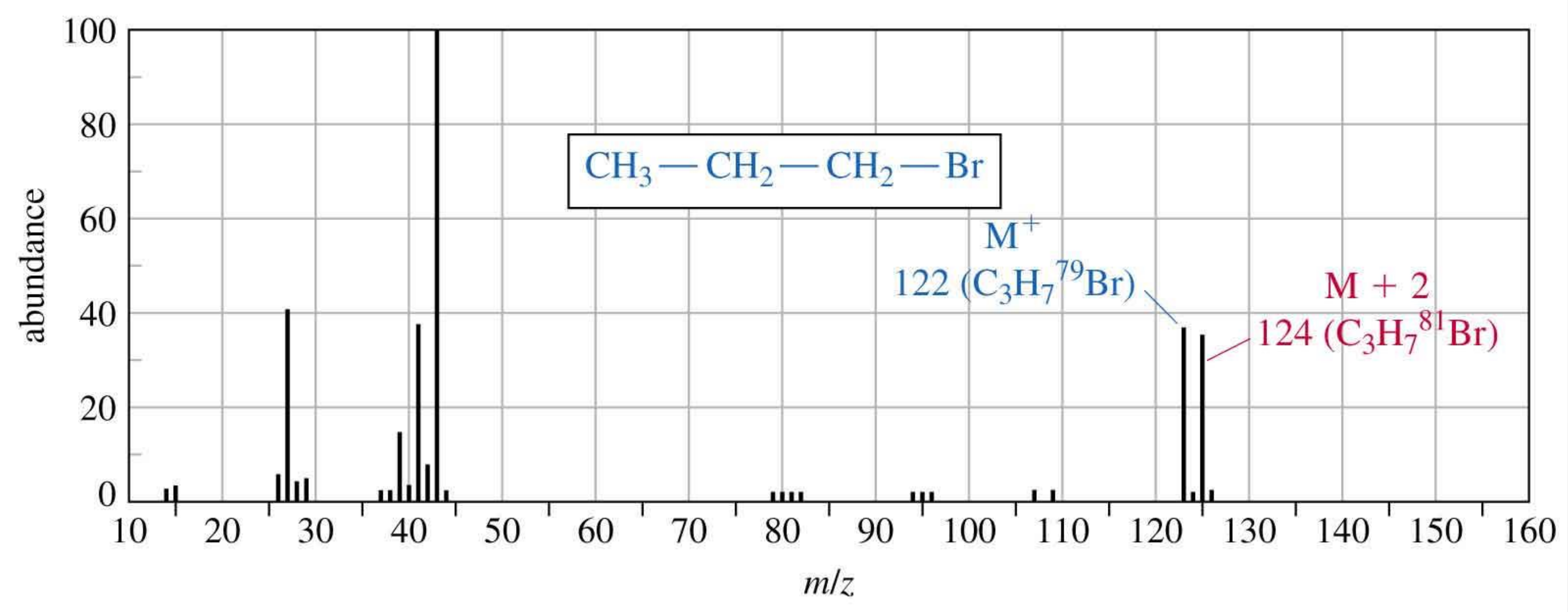


TABLE 12-4 Isotopic Composition of Some Common Elements

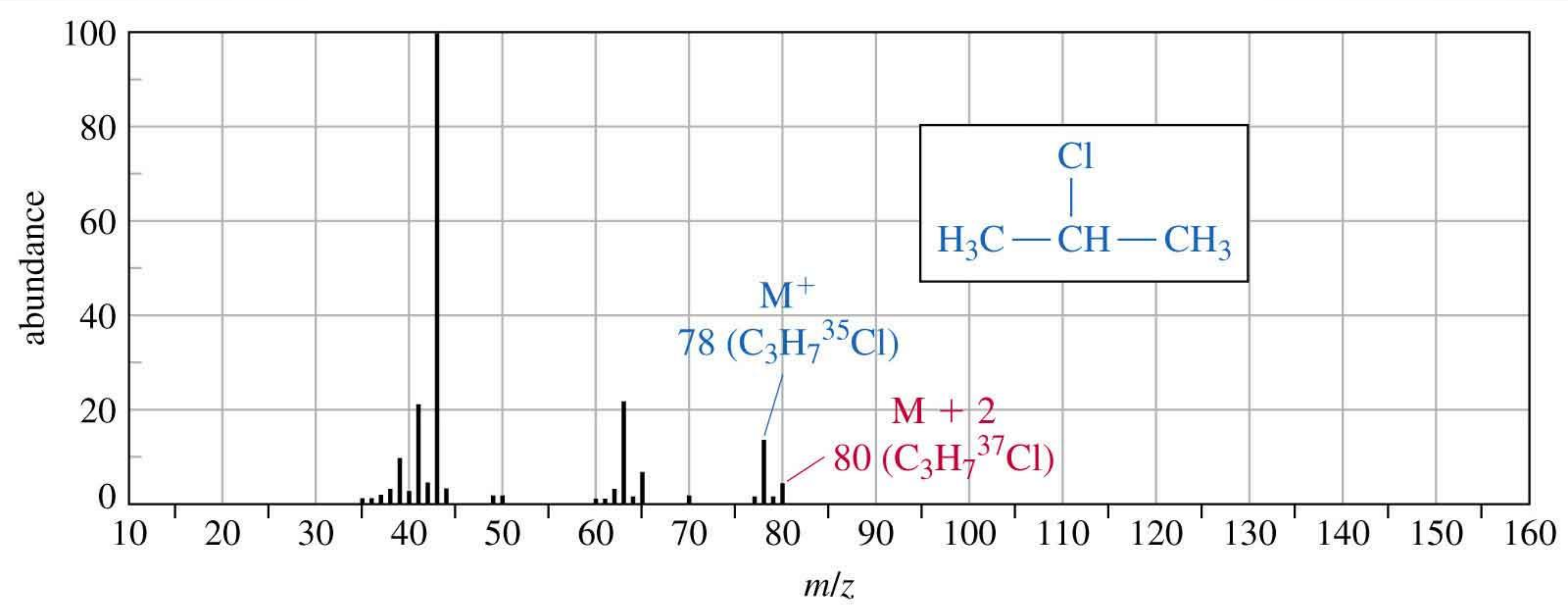
Element	*M*⁺		*M+1*		*M+2*	
hydrogen	^{1}H	100.0%				
carbon	^{12}C	98.9%	^{13}C	1.1%		
nitrogen	^{14}N	99.6%	^{15}N	0.4%		
oxygen	^{16}O	99.8%			^{18}O	0.2%
sulfur	^{32}S	95.0%	^{33}S	0.8%	^{34}S	4.2%
chlorine	^{35}Cl	75.5%			^{37}Cl	24.5%
bromine	^{79}Br	50.5%			^{81}Br	49.5%
iodine	^{127}I	100.0%				



Mass Spectrum with Bromine



Mass Spectrum with Chlorine



طيف الكتلة للمركبات العضوية الشائعة

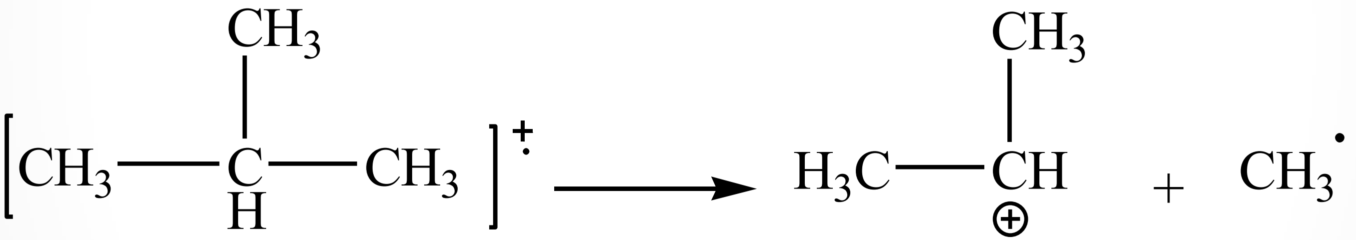
Hydrocarbons

$$[CH_3CH_2CH_2CH_2CH_3]^{+\cdot} \longrightarrow CH_3^{\cdot} + {}^{+}CH_2CH_2CH_3$$

m/e = 43

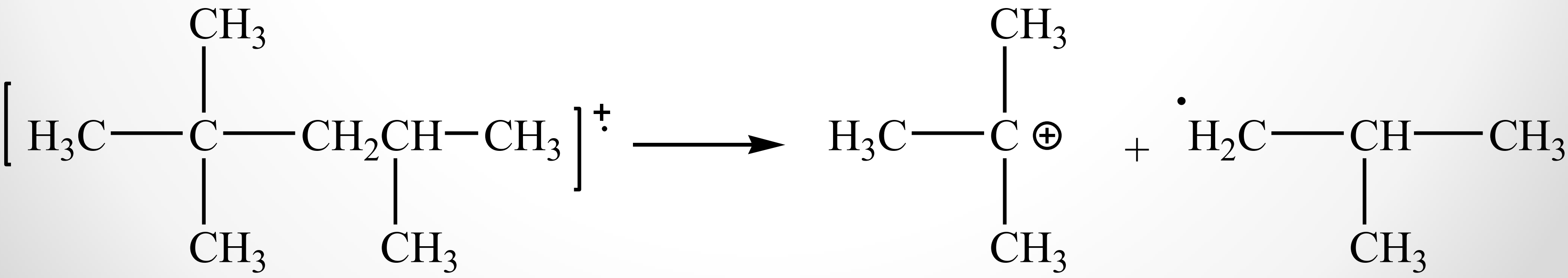
$$[CH_3CH_2CH_2CH_3]^{+\cdot} \longrightarrow CH_3CH_2^{\cdot} + {}^{+}CH_2CH_3$$

m/e = 29



$$[CH_3-CH(CH_3)-CH_3]^{+\cdot} \longrightarrow H_3C-\overset{\oplus}{C}H-CH_3 + CH_3^{\cdot}$$

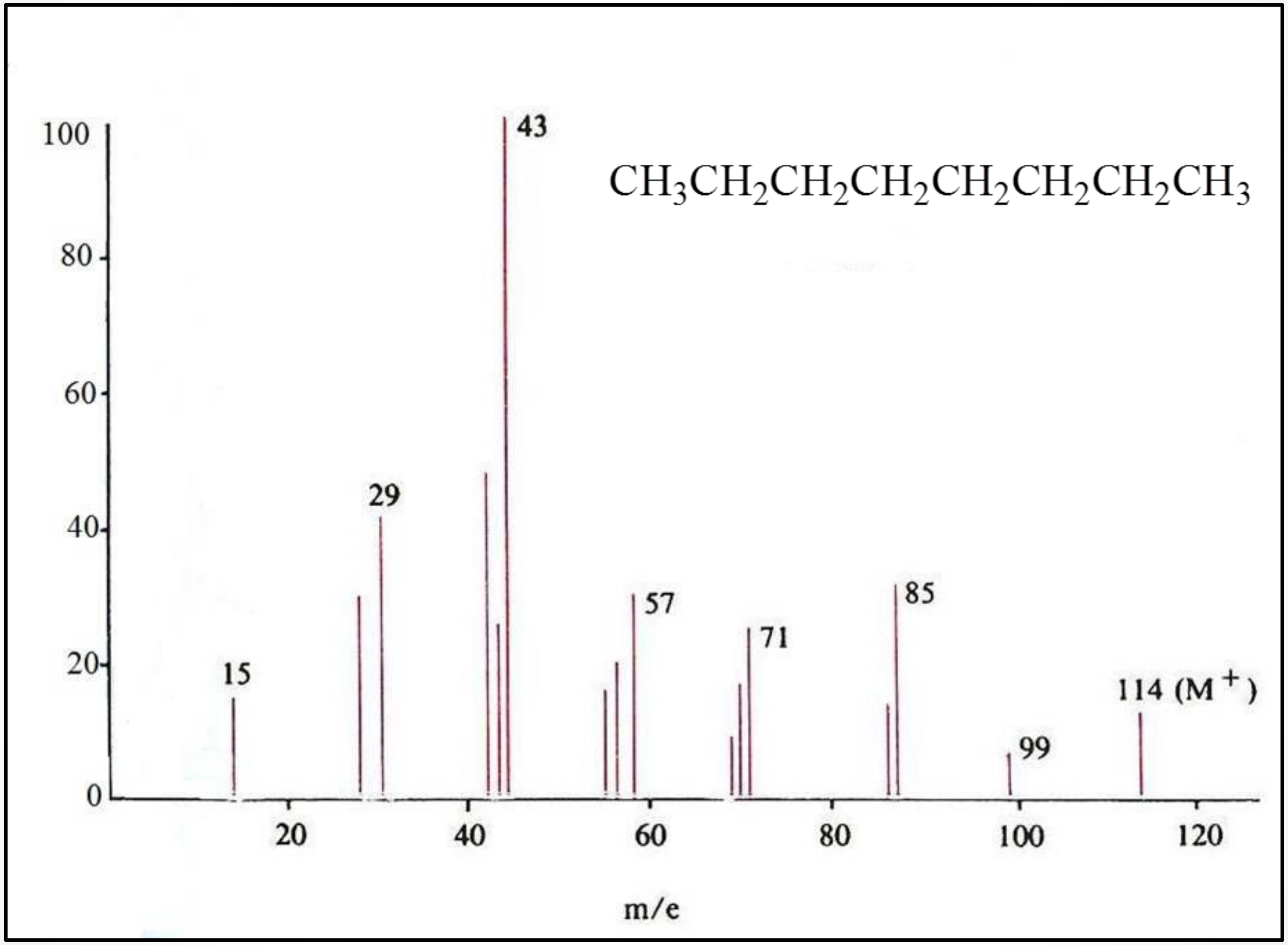
m/e = 43



$$[H_3C-C(CH_3)_2-CH_2CH(CH_3)-CH_3]^{+\cdot} \longrightarrow H_3C-C^{\oplus}(CH_3)_2 + {}^{\cdot}H_2C-CH(CH_3)-CH_3$$

m/e = 57

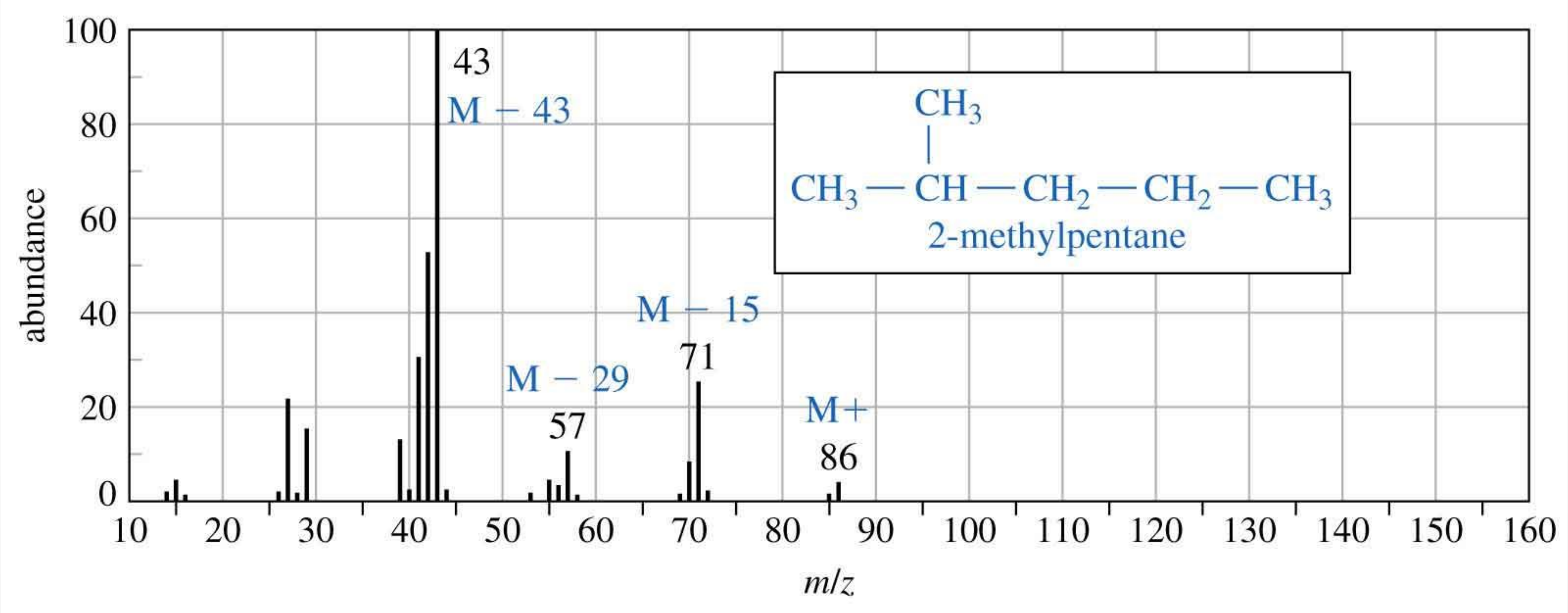
Mass Spectra of Alkanes



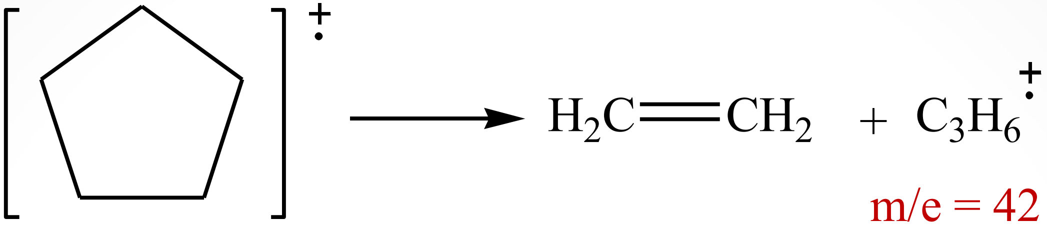
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Mass Spectra of Alkanes

More stable carbocations will be more abundant.

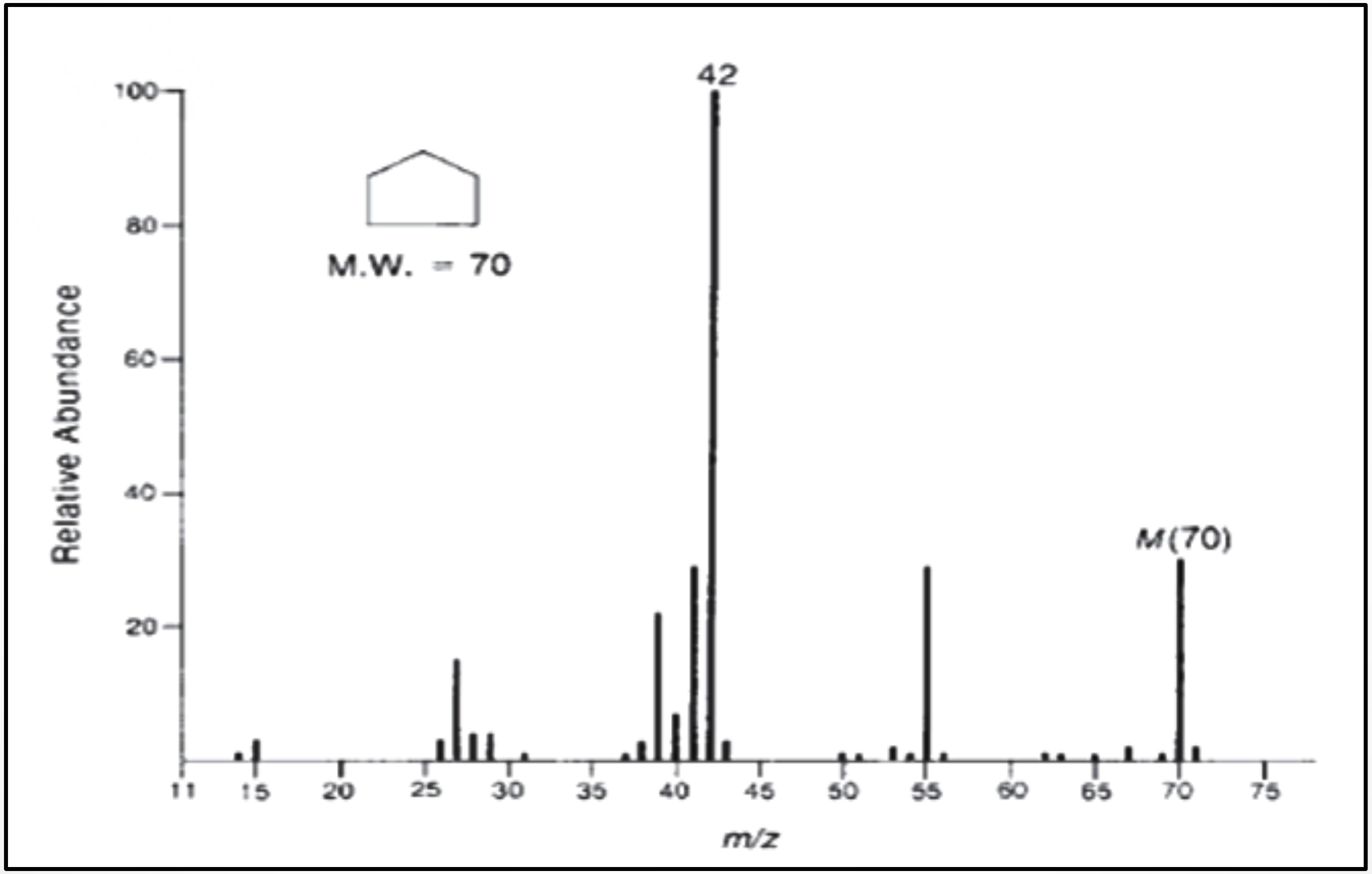


Cycloalkane

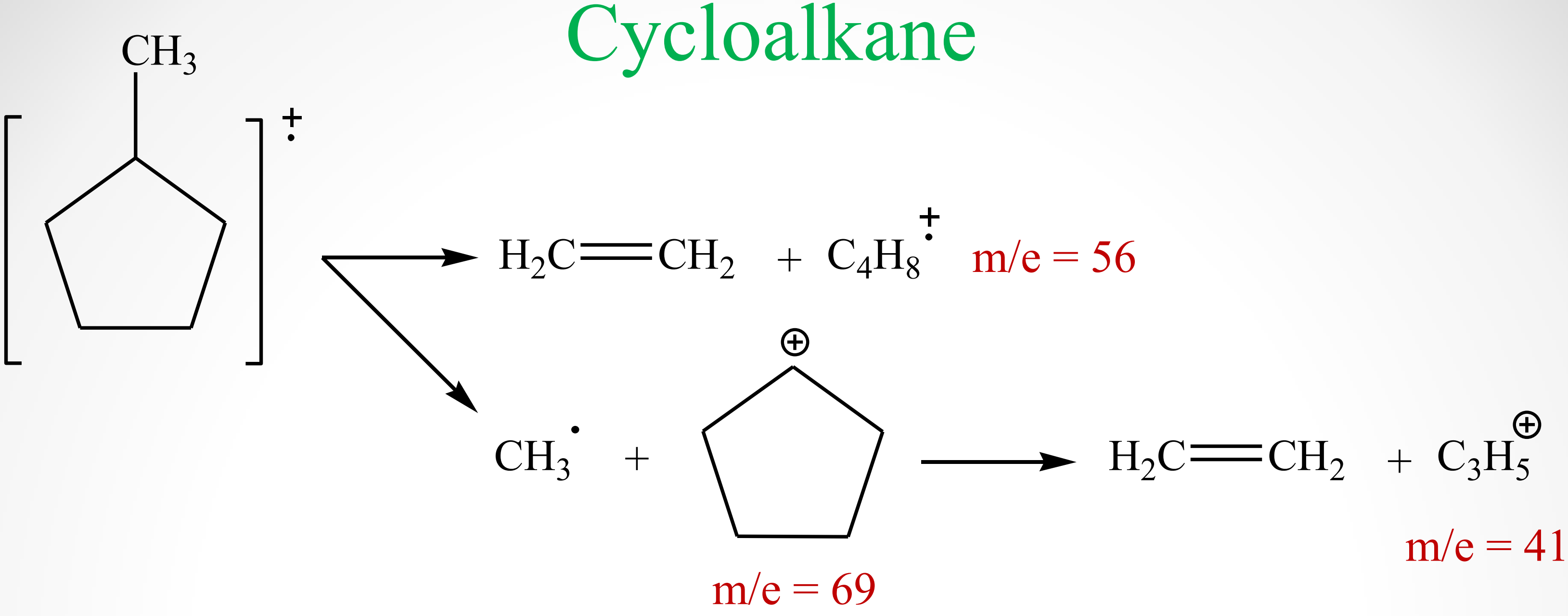


$$[C_5H_{10}]^{+\bullet} \longrightarrow H_2C{=}CH_2 + C_3H_6^{+\bullet}$$

m/e = 42



Cycloalkane



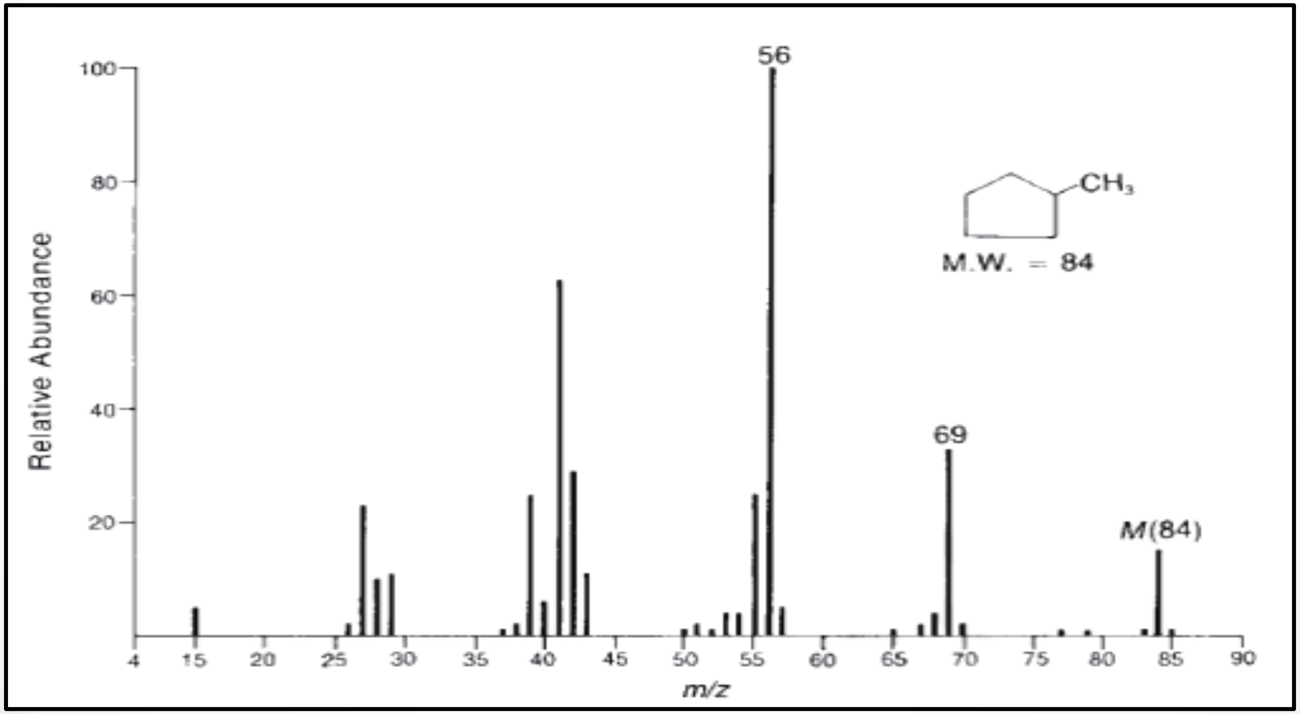
CH3

$H_2C{=}CH_2 + C_4H_8^{+\bullet}$ m/e = 56

$CH_3^{\bullet}$ + $\oplus$ $\longrightarrow$ $H_2C{=}CH_2 + C_3H_5^{\oplus}$

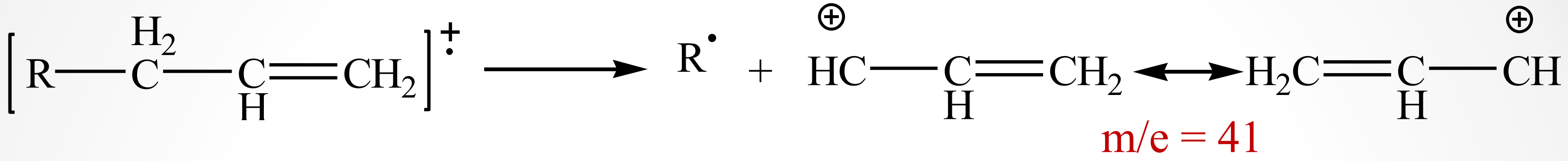
m/e = 69

m/e = 41



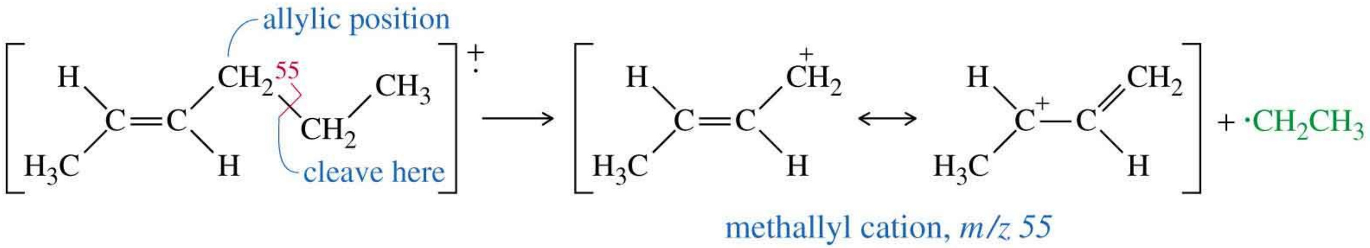
Alkene

allylic cleavage

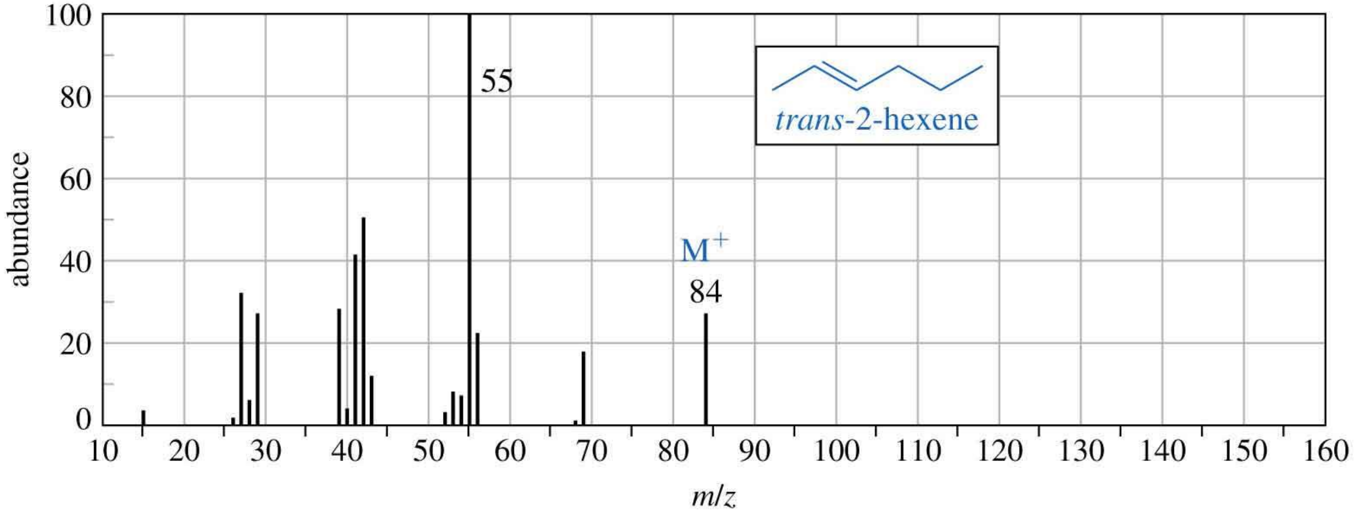


$$\left[R-\overset{H_2}{C}-\underset{H}{C}=CH_2\right]^{+\cdot} \longrightarrow R^{\cdot} + \overset{\oplus}{HC}-\underset{H}{C}=CH_2 \longleftrightarrow H_2C=\underset{H}{C}-\overset{\oplus}{CH}$$

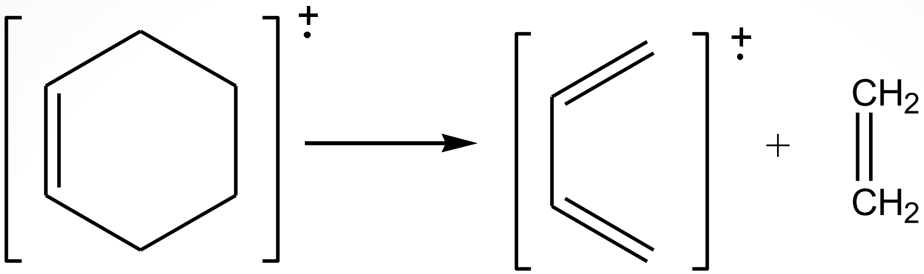
m/e = 41



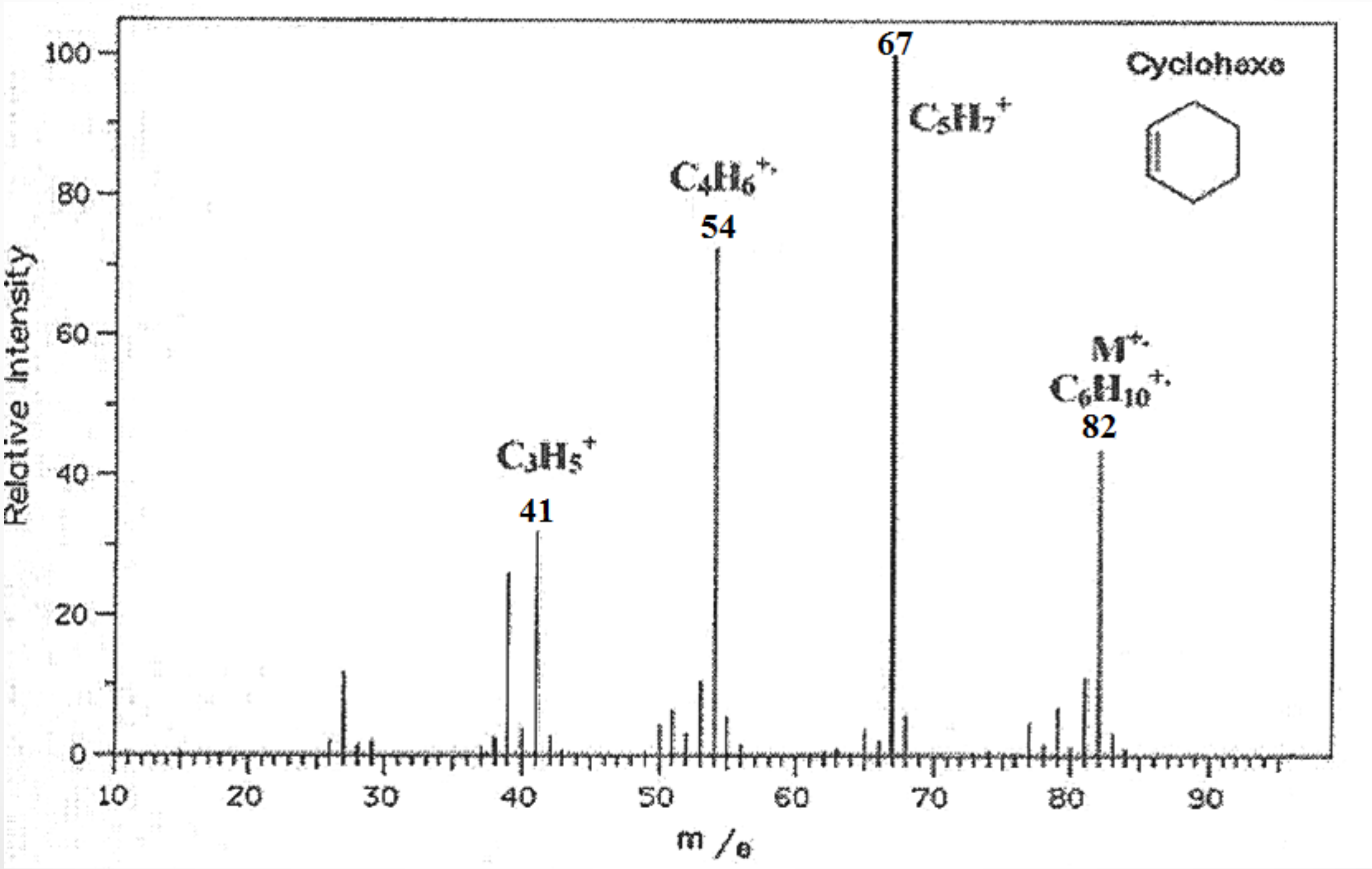
methallyl cation, *m/z* 55



Cycloalkene

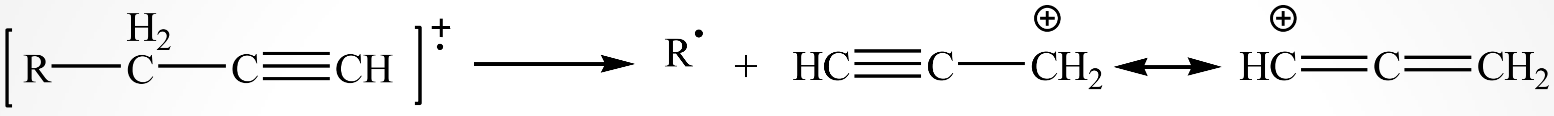


m/e = 54



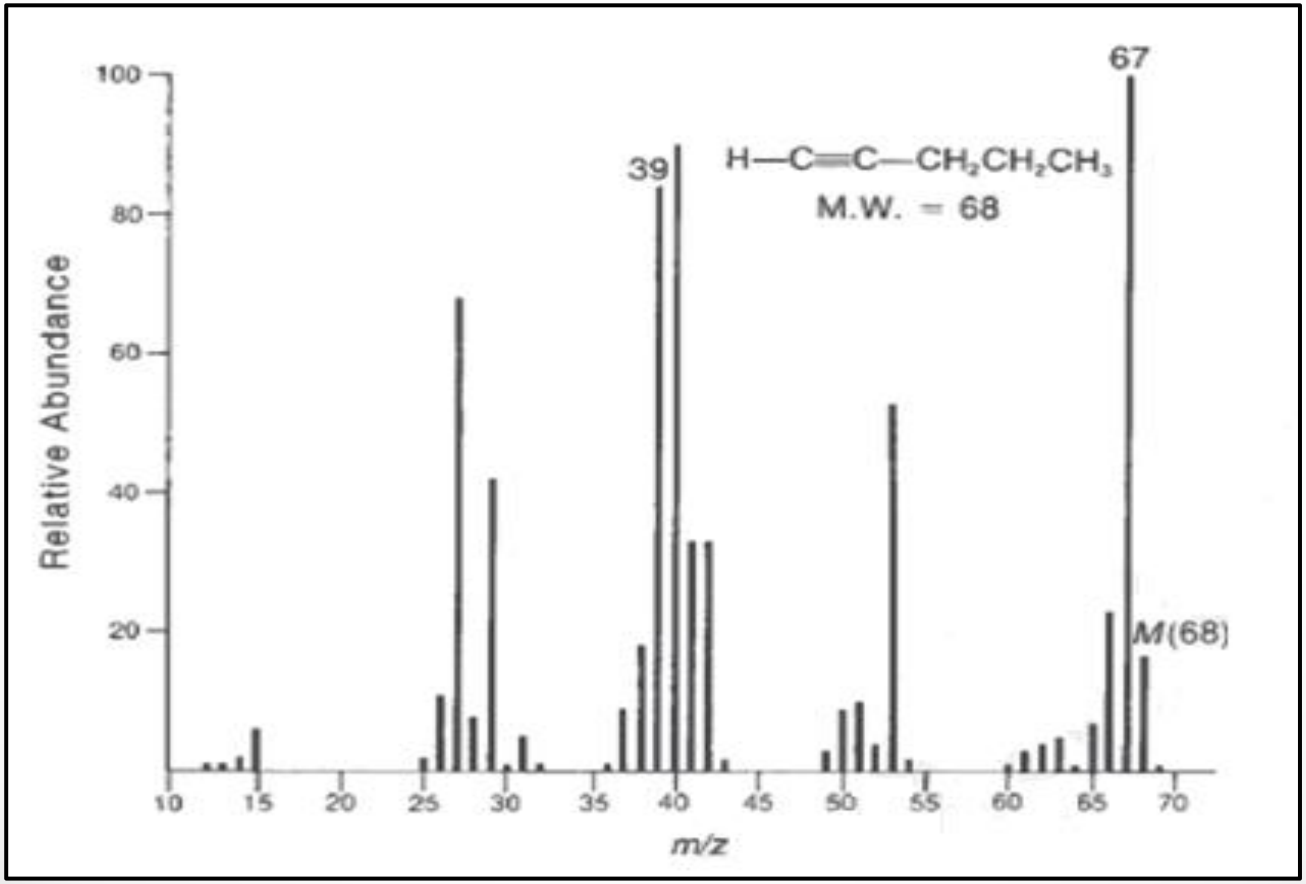
Alkyne

β- cleavage

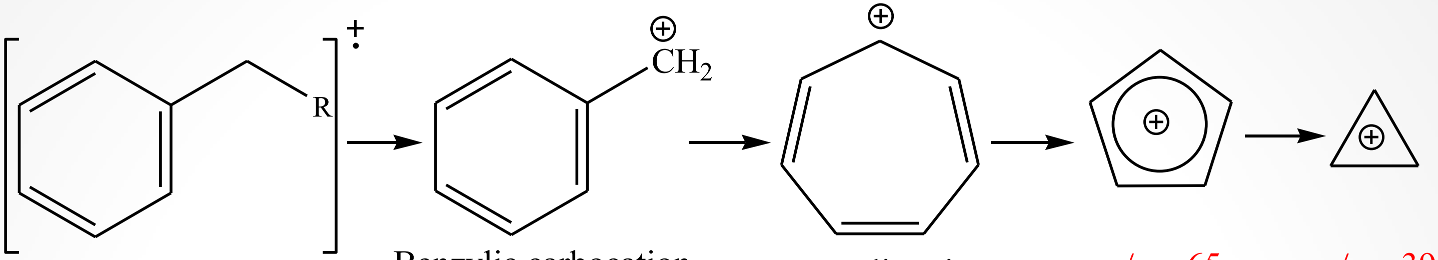


$$\left[R-\overset{H_2}{C}-C\equiv CH\right]^{+\bullet} \longrightarrow R^{\bullet} + HC\equiv C-\overset{\oplus}{C}H_2 \longleftrightarrow H\overset{\oplus}{C}=C=CH_2$$

m/e = 39



Aromatic Hydrocarbons



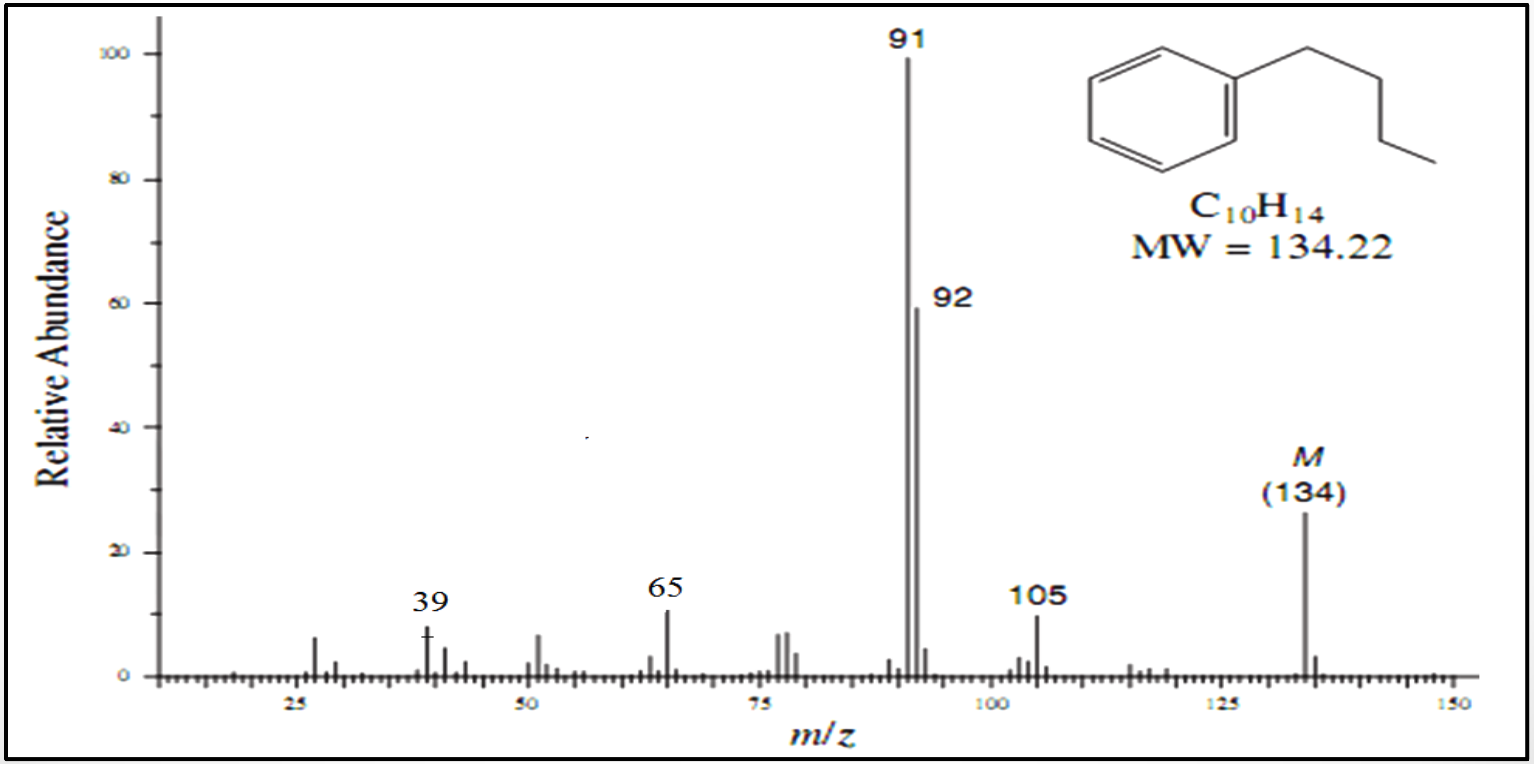
Benzylic carbocation

Tropylium ion

m/e = 65

m/e = 39

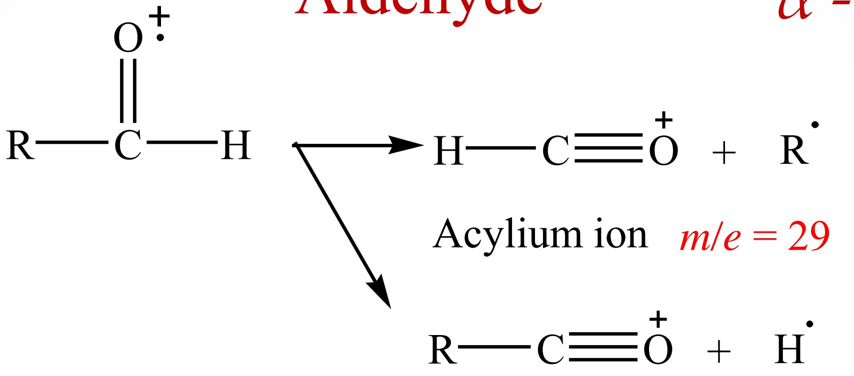
m/e = 91



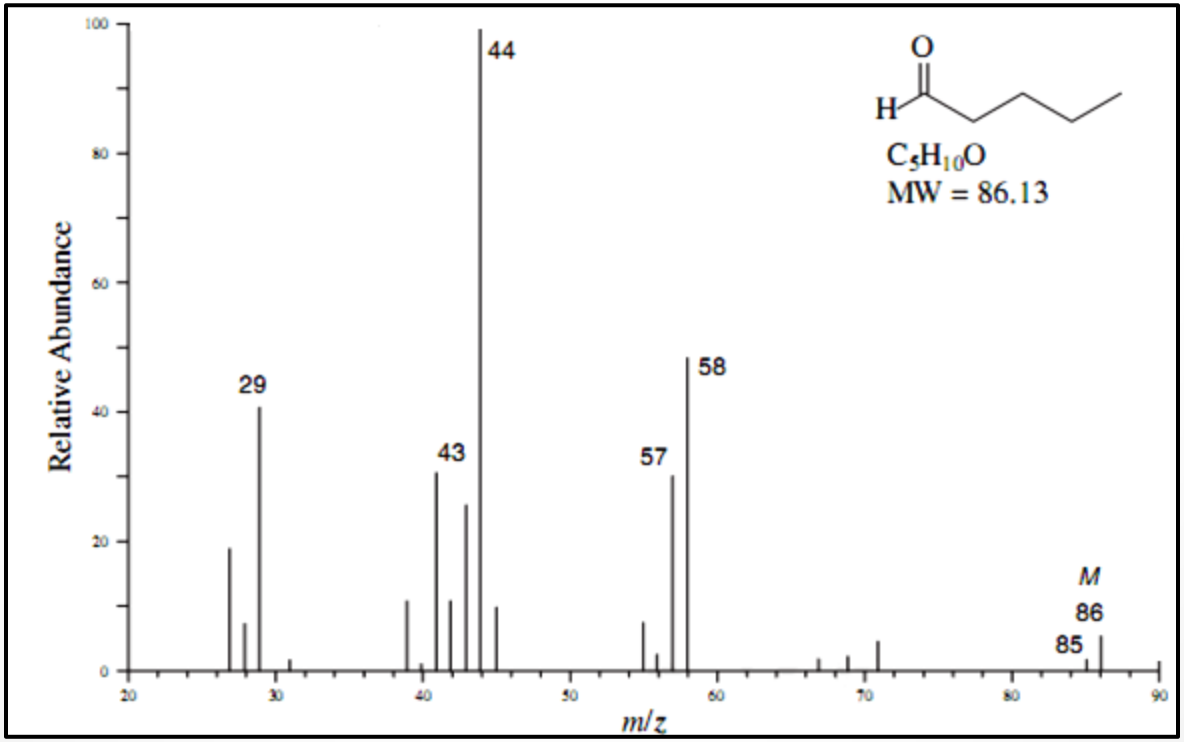
Aldehydes and Ketones

Aldehyde

α - cleavage

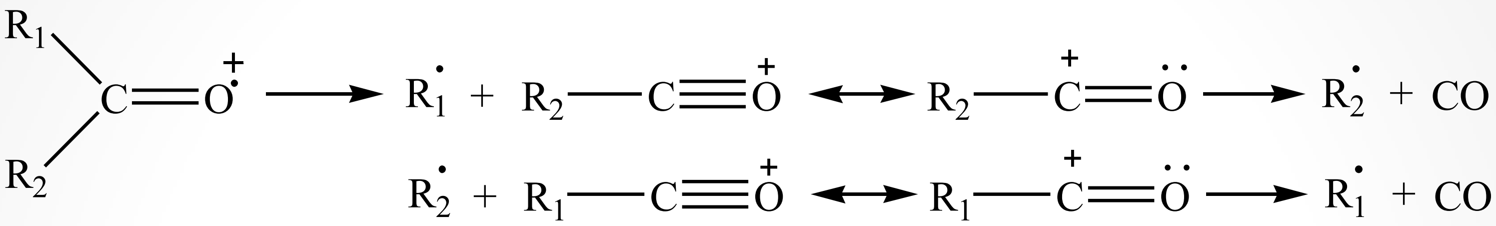


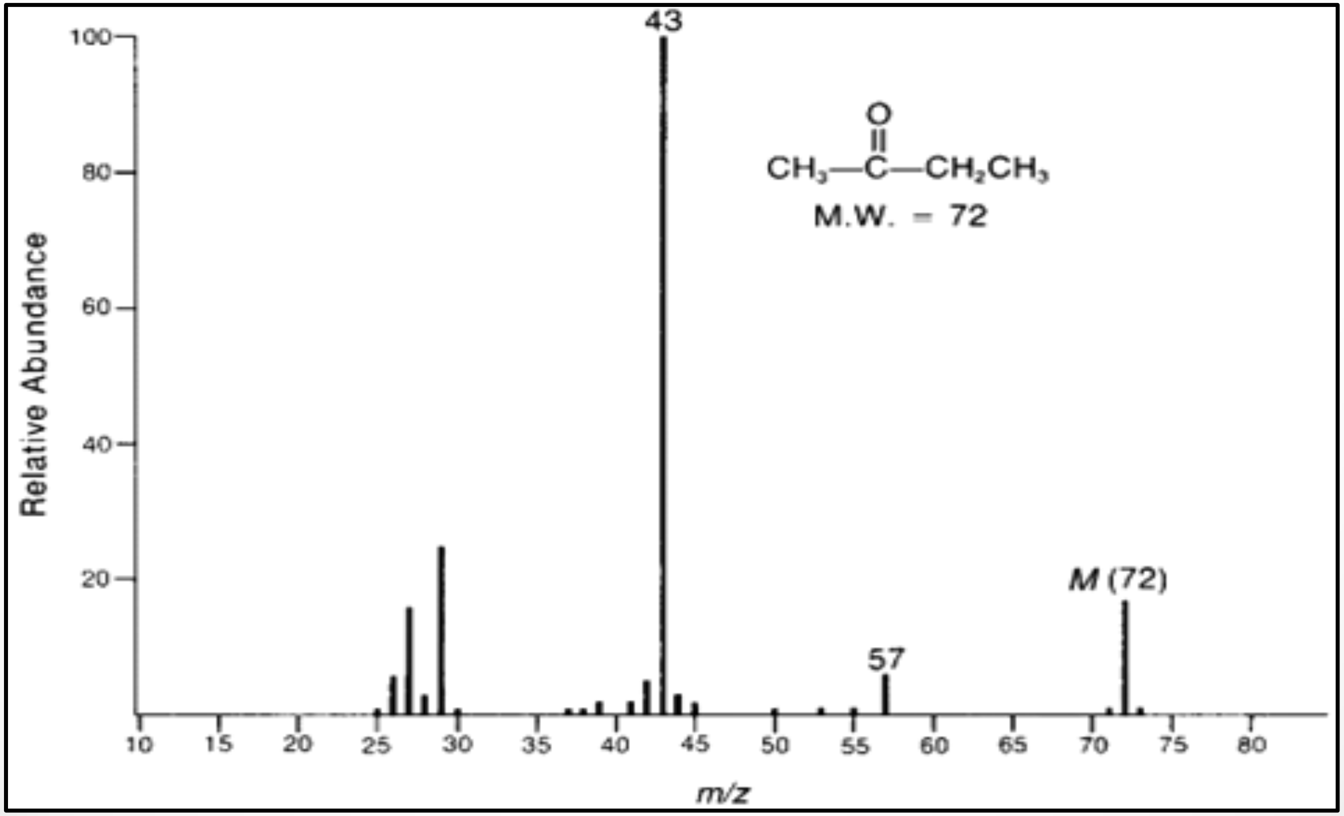
Acylium ion *m/e* = 29



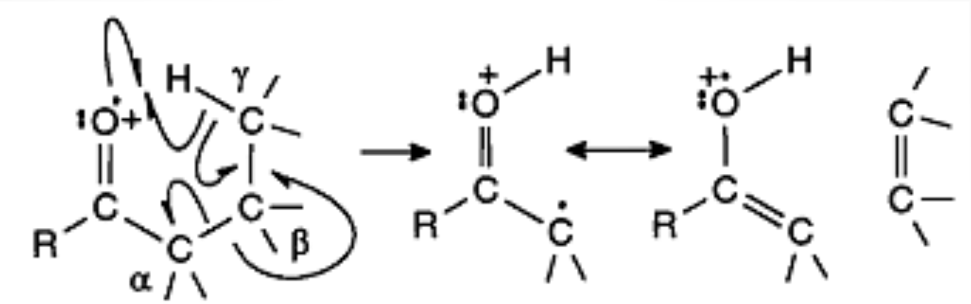
Ketone

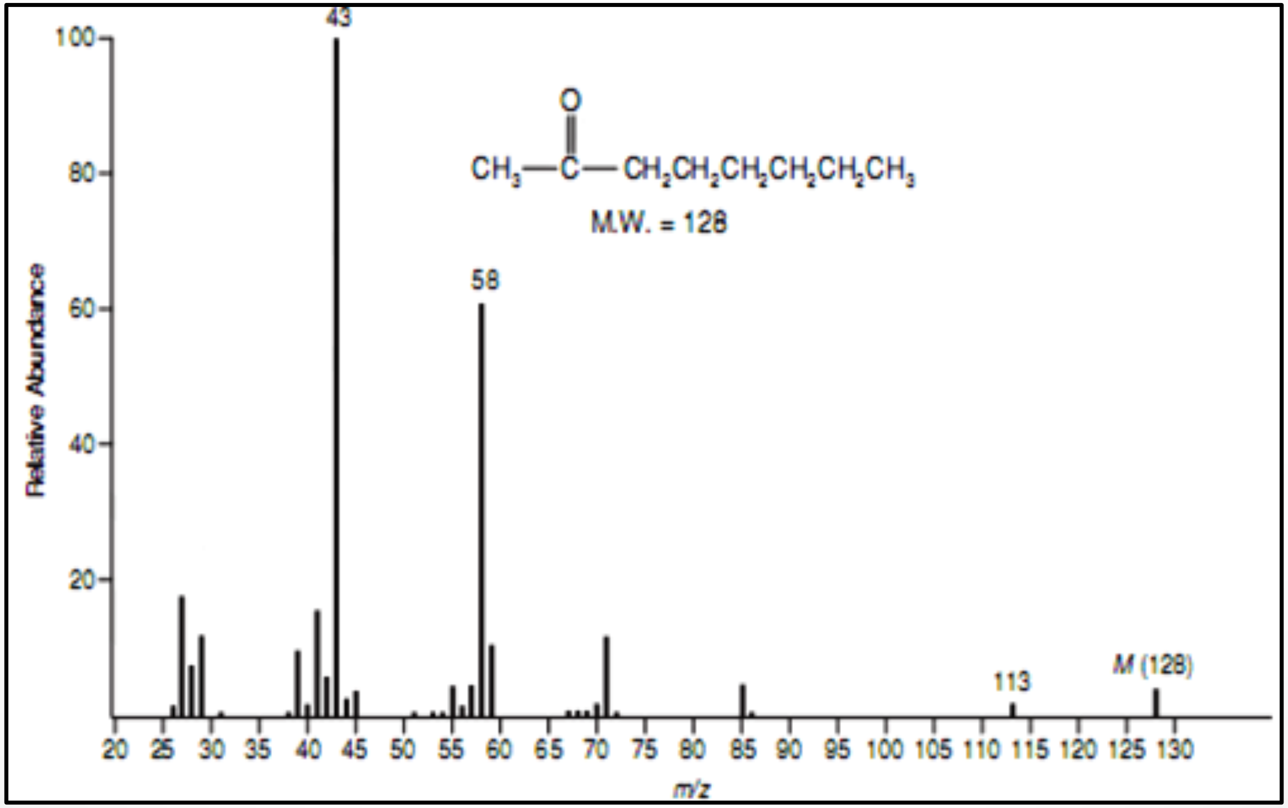
α - cleavage



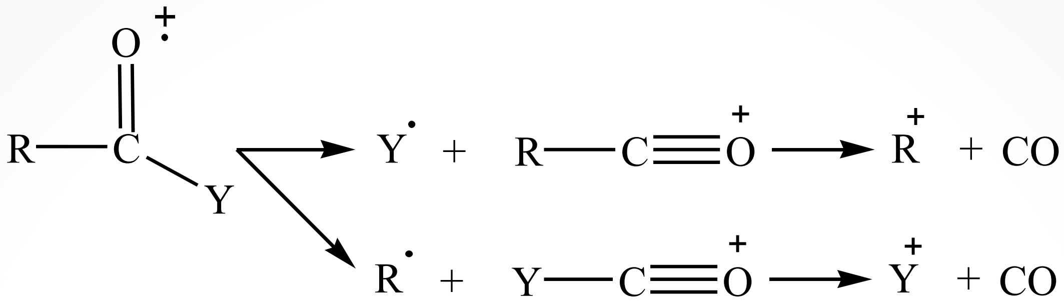


McLafferty rearrangment





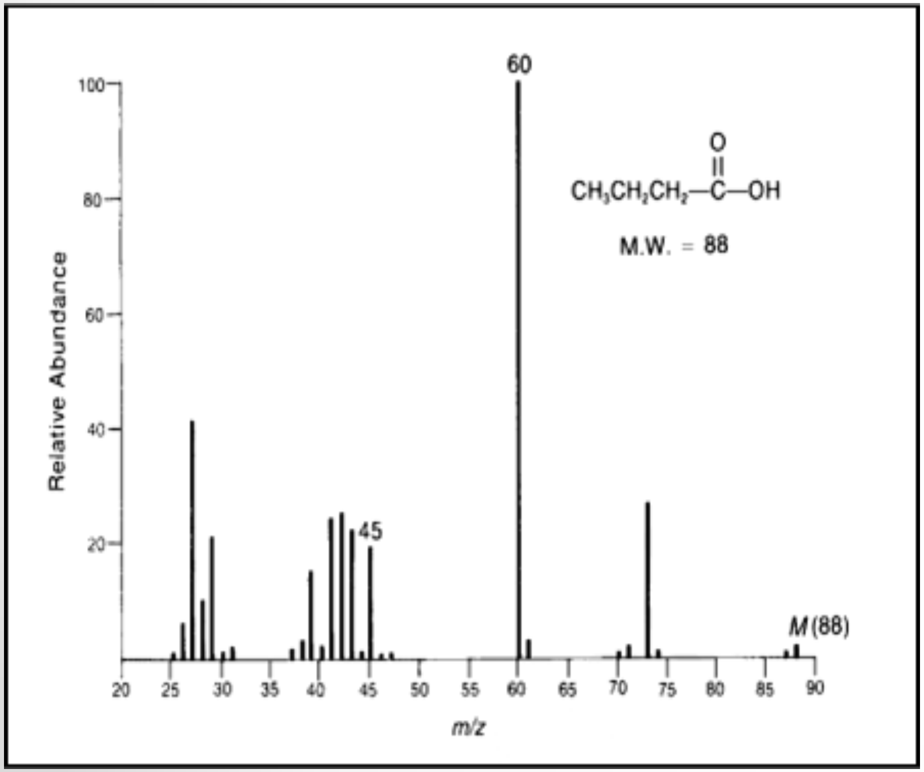
Carboxylic acids and Deriv.



$$R{-}C({=}O)Y^{+\bullet} \longrightarrow Y^{\bullet} + R{-}C{\equiv}O^{+} \longrightarrow R^{+} + CO$$

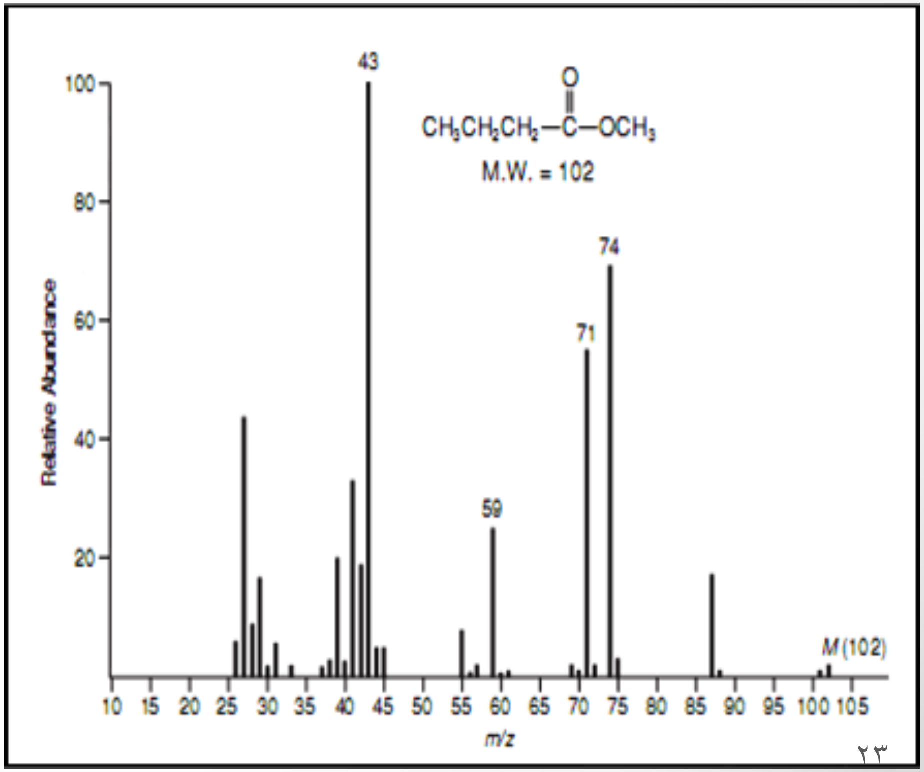
$$R{-}C({=}O)Y^{+\bullet} \longrightarrow R^{\bullet} + Y{-}C{\equiv}O^{+} \longrightarrow Y^{+} + CO$$

Y = OH, OR, NH_2, NHR, X



$CH_3CH_2CH_2{-}C({=}O){-}OH$

M.W. = 88

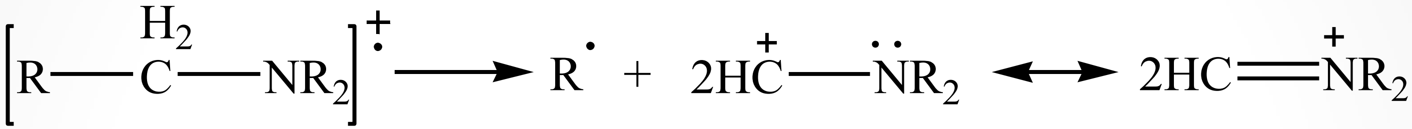


$CH_3CH_2CH_2{-}C({=}O){-}OCH_3$

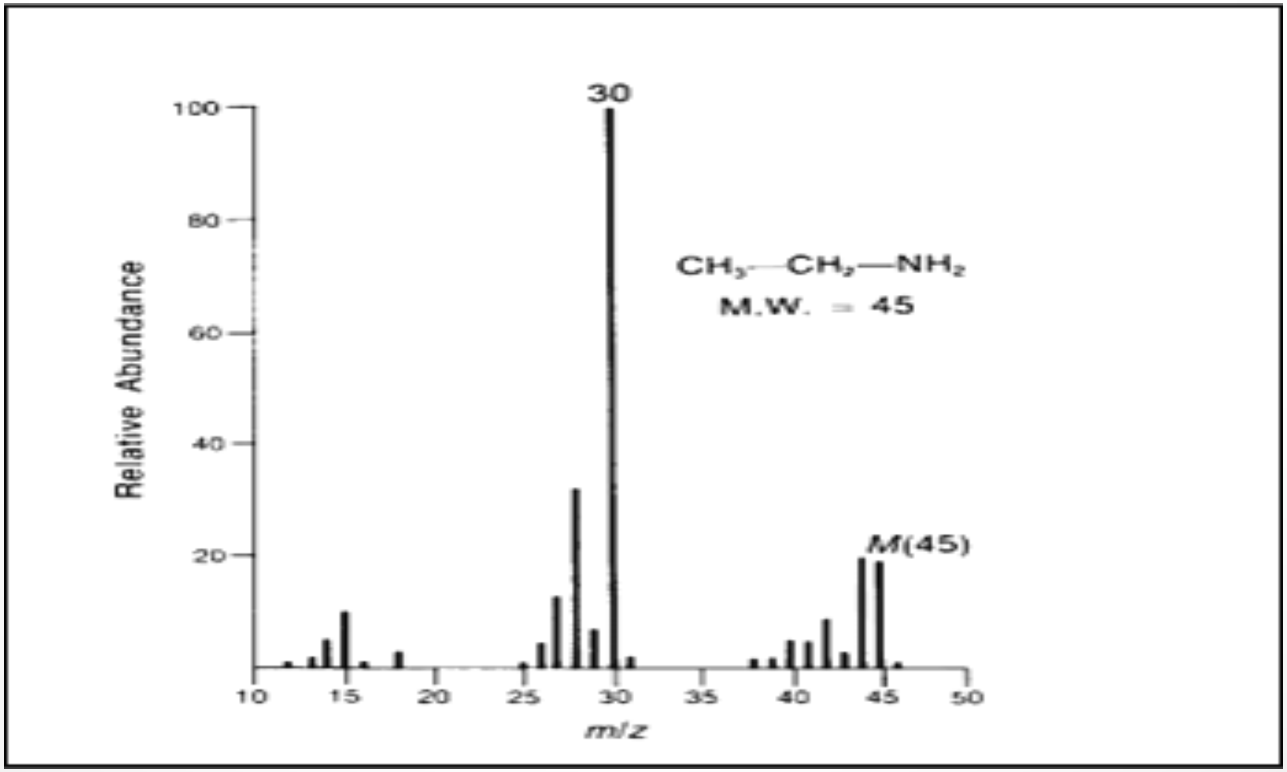
M.W. = 102

Amines

β - cleavage

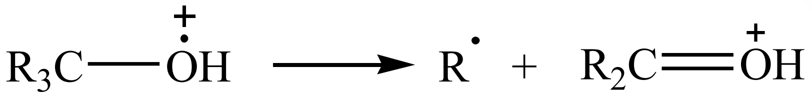


$$\left[R-\overset{H_2}{C}-NR_2\right]^{+\bullet} \longrightarrow R^{\bullet} + 2H\overset{+}{C}-\ddot{N}R_2 \longleftrightarrow 2HC=\overset{+}{N}R_2$$



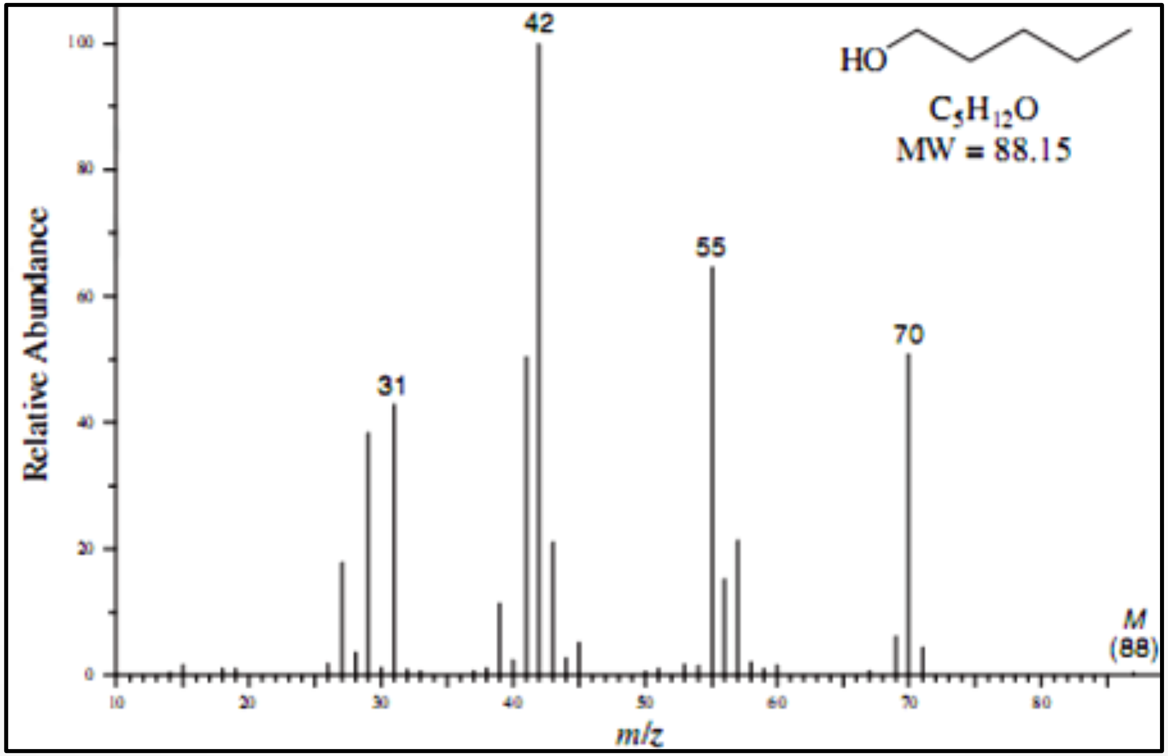
Alcohols

β - cleavage

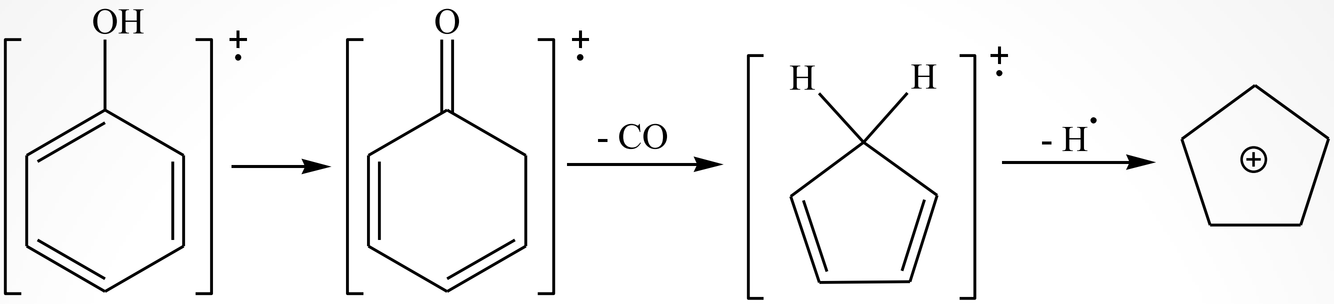


$$R_3C-\overset{+}{\dot{O}}H \longrightarrow R^{\cdot} + R_2C=\overset{+}{O}H$$

Oxonium ion



Phenol

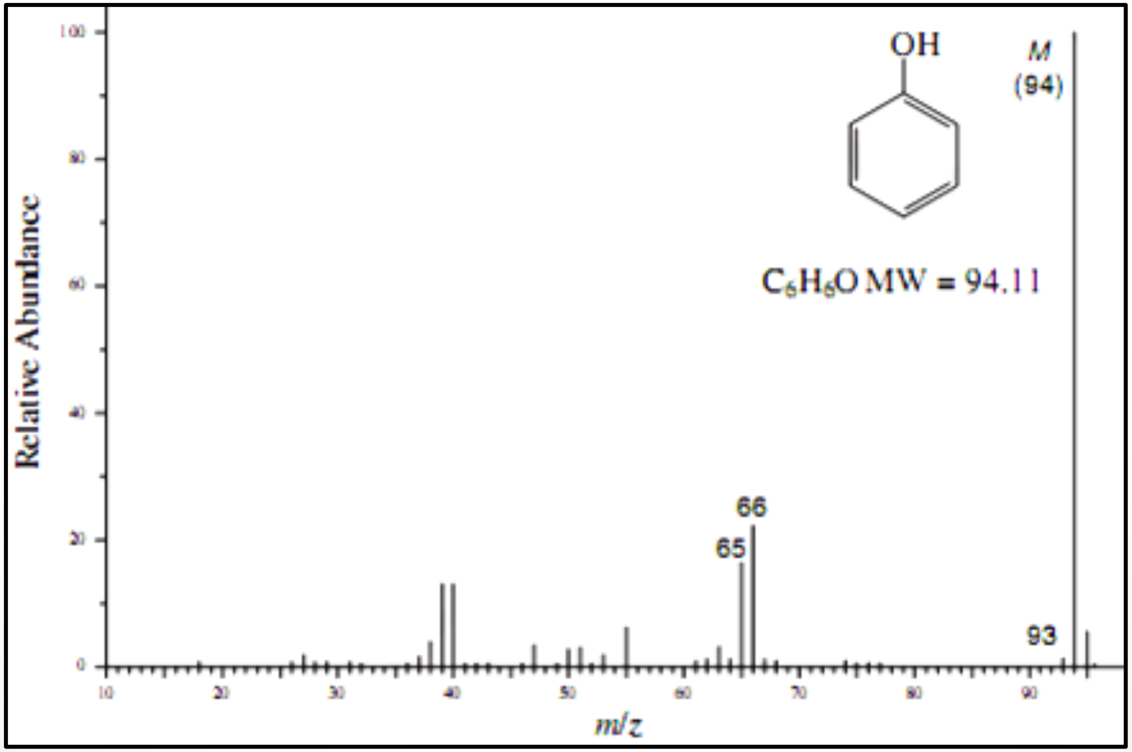


enol form

keto form

m/*e* = 66

m/*e* =65

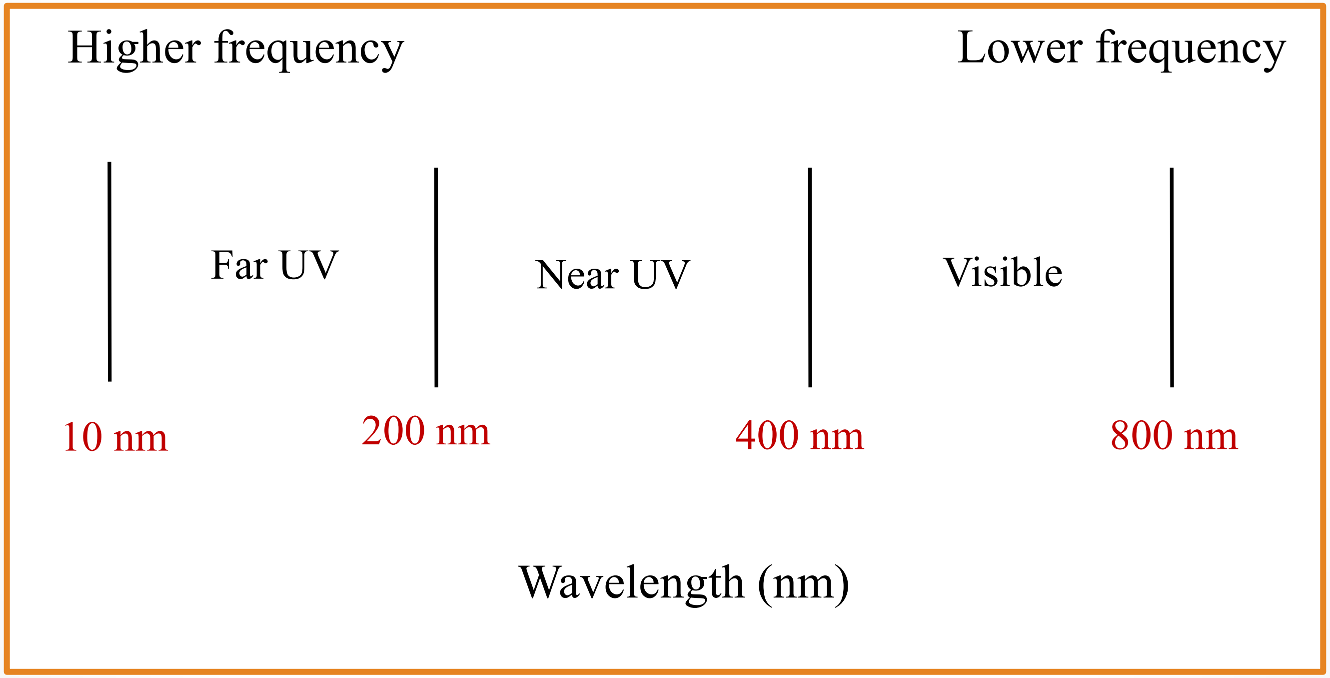


441 Chem

CH-2

Ultraviolet
and
Visible Spectroscopy

The Ultraviolet and Visible Spectrum



Higher frequency

Lower frequency

Far UV

Near UV

Visible

10 nm

200 nm

400 nm

800 nm

Wavelength (nm)

Ultraviolet and Visible Spectroscopy

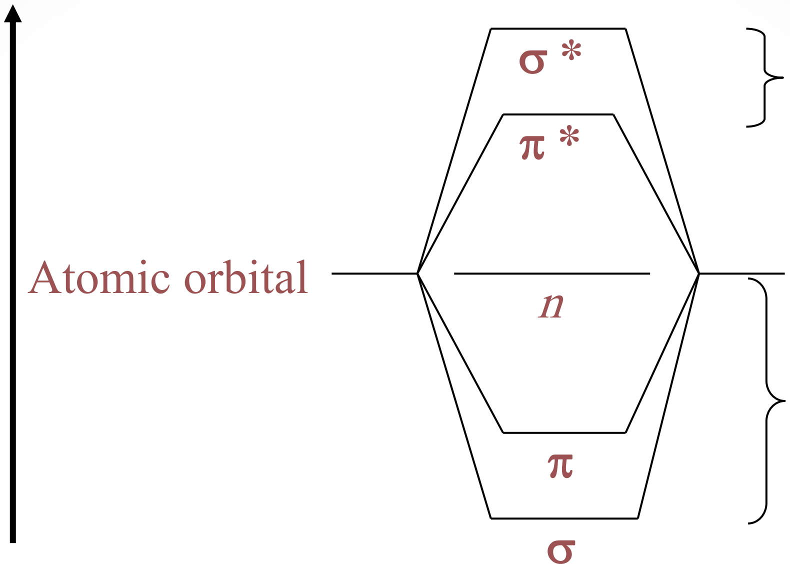
- ❑ The absorption of ultraviolet and visible radiation by molecules is dependent upon the electronic structure of the molecule.
- ❑ So the ultraviolet and visible spectrum is called:

Electronic Spectrum

- ❑ The absorption of light energy by organic compounds in the visible and ultraviolet region involves the promotion of electrons in σ, π, and n-orbitals from the ground state to higher energy states. This is also called

Energy Transition

Electron Transitions



Energy

Atomic orbital

σ^*

π^*

n

π

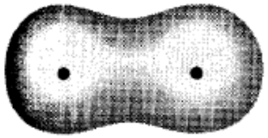
σ

Atomic orbital

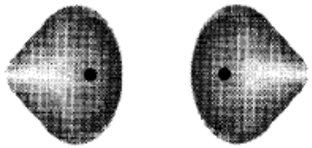
Anti-bonding

Bonding

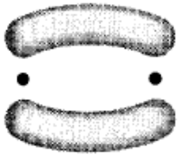
Molecular orbitals



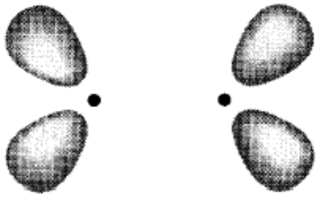
(a) σ orbital



(c) σ^* orbital

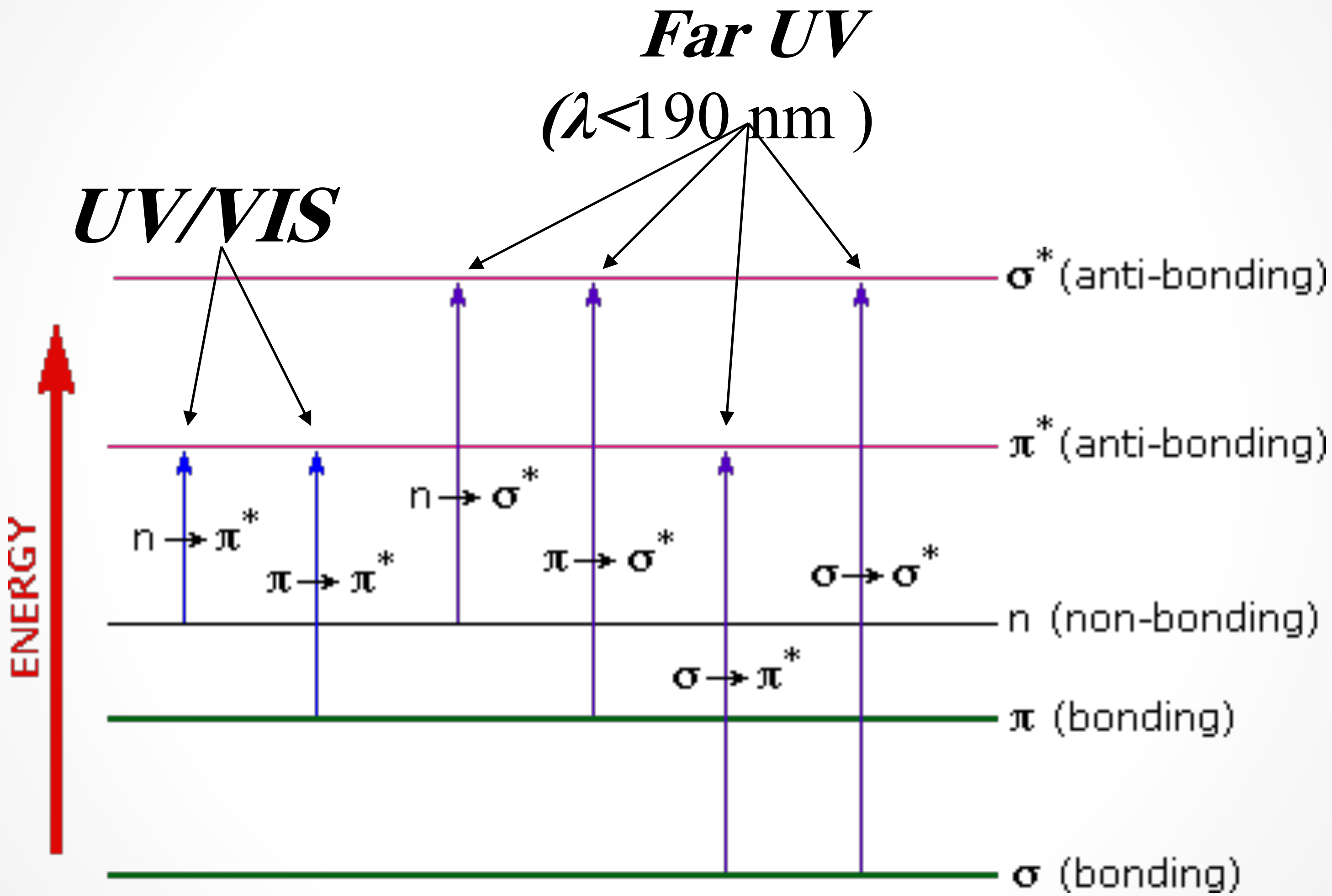


(b) π orbital

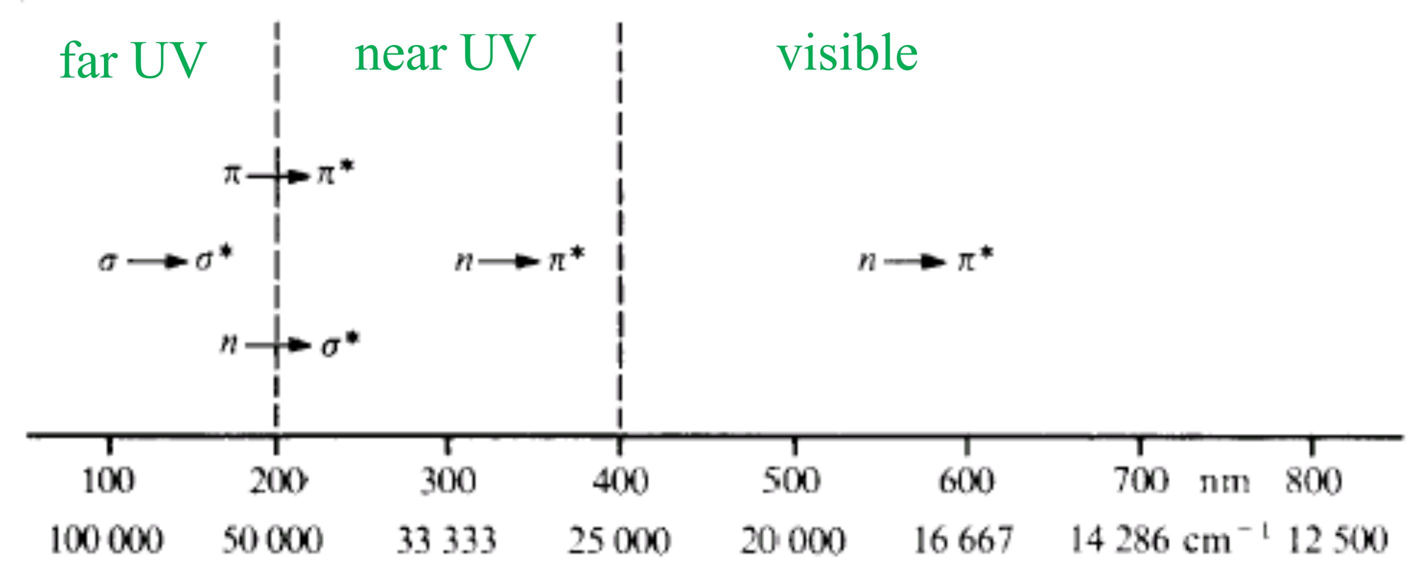


(d) π^* orbital

Electron transitions



The region of the electronic spectrum and the type of transitions that occur in each.

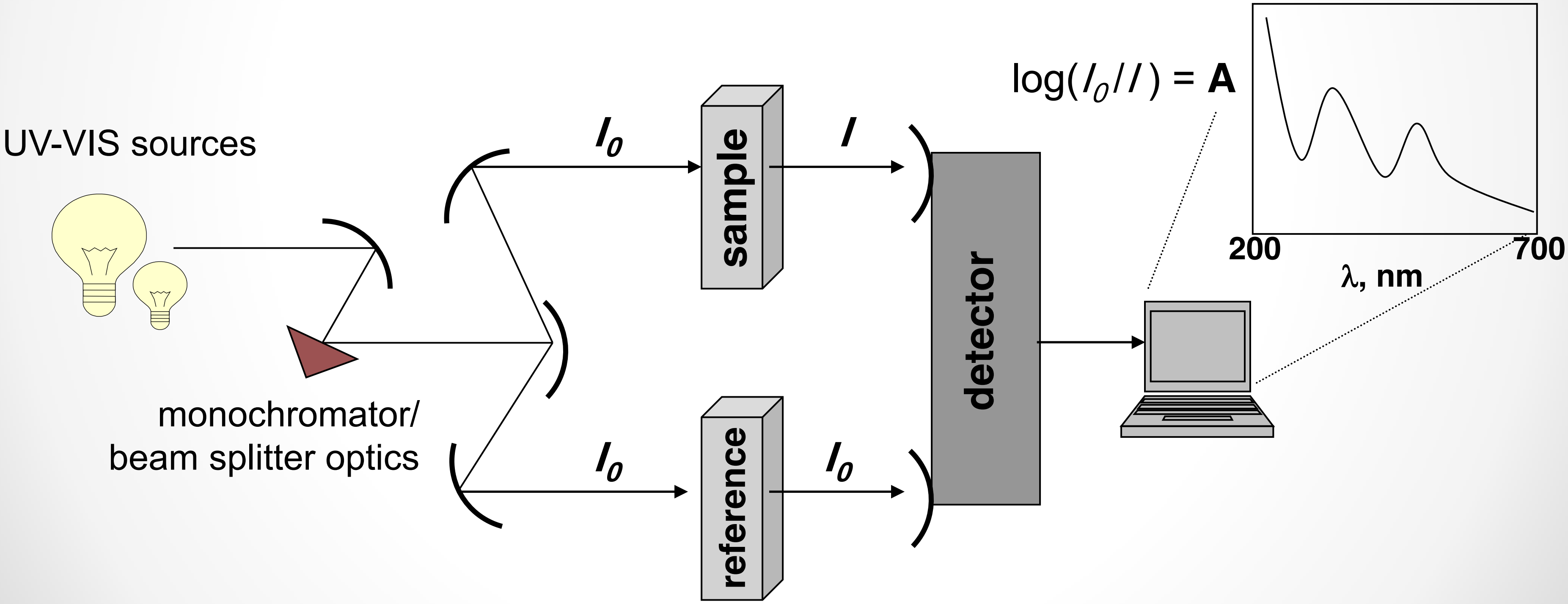


Some of the most important transitions:

$\sigma \longrightarrow \sigma^*$	In alkanes
$\sigma \longrightarrow \pi^*$	In carbonyl compounds
$\pi \longrightarrow \pi^*$	In unsaturated compounds
$n \longrightarrow \sigma^*$	In O, N, S and halogen compounds
$n \longrightarrow \pi^*$	In carbonyl compounds

Spectrometer

An instrument which can measure the absorbance of a sample at any wavelength.



Absorption laws

Beer – Lambert Law

$$\text{Absorbance (A)} = \text{Log}\ \frac{I_0}{I}$$

$$A = ECL$$

I_0 = Original light intensity

I = Transmitted light intensity

E = Molar Extinction Coefficient

C = Concentration (moles/L)

L = Length of sample cell (cm)

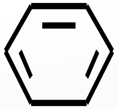
Solvents

Common solvents :

solvent	λ nm
acetonitrile	190
chloroform	240
cyclohexane	195
1,4-dioxane	215
95% ethanol	205
n-hexane	201
methanol	205
isooctane	195
water	190

Terms describing UV absorptions

1. **Chromophores**: functional groups that give electronic transitions.

Group	Structure	nm
Carbonyl	> C = O	280
Azo	-N = N-	262
Nitro	-N=O	270
Thioketone	-C =S	330
Nitrite	-NO2	230
Conjugated Diene	-C=C-C=C-	233
Conjugated Triene	-C=C-C=C-C=C-	268
Conjugated Tetraene	-C=C-C=C-C=C-C=C-	315
Benzene		261

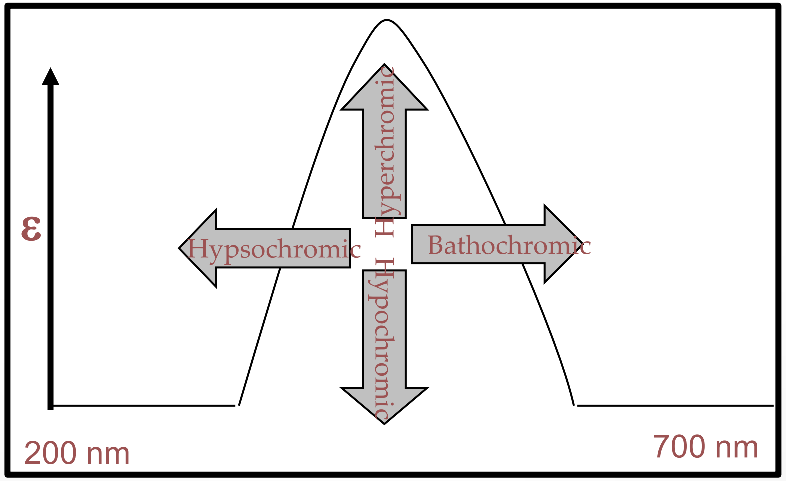
2. **Auxochromes**: substituents with unshared paire's like OH, NH, SH ..., when attached to π chromophore they generally move the absorption max. to longer λ.

3. **Bathochromic shift**: shift to longer λ, also called red shift.

4. **Hypsochromic shift**: shift to shorter λ, also called blue shift.

5. **Hyperchromic effect**: increase in absorption intensity.

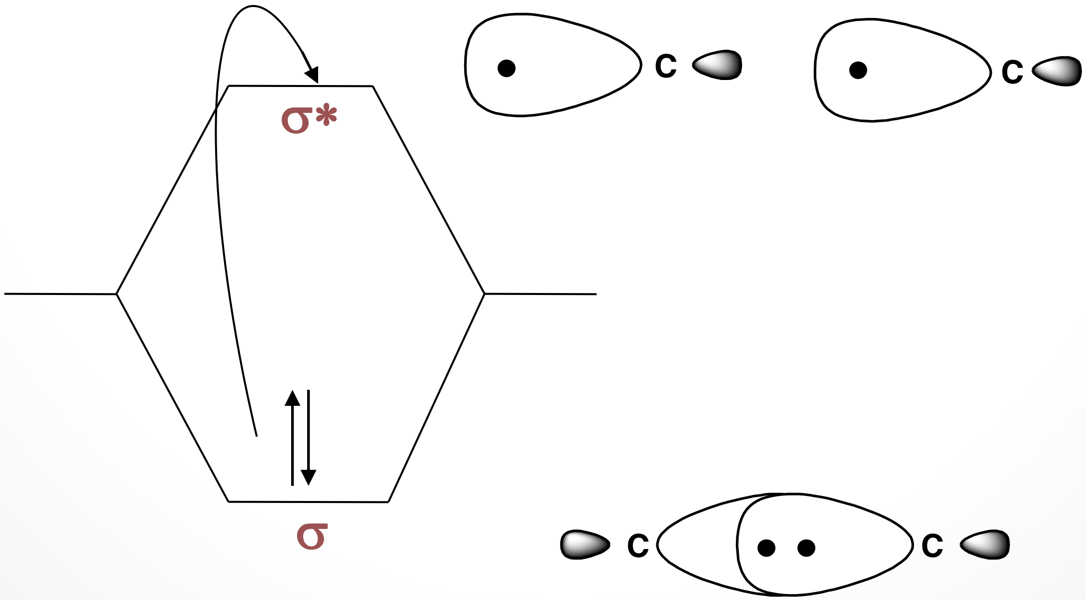
6. **Hypochromic effect**: decrease in absorption intensity.



Absorption of Ultraviolet and Visible Radiation in Organic Compounds

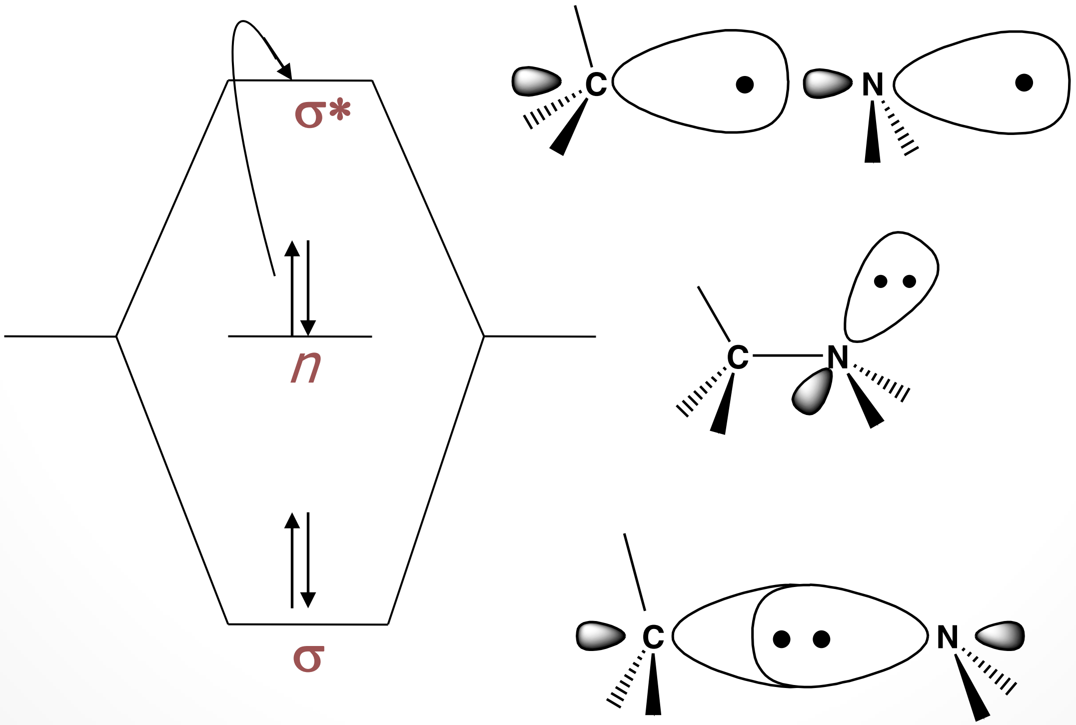
1- Saturated compounds

Alkanes – only posses σ-bonds and no lone pairs of electrons, so only the high energy σ → σ* transition is observed in the far UV.



2. Saturated compounds with unshared e^-

Alcohols, ethers, amines and sulfur compounds – in the cases of simple, aliphatic examples of these compounds the $n \rightarrow \sigma^*$ is the most often observed transition; like the alkane $\sigma \rightarrow \sigma^*$ it is most often at shorter λ than 200 nm.

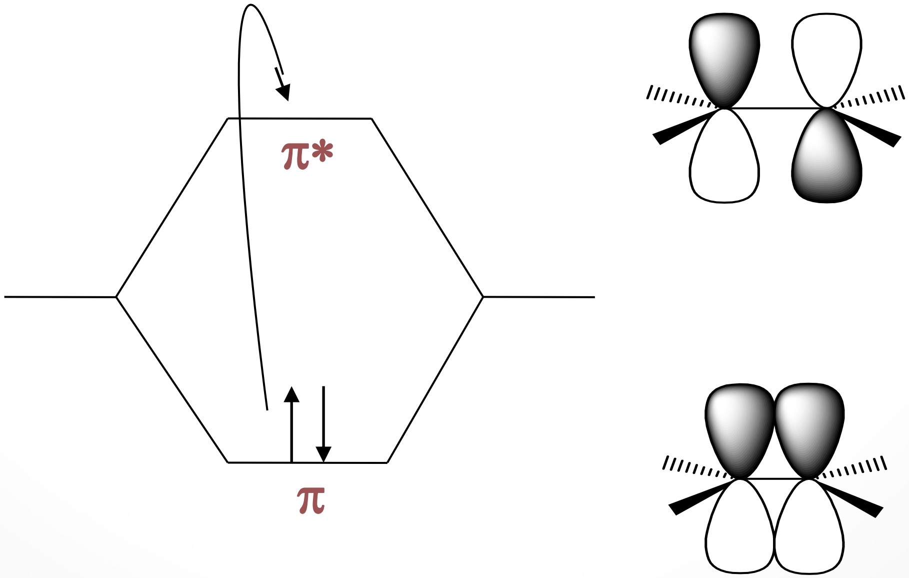


3. Unsaturated compounds

- Alkenes– in the case of isolated examples of these compounds the $\pi \rightarrow \pi^*$ is observed at 175 nm.

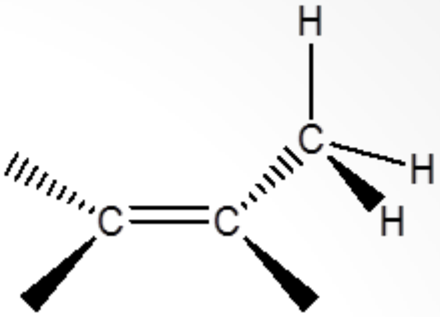
$CH_2{=}CH_2$ at 175 nm

- Even though this transition is of lower energy than $\sigma \rightarrow \sigma^*$, it is still in the far UV – however, the transition energy is sensitive to substitution.



Substituent Effects

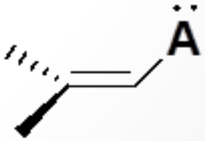
$CH_2{=}CHR$ at 180 nm
cis $CHR{=}CHR$ at 183 nm
trans $CHR{=}CHR$ at 180 nm
$CR_2{=}CR_2$ at 200 nm



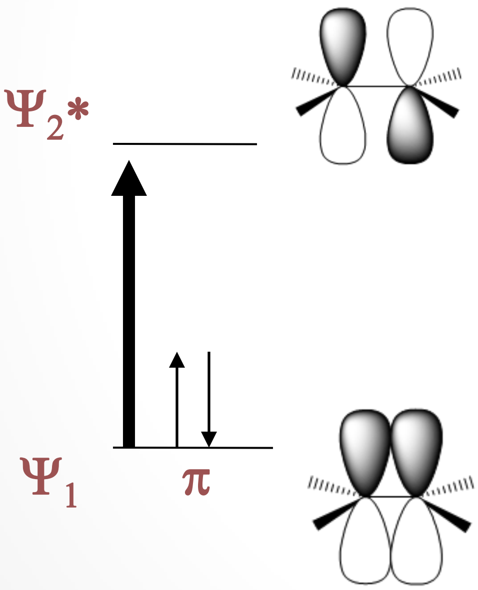
- This effect is thought to be through what is termed "hyperconjugated" or sigma bond resonance

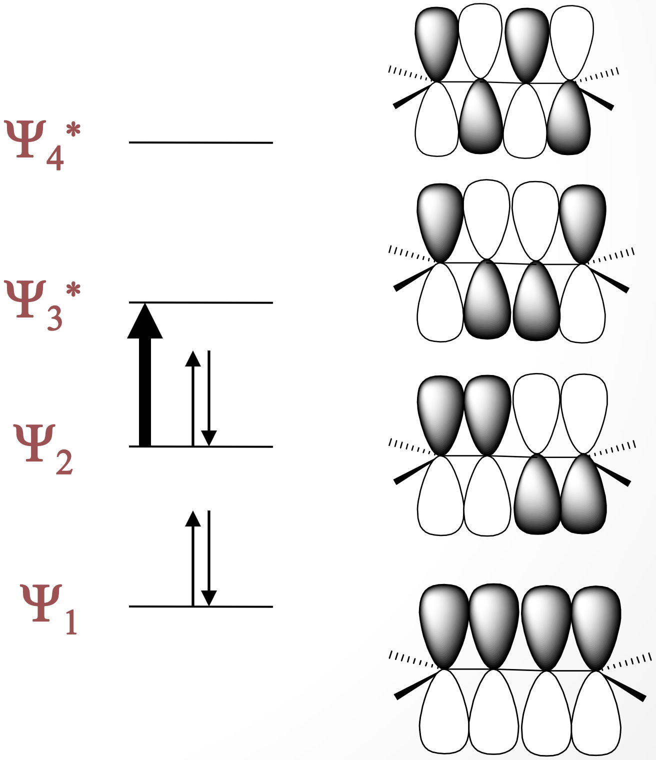
- Similarly, the lone pairs of electrons on N, O, S, X can extend conjugated systems

Substituent	Increment of Substituent
-SR	45
$-NR_2$	40
-OR	30
-Cl	5

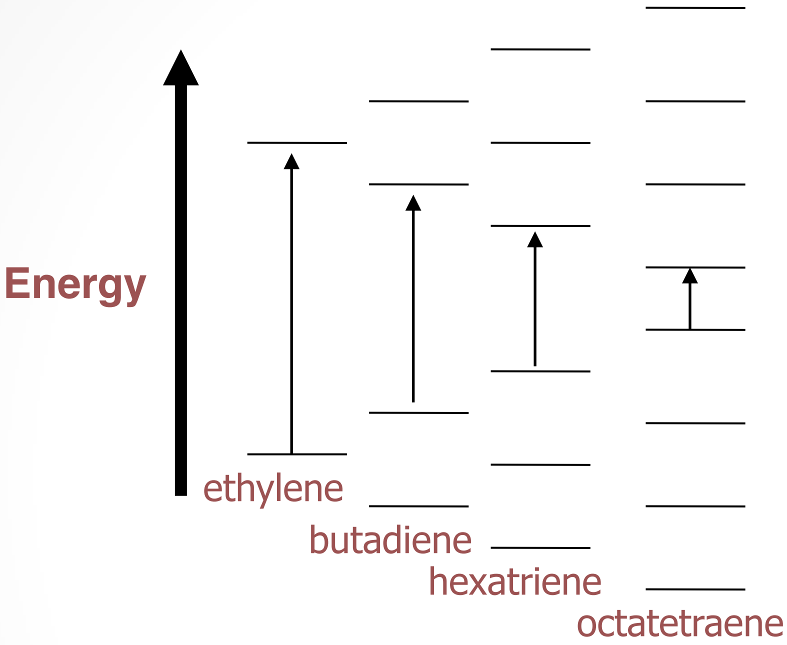


- Dienes– in the case of isolated examples of these compounds the $\pi \rightarrow \pi^*$ is observed in the far UV.
- Conjugated dienes–The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation.





- Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller.



Energy

ethylene

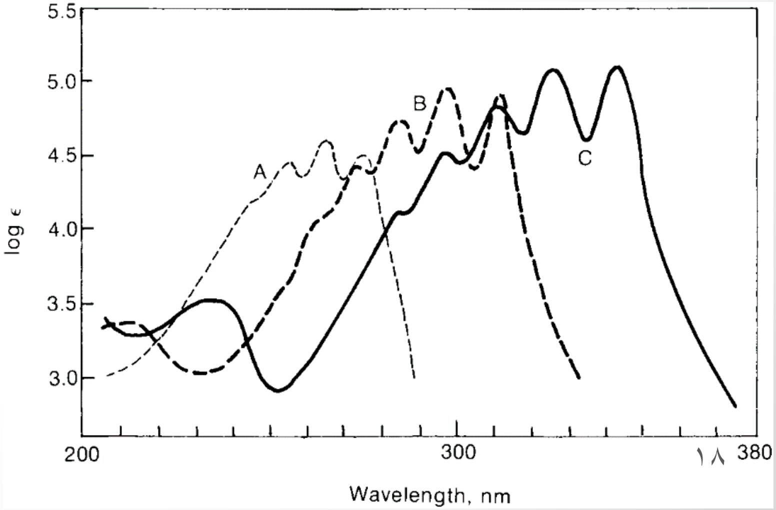
butadiene

hexatriene

octatetraene

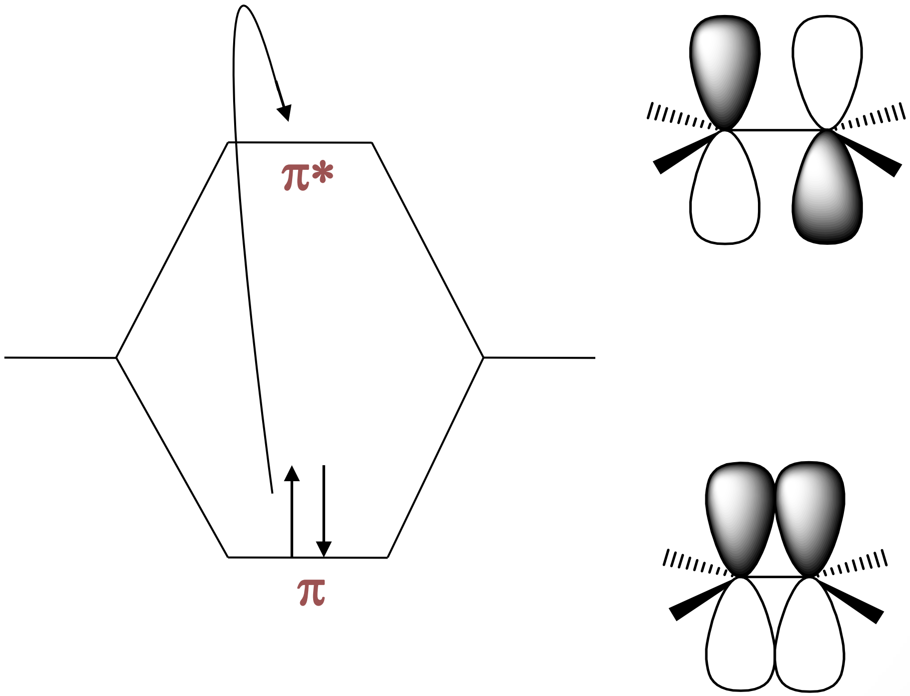
Lower energy =
Longer wavelengths

$\pi \rightarrow \pi^*$ is observed in the region from 217 to 245 nm.

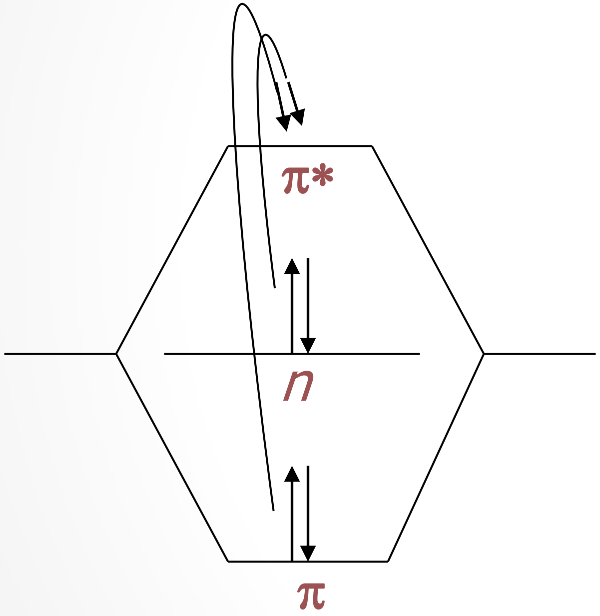


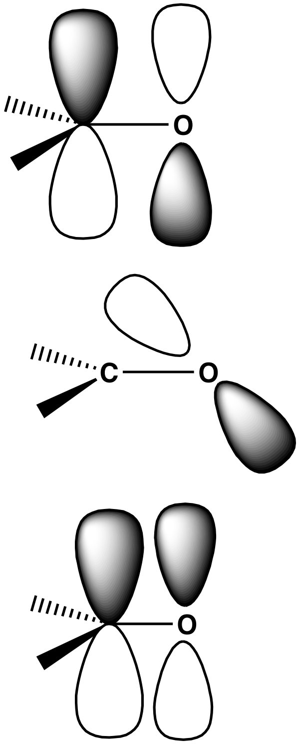
- Alkynes– in the case of isolated examples of these compounds the π → π* is observed in the far UV.

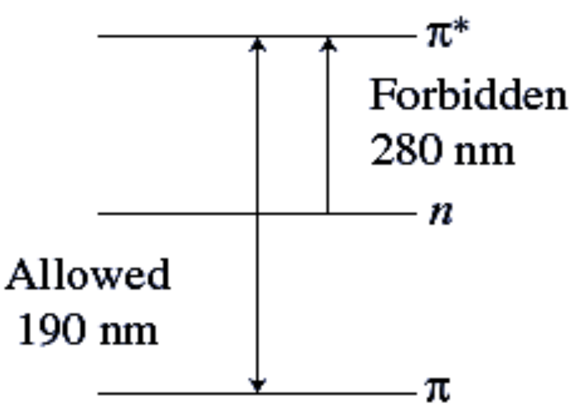
CH≡CH at 170 nm



- Carbonyl compounds – unsaturated systems incorporating N or O can undergo *n* → π* transition (~280 nm) in addition to π → π* transition (190 nm). Most *n* → π* transitions are forbidden and hence are of low intensity.

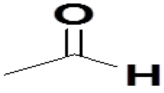
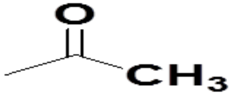
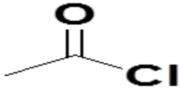
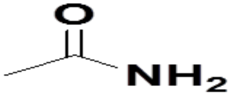
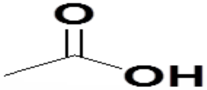




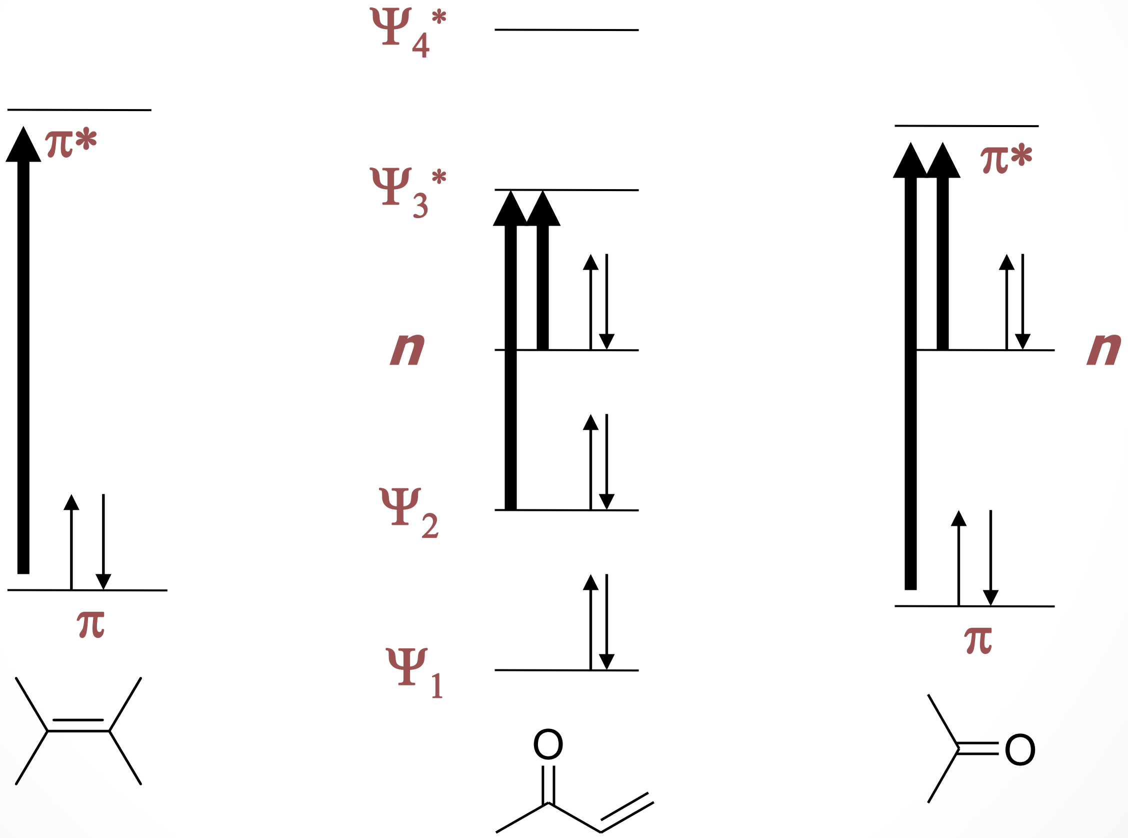


- For auxochromic substitution on the carbonyl, such as $-NR_2$, -OH, -OR, -X, gives a pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transition and a lesser bathochromic effect on the $\pi \rightarrow \pi^*$ transition.

Hypsochromic effect on the $n \rightarrow \pi^*$ transition

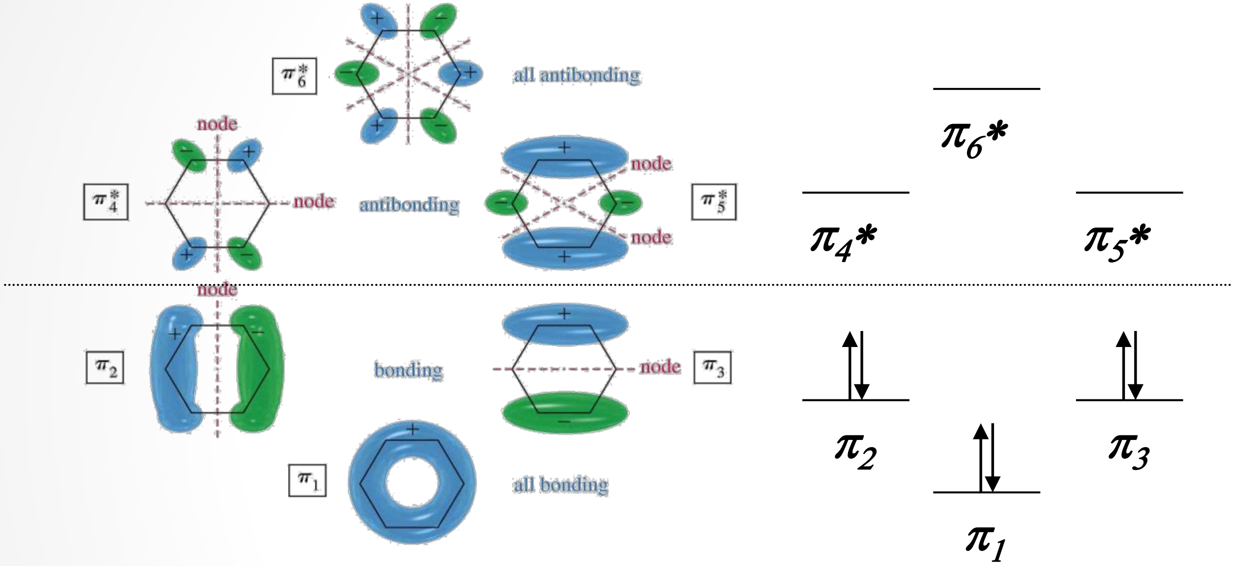
	293 nm
	279
	235
	214
	204
	204

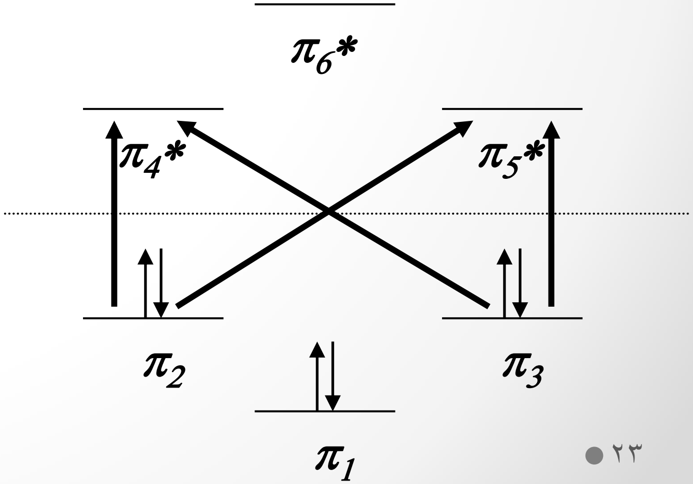
- Enones compounds – Conversely, if the C=O system is conjugated both the *n* → π* and π → π* bands are bathochromically shifted.



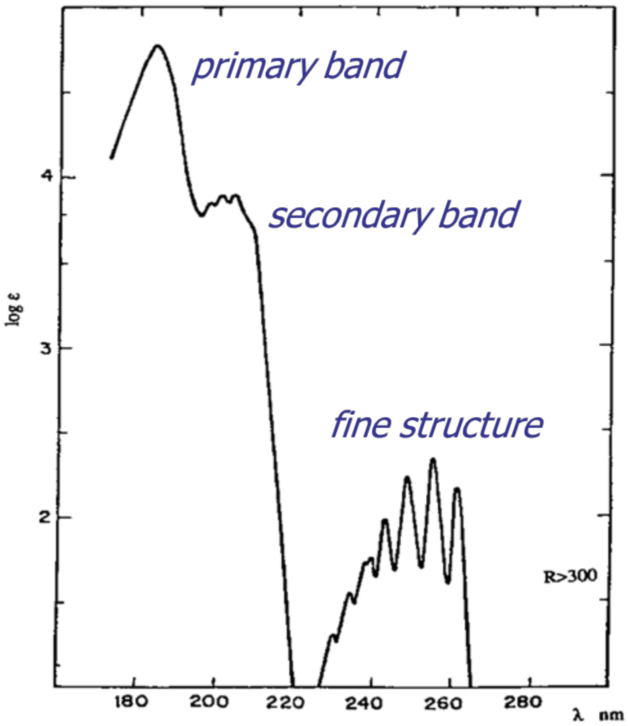
4. Aromatic Compounds

- On first inspection, benzene has six π -MOs, 3 filled π, 3 unfilled π *



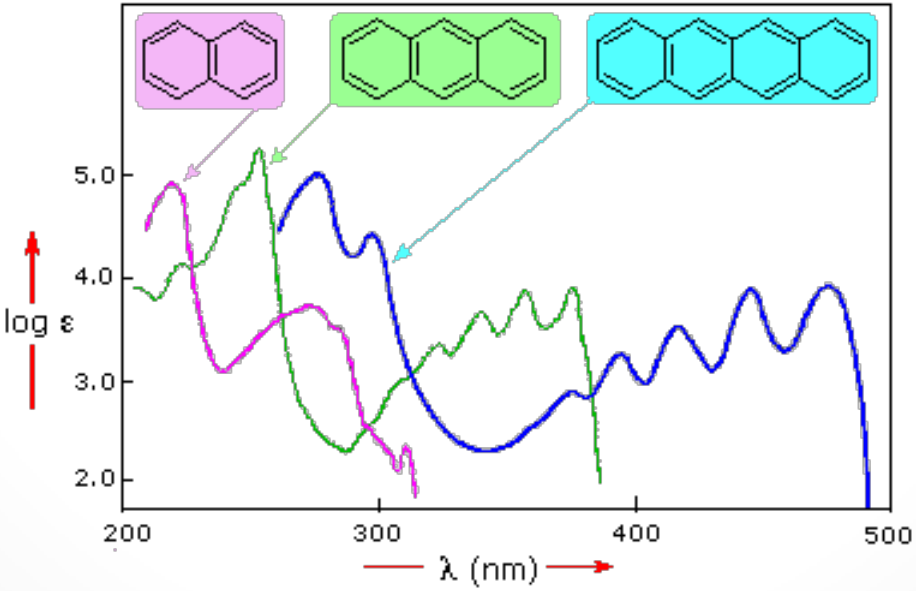


- The spectrum of Benzene has two bands at 204, 254 nm and transition i fleetingly allowed due to the disruption of symmetry by the vibrational energy states, the overlap of which is observed in what is called fine structure



- Substituent Effects
  - Polynuclear aromatics

- When the number of fused aromatic rings increases, the λ for the primary and secondary bands also increase



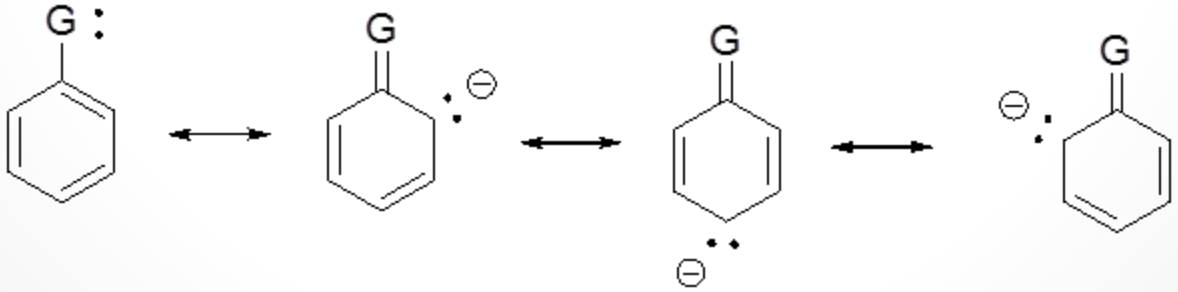
Substituent Effects

Substituents with Unshared Electrons

- If the group attached to the ring bears *n* electrons, they can induce a shift in the primary and secondary absorption bands.

- Non-bonding electrons extend the π -system through resonance – lowering the energy of transition π → π*

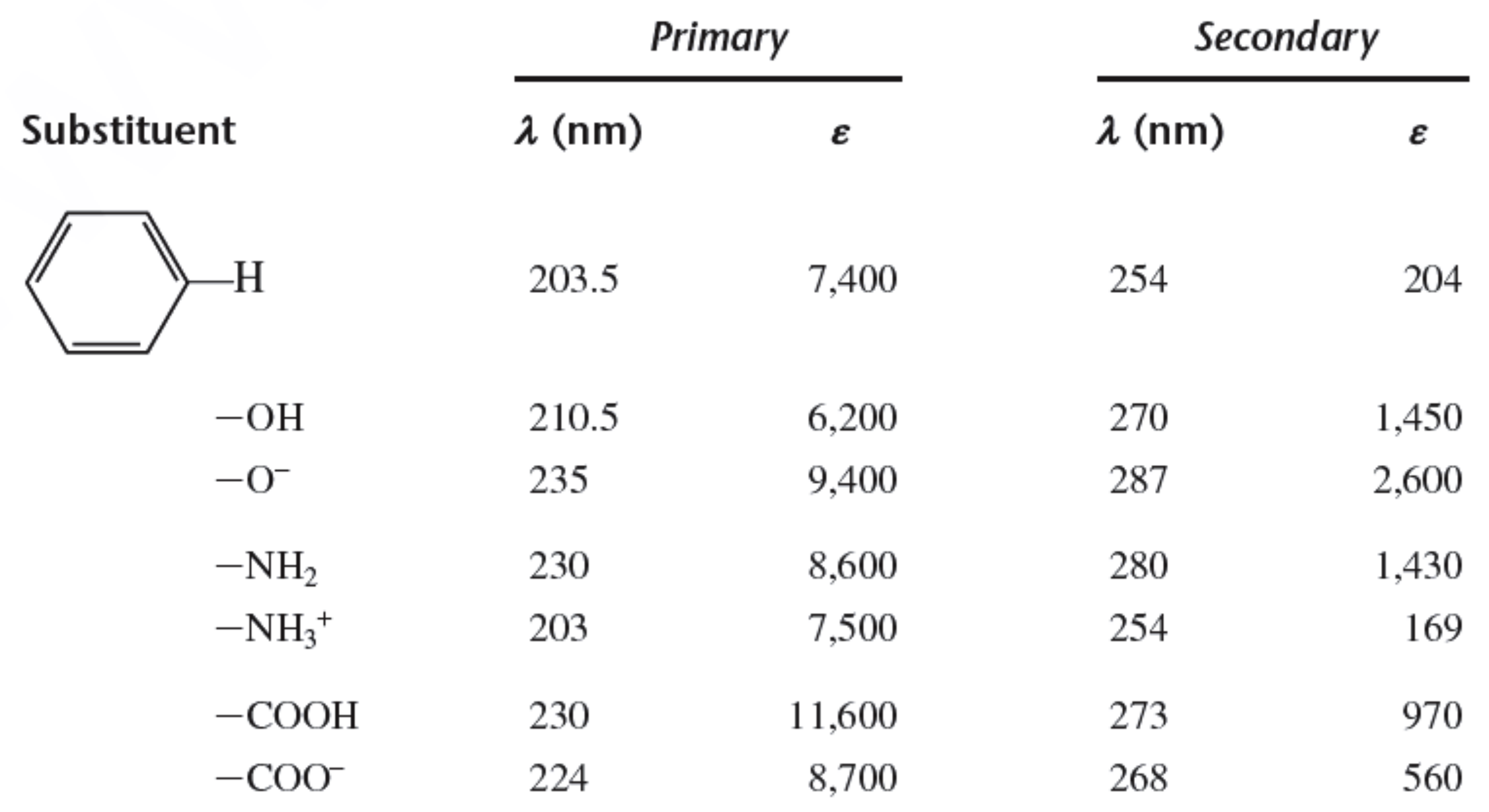
- More available n-pairs of electrons give greater shifts.



- Substituent Effects
  - Electron-donating and electron-withdrawing effects

	Substituent	*Primary*		*Secondary*	
		λ_{max}	ε	λ_{max}	ε
Electron donating	-H	203.5	7,400	254	204
	$-CH_3$	207	7,000	261	225
	-Cl	210	7,400	264	190
	-Br	210	7,900	261	192
	-OH	211	6,200	270	1,450
	$-OCH_3$	217	6,400	269	1,480
	$-NH_2$	230	8,600	280	1,430
Electron withdrawing	-CN	224	13,000	271	1,000
	C(O)OH	230	11,600	273	970
	-C(O)H	250	11,400		
	$-C(O)CH_3$	224	9,800		
	$-NO_2$	269	7,800		

- Substituent Effects
  - pH effects



Substituent	*Primary* λ (nm)	*Primary* ε	*Secondary* λ (nm)	*Secondary* ε
—H	203.5	7,400	254	204
$-OH$	210.5	6,200	270	1,450
$-O^-$	235	9,400	287	2,600
$-NH_2$	230	8,600	280	1,430
$-NH_3^+$	203	7,500	254	169
$-COOH$	230	11,600	273	970
$-COO^-$	224	8,700	268	560

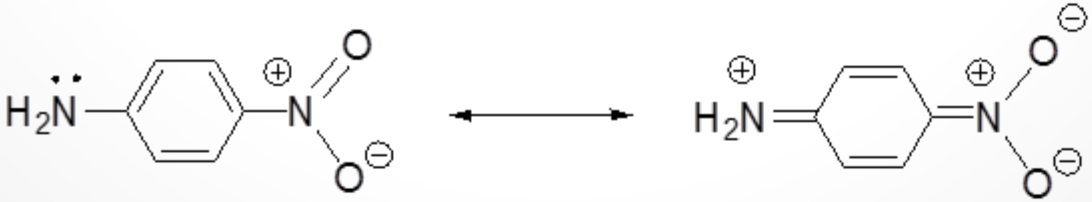
Substituent Effects

Di-substituted and multiple group effects

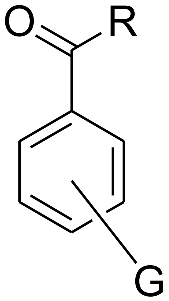
•If the two electonically dissimilar groups are ortho- or meta- to one another, the effect is usually the sum of the two individual effects (meta- no resonance; ortho-steric hind).

•If both groups are electron donating or withdrawing, the effect is similar to the effect of the stronger of the two groups as if it were a mono-substituted ring.

•If one group is electron withdrawing and one group electron donating and they are para- to one another, the magnitude of the shift is greater than the sum of both the group effects



Parent Chromophore	λ_{max}
R = alkyl or ring residue	246
R = H	250
R = OH or O-Alkyl	230



G	Substituent increment *o*	*m*	*p*
Alkyl or ring residue	3	3	10
-O-Alkyl, -OH, -O-Ring	7	7	25
$-O^-$	11	20	78
-Cl	0	0	10
-Br	2	2	15
$-NH_2$	13	13	58
$-NHC(O)CH_3$	20	20	45
$-NHCH_3$			73
$-N(CH_3)_2$	20	20	85

441 Chem

CH-4

Nuclear Magnetic Resonance

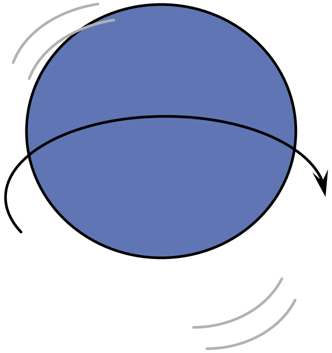
Introduction

- ❑ NMR is the most powerful tool available for organic structure determination.

- ❑ It is used to study a wide variety of nuclei:
  - ^{1}H
  - ^{13}C
  - ^{15}N
  - ^{19}F
  - ^{31}P

Nuclear Spin

The nuclei of some atoms have a property called "Spin".



- Elements with either odd mass or odd atomic number have the property of nuclear "spin".
- Each spin-active nucleus has a number of spins defined by its spin quantum number, **I**
- The number of spin states is $2\mathbf{I} + 1$

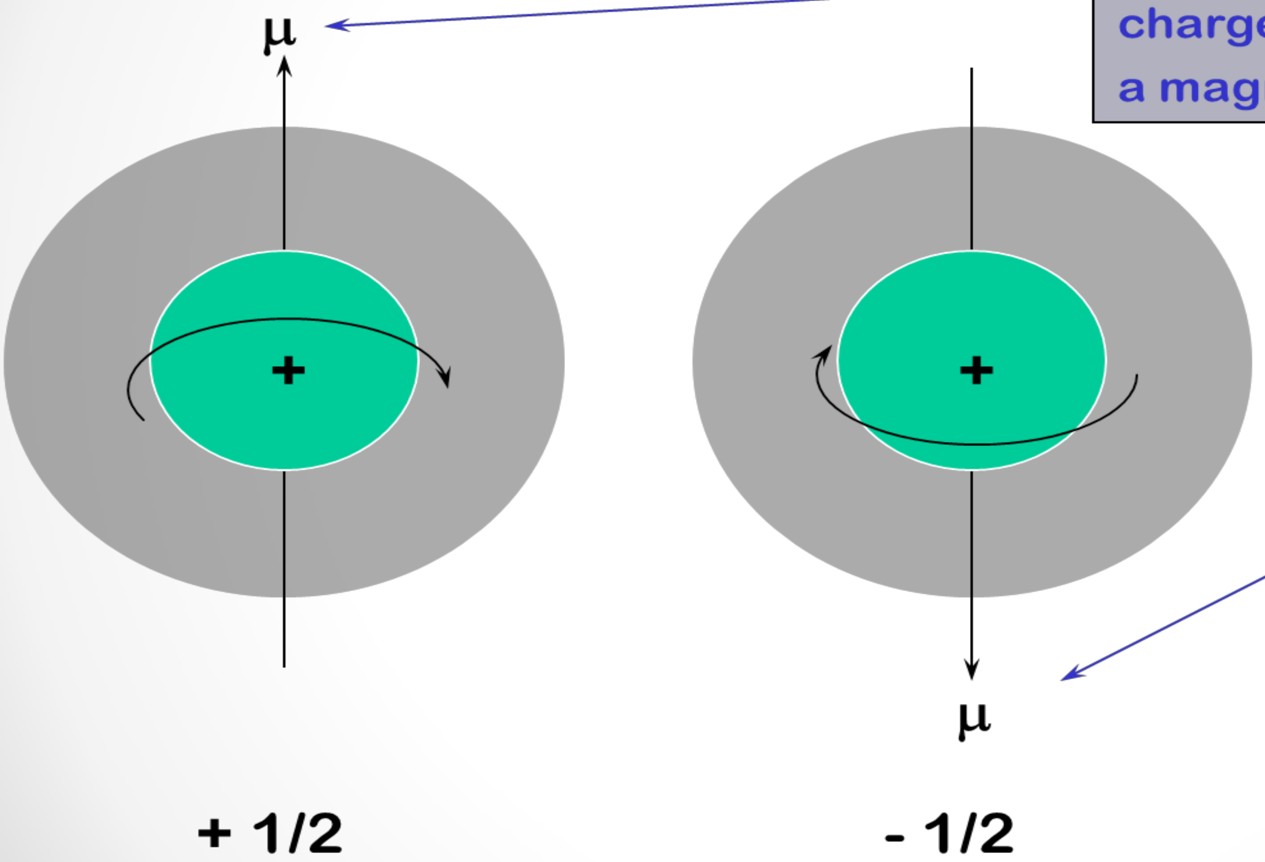
Spin Quantum Numbers of Some Common Nuclei

Mass No	**Atomic No**	**I**
Odd	Odd or Even	1/2 , 3/2, 5/2
Even	Even	0
Even	Odd	1 , 2 ,3

Element	**^{1}H**	**^{2}H**	**^{12}C**	**^{13}C**	**^{14}N**	**^{16}O**	**^{17}O**	**^{19}F**	**^{31}P**
Nuclear Spin Quantum No (I)	1/2	1	0	1/2	1	0	5/2	1/2	1/2
No. of Spin States	2	3	0	2	3	0	6	2	2

The Proton

Nuclear Spin States - Hydrogen Nucleus



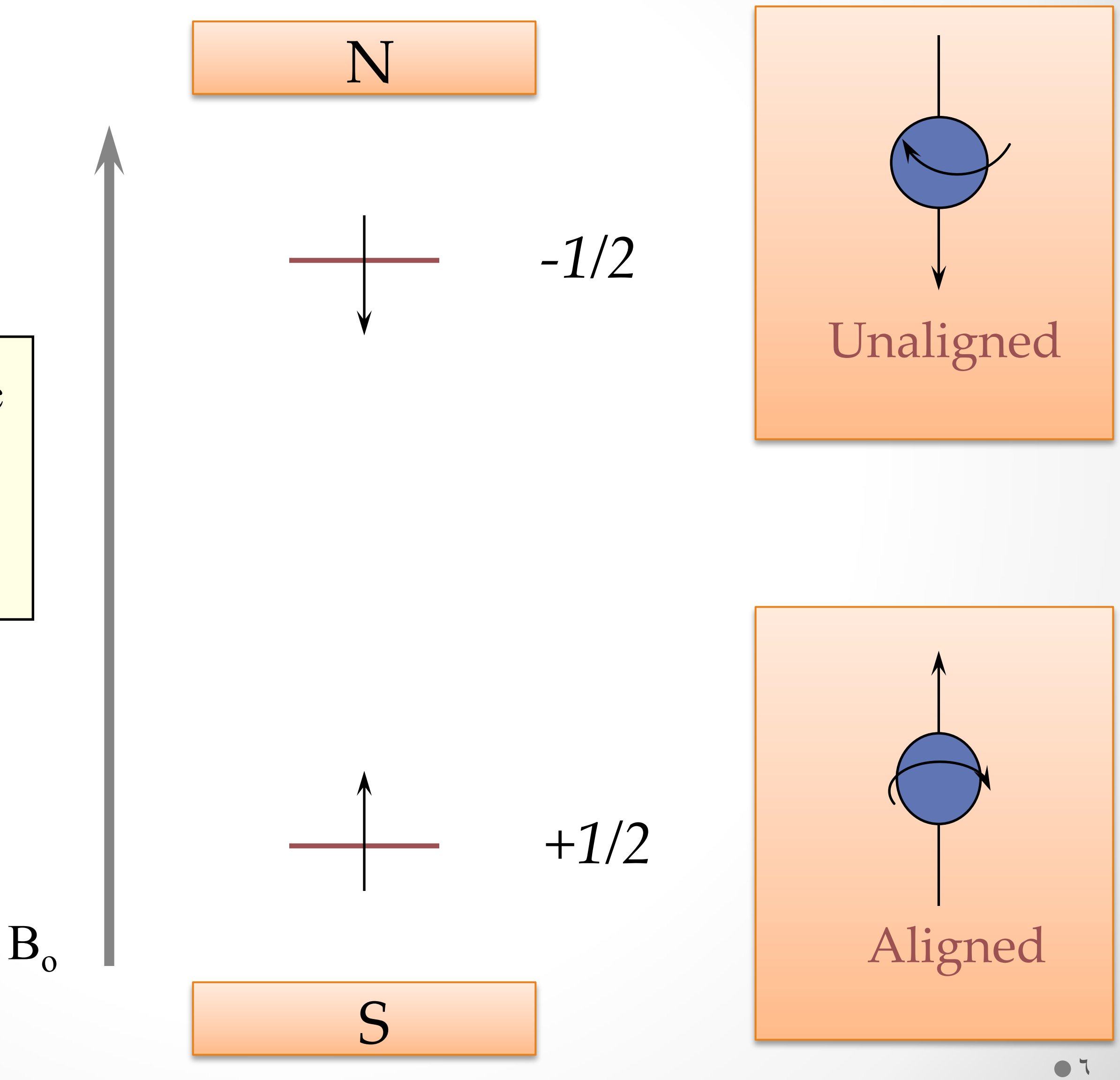
The spin of the positively charged nucleus generates a magnetic moment vector, μ.

The two states are equivalent in energy in the absence of a magnetic or an electric field.

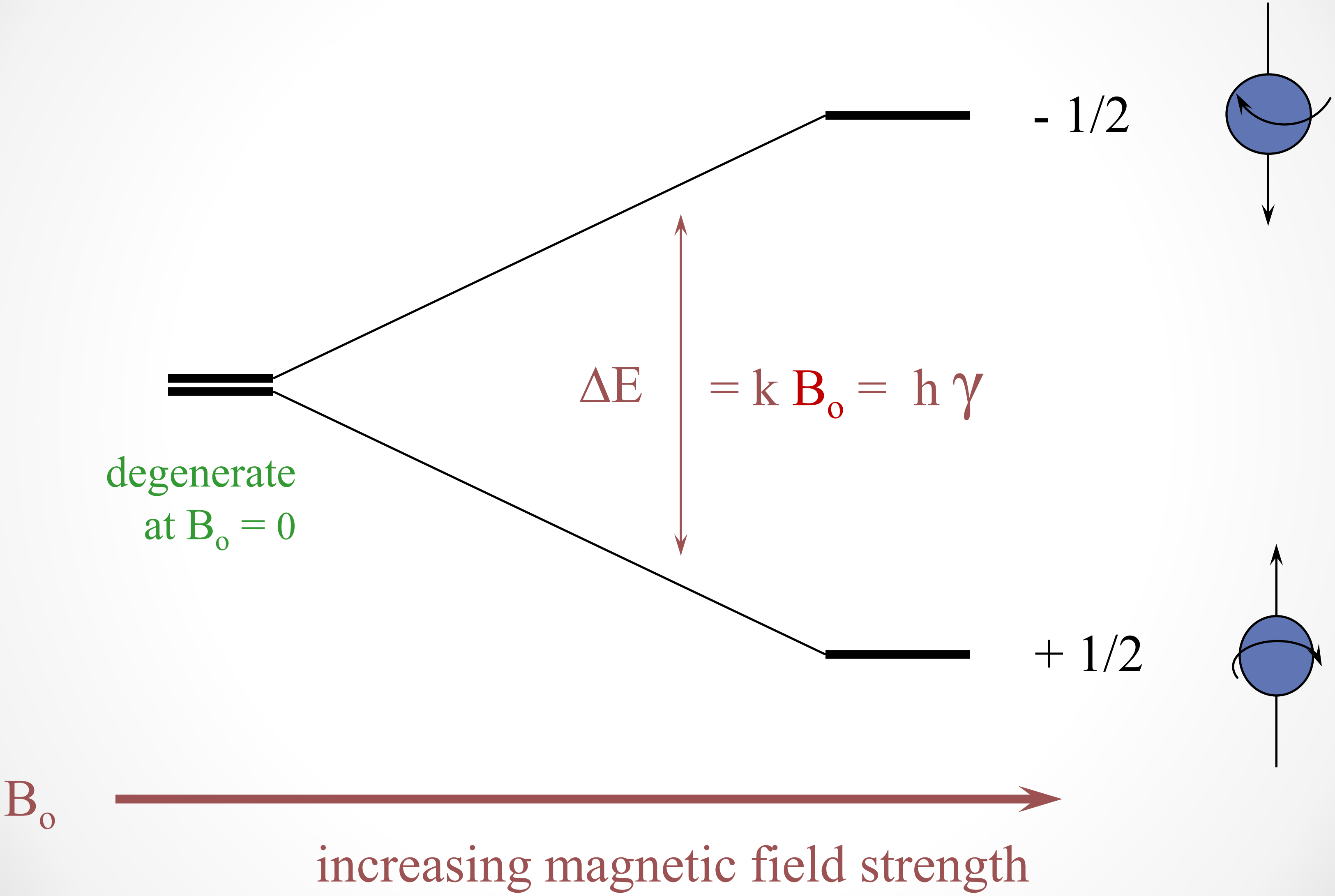
TWO SPIN STATES

Nuclear Spin Energy Levels

In a strong magnetic field (B_o) the two spin states differ in energy.



The Energy Separation Depends on B_o



- 1/2

$\Delta E = k B_o = h \gamma$

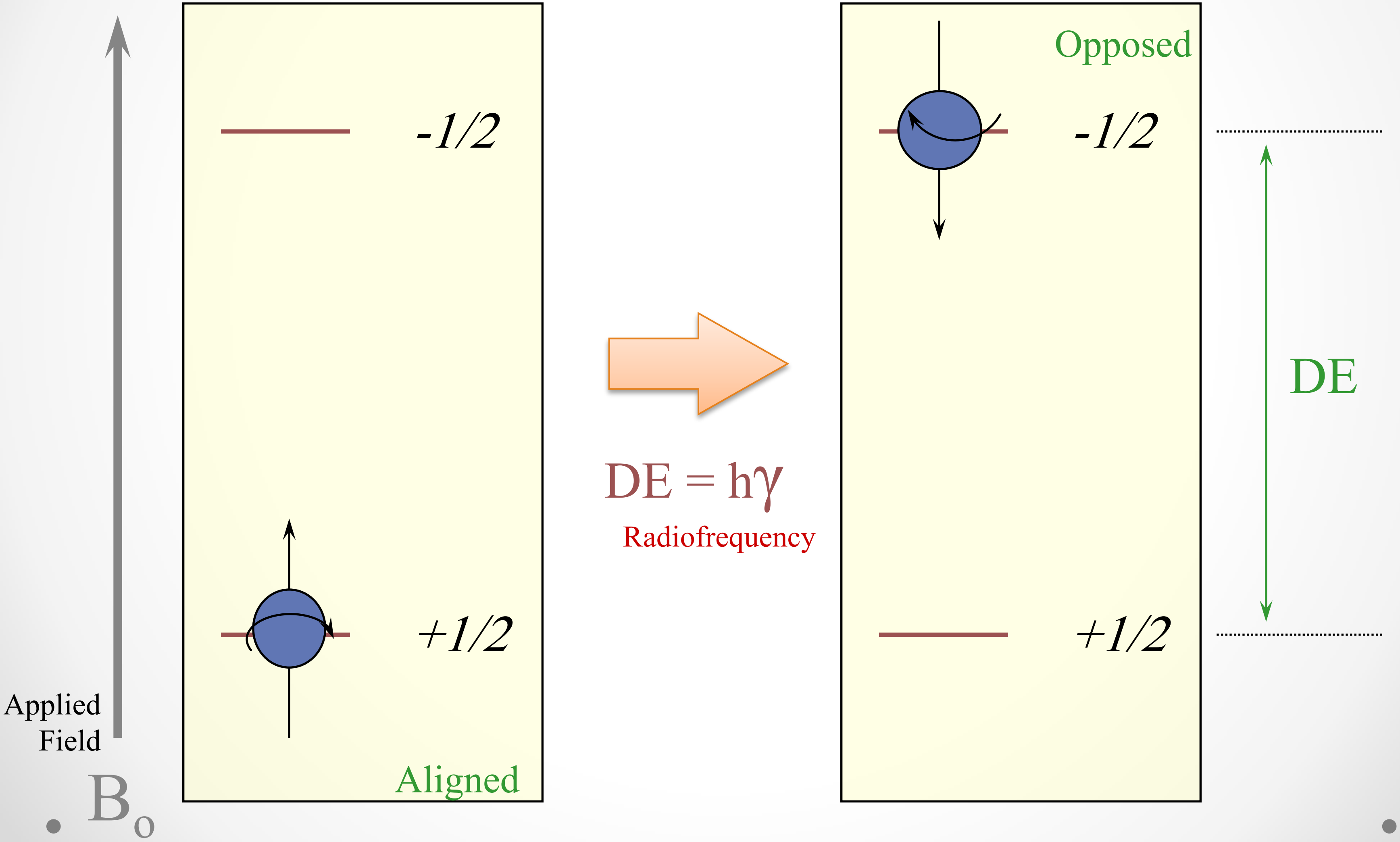
degenerate
at $B_o = 0$

+ 1/2

B_o

increasing magnetic field strength

Absorption of Energy



Applied Field

B_o

-1/2

+1/2

Aligned

$DE = h\gamma$

Radiofrequency

Opposed

-1/2

+1/2

DE

The Larmor Equation!!!

$\Delta E = kB_o = h\nu$ can be transformed into

frequency of the incoming radiation that will cause a transition

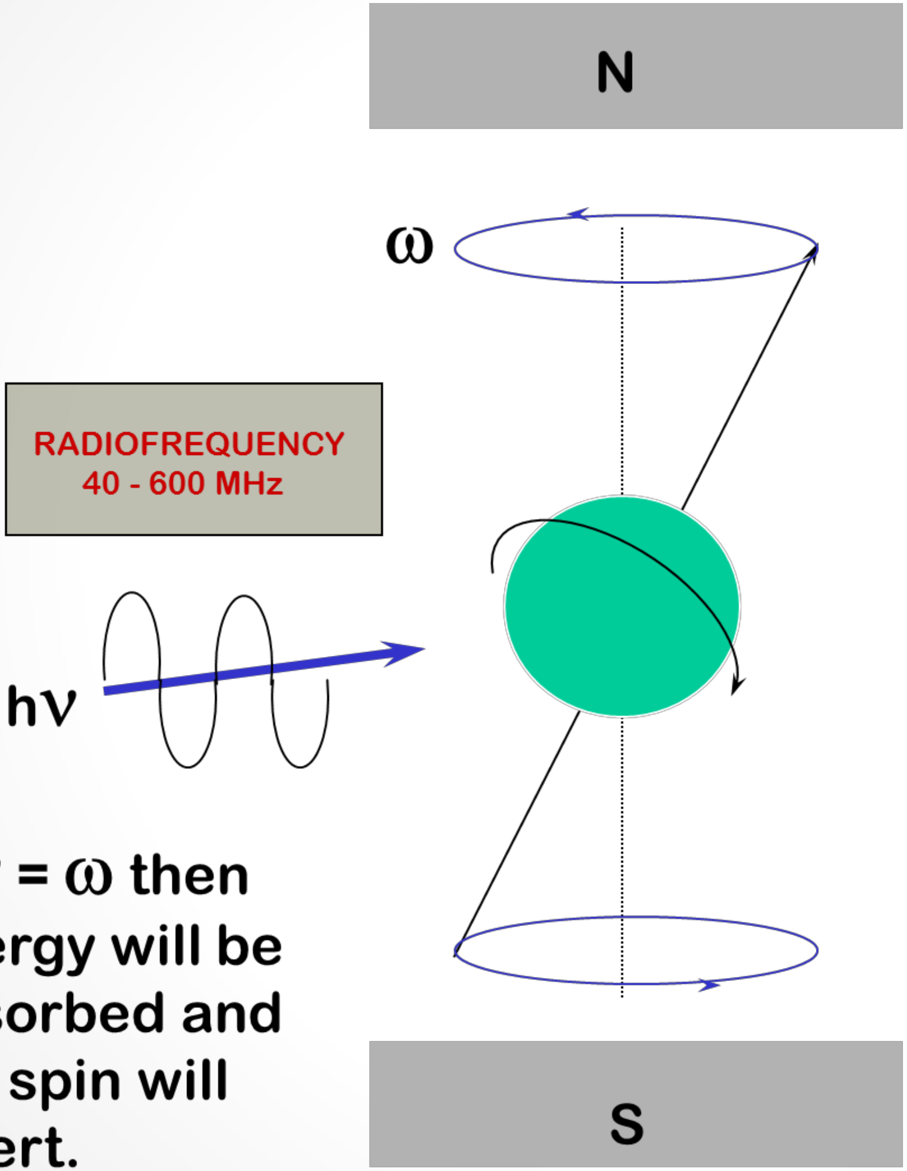
$$\nu = \left(\frac{\gamma}{2\pi}\right) B_o$$

gyromagnetic ratio γ

strength of the magnetic field

γ is a constant which is different for each atomic nucleus (H, C, N, etc)

The “Resonance” Phenomenon



Nuclei precess at frequency ω when placed in a strong magnetic field.

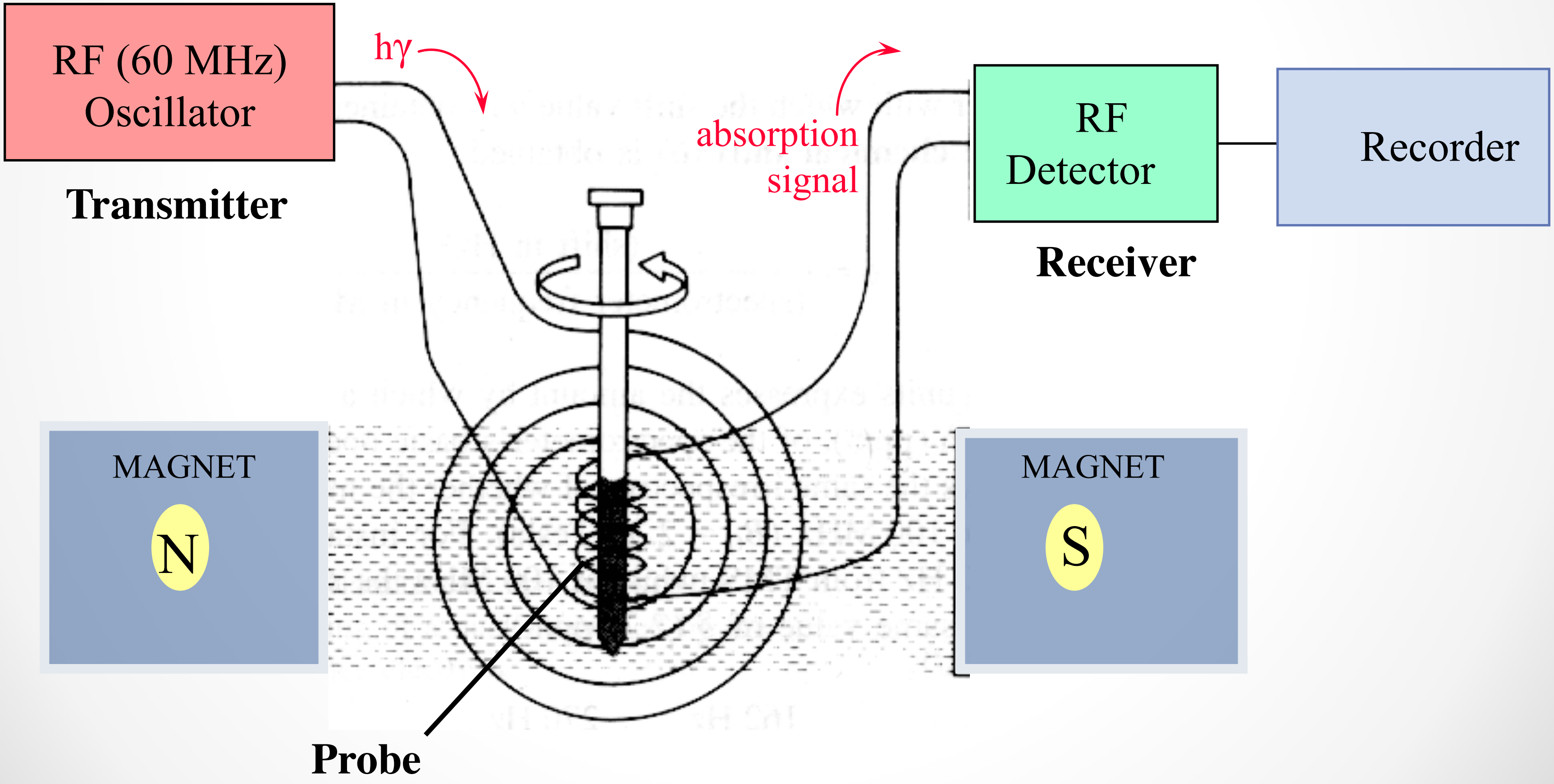
If ν = ω then energy will be absorbed and the spin will invert.

NUCLEAR MAGNETIC RESONANCE

NMR

NMR Spectrometers

1- The Continuous-Wave (CW) Instruments



RF (60 MHz) Oscillator

Transmitter

hγ

absorption signal

RF Detector

Receiver

Recorder

MAGNET

N

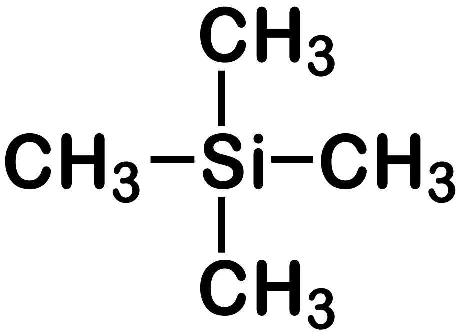
MAGNET

S

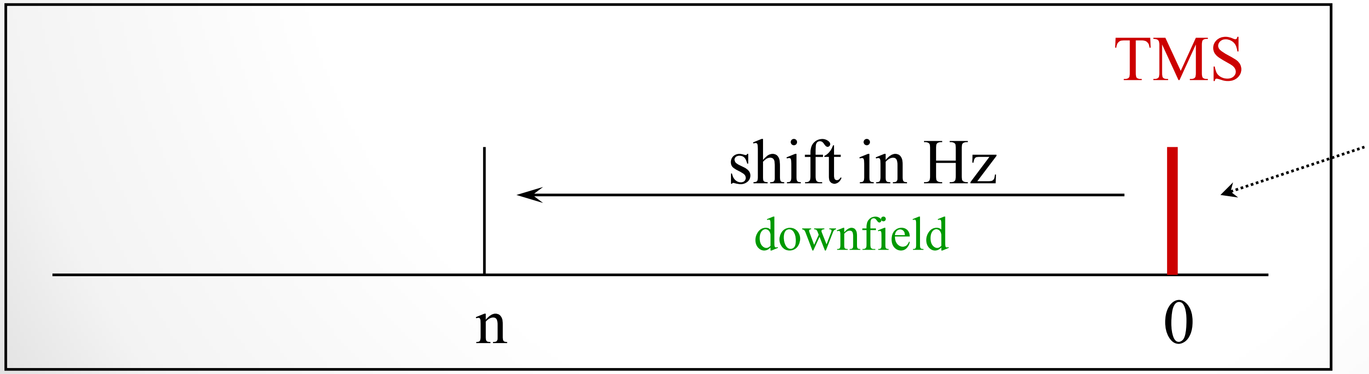
Probe

Peaks are Measured Relative to TMS (Tetramethylsilane)

Reference compound



$$\begin{array}{c} CH_3 \\ | \\ CH_3-Si-CH_3 \\ | \\ CH_3 \end{array}$$

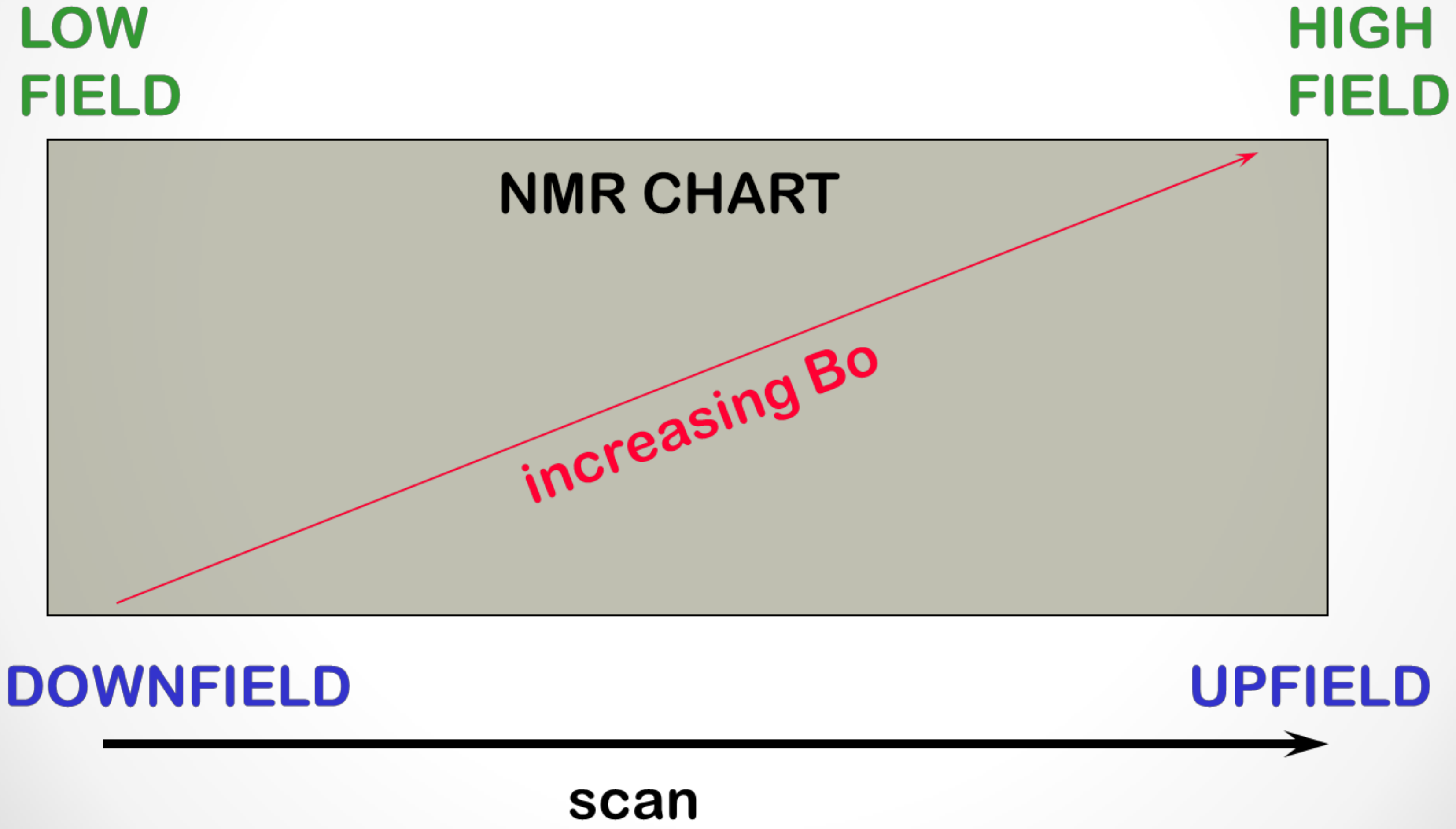


Chemists originally thought no other compound would come at a higher field than TMS.

Solvents

Solvent		δ value
Tetrachlorocarbon	CCl_4	-
Carbon disulfide	CS_2	-
Acetone	$(CD_3)_2CO$	2.0
Dimethysulfoxide	$(CD_3)_2SO$	2.0
Acetonitrile	CD_3CN	2.0
Water	D_2O	5.0
Chloroform	$CDCl_3$	7.2
Benzene	C_6D_6	7.3

IN THE CLASSICAL NMR EXPERIMENT THE INSTRUMENT SCANS FROM “LOW FIELD” TO “HIGH FIELD”



LOW FIELD

HIGH FIELD

NMR CHART

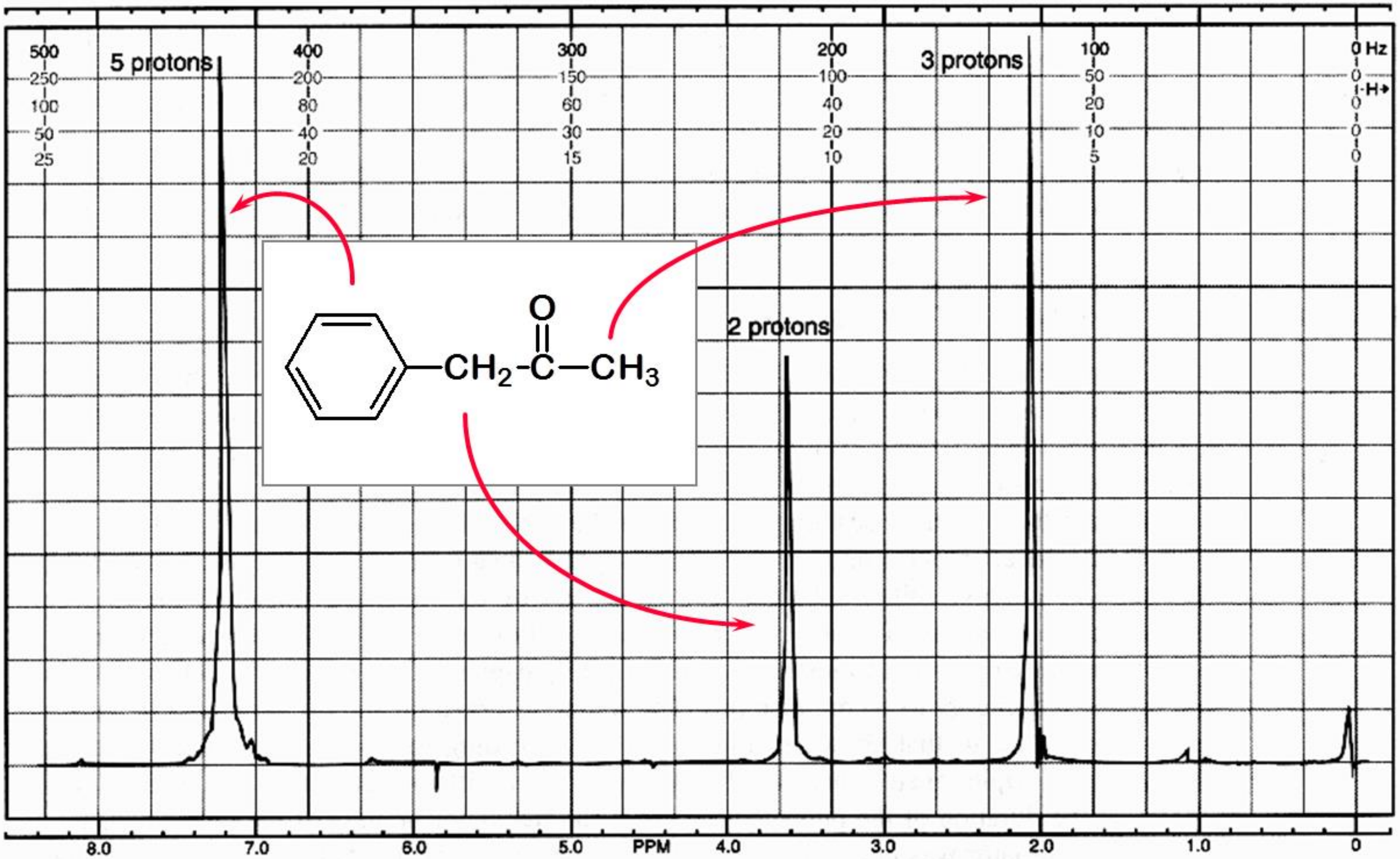
increasing Bo

DOWNFIELD

UPFIELD

scan

NMR Spectrum of Phenylacetone

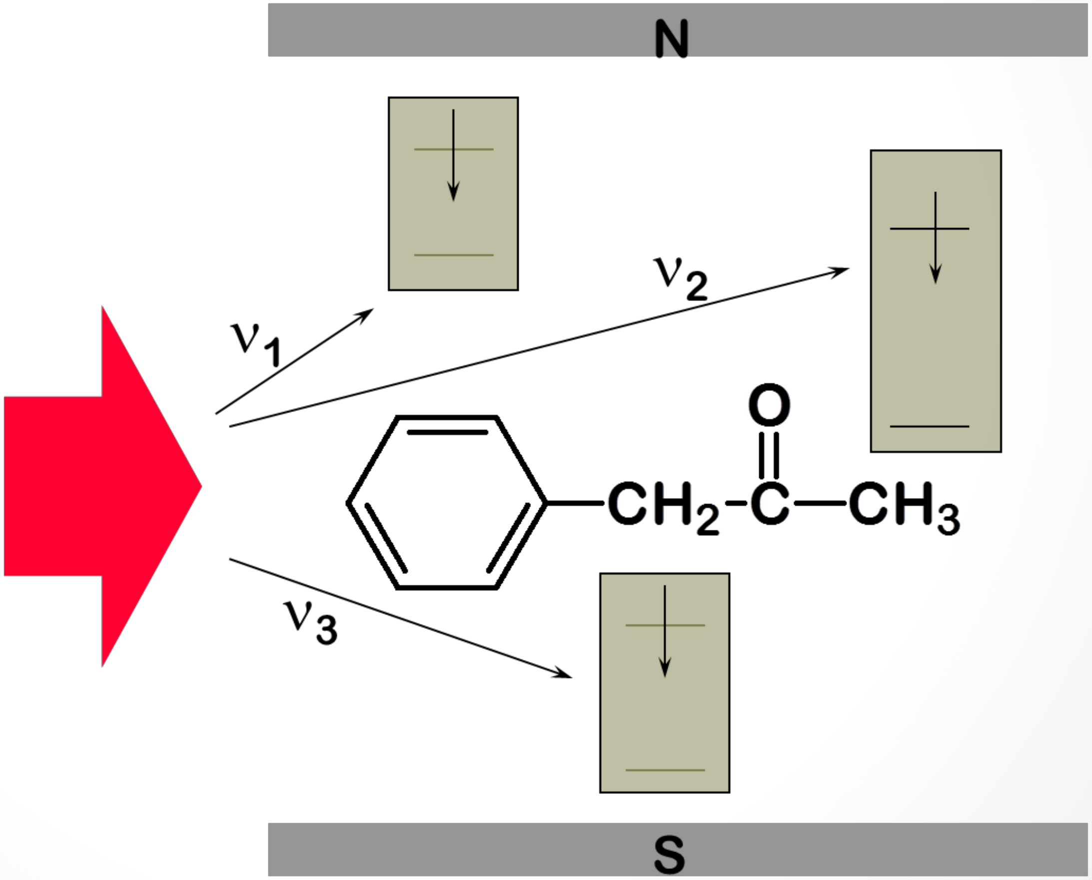


NMR Spectrometers
2- Fourier Transform (FT) Instruments

PULSED EXCITATION

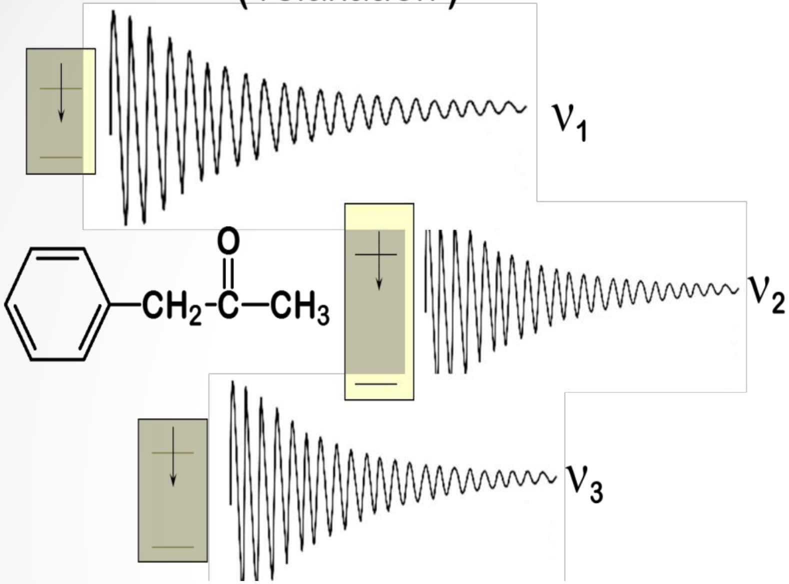
BROADBAND RF PULSE

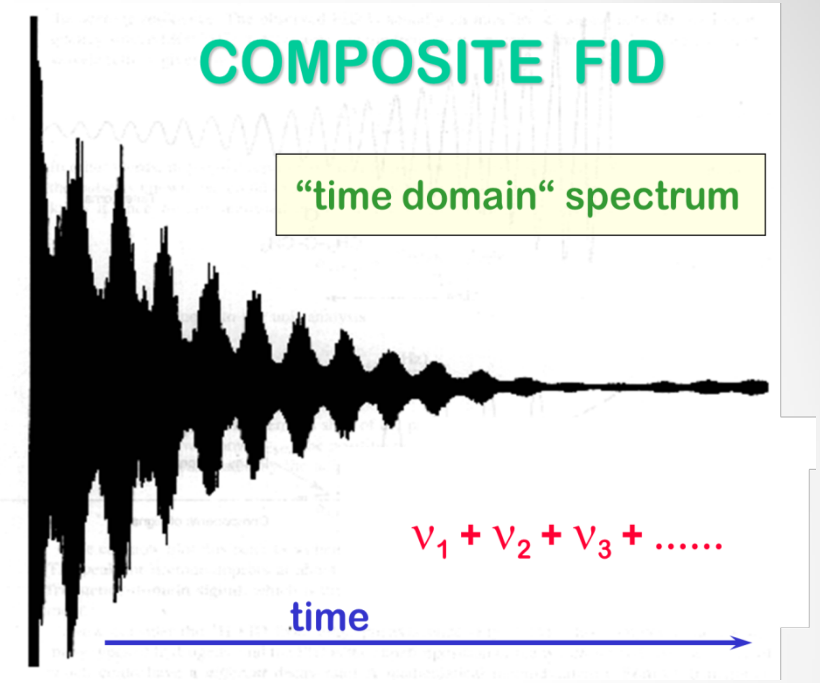
contains a range of frequencies ($\nu_1 \ldots\ldots \nu_n$)



All types of hydrogen are excited simultaneously with the single RF pulse.

FREE INDUCTION DECAY
(relaxation)





A mathematical technique that resolves a complex FID signal into the individual frequencies that add together to make it.

TIME DOMAIN converted to → **FREQUENCY DOMAIN**

FID NMR SPECTRUM

DOMAINS ARE MATHEMATICAL TERMS

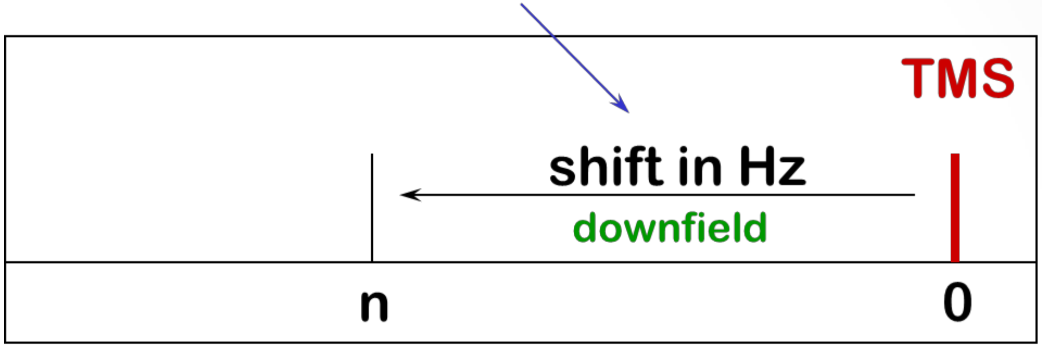
NMR—The Spectrum

There are three kinds each of which we will consider each of these separately:

- Position of Signals (Chemical shift)
- Integrations
- Coupling constant

1- Position of Signals (Chemical shift)

- The shift observed for a given proton in Hz also depends on the frequency of the instrument used.



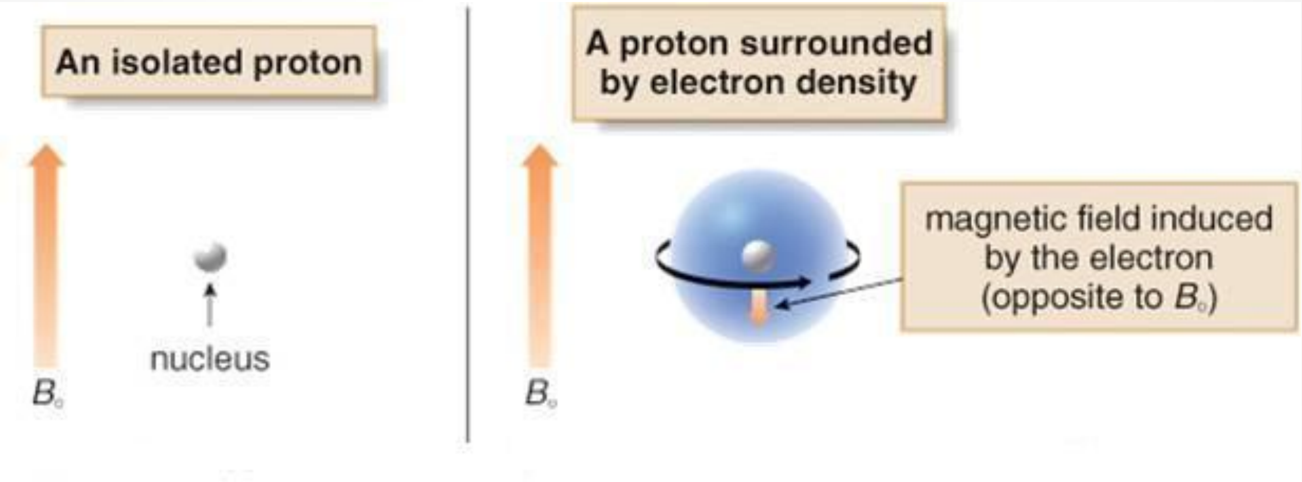
Higher frequencies = larger shifts in Hz.

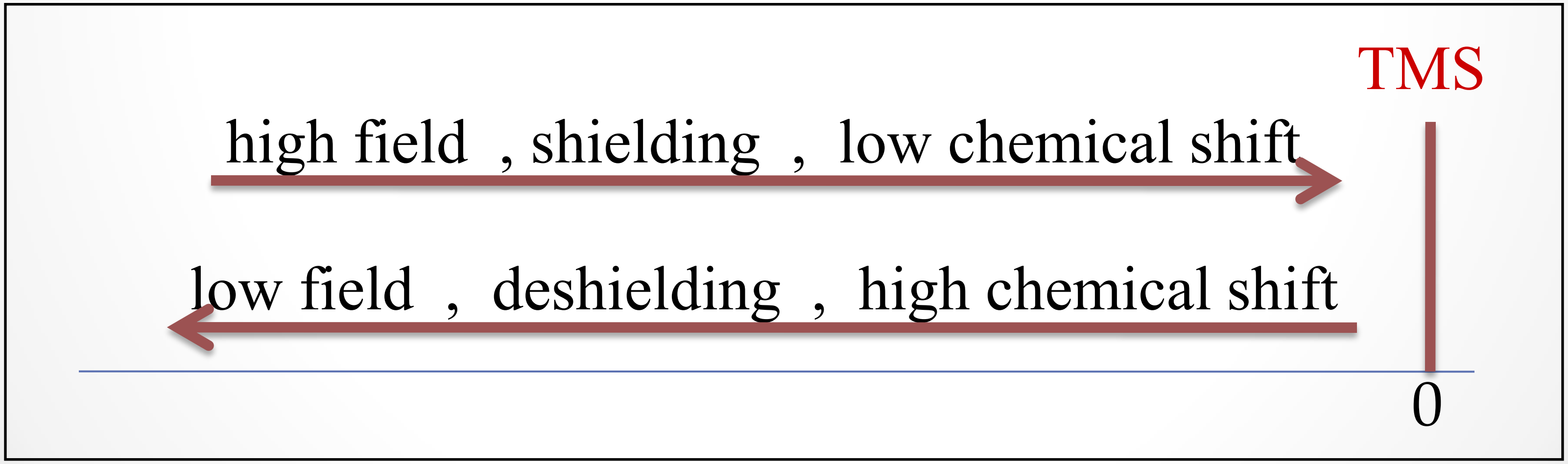
- We can adjust the shift to a field-independent value, the “chemical shift” in the following way:

$$\text{Chemical shift} = \delta = \frac{\text{shift in Hz}}{\text{spectrometer frequency in MHz}} = \textbf{ppm}$$

Protons Differ in Their Shielding

- All different types of protons in a molecule have a different amounts of shielding.
- They all respond differently to the applied magnetic field and appear at different places in the spectrum.
- This is why an NMR spectrum contains useful information (different types of protons appear in predictable places).





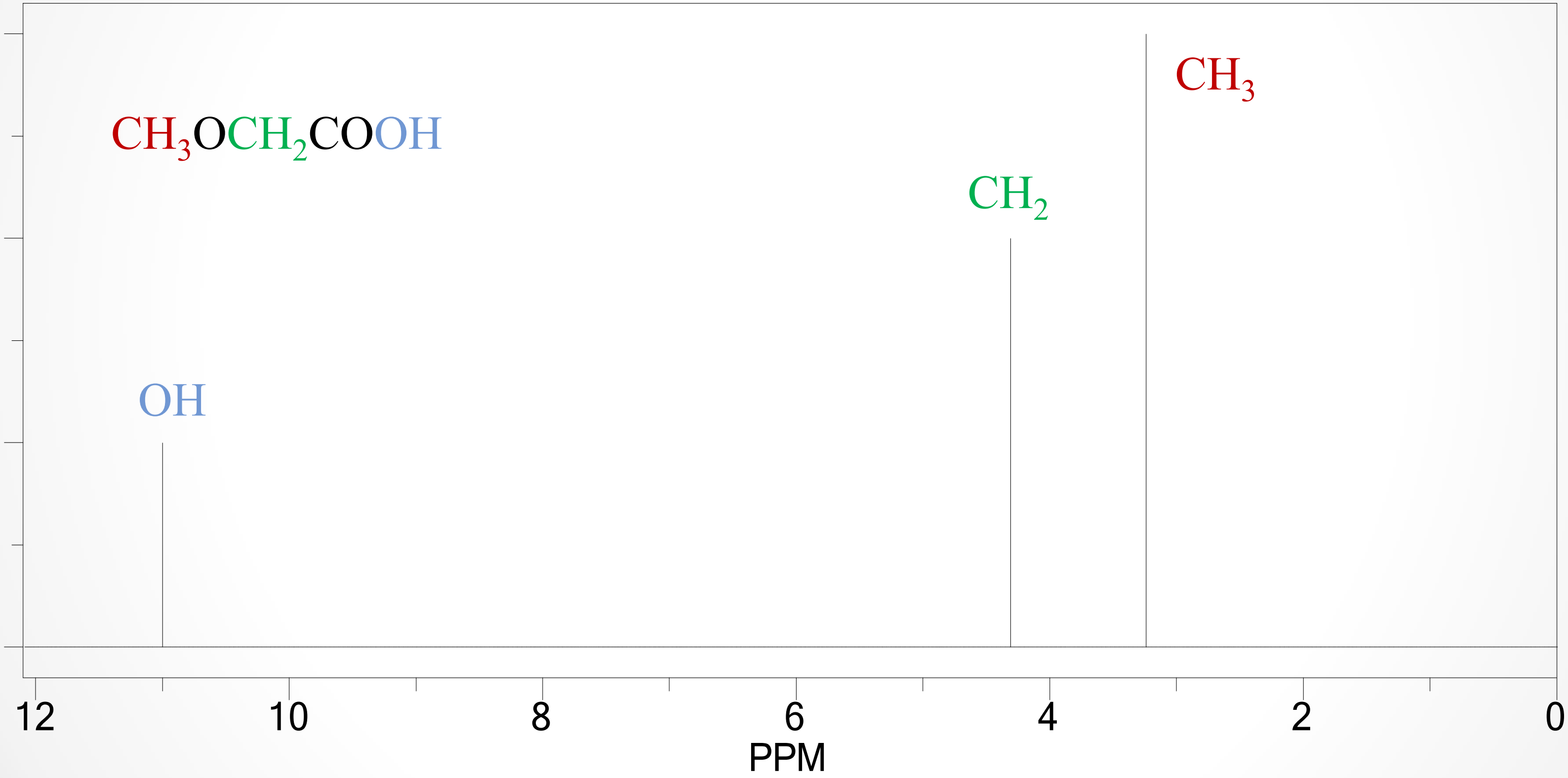
TMS

high field , shielding , low chemical shift

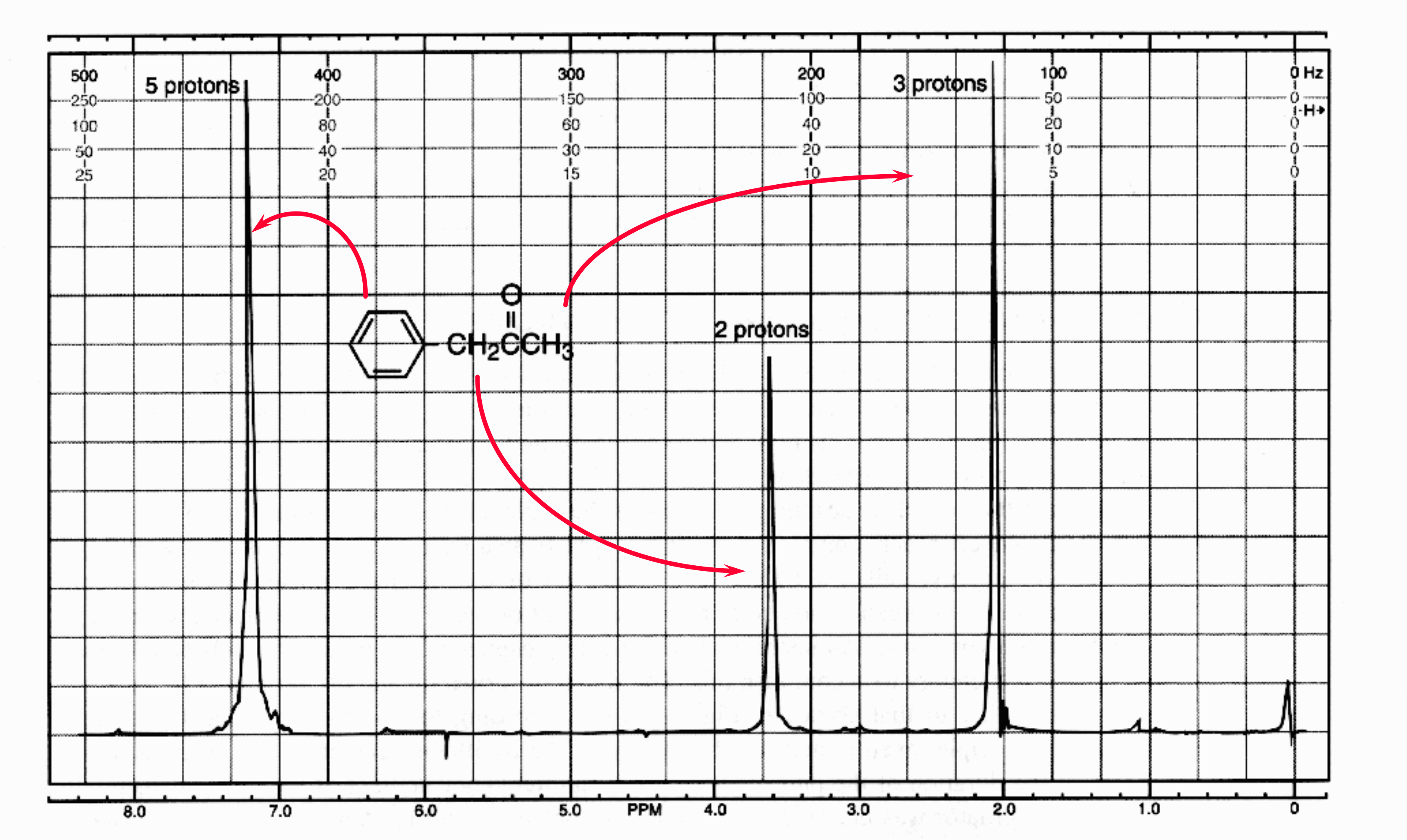
low field , deshielding , high chemical shift

0

NMR Spectrum of Methylacetic acid



NMR Spectrum of Phenylacetone

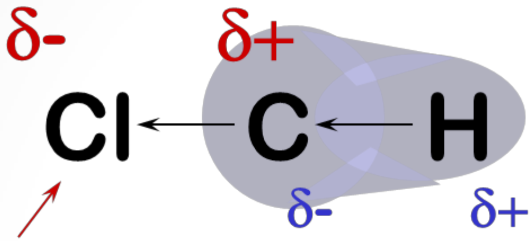


Factors Influencing Chemical Shifts

- Three major factors account for the resonance positions (on the ppm scale) of most protons.

1. Deshielding by electronegative elements.
2. Anisotropic fields usually due to pi-bonded electrons in the molecule.
3. Deshielding due to hydrogen bonding.

1. Deshielding by electronegative elements.



electronegative
element

Chlorine "deshields" the proton, that is, it takes valence electron density away from carbon, which in turn takes more density from hydrogen deshielding the proton.

NMR CHART

"deshielded" protons appear at low field

highly shielded protons appear at high field

←

deshielding moves proton resonance to lower field

Electronegativity Dependence of 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	$(CH_3)_4Si$
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

TMS

deshielding increases with the electronegativity of atom X

Substitution Effects on Chemical Shift

most
deshielded

$CHCl_3$	CH_2Cl_2	CH_3Cl	
7.27	5.30	3.05	ppm

The effect increases with greater numbers of electronegative atoms.

most
deshielded

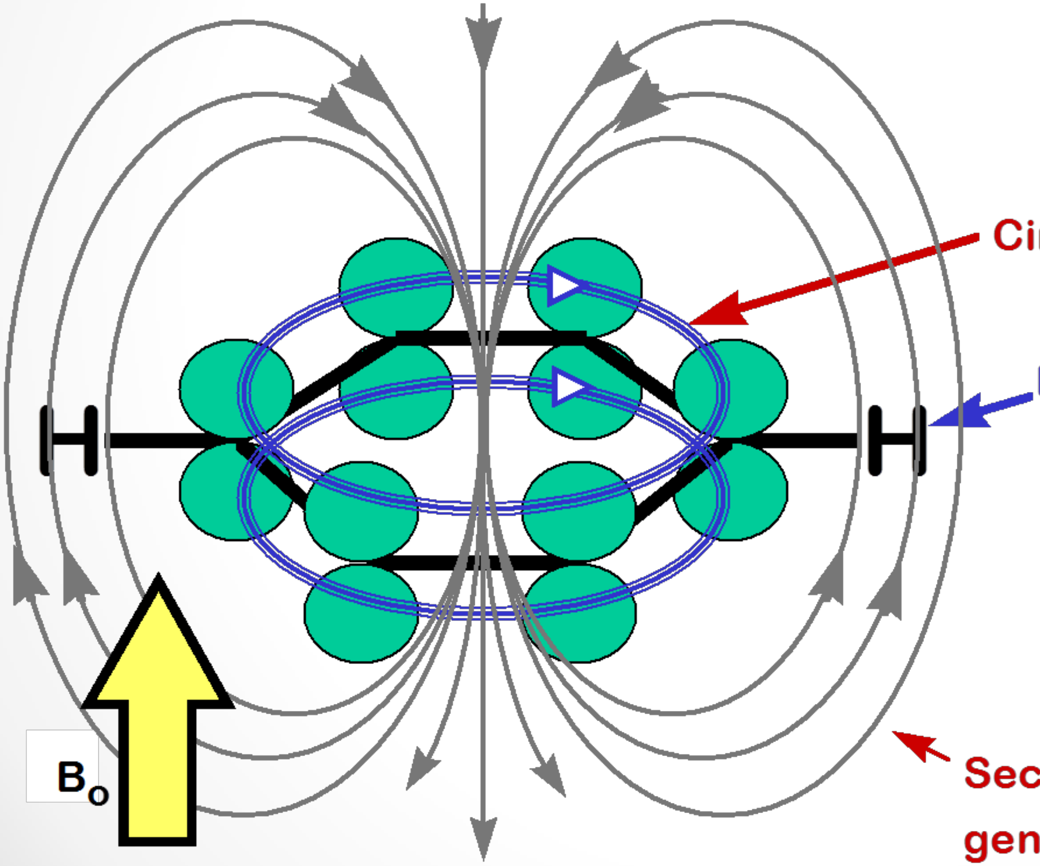
$-CH_2-Br$	$-CH_2-CH_2Br$	$-CH_2-CH_2CH_2Br$	
3.30	1.69	1.25	ppm

The effect decreases with incresing distance.

2. Anisotropic fields

The presence of a nearby pi bond or pi system greatly affects the chemical shift.

Benzene rings have the greatest effect

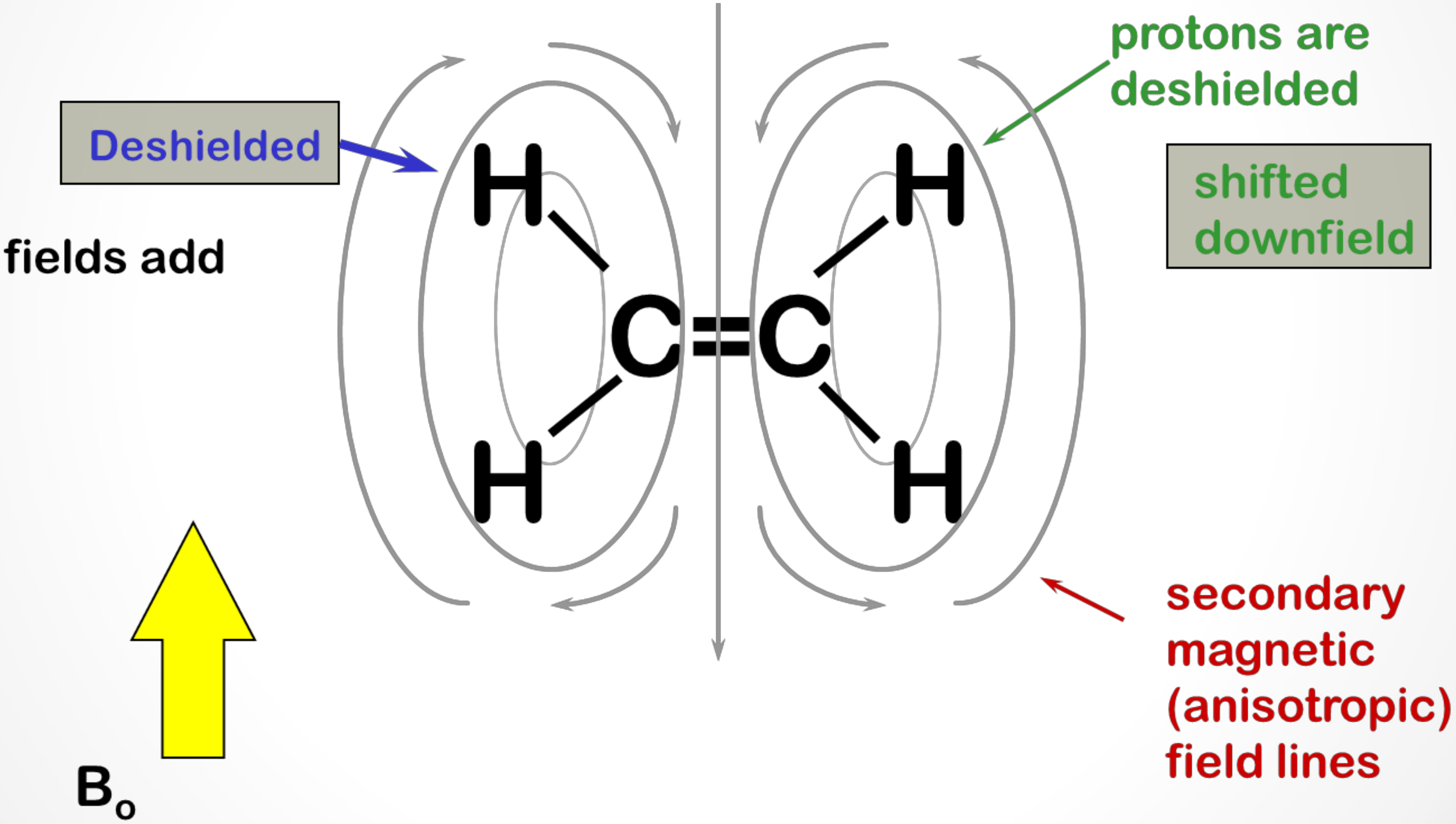


Circulating π electrons

Deshielded

Secondary magnetic field generated by circulating π electrons deshields aromatic protons

Anisotropic fields in an Alkene



Deshielded

fields add

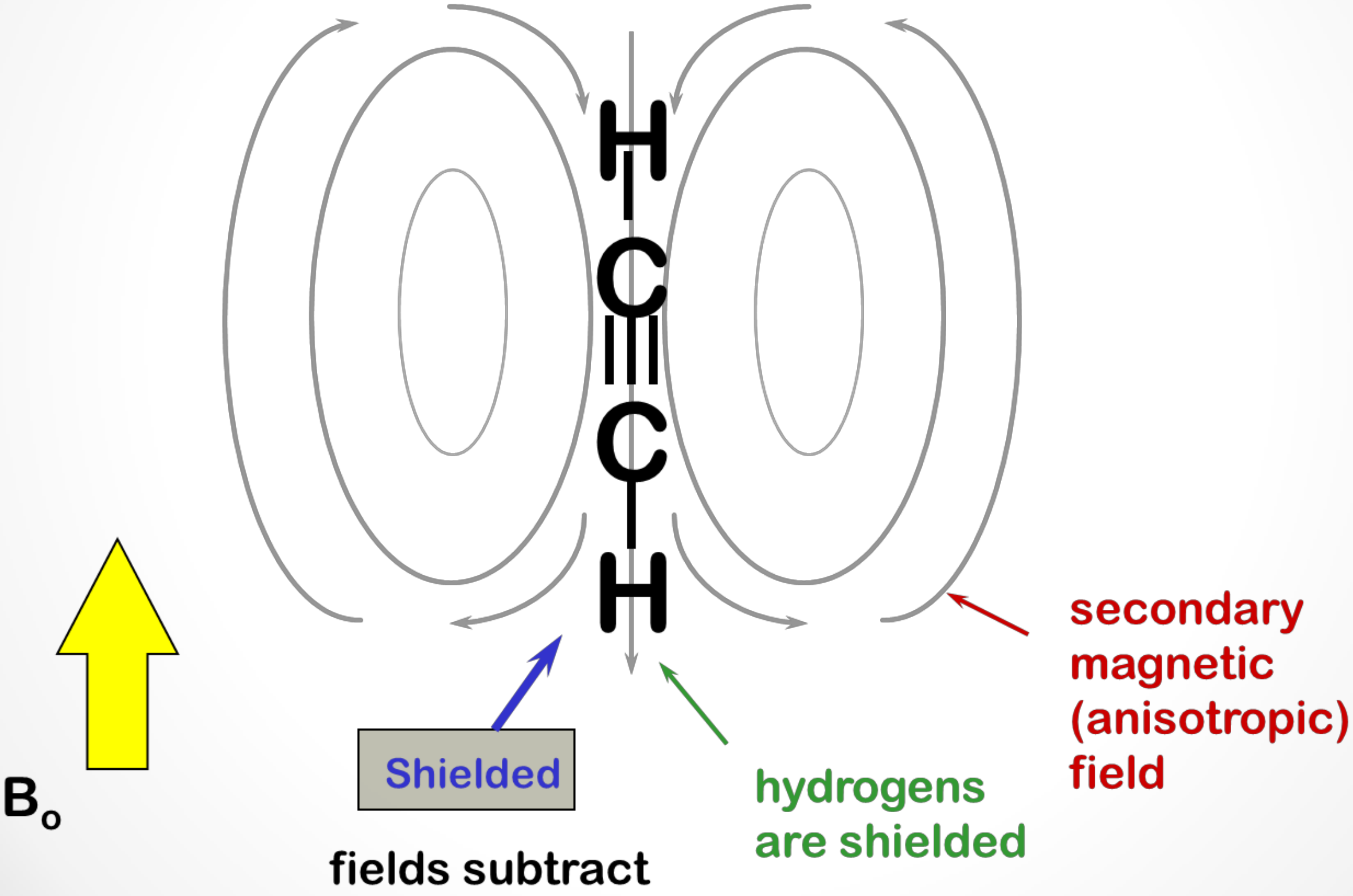
B_o

protons are deshielded

shifted downfield

secondary magnetic (anisotropic) field lines

Anisotropic fields in an Alkyne



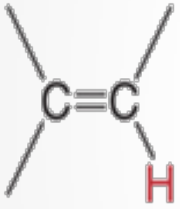
B_o

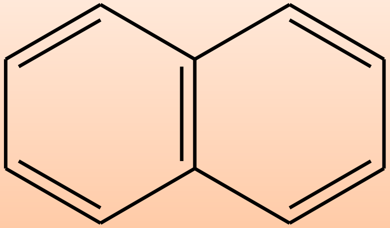
Shielded

fields subtract

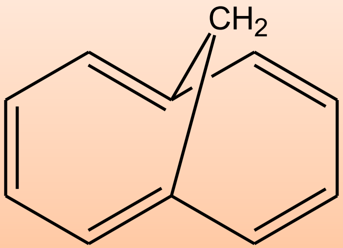
hydrogens are shielded

secondary magnetic (anisotropic) field

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



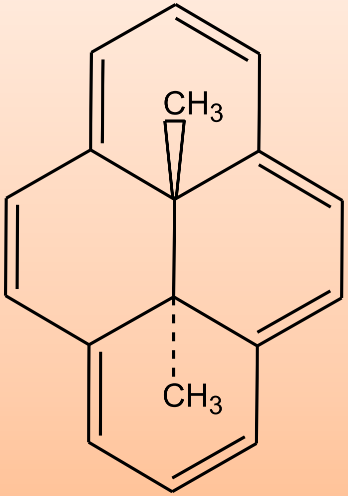
Naphthalene



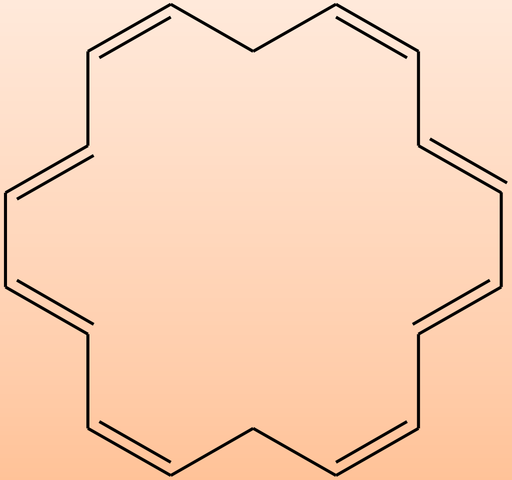
Bicyclo[4.4.1]undeca-1(10),2,4,6,8-pentaene

>7.27δ

CH_2 at ~ -1.2 δ



10b,10c-Dimethyl-10b,10c-dihydro-pyrene



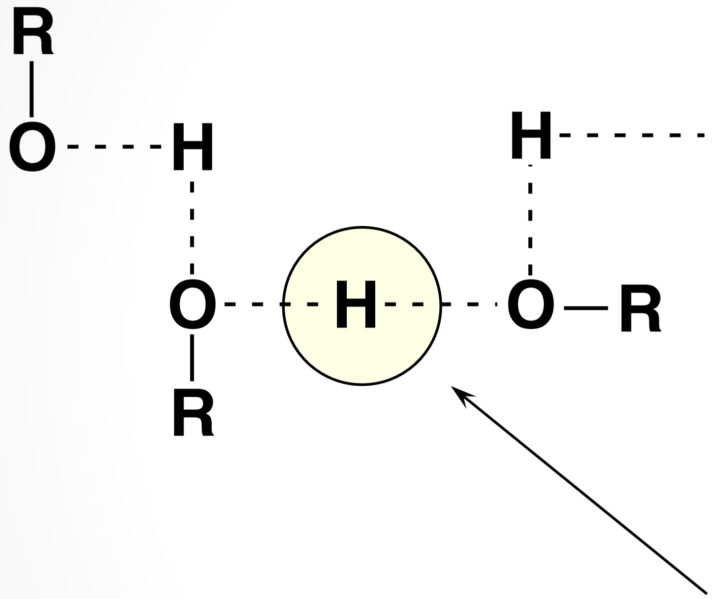
Cyclooctadecanonaene

2CH_3 at ~ -4.2 δ

Inner hydrogens ~ -1.8 δ
Outer hydrogens ~ 8.9 δ

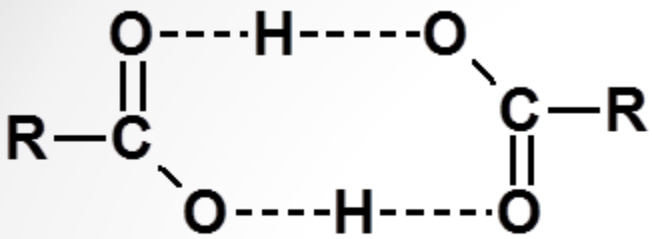
3. Deshielding due to hydrogen bonding

The chemical shift depends on how much hydrogen bonding is taking place.



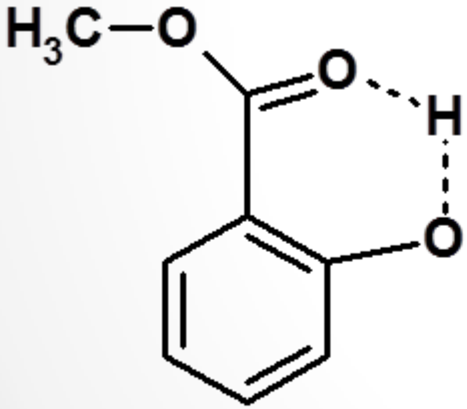
Alcohols vary in chemical shift from 0.5 ppm (free OH) to about 5.0 ppm (lots of H bonding).

Hydrogen bonding lengthens the O-H bond and reduces the valence electron density around the proton - it is deshielded and shifted downfield in the NMR spectrum.



Carboxylic acids have strong hydrogen bonding – they form dimers.

With carboxylic acids the O-H absorptions are found between 10 and 12 ppm very far downfield



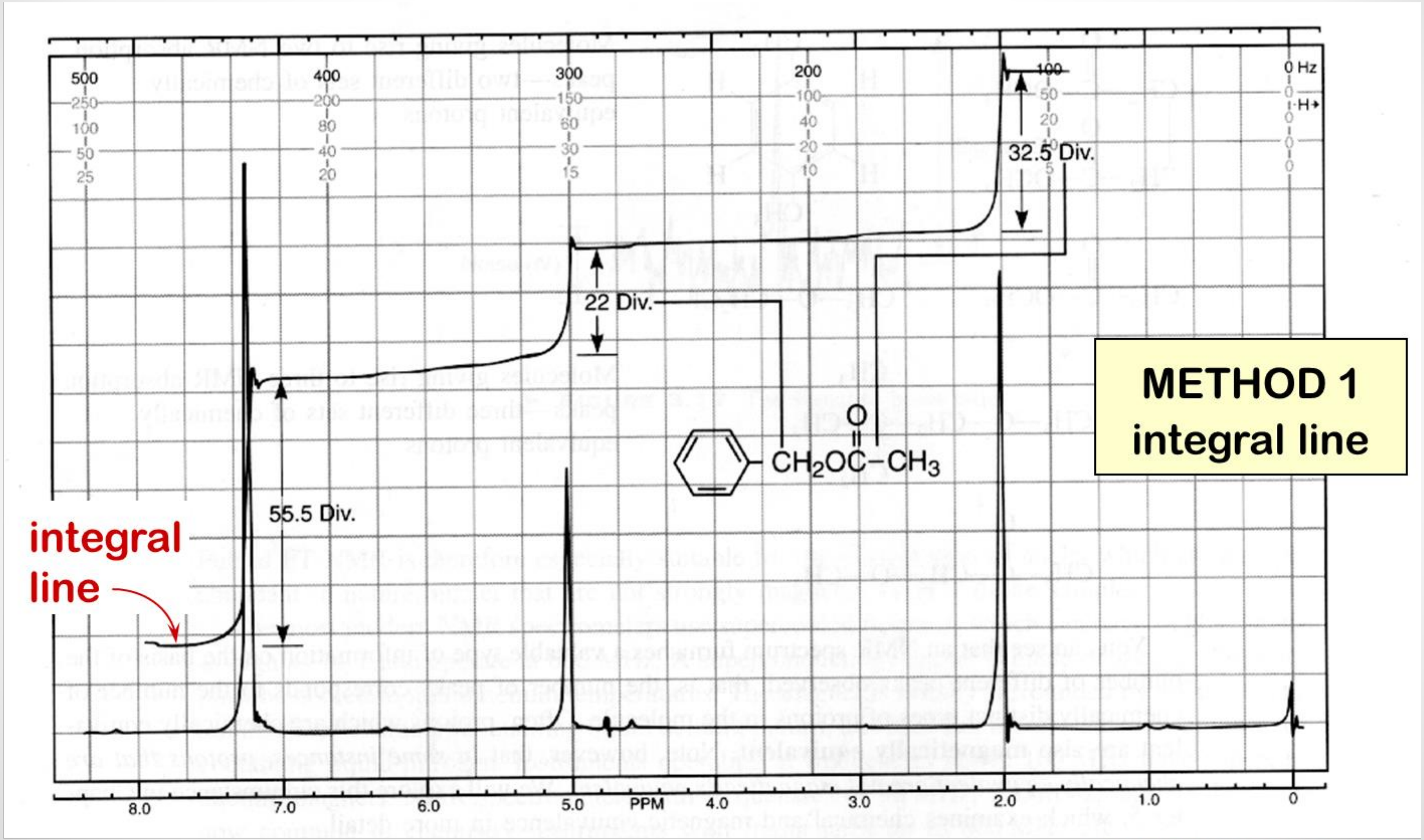
In methyl salicylate, which has strong internal hydrogen bonding, the NMR absorption for O-H is at about 14 ppm, very far downfield.

2- Integration of Peak

- The NMR spectrum can also tell the relative numbers of each type of hydrogen by a process called Integration.

Integration = determination of the area under a peak

The integral line rises an amount proportional to the number of H in each peak



METHOD 1
integral line

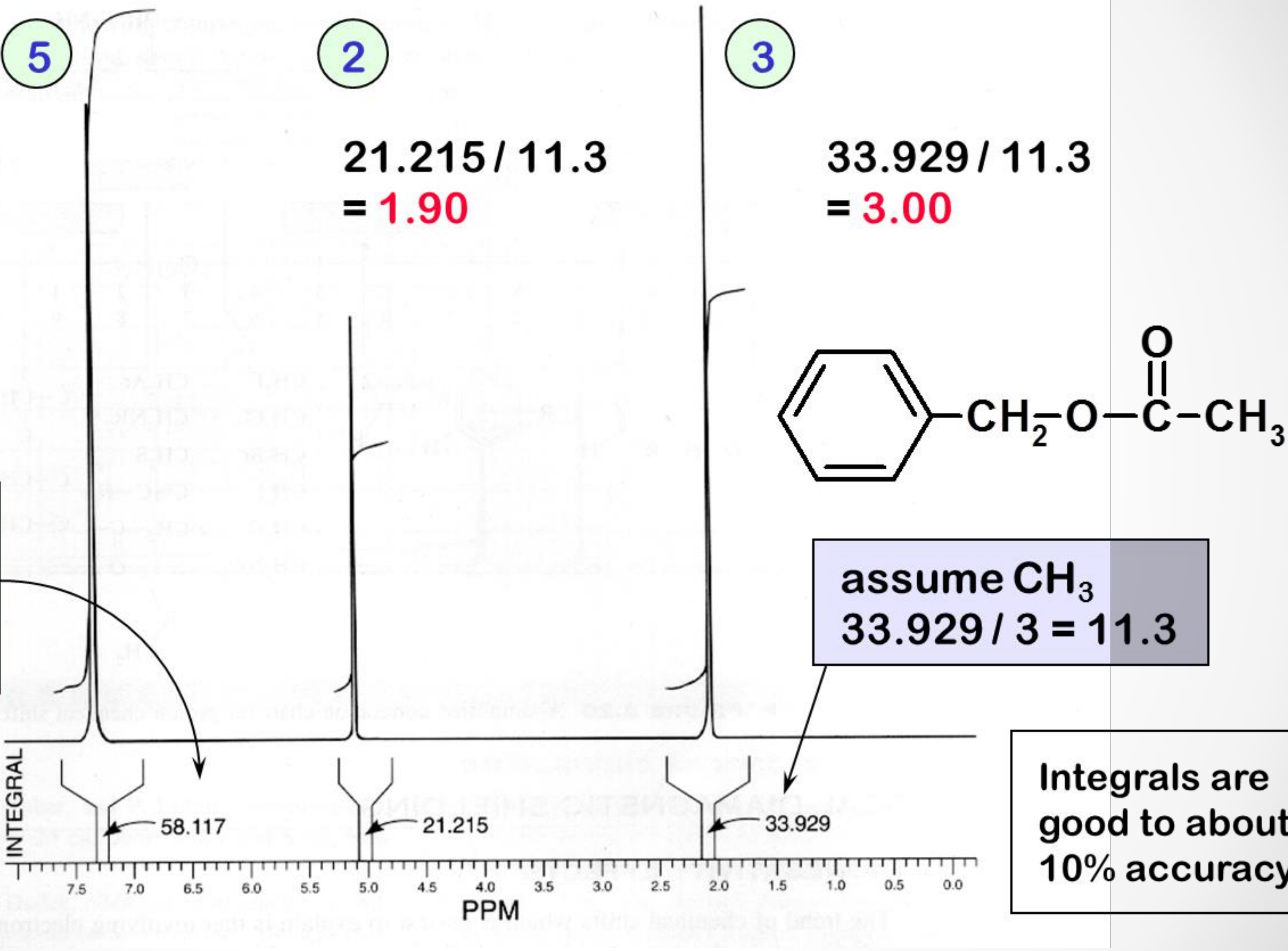
integral line

55 : 22 : 33 = 5 : 2 : 3

simplest ratio of the heights

Modern instruments FT-NMR report the integral as a number

Actually :



⑤ 58.117 / 11.3 = 5.14

② 21.215 / 11.3 = 1.90

③ 33.929 / 11.3 = 3.00

METHOD 2

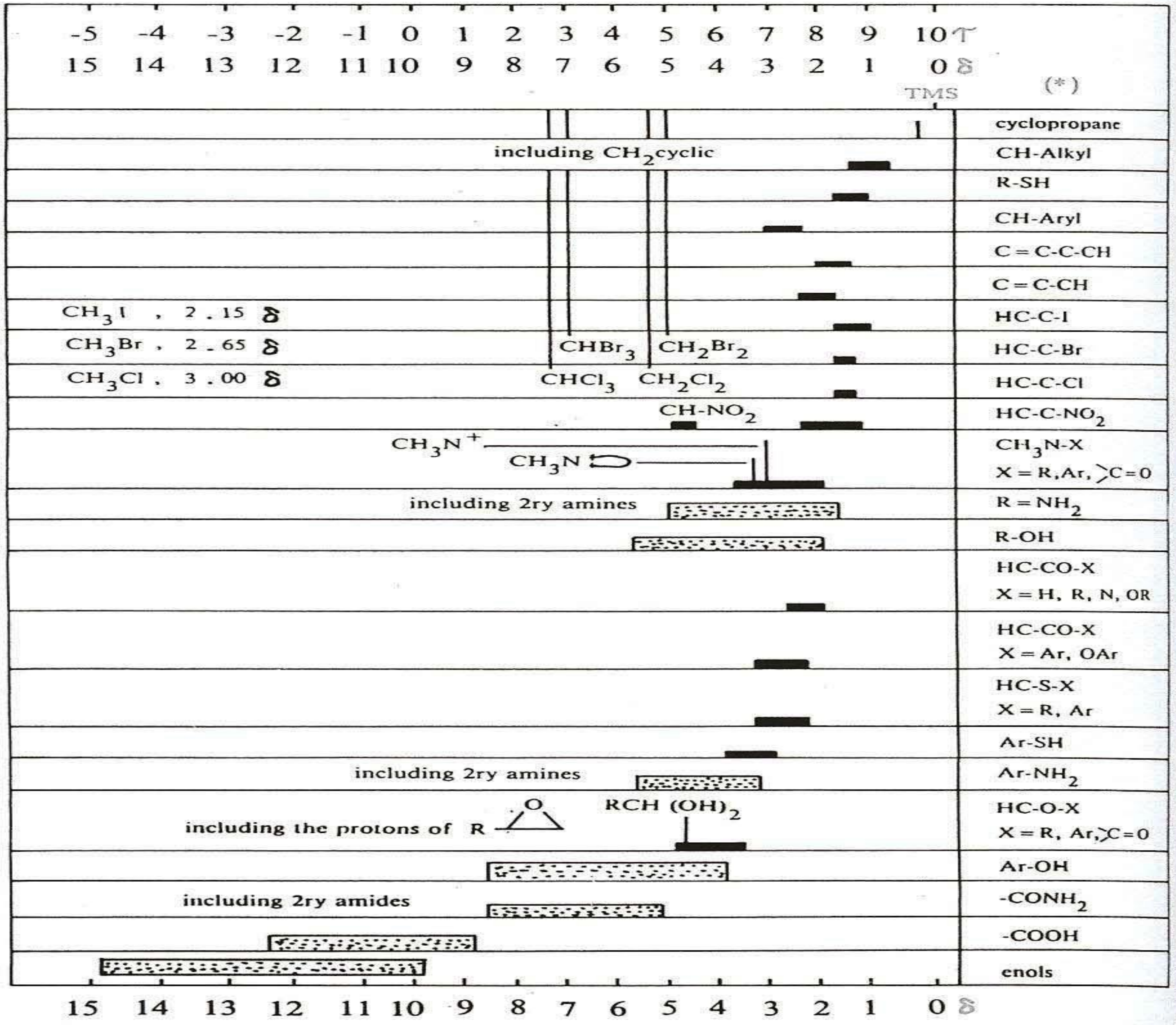
digital integration

assume CH_3
33.929 / 3 = 11.3

Integrals are good to about 10% accuracy.

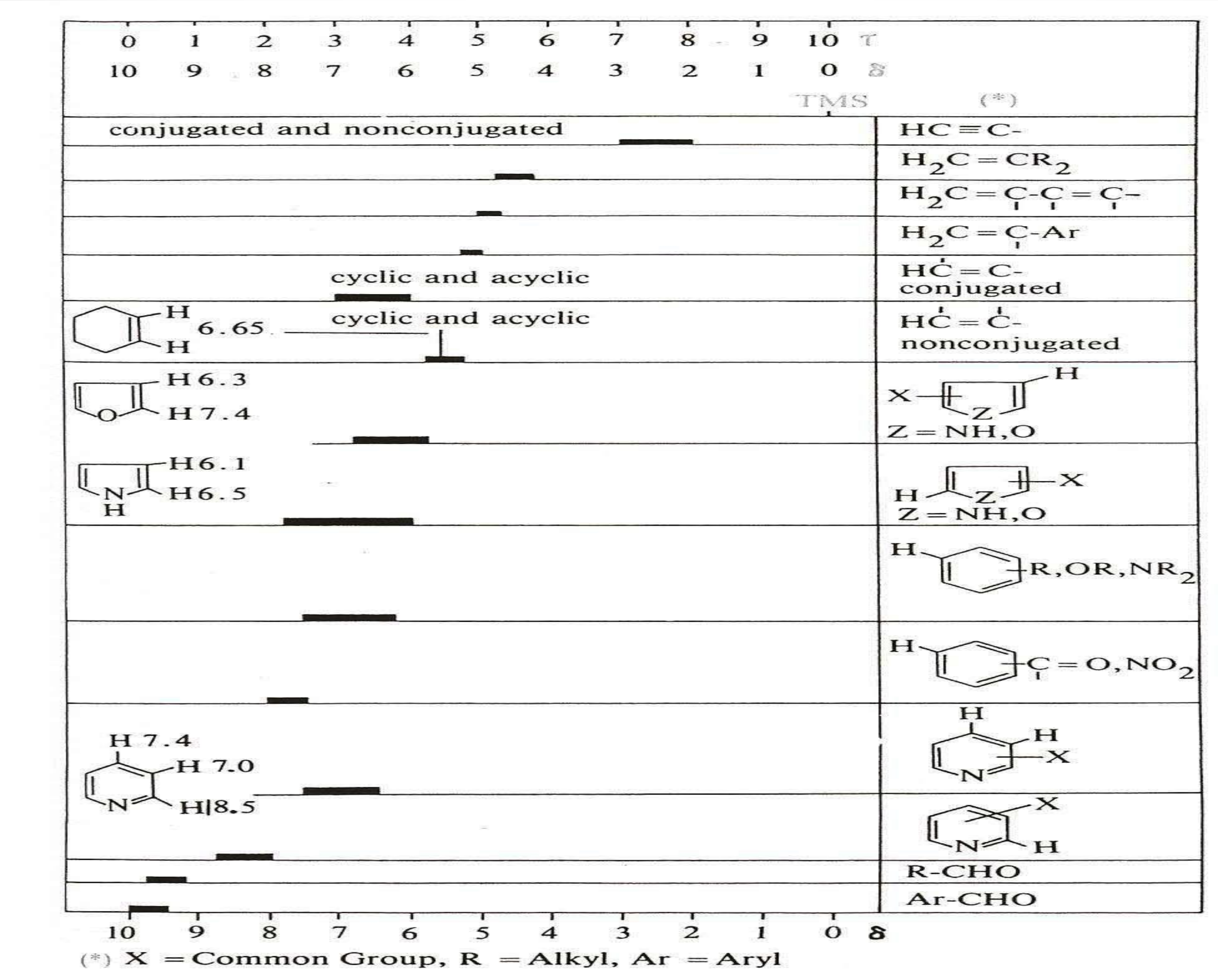
NMR - Position of Signals (Chemical shift values)

Chart .1 Chemical shifts of Protons



(*) R = Alkyl, Ar = Aryl

Chart .2 Chemical shifts of Protons



(*) X = Common Group, R = Alkyl, Ar = Aryl

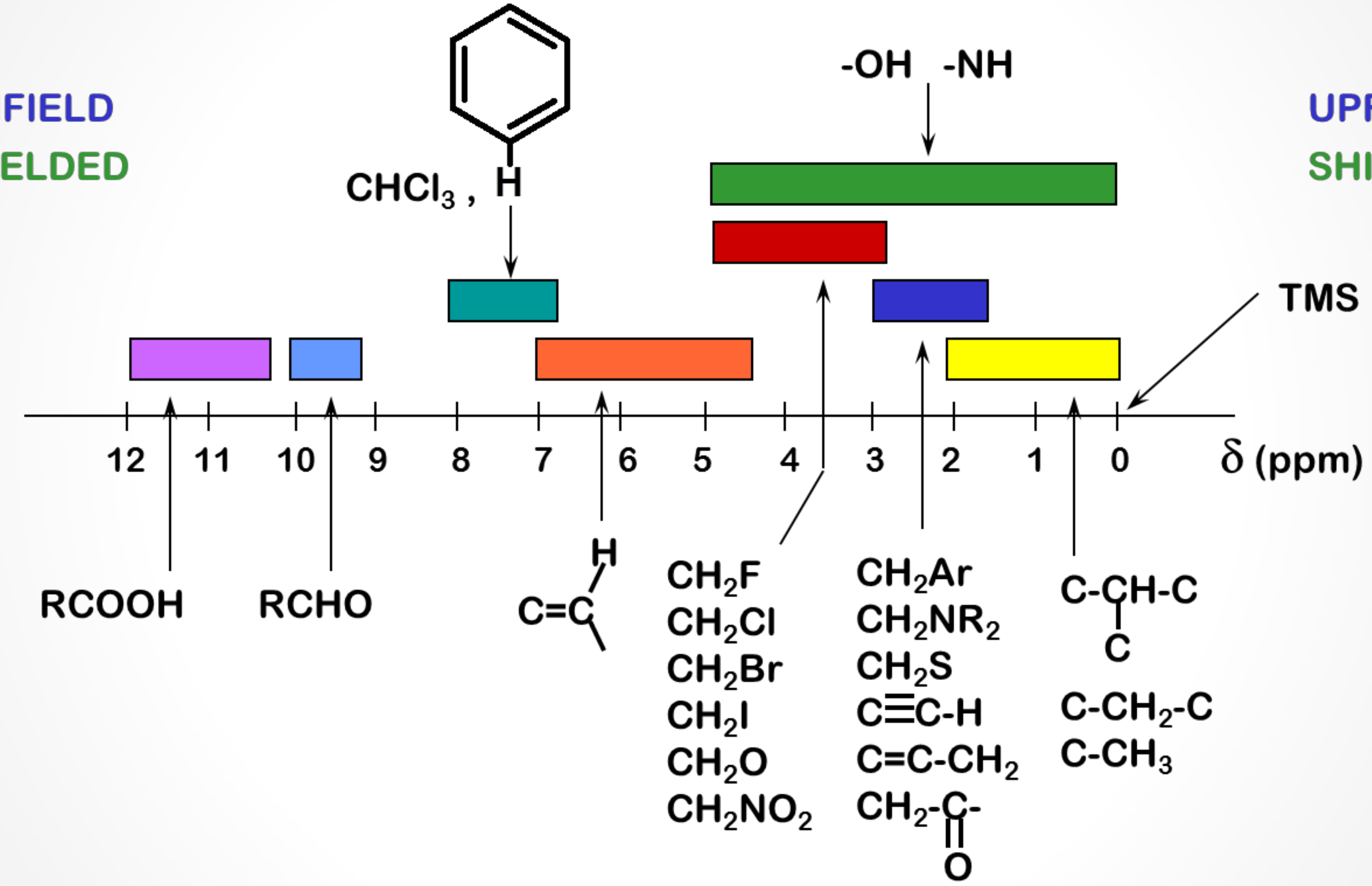
NMR Correlation Chart

DOWNFIELD

DESHIELDED

UPFIELD

SHIELDED



$CHCl_3$, H

-OH -NH

TMS

12 11 10 9 8 7 6 5 4 3 2 1 0 δ (ppm)

RCOOH

RCHO

H
C=C

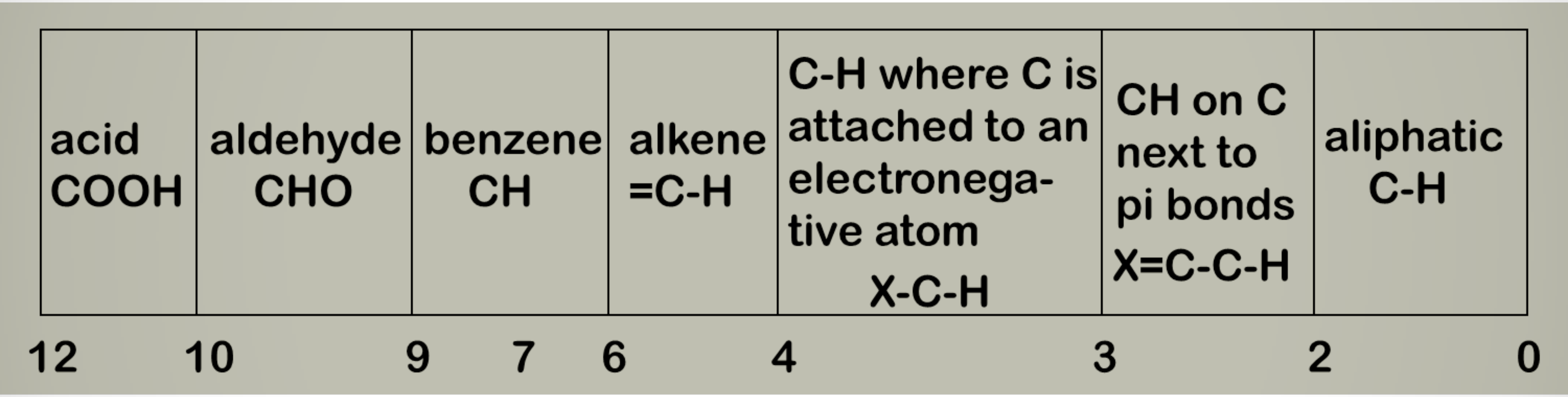
CH_2F
CH_2Cl
CH_2Br
CH_2I
CH_2O
CH_2NO_2

CH_2Ar
CH_2NR_2
CH_2S
C≡C-H
C=C-CH_2
CH_2-C-
O

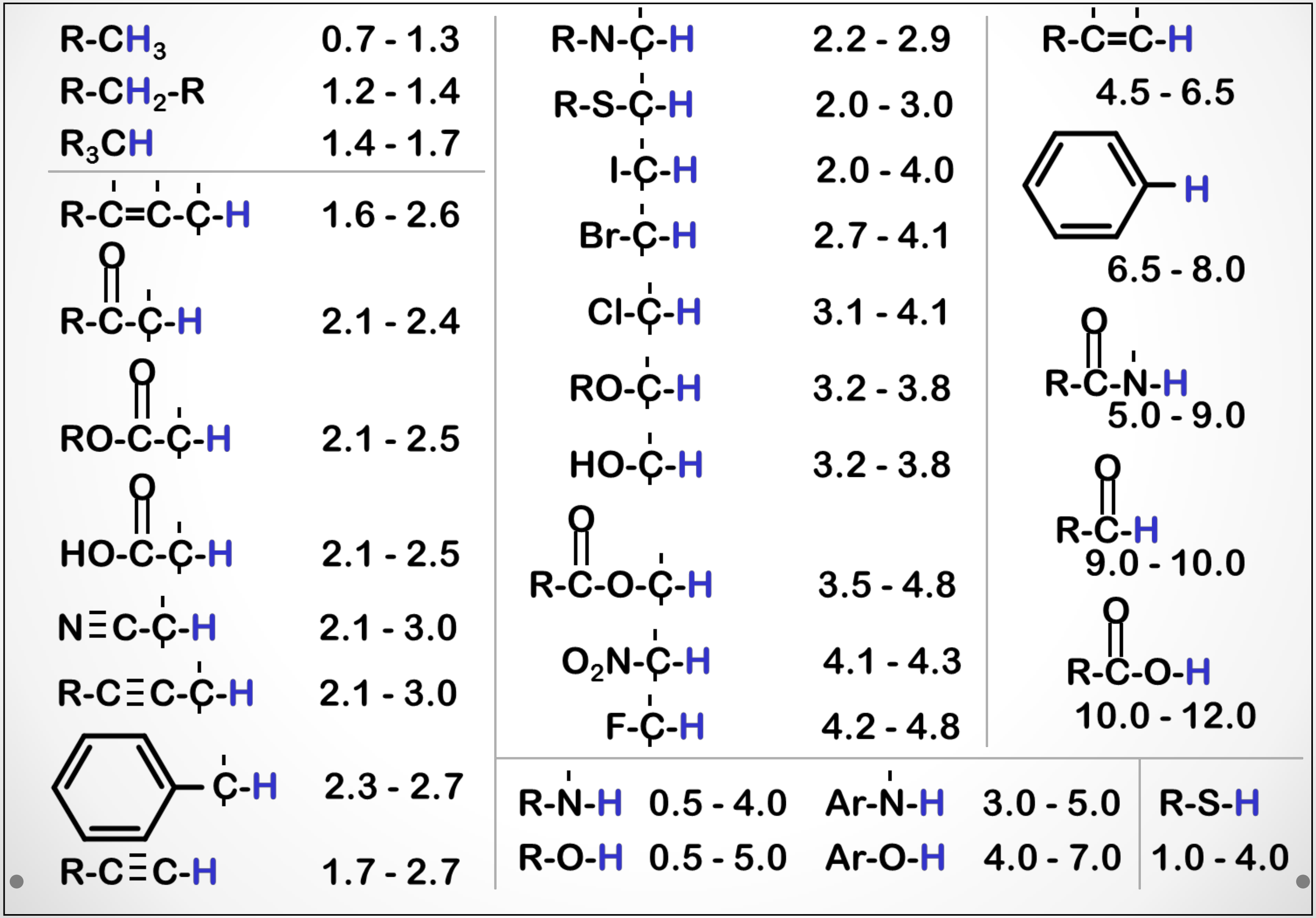
C-CH-C
C

C-CH_2-C
C-CH_3

It is usually sufficient to know what types of Hydrogens come in selected areas of the NMR Chart.



Approximate Chemical Shift Ranges (ppm) for Selected Types of Protons.



$R\text{-}CH_3$	0.7 - 1.3
$R\text{-}CH_2\text{-}R$	1.2 - 1.4
R_3CH	1.4 - 1.7
$R\text{-}C{=}C\text{-}C\text{-}H$	1.6 - 2.6
$R\text{-}C(=O)\text{-}C\text{-}H$	2.1 - 2.4
$RO\text{-}C(=O)\text{-}C\text{-}H$	2.1 - 2.5
$HO\text{-}C(=O)\text{-}C\text{-}H$	2.1 - 2.5
$N{\equiv}C\text{-}C\text{-}H$	2.1 - 3.0
$R\text{-}C{\equiv}C\text{-}C\text{-}H$	2.1 - 3.0
$C_6H_5\text{-}C\text{-}H$	2.3 - 2.7
$R\text{-}C{\equiv}C\text{-}H$	1.7 - 2.7
$R\text{-}N\text{-}C\text{-}H$	2.2 - 2.9
$R\text{-}S\text{-}C\text{-}H$	2.0 - 3.0
$I\text{-}C\text{-}H$	2.0 - 4.0
$Br\text{-}C\text{-}H$	2.7 - 4.1
$Cl\text{-}C\text{-}H$	3.1 - 4.1
$RO\text{-}C\text{-}H$	3.2 - 3.8
$HO\text{-}C\text{-}H$	3.2 - 3.8
$R\text{-}C(=O)\text{-}O\text{-}C\text{-}H$	3.5 - 4.8
$O_2N\text{-}C\text{-}H$	4.1 - 4.3
$F\text{-}C\text{-}H$	4.2 - 4.8
$R\text{-}C{=}C\text{-}H$	4.5 - 6.5
$C_6H_5\text{-}H$	6.5 - 8.0
$R\text{-}C(=O)\text{-}N\text{-}H$	5.0 - 9.0
$R\text{-}C(=O)\text{-}H$	9.0 - 10.0
$R\text{-}C(=O)\text{-}O\text{-}H$	10.0 - 12.0
$R\text{-}N\text{-}H$	0.5 - 4.0
$R\text{-}O\text{-}H$	0.5 - 5.0
$Ar\text{-}N\text{-}H$	3.0 - 5.0
$Ar\text{-}O\text{-}H$	4.0 - 7.0
$R\text{-}S\text{-}H$	1.0 - 4.0

Spin-Spin Splitting

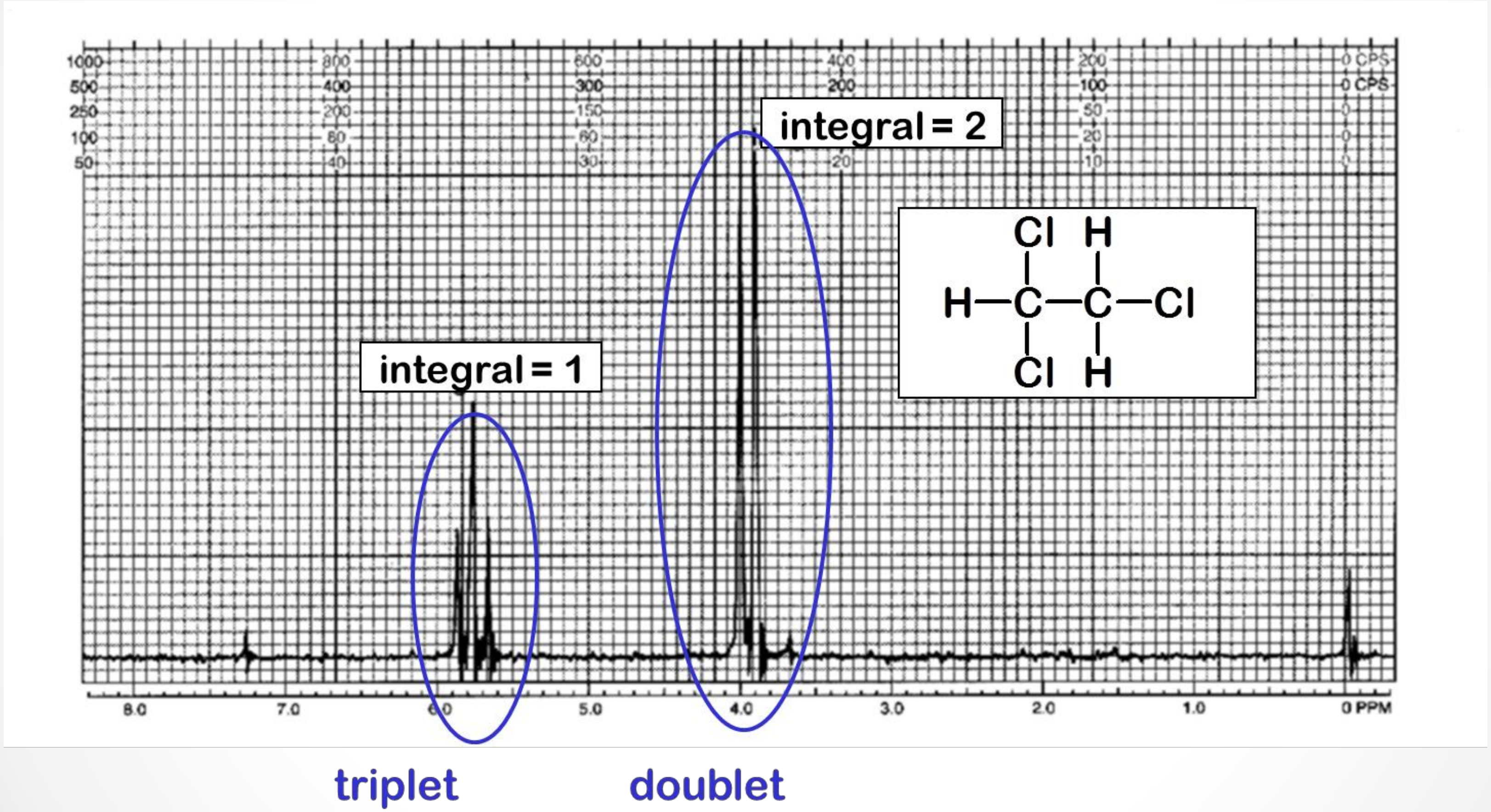
- Often a group of hydrogens will appear as a multiplet rather than as a single peak.
- Multiplets are named as follows:

Single
Doublet
Triplet
Quartet
Quintet
Sextet
Septet
Octet
Nonet

- This happens because of interaction with neighboring hydrogens and is called Spin-Spin Splitting

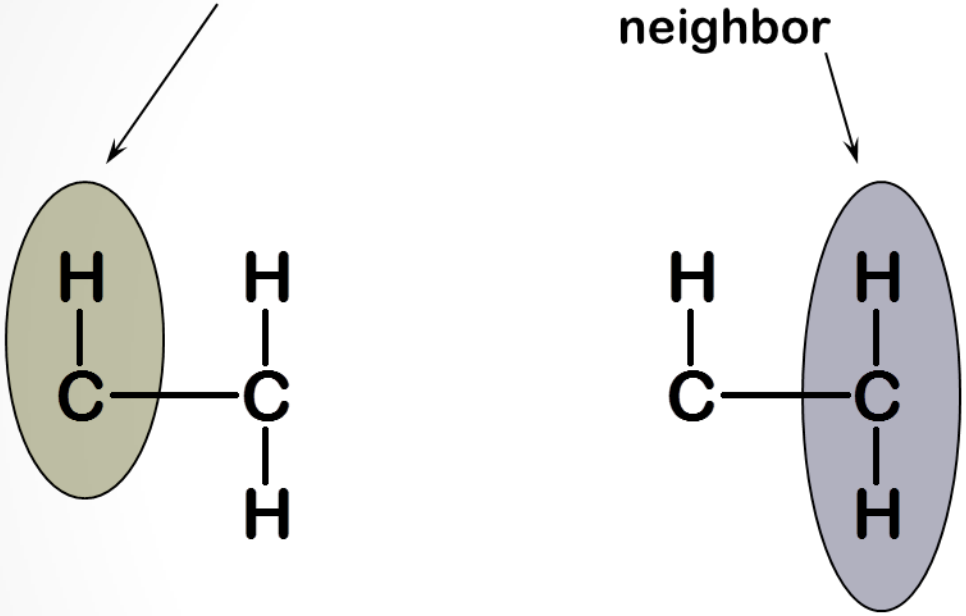
1,1,2-Trichloroethane

The two kinds of hydrogens do not appear as single peaks, rather there is a “triplet” and a “doublet”.



The subpeaks are due to spin-spin splitting and are predicted by the n+1 rule.

n + 1 Rule



this hydrogen's peak
is split by its two neighbors

these hydrogens are
split by their single
neighbor

two neighbors
n+1 = 3
triplet

one neighbor
n+1 = 2
doublet

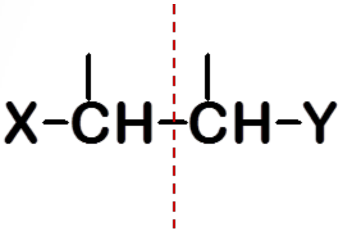
Multiplets

- singlet
- doublet
- triplet
- quartet
- quintet
- sextet
- septet

Exceptions to the n+1 Rule

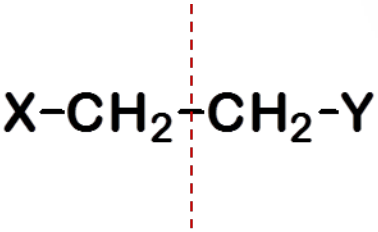
IMPORTANT !

1) Protons that are equivalent by symmetry usually do not split one another.



$X-CH-CH-Y$

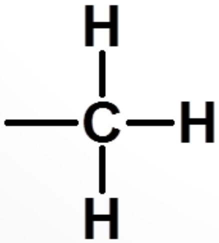
no splitting if x=y



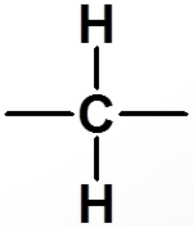
$X-CH_2-CH_2-Y$

no splitting if x=y

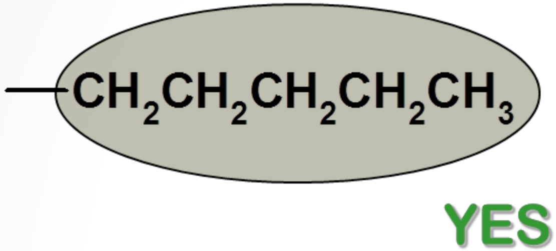
2) Protons in the same group usually do not split one another.



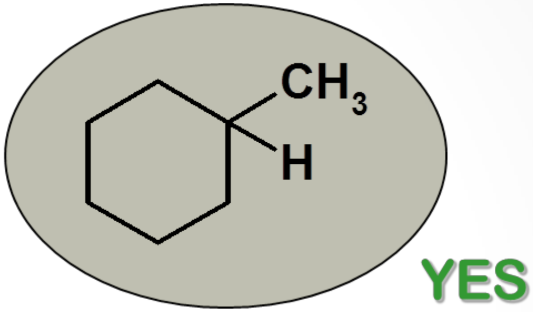
or



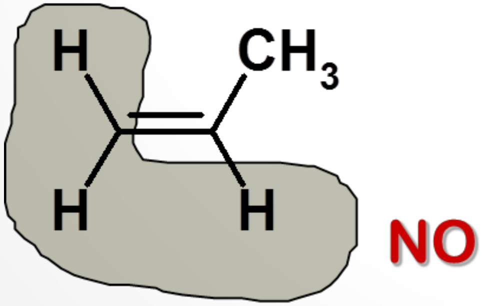
3) The n+1 rule applies principally to protons in aliphatic (saturated) chains or on saturated rings.

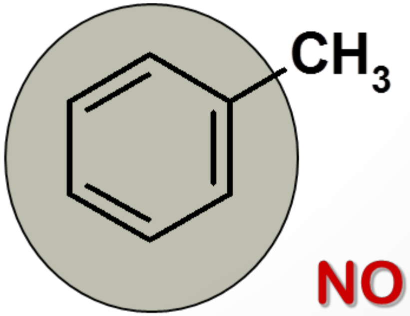


or

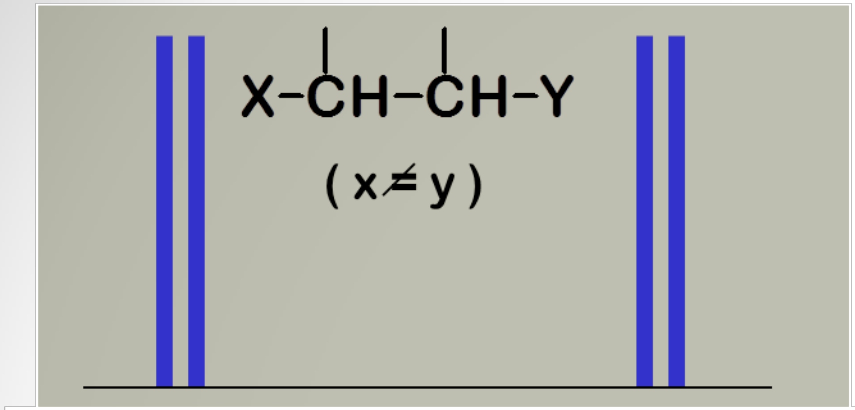


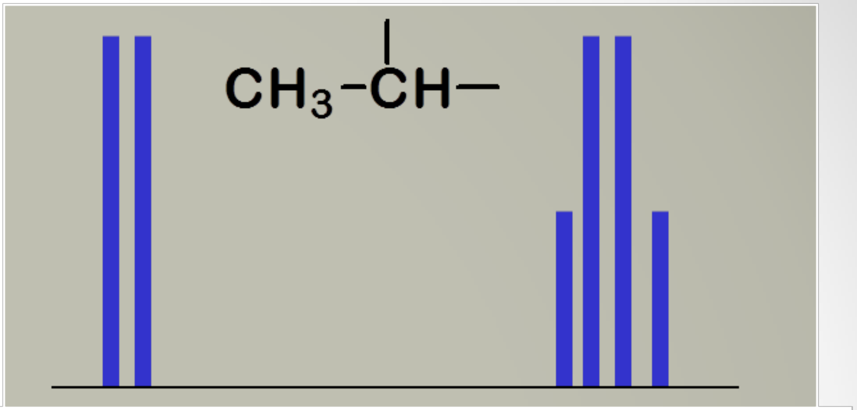
but does not apply (in the simple way shown here) to protons on double bonds or on benzene rings.

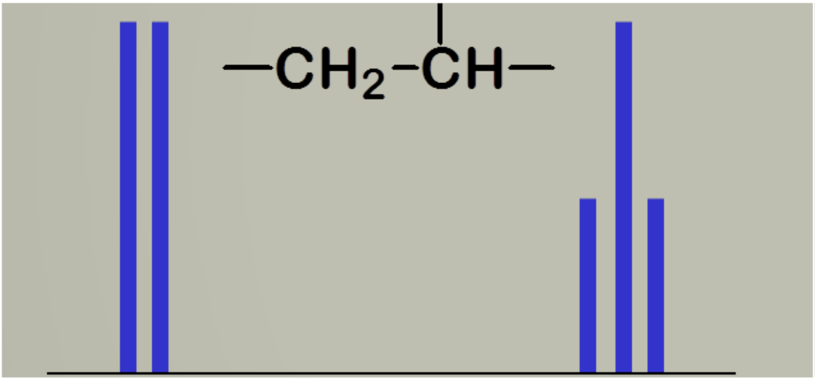


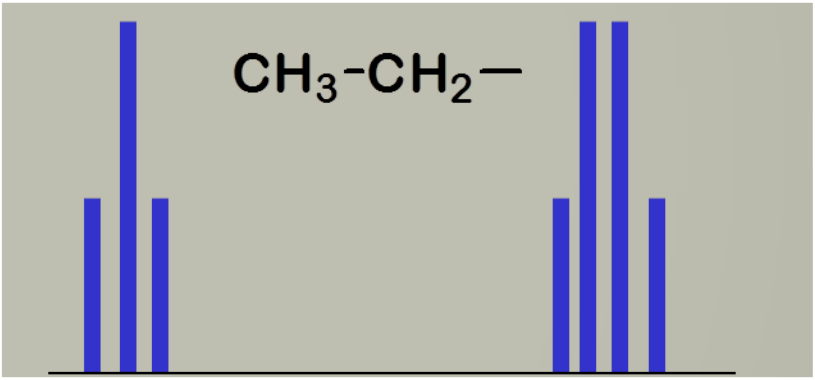


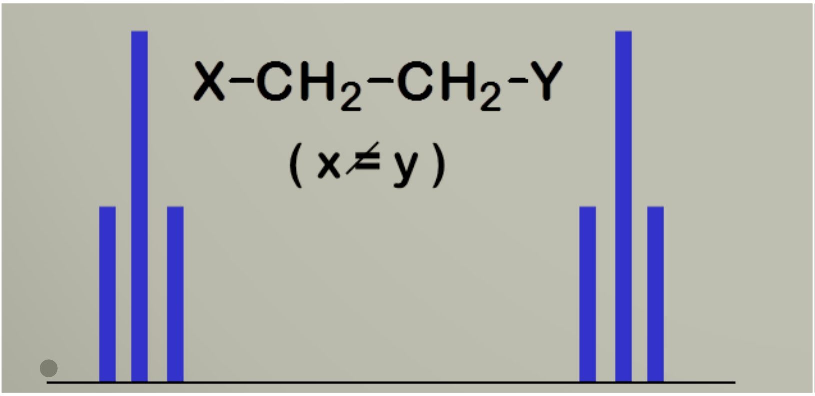
Some Common Splitting Patterns

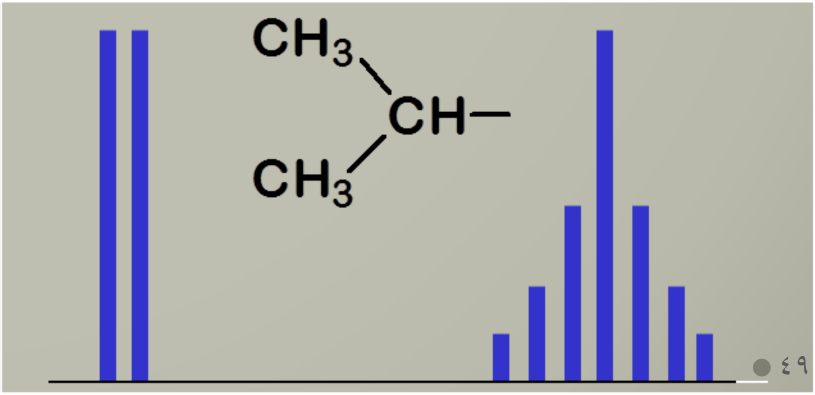












Intensities of multiplet peaks

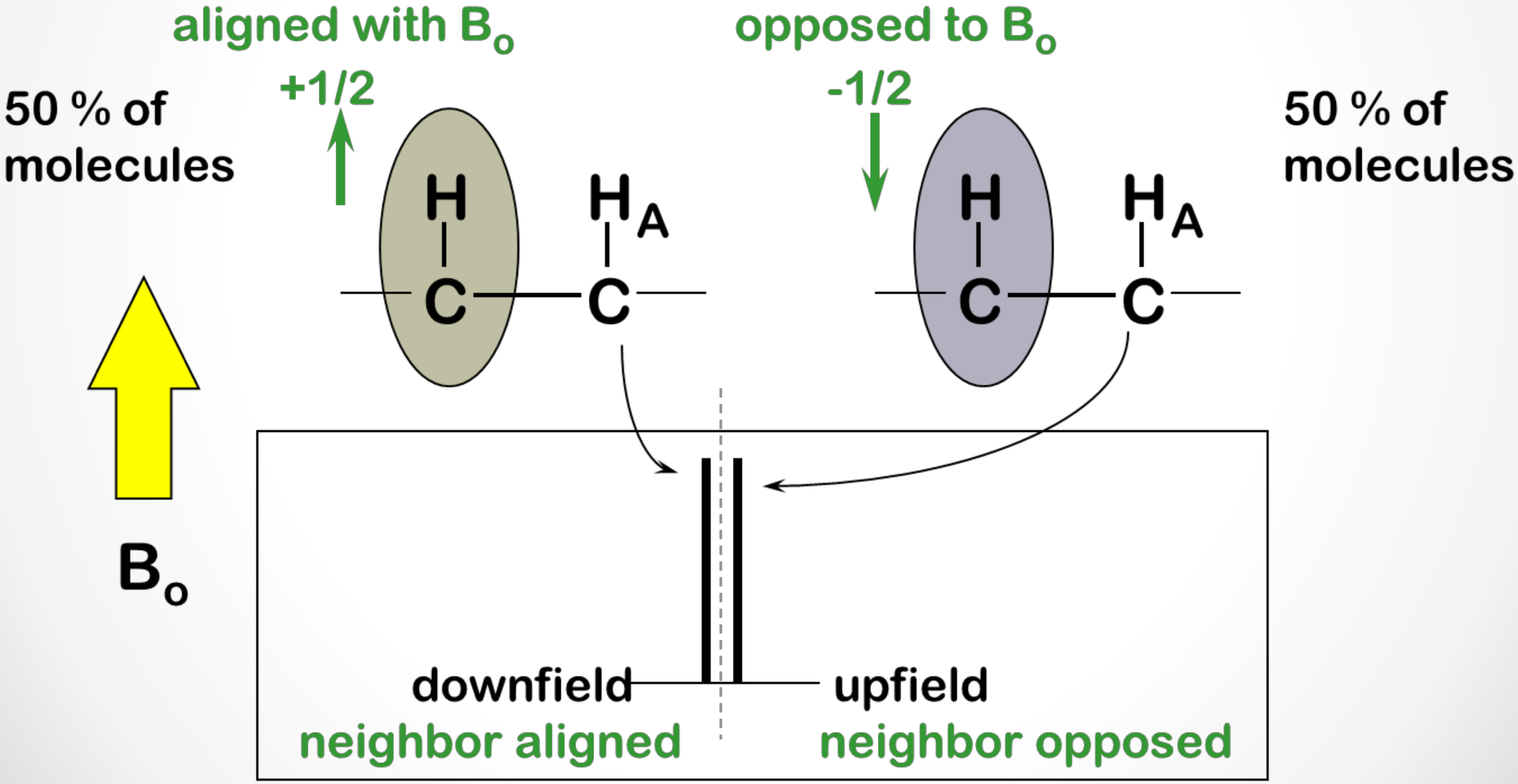
PASCAL’S TRIANGLE

1	singlet
1 1	doublet
1 2 1	triplet
1 3 3 1	quartet
1 4 6 4 1	quintet
1 5 10 10 5 1	sextet
1 6 15 20 15 6 1	septet
1 7 21 35 35 21 7 1	octet

The interior entries are the sums of the two numbers immediately above.

The Origin of ^{1}H NMR—Spin-Spin Splitting

The Chemical Shift of Proton H_A is affected by the Spin of its Neighbors.



aligned with B_o

+1/2

opposed to B_o

-1/2

50 % of molecules

50 % of molecules

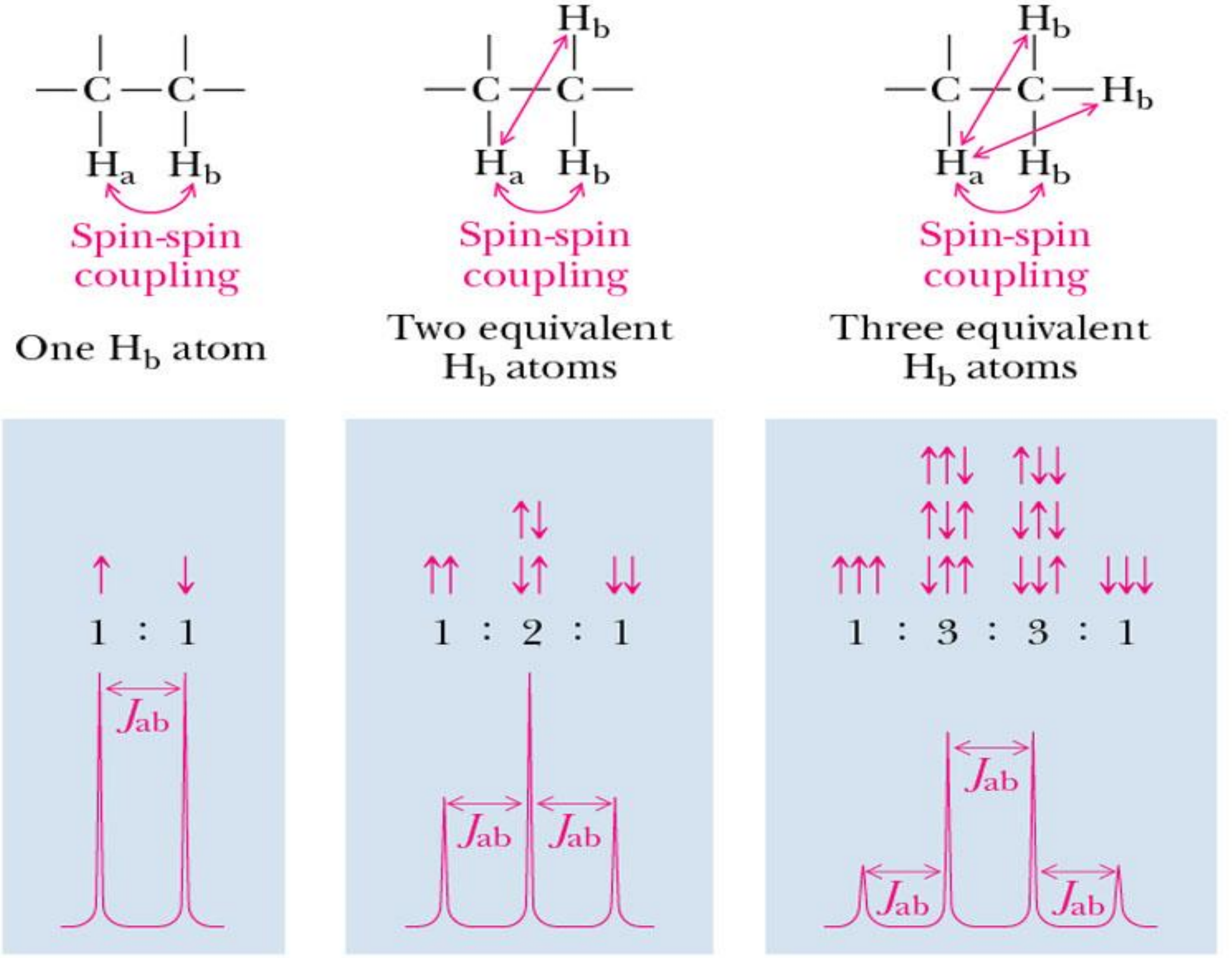
B_o

downfield

neighbor aligned

upfield

neighbor opposed

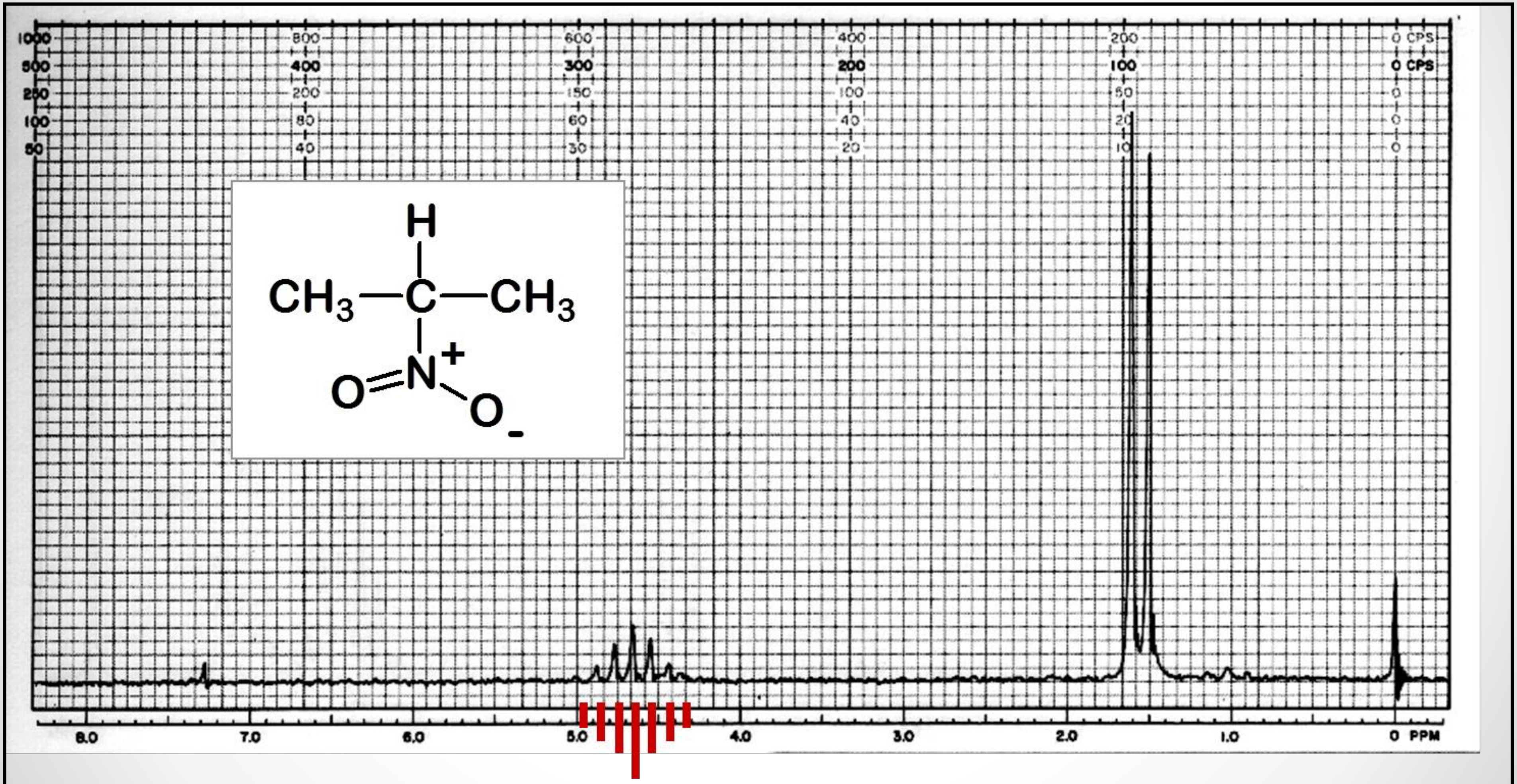


Observed splitting in signal of H_a

Some Example Spectra with Splitting

NMR Spectrum of Bromoethane

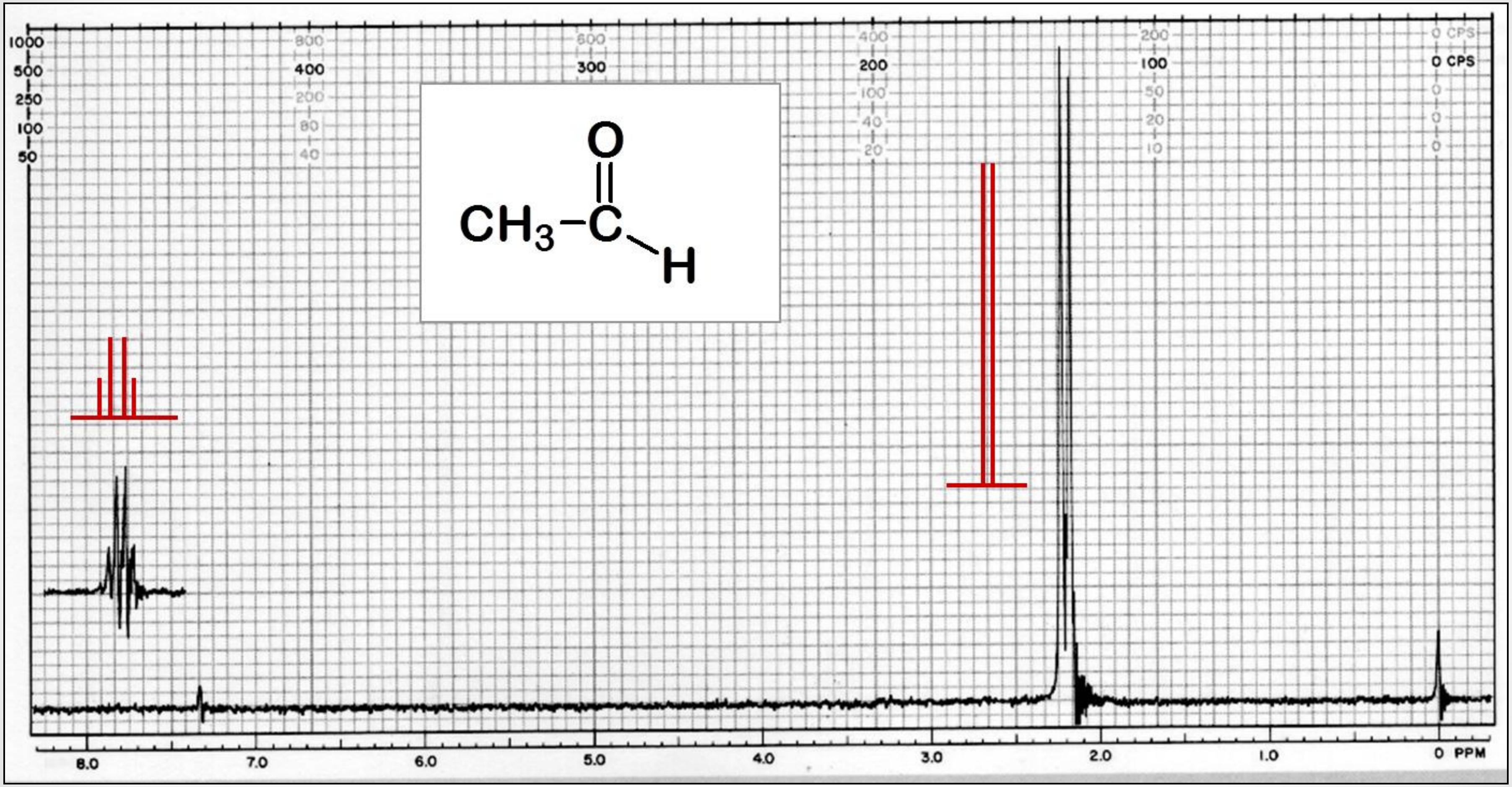
NMR Spectrum of 2-Nitropropane



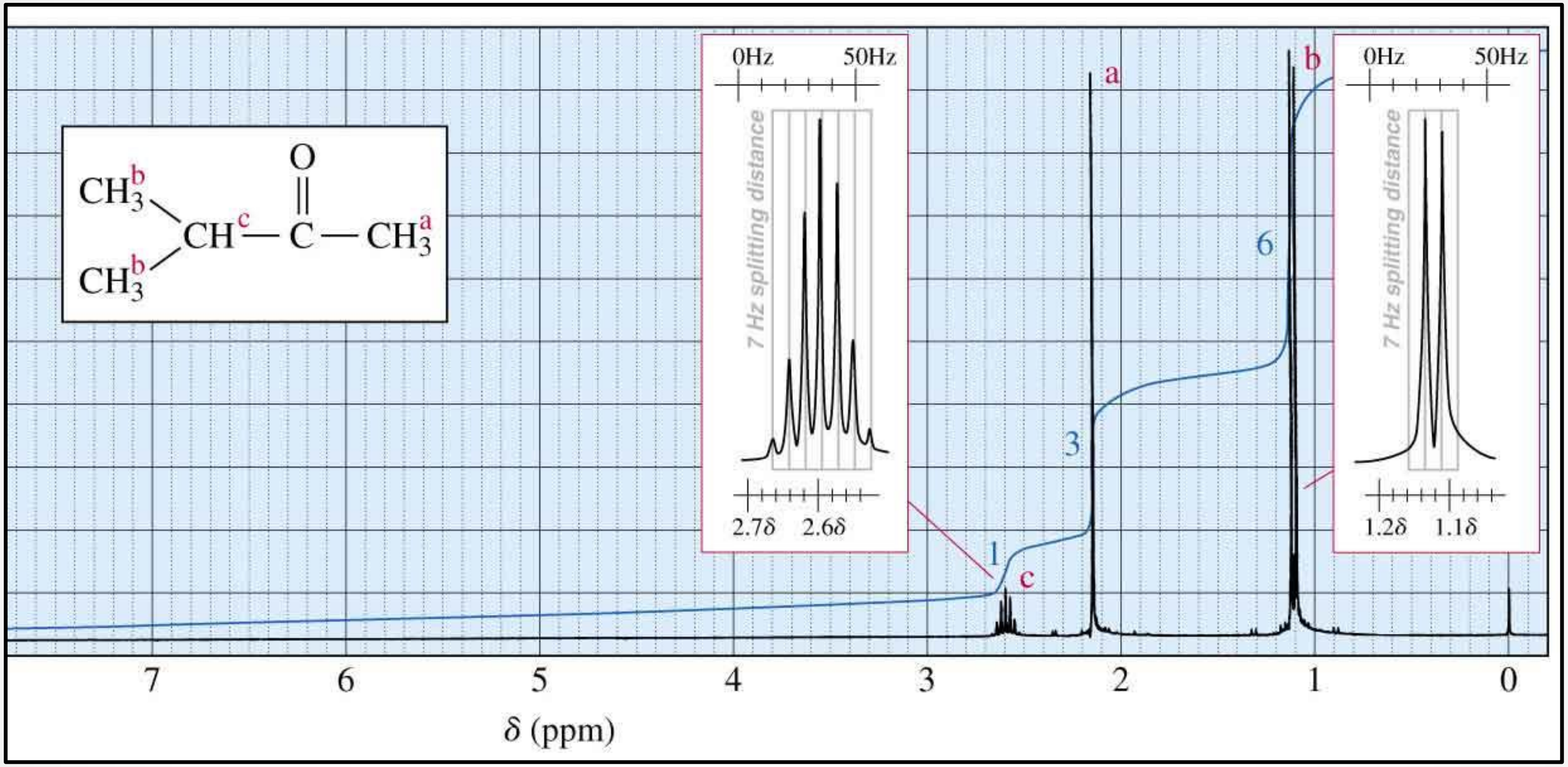
1:6:15:20:16:6:1

in higher multiplets the outer peaks are often nearly lost in the baseline

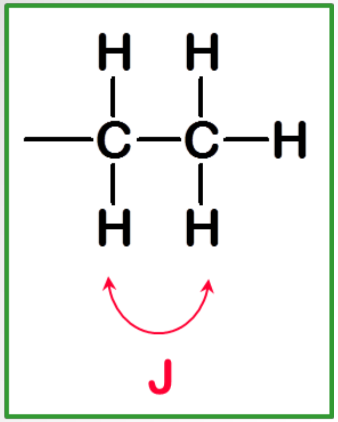
NMR Spectrum of Acetaldehyde



NMR Spectrum of 3-Methyl-butan-2-one

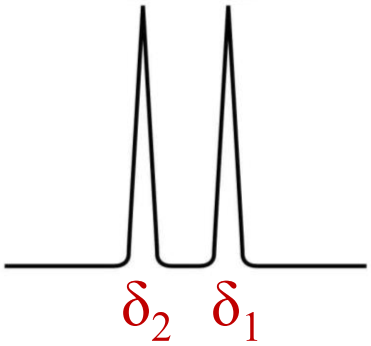


Coupling Constants



- Distance between the peaks of multiplet
- Measured in Hz
- J is a measure of the amount of interaction between the two sets of hydrogens creating the multiplet.
- Not dependent on strength of the external field

How to count J from spectrum:

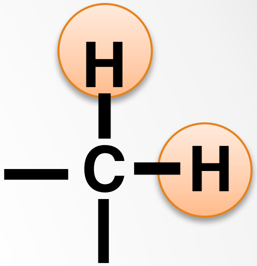


$J = (\delta_2 - \delta_1) \times$ spectrometer frequency Hz

Types of Coupling Constants

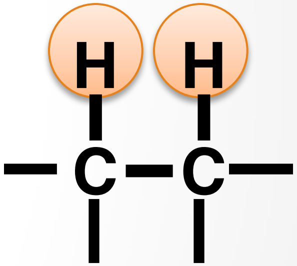
1. ^{2}J or geminal coupling

It is designated ^{2}J since two bonds intervene between the two hydrogens but the two hydrogens are not equivalent



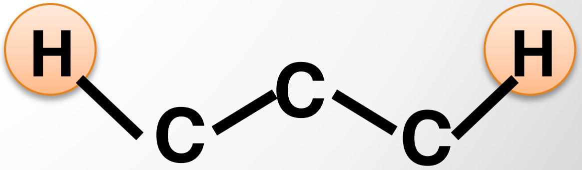
2. ^{3}J or vicinal coupling

It is designated ^{3}J since three bonds intervene between the two hydrogens

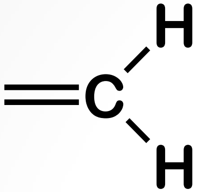
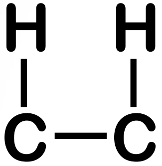
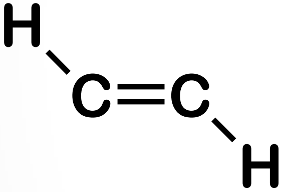
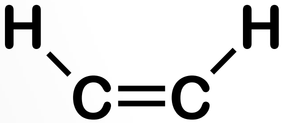
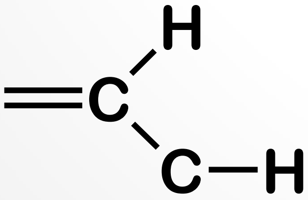


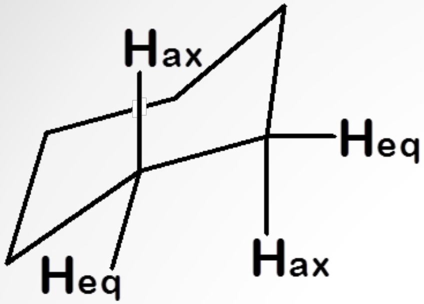
3. ^{4}J - ^{n}J or Long Range Coupling

Couplings larger than ^{3}J since more than three bonds intervene between the two hydrogens



Some Representative Coupling Constants

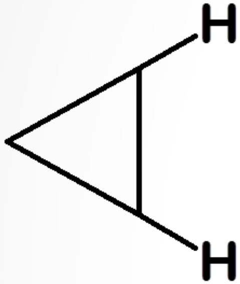
geminal		0 to 5 Hz	two bond	^2J
vicinal		6 to 8 Hz	three bond	^3J
trans		11 to 18 Hz	three bond	^3J
cis		6 to 15 Hz	three bond	^3J
vicinal		4 to 10 Hz	three bond	^3J



Hax , Hax = 8 to 14

Hax , Heq = 0 to 7 three bond ^3J

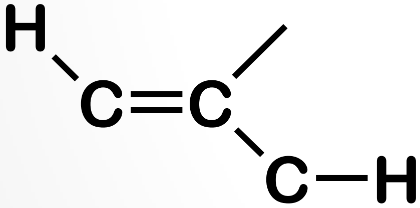
Heq , Heq = 0 to 5



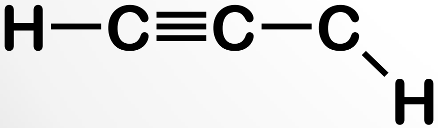
cis 6 to 12 Hz

three bond ^3J

trans 4 to 8 Hz



0 to 3 Hz four bond ^4J



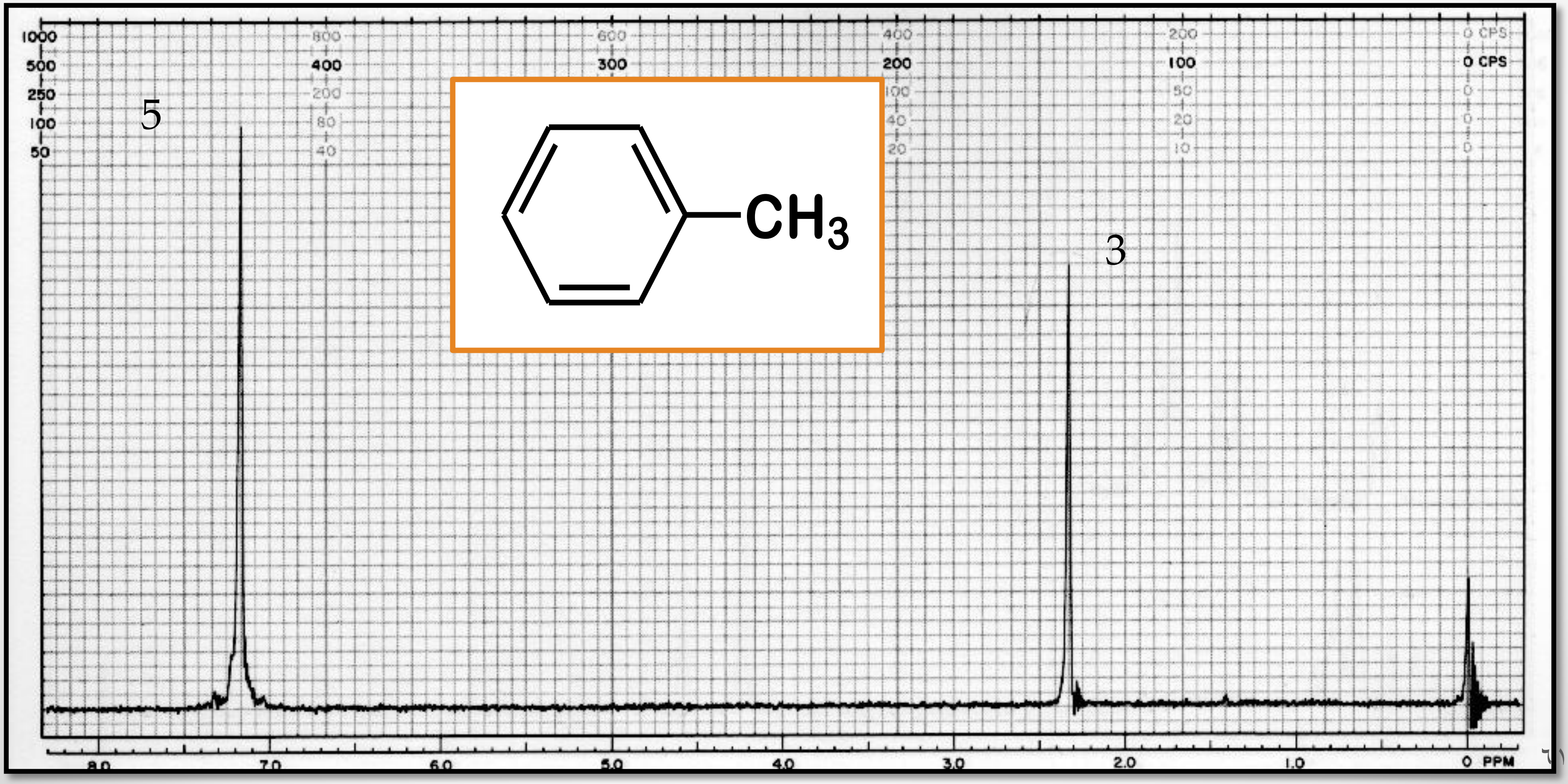
0 to 3 Hz four bond ^4J

Spectra of Aromatic Compounds

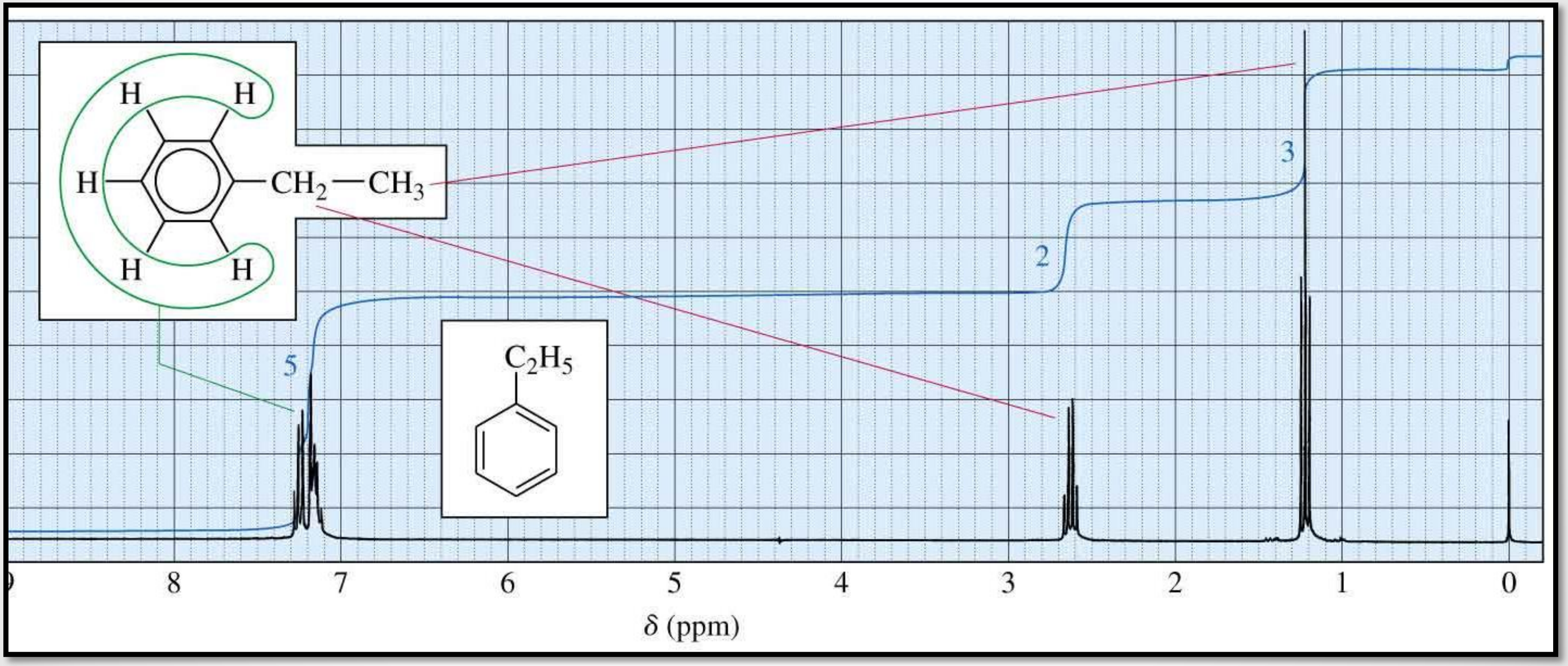
The *mono*-substituted Pattern

Alkyl - Substituted Rings

NMR Spectrum of Toluene

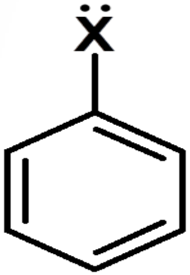


NMR Spectrum of Ethyl-benzene



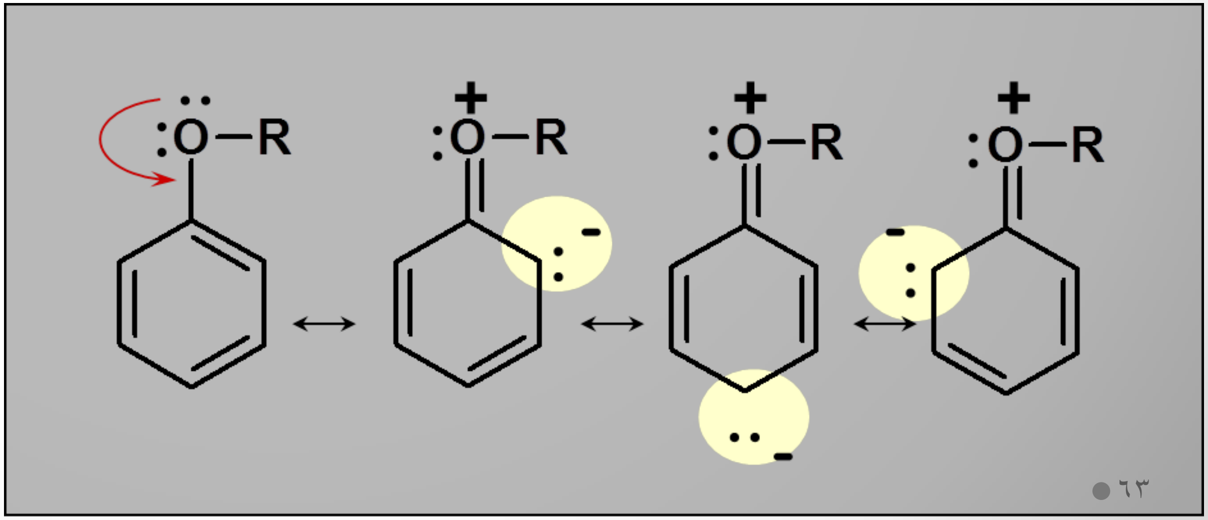
Substituents with Unshared Pairs

- Electronegative elements with unshared pairs shield the *o*- and *p*- ring positions

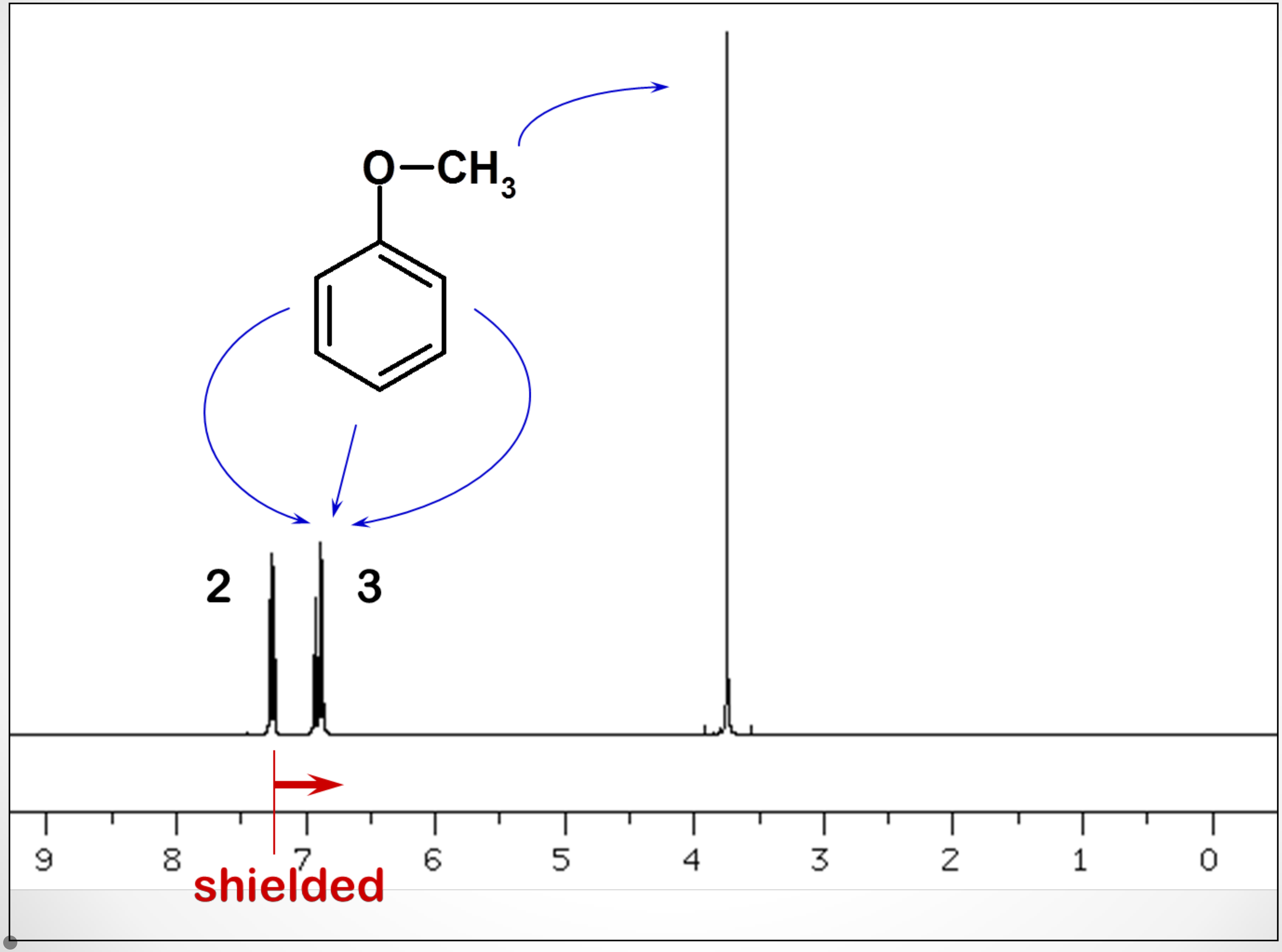


$X = \ddot{\underset{..}{O}}H, \ddot{O}R, \ddot{N}H_2, \ddot{N}R_2, -\ddot{\underset{..}{O}}(CO)CH_3$

Electron-donating groups shield the *o*-, *p*- positions due to resonance

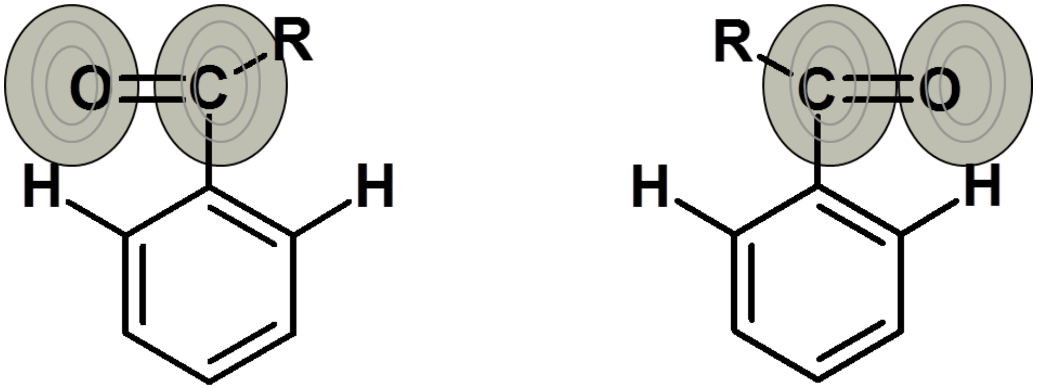


NMR Spectrum of Anisole



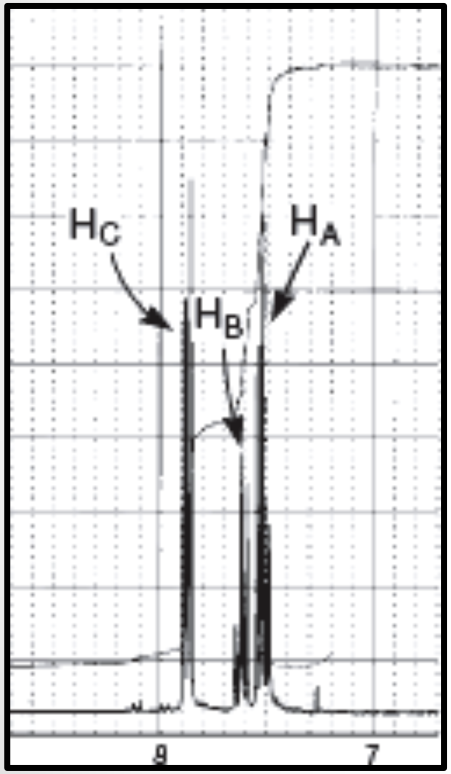
The Effect of Carbonyl Substituents

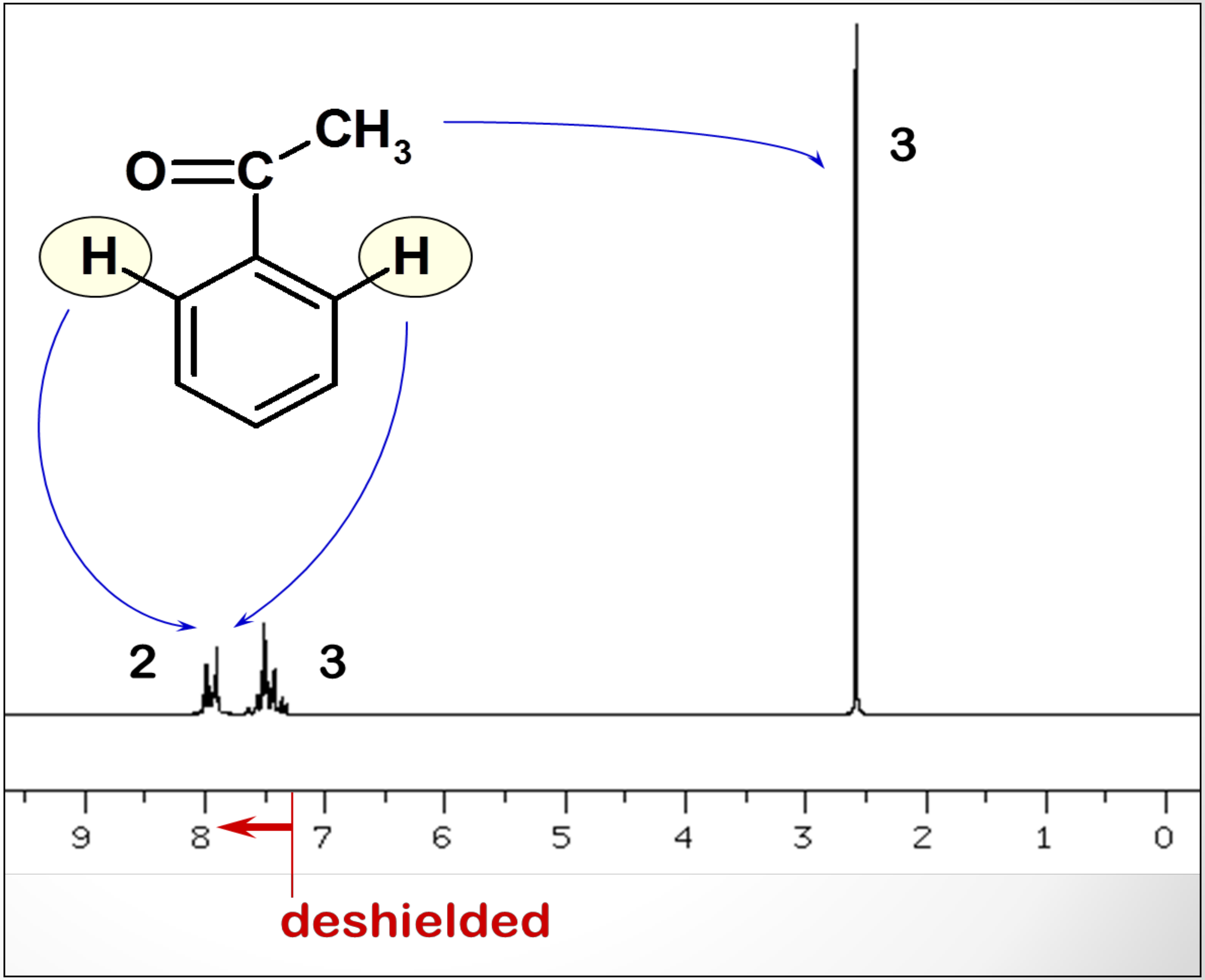
- When a carbonyl group is attached to the ring the *o*- and *p*- protons are deshielded by the anisotropic field of C=O



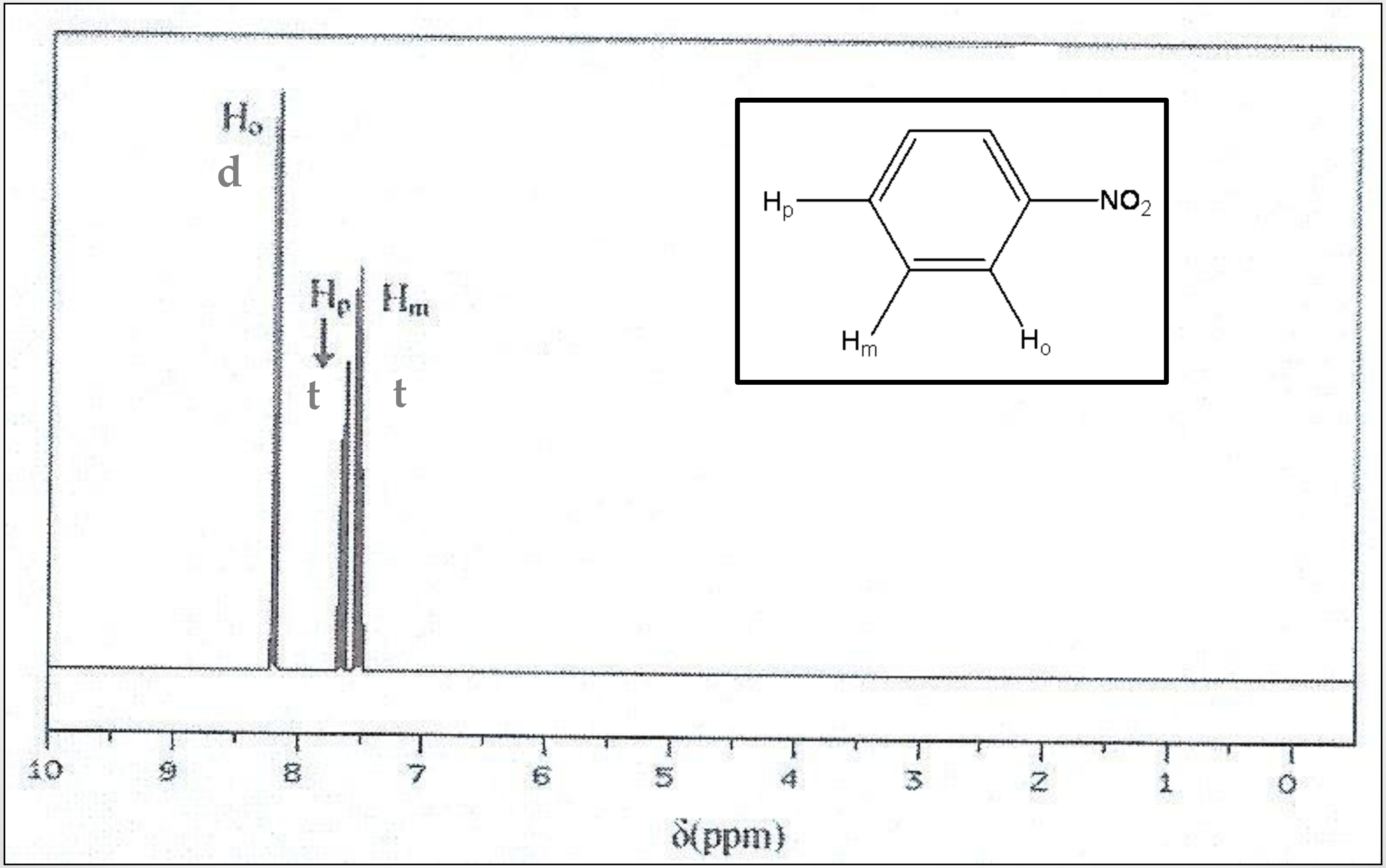
- The same effect is sometimes seen with C=C bonds.

NMR Spectrum of Acetophenone

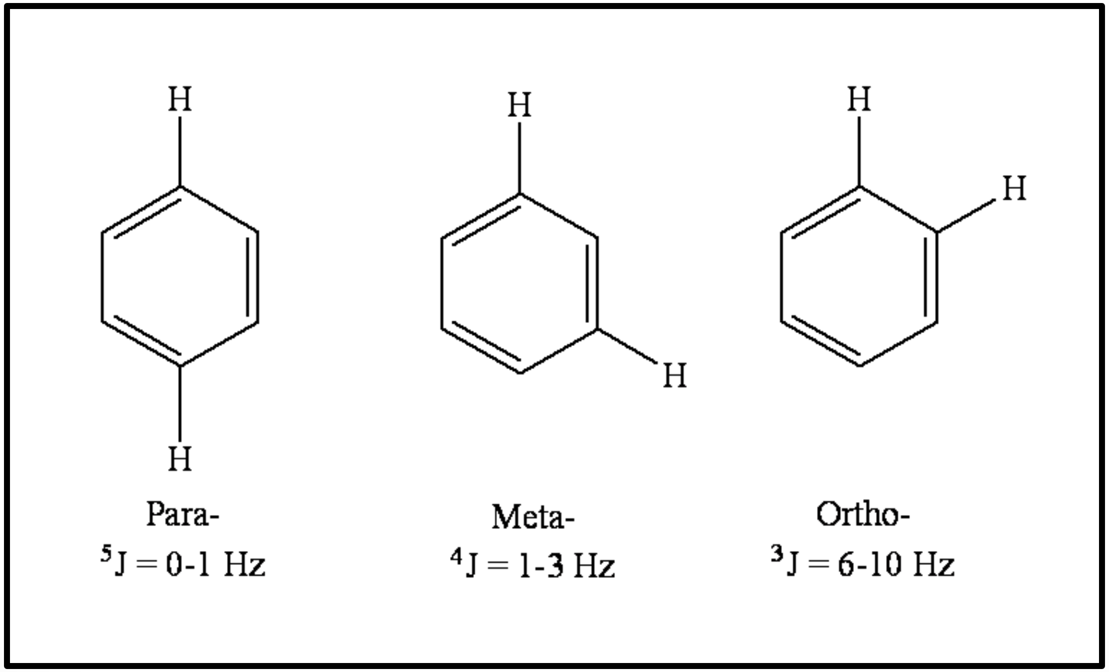




NMR Spectrum of Nitrobenzene



Coupling Constants in Aromatic Rings



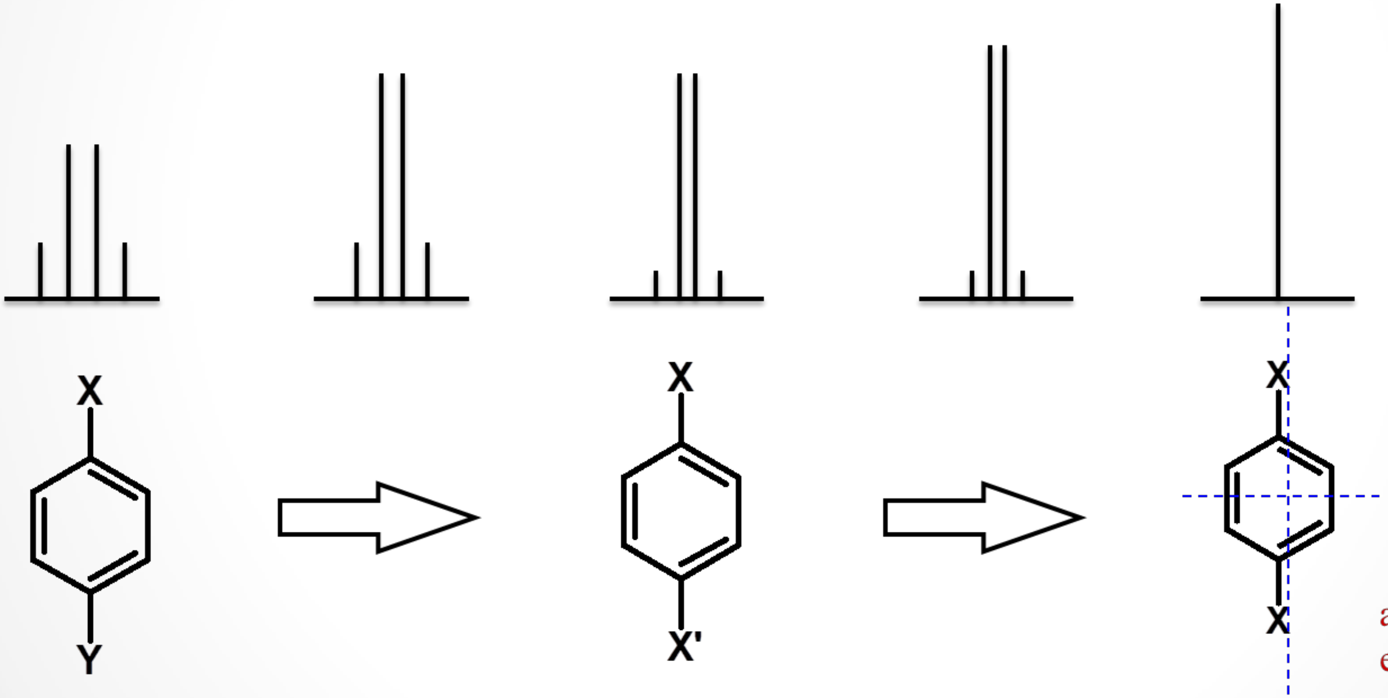
Para- $^{5}J = 0\text{-}1$ Hz

Meta- $^{4}J = 1\text{-}3$ Hz

Ortho- $^{3}J = 6\text{-}10$ Hz

The *p*-Disubstituted Rings

- 1,4-Disubstituted benzene rings will show a pair of doublets, when the two groups on the ring are very different



all H equivalent

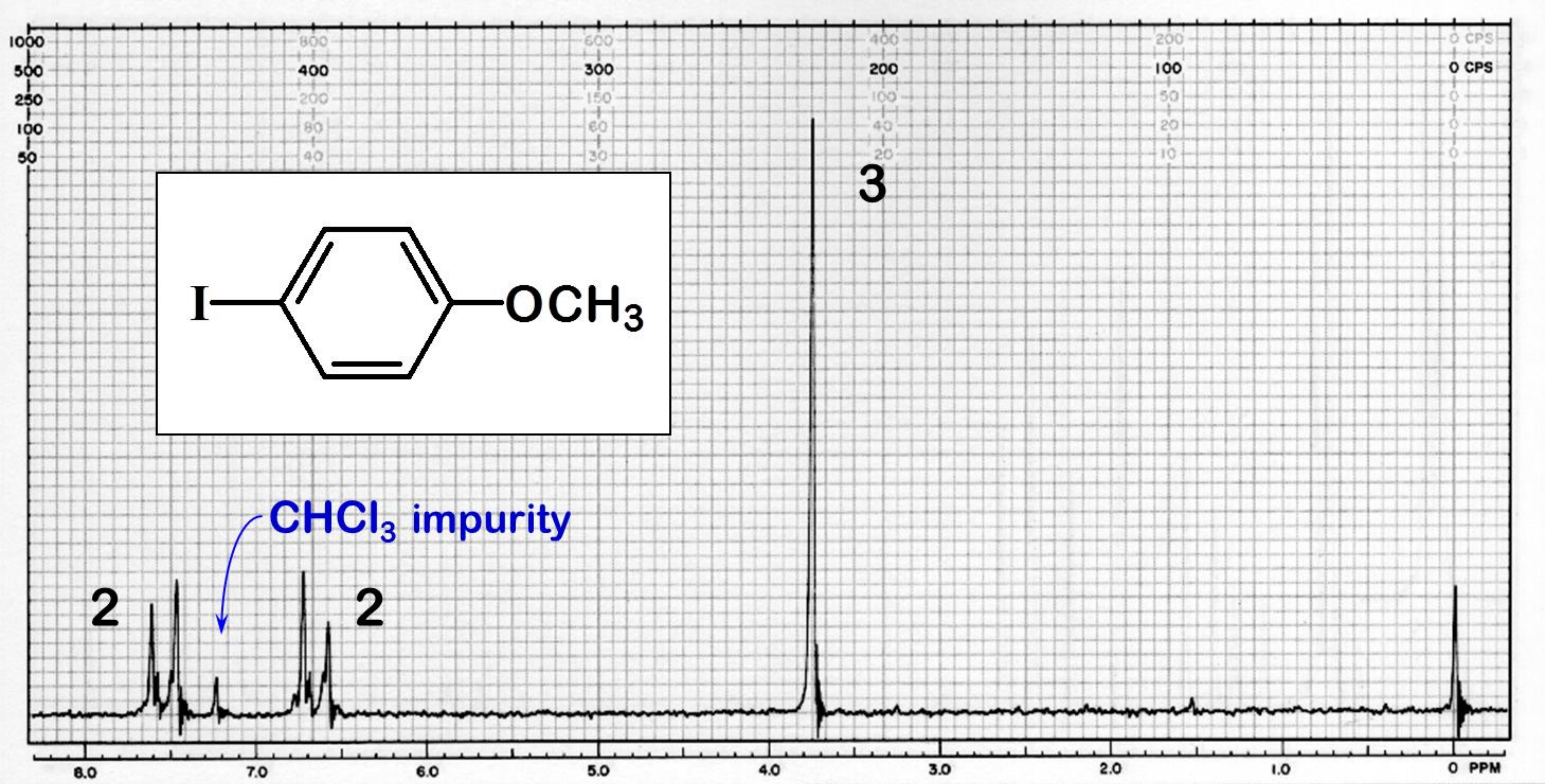
X ≠Y

X ≈ X’

X = X

same groups

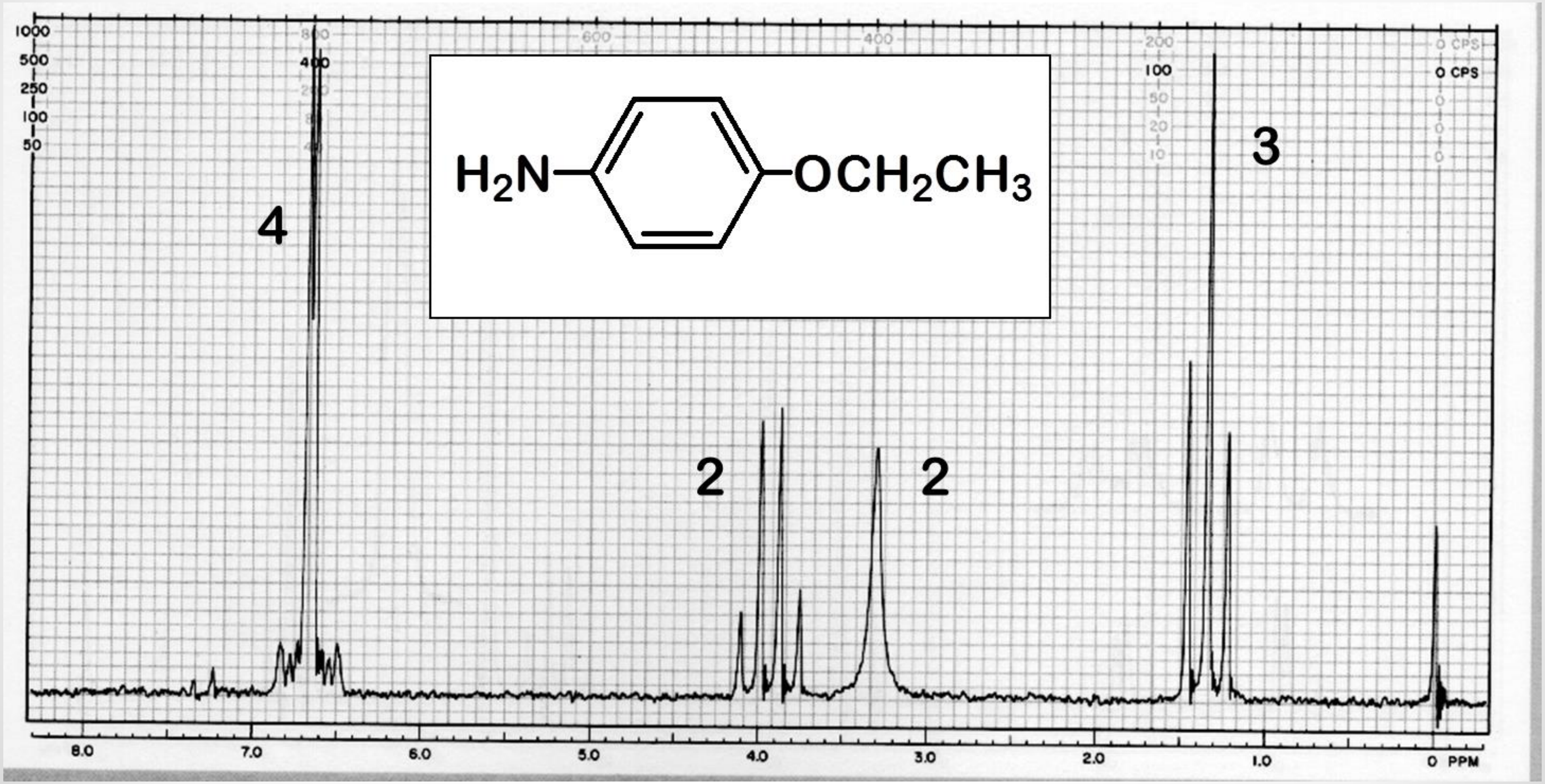
NMR Spectrum of 1-iodo-4-methoxybenzene



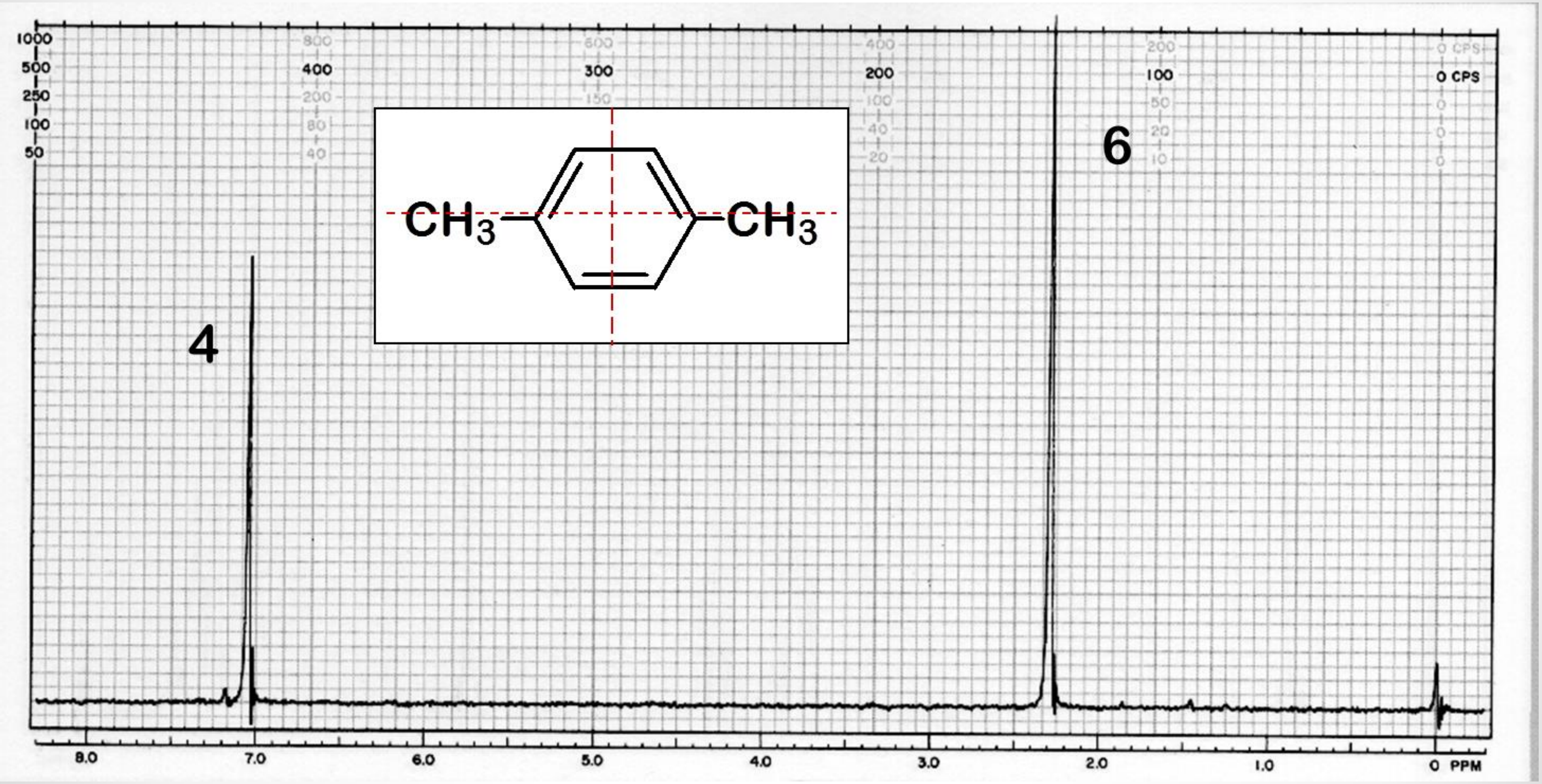
$CHCl_3$ impurity

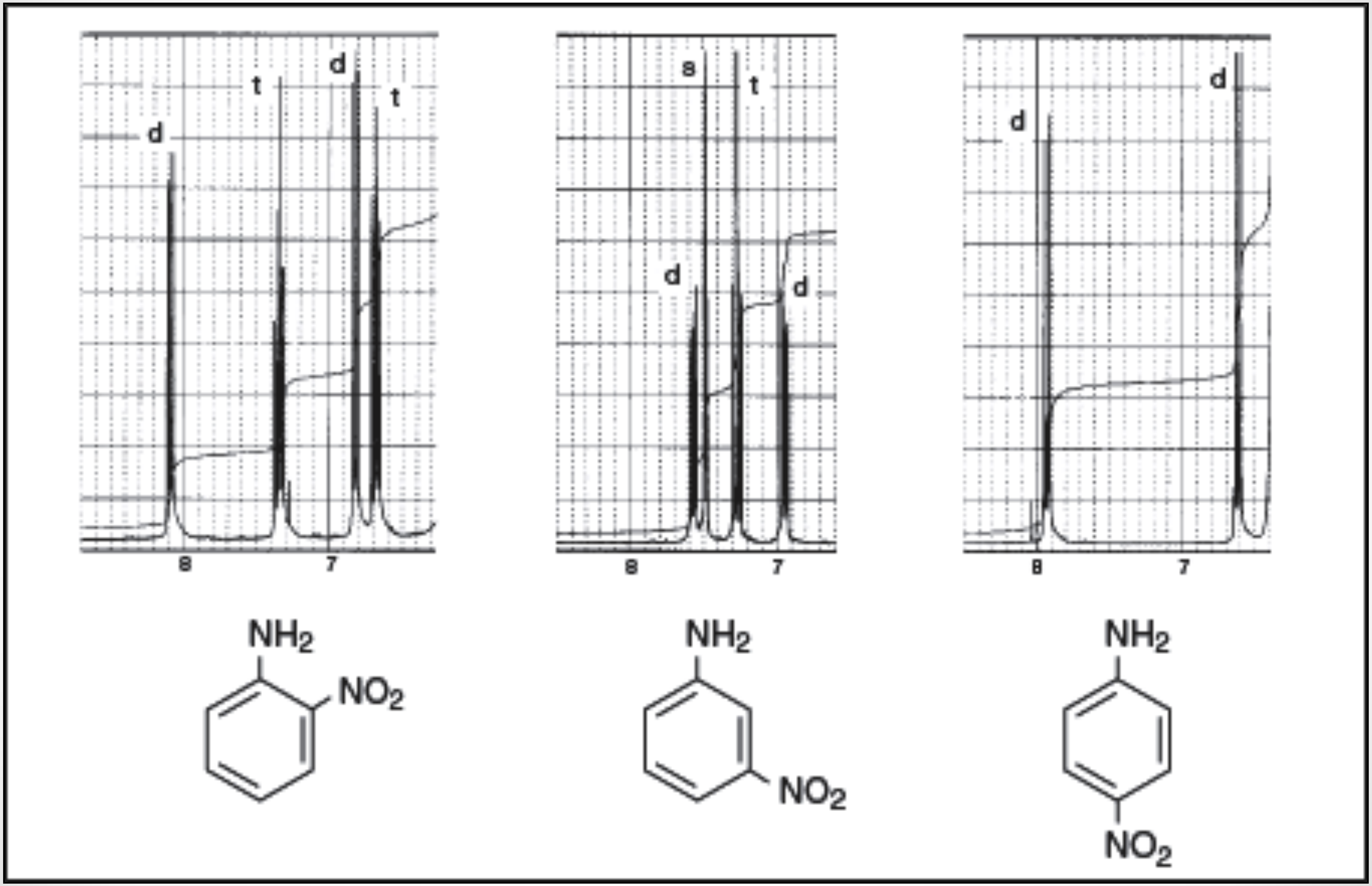
AA`BB` pattern

NMR Spectrum of 1-amino-4-ethoxybenzene

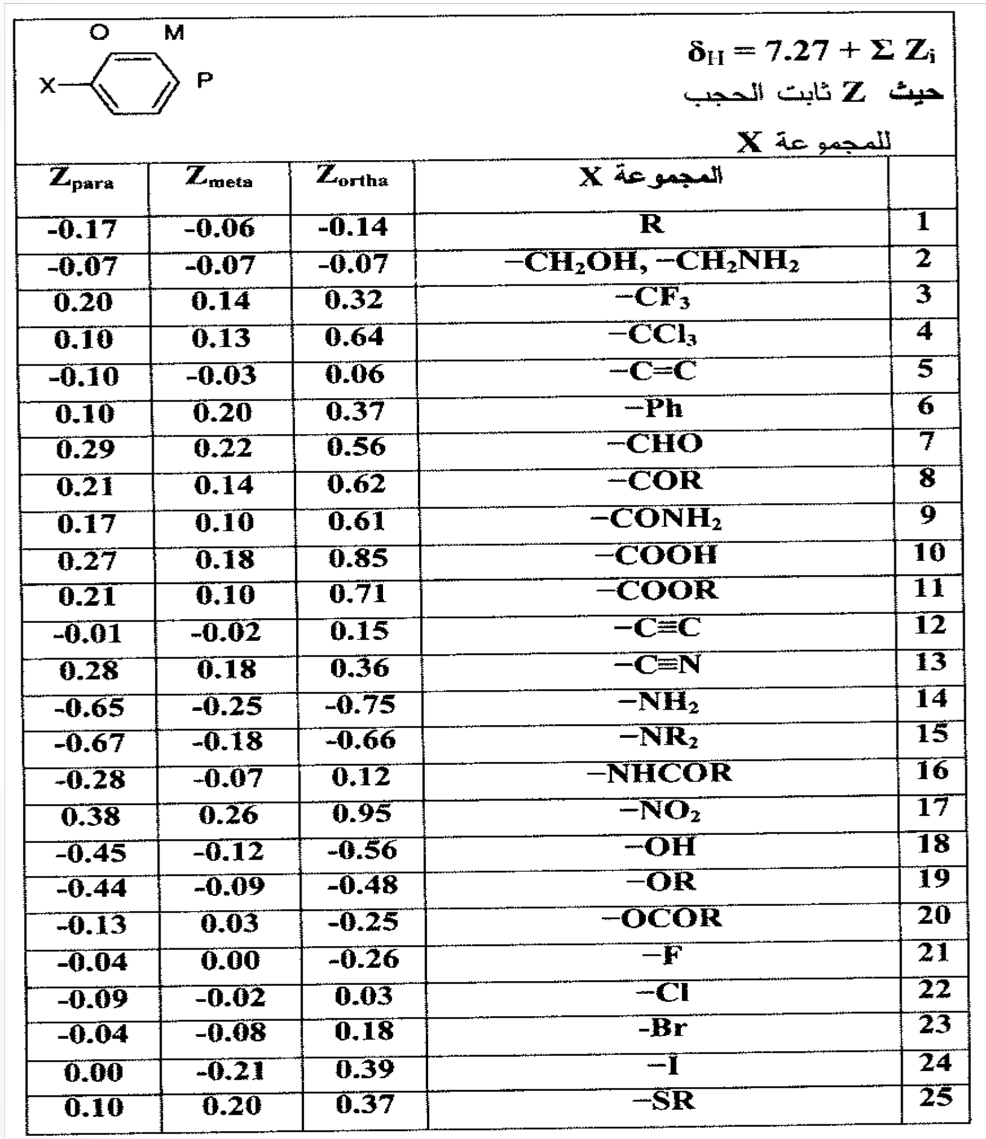


NMR Spectrum of *p*-Xylene (1,4-dimethylbenzene)




d
t
d
t
8
7
NH2
NO2
s
t
d
d
8
7
NH2
NO2
d
d
8
7
NH2
NO2

Estimation of Proton Chemical shifts in Substituted Benzene



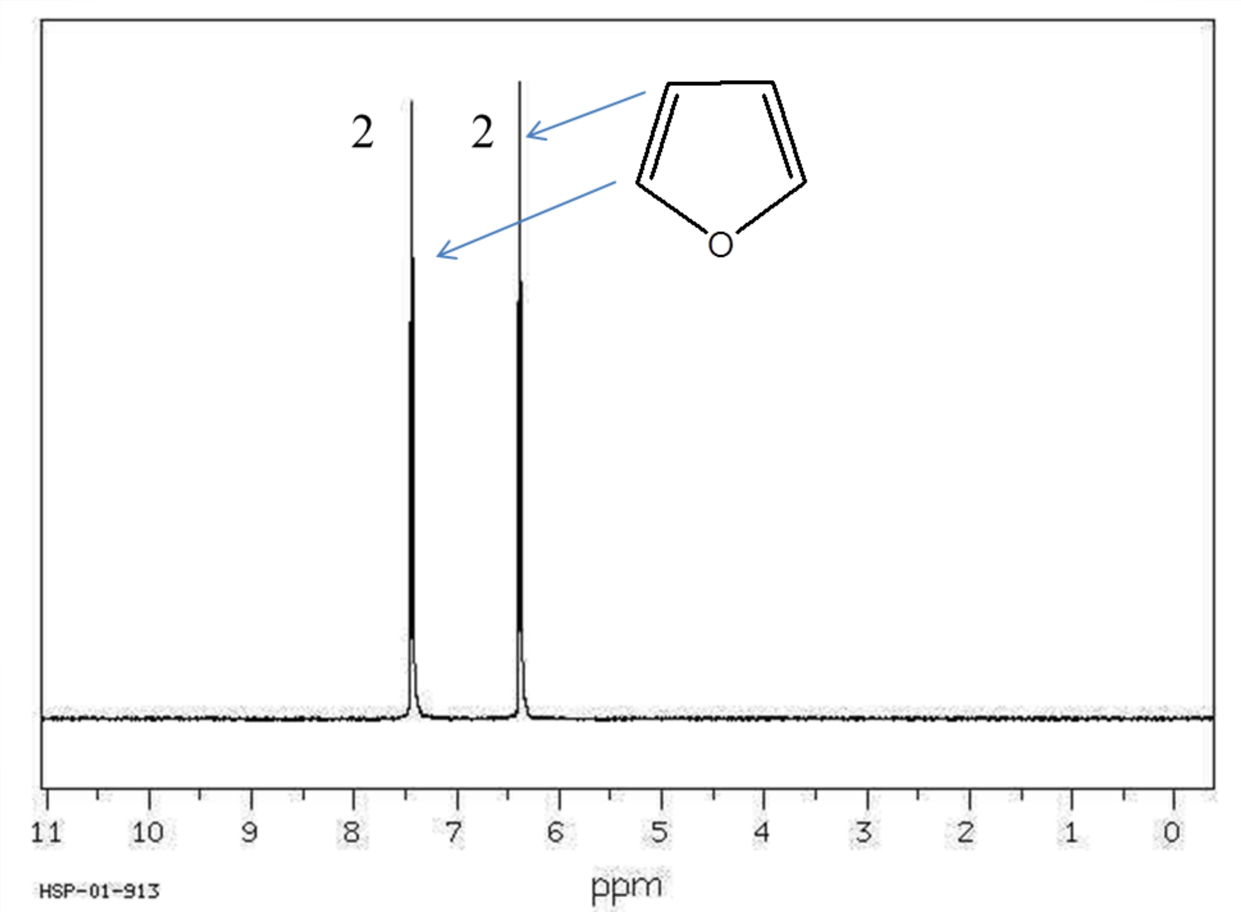
$\delta_H = 7.27 + \Sigma Z_i$

حيث Z ثابت الحجب

للمجموعة X

	المجموعة X	Z_{ortha}	Z_{meta}	Z_{para}
1	R	-0.14	-0.06	-0.17
2	$-CH_2OH$, $-CH_2NH_2$	-0.07	-0.07	-0.07
3	$-CF_3$	0.32	0.14	0.20
4	$-CCl_3$	0.64	0.13	0.10
5	$-C=C$	0.06	-0.03	-0.10
6	$-Ph$	0.37	0.20	0.10
7	$-CHO$	0.56	0.22	0.29
8	$-COR$	0.62	0.14	0.21
9	$-CONH_2$	0.61	0.10	0.17
10	$-COOH$	0.85	0.18	0.27
11	$-COOR$	0.71	0.10	0.21
12	$-C\equiv C$	0.15	-0.02	-0.01
13	$-C\equiv N$	0.36	0.18	0.28
14	$-NH_2$	-0.75	-0.25	-0.65
15	$-NR_2$	-0.66	-0.18	-0.67
16	$-NHCOR$	0.12	-0.07	-0.28
17	$-NO_2$	0.95	0.26	0.38
18	$-OH$	-0.56	-0.12	-0.45
19	$-OR$	-0.48	-0.09	-0.44
20	$-OCOR$	-0.25	0.03	-0.13
21	$-F$	-0.26	0.00	-0.04
22	$-Cl$	0.03	-0.02	-0.09
23	$-Br$	0.18	-0.08	-0.04
24	$-I$	0.39	-0.21	0.00
25	$-SR$	0.37	0.20	0.10

NMR Spectrum of Furan



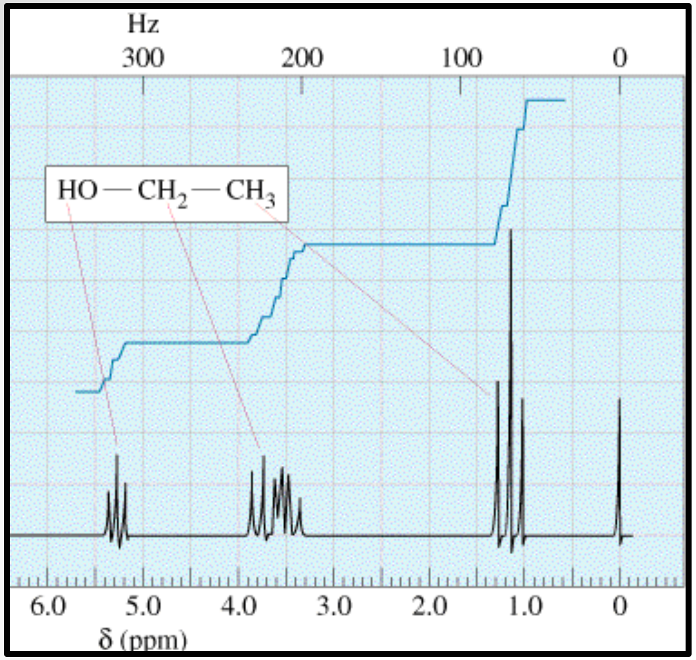
Hydroxyl and Amino Protons

- Hydroxyl and amino protons can appear almost anywhere in the spectrum (H-bonding).

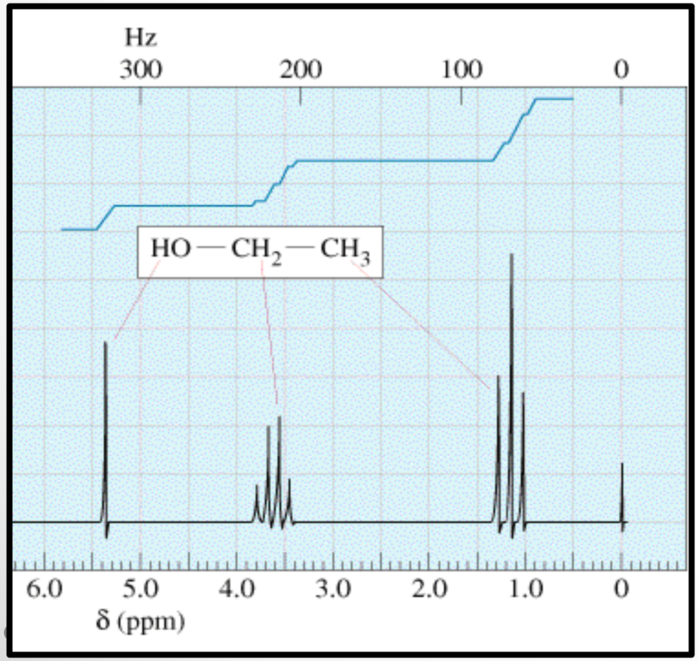
- These absorptions are usually broader than other proton peaks and can often be identified because of this fact.

- Carboxylic acid protons generally appear far downfield near 10 to 12 ppm.

O-H Proton

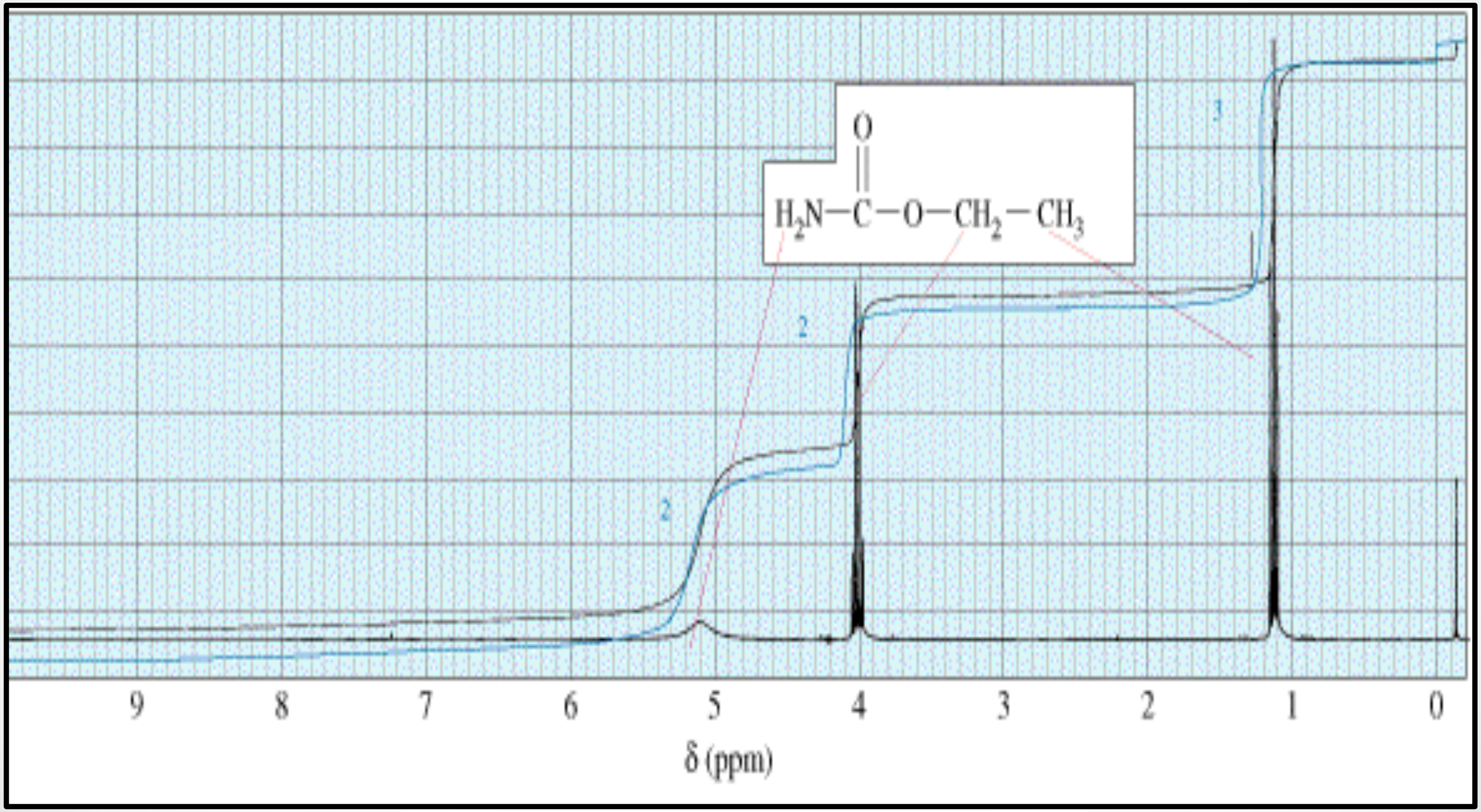


Ultrapure samples of ethanol show splitting.

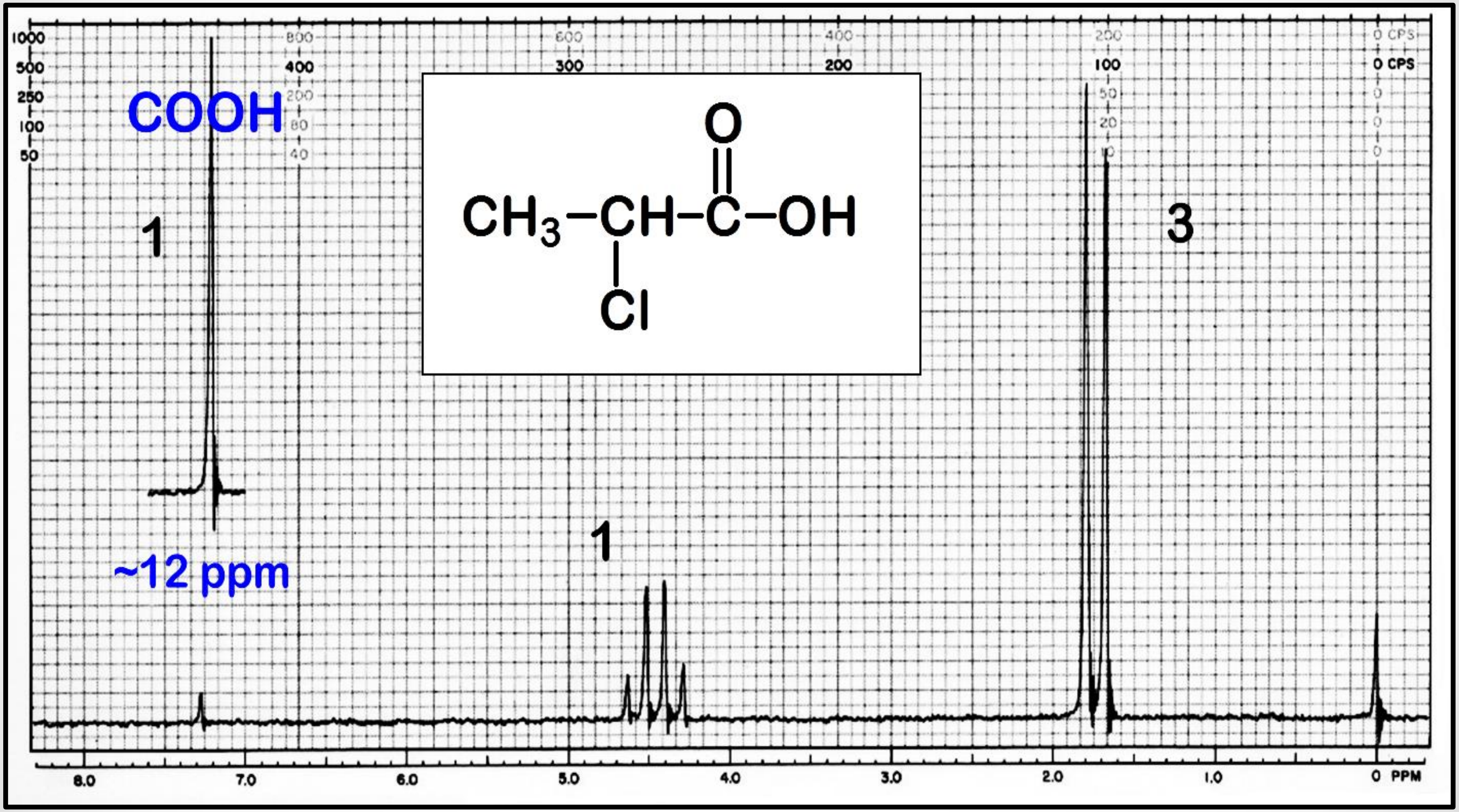


Ethanol with a small amount of acidic or basic impurities will not show splitting.

N-H Proton



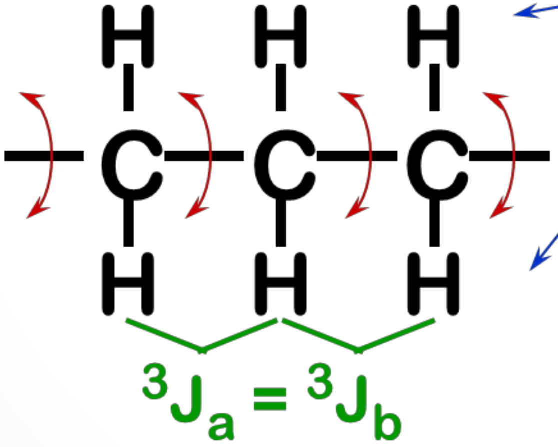
NMR Spectrum of 2-Chloropropanoic Acid



Unequal Coupling Tree Diagrams

Splitting Diagrams aka " Tree Diagrams "

The Typical Situation where the n+1 Rule Applies



Hydrogens can interchange their positions by rotations about the C-C bonds.

This makes all the hydrogens on each of the carbon atoms equivalent.

All the couplings along the chain have the same J value.

The n+1 rule is followed .....

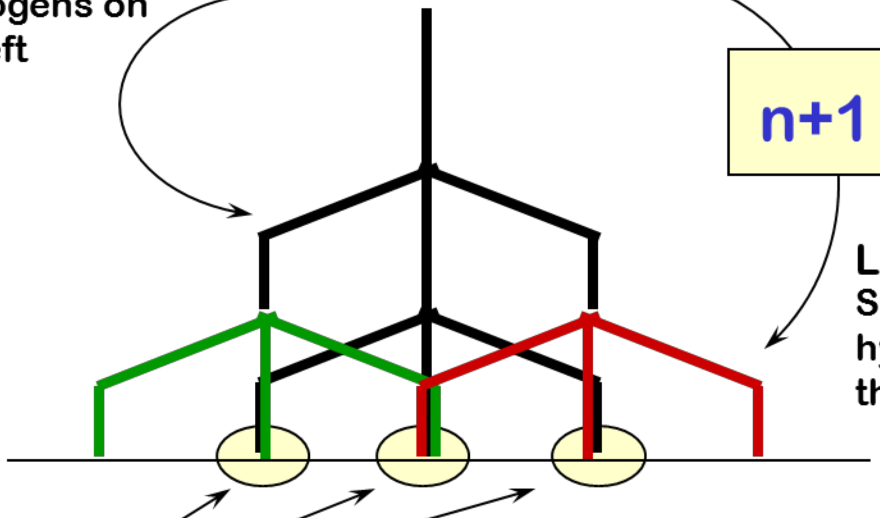
INTENSITIES

1:2:1
1:2:1
1:2:1
+ 1:2:1

1:4:6:4:1

LEVEL ONE
Splitting from hydrogens on the left

-CH_2-CH_2-CH_2-



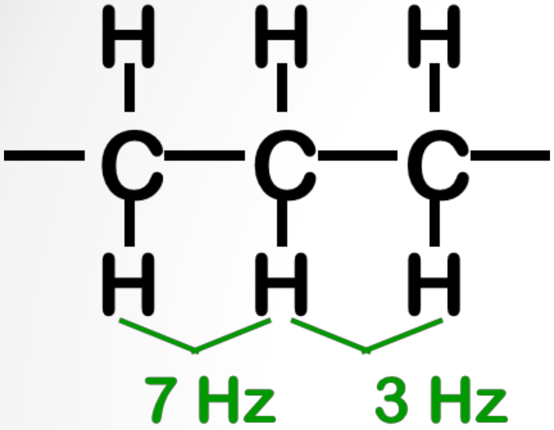
$n+1 = (4 + 1) = 5$

LEVEL TWO
Splitting from hydrogens on the right

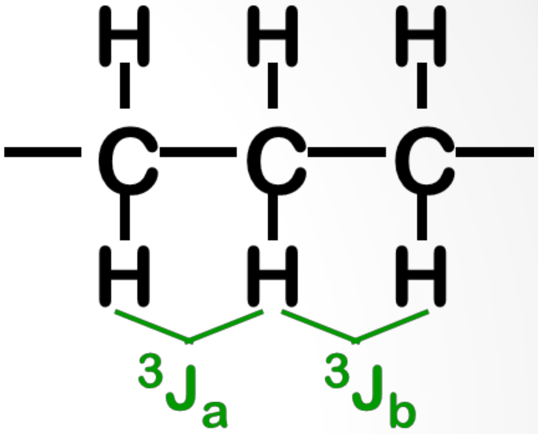
Splittings overlap

..... because of overlapping legs. You get the quintet predicted by the n+1 rule.

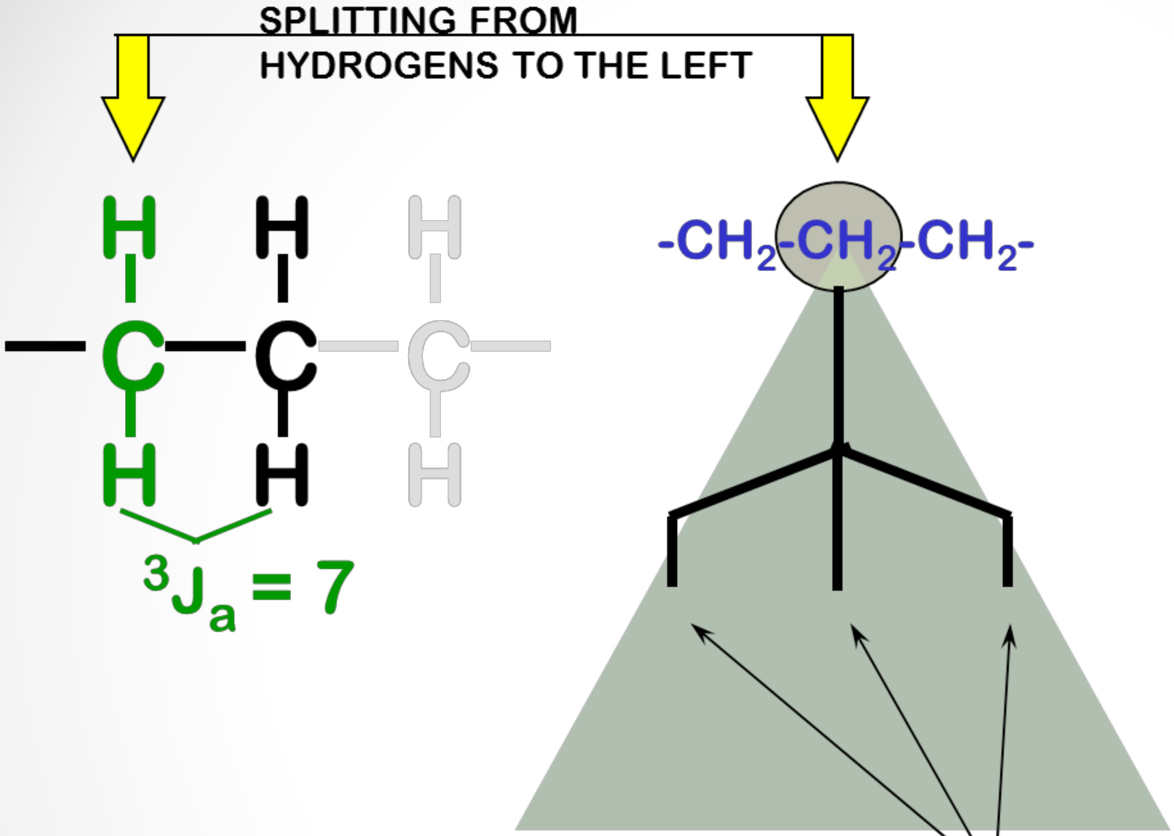
What happens when the J values are not equal ?



$^3J_a \neq {}^3J_b$



A “ Splitting Tree ” is constructed



SPLITTING FROM
HYDROGENS TO THE LEFT

LEVEL ONE

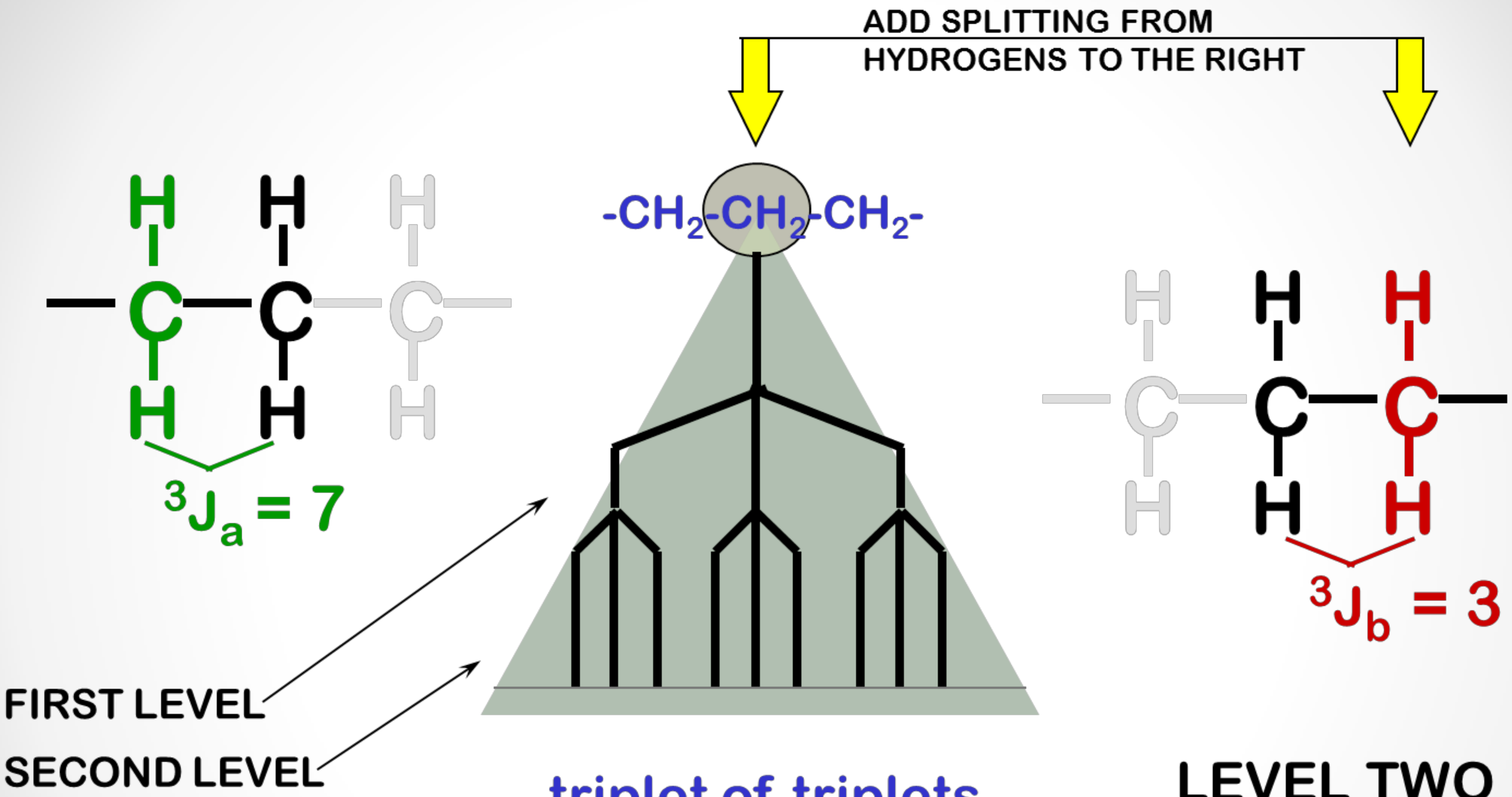
The largest J value is usually used first.

Two neighbors gives a triplet.

The next splittings will be added to <u>each</u> <u>leg</u> of the first splitting.

Each level of the splitting uses the n+1 rule.

ADD SPLITTING FROM HYDROGENS TO THE RIGHT



FIRST LEVEL

SECOND LEVEL

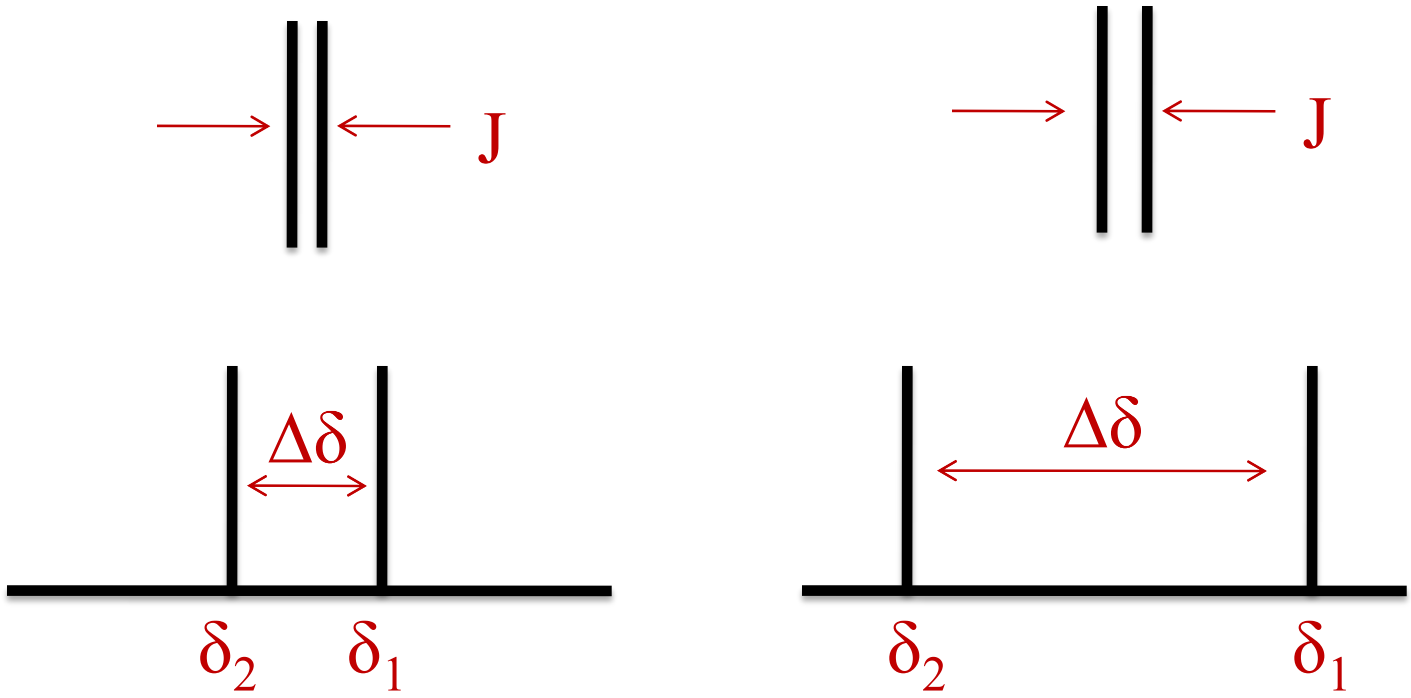
triplet of triplets

LEVEL TWO

The smaller splitting is used second.

It is also a triplet.

Simple and Complex Spectra



$\Delta\delta/J < 10$

Second-order spectra

$\Delta\delta/J > 10$

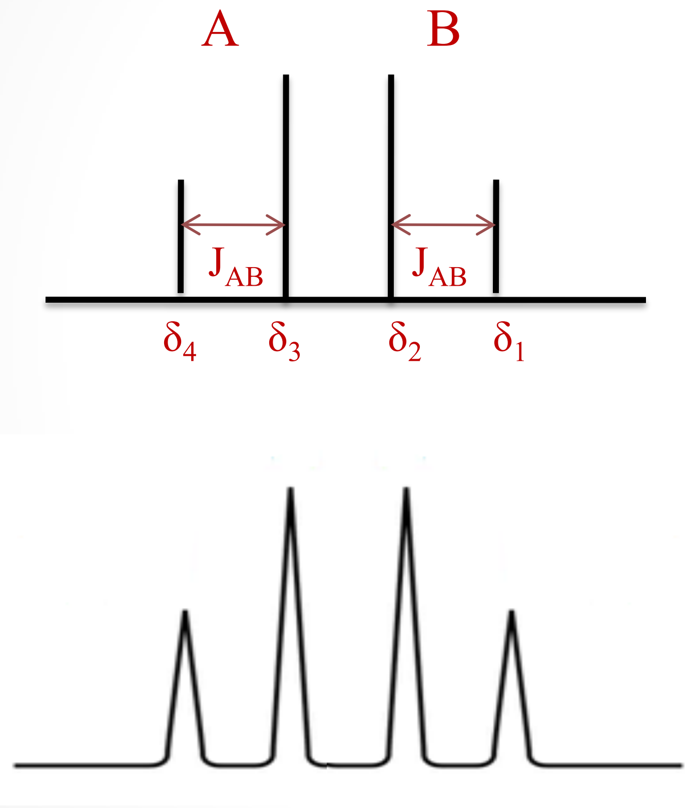
First-order spectra

Classification of splitting systems

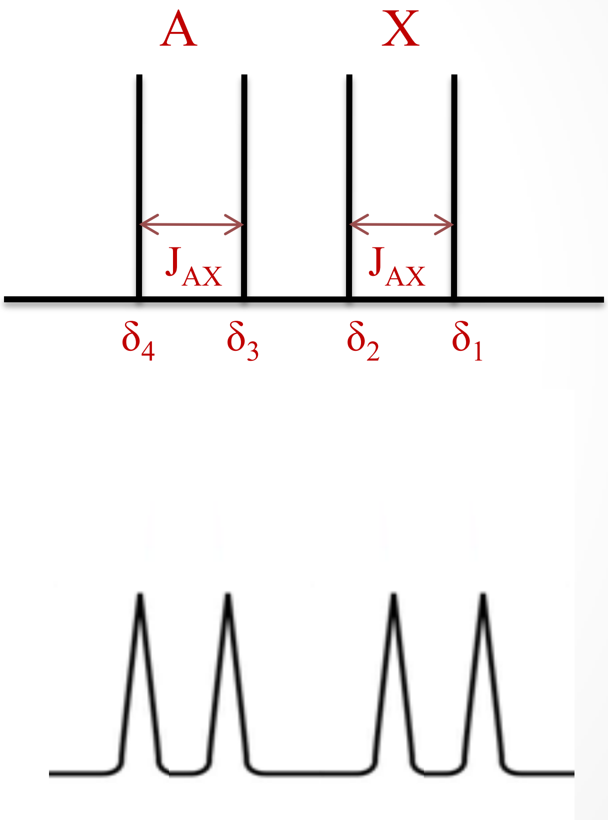
- AB pattern
- AX pattern
- ABC pattern
- ABX pattern
- AMX pattern

AB and AX patterns

$\Delta\delta \approx J$

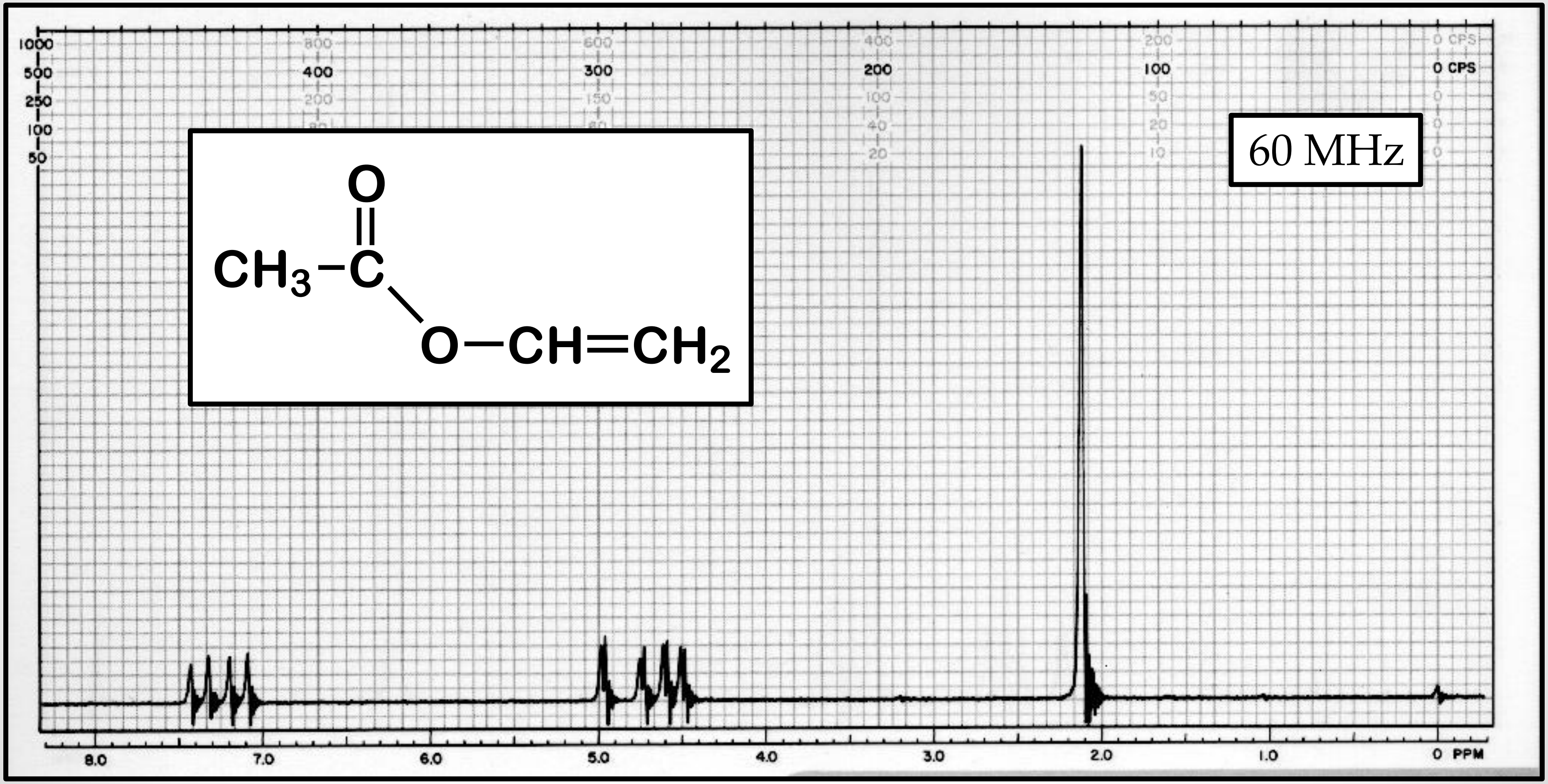


$\Delta\delta > J$

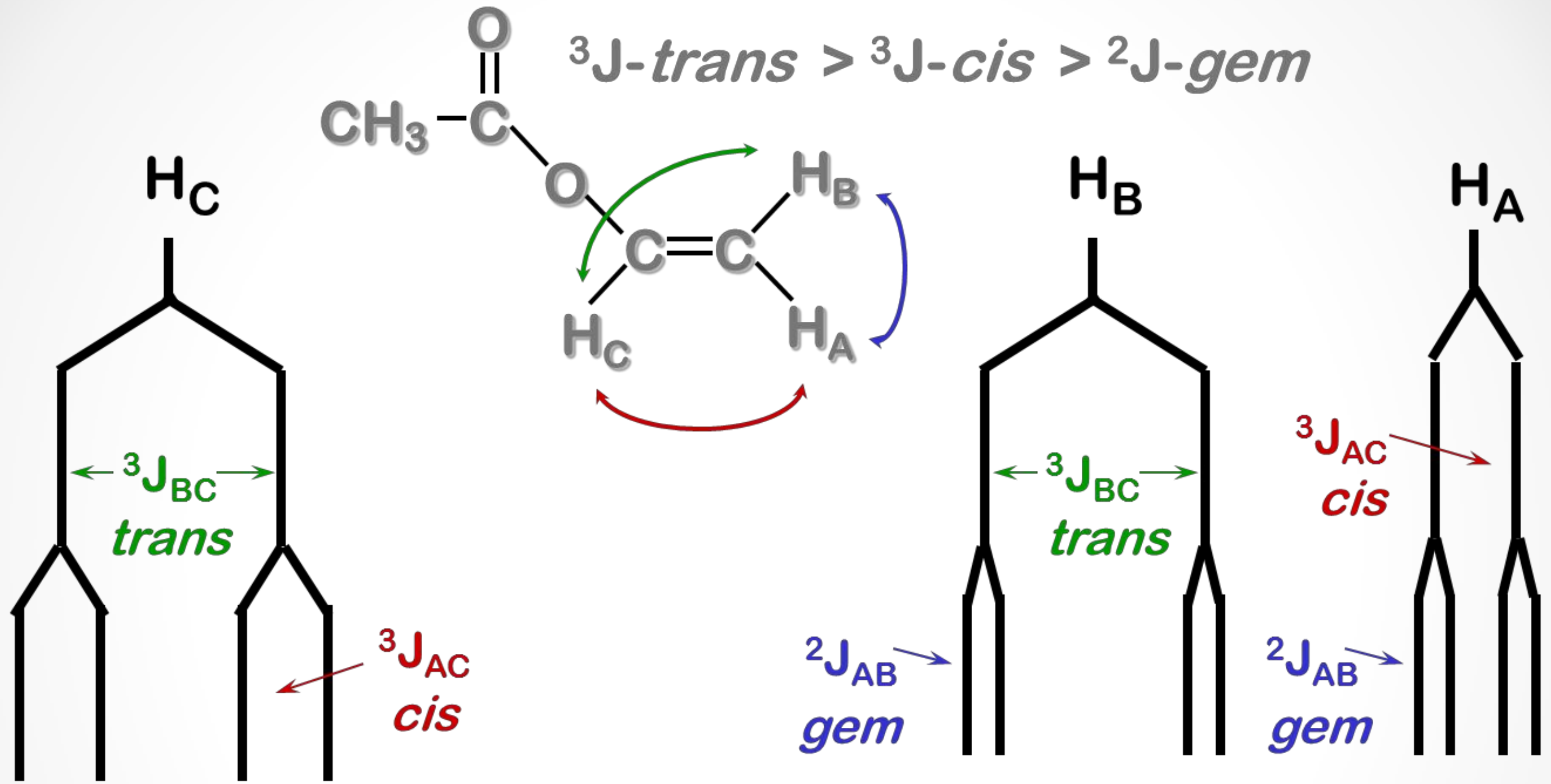


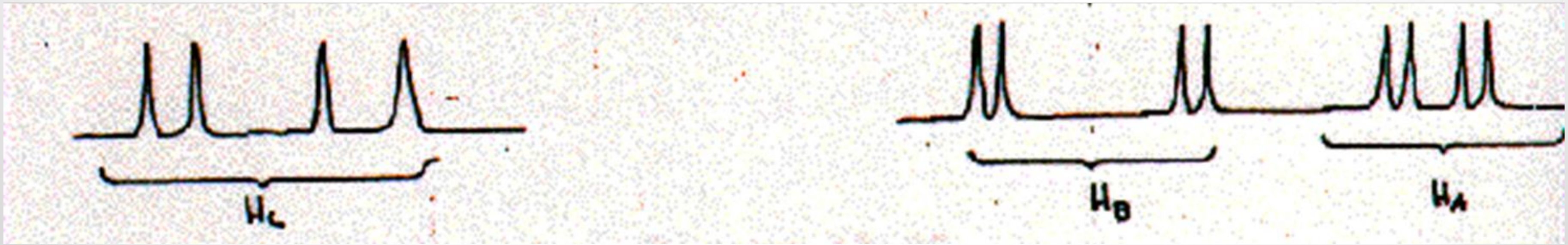
AMX pattern

NMR Spectrum of Vinyl Acetate

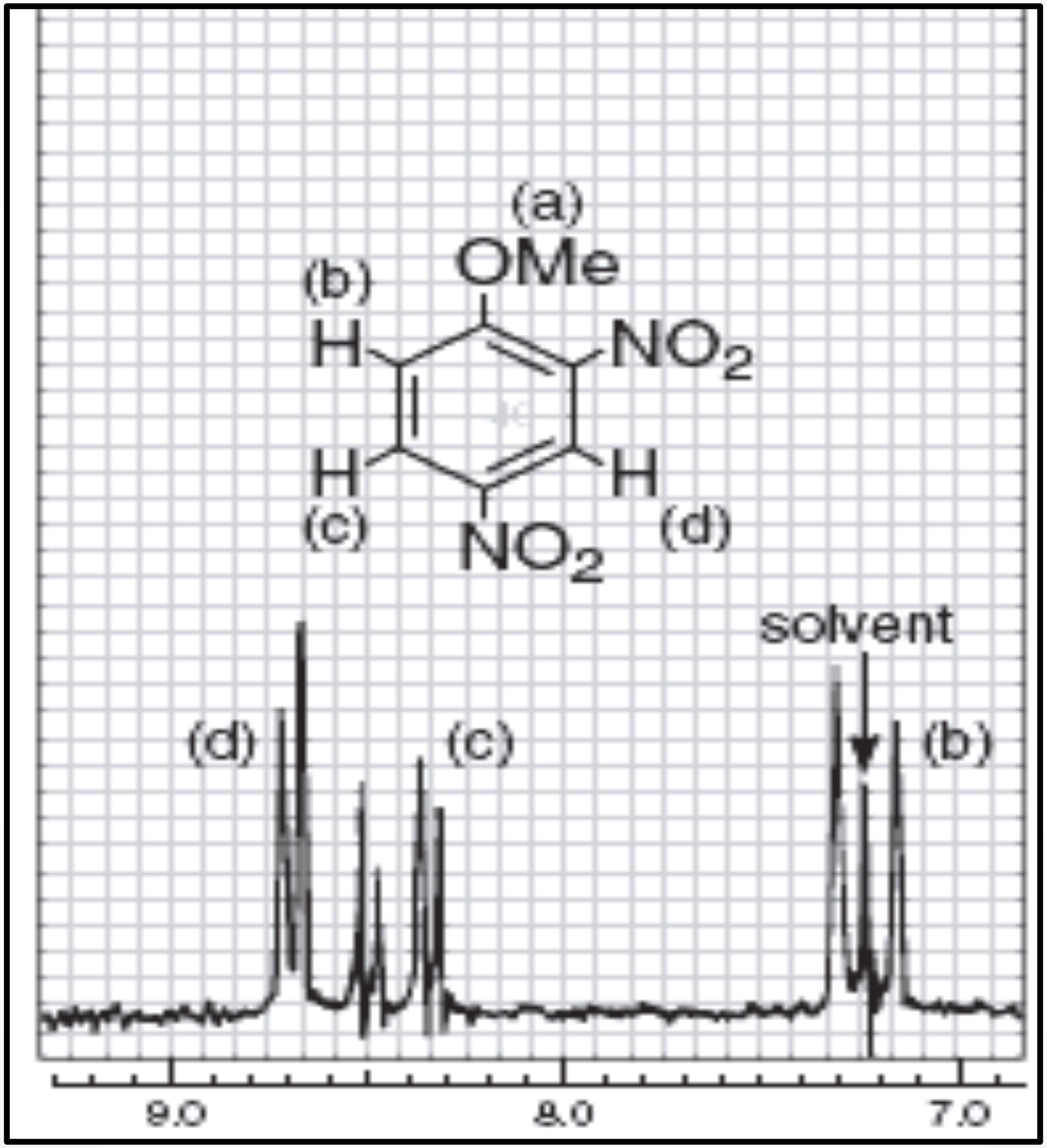


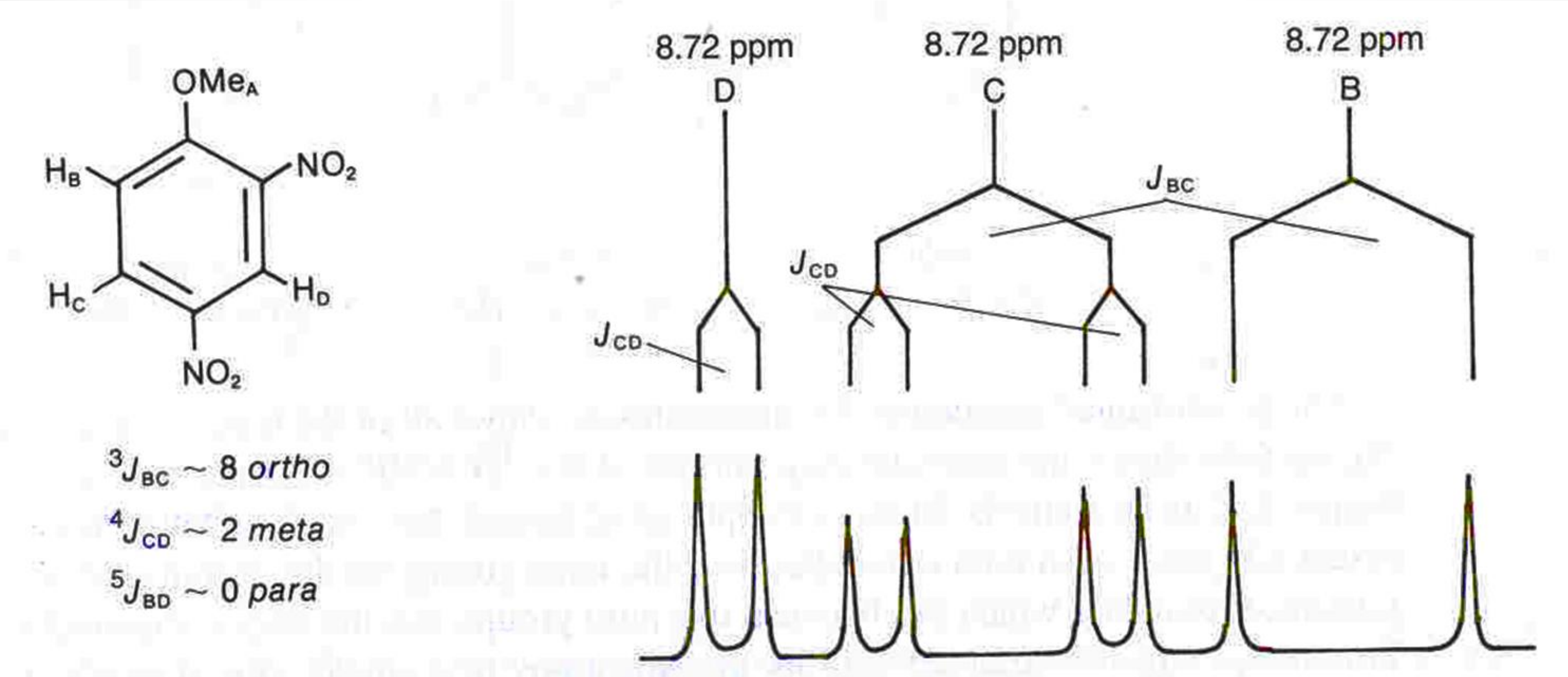
^{3}J-*trans* > ^{3}J-*cis* > ^{2}J-*gem*





2,4-Dinitroanisole





$^{3}J_{BC} \sim 8$ *ortho*

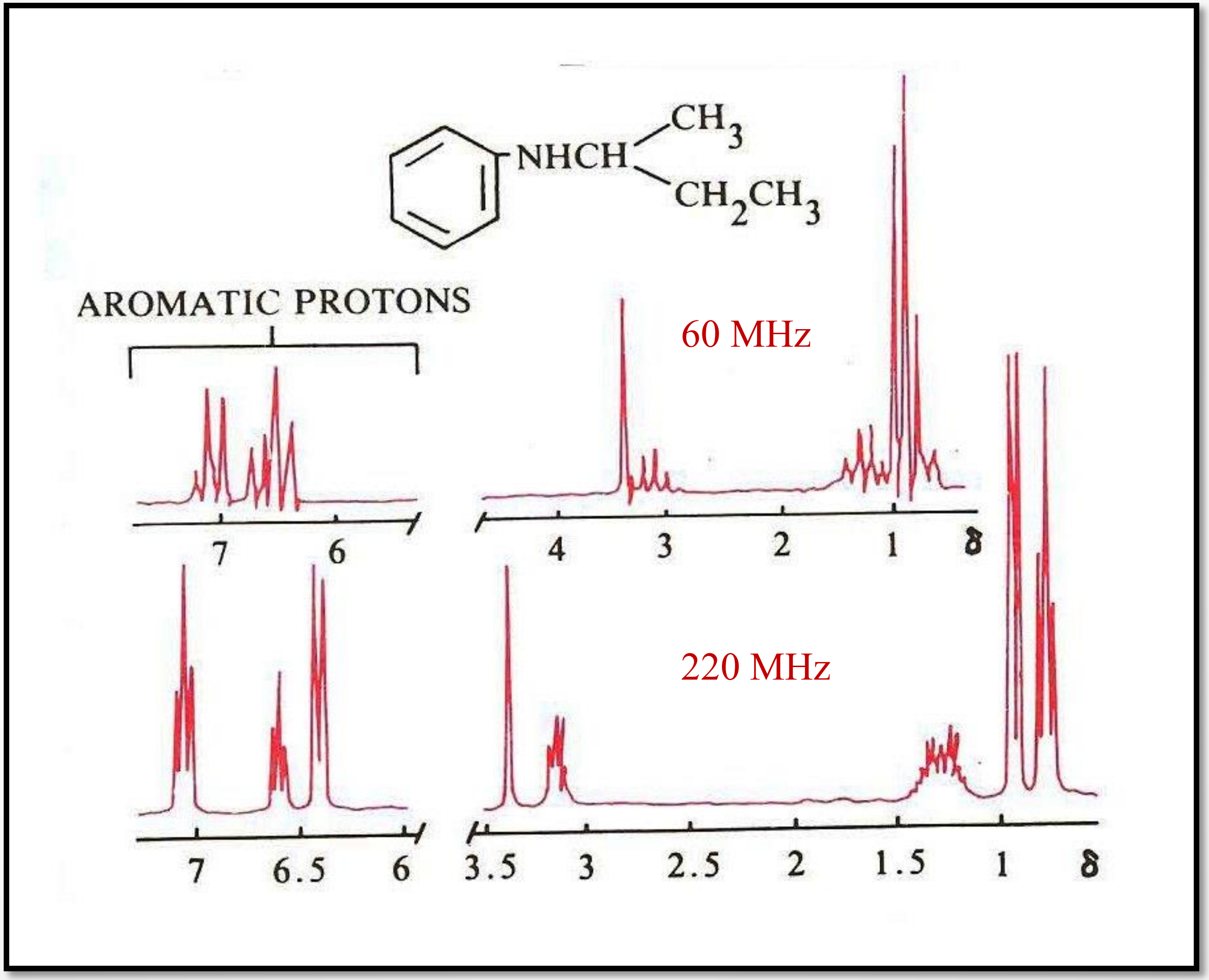
$^{4}J_{CD} \sim 2$ *meta*

$^{5}J_{BD} \sim 0$ *para*

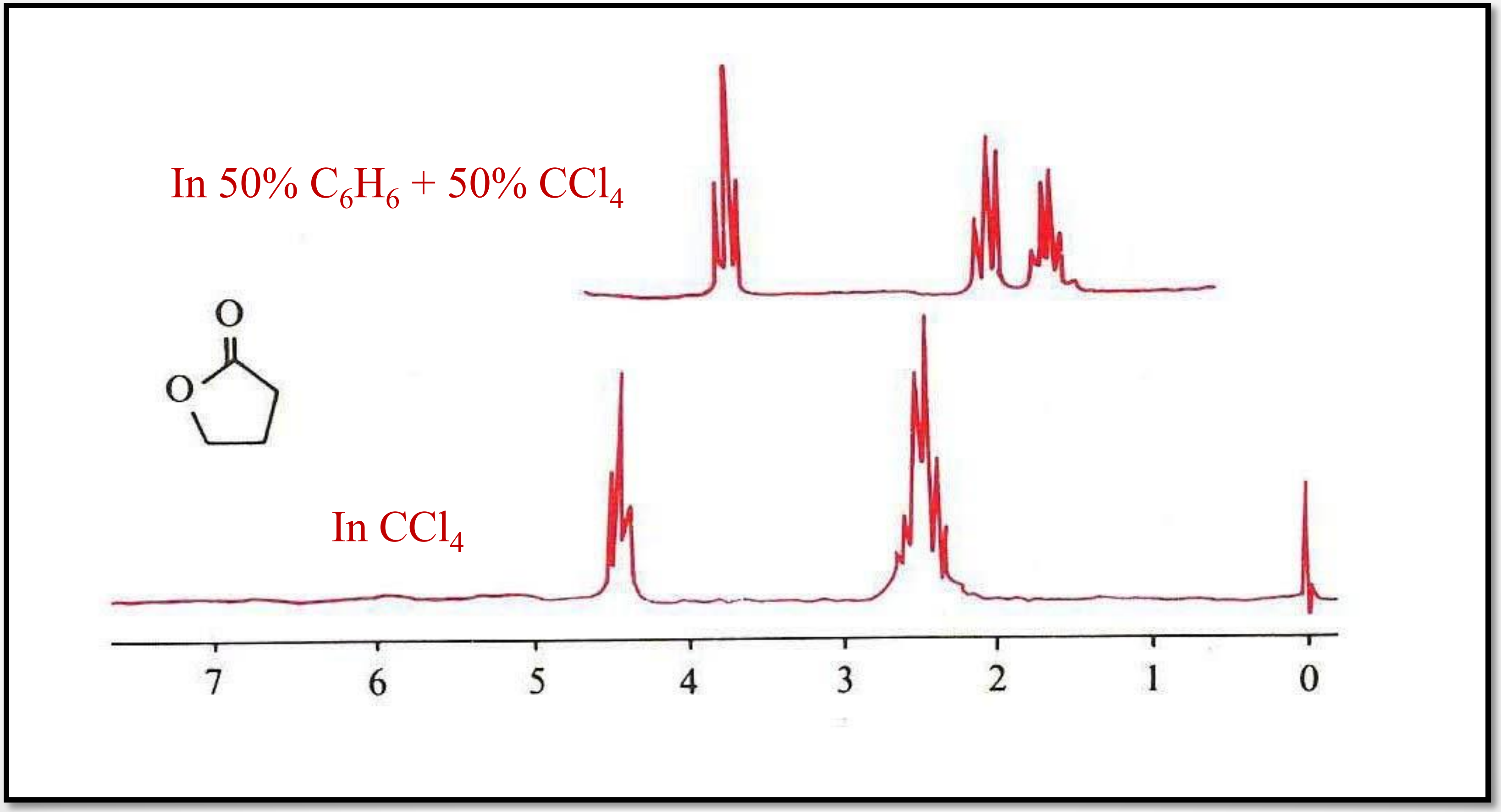
Simplification of Complex ^{1}H-NMR Spectra

- Increasing the Frequency of the Instrument
- Deuteration
- Change the Solvent
- Double resonance
- Shift reagents

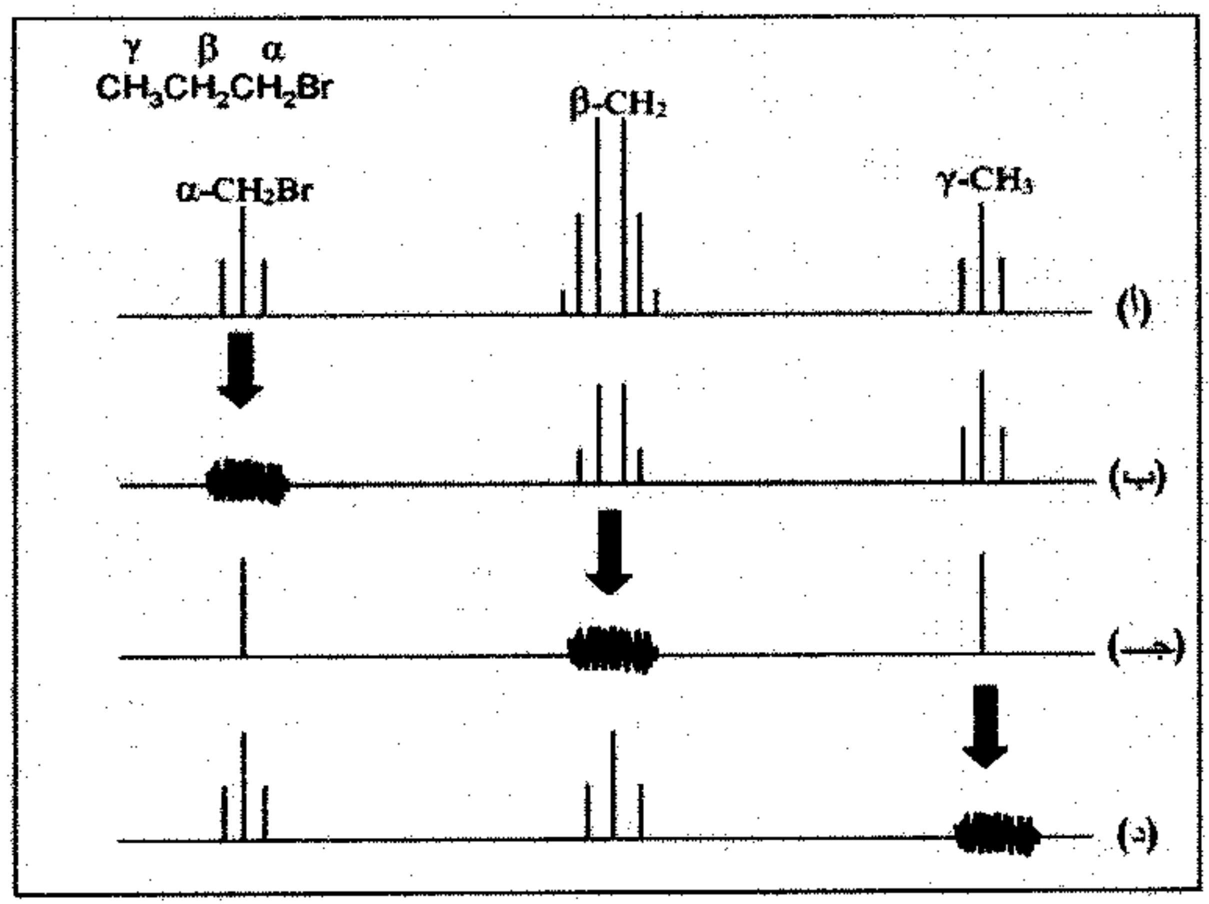
Increasing the Frequency of the Instrument



Change the Solvent



Double resonance



Carbon-13

- ^{12}C is not NMR-active (no magnetic spin (I = 0))
- ^{13}C has a magnetic spin (I = 1/2 , odd mass)
- ^{13}C signals are 6000 times weaker than ^{1}H because:
  1. Natural abundance of ^{13}C is small (1.08%)
  2. Magnetic moment of ^{13}C is small
- The gyromagnetic constant of ^{13}C is one-fourth of that of ^{1}H
- The chemical shift range is larger than for protons

^{13}C $\gamma = 6.72$
^{1}H $\gamma = 26.75$

0 - 200 ppm

- The number of different signals indicates the number of different kinds of carbon
- PULSED FT-NMR is required

The Larmor Equation!!!

$\Delta E = kB_o = h\nu$ can be transformed into

$$\nu = \left(\frac{\gamma}{2\pi}\right) B_o$$

frequency of the incoming radiation that will cause a transition

gyromagnetic ratio γ

strength of the magnetic field

γ is a constant which is different for each atomic nucleus (H, C, N, etc)

Coupling Constants

^{13}C - ^{13}C coupling NO!

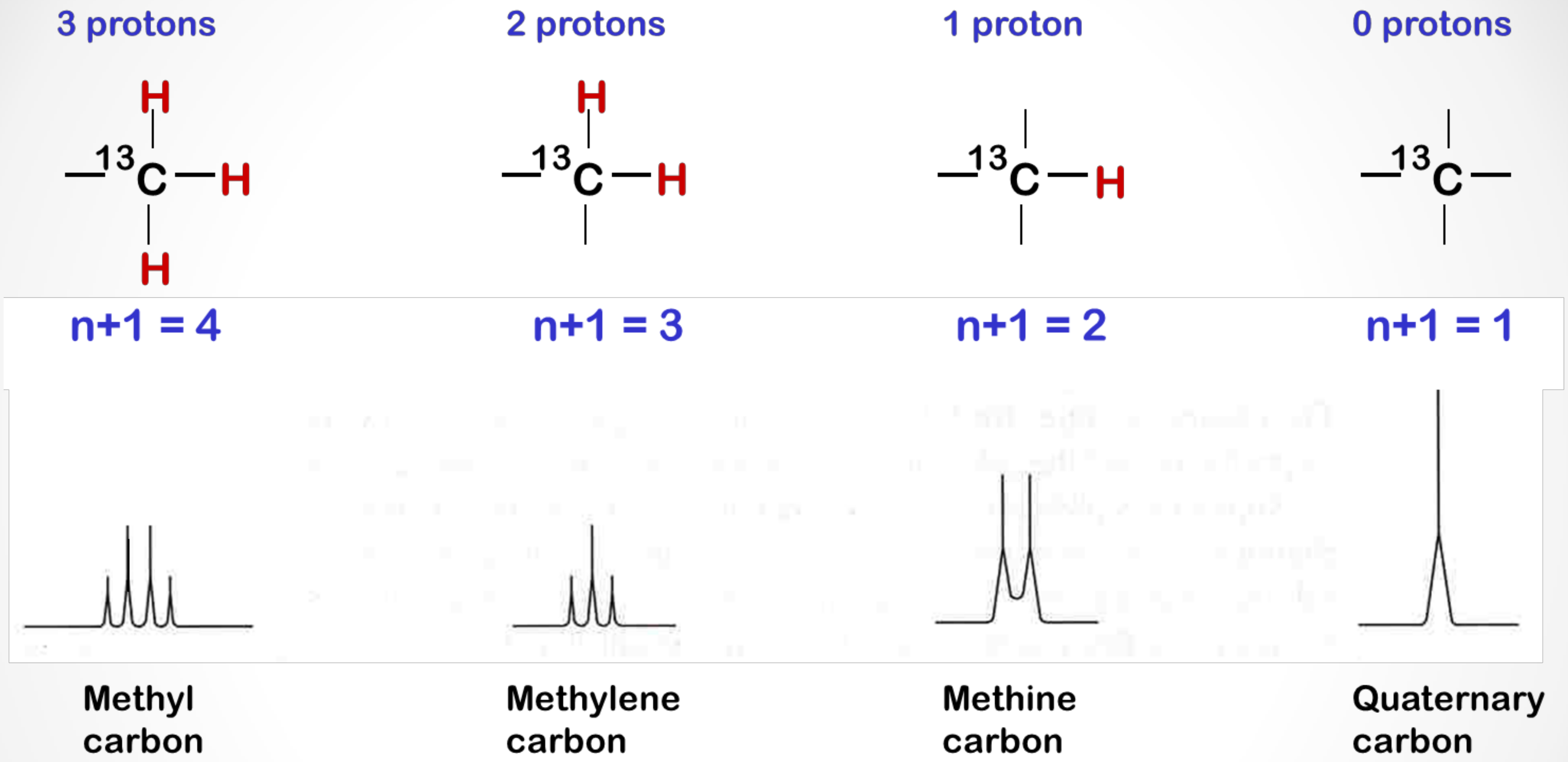
not probable

However, ^{13}C does couple to hydrogen atoms ($I = 1/2$)

^{13}C – ^{1}H coupling YES!

very common

Coupling to attached Protons



3 protons — n+1 = 4 — Methyl carbon

2 protons — n+1 = 3 — Methylene carbon

1 proton — n+1 = 2 — Methine carbon

0 protons — n+1 = 1 — Quaternary carbon

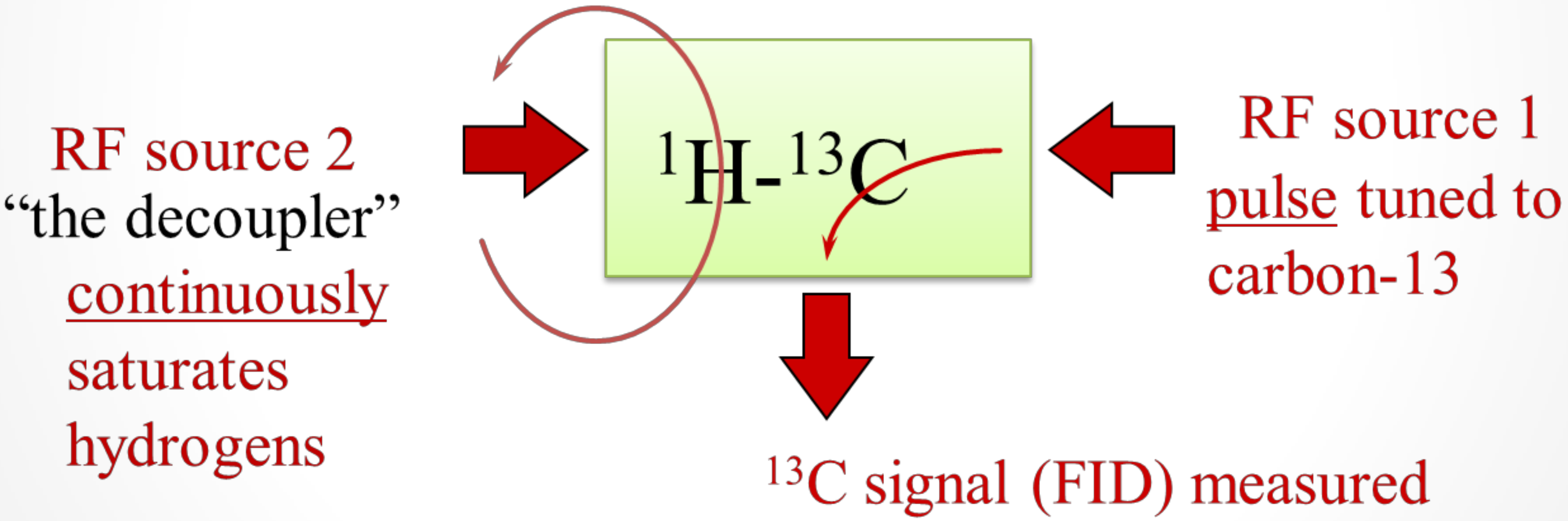
The effect of attached protons on ^{13}C resonances

(n+1 rule applies)   (J's are large ~ 100 - 200 Hz)

Decoupling the Proton Spins

Proton-Decoupled Spectra

Off-resonance decoupling



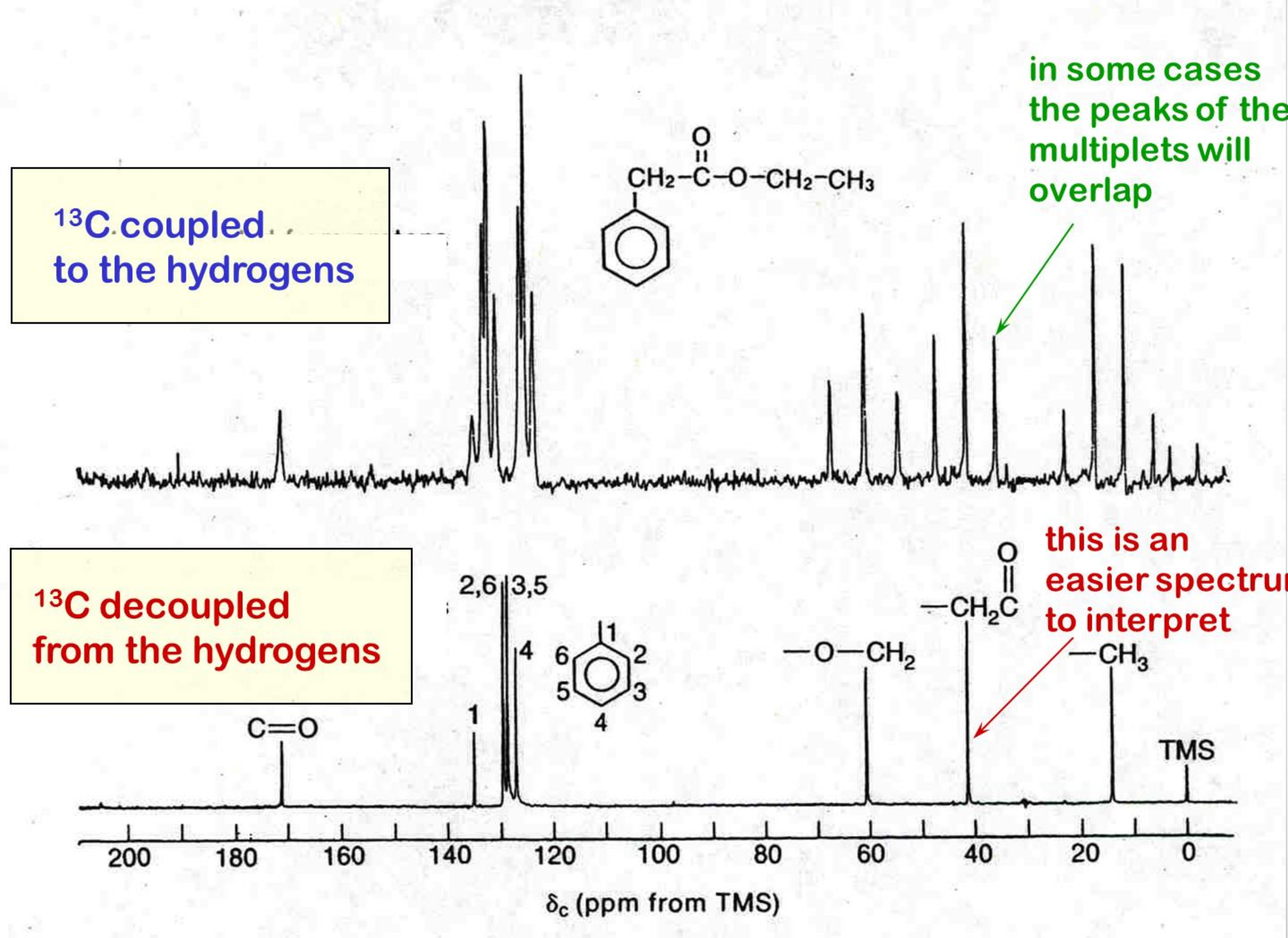
RF source 2
"the decoupler"
continuously
saturates
hydrogens

^1H-^{13}C

RF source 1
pulse tuned to
carbon-13

^{13}C signal (FID) measured

Ethylphenylacetate



^{13}C coupled
to the hydrogens

in some cases
the peaks of the
multiplets will
overlap

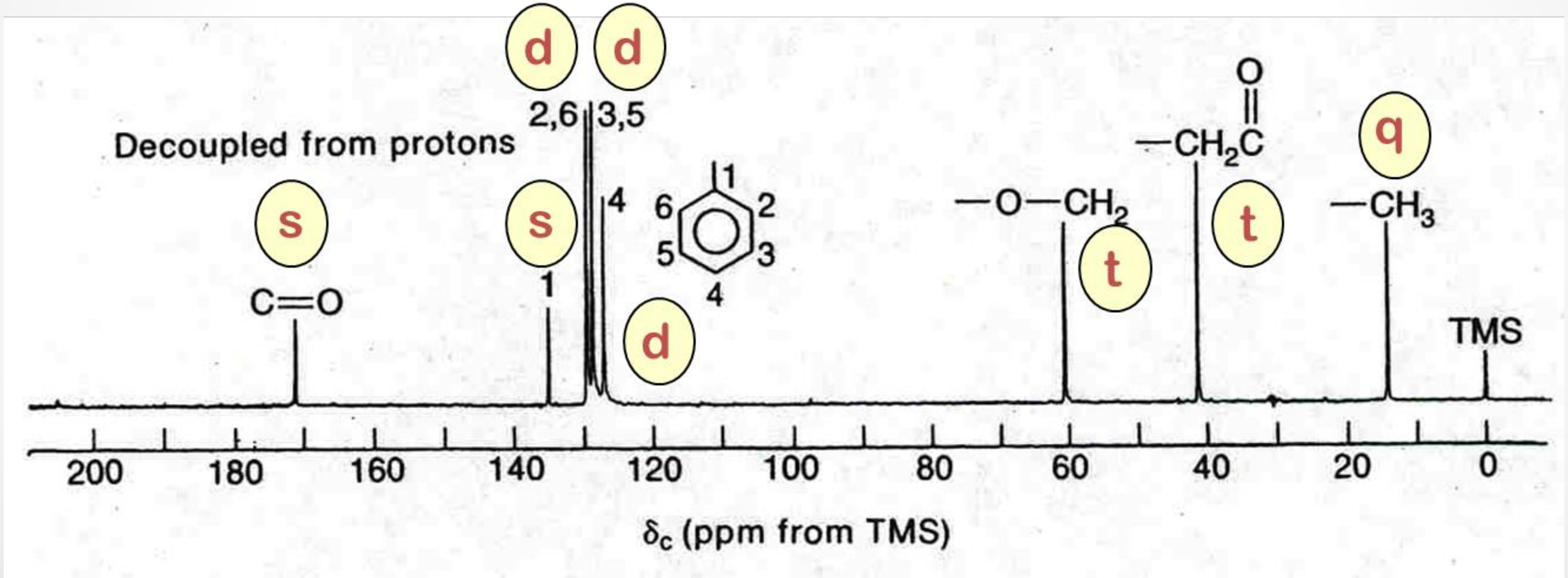
^{13}C decoupled
from the hydrogens

this is an
easier spectrum
to interpret

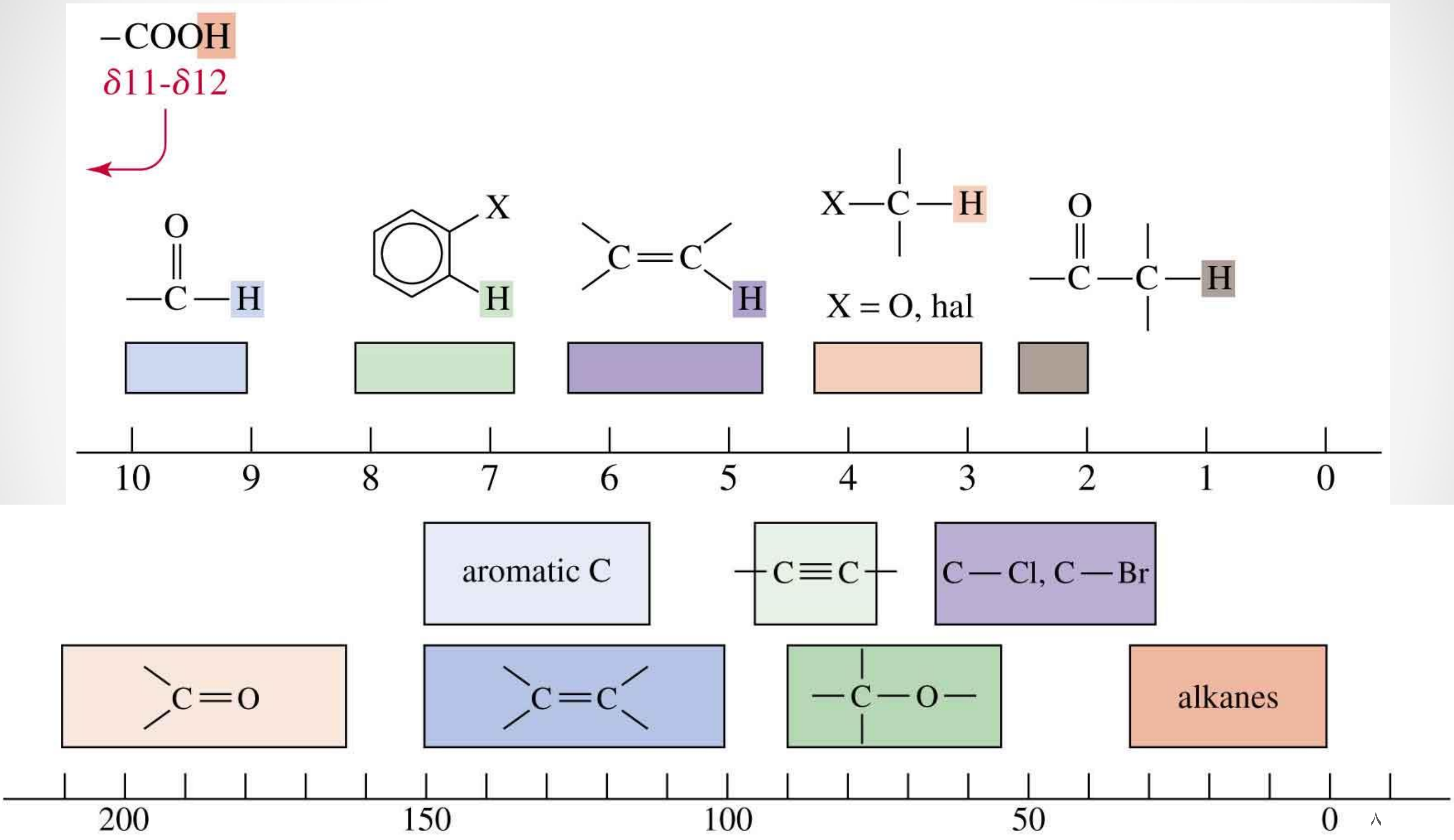
Some Instruments Show The Multiplicities of The Peaks on The Decoupled Spectra

CODE :

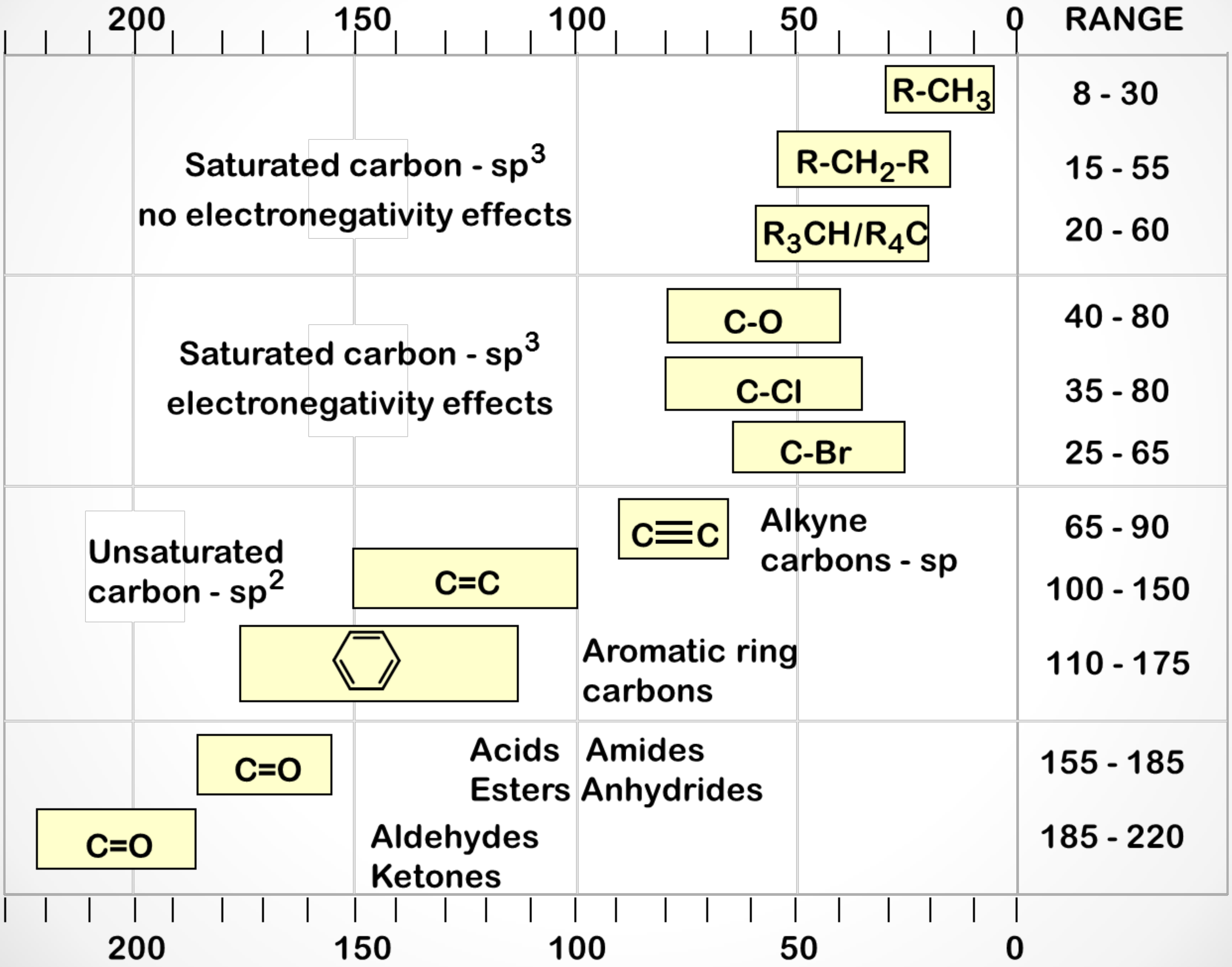
s = singlet
d = doublet
t = triplet
q = quartet



Hydrogen and Carbon Chemical Shifts

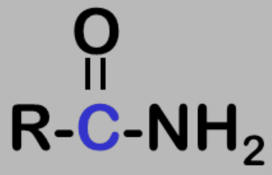
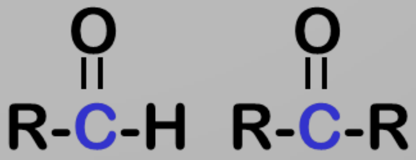


Correlation chart for ^{13}C Chemical Shifts (ppm)



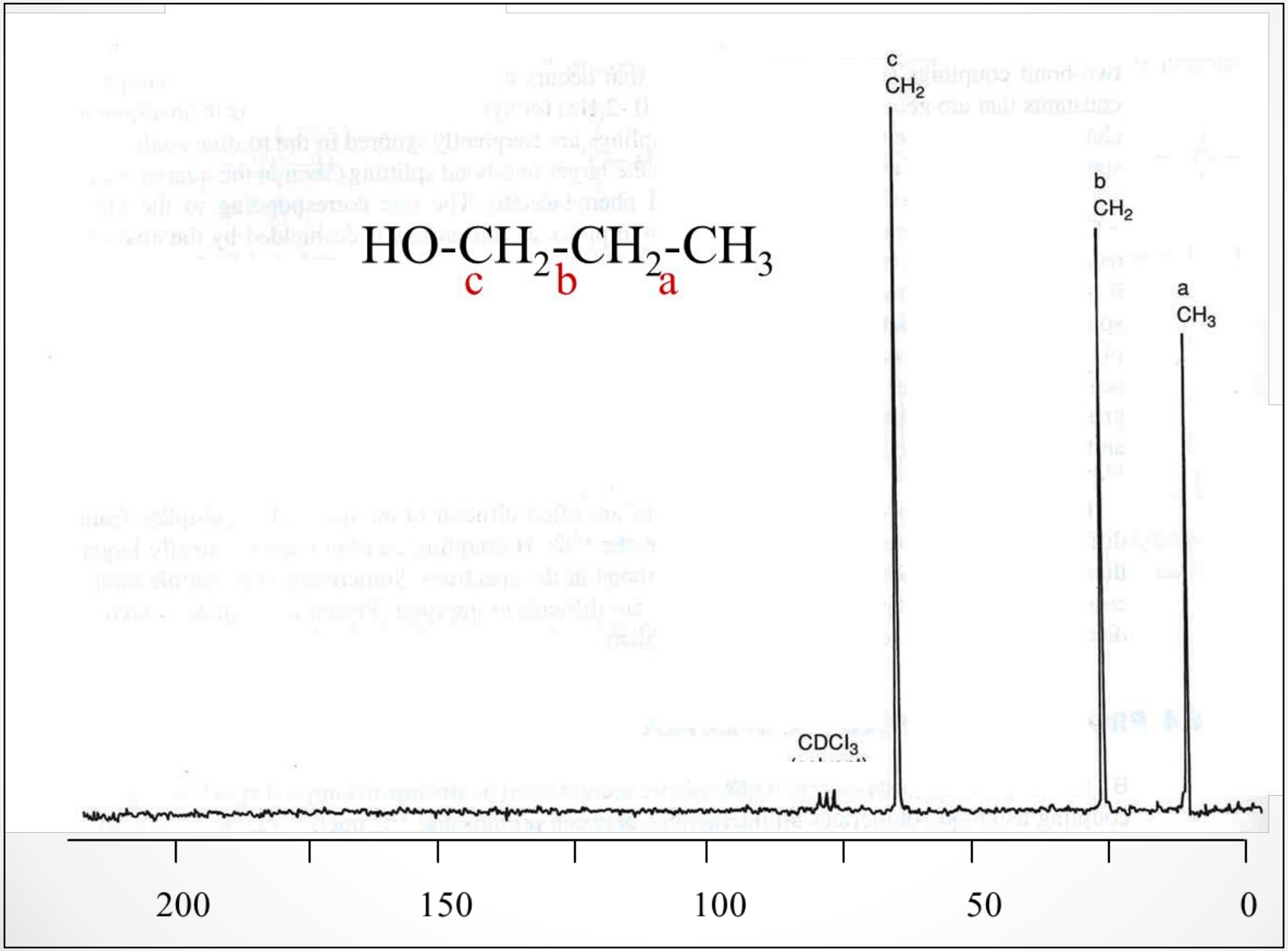
Approximate Chemical Shift Ranges (ppm) for Selected Types of Carbon.

$R-CH_3$	8 - 30
R_2CH_2	15 - 55
R_3CH	20 - 60
C-I	0 - 40
C-Br	25 - 65
C-Cl	35 - 80
C-N	30 - 65
C-O	40 - 80

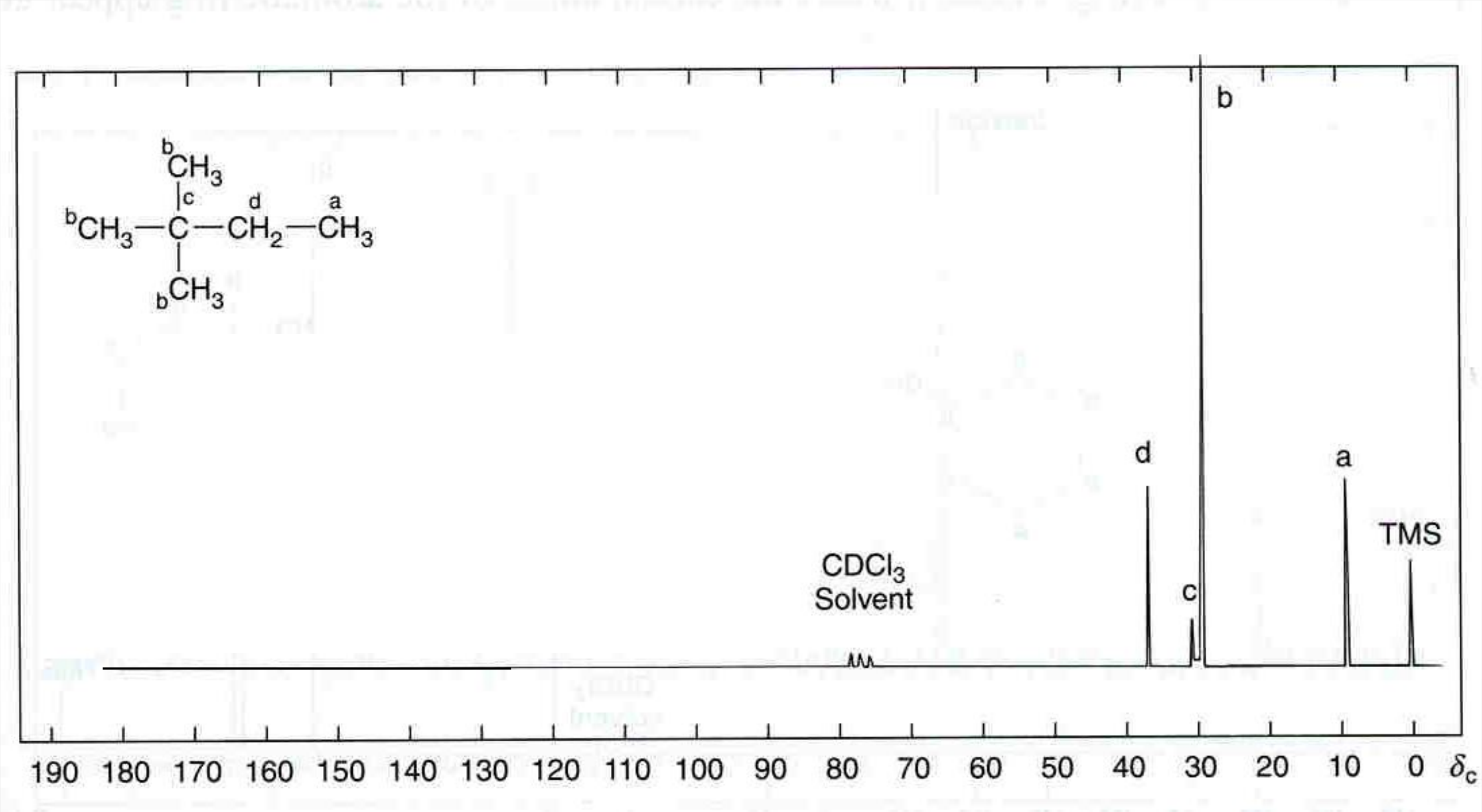
$C\equiv C$	65 - 90
$C=C$	100 - 150
$C\equiv N$	110 - 140
	110 - 175
 $R-\overset{O}{\overset{\|}{C}}-OR$ $R-\overset{O}{\overset{\|}{C}}-OH$	155 - 185
 $R-\overset{O}{\overset{\|}{C}}-NH_2$	155 - 185
 $R-\overset{O}{\overset{\|}{C}}-H$ $R-\overset{O}{\overset{\|}{C}}-R$	185 - 220

1-Propanol

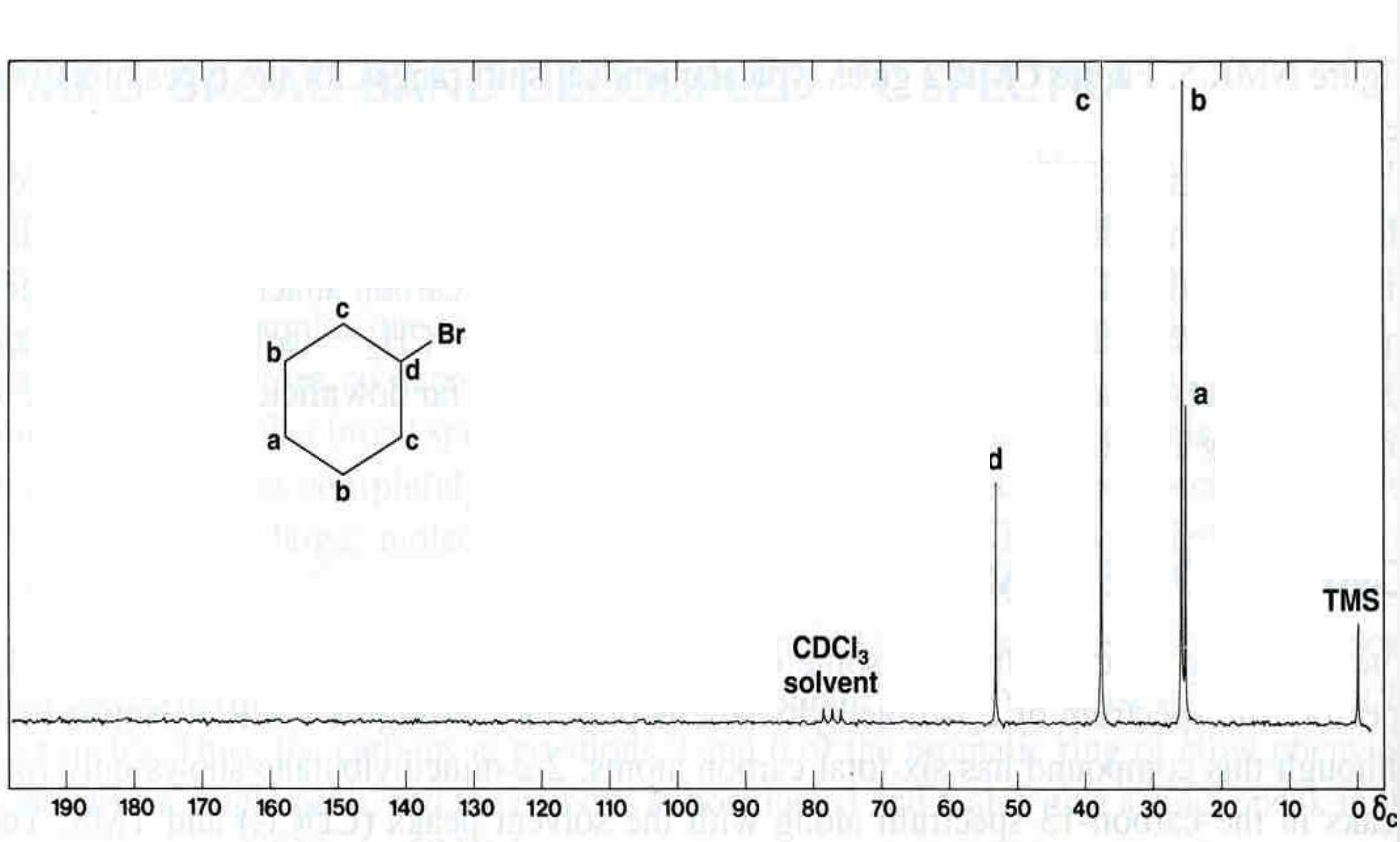
$HO\text{-}\underset{c}{CH_2}\text{-}\underset{b}{CH_2}\text{-}\underset{a}{CH_3}$



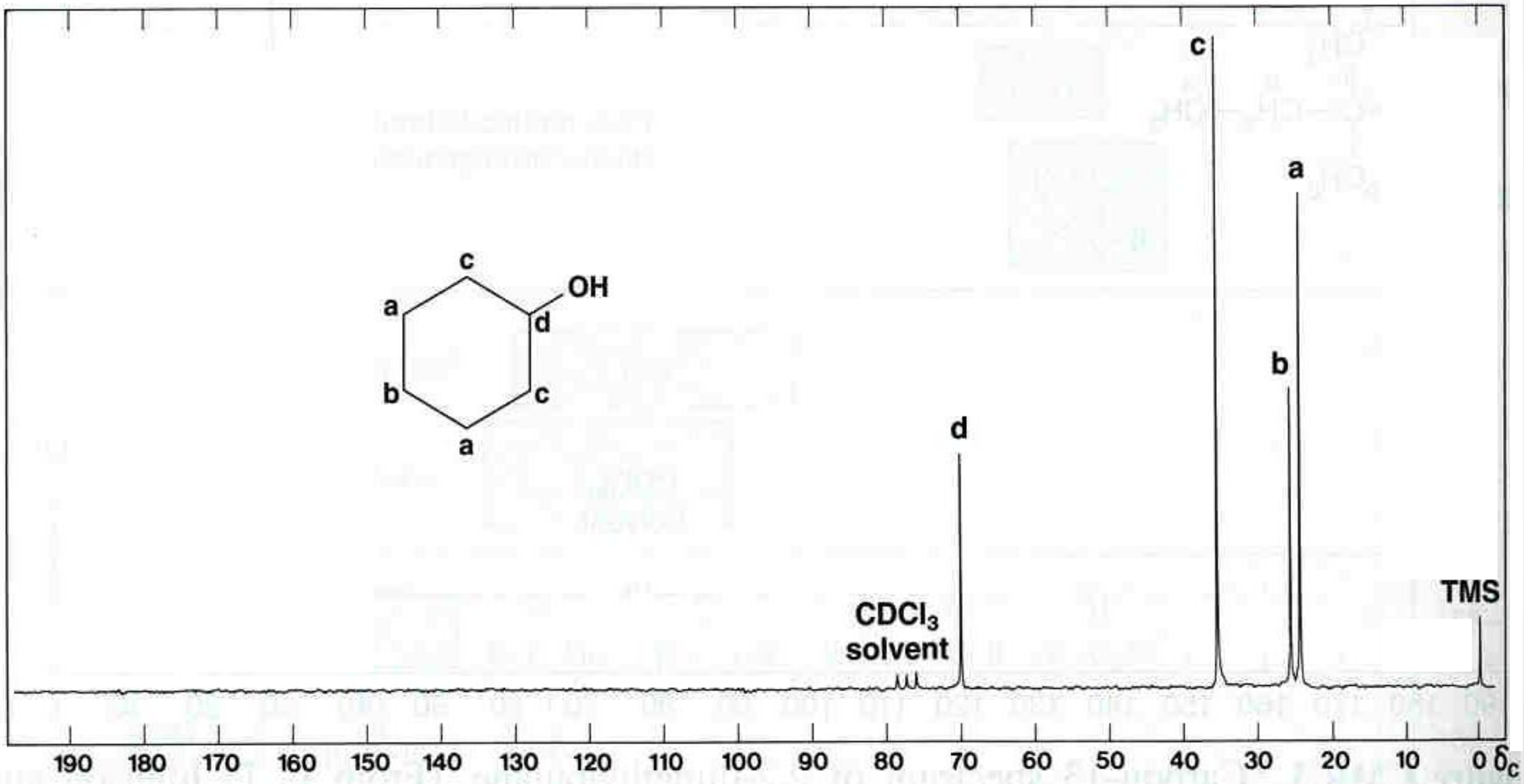
2,2-Dimethylbutane



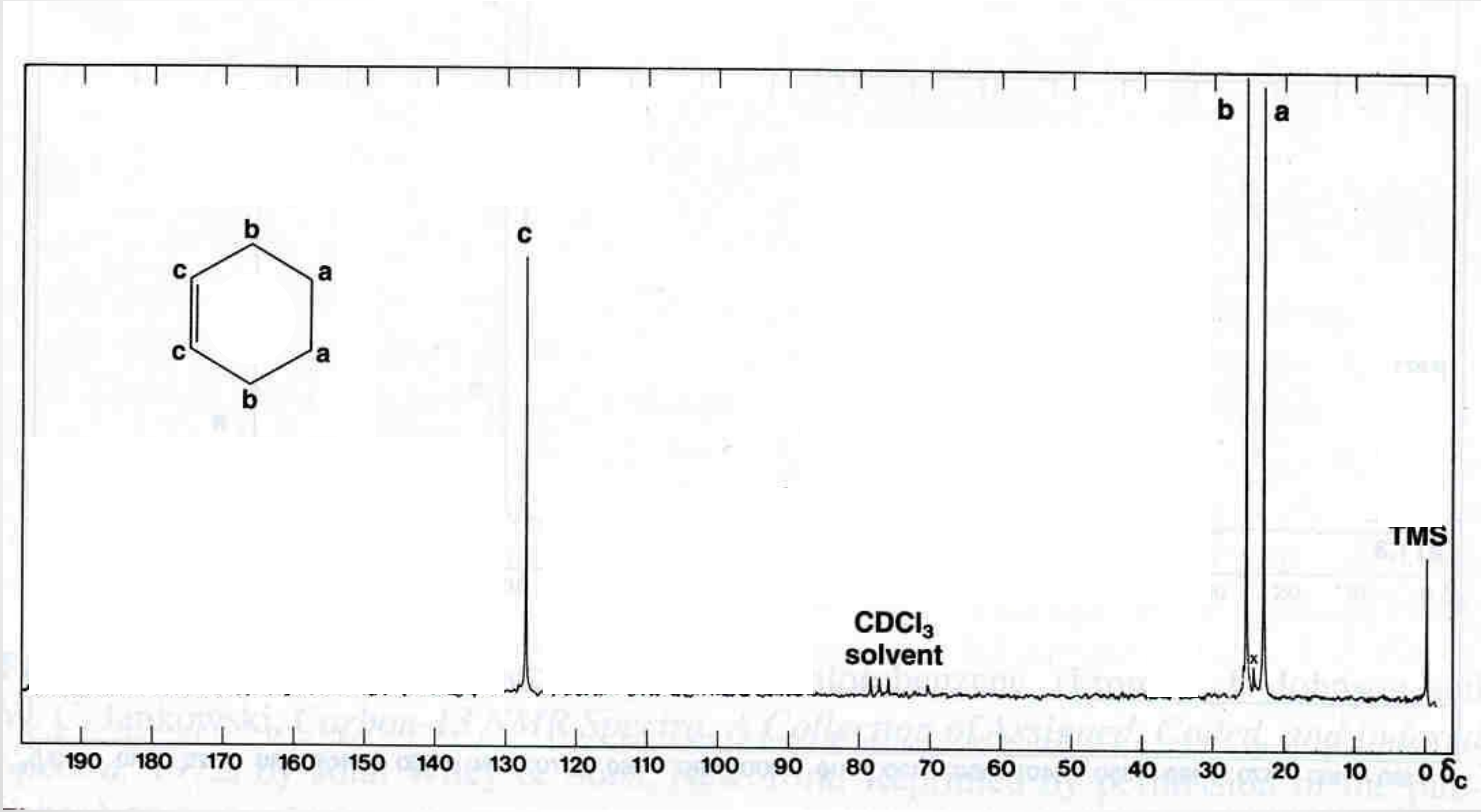
Bromocyclohexane



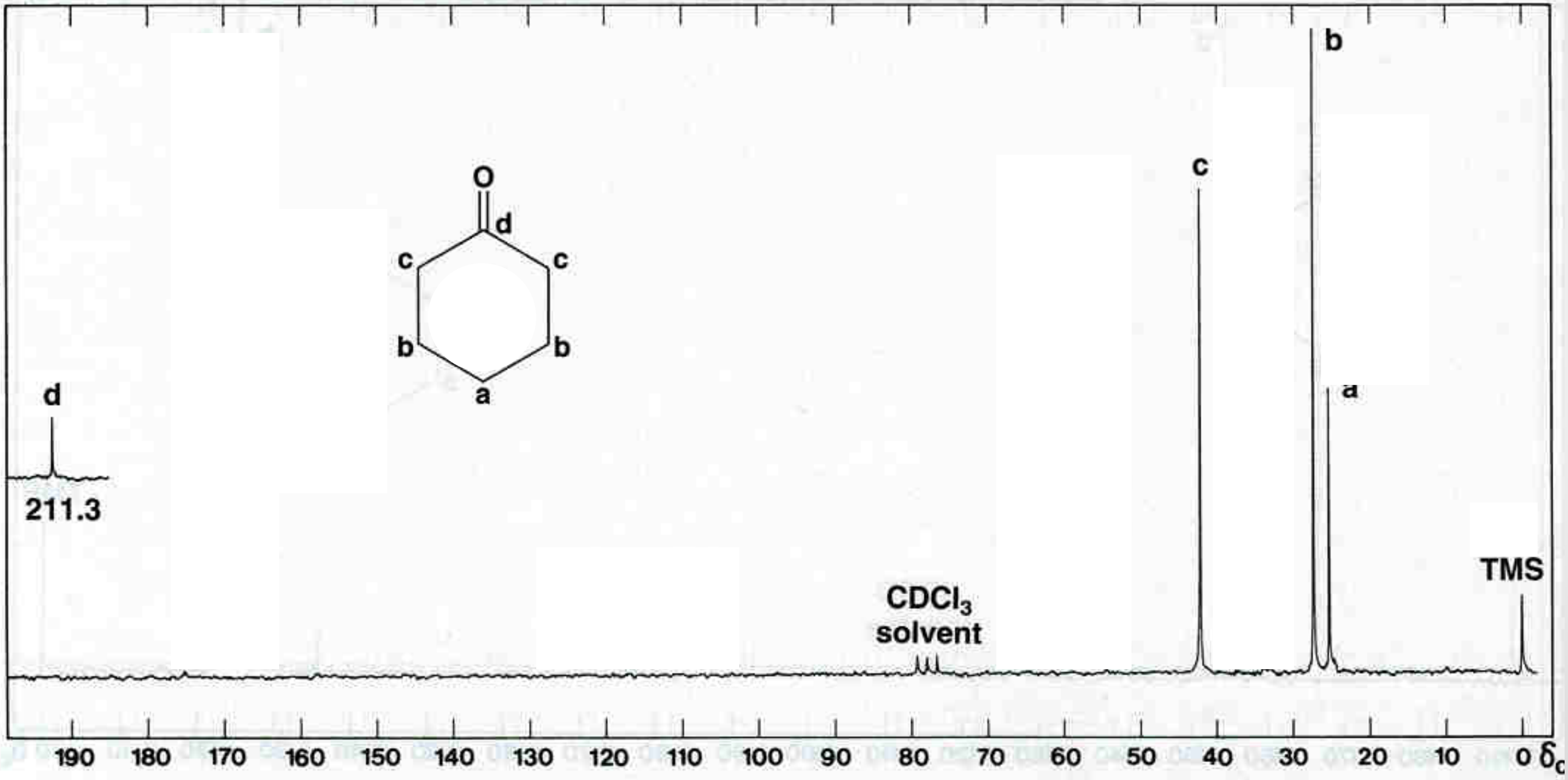
Cyclohexanol



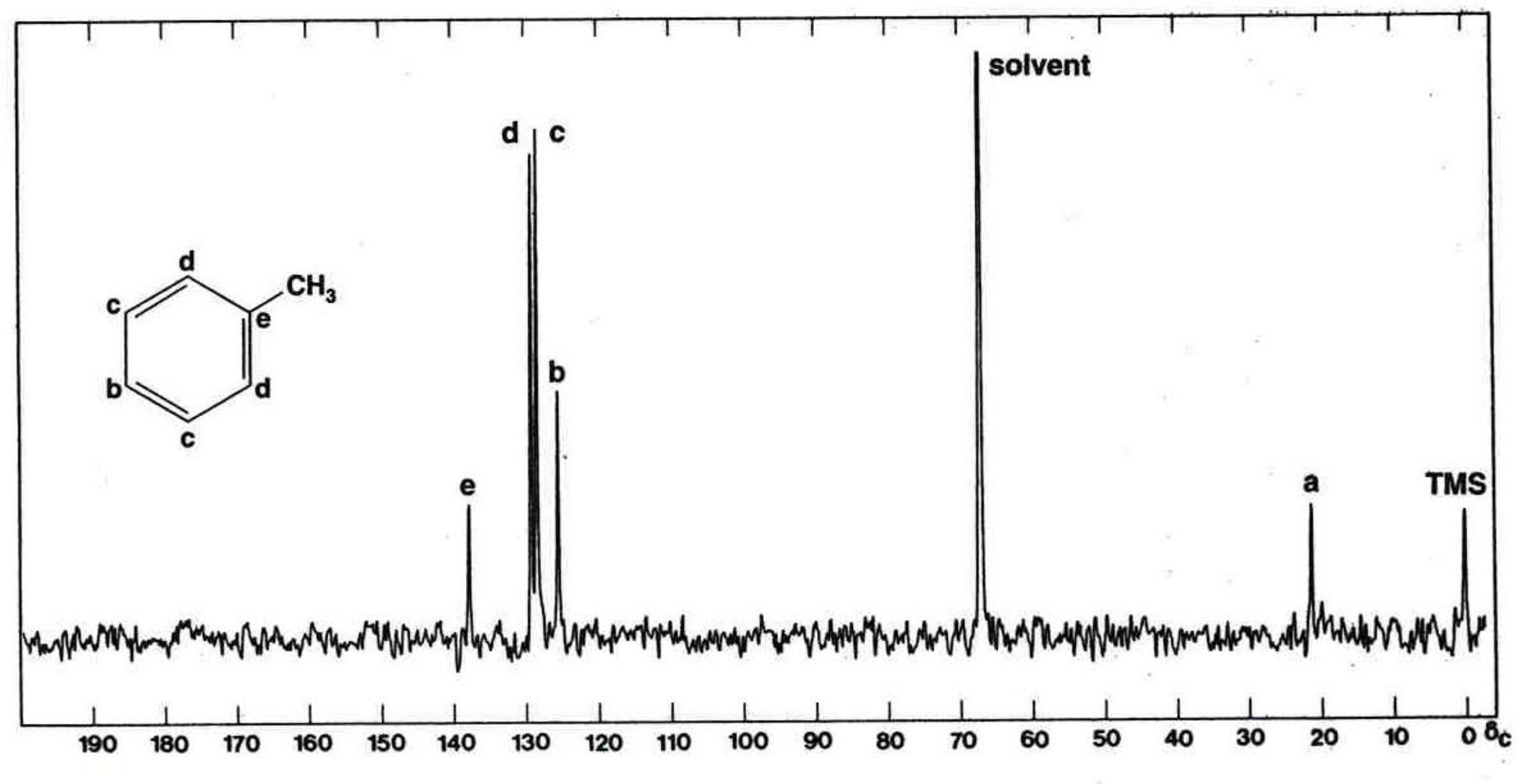
Cyclohexene



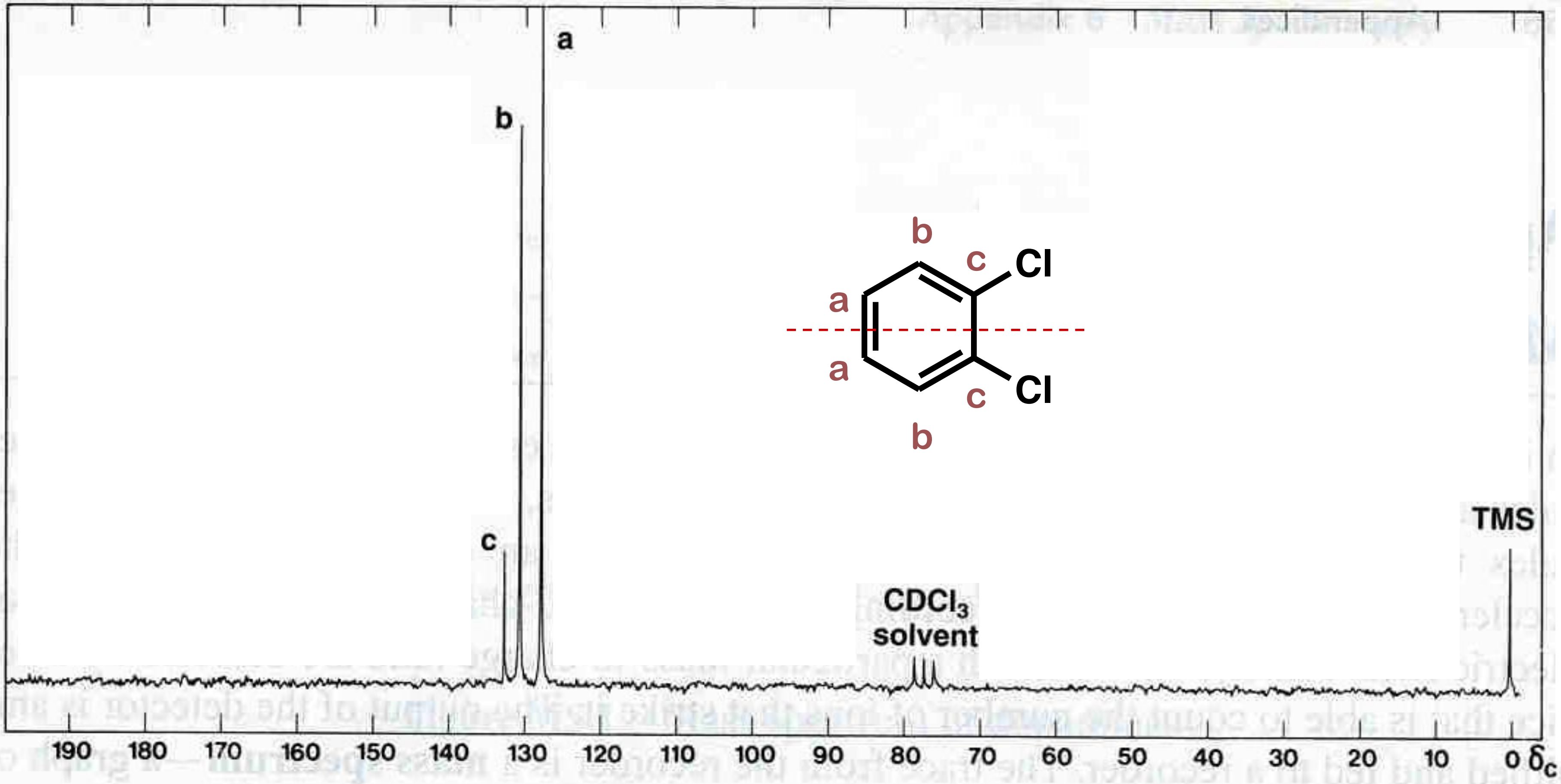
Cyclohexanone



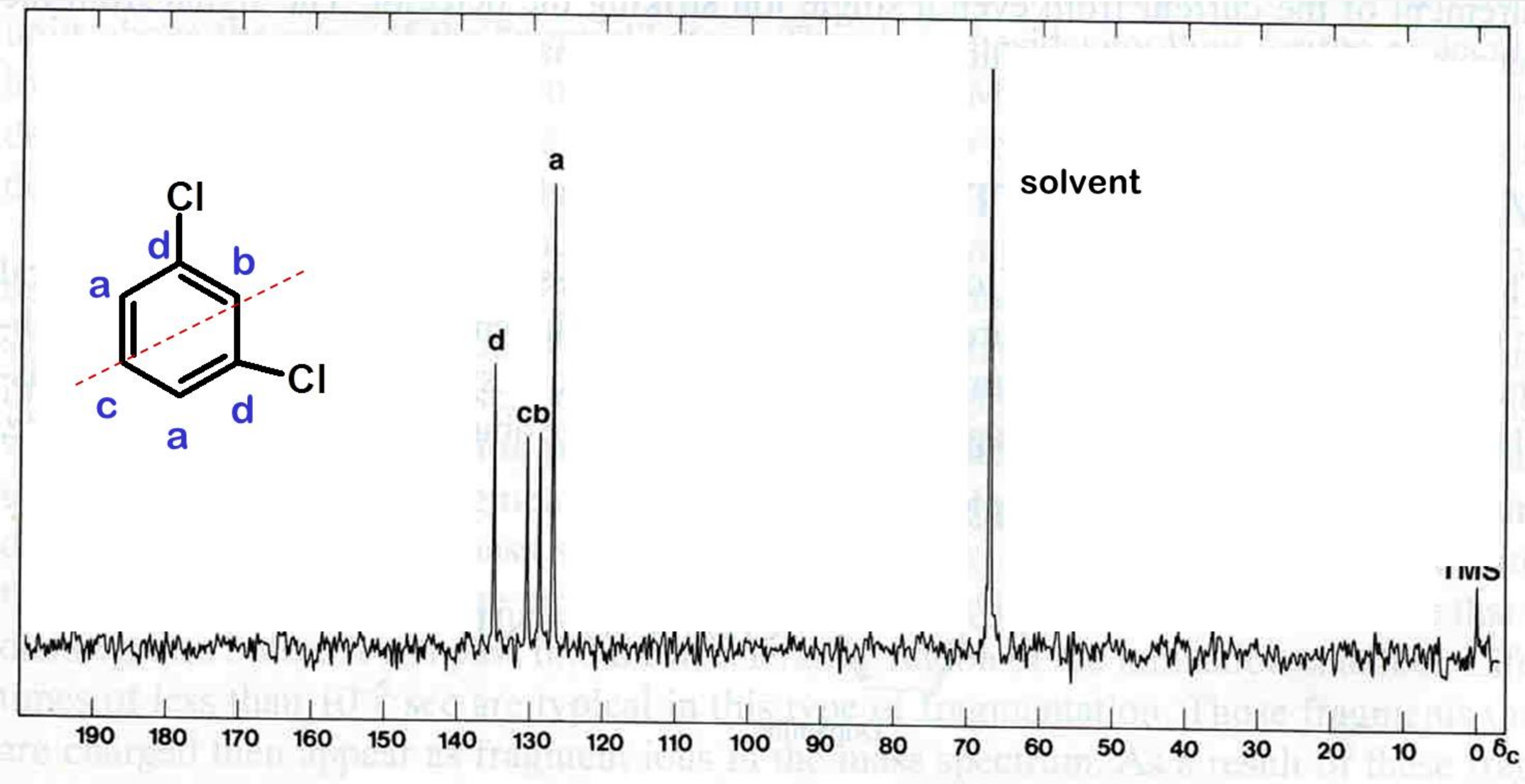
Toluene


solvent
d
c
b
e
a
TMS
CH_3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ_C

1,2-Dichlorobenzene



1,3-Dichlorobenzene



Estimation of Carbon Chemical shifts in Substituted Benzene

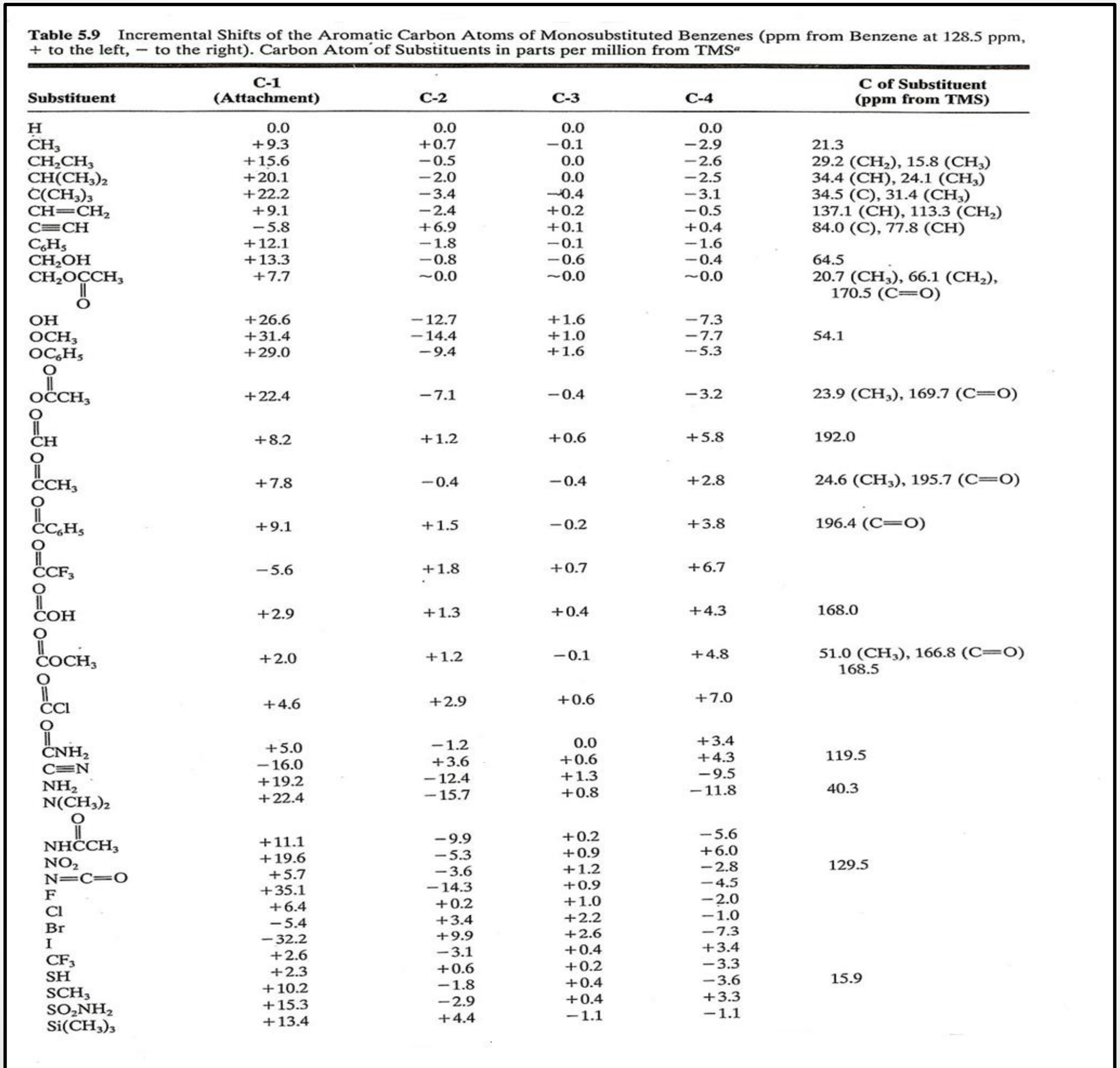


Table 5.9 Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm, + to the left, − to the right). Carbon Atom of Substituents in parts per million from TMS[a]

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	+9.3	+0.7	−0.1	−2.9	21.3
CH_2CH_3	+15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	+22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH_3)
$CH{=}CH_2$	+9.1	−2.4	+0.2	−0.5	137.1 (CH), 113.3 (CH_2)
$C{\equiv}CH$	−5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C_6H_5	+12.1	−1.8	−0.1	−1.6	
CH_2OH	+13.3	−0.8	−0.6	−0.4	64.5
$\mathrm{CH_2O\underset{\underset{O}{\Vert}}{C}CH_3}$	+7.7	~0.0	~0.0	~0.0	20.7 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	+26.6	−12.7	+1.6	−7.3	
OCH_3	+31.4	−14.4	+1.0	−7.7	54.1
OC_6H_5	+29.0	−9.4	+1.6	−5.3	
$\mathrm{O\overset{\overset{O}{\Vert}}{C}CH_3}$	+22.4	−7.1	−0.4	−3.2	23.9 (CH_3), 169.7 (C=O)
$\mathrm{\overset{\overset{O}{\Vert}}{C}H}$	+8.2	+1.2	+0.6	+5.8	192.0
$\mathrm{\overset{\overset{O}{\Vert}}{C}CH_3}$	+7.8	−0.4	−0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
$\mathrm{\overset{\overset{O}{\Vert}}{C}C_6H_5}$	+9.1	+1.5	−0.2	+3.8	196.4 (C=O)
$\mathrm{\overset{\overset{O}{\Vert}}{C}CF_3}$	−5.6	+1.8	+0.7	+6.7	
$\mathrm{\overset{\overset{O}{\Vert}}{C}OH}$	+2.9	+1.3	+0.4	+4.3	168.0
$\mathrm{\overset{\overset{O}{\Vert}}{C}OCH_3}$	+2.0	+1.2	−0.1	+4.8	51.0 (CH_3), 166.8 (C=O) 168.5
$\mathrm{\overset{\overset{O}{\Vert}}{C}Cl}$	+4.6	+2.9	+0.6	+7.0	
$\mathrm{\overset{\overset{O}{\Vert}}{C}NH_2}$	+5.0	−1.2	0.0	+3.4	
$C{\equiv}N$	−16.0	+3.6	+0.6	+4.3	119.5
NH_2	+19.2	−12.4	+1.3	−9.5	
$N(CH_3)_2$	+22.4	−15.7	+0.8	−11.8	40.3
$\mathrm{NH\overset{\overset{O}{\Vert}}{C}CH_3}$	+11.1	−9.9	+0.2	−5.6	
NO_2	+19.6	−5.3	+0.9	+6.0	
$N{=}C{=}O$	+5.7	−3.6	+1.2	−2.8	129.5
F	+35.1	−14.3	+0.9	−4.5	
Cl	+6.4	+0.2	+1.0	−2.0	
Br	−5.4	+3.4	+2.2	−1.0	
I	−32.2	+9.9	+2.6	−7.3	
CF_3	+2.6	−3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	−3.3	
SCH_3	+10.2	−1.8	+0.4	−3.6	15.9
SO_2NH_2	+15.3	−2.9	+0.4	+3.3	
$Si(CH_3)_3$	+13.4	+4.4	−1.1	−1.1	

441 Chem

CH-1

Introduction to Spectroscopy

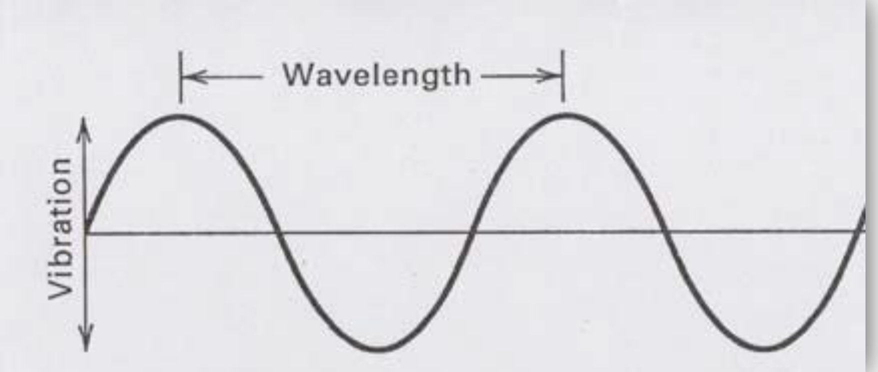
Introduction to Spectroscopy

Set of methods where interaction of electromagnetic radiation with chemical molecules.

Electromagnetic Radiation

$$\upsilon = \frac{C}{\lambda}$$

$$V = \frac{\upsilon}{C} = \frac{1}{\lambda}$$



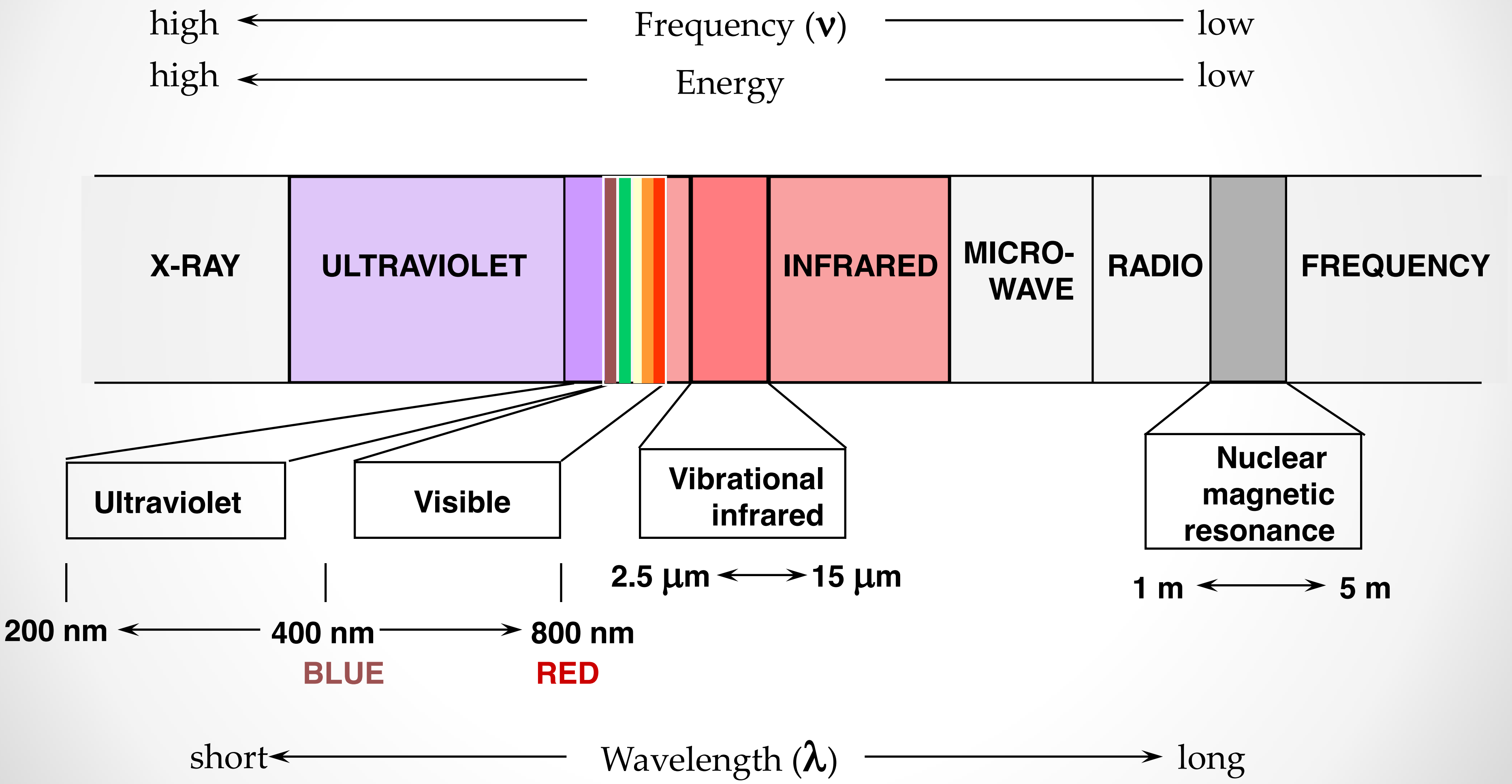
υ = Frequency of Radiation (Hertz or S^{-1})
λ = Wave Length (cm)
V = Wave Number (cm^{-1})
C = Velocity of light (constant) = 3×10^{10} cm/sec

The energy of quantum:

$$E = h\upsilon = h\frac{C}{\lambda}$$

h (Planck's constant) = 6.62×10^{-27} (Erg/sec)

The Electromagnetic Spectrum



high ← Frequency (ν) → low

high ← Energy → low

X-RAY

ULTRAVIOLET

INFRARED

MICRO-
WAVE

RADIO

FREQUENCY

Ultraviolet

Visible

Vibrational
infrared

Nuclear
magnetic
resonance

2.5 µm ⟷ 15 µm

1 m ⟷ 5 m

200 nm ← 400 nm → 800 nm

BLUE

RED

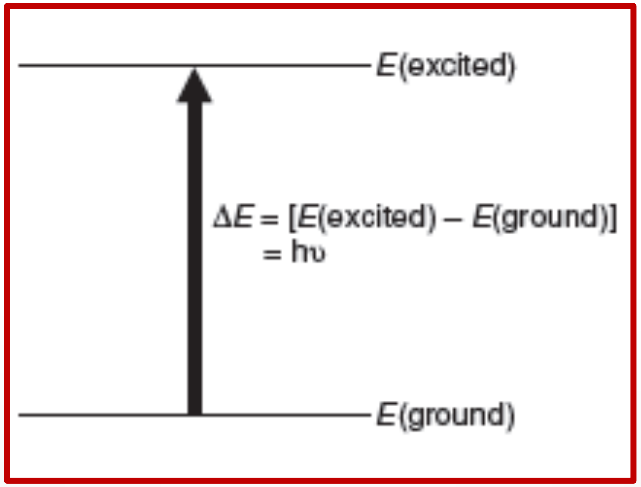
short ← Wavelength (λ) → long

Internal Energy of Molecules:

$$E_{total} = E_{elec} + E_{vib} + E_{rot}$$

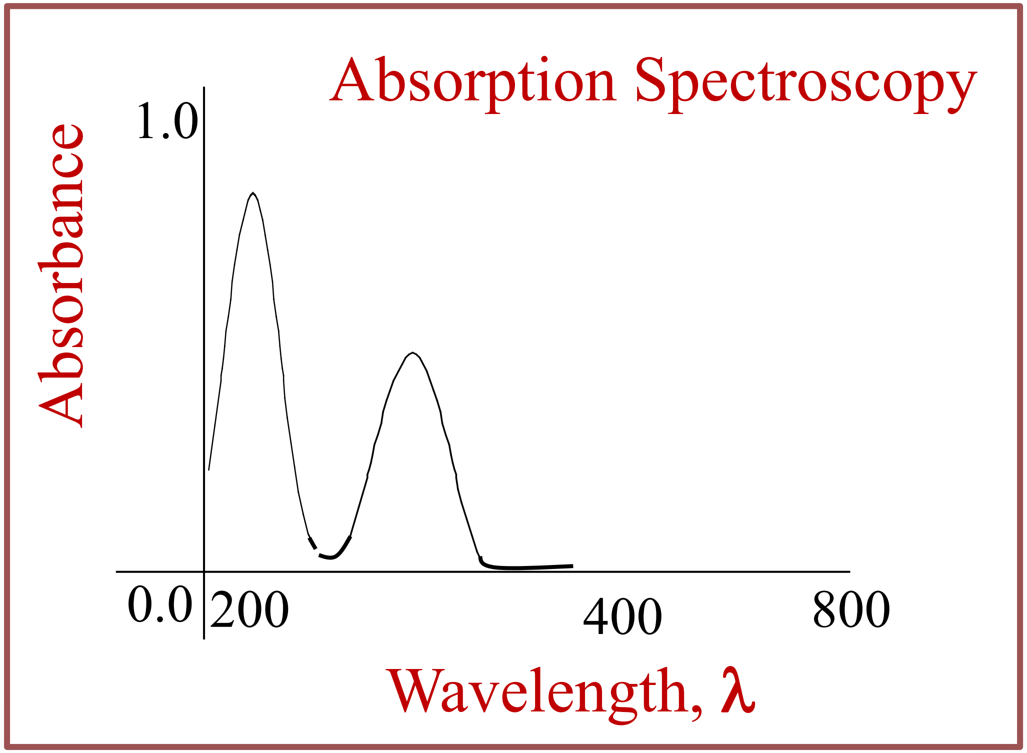
E_{elec}: *Electronic transitions*
E_{vib}: *Vibrational transitions*
E_{rot}: *Rotational transitions*

The Excitation process



Type of Spectroscopy:

1- Emission Spectroscopy
2- Absorption Spectroscopy



Types of Energy Transitions in Each Region of the Electromagnetic Spectrum

REGION	ENERGY TRANSITIONS
X-ray	Bond-breaking
UV/Visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radio Frequency	Nuclear and Electronic Spin

Summary of Spectroscopic Methods in Organic Chemistry

Electromagnetic Radiation	Wavelength And (Frequency)	The effect of radiation on molecular	Information learned
Ultraviolet and Visible	200-800 nm (1.5x10^{15}- 3.7x10^{14}Hz)	Changes in the electronic energy levels within the molecule	Unsaturated bonds alternating with nonbonding electrons
Infrared	2.5-15 um (1.2x10^{14}- 2.0x10^{13}Hz)	Changes in the vibrational and rotational energy levels in the molecule	Detection of functional groups in the compound
Radio Frequency Nuclear Magnetic Resonance	5-0.5 m (60-600 MHz)	Changes in the magnetic properties of some nuclei of atoms	Detect the type and number of hydrogen and carbon atoms in the compound and find out different chemical environments
Mass Spectrum	---	Ionization and fragmentation of compound to ions Broken	Determination of Molecular weight of the compound and detection of the molecular structure from broken molecules resulting