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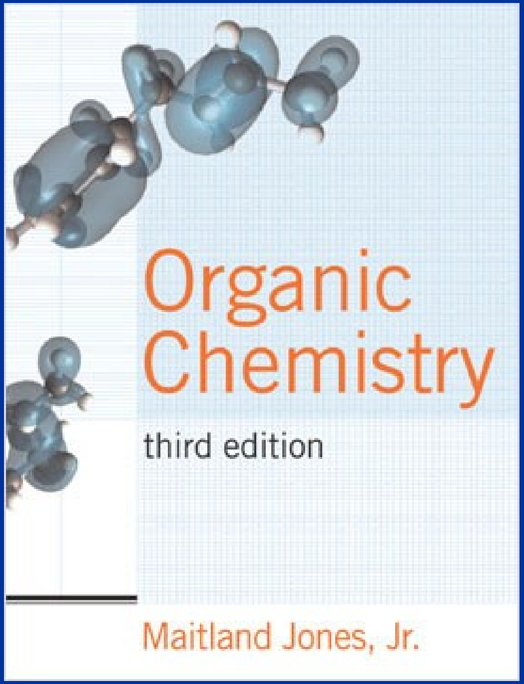

Organic Chemistry
third edition
Maitland Jones, Jr.

Chapter 15
Organic Chemistry

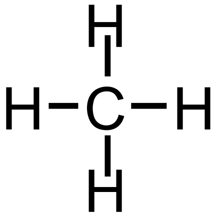
Third Edition

Maitland Jones, Jr.

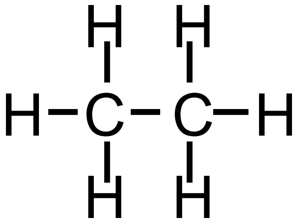
Degree of Unsaturation

- Degree of Unsaturation (or “Double Bond Equivalents”, DBE) is the number of π-bonds and/or rings present in a molecule
- For the formula $C_CH_HX_XN_NO_O$, where X = halogen:

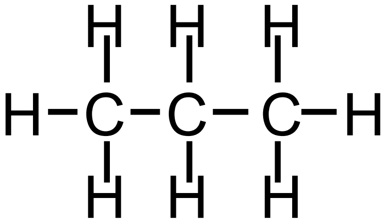
$$DBE = C - \frac{H+X-N}{2} + 1$$



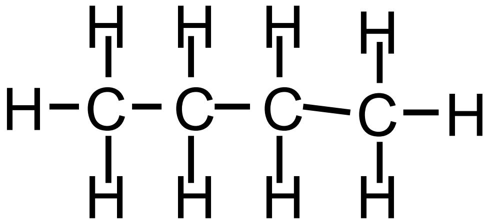
C_1H_4



C_2H_6



C_3H_8

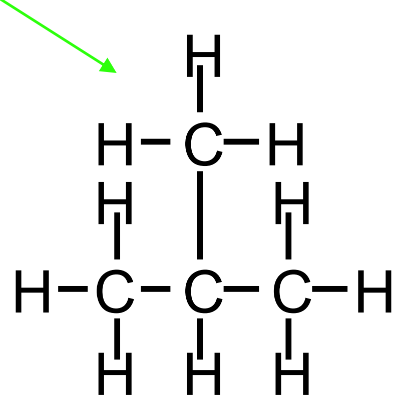


C_4H_{10}

Saturated alkanes (CH-only compounds) have the general formula:

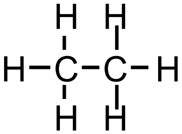
$$C_nH_{2n+2}$$

Note: it doesn't matter how the atoms are configured:

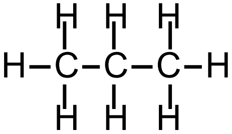


C_4H_{10}

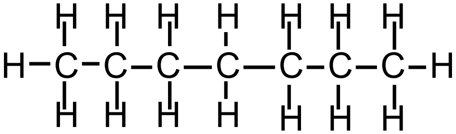
C_nH_{2n+2}



C_2H_6

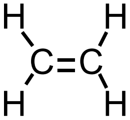


C_3H_8

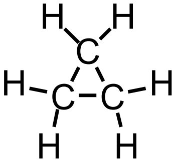


C_7H_{16}

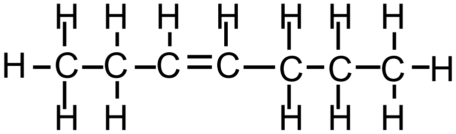
C_nH_{2n}



C_2H_4



C_3H_6

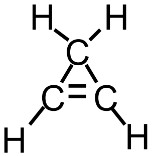


C_7H_{14}

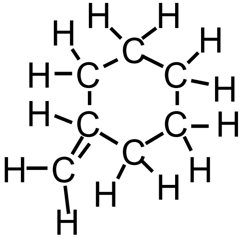
C_nH_{2n-2}

$HC\equiv CH$

C_2H_2



C_3H_6



C_7H_{12}

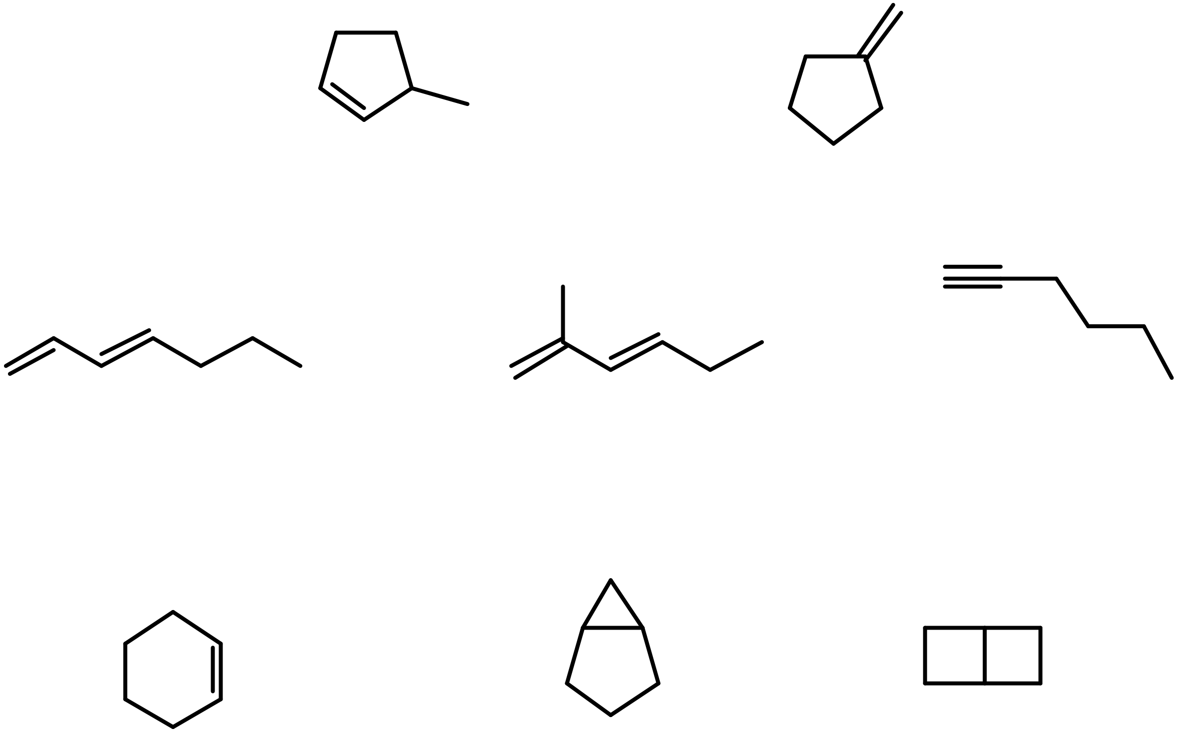
Two less hydrogens per double bond or ring!

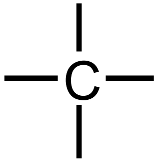
Example: C_6H_{10}

$$DBE=6-\frac{10}{2}+1=2$$

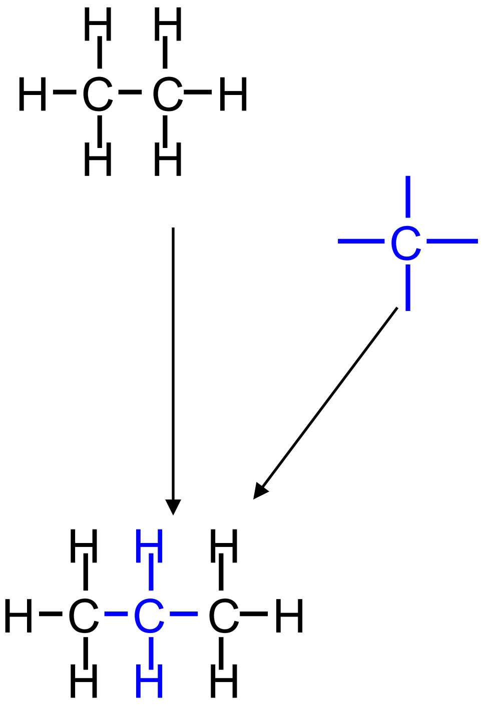
(or: missing 2 pairs of H from fully-saturated C_6H_{14})

- Two double bonds
- Two rings
- One triple bonds
- One double bond plus one ring





For each Carbon (valence =4) you add to a structure requires the addition of two more Hydrogens



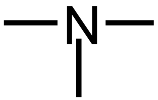
—H

X = —F —Cl —Br —I

Each halogen (valance = 1), takes the place of a hydrogen

—O—

Oxygen (valance = 2) can be added into a structure without changing the number of hydrogens



Each added nitrogen (valence =3) requires one additional hydrogen

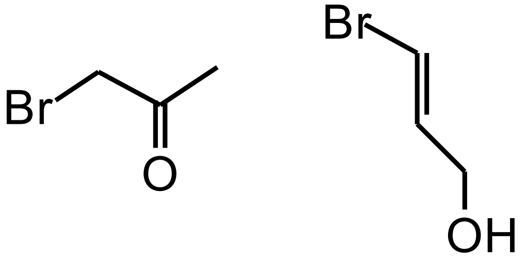
$$DBE = C - \frac{H+X-N}{2} + 1$$

Example:

C_3H_5BrO

$$DBE = 3 - \frac{5+1}{2} + 1$$

DBE = 1

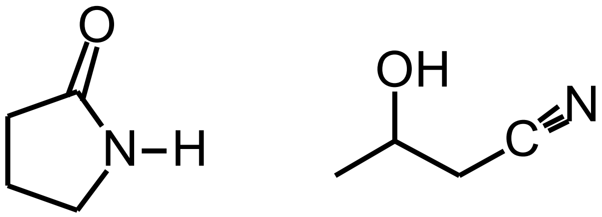


Example:

C_4H_7NO

$$DBE = 4 - \frac{7-1}{2} + 1$$

DBE = 2

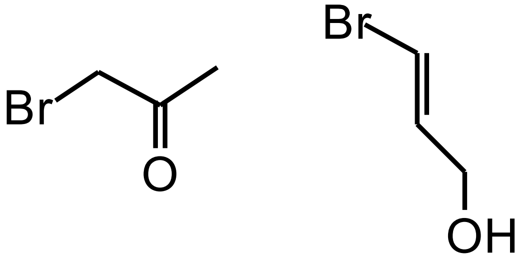


Example:

C_3H_5BrO

C_3: saturated = 8H
5H+Br =“6H”
2H missing so 1DBE

DBE = 1

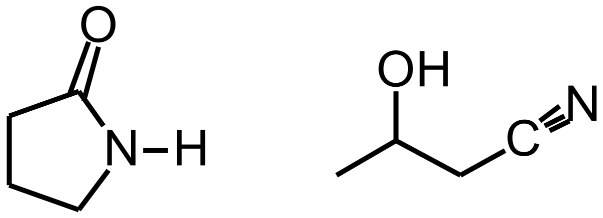


Example:

C_4H_7NO

C_4N: Sat’d = 10+1 = 11H
4H missing so 2 DBE

DBE = 2



Mass Spectrometry

- Molecules are ionized and “shot” through a magnetic field

- How far they’re deflected depends on the magnet’s strength, and the ion’s mass-to-charge (*m/z*) ratio

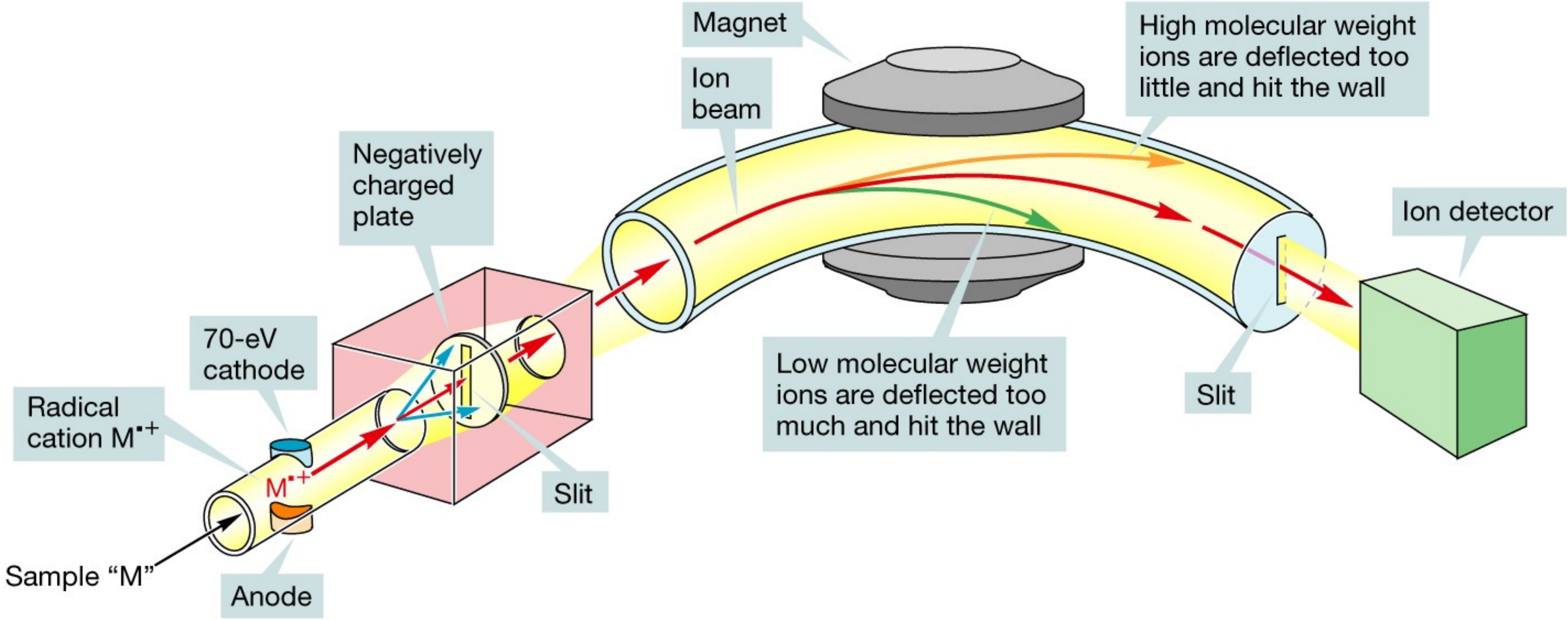
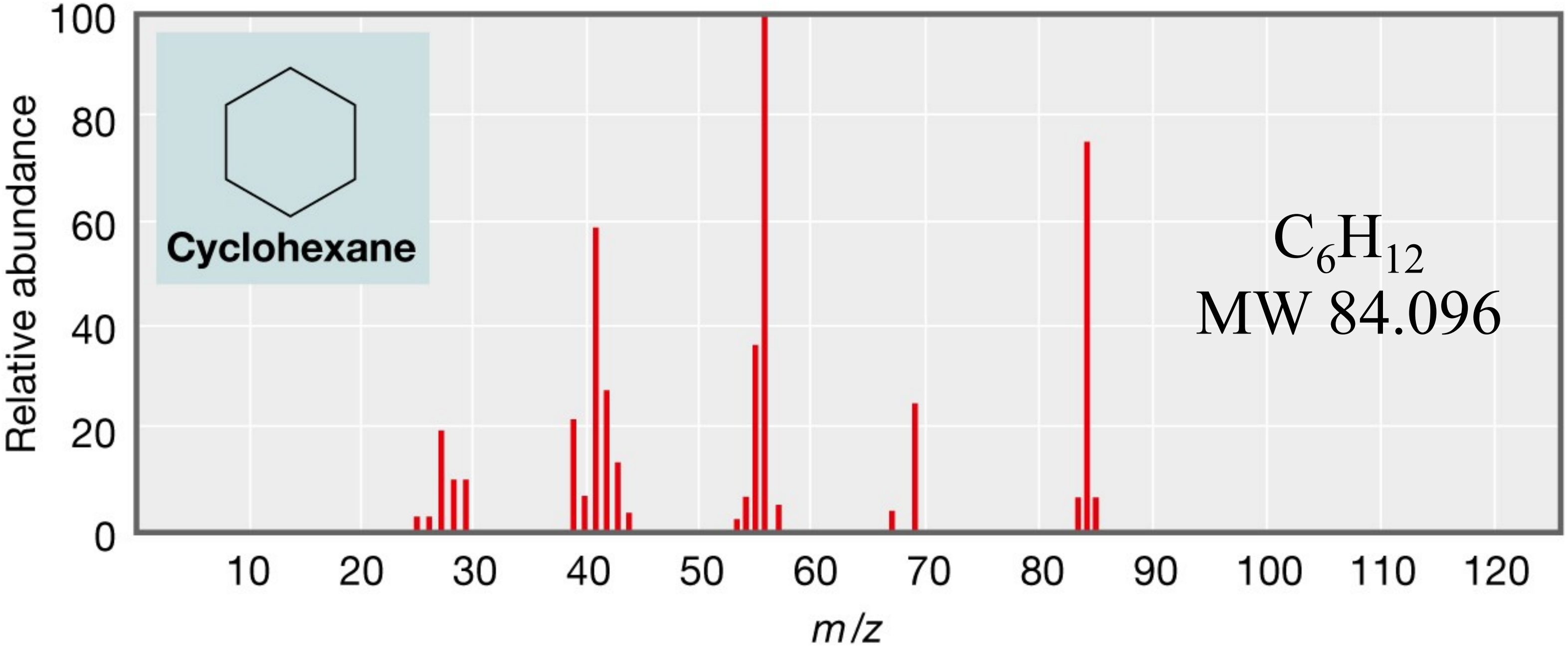

Magnet
Ion beam
High molecular weight ions are deflected too little and hit the wall
Negatively charged plate
Ion detector
70-eV cathode
Radical cation M•+
M•+
Slit
Low molecular weight ions are deflected too much and hit the wall
Slit
Sample "M"
Anode

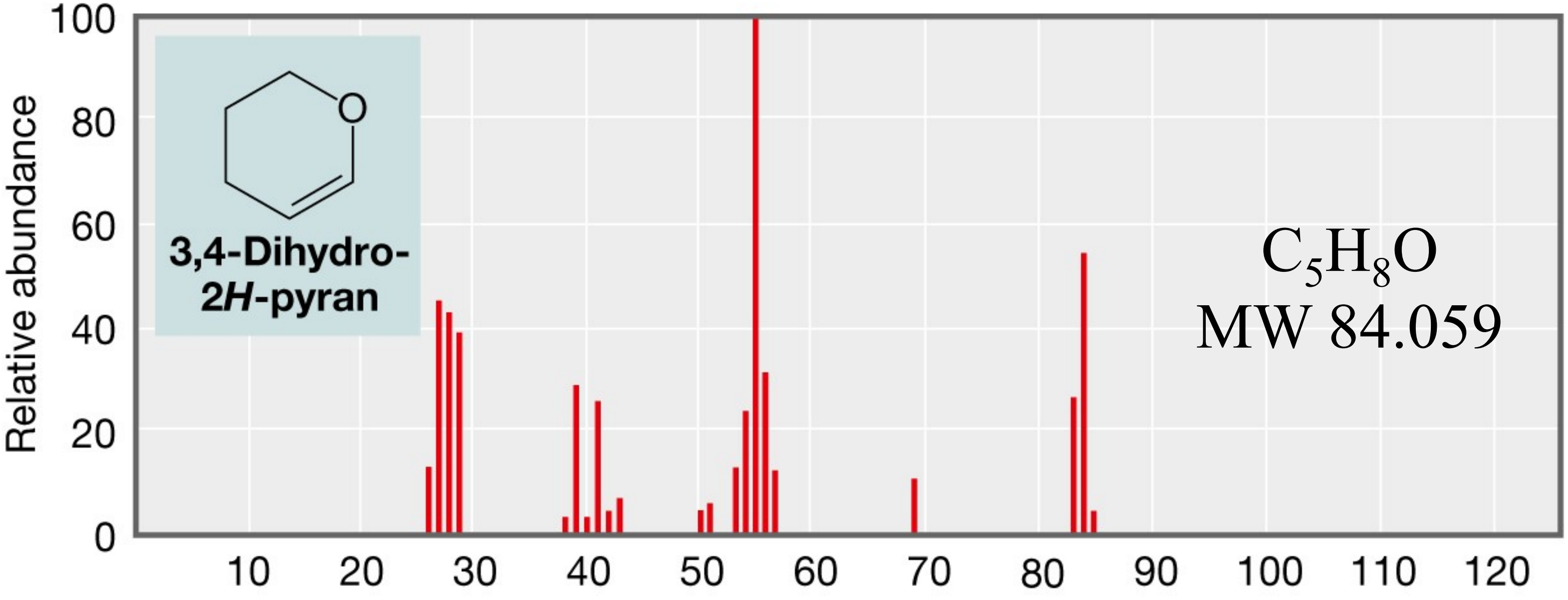
Figure 15.04

Isotope	Abundance	Isotope	Abundance
^{1}H	99.985	^{17}O	0.038
^{2}H (D)	0.015	^{18}O	0.200
^{12}C	98.90	^{35}Cl	75.77
^{13}C	1.10	^{37}Cl	24.23
^{14}N	99.63	^{79}Br	50.69
^{15}N	0.37	^{81}Br	49.31
^{16}O	99.762	^{127}I	100

TABLE 15.1 Some Common Isotopes and Their Abundances



C_6H_{12}
MW 84.096



C_5H_8O
MW 84.059

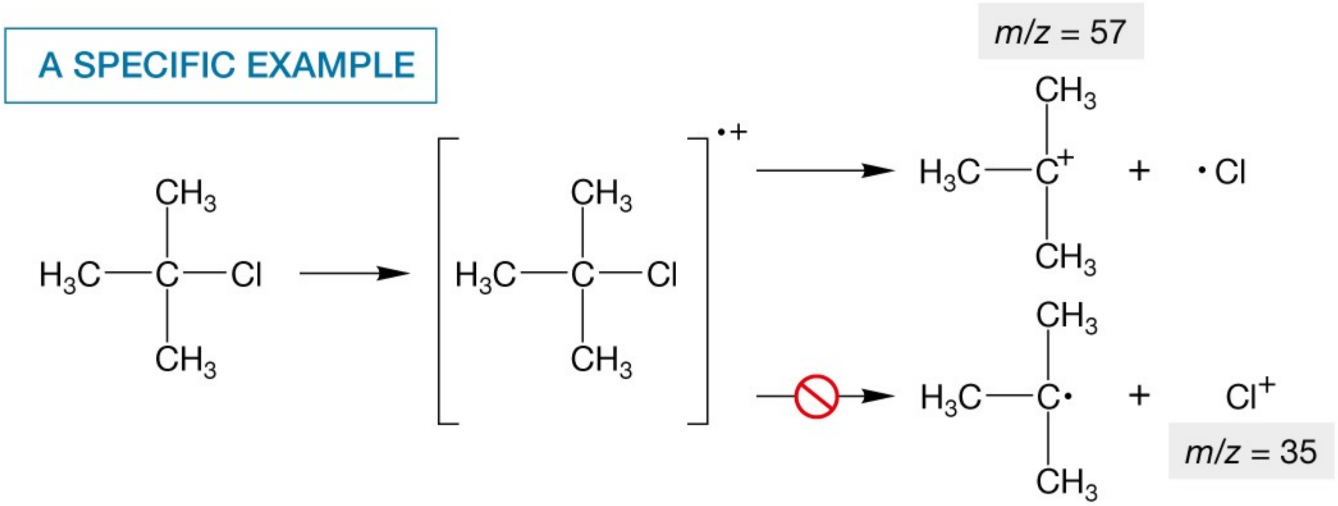
High-Resolution MS can determine the exact molecular formula

THE GENERAL CASE

$$[A{-}B]^{\bullet +} \longrightarrow A\bullet + B^{+}$$

$$[A{-}B]^{\bullet +} \longrightarrow A^{+} + B\bullet$$

A SPECIFIC EXAMPLE



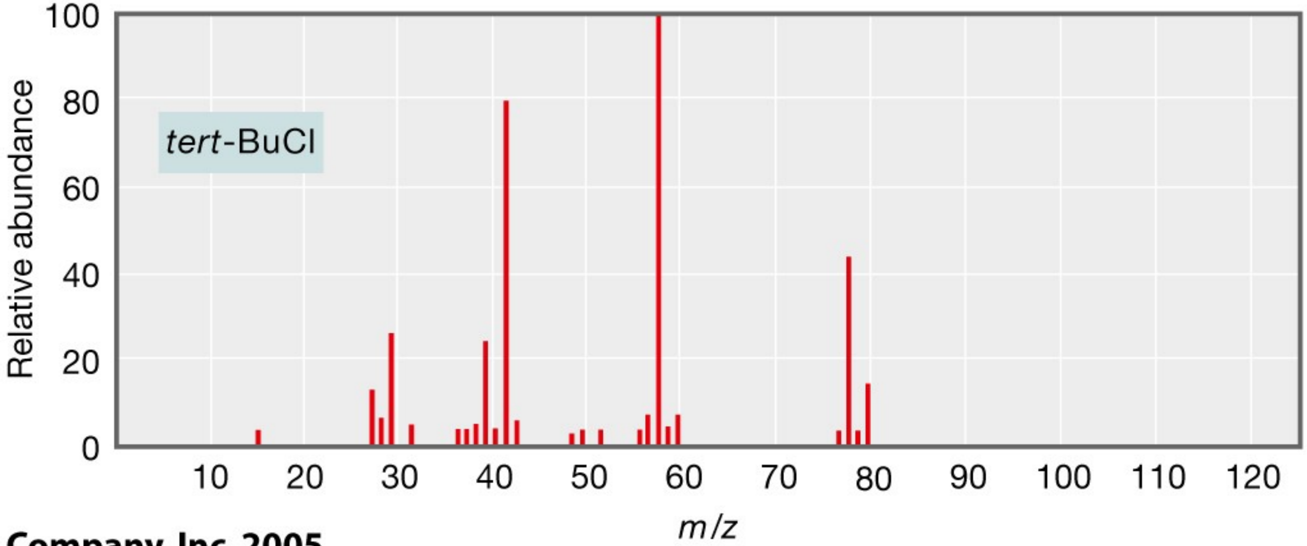


Figure 15.08

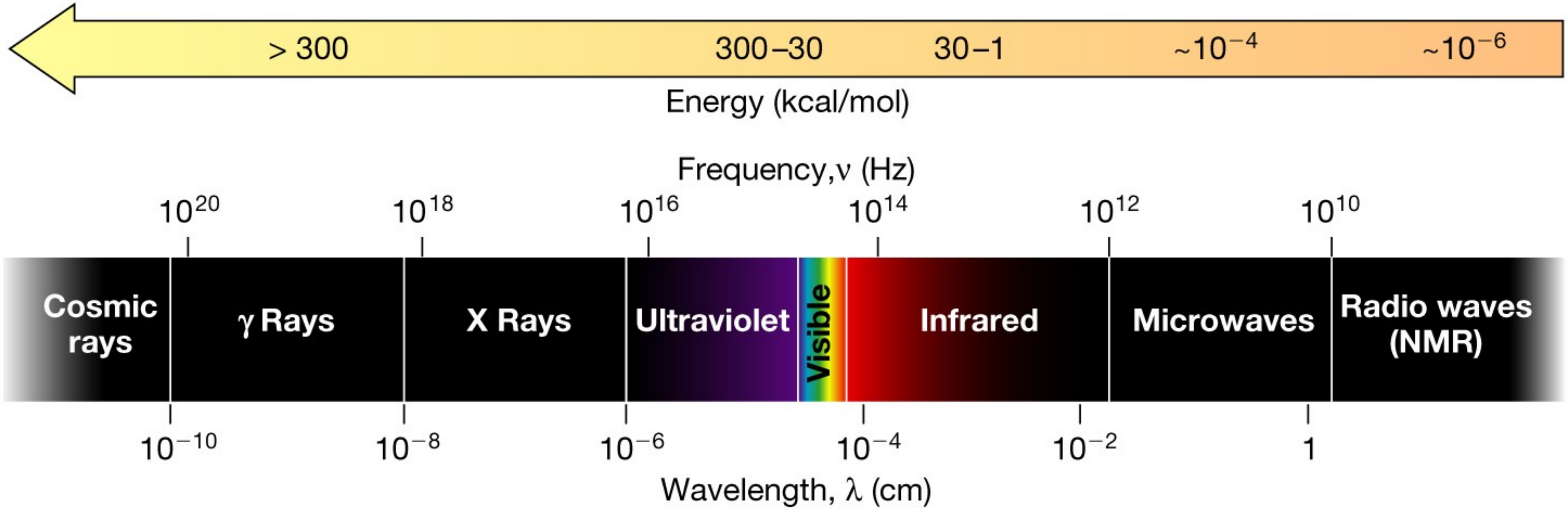

> 300
300–30
30–1
~10^−4
~10^−6
Energy (kcal/mol)
Frequency, ν (Hz)
10^20
10^18
10^16
10^14
10^12
10^10
Cosmic rays
γ Rays
X Rays
Ultraviolet
Visible
Infrared
Microwaves
Radio waves (NMR)
10^−10
10^−8
10^−6
10^−4
10^−2
1
Wavelength, λ (cm)

Figure 15.16

Infrared Spectroscopy

- Bond lengths and bond angles are not constant. Molecular vibrations cause changes in bond lengths and angles to oscillate:

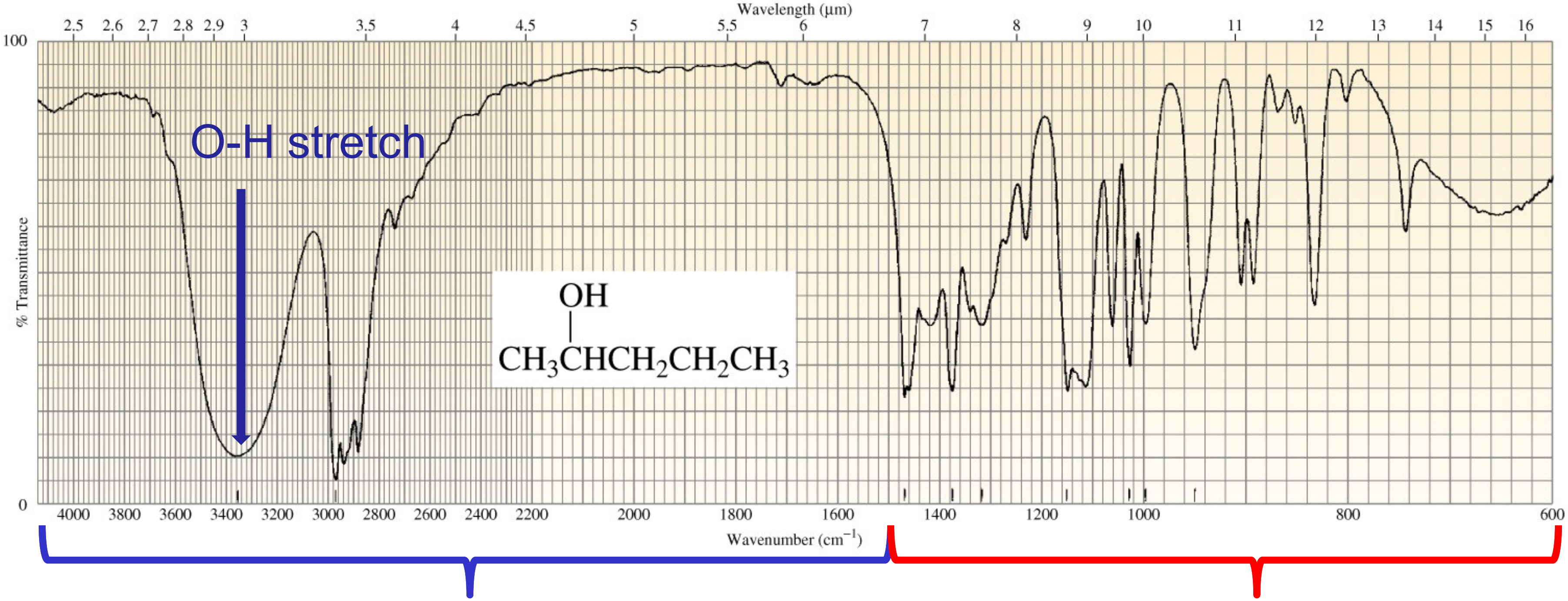
- If a bond stretch causes a change in the size of the molecule's dipole moment, then it is capable of absorbing infrared. Different types of bond stretches absorb at different frequencies.

- **IR can be used to identify functional groups in the molecule**

Some Useful IR Stretching Frequencies

Bond	Frequency (cm^{-1})	Intensity
O-H (alcohol)	3650-3200	Strong, broad
O-H (carboxylic acid)	3300-2500	Strong, **very** broad
N-H	3500-3300	Medium, broad
C-H	3300-2700	Medium
C≡N	2260-2220	Medium
C≡C	2260-2100	Medium to weak
C=O	1780-1650	Strong
C-O	1250-1050	strong

a.

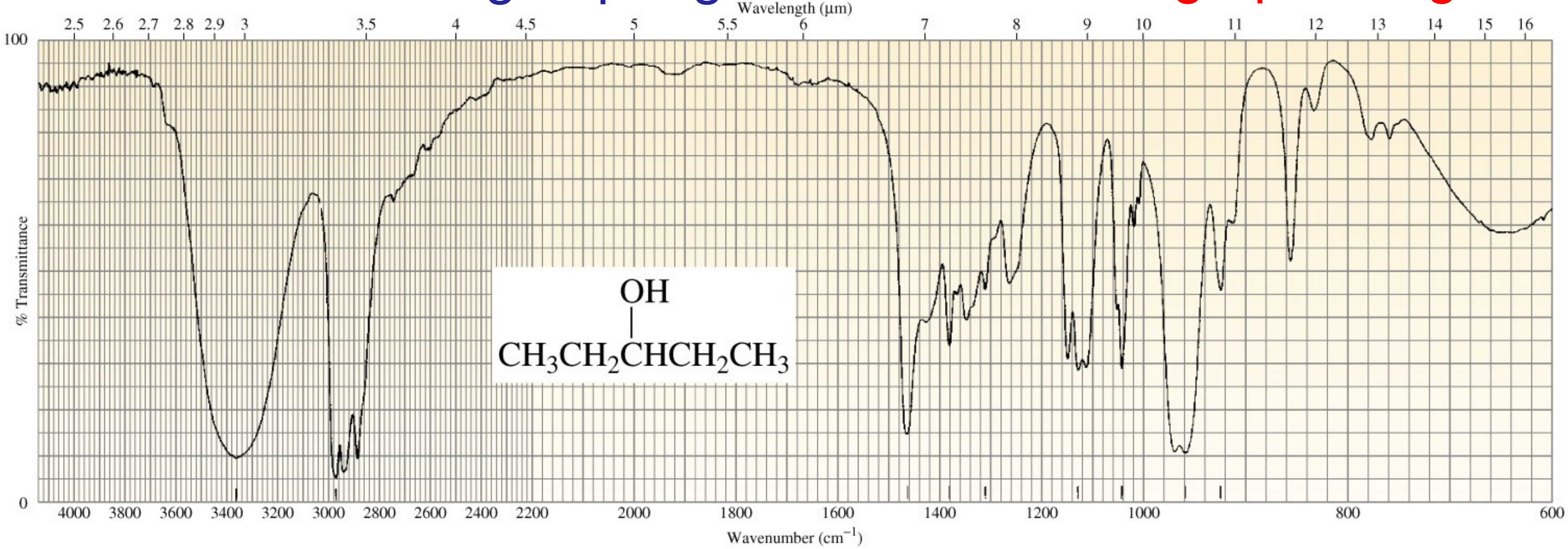


O-H stretch

The functional group region

The fingerprint region

b.



Carbonyls have very strong absorptions at ~1650-1780 cm^{-1}

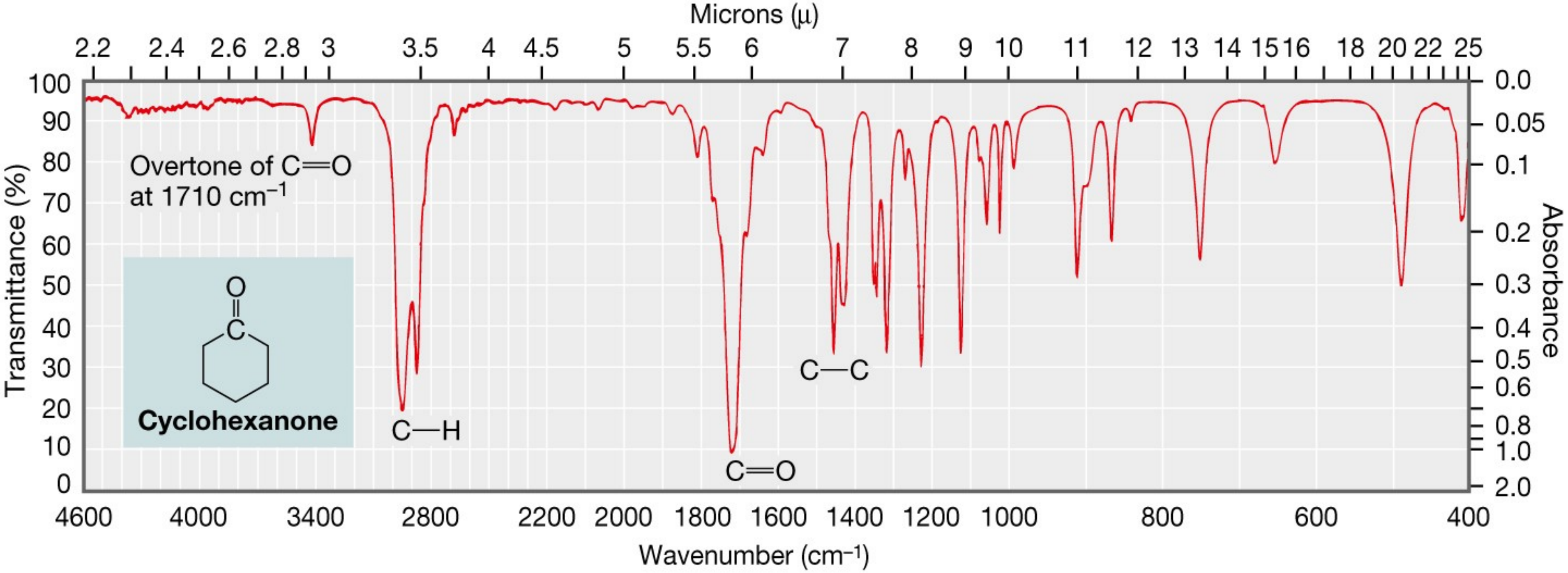
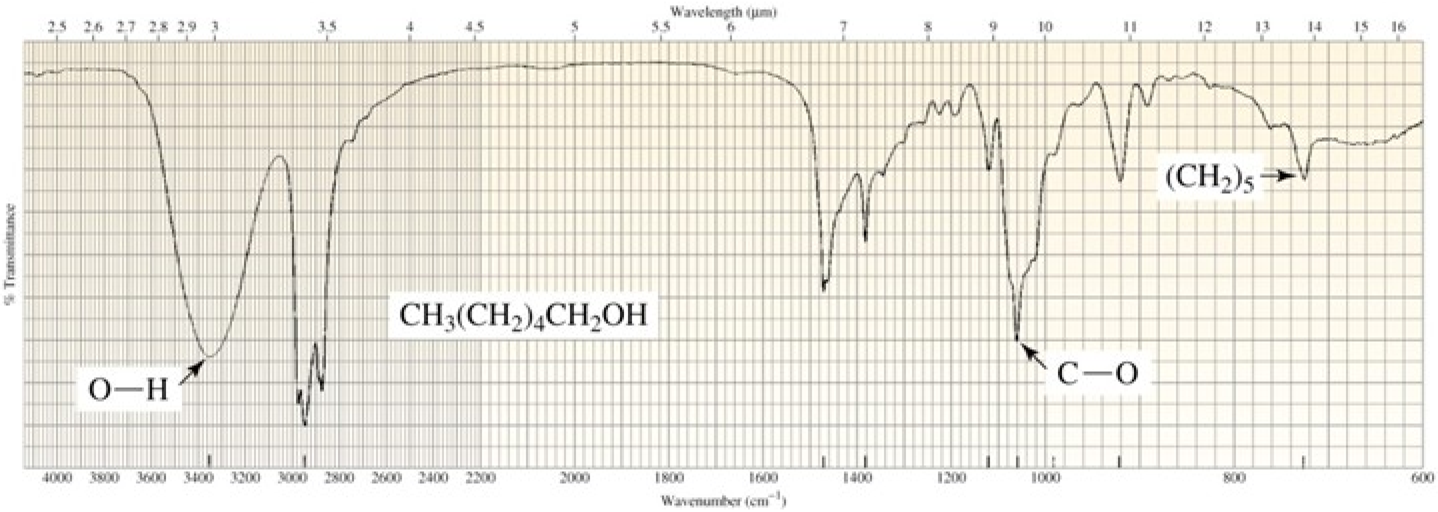
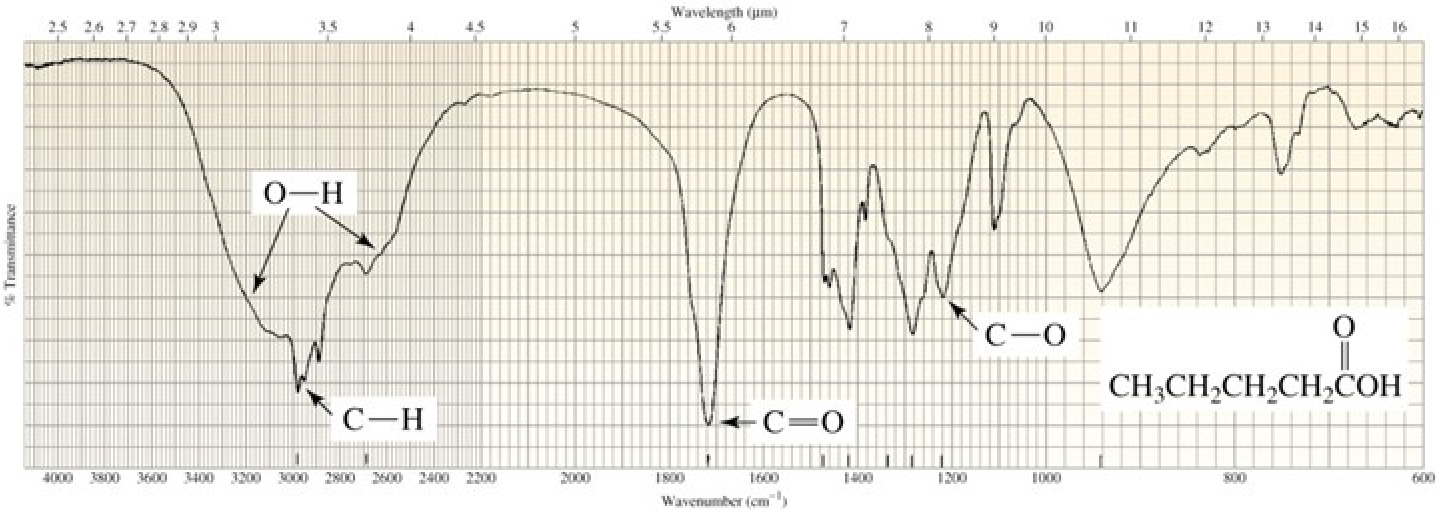


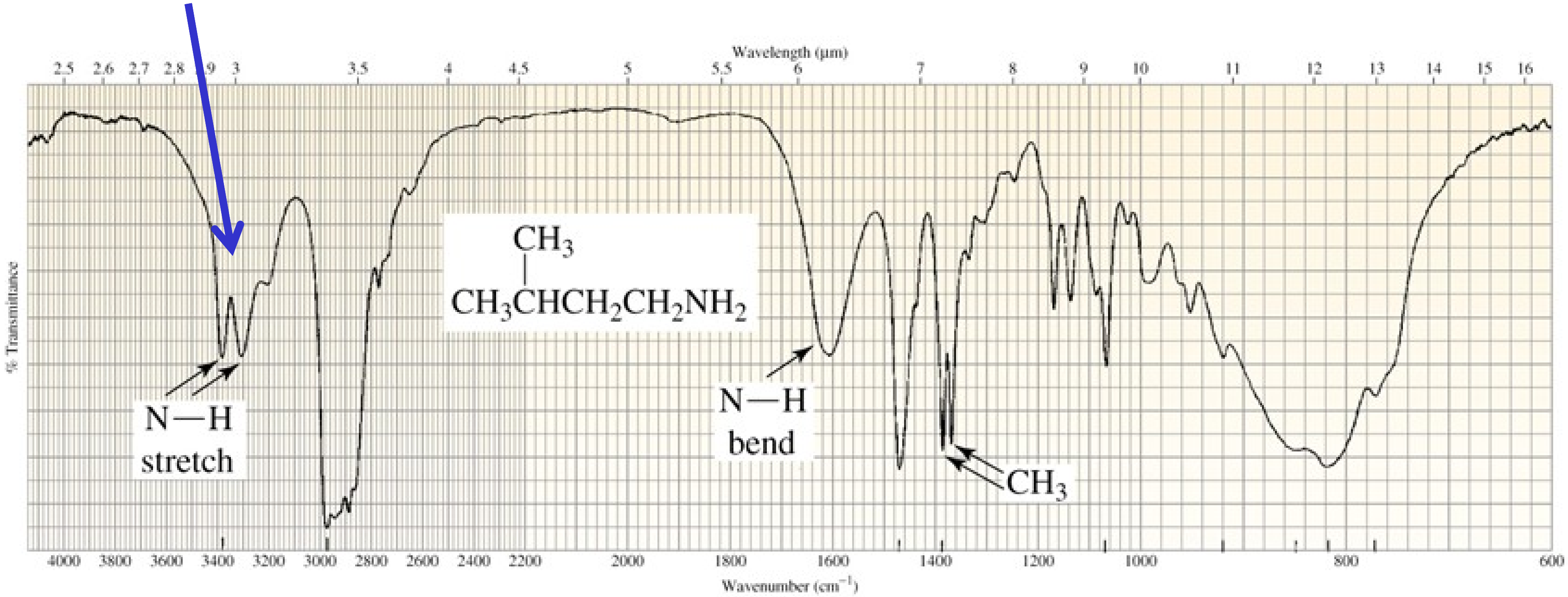
Figure 15.17



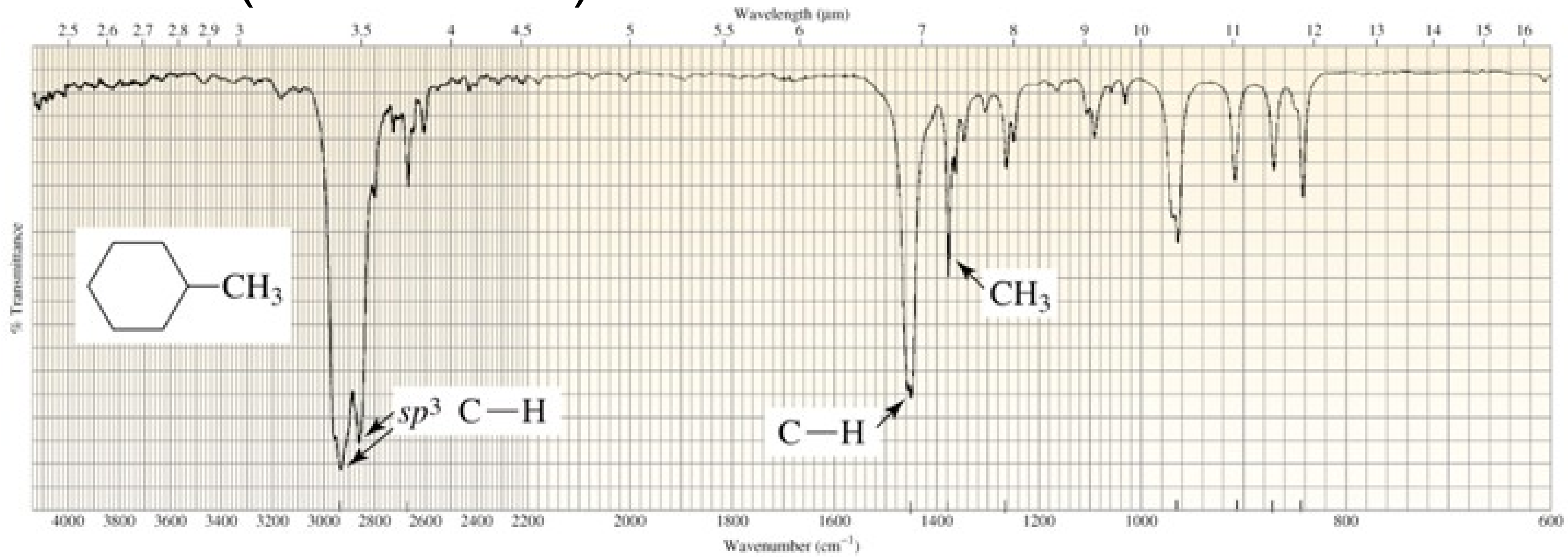
A carboxylic has a very broad O-H stretch (plus a C=O stretch)



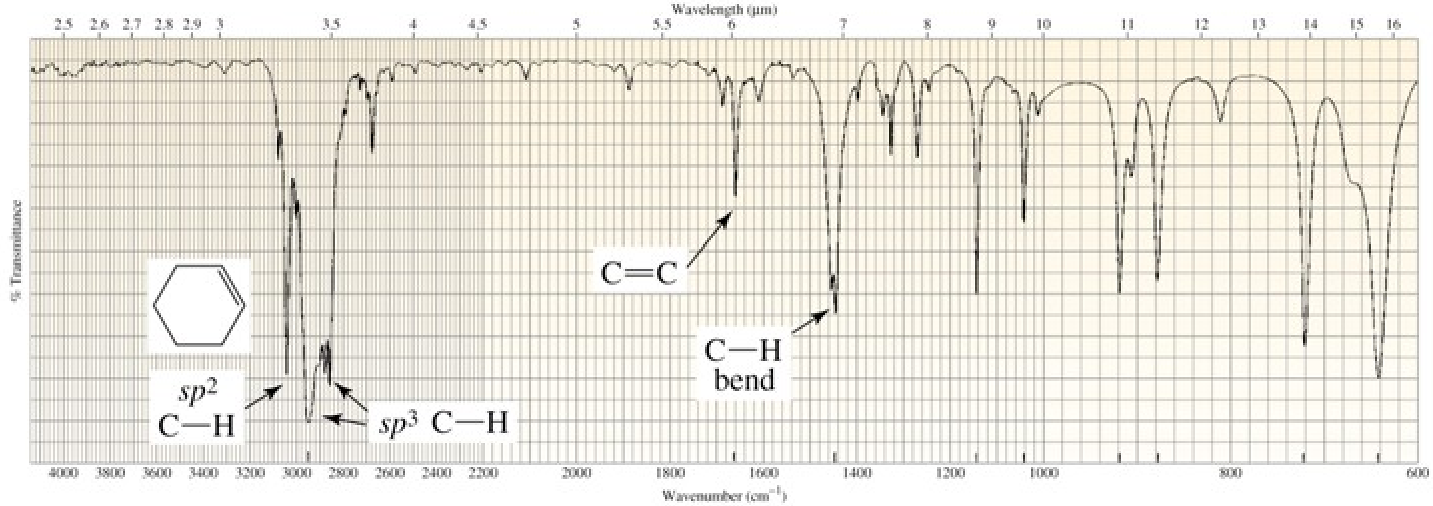
- NH stretches are similar in frequency to –OH stretches, but usually weaker
- An NH_2 group has a double peak



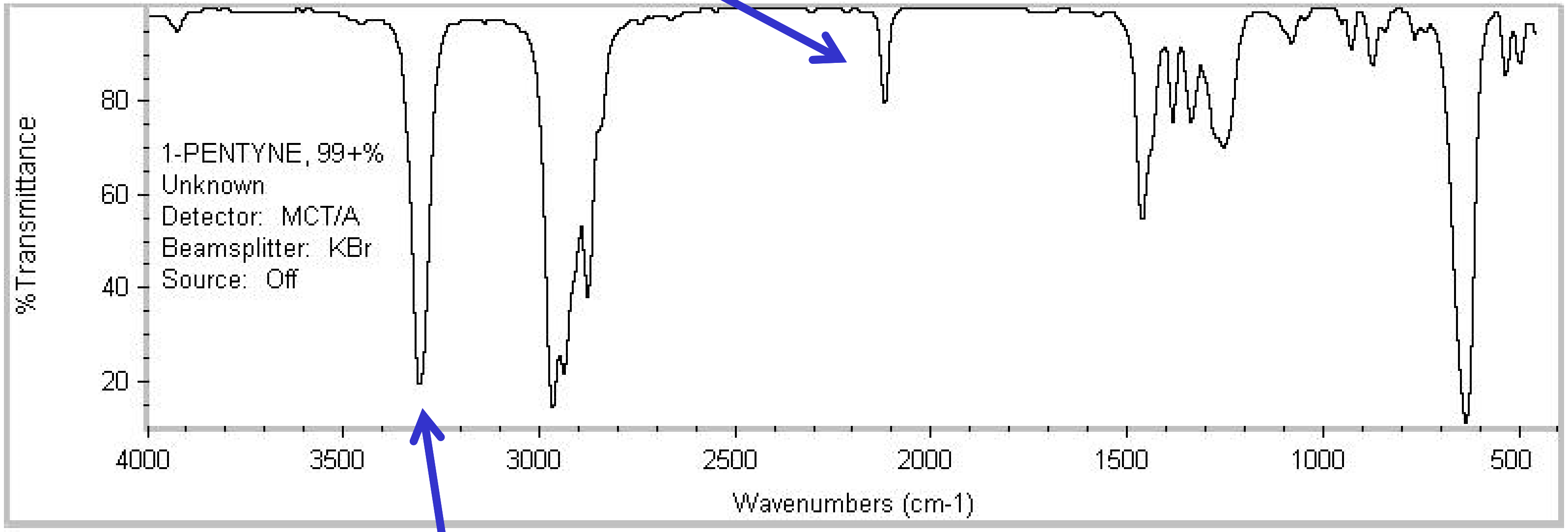
Absorption at ~ 3000 cm^{-1} will practically always be seen (C-H stretch)



sp^3 C-H <3000 cm^{-1}
sp^2 C-H >3000 cm^{-1}



Absorption in the 2100-2300 cm-1 region is uncommon but significant—C≡C or C≡N. Alkynes aren't very polar, so their C≡C stretches tend to be weak.

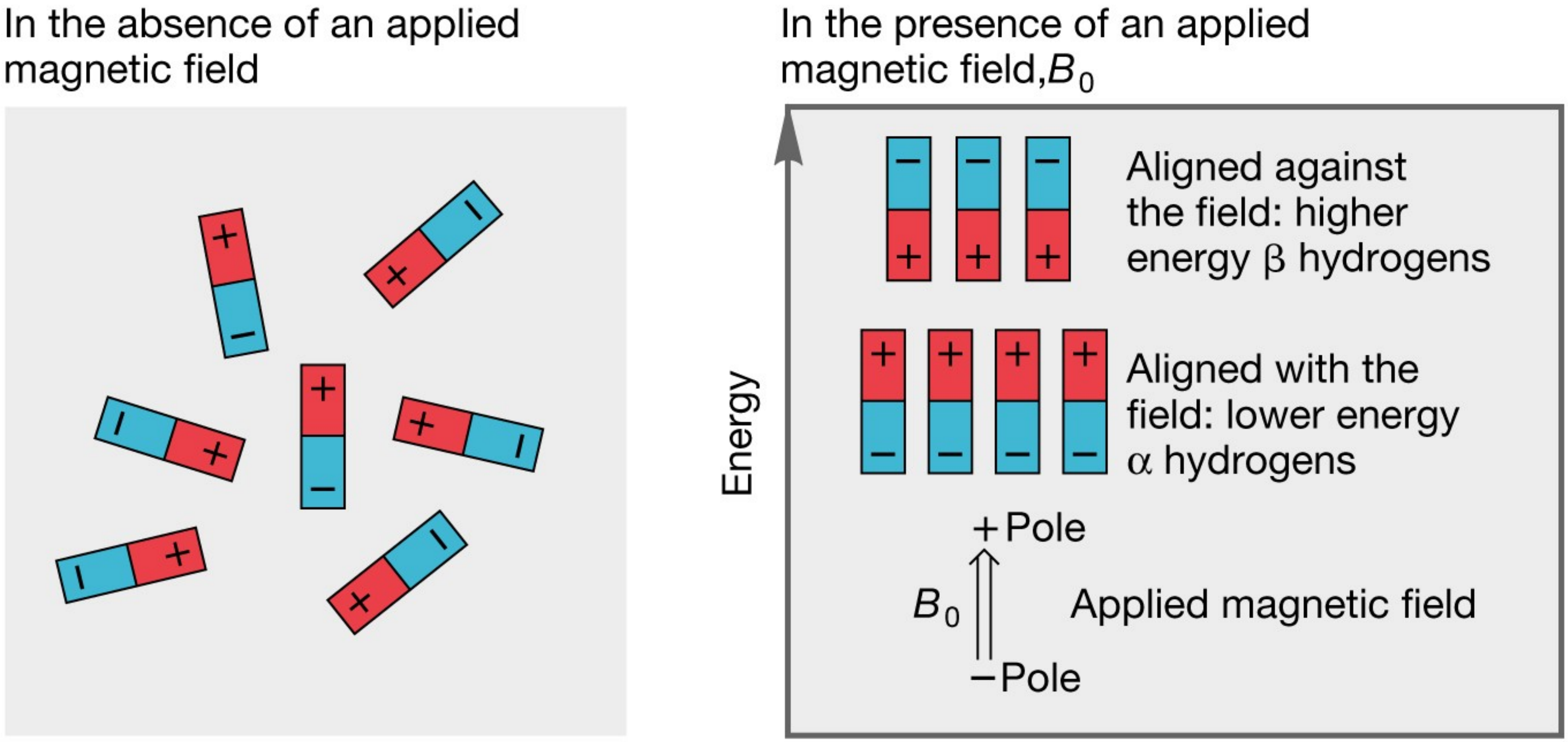


Terminal alkyne C-H stretches are higher frequency than sp^2- or sp^3-C-H stretches

Nuclear Magnetic Resonance (NMR) Spectroscopy

- Some subatomic particles (e.g. : electrons, protons, some nuclei) have a property called “spin”
  - ^{1}H, ^{13}C: S = ½
  - ^{2}H : S = 1

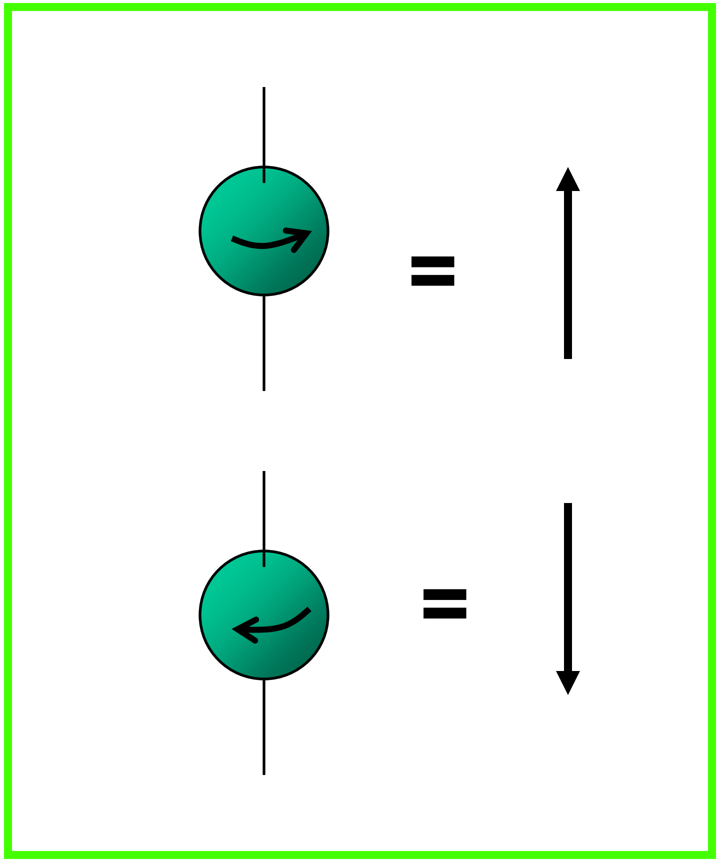
- Spin gives the particle a magnetic dipole moment

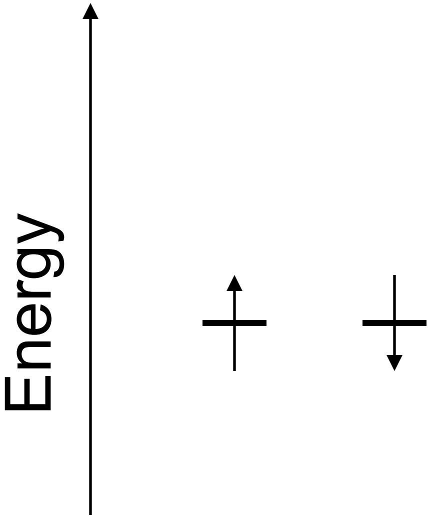


In the absence of an applied magnetic field

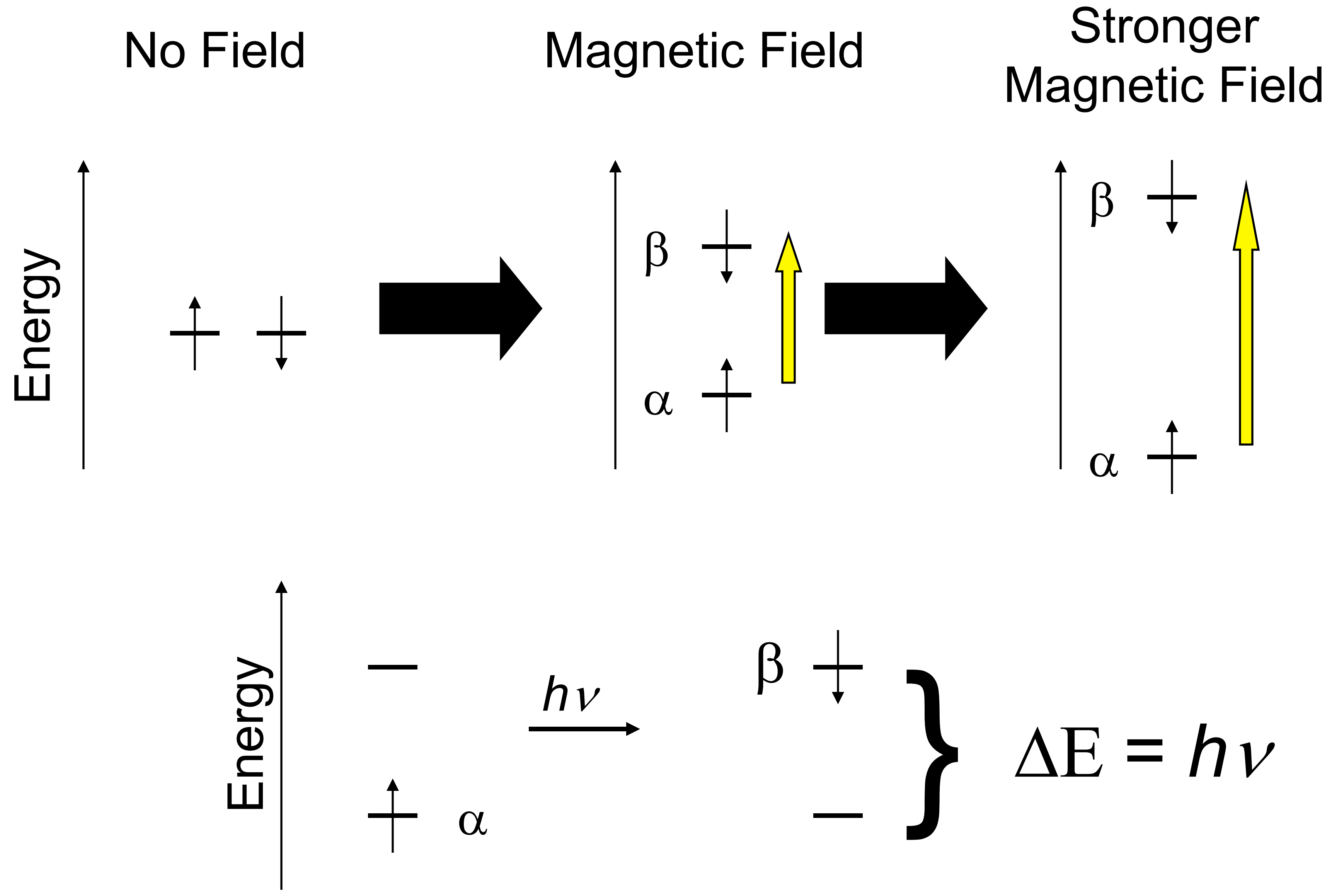
In the presence of an applied magnetic field, B_0

Figure 15.18





In the absence of a magnetic field, both spin states have equal energy



$$\Delta E = h\nu$$

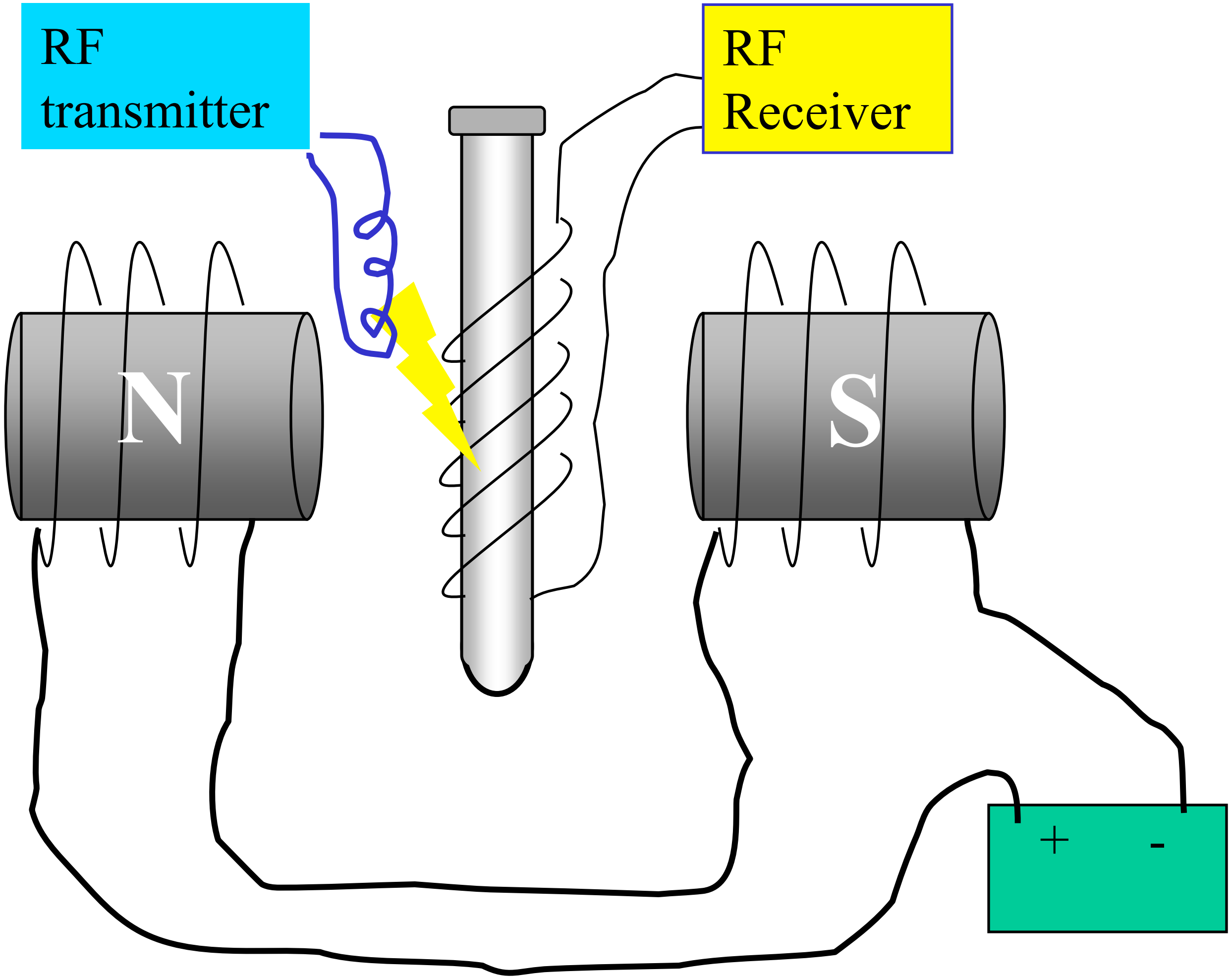
In a strong magnetic field, the energy level difference corresponds to the energy of radio waves

The frequency that a nucleus absorbs or emits radio waves depends on:

- The type of nucleus
- The strength of the magnet

For example, a “300-MHz NMR spectrometer” uses a 7-Tesla magnet, causing protons to absorb/emit radio waves at 300 MHz

How an NMR spectrometer works:



Note modern NMRs use superconducting magnets to attain very strong magnetic fields

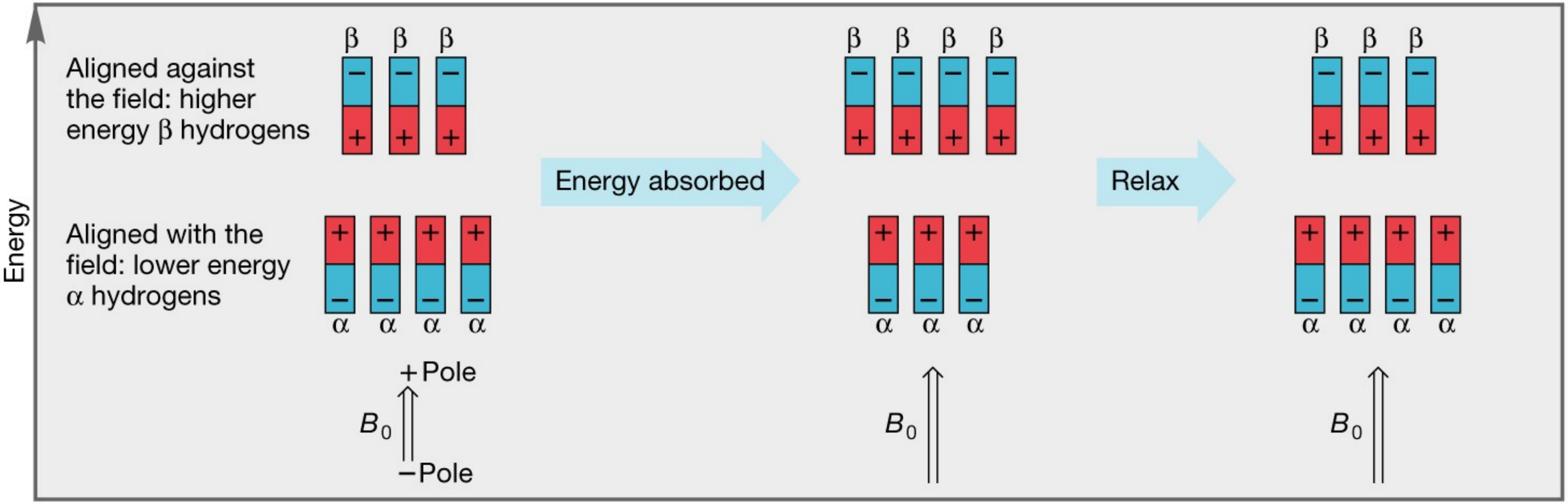
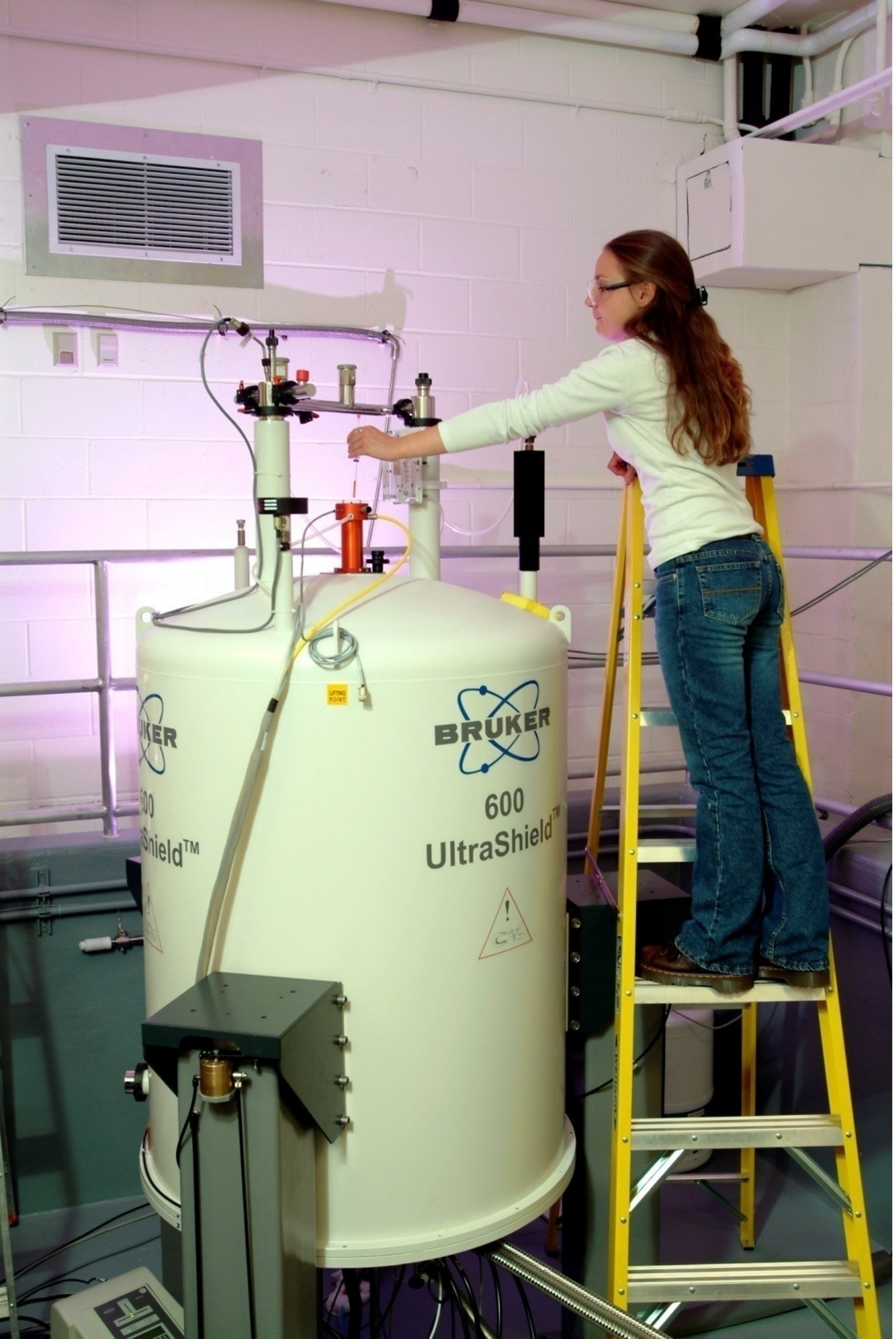

Energy
Aligned against the field: higher energy β hydrogens
Aligned with the field: lower energy α hydrogens
β β β
− − −
+ + +
+ + + +
− − − −
α α α α
+Pole
B_0
−Pole
Energy absorbed
β β β β
α α α
B_0
Relax
β β β
α α α α
B_0

Figure 15.19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UltraShield™
LIFTING POINT


BRUKER
600
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^{1}H (Proton) NMR

- Hydrogen atoms are more than 99% ^{1}H.
- ^{1}H is particularly sensitive to NMR
- Almost all organic compounds contain H
- Can use size of peaks to determine # of H
- Signal splitting provides extra information

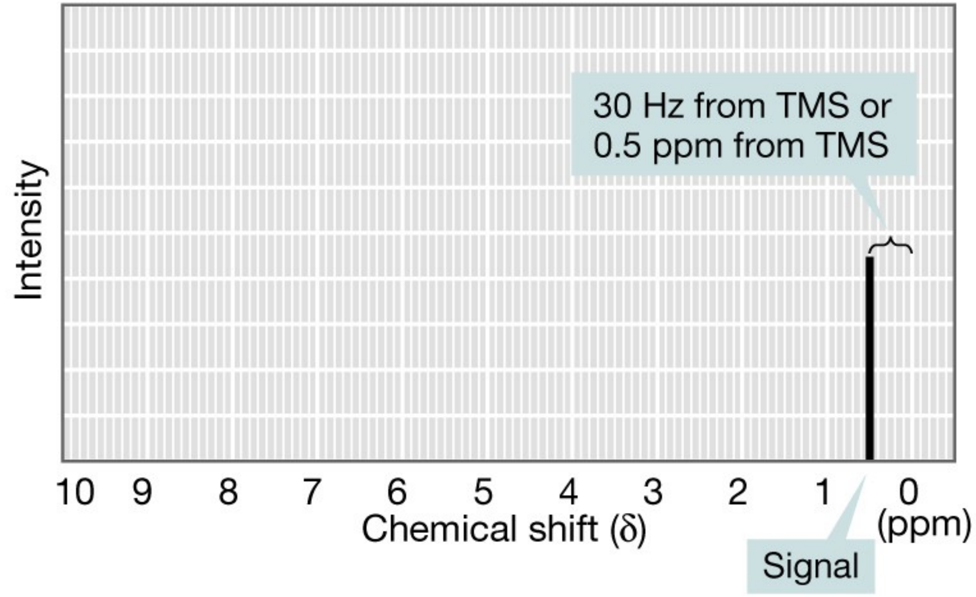
Proton NMR has been developed into a very powerful analytical technique

The frequency that a nucleus absorbs or emits radio waves is also slightly altered by other features in the molecule.

The NMR spectrum is a plot of signal intensity versus frequency. However, different spectrometers use different magnets, and detect different frequencies

We use a standard scale that works across all spectrometers: “chemical shift” unit: δ (also “ppm” for “parts per million”)

Spectrum taken at 60 MHz



At 60 MHz,
1 ppm = 60 Hz

At 300 MHz,
1 ppm = 300 Hz

Spectrum taken at 300 MHz

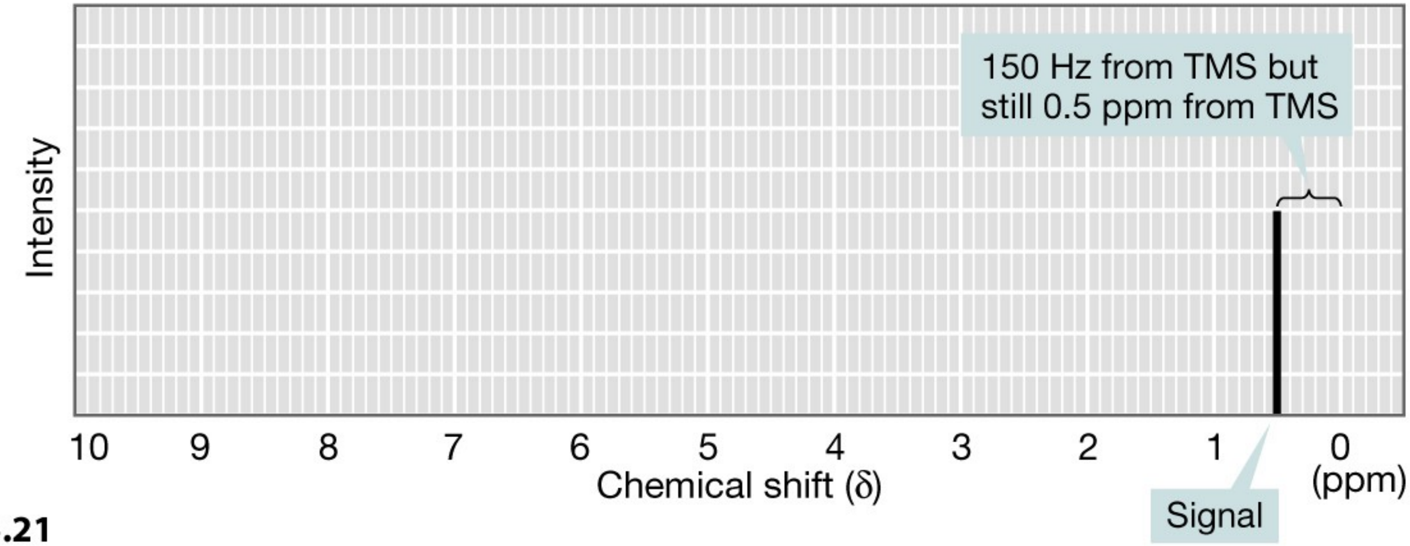
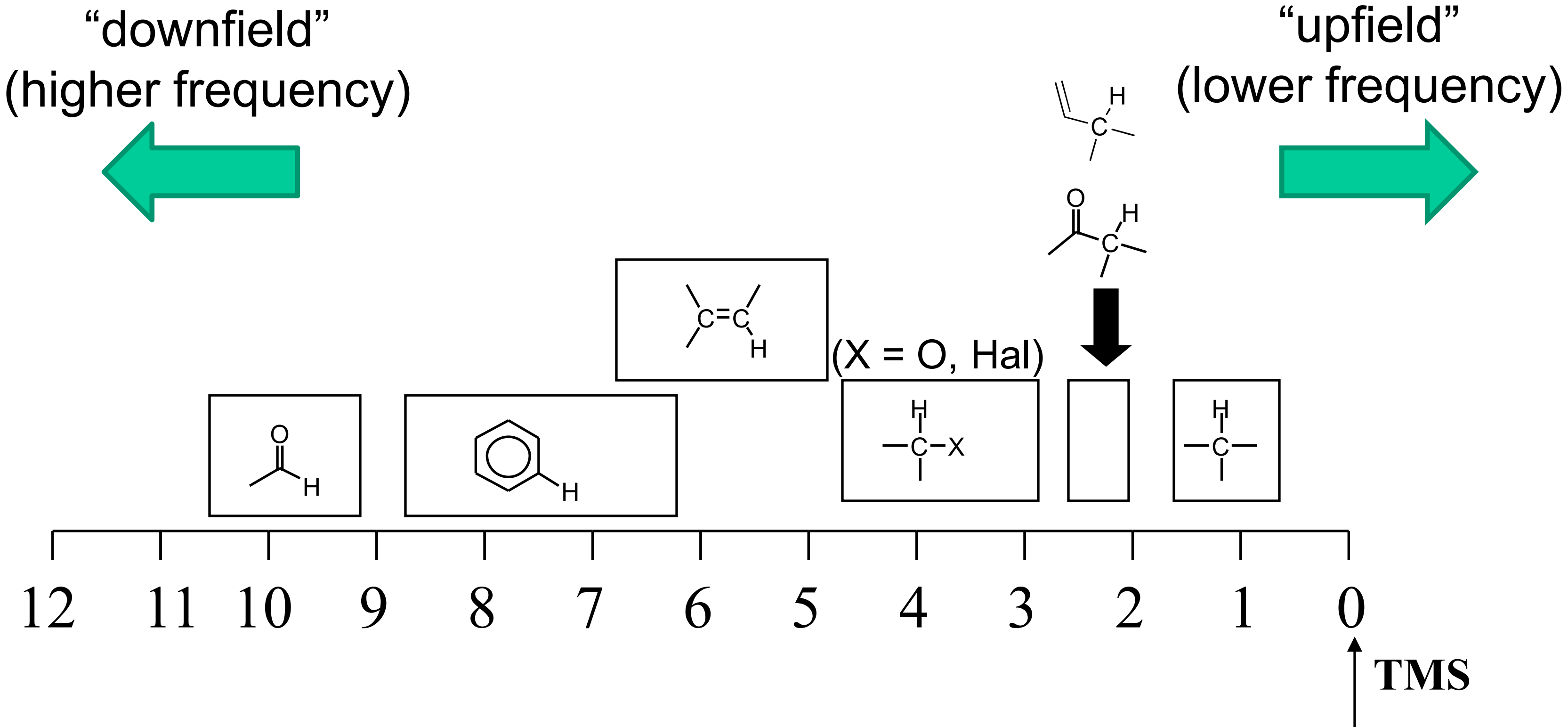


Figure 15.21

Tetramethylsilane {$(CH_3)_4Si$, TMS} is used as a reference for NMR spectra. Its chemical shift is defined as 0 ppm.

Most protons in organic compounds fall in the range of 1-12 ppm.

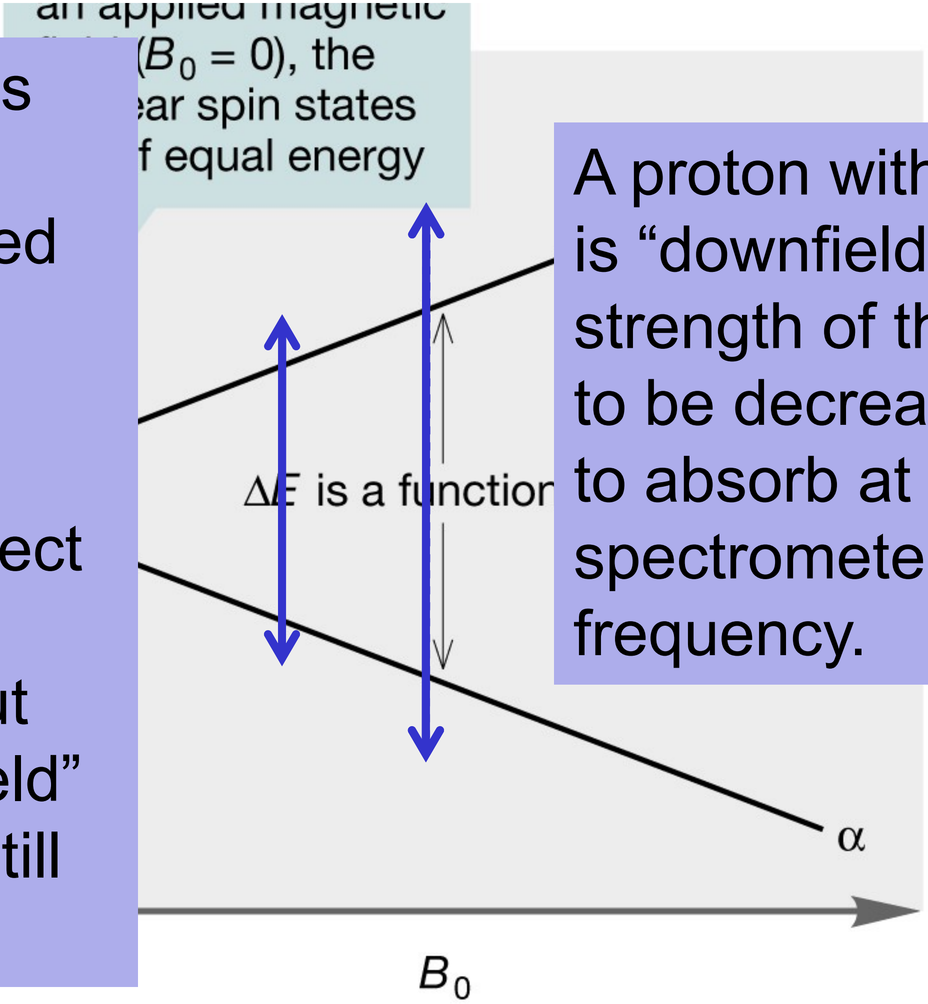
Typical locations of ^{1}H-NMR resonances



Old spectrometers used a single frequency of radio waves, and changed the strength of the magnet.

At lower field, ΔE is now at the spectrometer's fixed frequency.

Modern spectrometers detect all frequencies simultaneously, but the terms "downfield" and "upfield" are still used.



A proton with a higher ΔE is "downfield" because the strength of the magnet has to be decreased in order to absorb at the spectrometer's fixed frequency.

Figure 15.20
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TABLE 15.4 Chemical Shifts of Various Hydrogens[a,b]

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
$C{=}C{-}CH$ (allylic hydrogens)	1.8–2.3
$O{=}C{-}CH$	2.0–2.5
$Ph{-}CH$ (benzylic hydrogens)	2.3–2.8
$\equiv C{-}H$	2.5
$R_2N{-}CH$	2.0–3.0
$I{-}CH$	2.8–3.3
$Br{-}CH$	2.8–3.5
$Cl{-}CH$	3.1–3.8
$F{-}CH$	4.1–4.7
$O{-}CH$	3.1–3.8
$=CH_2$ (terminal alkene)	5.0
$C{=}CH$ (internal alkene)	4.5–5.5
$Ph{-}H$ (aromatic hydrogens)	7.0–7.5
$O{=}CH$ (aldehyde hydrogens)	9.0–10.0
RCOOH	10–13

[a] These values are approximate. There will surely be examples that lie outside the ranges indicated. Use them as guidelines, not "etched in stone" inviolable numbers.

[b] Watch out for loose talk. For example, "aromatic hydrogen" means a hydrogen attached to a benzene ring.

Alkanes: $CH_3 \sim \delta$ 0.8-1.0

$CH_2 \sim \delta$ 1.2-1.5

$CH \sim \delta$ 1.4-1.7

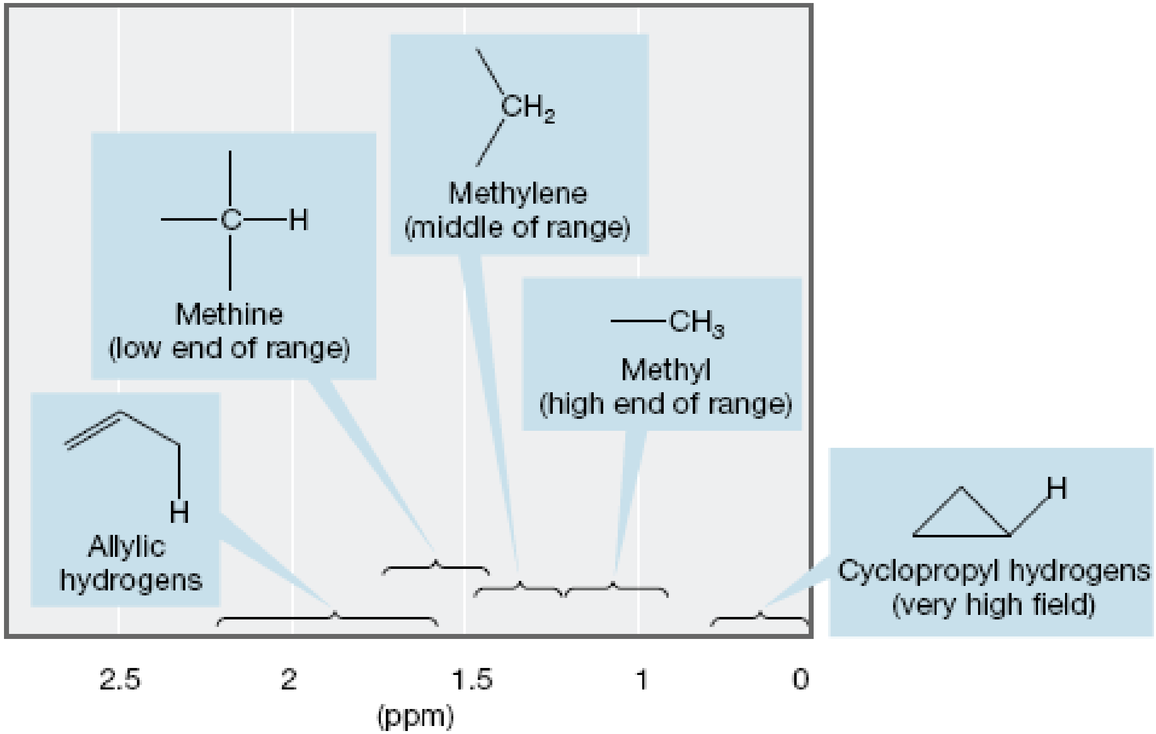
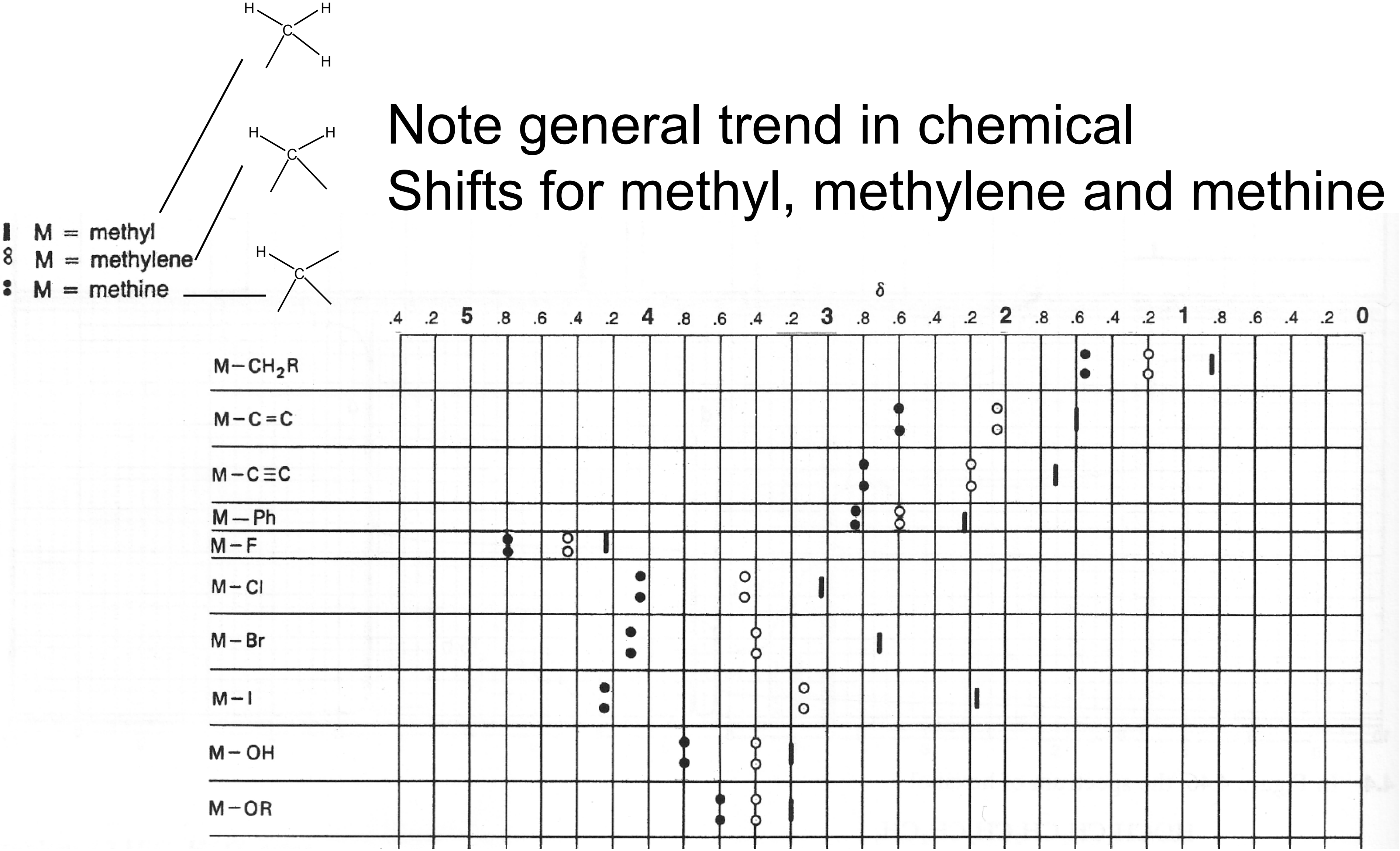


FIGURE 15.27 The ^1H NMR chemical shifts of alkanes.

Note general trend in chemical
Shifts for methyl, methylene and methine



Factors that Affect Chemical Shift

- The electrons around a nucleus “shield” it from the full strength of the applied magnetic field

- Electron-withdrawing groups “deshield” nearby nuclei, and shift their absorbance downfield (higher δ)

B_0 causes the electrons to circulate. This generates an induced magnetic field B_i at the nucleus, which opposes B_0.

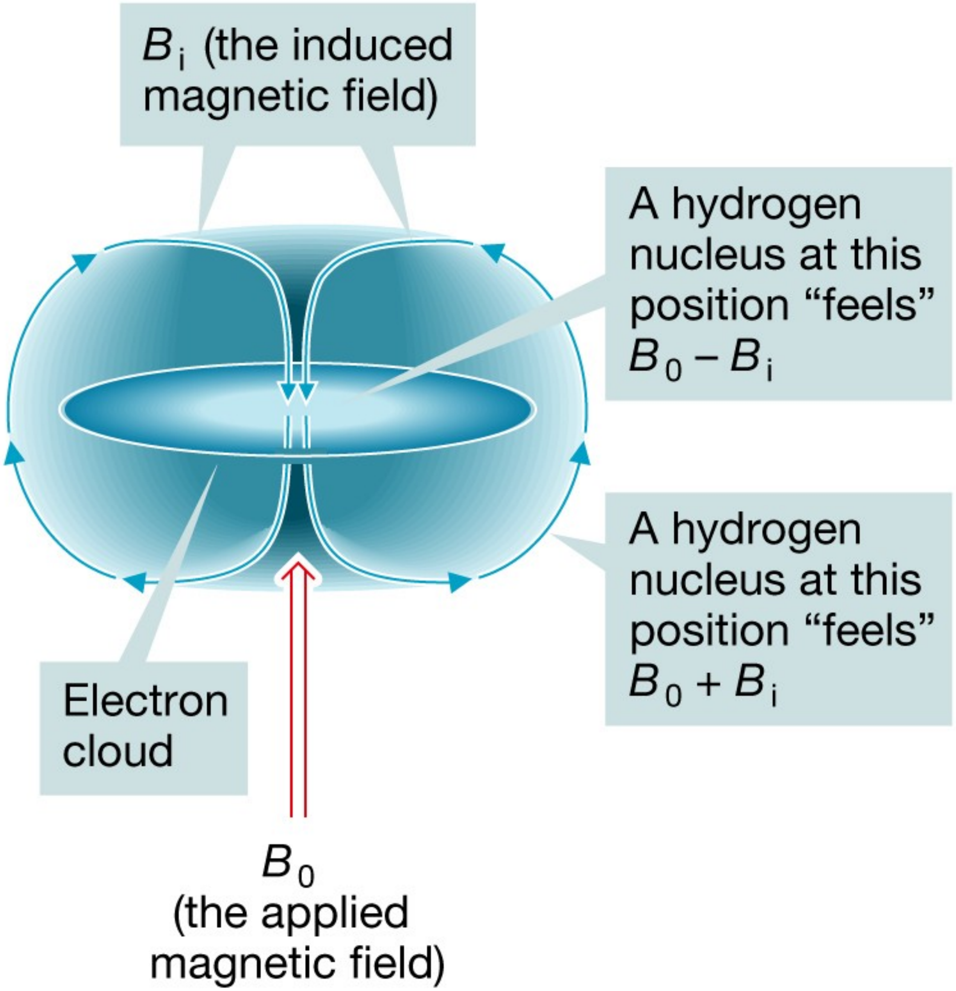
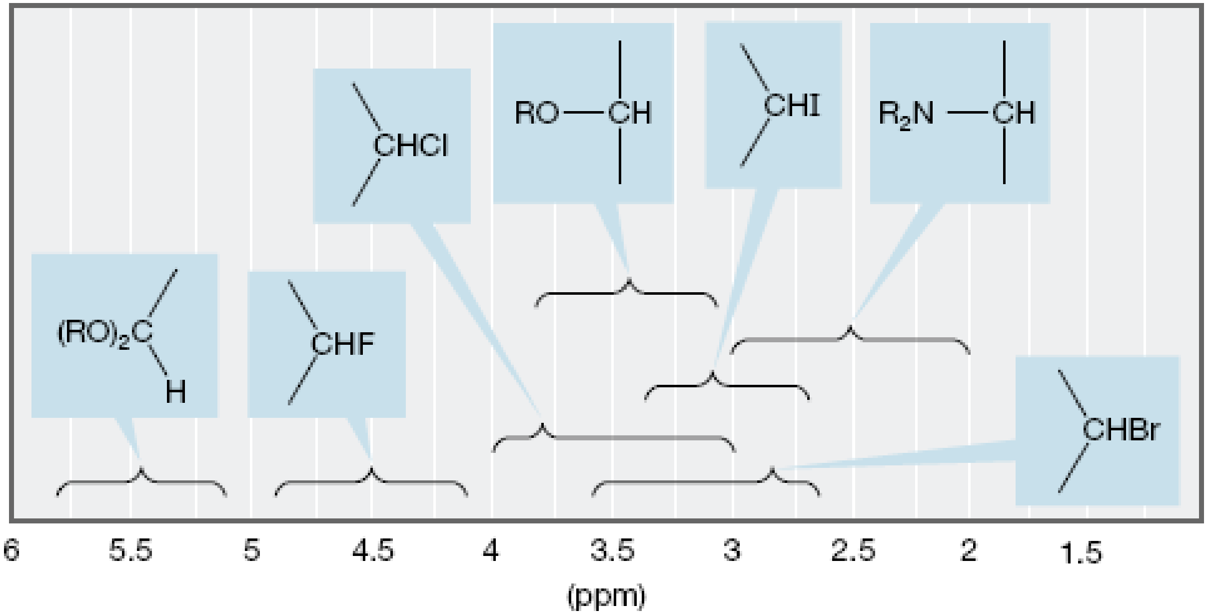


Figure 15.22

Electronegative atoms deshield protons, moving them downfield.

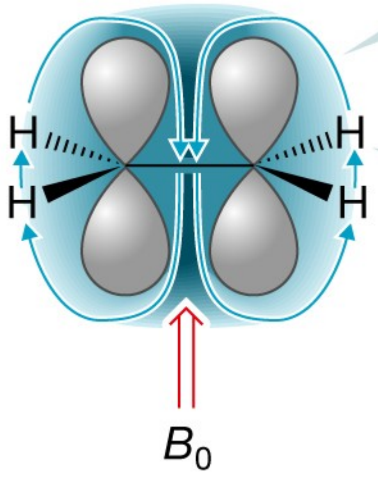
Especially note the typical shifts for protons next to O and Cl (~3-4 ppm)



	X=F	X=Cl	X=Br	X=I
CH_3X	4.26	3.05	2.68	2.16
CH_2X_2		5.31	4.96	3.88
CHX_3		7.28	6.86	5.36

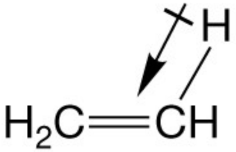
FIGURE 15.28 The ^{1}H NMR chemical shifts of alkanes substituted with electron-withdrawing groups.

- The circulation of p-electrons in a magnetic field produce particularly strong chemical-shift effects



Induced magnetic field, B_i

At this point, B_0 is augmented by B_i. The hydrogen will “feel” a net $B_{net} = B_0 + B_i$, and require a reduced B_0 to come into resonance. It appears at relatively low field



The sp^2 carbon has high *s* character and withdraws electrons, deshielding the hydrogen

Figure 15.30

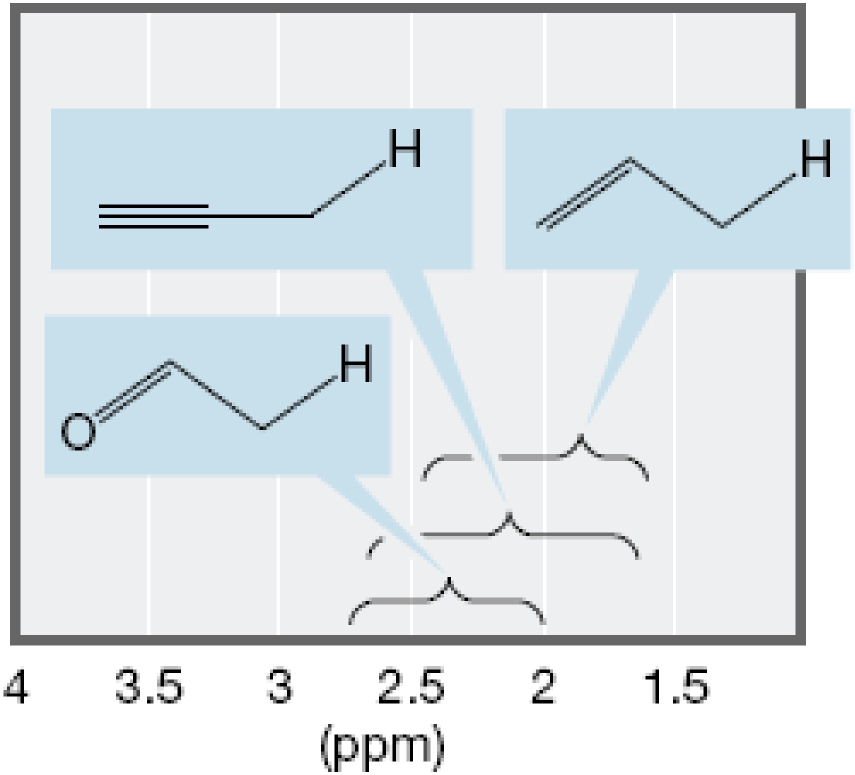


FIGURE 15.29 The ^{1}H NMR chemical shifts of hydrogens adjacent to double and triple bonds.

Allylic and propargylic hydrogens generally appear on either side of 2 ppm.

Hydrogens next to a carbonyl, or at a benzylic position, are generally in the 2-3 ppm range.

- Vinylic hydrogens appear ~δ 4.5-6
- Hydrogens on an aromatic ring appear ~δ 7-8

- Aldehyde protons ~δ 9-10 ppm
- Carboxylic acid shifts vary, but are typically ~δ 10-13

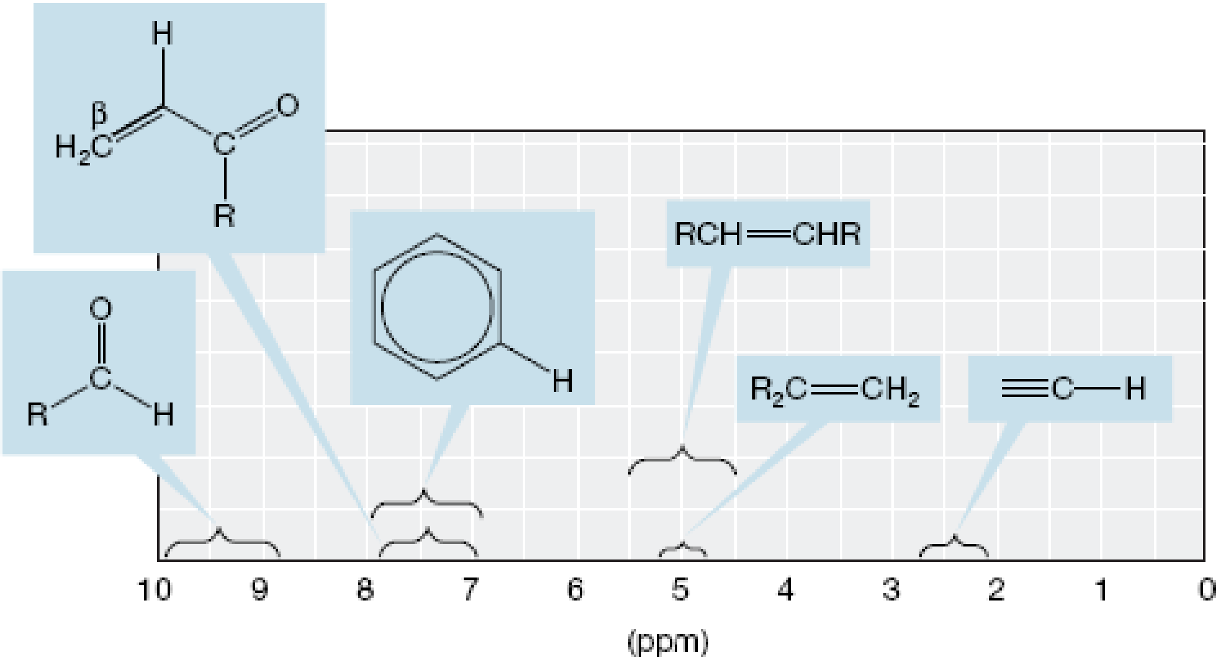
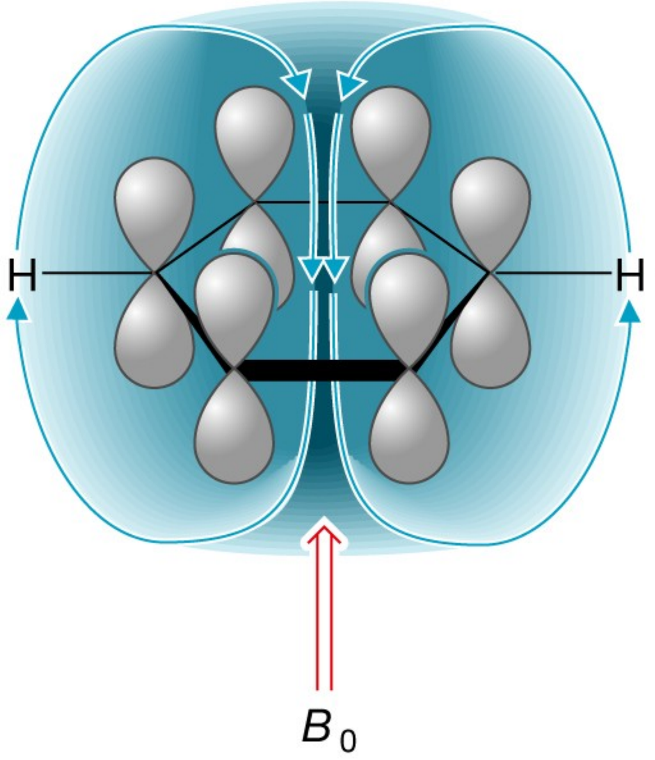


FIGURE 15.31 The ^1H NMR chemical shifts of alkenes and alkynes.

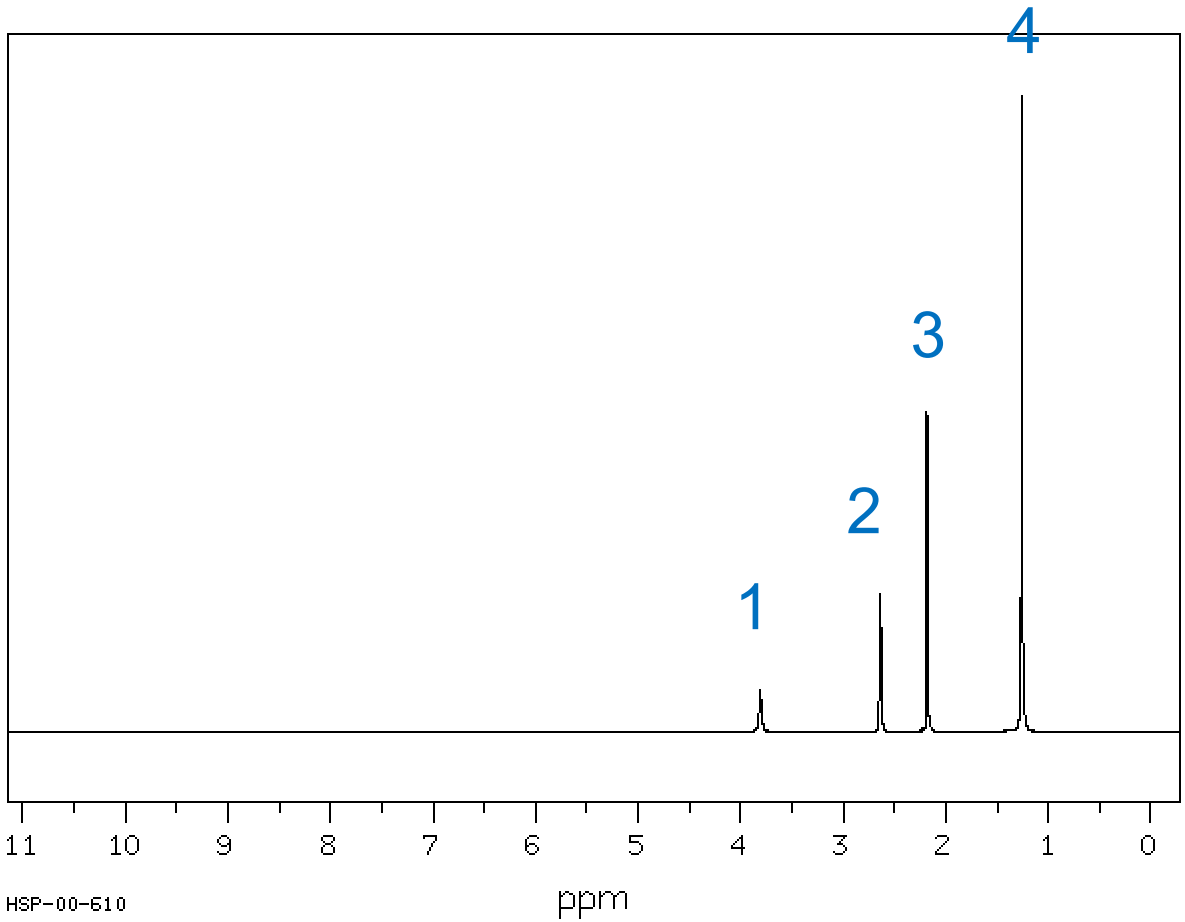
A magnetic field induces a “ring current” of π-electrons around an aromatic ring…



At this point the induced magnetic field, B_i augments the applied field B_0; the hydrogen will “feel” a net magnetic field, $B_{net} = B_0 + B_i$, and require a reduced applied field to come into resonance

…resulting in a pronounced downfield chemical shift (~7-8 ppm)

Figure 15.32

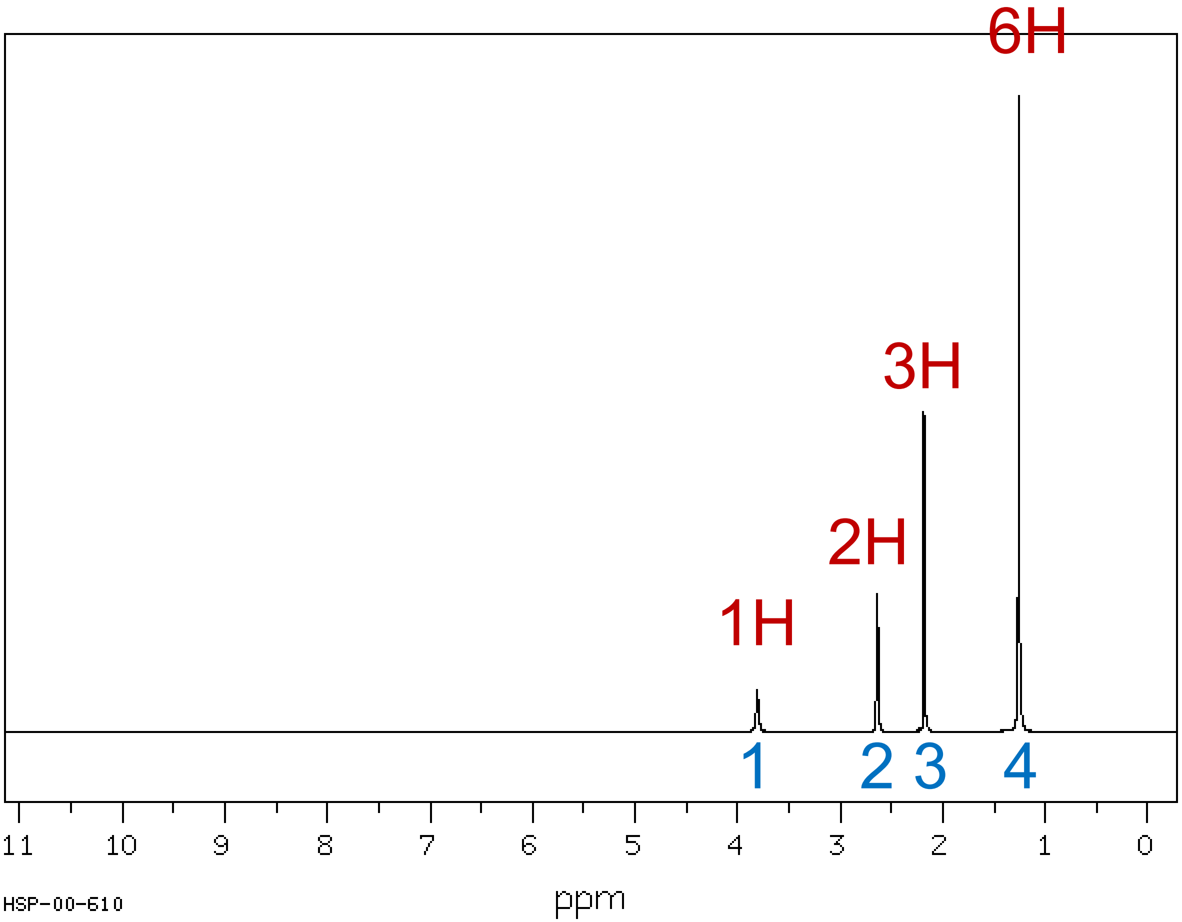

1
2
3
4
11
10
9
8
7
6
5
4
3
2
1
0
ppm
HSP-00-610

Protons that are interchangeable via bond rotation or symmetry have the same chemical shift and appear as one signal.

Integration of NMR Signals

The area under an NMR signal is proportional to the number of H that cause the signal.

Computers can “integrate” (calculate the areas of) NMR signals, and allow ratios to be calculated.


6H
3H
2H
1H
1
2
3
4
11
10
9
8
7
6
5
4
3
2
1
0
ppm
HSP-00-610

The “Old School” method of integration involved measuring the heights of computer-traced curves and calculating the ratio of heights

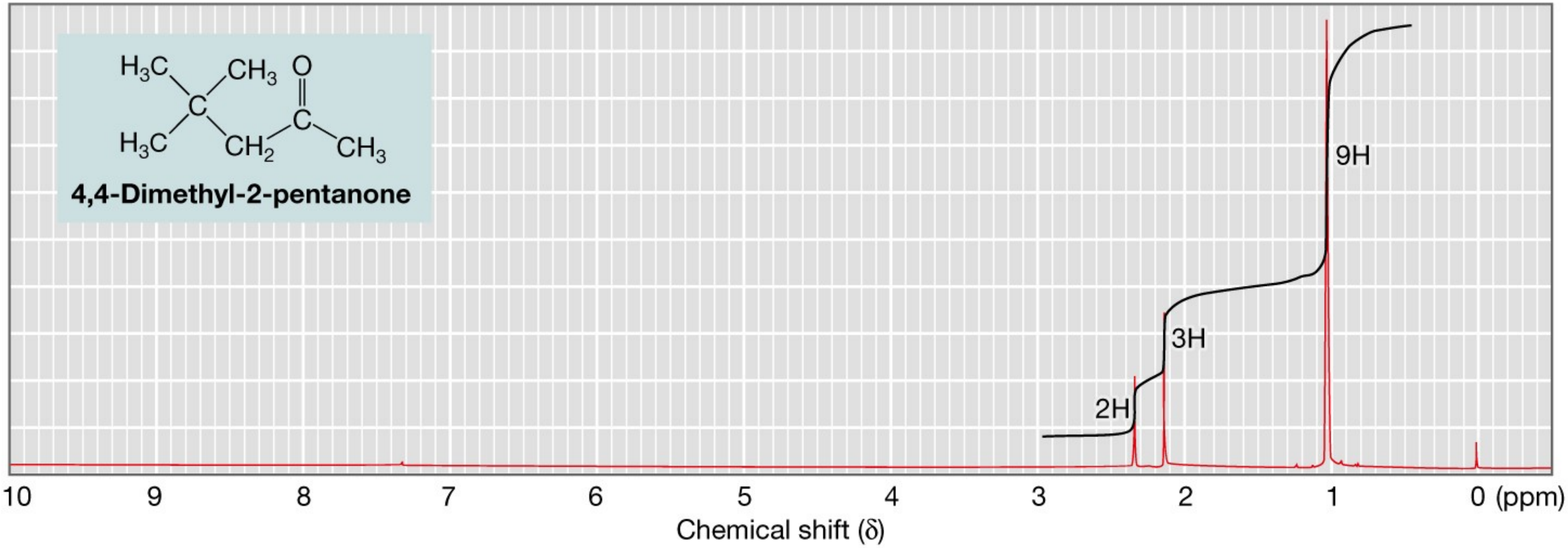
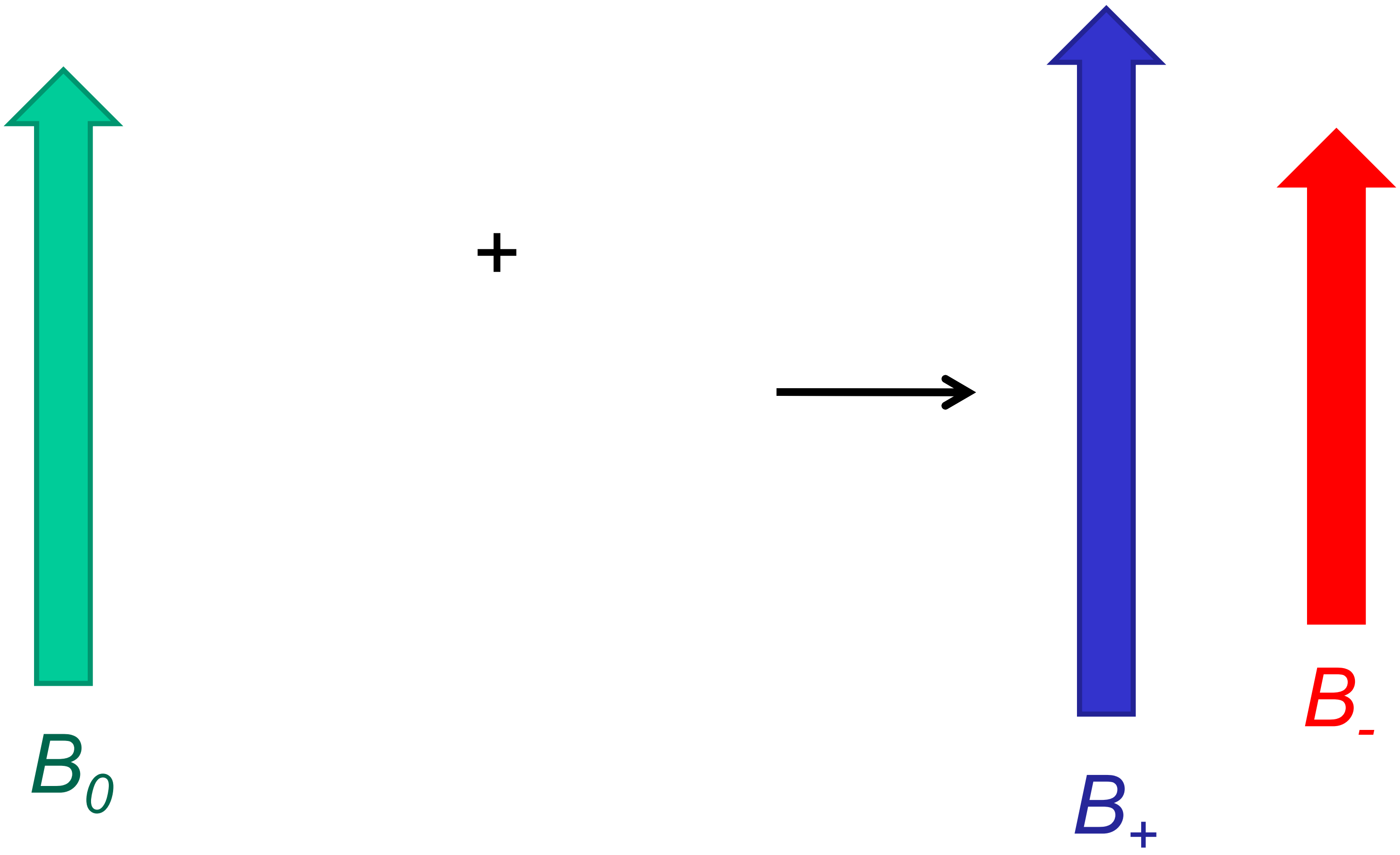


Figure 15.26

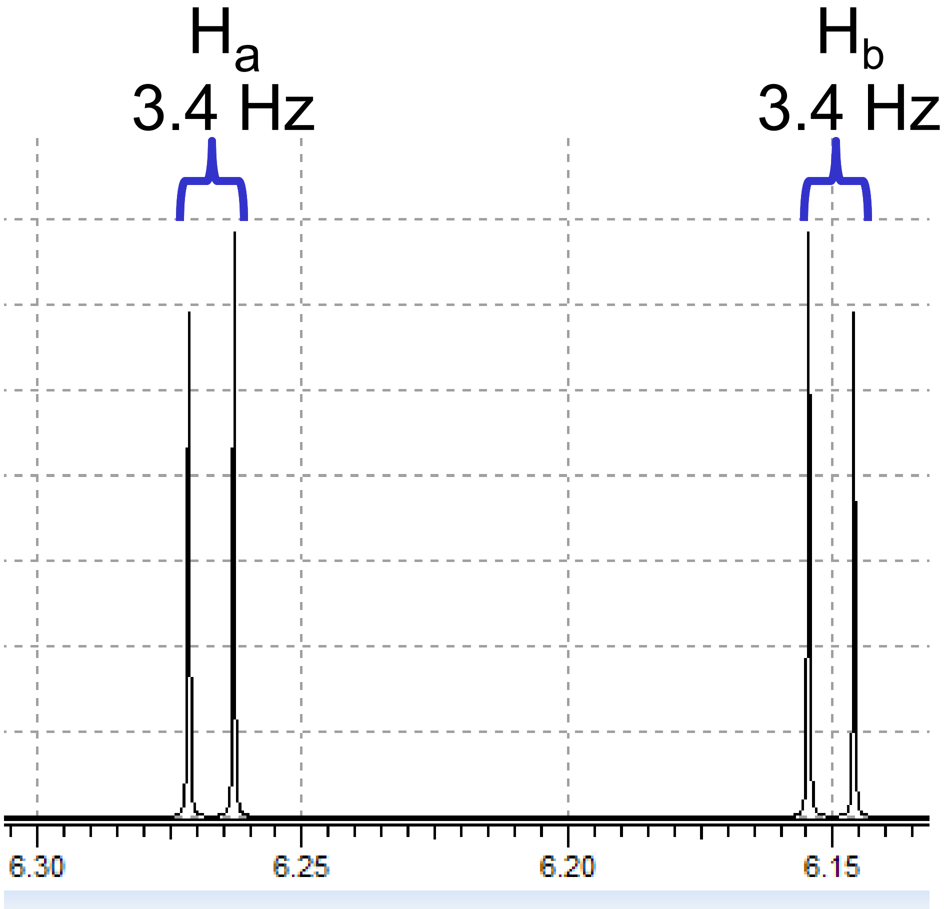
Spin-Spin Coupling

- Protons in a magnetic field are almost equally divided between α- and β- spin states (i.e. +1/2, -1/2).

- If two hydrogens are separated by 2-3 bonds, they feel each other’s magnetic spin—i.e. they are “spin-spin coupled”



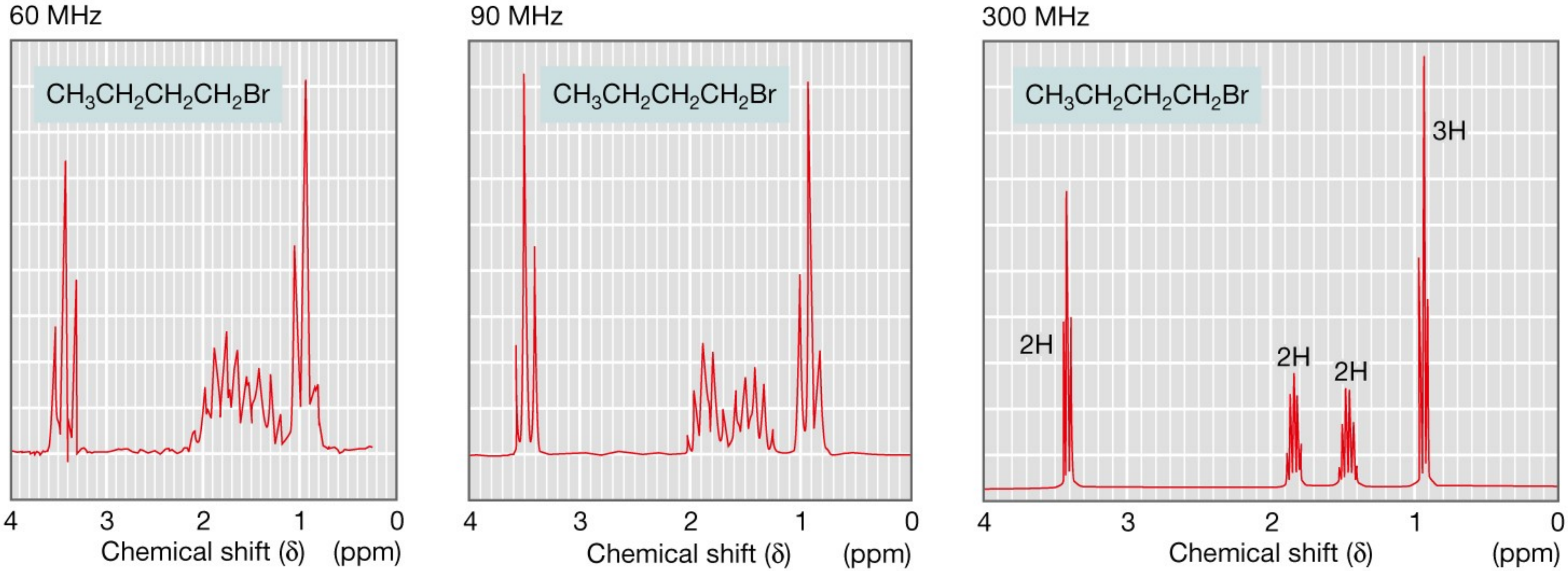
- •50% chance H_2's magnetic dipole adds to B_0
- •50% chance H_2's magnetic dipole subtracts from B_0
- •H_1 feels 2 different net magnetic fields. Half of its signal appears slightly upfield, and half slightly downfield —i.e. it's split to a "doublet"



The size of couplings (***J* values**) are expressed in Hz. **The size of *J* in Hz is the same regardless of the strength of the magnetic field.**

Coupled protons split each other to the same extent. Here, $J_{AB} = J_{BA} =$ 3.4 Hz

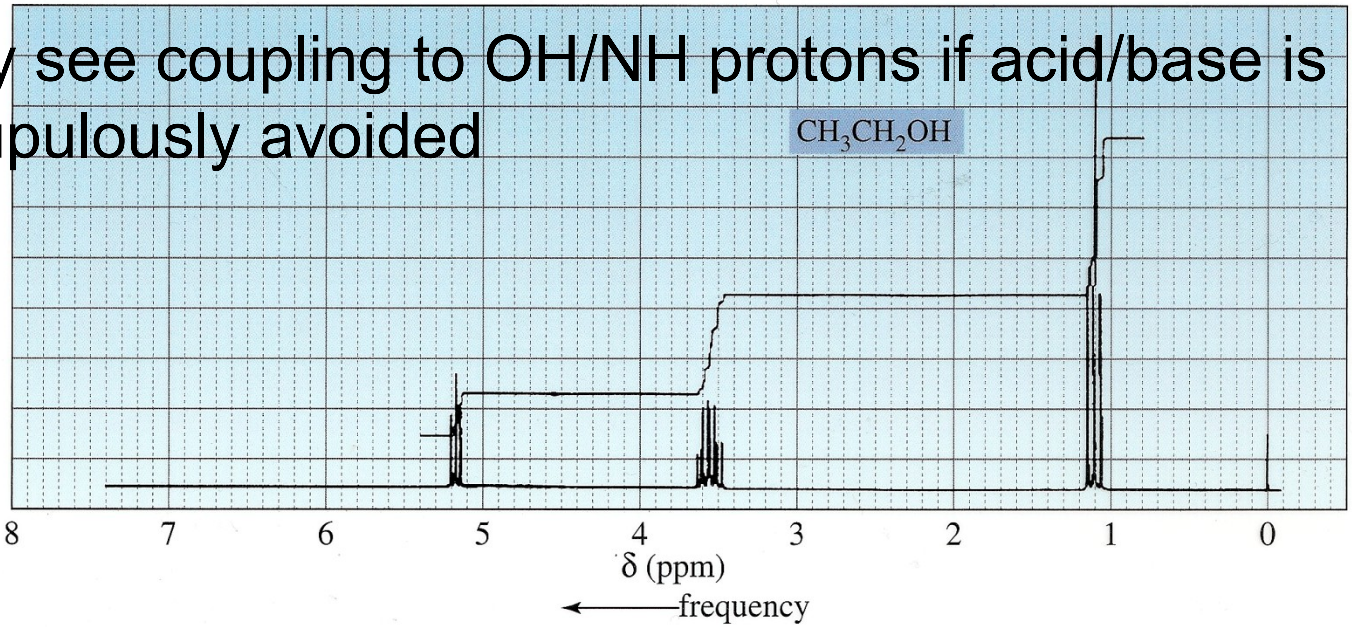
As the magnetic field increases, chemical shifts ***in Hz*** (not δ) increase, but *J*-splittings are constant.



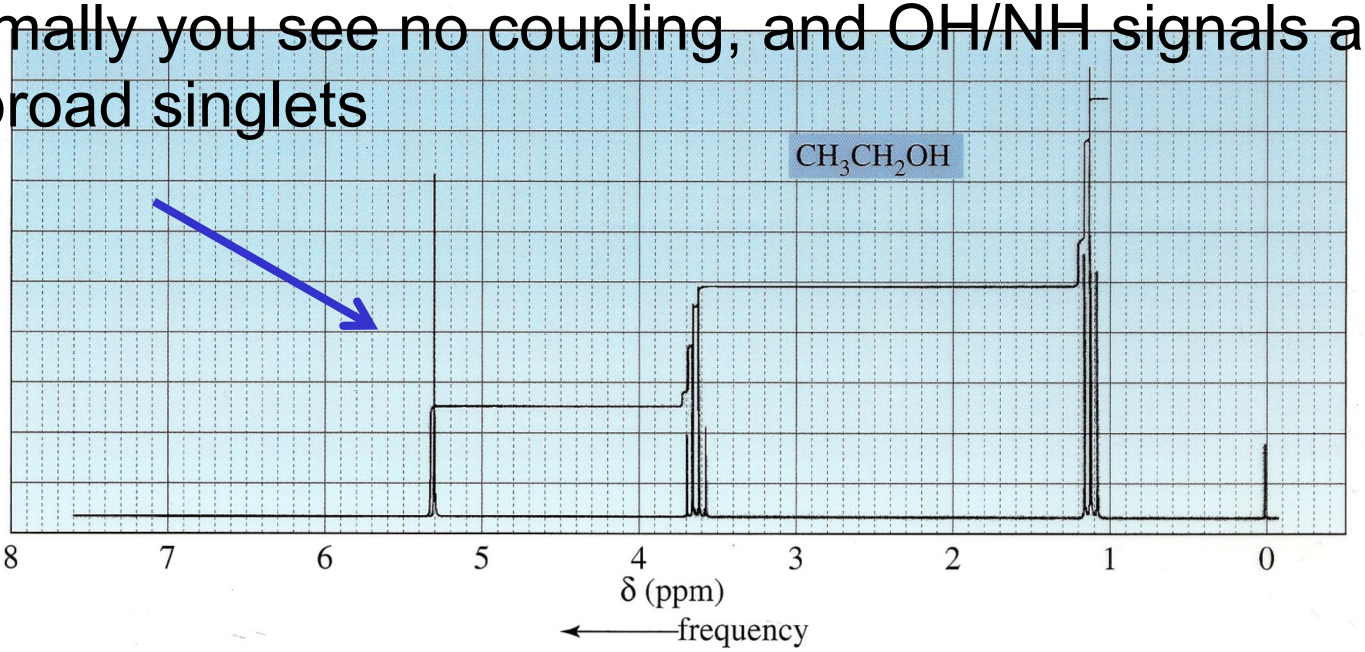
Therefore, more powerful magnets give better resolution

Figure 15.54

Only see coupling to OH/NH protons if acid/base is scrupulously avoided



Normally you see no coupling, and OH/NH signals appear as broad singlets



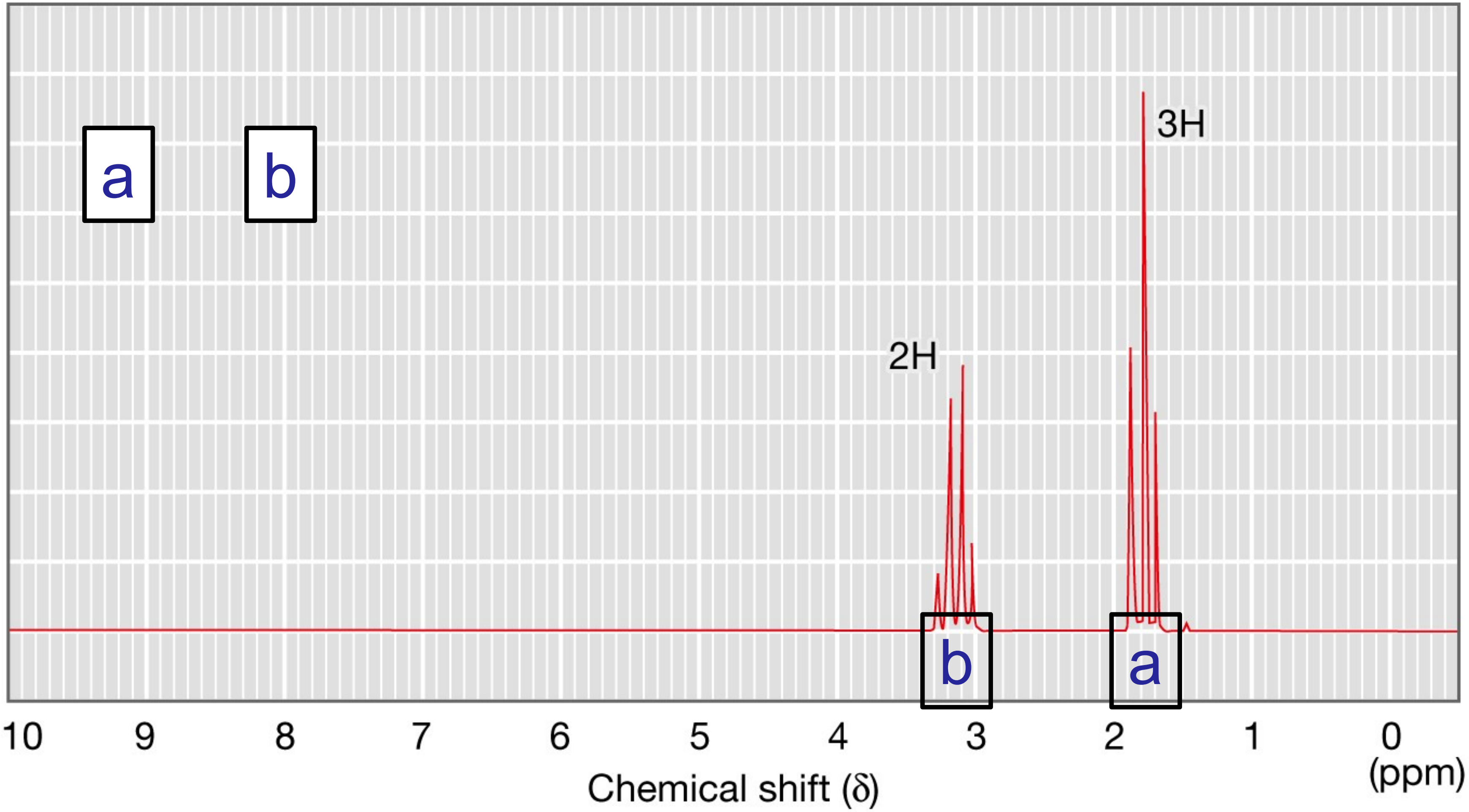
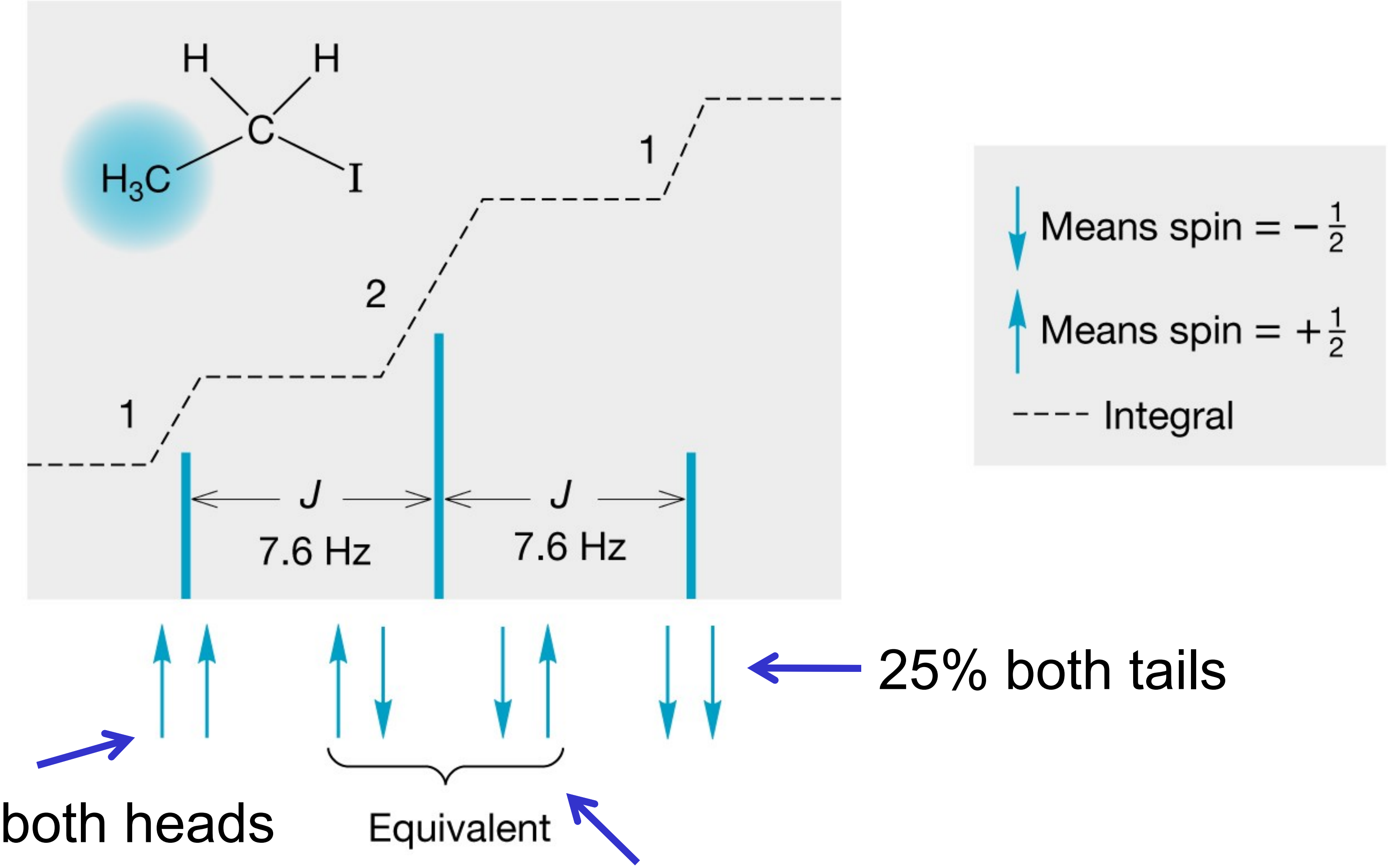


Figure 15.34

Compare this with the results of flipping a coin twice:



25% both tails

25% both heads

50% one head, one tail

Figure 15.36

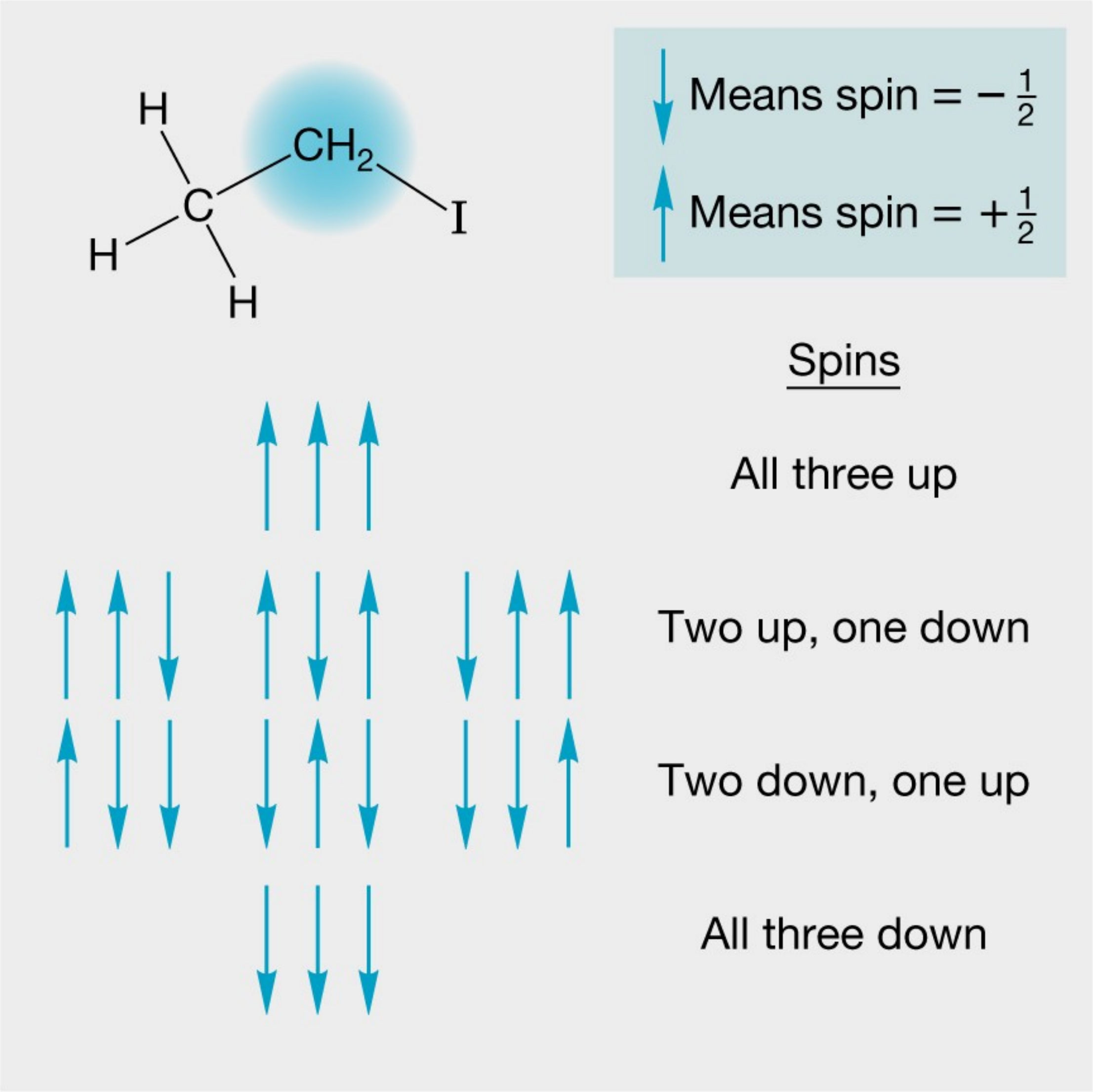

H
CH$_2$
C
I
H
H
Means spin = $-\frac{1}{2}$
Means spin = $+\frac{1}{2}$
Spins
All three up
Two up, one down
Two down, one up
All three down

Figure 15.37

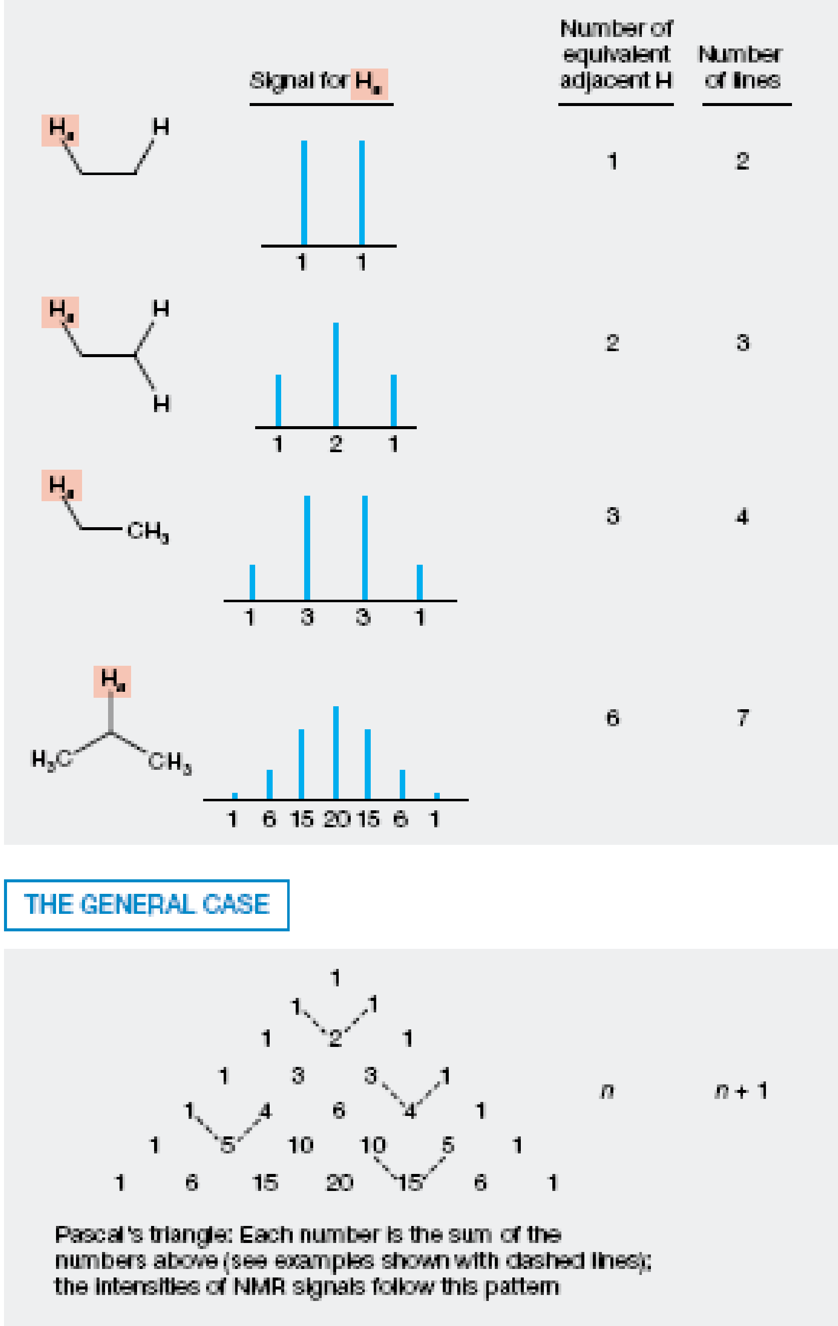


FIGURE 15.39 In the general case, there will be $n + 1$ lines for a hydrogen adjacent to n equivalent hydrogens.

n+1 rule: the number of peaks in a proton's signal = the number of neighboring protons (n) +1

This assumes that all *J*s are the same size. It generally holds true for simple acyclic alkyl groups.

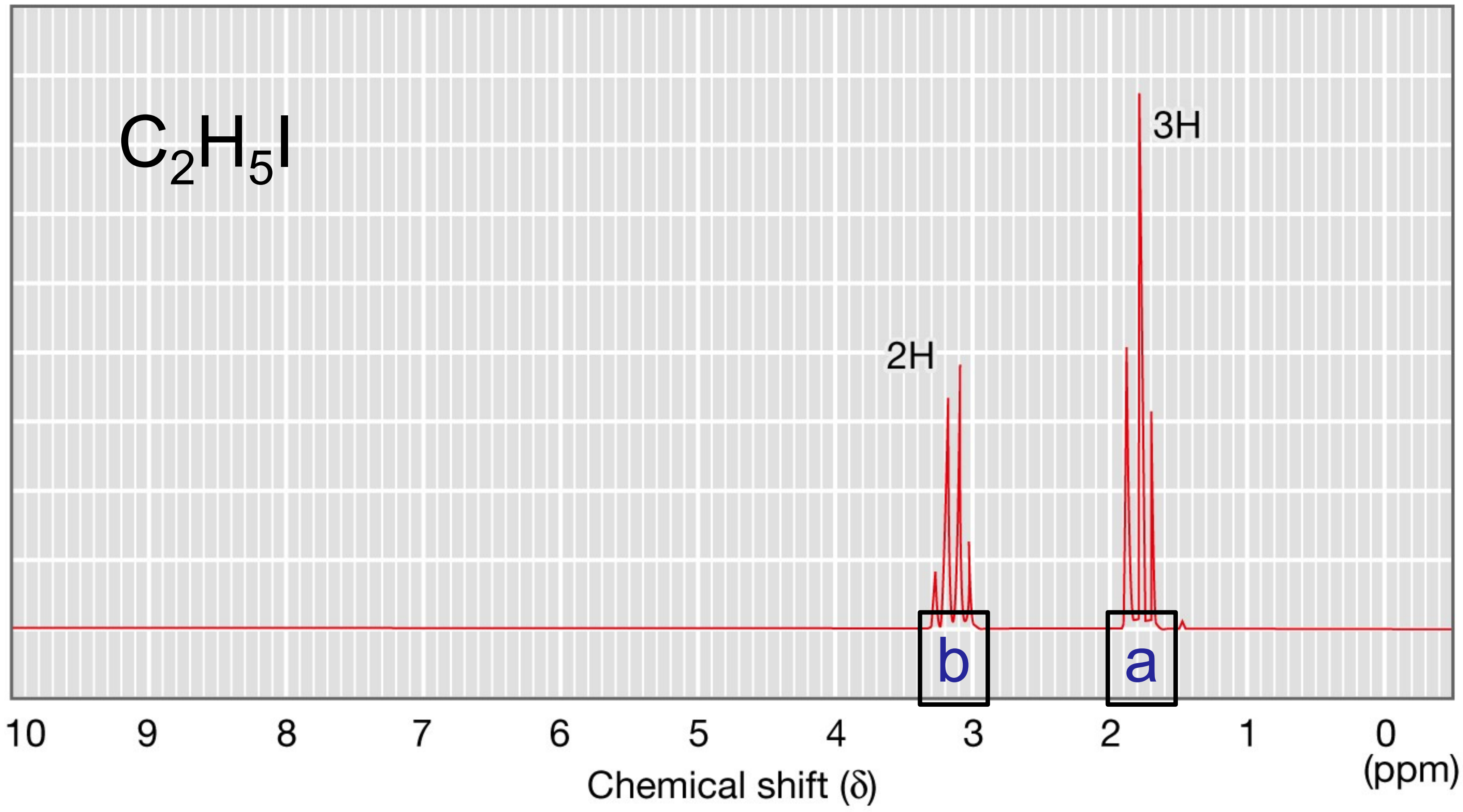
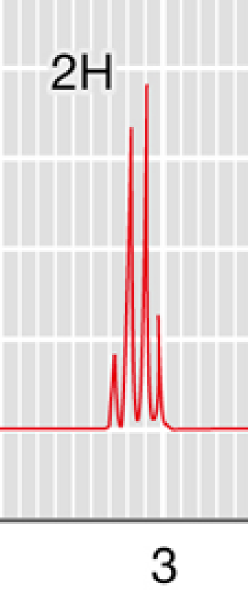


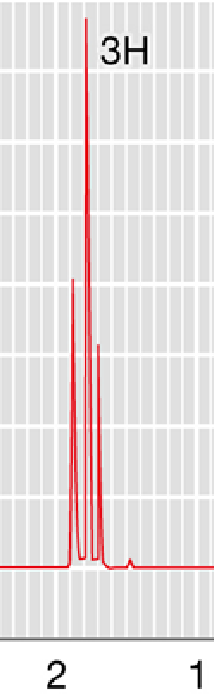
Figure 15.34



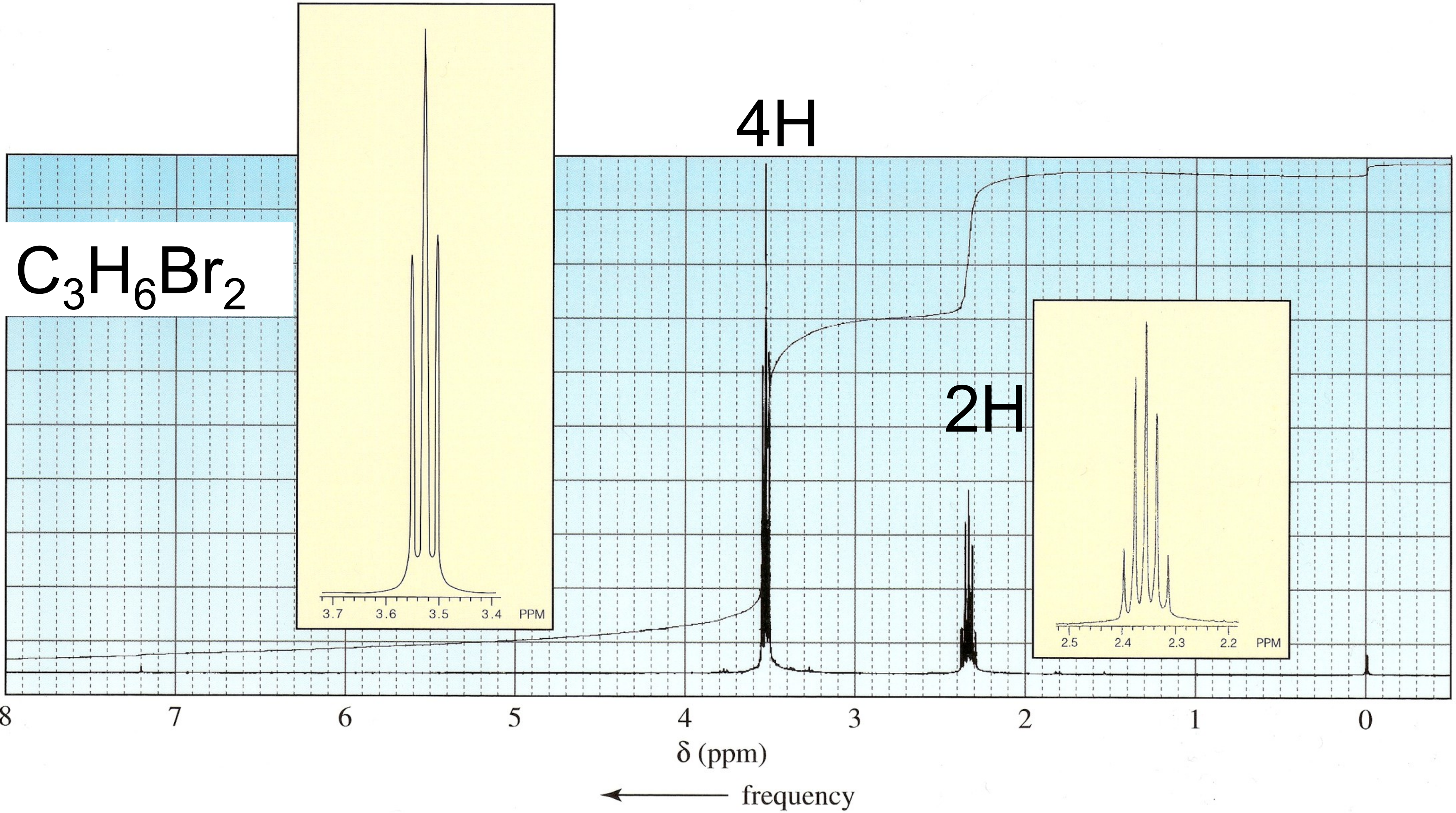
Analyzing the NMR Spectrum

Construct a table:

δ	Integration	Multiplicity	assignment
3.1	2H	q (quartet)	$X\text{-}C\underline{H}_2\text{-}CH_3$ $(I\text{-}C\underline{H}_2\text{-}CH_3)$
1.8	3H	t (triplet)	$C\underline{H}_3\text{-}CH_2$



$C_3H_6Br_2$

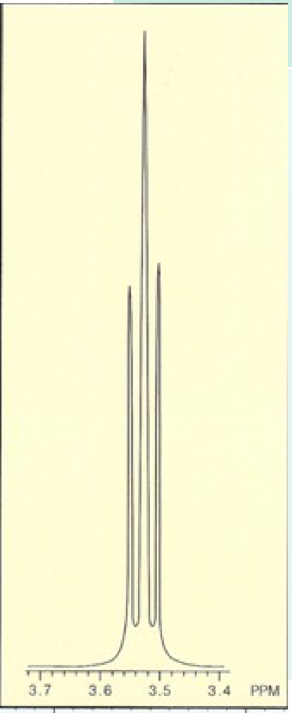


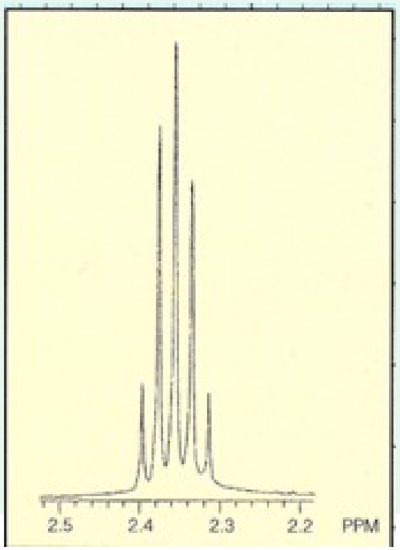
4H

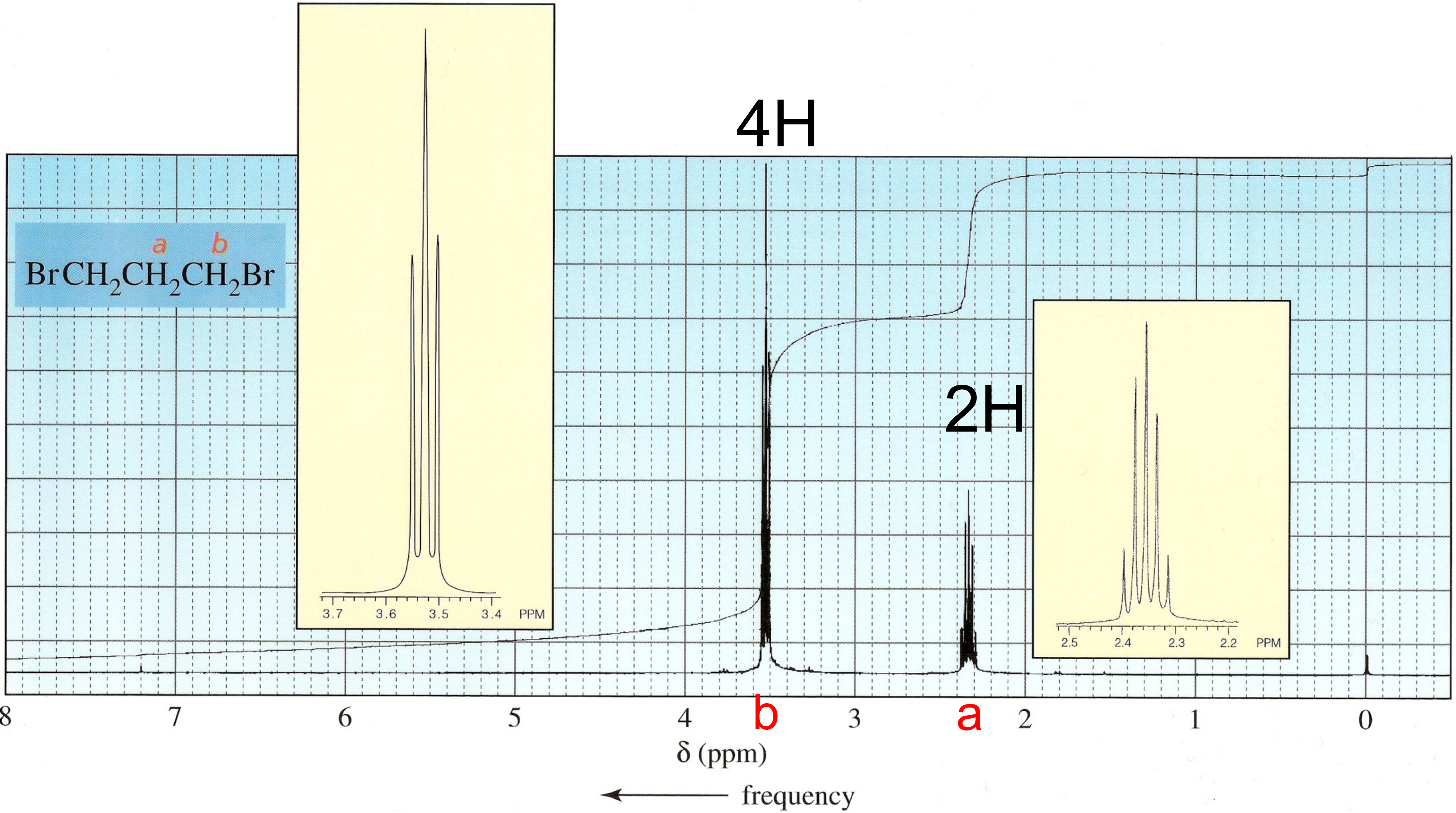
2H

δ	Integration	Multiplicity	assignment
3.5	4H	t	$X\text{-}C\underline{H_2}\text{-}CH_2$ $(Br\text{-}C\underline{H_2}\text{-}CH_2)$ **×2**
2.3	2H	pentet	$CH_2\text{-}C\underline{H_2}\text{-}CH_2$ or $CH_3\text{-}C\underline{H_2}\text{-}CH$

$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br$






4H
2H
a b
BrCH₂CH₂CH₂Br
3.7 3.6 3.5 3.4 PPM
2.5 2.4 2.3 2.2 PPM
8 7 6 5 4 b 3 a 2 1 0
δ (ppm)
frequency

How to Solve Spectroscopy Problems

- You’ll typically be given the molecular formula for the unknown compound, plus possibly IR and/or ^{13}C data.

- Calculate the DBE from the molecular formula. This can sometimes indicate the presence of functional groups not directly detectable by NMR (e.g. C=O)

- Look at the IR data for functional groups. Evidence of C=O, C≡C or C≡N is particularly helpful because these groups aren’t directly detected by proton NMR.

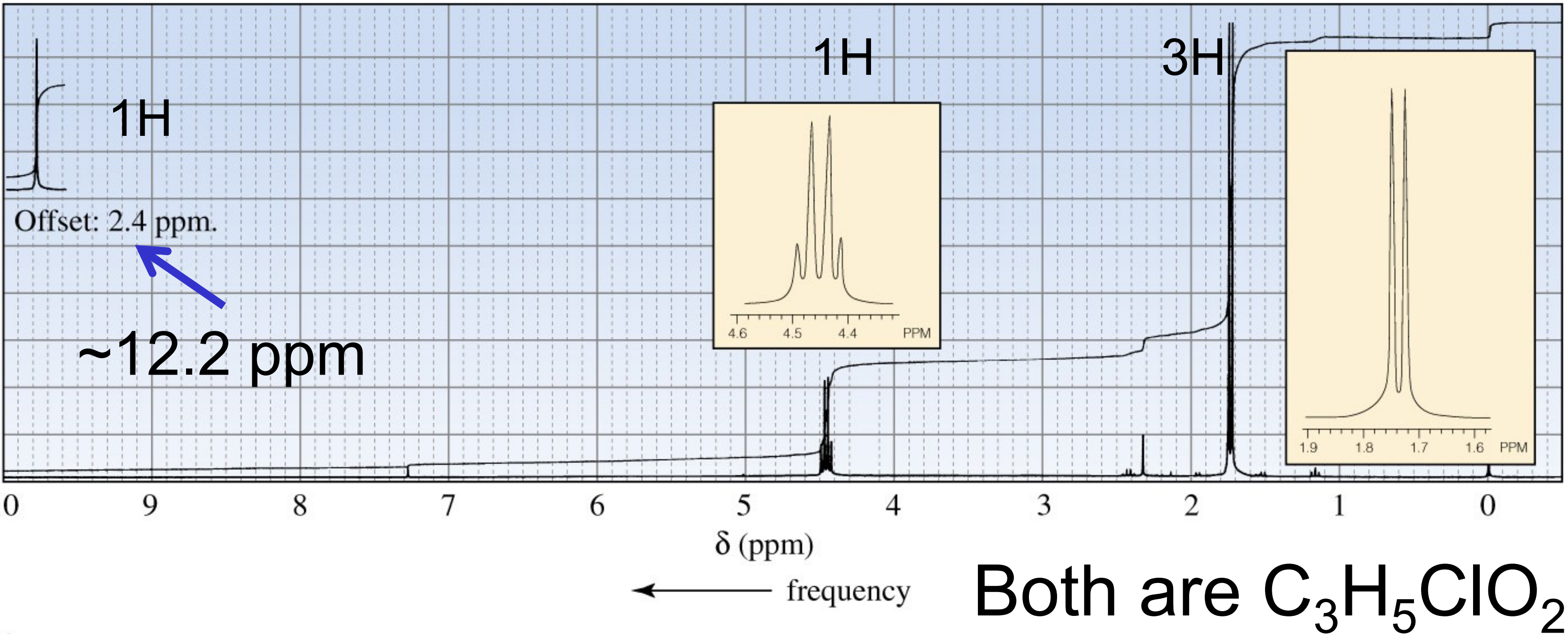
- The ^{13}C spectrum can tell you how many different kinds of carbon are in the molecule, and their chemical shifts may provide additional insight. In particular, carbon signals above 150 ppm often indicate the presence of a carbonyl group.

Analyzing the NMR spectrum

Construct a table:

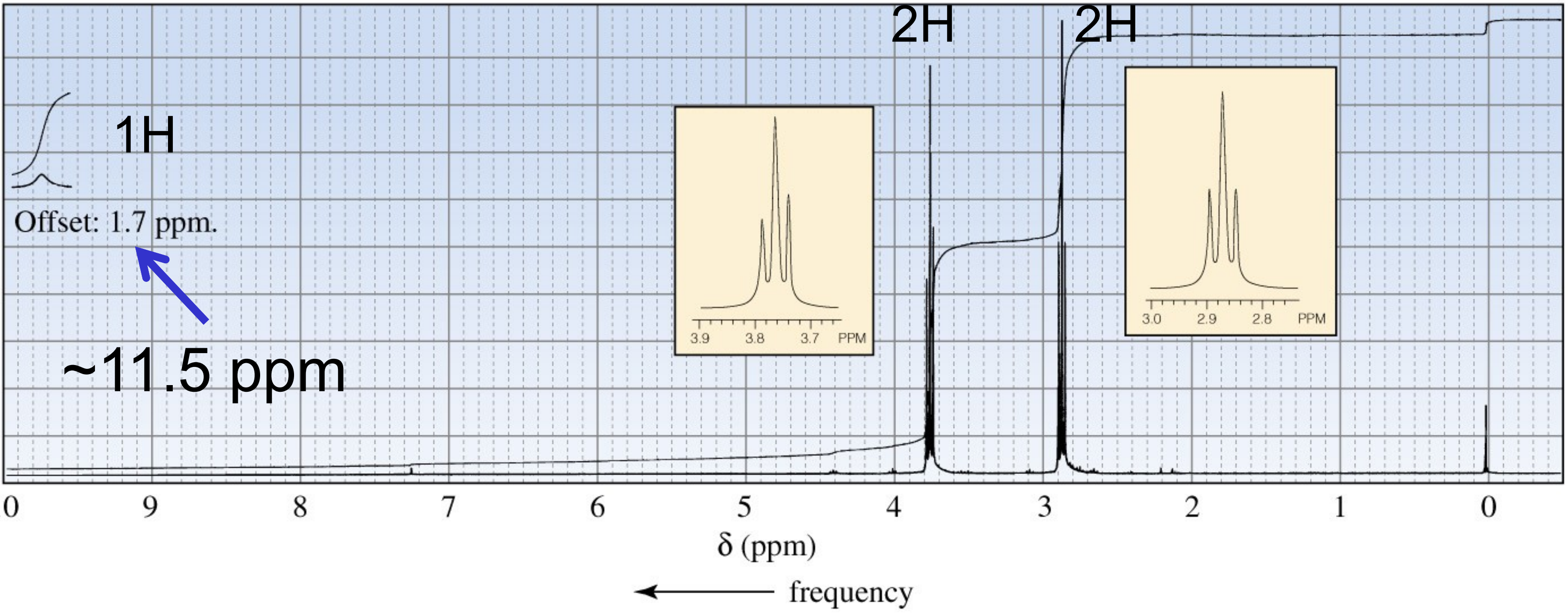
δ	Integration	Multiplicity	Assignment

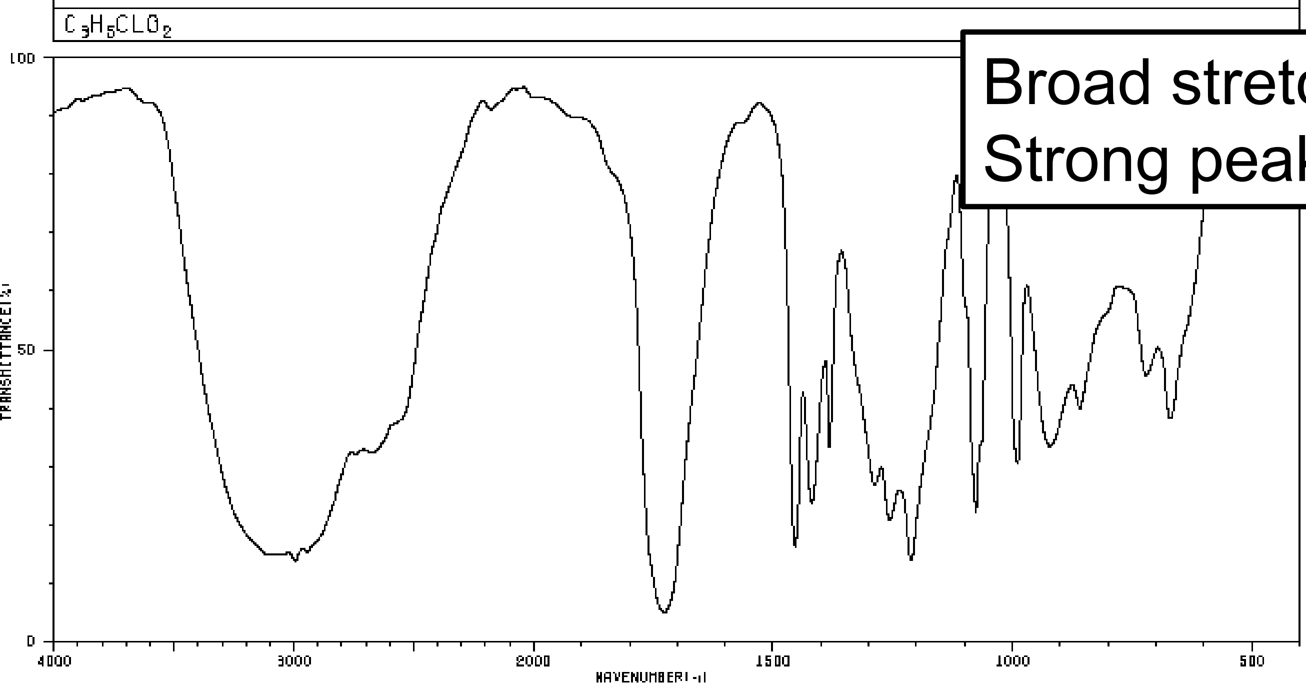
a.



Both are $C_3H_5ClO_2$

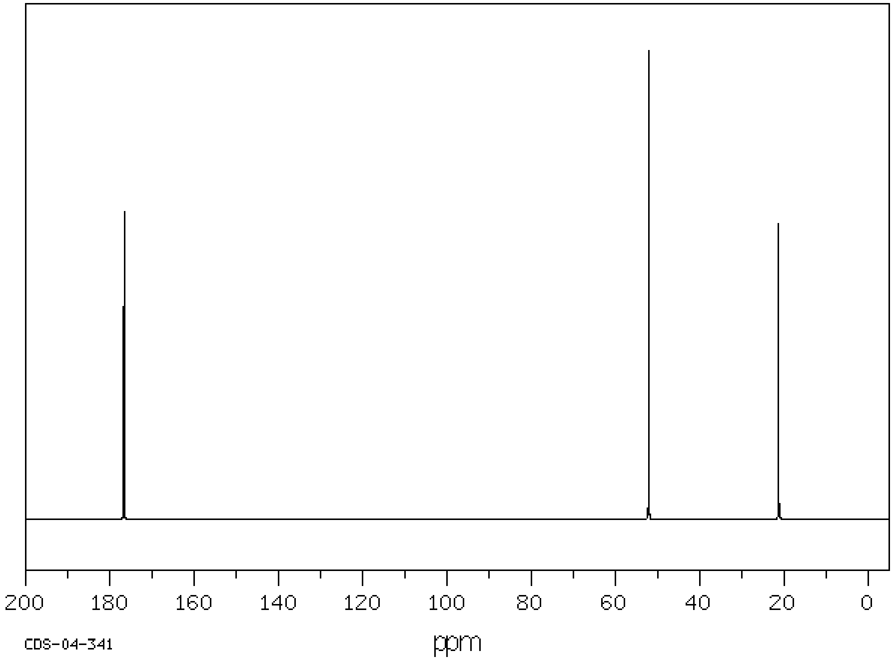
b.





Broad stretch 3500-2100 cm^{-1}
Strong peak ~1730 cm^{-1}

Compound “a”



^{13}C: ~δ 177, 52, 21

Compound “a” Analysis

DBE for $C_3H_5ClO_2$: 1
IR: 3500-2100 cm^{-1} (v. broad OH stretch)
+1730 cm^{-1} (carbonyl)
= carboxylic acid

^{13}C NMR: -3 carbons
-177 ppm: carbonyl
-(52: next to EWG)

^{1}H NMR:

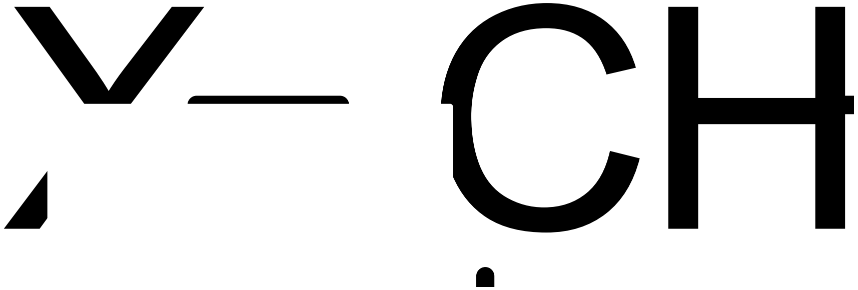
δ	integration	multiplicity	assignment
δ12.2	1H	br s	$CO_2\underline{H}$
δ4.4	1H	q	
δ1.7	3H	d	$C\underline{H_3}$-CH

“br s” = “broad singlet”

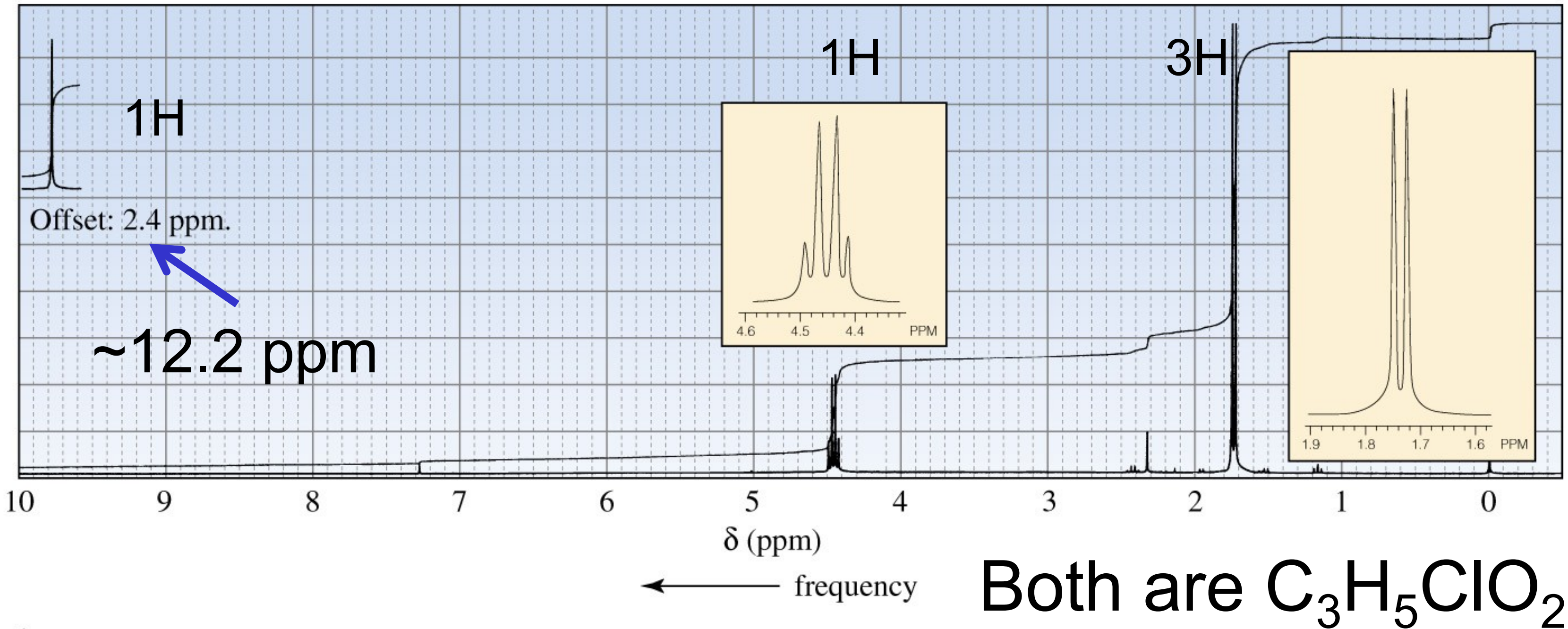
DBE + IR + ^{13}C NMR + ^{1}H NMR all indicate CO_2H— C_2H_4Cl remain.

^{1}H NMR:

δ4.4	1H	q	✖
δ1.7	3H	d	$C\underline{H_3}$-CH

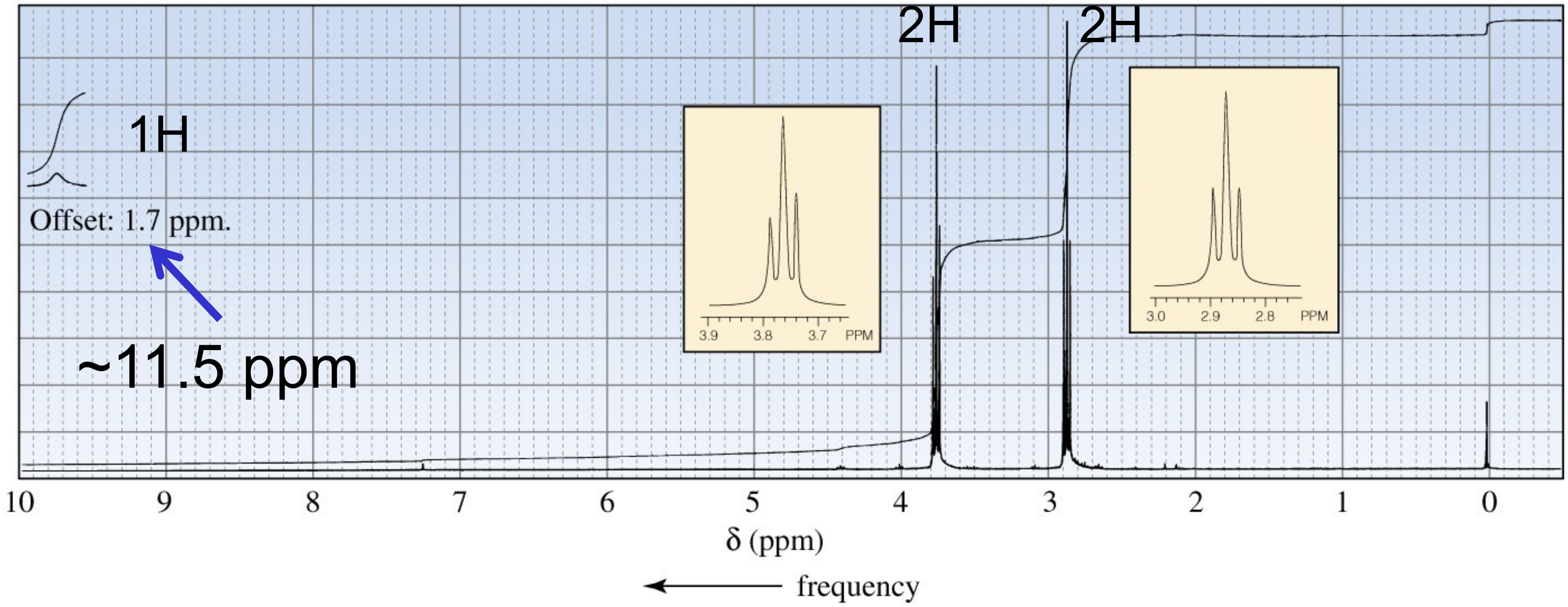


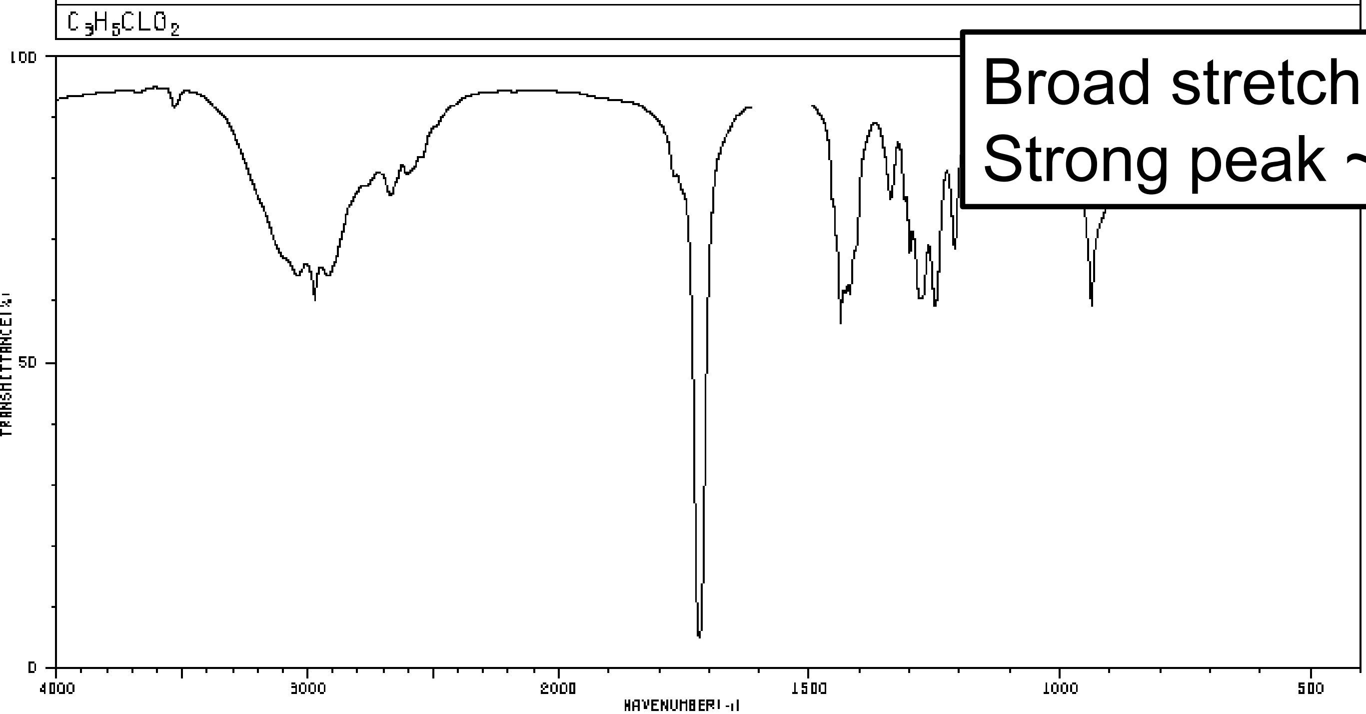
a.



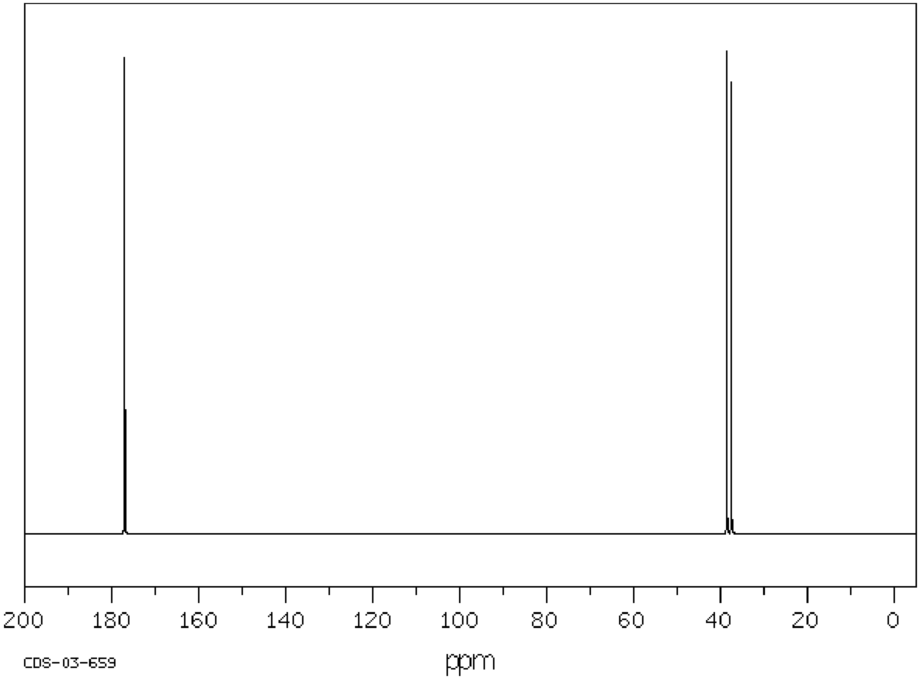
Both are $C_3H_5ClO_2$

b.





Broad stretch 3500-2100 cm^{-1}
Strong peak ~1720 cm^{-1}



^{13}C: ~δ 177, 39, 37

Compound “b” Analysis

DBE for $C_3H_5ClO_2$: 1

IR: 3500-2100 cm^{-1} (v. broad OH stretch)
+1720 cm^{-1} (carbonyl)
= carboxylic acid

^{13}C NMR: -3 carbons
-177 ppm: carbonyl
-(39,37: next to EWG)

^1H NMR:

δ	integration	multiplicity	assignment
δ11.5	1H	br s	$CO_2\underline{H}$
δ3.8	2H	t	
δ2.9	2H	t	

DBE + IR + ^{13}C NMR + ^{1}H NMR all indicate CO_2H—C_2H_4Cl remain.

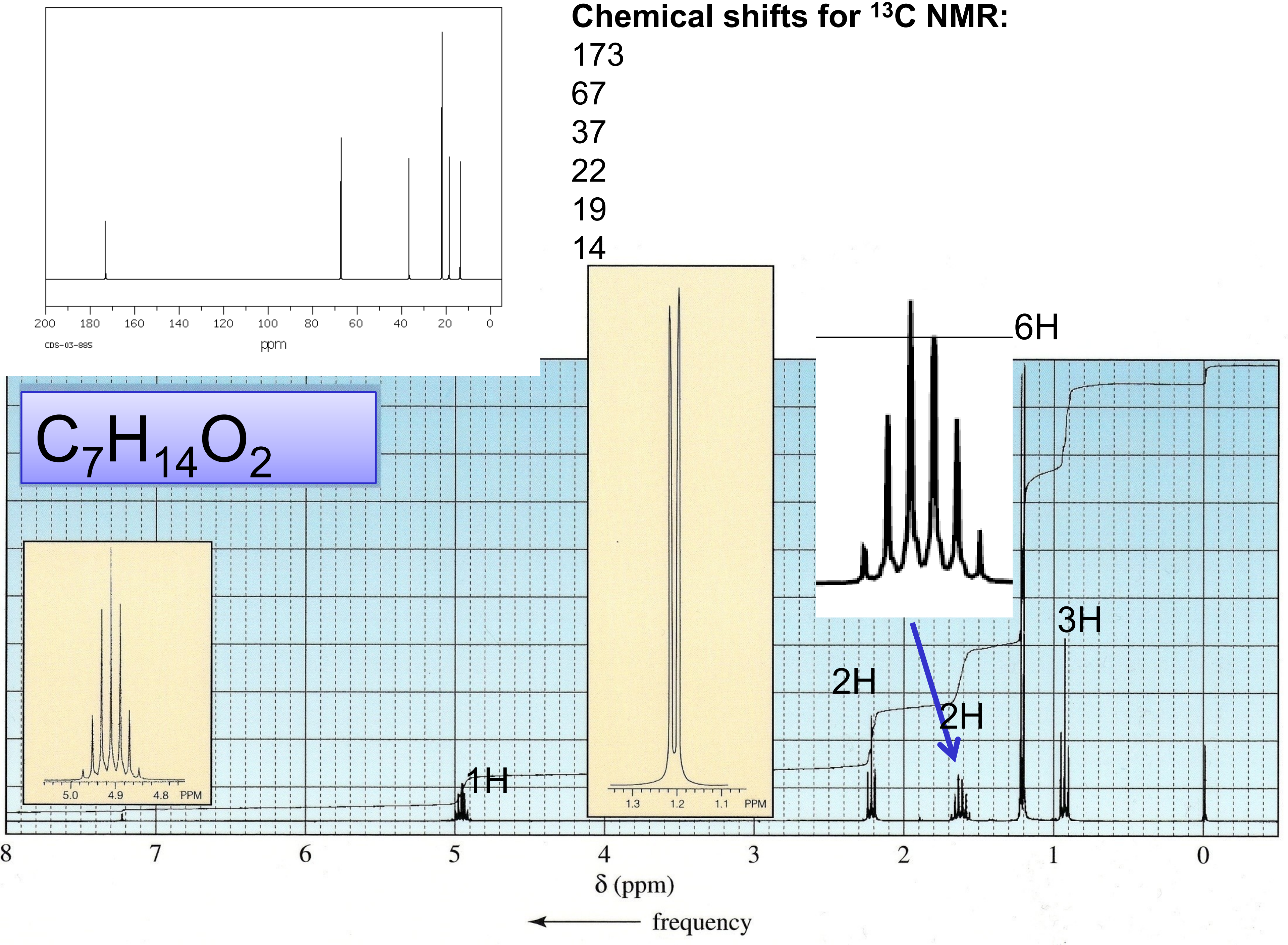
^{1}H NMR:

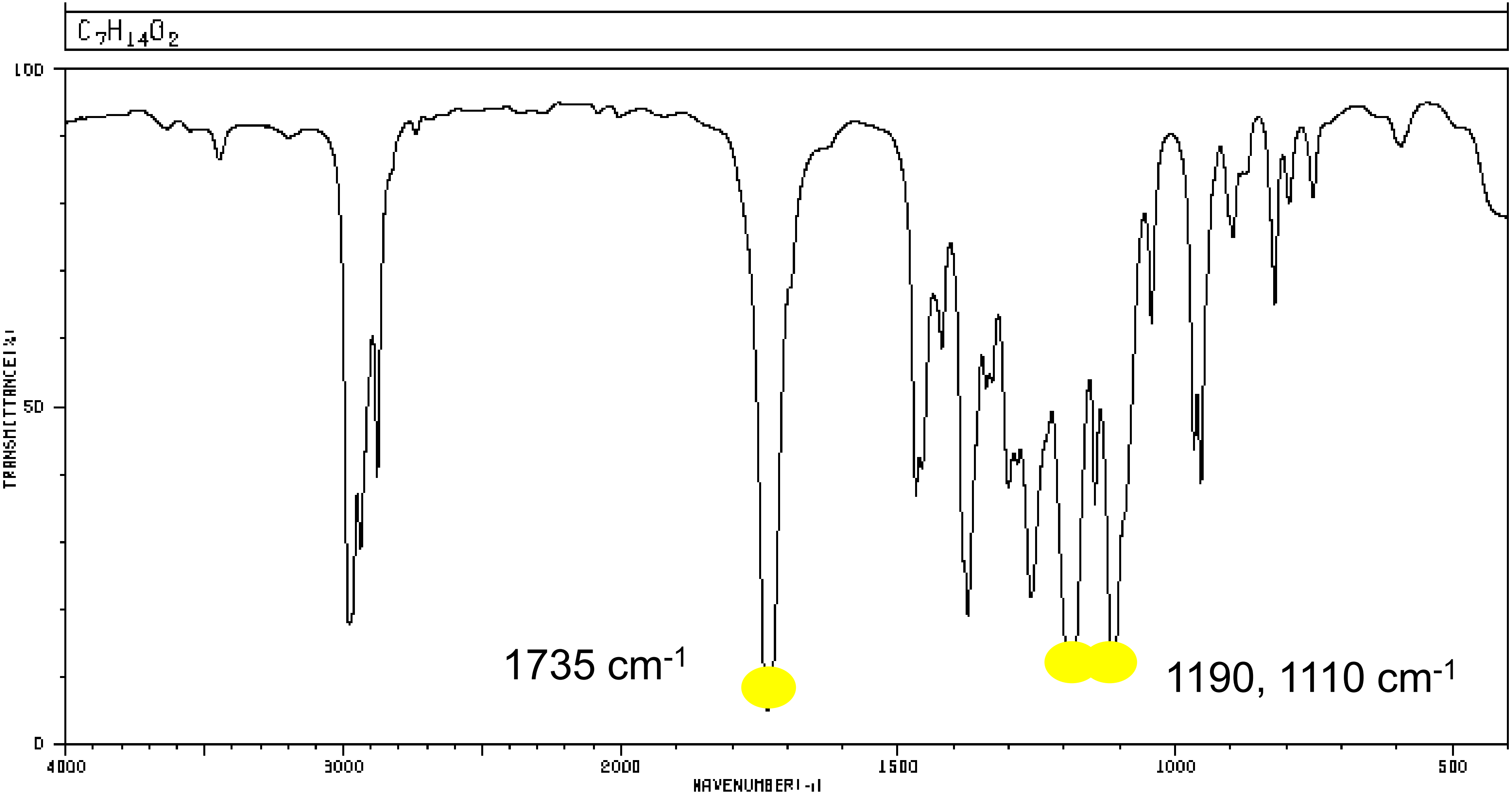
δ3.8	2H	t
δ2.9	2H	t

Chemical shifts for ^{13}C NMR:

173
67
37
22
19
14

$C_7H_{14}O_2$





1735 cm^{-1}

1190, 1110 cm^{-1}

DBE for $C_7H_{14}O_2$: 1

IR: 1735 cm^{-1} (C=O)
+1190, 1110 cm^{-1} (C-O)

^{13}C NMR: -6 kinds of carbon
(but C_7, so hints at symmetry)
-173 ppm: carbonyl (suggests ester)

^1H NMR:

δ	integration	multiplicity	assignment
$\delta 4.9$	1H	septet	
$\delta 2.2$	2H	t	
$\delta 1.6$	2H	sextet	$CH_3\text{-}C\underline{H_2}\text{-}CH_2$

δ	integration	multiplicity	assignment
δ1.2	6H	d	
δ0.9	3H	t	CH_3-CH_2

+ + O →

C_3H_7
(+O if you
determined
X=O)

C_4H_7O

•The n+1 rule assumes that the *J* values between all neighboring protons is the same. This will be true if all the neighboring protons are the same by exchange or by symmetry.

•The rule also holds relatively well for alkyl chains, particularly on less powerful spectrometers where slight differences in *J* couplings aren’t resolved.

When the coupling constants are different to different neighboring protons, more complex patterns result.

This is commonly seen in cyclic alkanes, alkenes, and substituted benzenes.

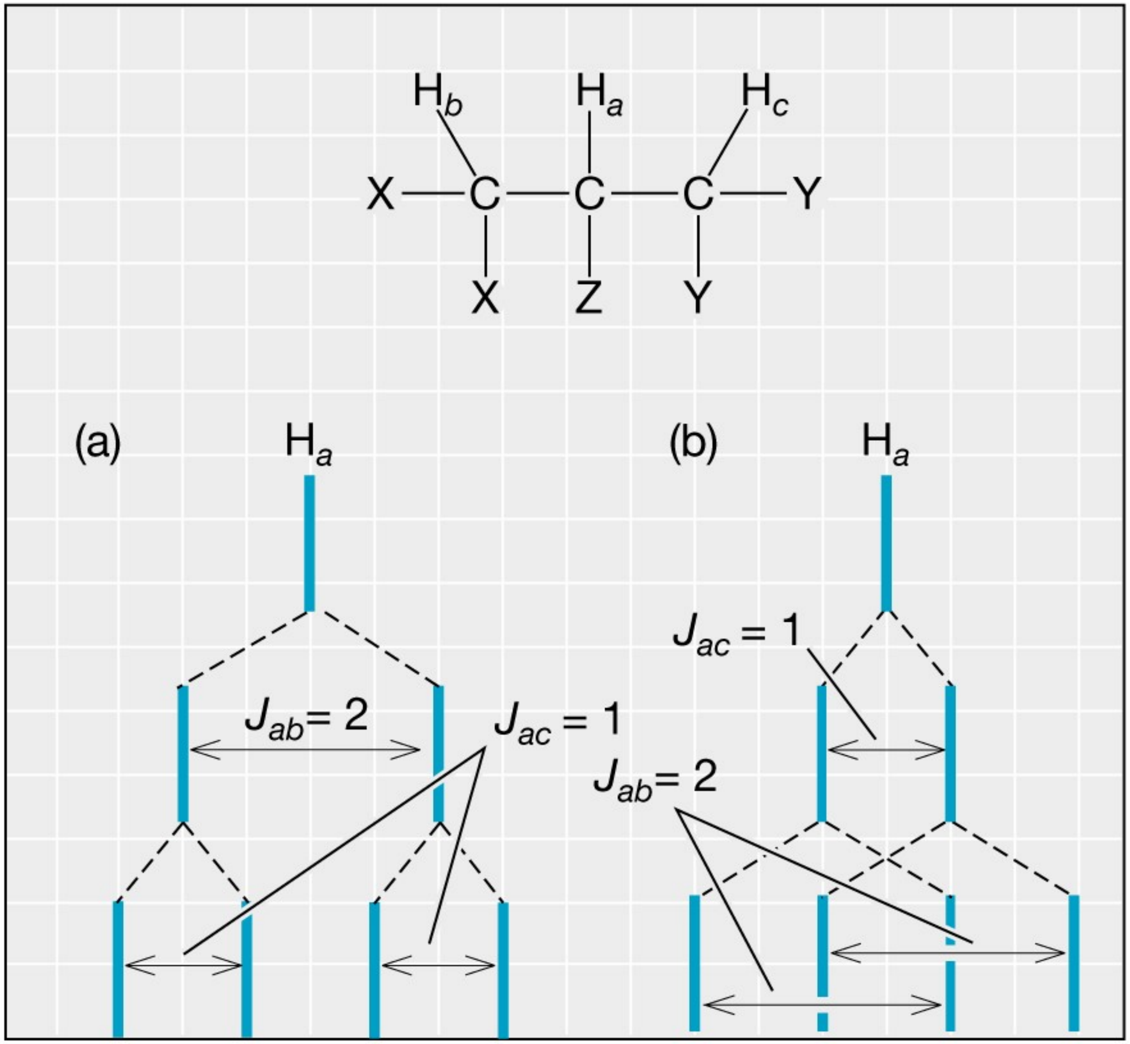
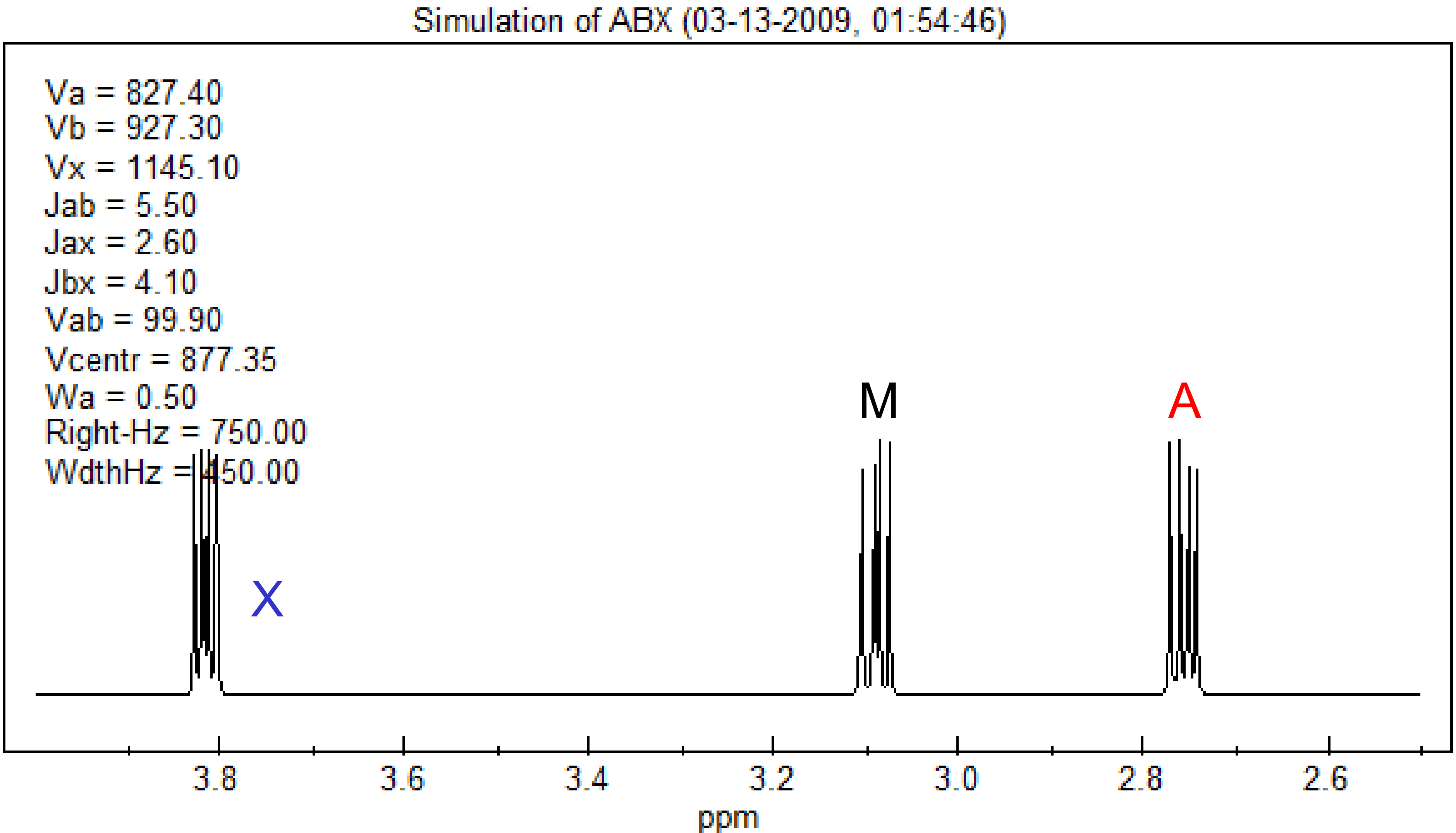


Figure 15.40

See:
http://orgchem.colorado.edu/hndbksupport/nmrtheory/splittingcomplex.html
for a discussion of the NMR of styrene oxide.



Simulation of ABX (03-13-2009, 01:54:46)

Va = 827.40
Vb = 927.30
Vx = 1145.10
Jab = 5.50
Jax = 2.60
Jbx = 4.10
Vab = 99.90
Vcentr = 877.35
Wa = 0.50
Right-Hz = 750.00
WdthHz = 450.00

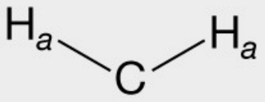
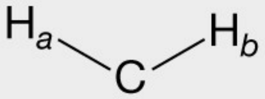
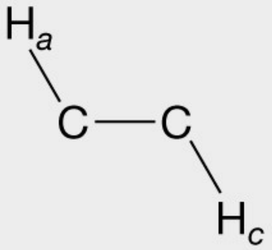
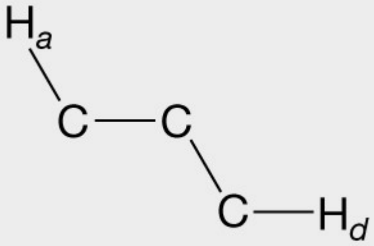
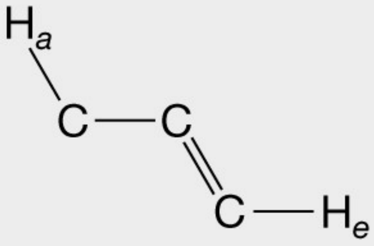
		Magnitude of J (Hz)
	Identical hydrogens do not couple	0
	H_a is two bonds away from H_b; coupling over this distance is usually observable	2–30
	H_a is three bonds away from H_c; coupling over this distance is usually observable	6–8
	H_a is four bonds away from H_d; coupling is not usually observable	0–1
	H_a is in the allylic position relative to H_e; coupling is usually observable	2–3

Figure 15.42

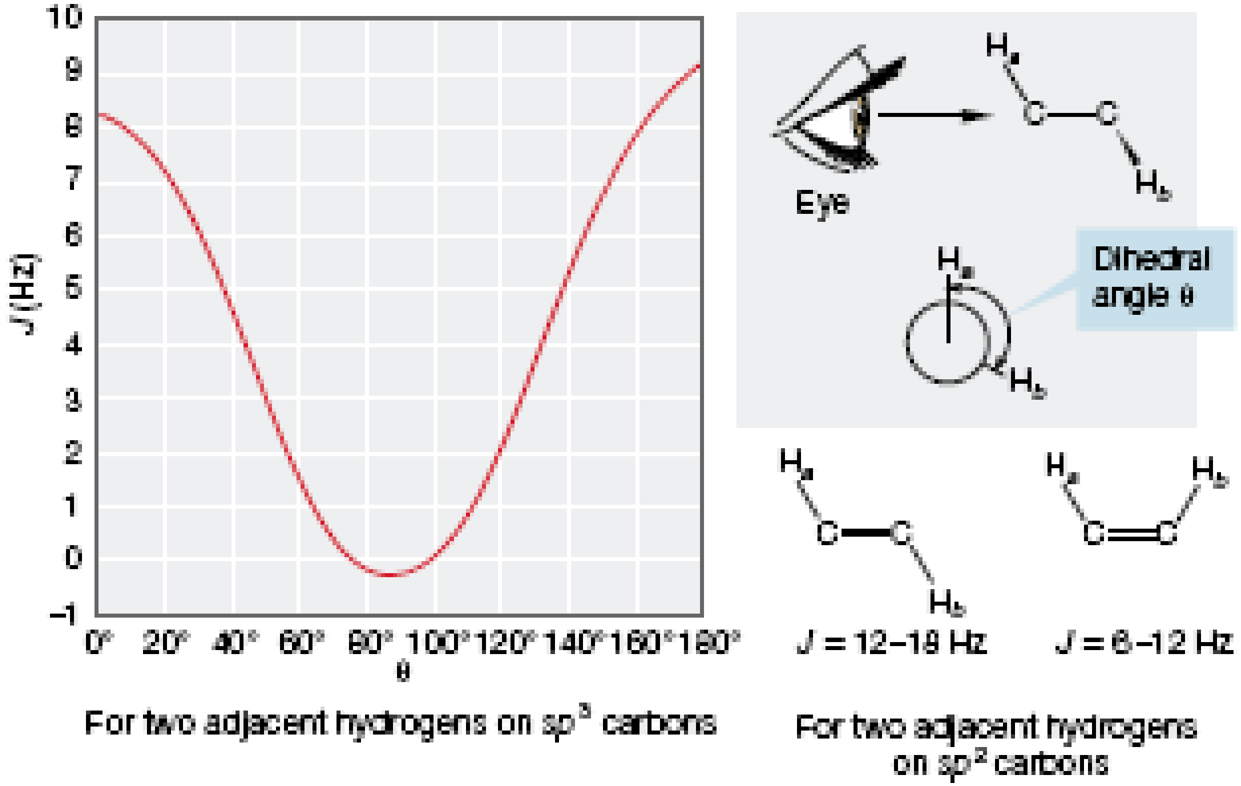
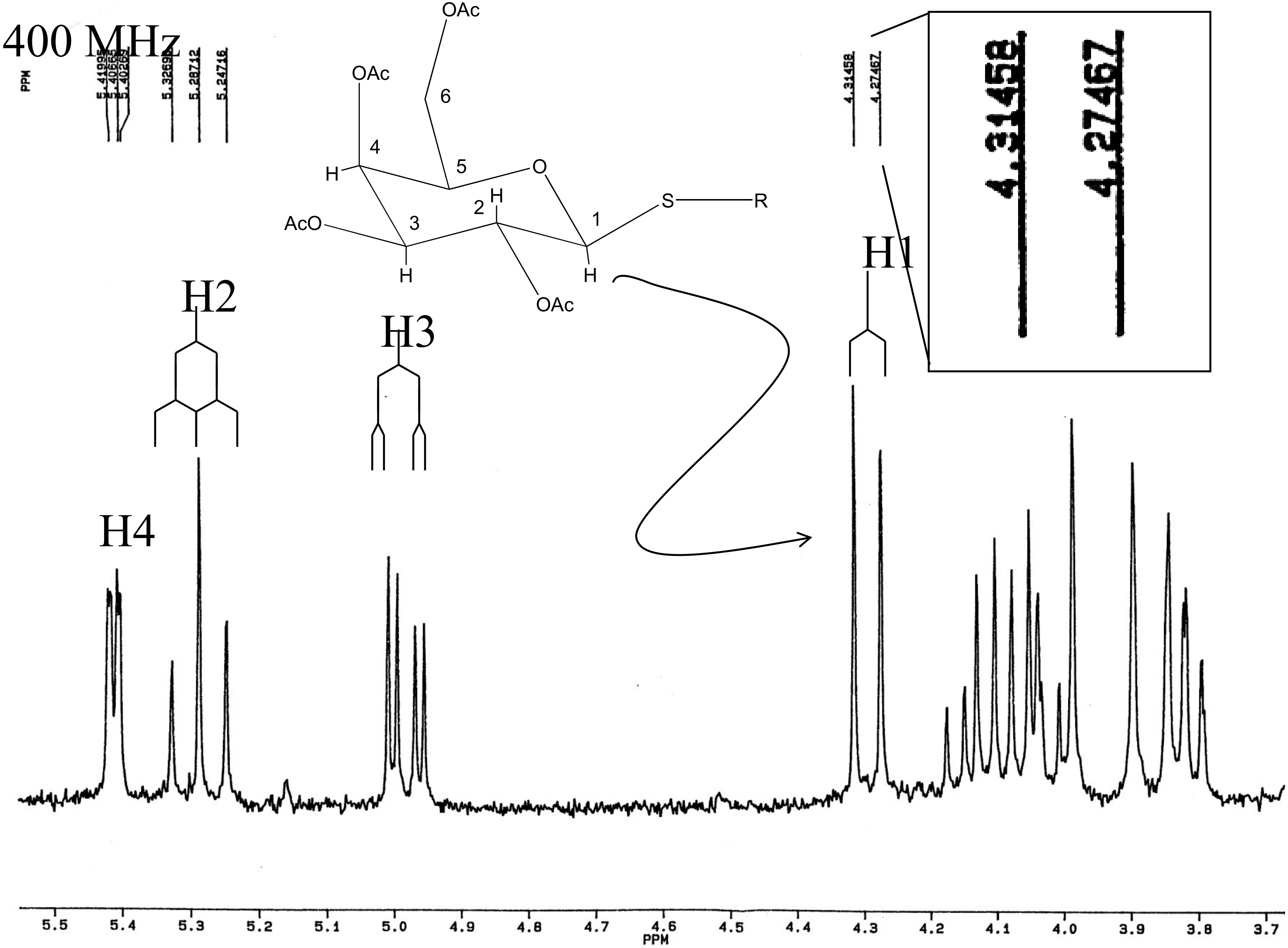
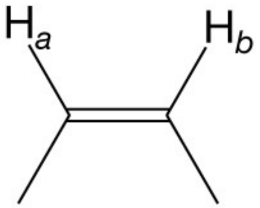


FIGURE 15.43 Coupling between two adjacent hydrogens is sensitive to the dihedral angle between them. The Karplus curve shows the calculated relationship between *J* and the dihedral angle.

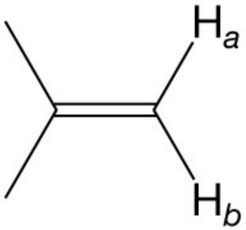
Note *J*s are largest when the dihedral angle is 0° or 180°.


400 MHz
PPM
5.41995
5.40665
5.40269
5.32698
5.28712
5.24716
4.31458
4.27467
OAc
OAc
6
4
5
O
H
2
H
S
R
AcO
3
1
H
H
OAc
H1
H2
H3
H4
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
PPM

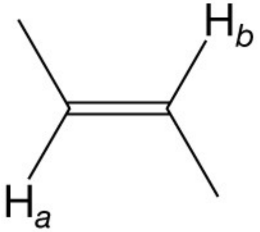
Alkenes: $J_{cis} < J_{trans}$



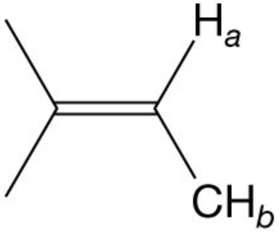
$J_{ab} = 6–12$ Hz



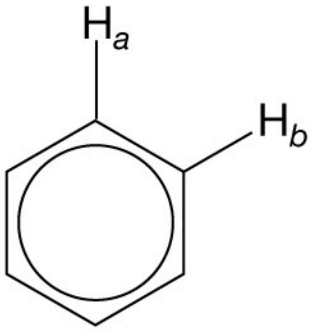
$J_{ab} = 0–3$ Hz



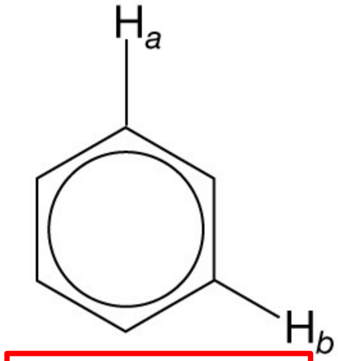
$J_{ab} = 12–18$ Hz



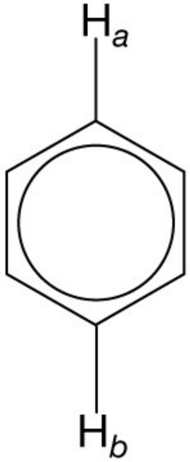
$J_{ab} = 4–10$ Hz



$J_{ab} = 6–8$ Hz



$J_{ab} = 1–3$ Hz

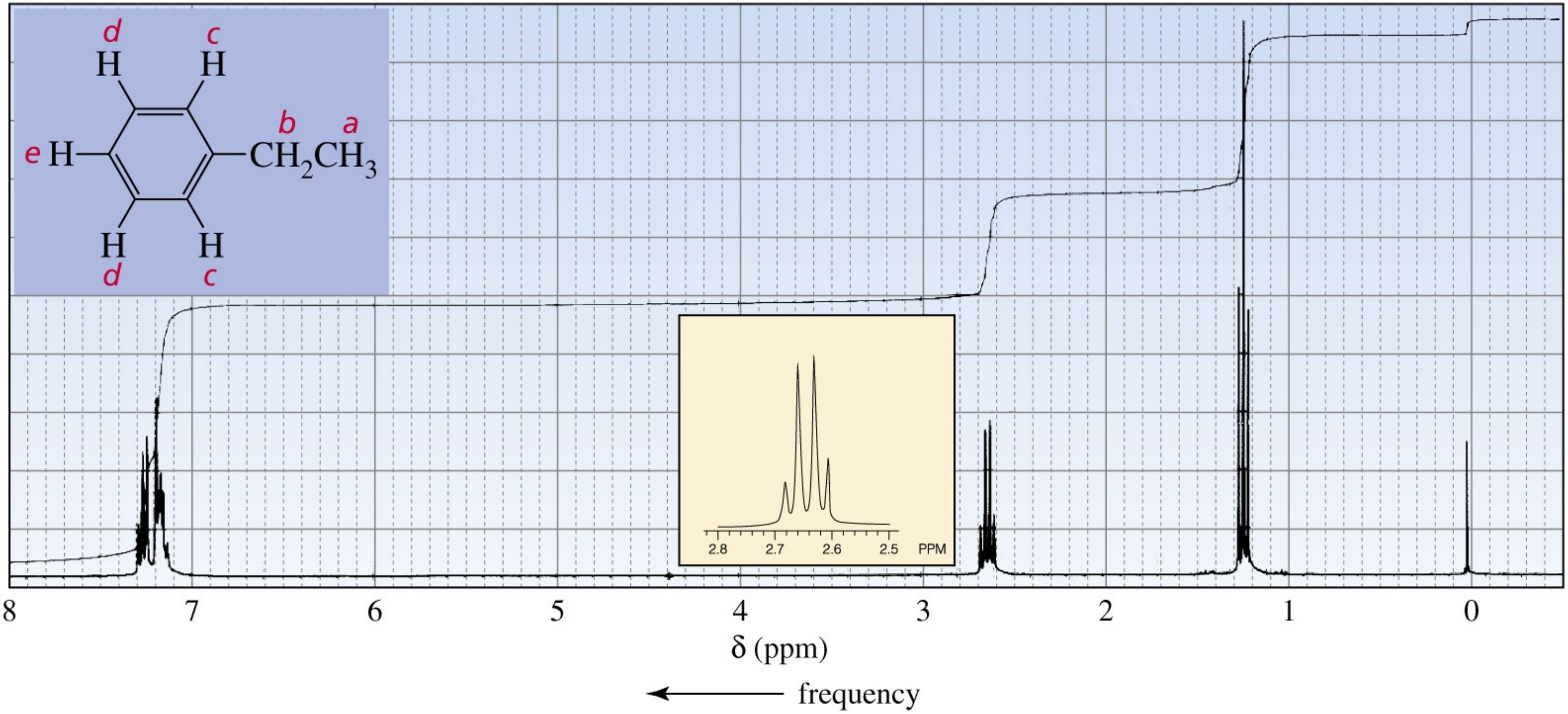


$J_{ab} = 0–1$ Hz

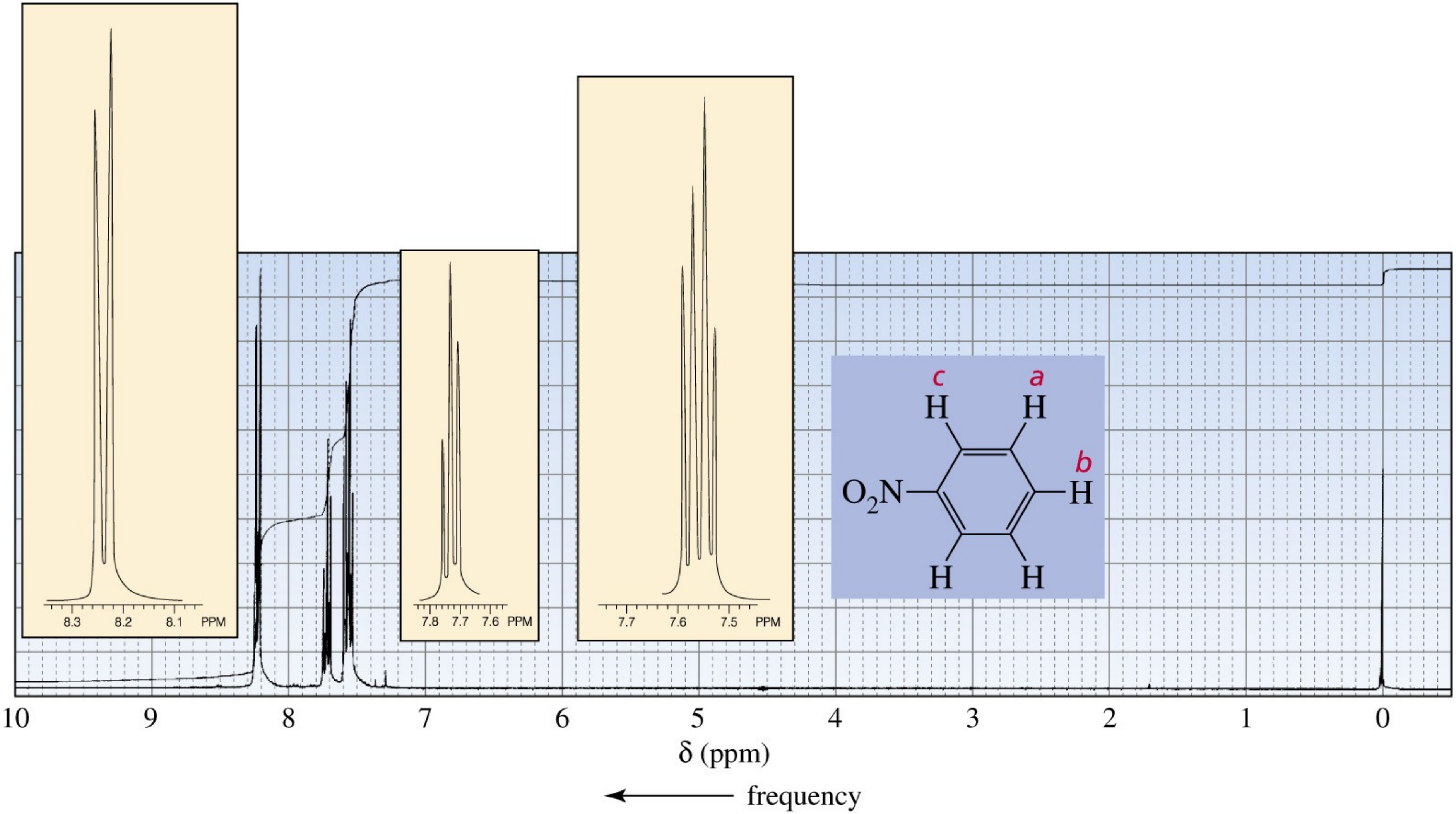
Benzenes: $J_{ortho} > J_{meta}$

Figure 15.44

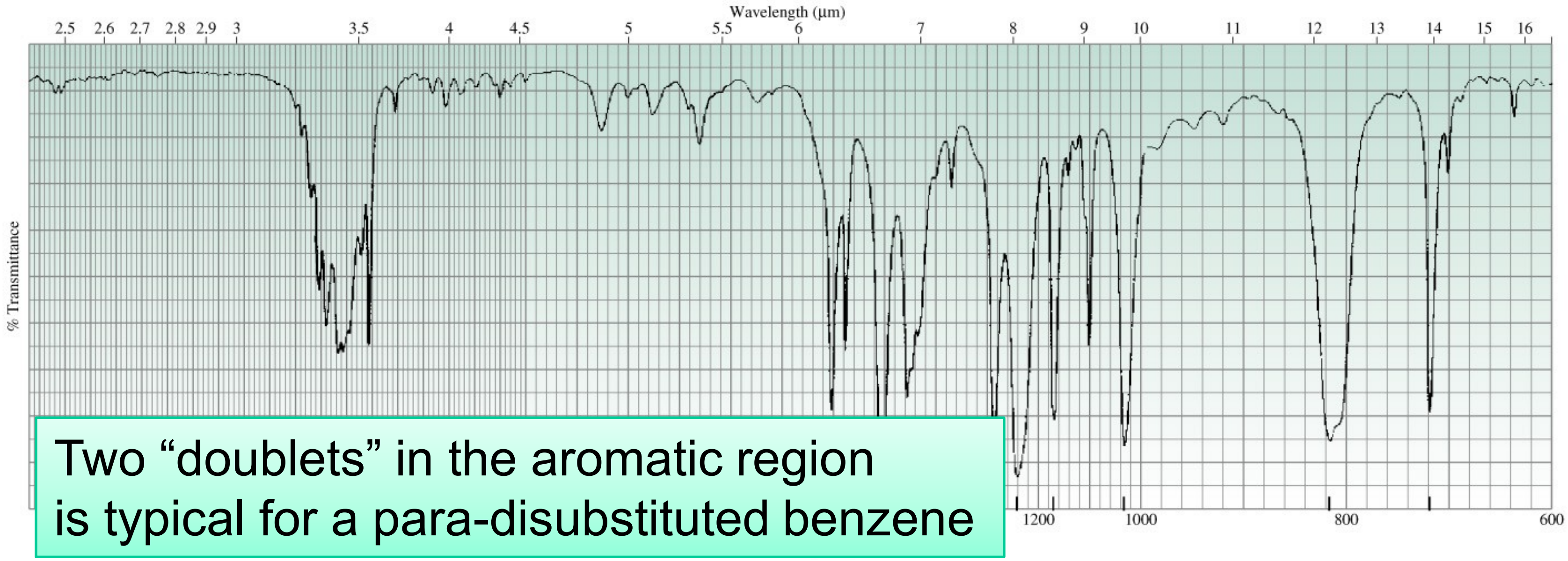
Alkyl benzenes usually have all the benzene hydrogens lumped together close to 7 ppm.



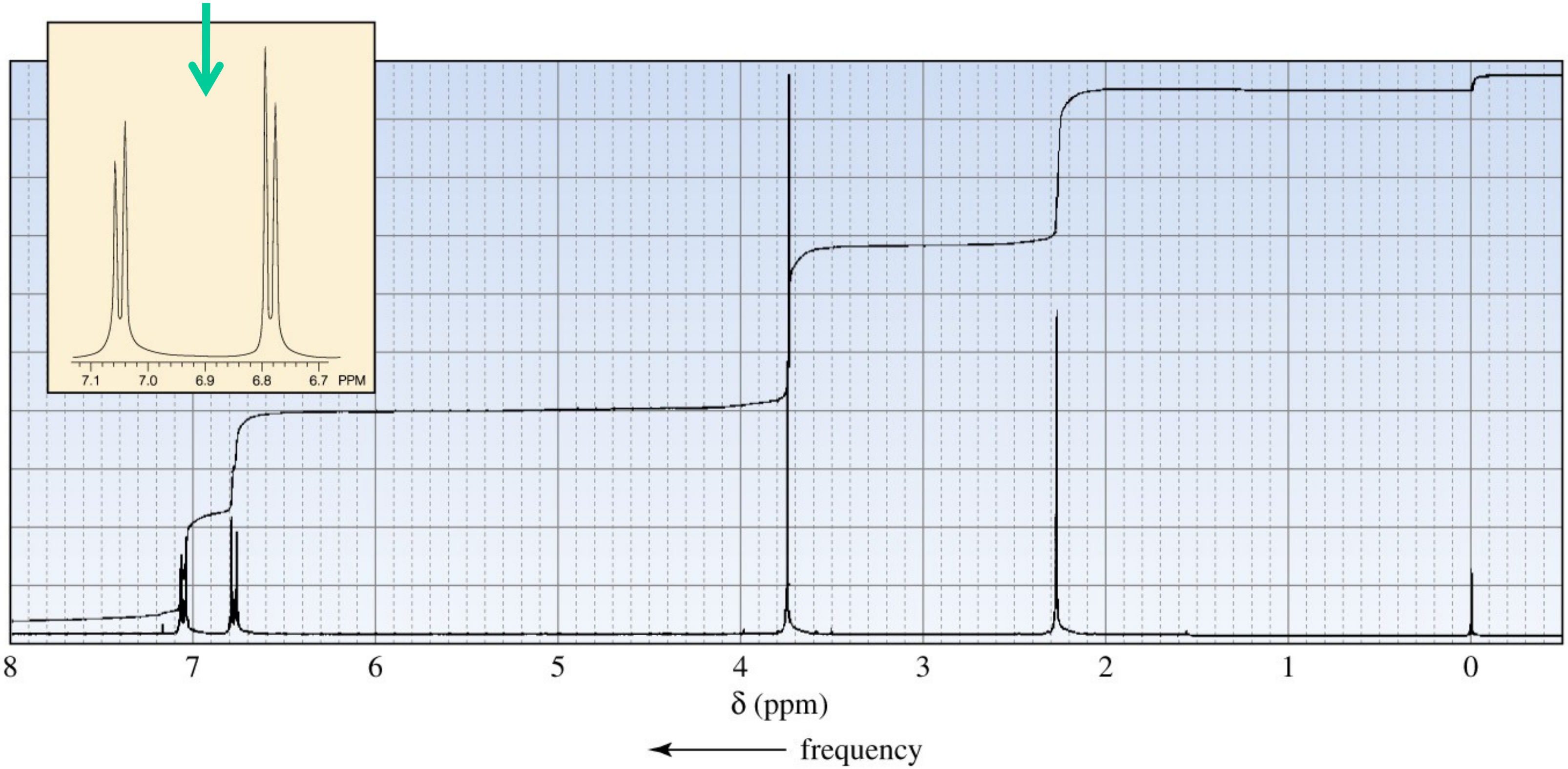
EDG or EWG on the benzene ring tend to create larger chemical shift differences between benzene hydrogens



In this spectrum, the meta-couplings are too small to be seen– c is a doublet, b is a triplet, and a is a doublet of doublets (2 different J_{ortho})

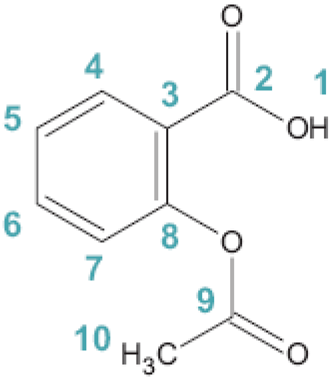


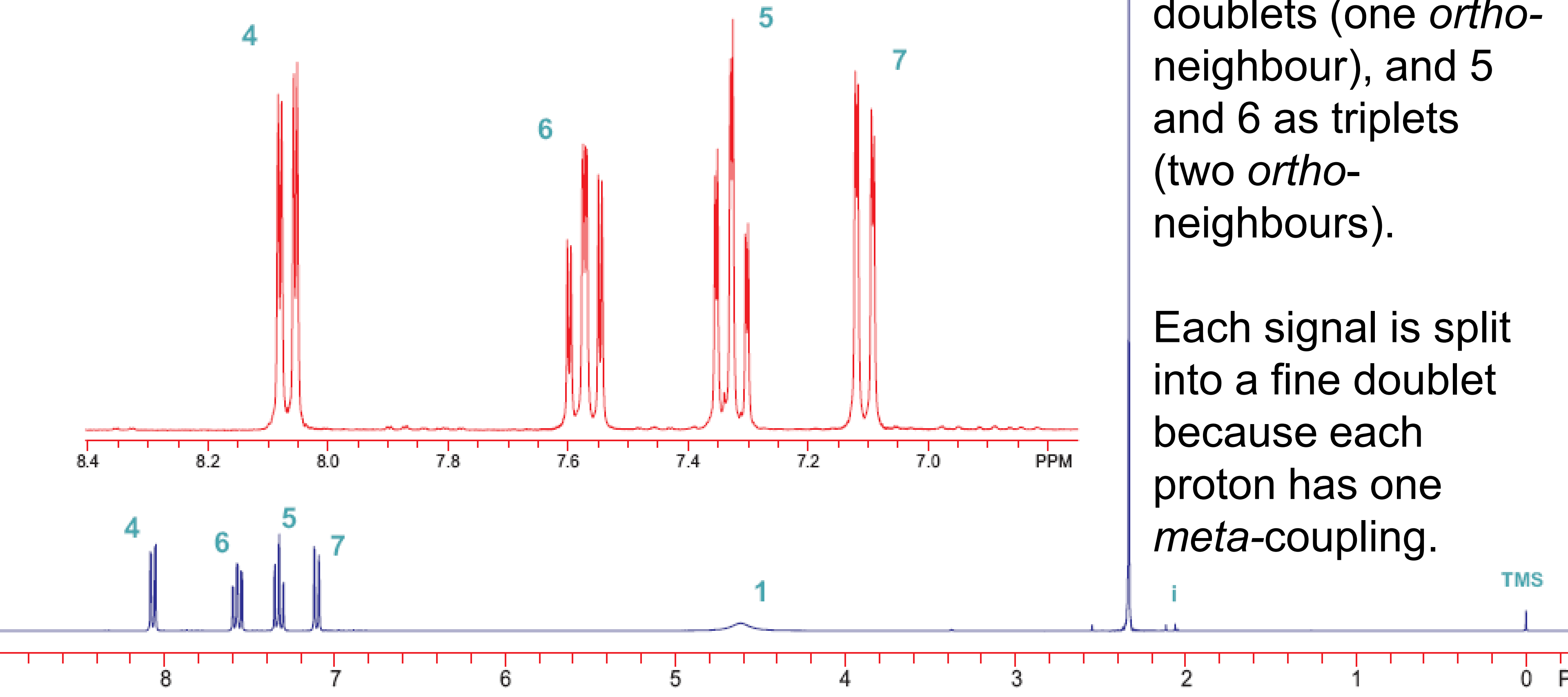
Two “doublets” in the aromatic region
is typical for a para-disubstituted benzene



Over-the-counter aspirin (acetylsalicylic acid) in $CDCl_3$

1H spectrum acquired at 250 MHz





Here, the smaller *meta*-couplings can be clearly seen.

On a poorer spectrometer, 4 and 7 would appear as doublets (one *ortho*-neighbour), and 5 and 6 as triplets (two *ortho*-neighbours).

Each signal is split into a fine doublet because each proton has one *meta*-coupling.

If two protons are coupled to each other, and their chemical shifts are close to each other, distortions start to appear and the signals no longer follow the basic “first-order” rules we’ve covered.

Such “second-order” spectra require special calculations to analyze properly, and are beyond the scope of this course.

The signals for two coupled hydrogens “lean” towards each other. The closer they are in chemical shift, the more pronounced the effect.

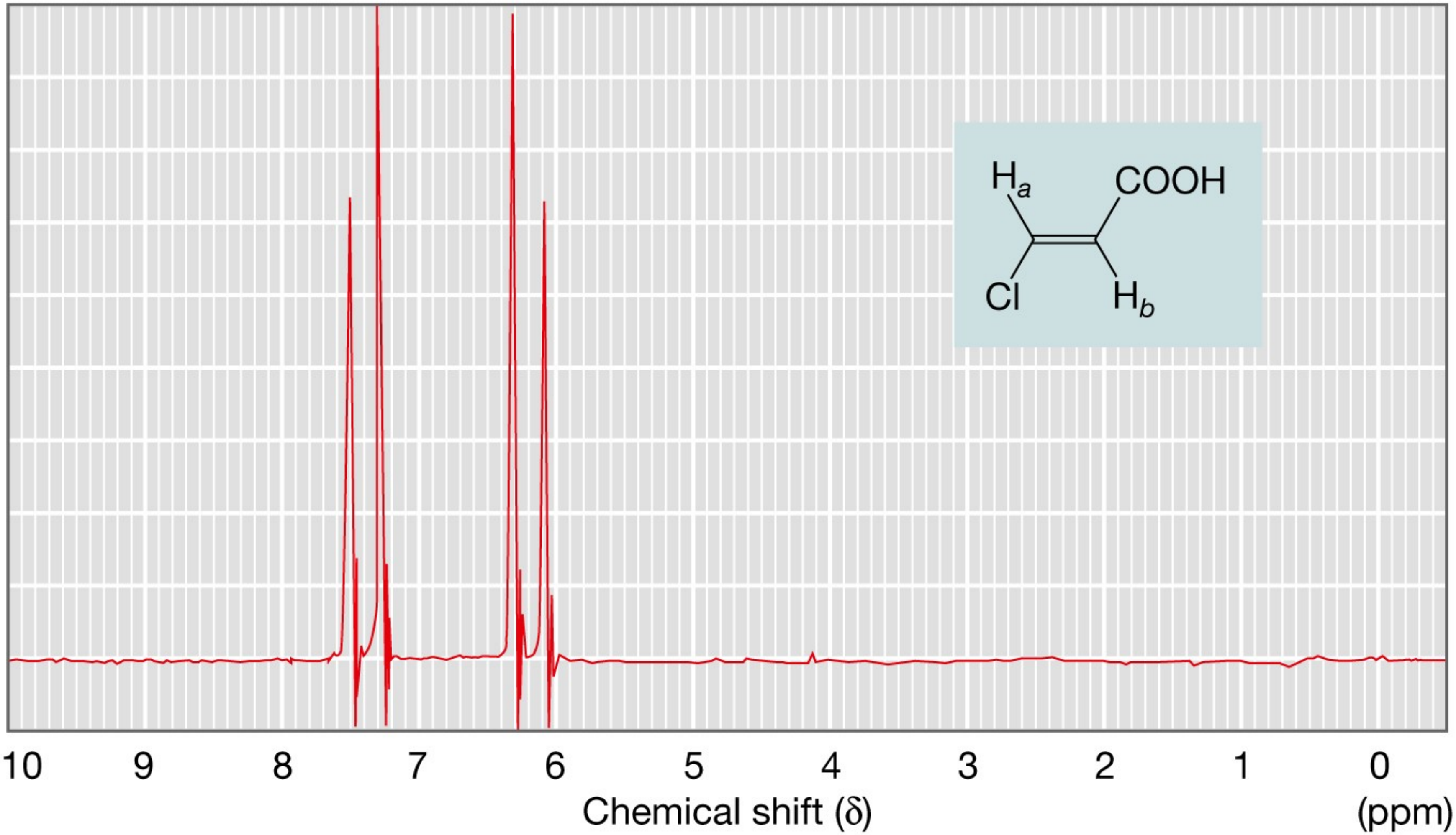


Figure 15.48

The closer the signals are to each other, the more extreme the distortion.

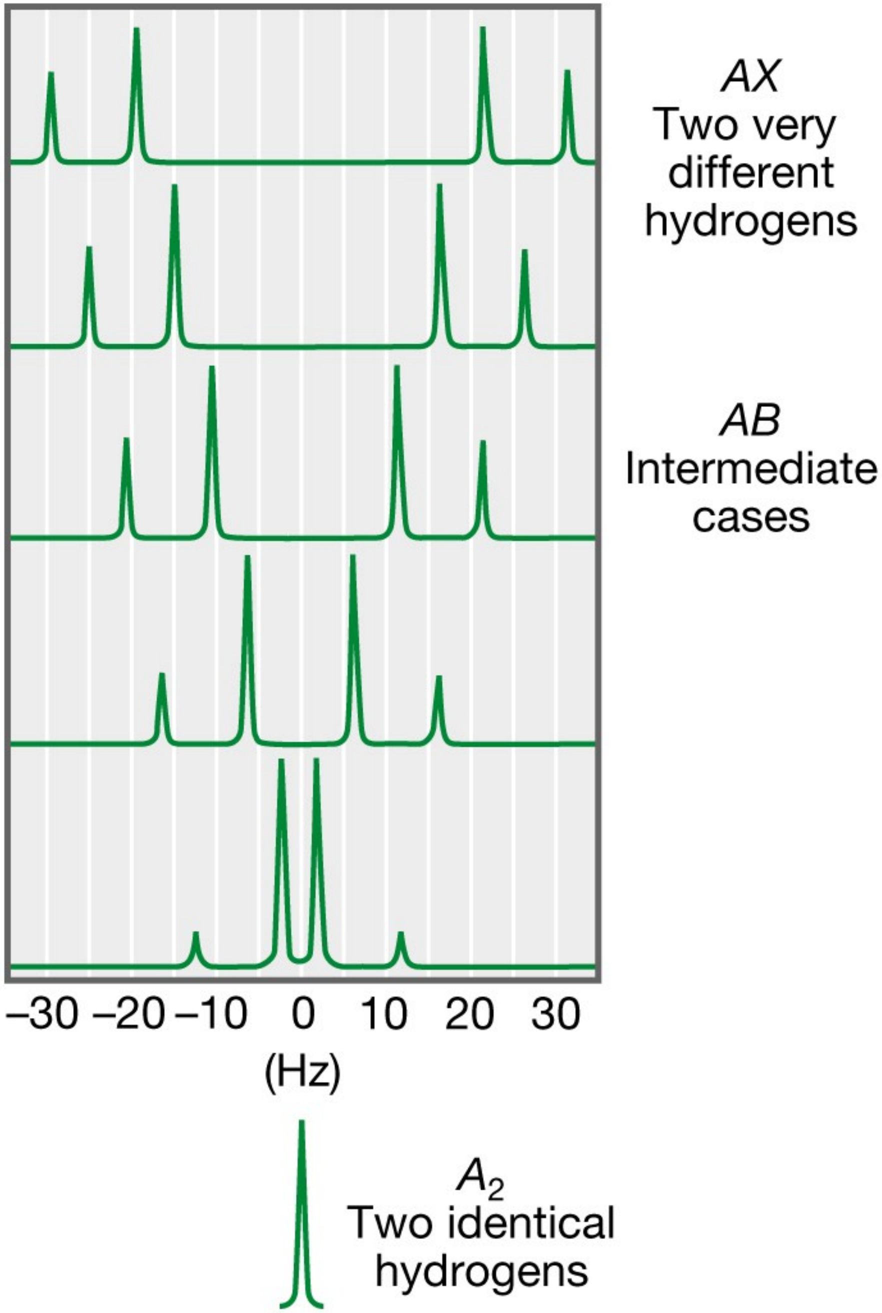
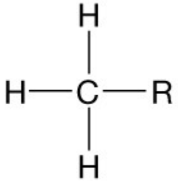
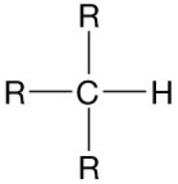
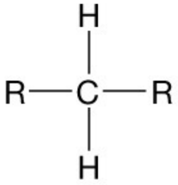
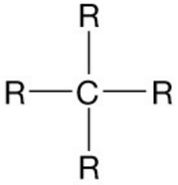
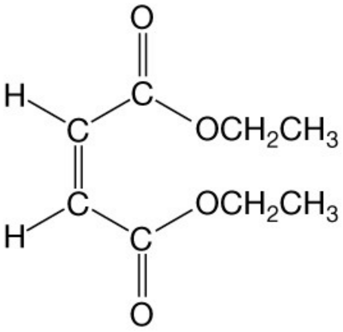


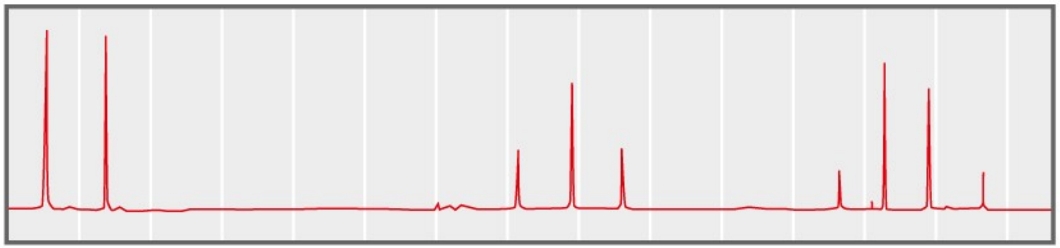
Figure 15.49

Broad-Band Decoupled		**Off-Resonance Decoupled**	**Broad-Band Decoupled**		**Off-Resonance Decoupled**
Singlet		This carbon is coupled to three hydrogens and will appear as a quartet	Singlet		This carbon is coupled to one hydrogen and will appear as a doublet
Singlet		This carbon is coupled to two hydrogens and will appear as a triplet	Singlet		This carbon is coupled to no hydrogens and will appear as a singlet

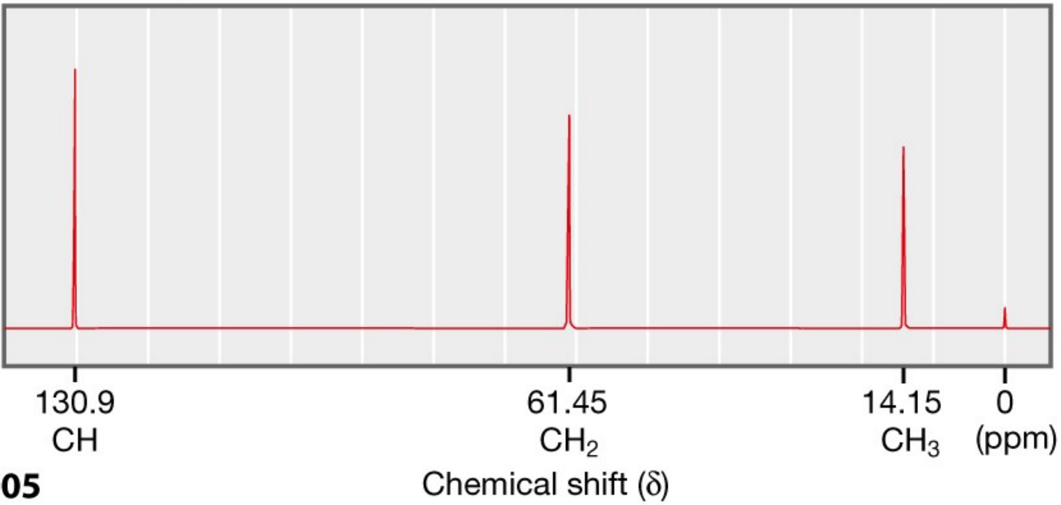
Decoupled and off-resonance decoupled ^{13}C NMR spectra of



Off-resonance decoupled spectrum



Decoupled spectrum



^{13}C spectra are normally "decoupled"-
Every carbon appears as a singlet.

Figure 15.57

TABLE 15.5 Some ^{13}C Chemical Shifts

Type of Carbon	**Chemical Shift (δ)**[a]	**Type of Carbon**	**Chemical Shift (δ)**[a]
Alkanes		Alcohols, ethers	
Methyl	0–30	C–O	50–90
Methylene	15–55	Amines	
Methine	25–55	C–N	40–60
Quaternary	30–40	Halogens	
Alkenes		C–F	70–80
C=C	80–145	C–Cl	25–50
Alkynes		C–Br	10–40
C≡C	70–90	C–I	–20–10
Aromatics	110–170	Carbonyls, C=O	
Benzene	128.7	$R_2C=O$	190–220
		RXC=O (X = O or N)	150–180

[a] The chemical shift δ is in parts per million (ppm) from TMS.

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