

Modern Techniques in Structural Elucidation of Compounds

(UV – Vis, IR, NMR)

- **Spectroscopy is the study of the interaction between matter and electromagnetic radiation**
- Ultraviolet light and visible light have just the right energy to cause an electronic transition
 - the promotion of an electron from one orbital to another of higher energy.

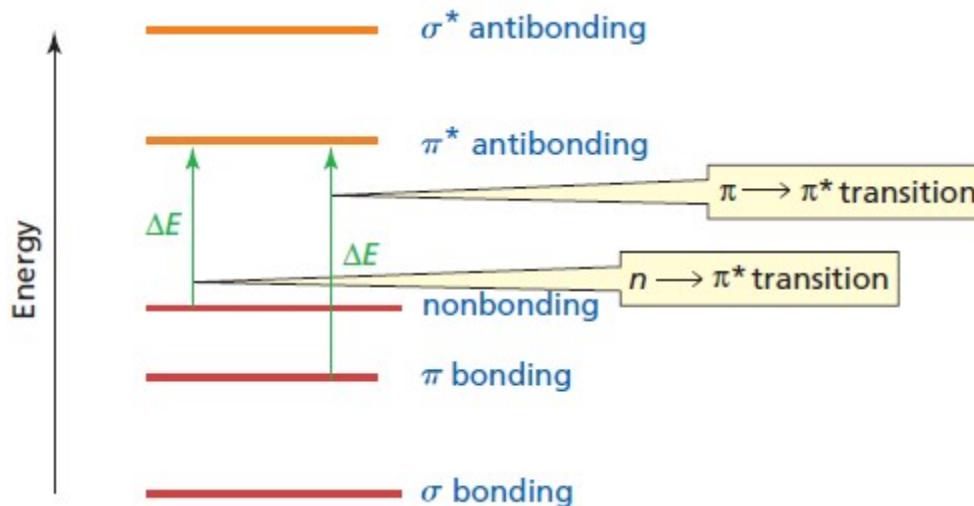
UV-Visible Spectroscopy

- Depending on the energy needed for the electronic transition, a molecule will absorb either ultraviolet or visible light.
- **Ultraviolet light** is electromagnetic radiation with wavelengths ranging from **180 to 400 nm** (nanometers);
- **visible light** has wavelengths ranging from **400 to 780 nm**.
- $1 \text{ nm} = 10^{-9} \text{ m}$ or 10\AA

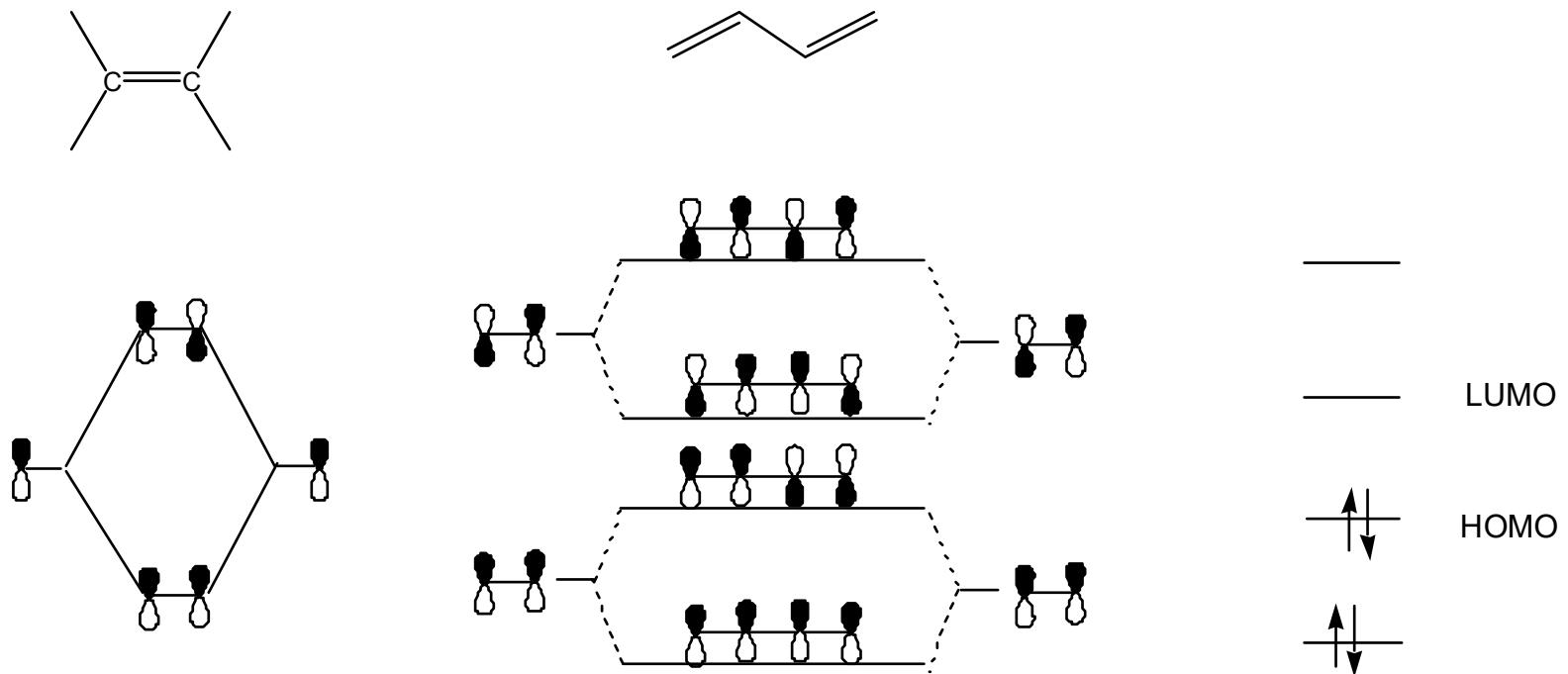
$$E = \frac{hc}{\lambda}$$

h = Planck's constant
 c = velocity of light
 λ = wavelength

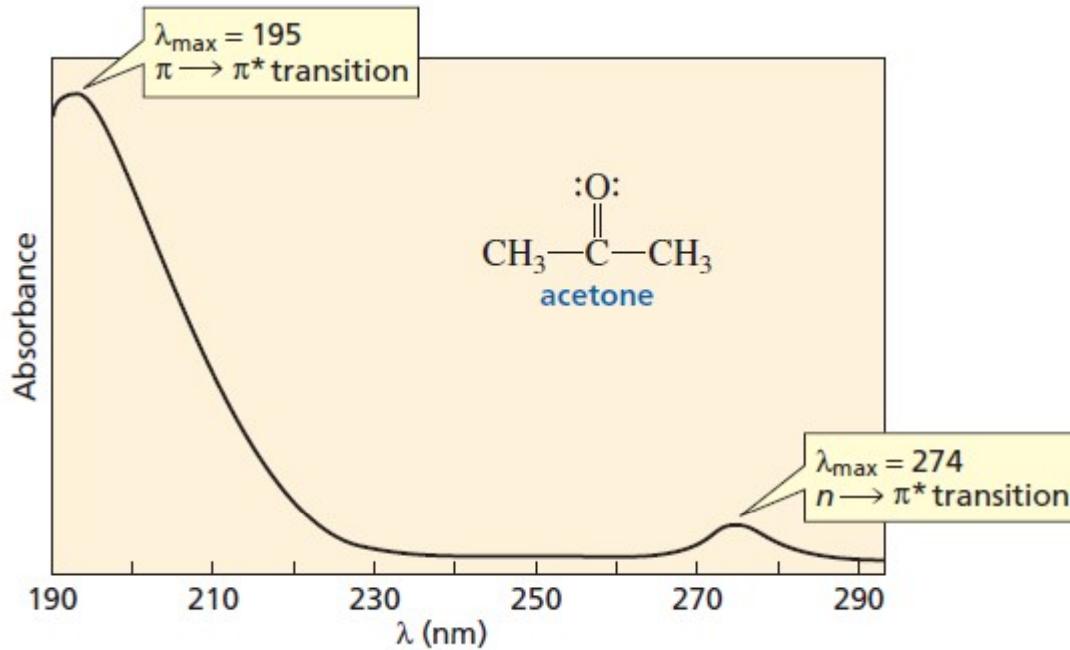
- normal electronic configuration of a molecule is known as its **ground state**
- When a molecule absorbs light of an appropriate wavelength and an electron is promoted to a higher energy molecular orbital, the molecule is then in an **excited state**.
- an electronic transition is the promotion of an electron to a higher energy MO



HOMO-LUMO



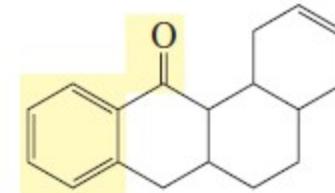
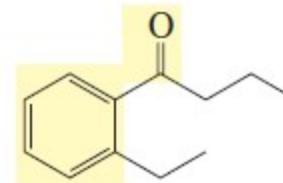
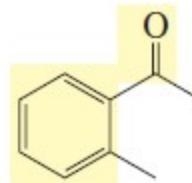
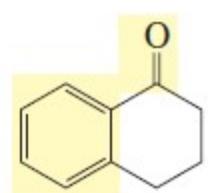
UV-Visible Spectroscopy



- only organic compounds with π electrons can produce UV Vis spectra.
 - diethyl ether does not have a UV spectrum, even though it has lone-pair electrons

UV-Visible Spectroscopy

- **Chromophore:** part of a molecule that absorbs UV or visible light.
 - The carbonyl group is the chromophore of acetone.
- If same chromophore, then approximately the same λ_{max} :the wavelength corresponding to the highest point (maximum absorbance) of the absorption band.



The Beer–Lambert Law

- At a given wavelength, the **absorbance** of a sample depends on the **amount of absorbing species** that the light encounters as it passes through a solution of the sample.

$$A = cl\epsilon$$

c = concentration of the sample, in moles/liter

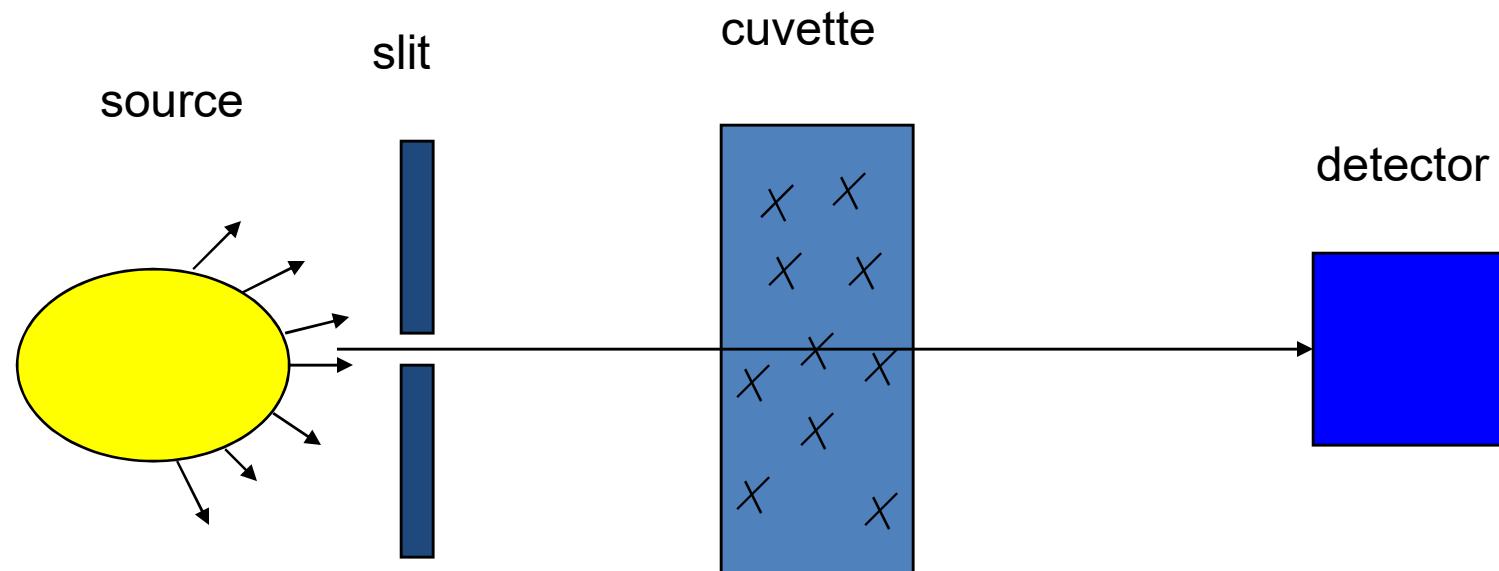
l = length of the light path through the sample, in centimeters

ϵ = molar absorptivity (liter mol⁻¹ cm⁻¹)

- molar absorptivity:** It is the absorbance that would be observed for a 1.00 M solution in a cell with a 1.00-cm path length.
- molar absorptivity:** constant that is characteristic of the compound at a particular wavelength.

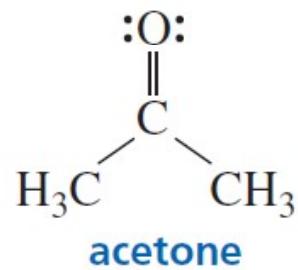
UV-Visible Spectroscopy

- Either glass or quartz cells can be used for visible spectra, but quartz cells must be used for UV spectra because glass absorbs UV light.

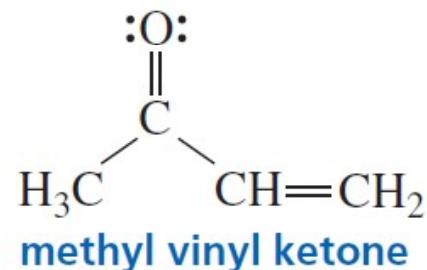


UV-Vis and conjugated double bonds

- UV/Vis spectroscopy provides information about compounds with conjugated double bonds.
- Effect of Conjugation on λ_{\max} .

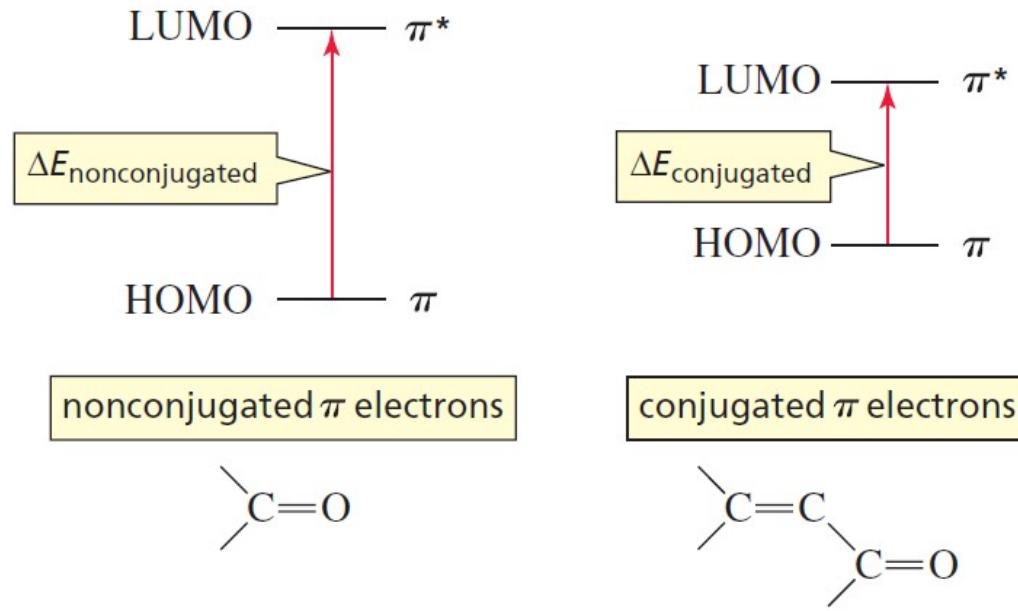


$n \longrightarrow \pi^*$ $\lambda_{\max} = 274 \text{ nm } (\varepsilon_{\max} = 13.6)$
 $\pi \longrightarrow \pi^*$ $\lambda_{\max} = 195 \text{ nm } (\varepsilon_{\max} = 9000)$



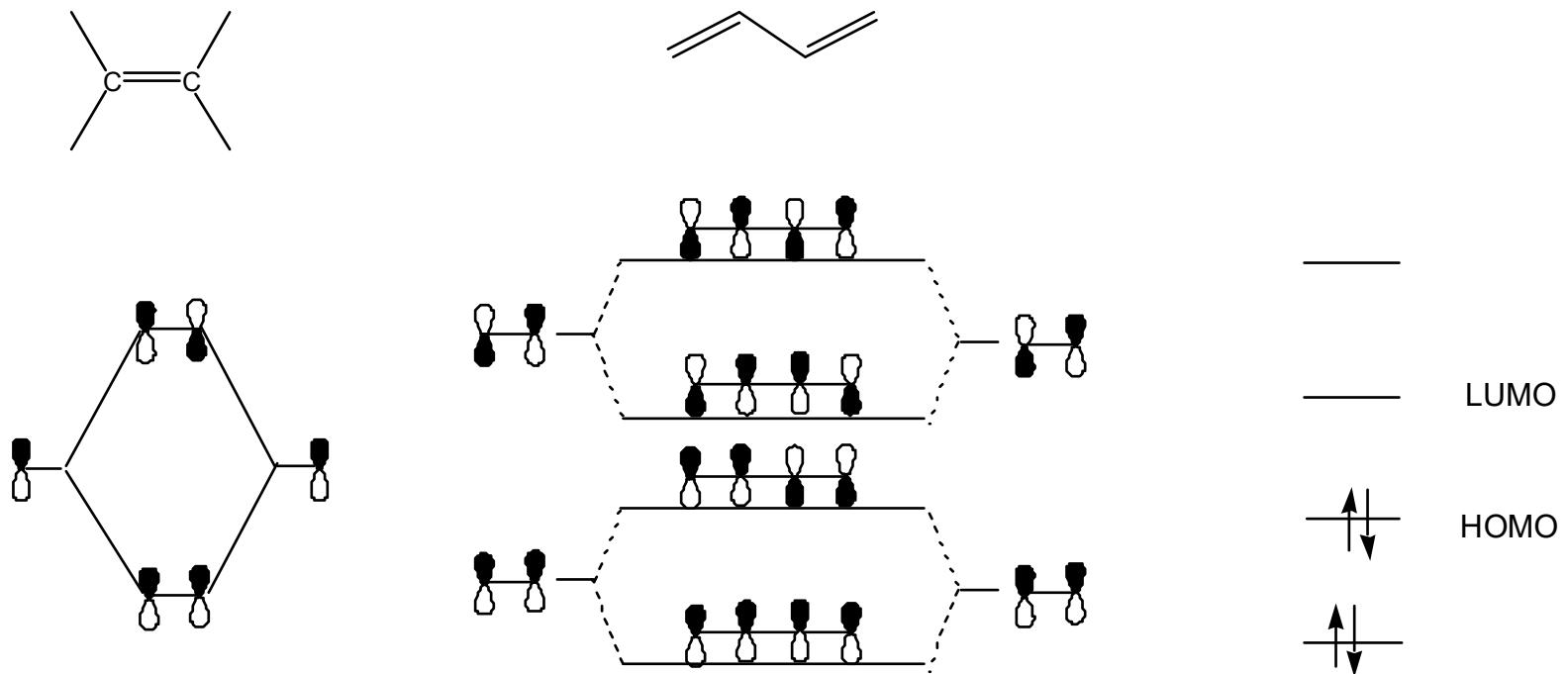
$\lambda_{\max} = 331 \text{ nm } (\varepsilon_{\max} = 25)$
 $\lambda_{\max} = 203 \text{ nm } (\varepsilon_{\max} = 9600)$

Effect of Conjugation on λ_{\max}



Conjugation **raises** the energy of the HOMO and **lowers** the energy of the LUMO

HOMO-LUMO



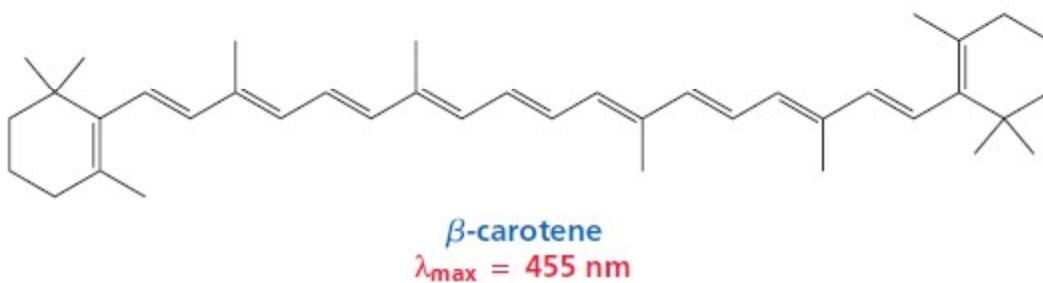
Effect of Conjugation

- both the λ_{\max} and the ϵ increase as the number of conjugated double bonds increases.

Table 8.3 Values of λ_{\max} and ϵ for Ethylene and Conjugated Dienes

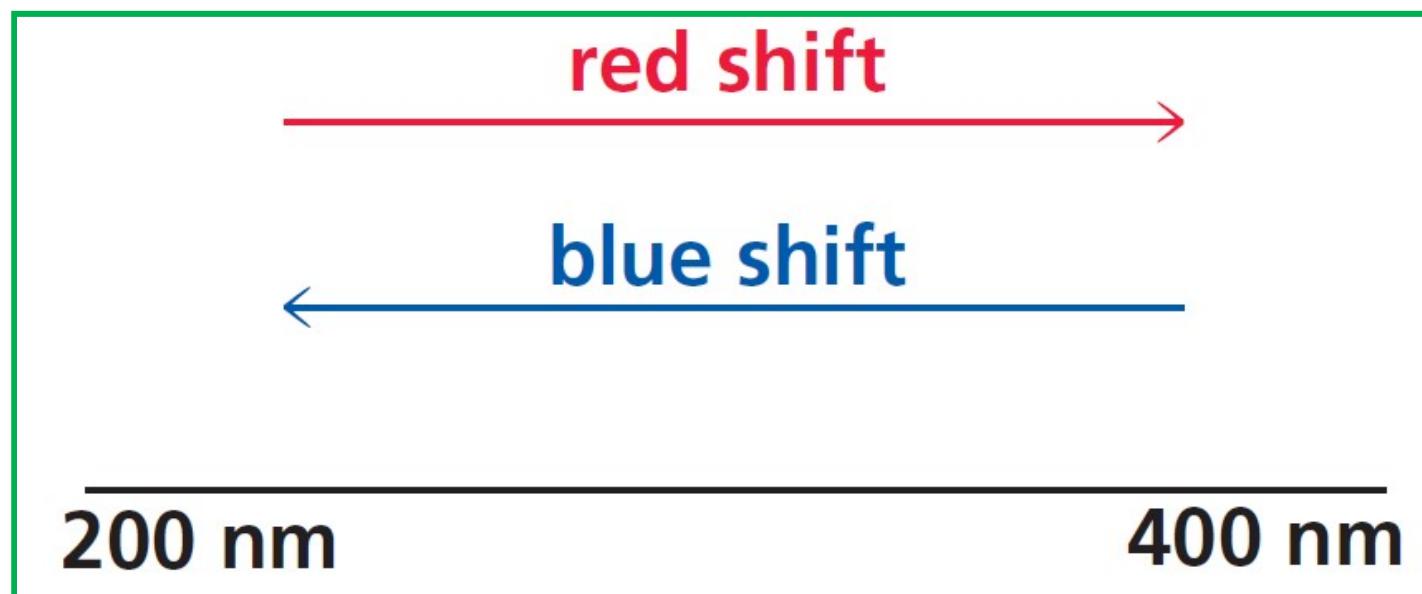
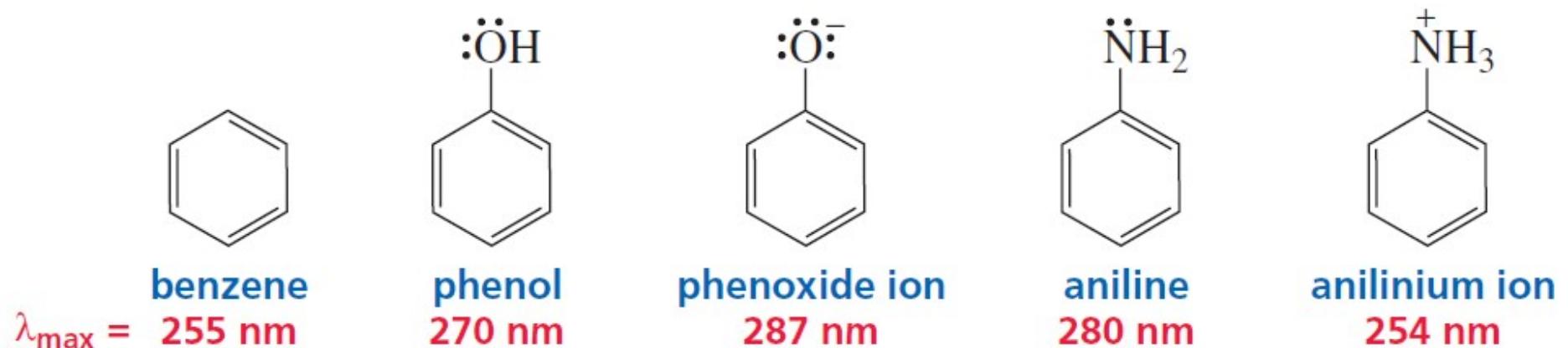
Compound	λ_{\max} (nm)	ϵ ($M^{-1} \text{ cm}^{-1}$)
$\text{H}_2\text{C}=\text{CH}_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

- If a compound has enough conjugated double bonds, it will absorb visible light ($\lambda_{\text{max}} > 400 \text{ nm}$) and the compound will be colored.

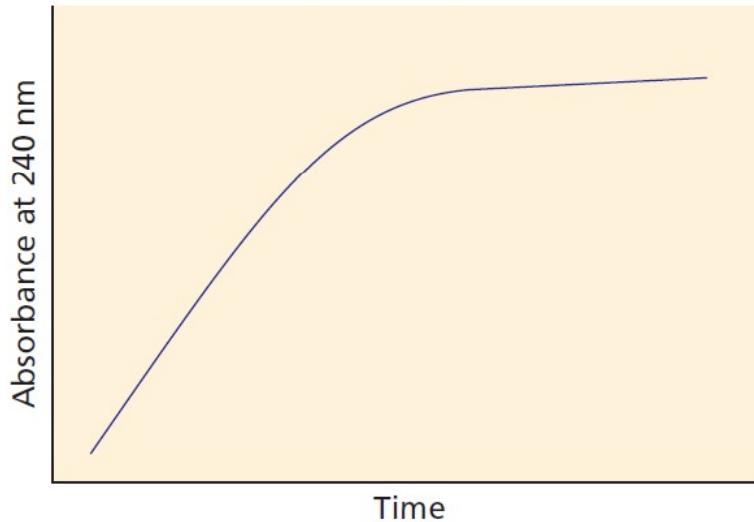
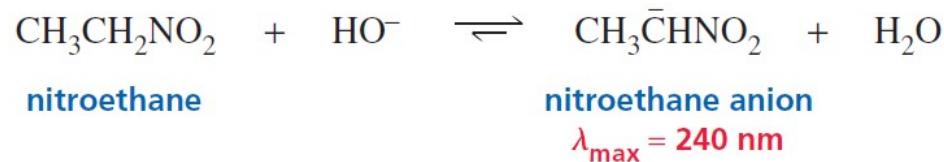


- **Auxochrome** : a substituent that when attached to a chromophore, alters the λ_{max} and the intensity of the absorption, usually increasing both.

Auxochrome

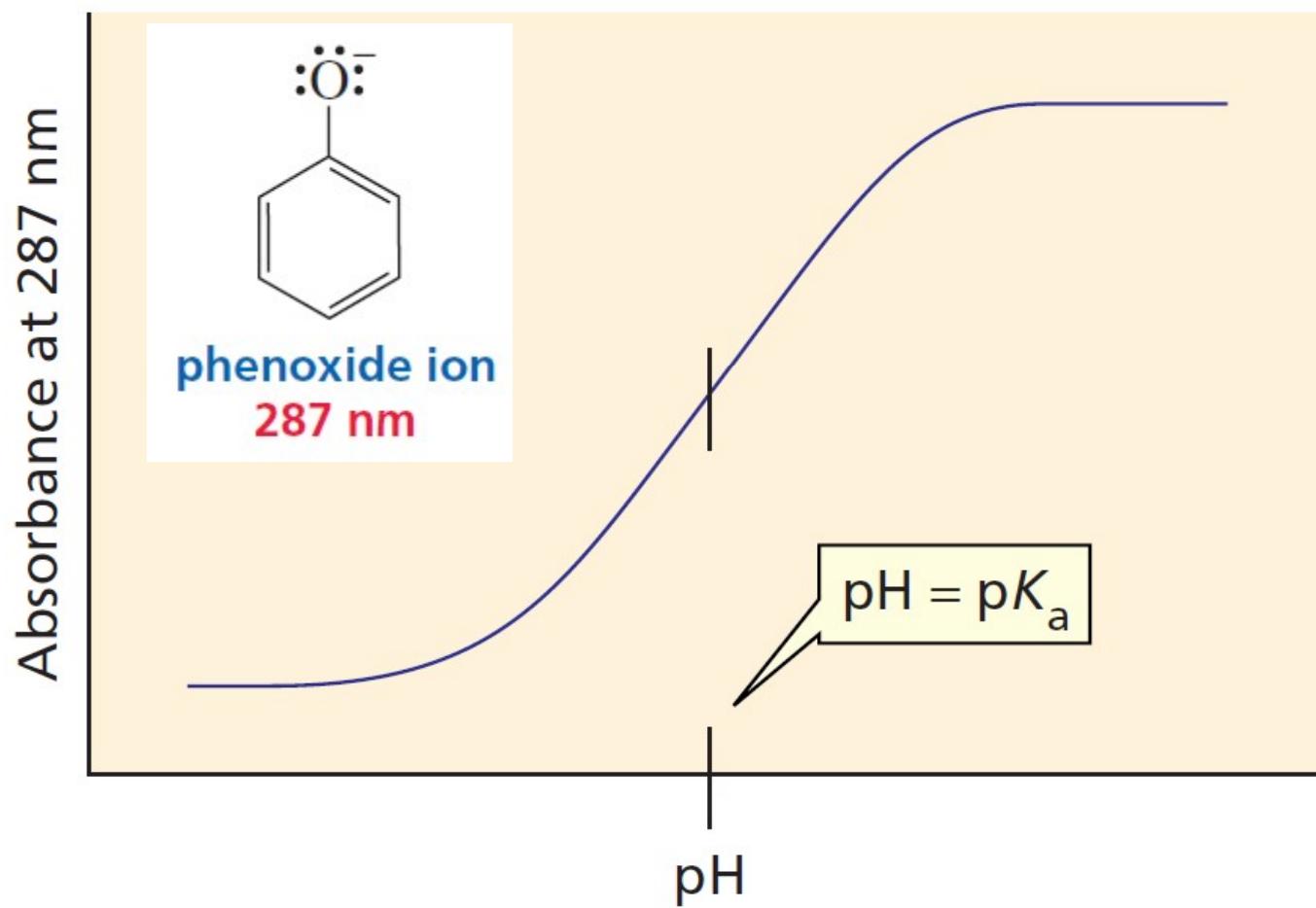


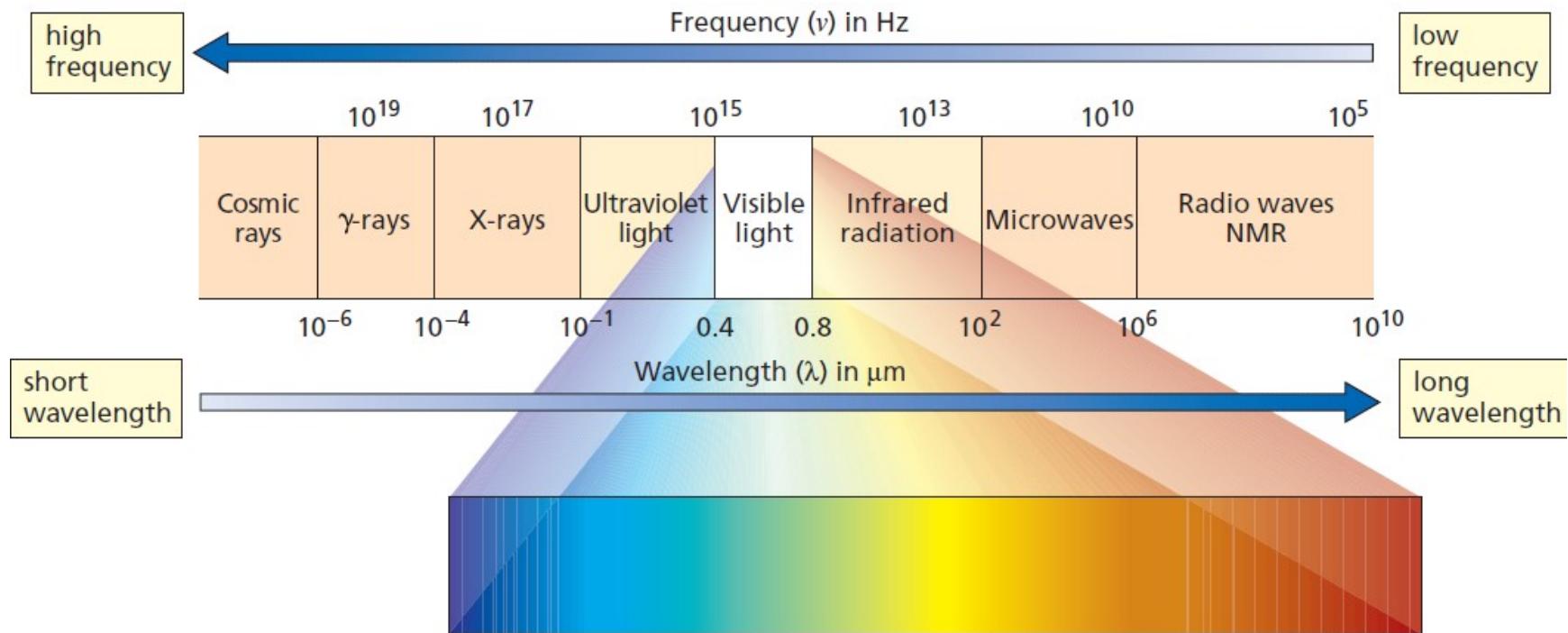
Uses of UV/VIS Spectroscopy

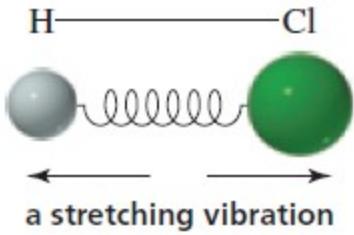


one of the reactants or one of the products absorbs UV or visible light at a wavelength at which the other reactants and products have little or no absorbance.

pK_a determination using UV/Vis spectroscopy



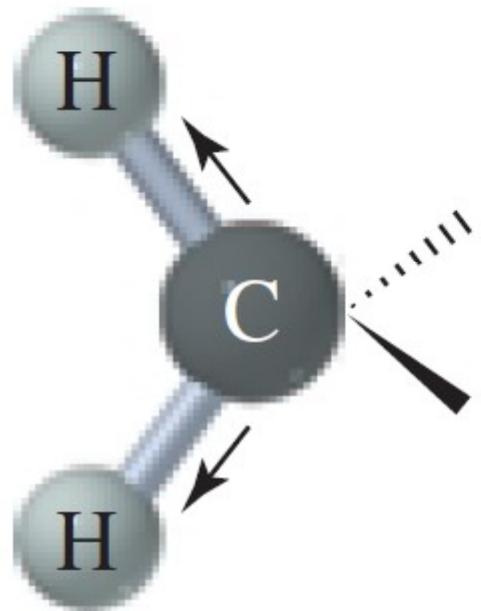




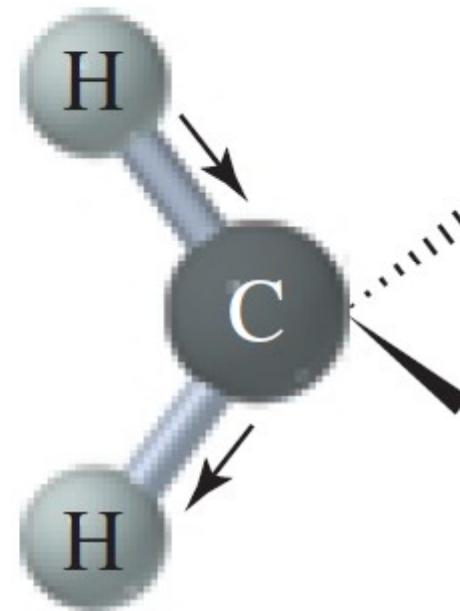
Infrared Spectroscopy

- The covalent bonds in molecules are constantly vibrating.
- A bond vibrates with both **stretching** and **bending** motions.
- A **stretch** is a vibration occurring along the line of the bond that changes the bond length.
- A **bend** is a vibration that does not occur along the line of the bond, but changes the bond angle.

Stretching Vibrations

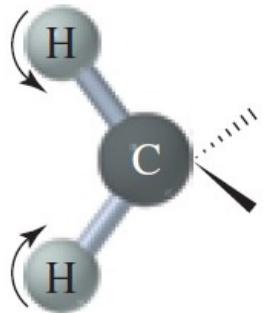


symmetric stretch

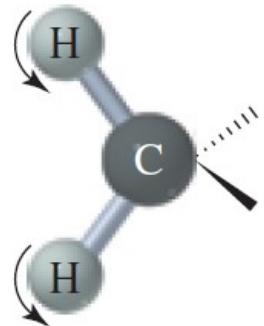


asymmetric stretch

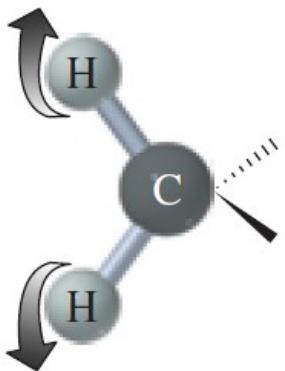
Bending Vibrations



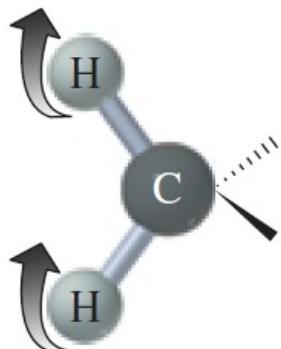
symmetric in-plane
bend (scissor)



asymmetric in-plane
bend (rock)



symmetric out-of-plane
bend (twist)

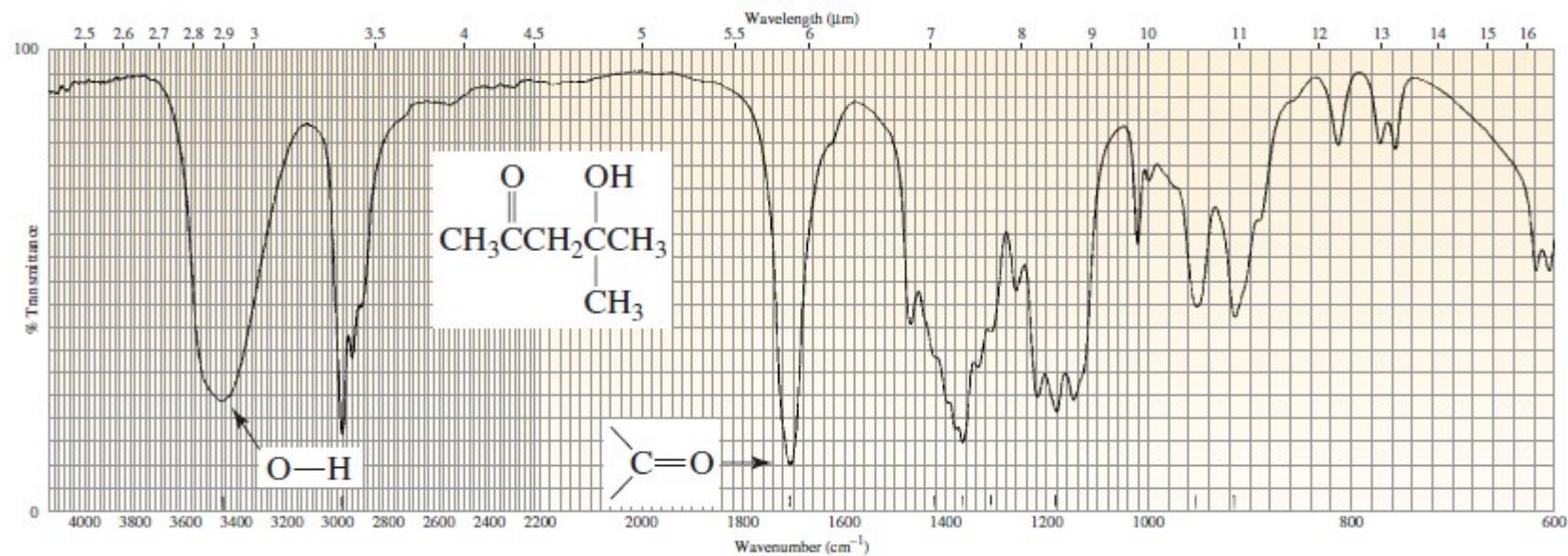


asymmetric out-of-plane
bend (wag)

Infrared Spectroscopy

- Each stretching and bending vibration of a bond in a molecule occurs with a characteristic frequency.
- When a compound is bombarded with radiation of a frequency that exactly matches the frequency of one of its vibrations, the molecule will absorb energy.
- By experimentally determining the wavenumbers of the energy absorbed by a particular compound, we can ascertain what kinds of bonds it has.

IR Spectrum



Electromagnetic radiation with wavenumbers from 4000 to 600 cm⁻¹ has just the right energy to correspond to the stretching and bending vibrations of organic molecules.

- An IR spectrum can be divided into two areas.
- Functional group region: 4000 to 1400 cm⁻¹ : most of the functional groups show absorption bands.
- Fingerprint region: 1400 to 600 cm⁻¹ : it is characteristic of the compound as a whole, just as a fingerprint is characteristic of an individual.
- Even if two different molecules have the same functional groups, their IR spectra will not be identical, since the functional groups are not in exactly the same environment; this difference is reflected in the pattern of absorption bands in the fingerprint regions.

Characteristic IR Absorption Bands

- Organic chemists generally do not try to identify all the absorption bands in an IR spectrum.
- They will look at some characteristic bands so that they will be able to tell something about the structure of a compound that gives a particular IR spectrum

Characteristic IR Absorption Bands

Type of bond	Wavenumber (cm^{-1})
$\text{C}\equiv\text{N}$	2260–2220
$\text{C}\equiv\text{C}$	2260–2100
$\text{C}=\text{C}$	1680–1600
$\text{C}=\text{N}$	1650–1550
	~1600 and ~1500–1430
$\text{C}=\text{O}$	1780–1650
$\text{C}—\text{O}$	1250–1050
$\text{C}—\text{N}$	1230–1020
$\text{O}—\text{H}$ (alcohol)	3650–3200
$\text{O}—\text{H}$ (carboxylic acid)	3300–2500
$\text{N}—\text{H}$	3500–3300
$\text{C}—\text{H}$	3300–2700

The Position of Absorption Bands

- The amount of energy required to stretch a bond depends on the strength of the bond and the masses of the bonded atoms

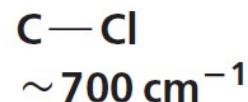
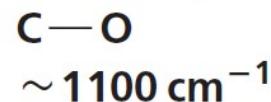
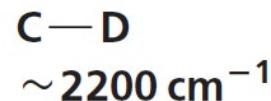
$$\tilde{\nu} = \frac{1}{2\pi c} \left[\frac{f(m_1 + m_2)}{m_1 m_2} \right]^{1/2}$$

- The equation shows that stronger bonds and lighter atoms give rise to higher frequencies/wavenumbers

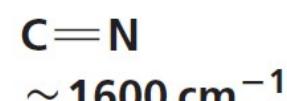
The Position of Absorption Bands

$$\tilde{\nu} = \frac{1}{2\pi c} \left[\frac{f(m_1 + m_2)}{m_1 m_2} \right]^{1/2}$$

Lighter atoms show absorption bands at larger wavenumbers.



Stronger bonds show absorption bands at larger wavenumbers.

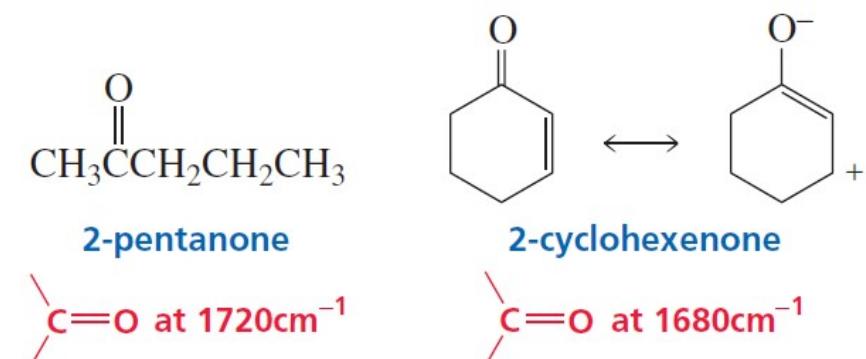


Characteristic IR Absorption Bands

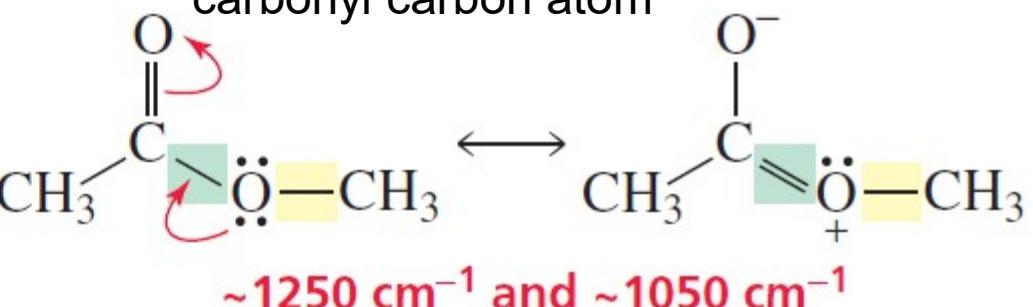
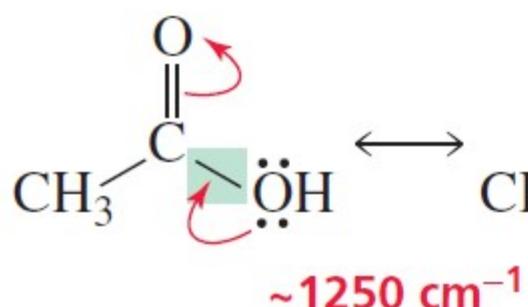
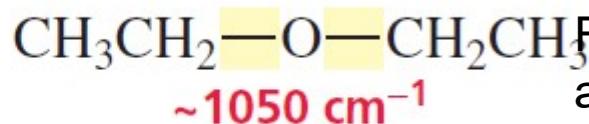
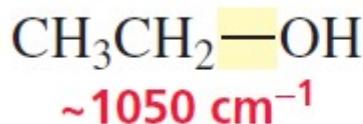
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$\text{C}—\text{H}$	3300–2700

Effect of Bond Order

Resonance and Inductive Electronic Effects

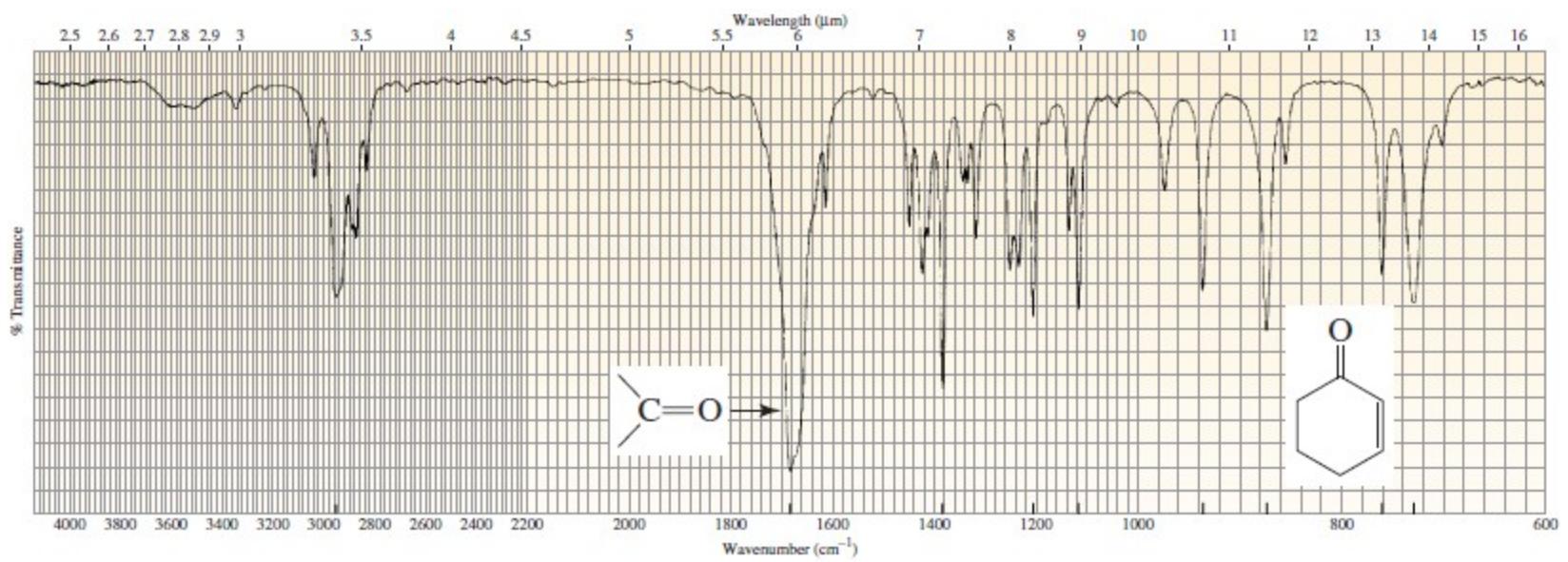
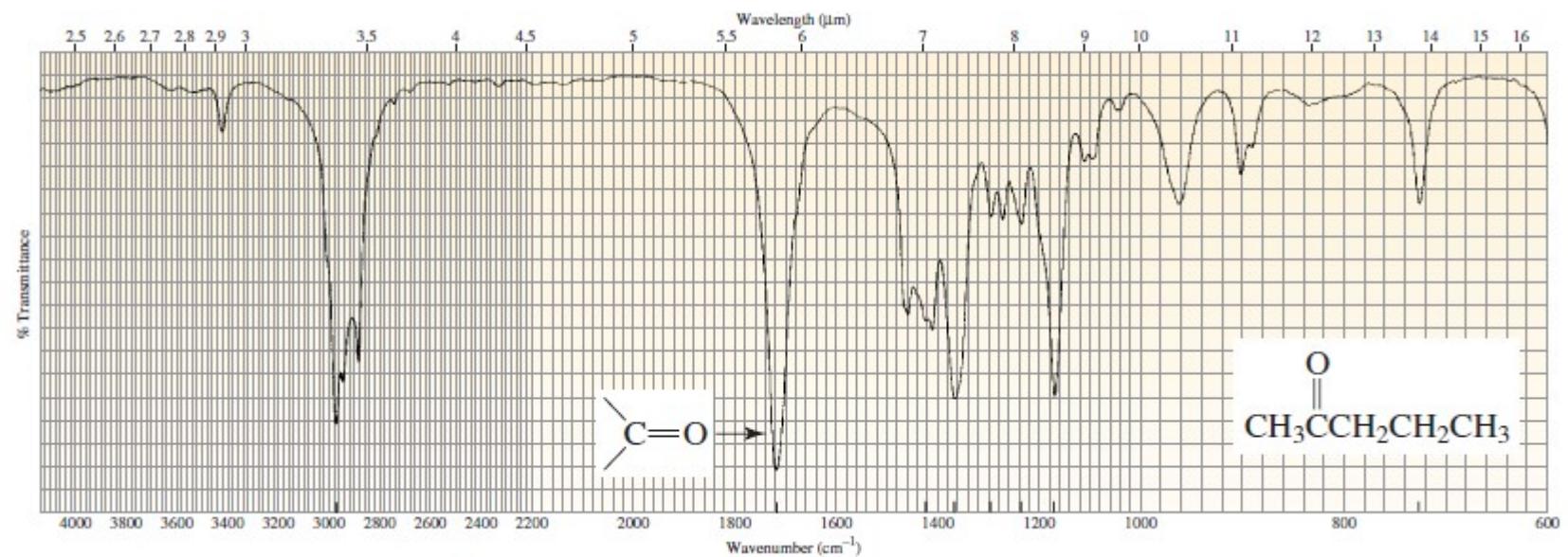


C — O absorption



Since less energy is required to stretch a single bond than a double bond, any structural feature that stabilizes the contributing polar resonance form with a carbon-oxygen single bond will cause the infrared absorption to occur at lower wavenumber position. In other words, any group that donates electrons by resonance causes a shift in the absorption to lower wavenumbers.

For example, the nitrogen atom of amides is very effective in donation of electrons to the carbonyl carbon atom

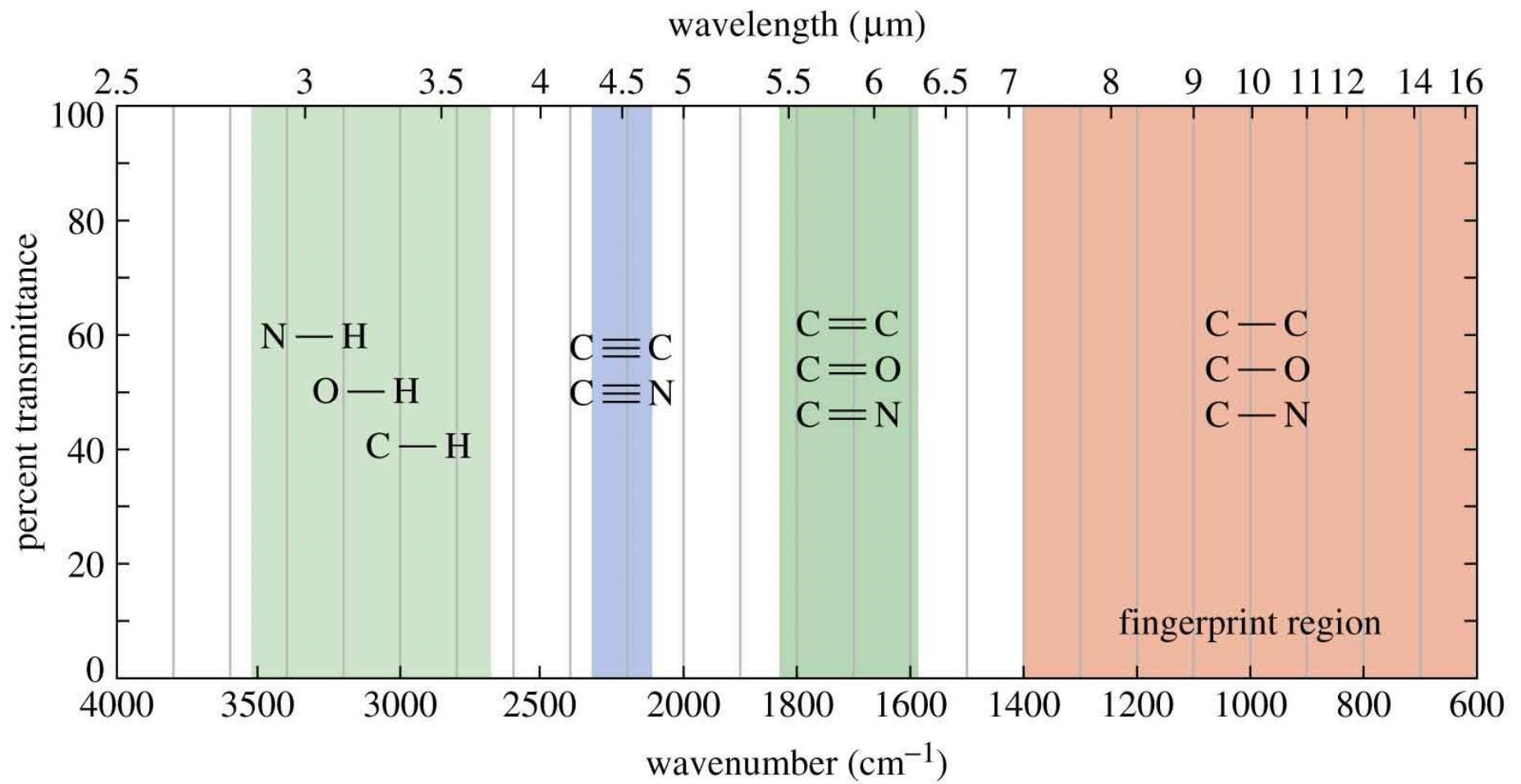


C-H Absorption Bands

Carbon–Hydrogen Stretching Vibrations	Wavenumber (cm ⁻¹)
$\text{C}\equiv\text{C}-\text{H}$	~3300
$\text{C}=\text{C}-\text{H}$	3100–3020
$\text{C}-\text{C}-\text{H}$	2960–2850

- The strength of a C-H bond depends on the hybridization of the carbon
 - The greater the s character of the carbon, the stronger the bond it forms

Summary of IR Absorptions



Alcohol and amine peaks are broad at around 3300-3500

NMR Spectroscopy

- Nuclear Magnetic Resonance
- Electrons are charged, spinning particles with two allowed spin states: $+1/2$ and $-1/2$.
- Certain nuclei also have allowed spin states of $+1/2$ and $-1/2$ and this property allows them to be studied by NMR. Examples of such nuclei are ^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P .

- When there are even number of protons and even number of neutrons in the nucleus, the net spin is equal to **zero**.
- When there are odd number of neutrons and odd number of protons in the nucleus, it will have an integer spin (i.e. 1, 2, 3)
- If the sum of the number of neutrons and the number of protons is odd number, the nucleus will have a half-integer spin (i.e. $1/2$, $3/2$, $5/2$).

Nuclear Magnetic Resonance Spectroscopy

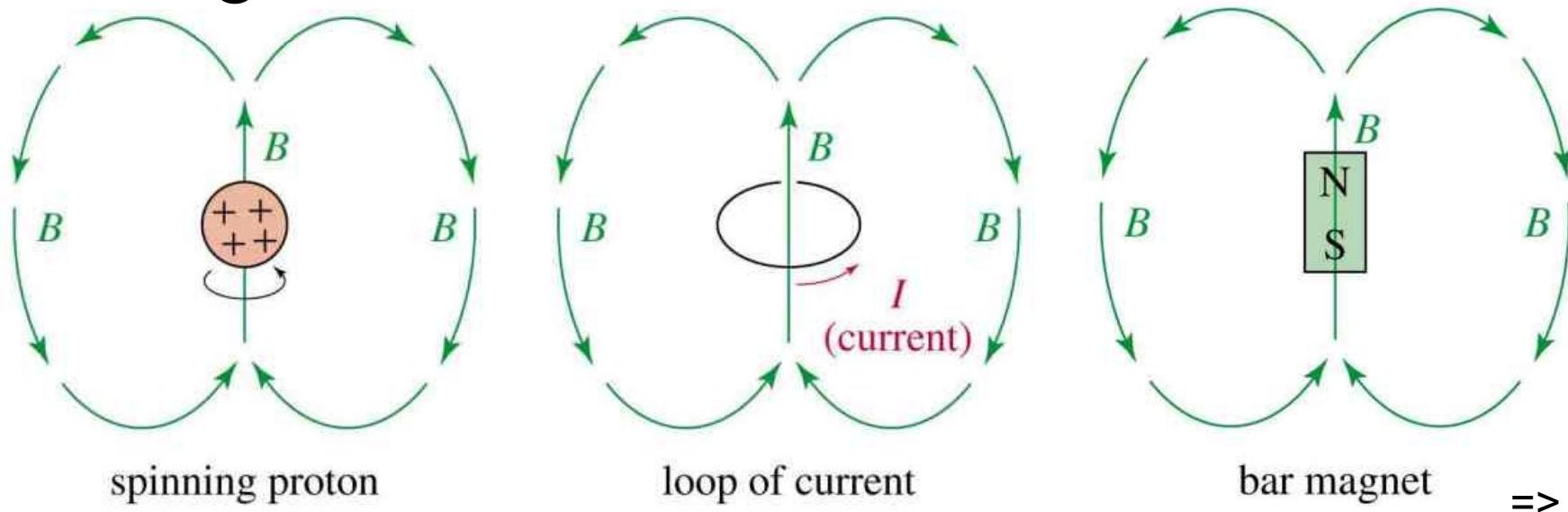
- NMR is one of the most powerful tool available for organic structure determination.
- It is used to study a wide variety of nuclei:
 - ^1H
 - ^{13}C
 - ^{15}N
 - ^{19}F
 - ^{31}P



Magnetic shielding of nucleus by surrounding electron cloud

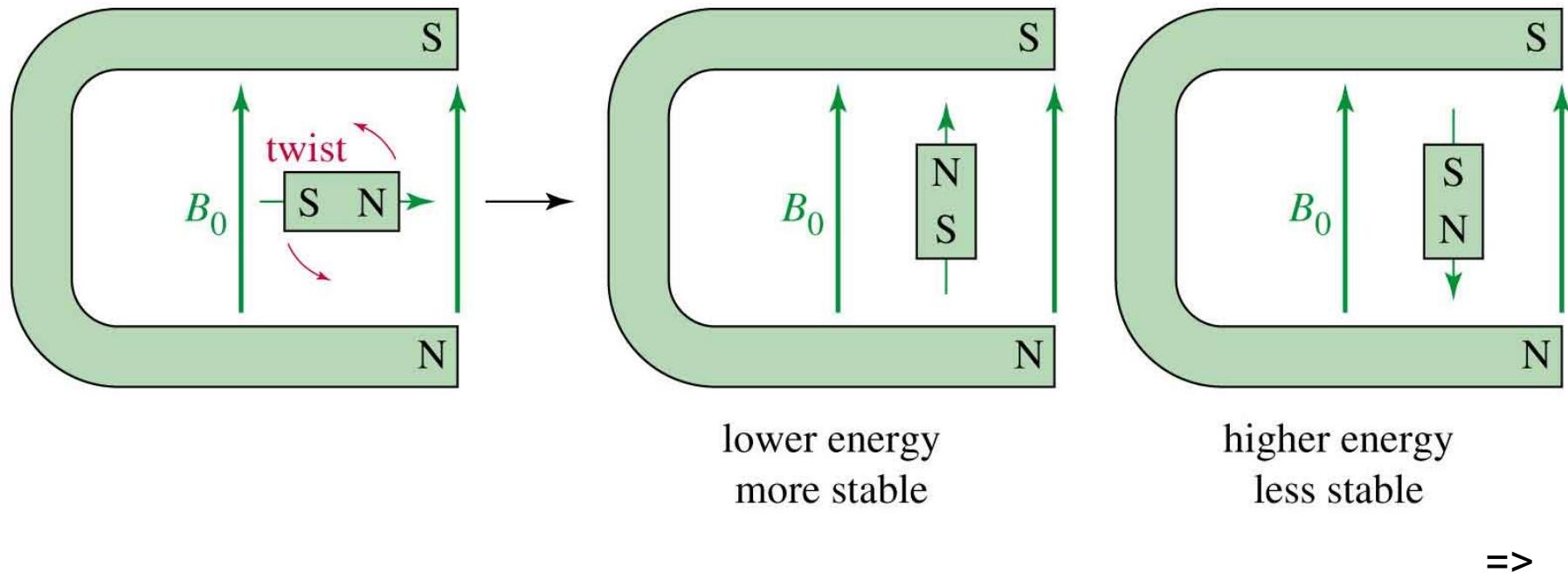
Nuclear Spin

- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.



External Magnetic Field

When placed in an external field, spinning protons act like bar magnets.

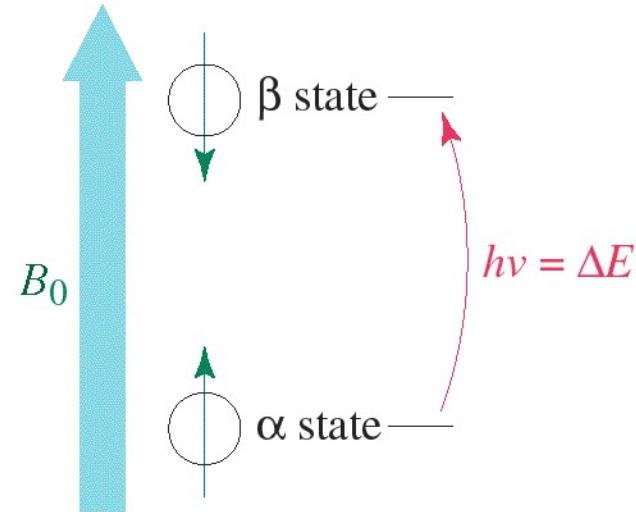


Two Energy States

The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.

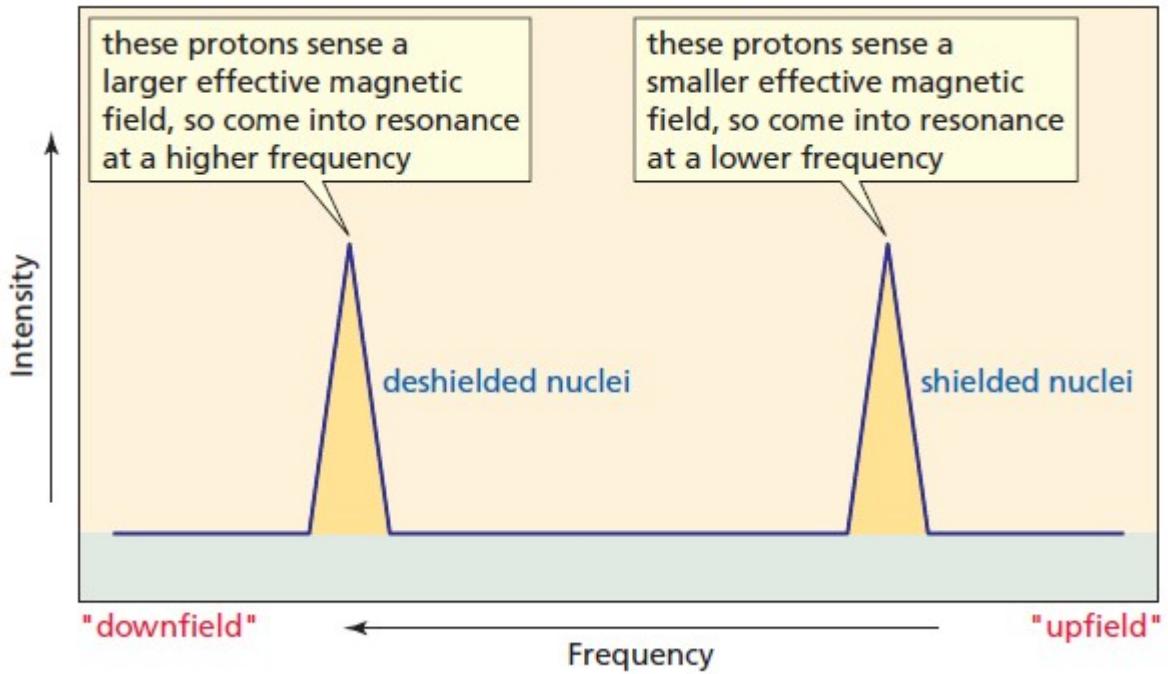
- Energy difference is proportional to the magnetic field strength.
- $\Delta E \propto B_0$



Magnetic Shielding

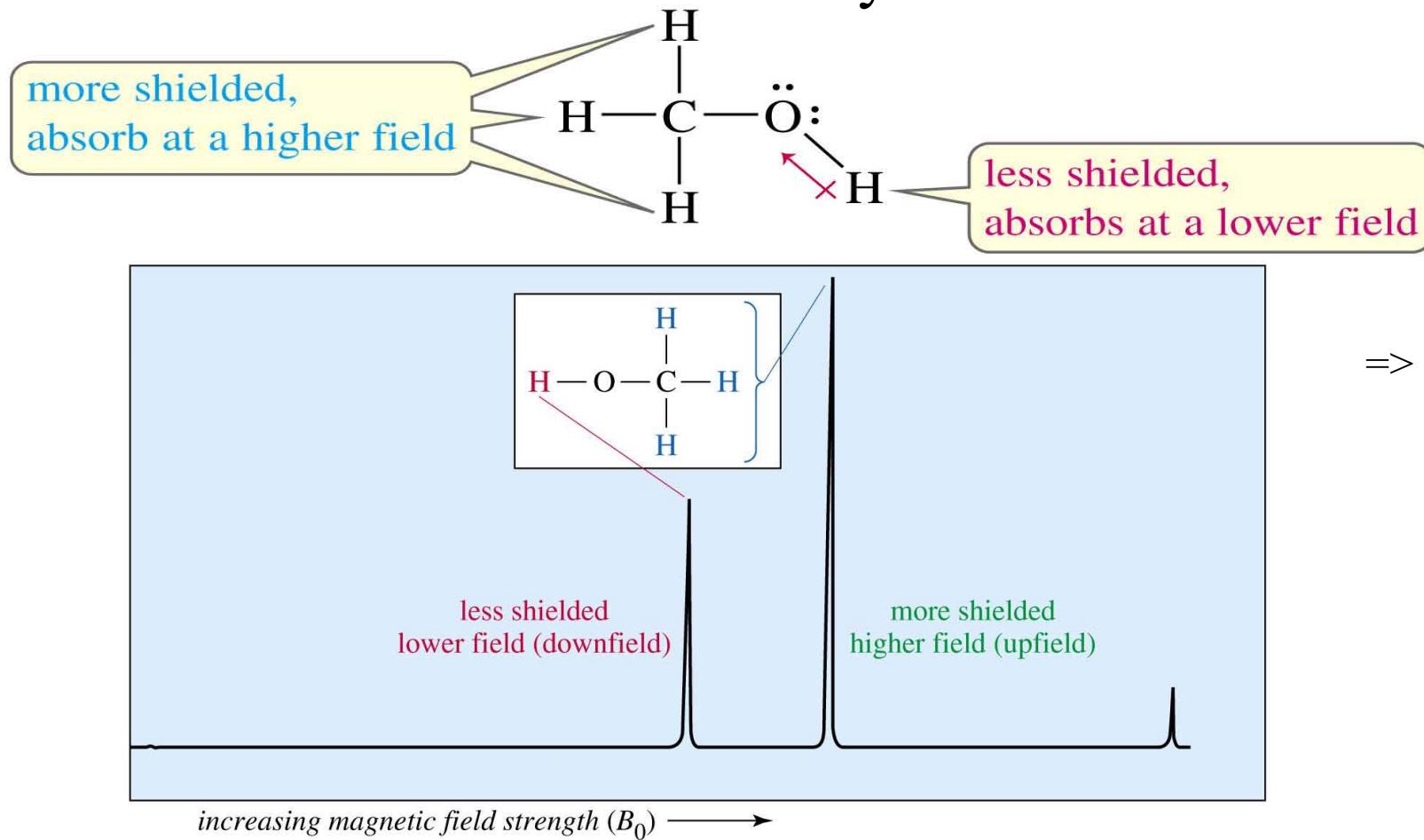
- If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.
- But protons are surrounded by electrons that shield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field.

- Protons in **electron-dense environments** sense a **smaller effective magnetic field**. They, therefore, will require a **lower frequency** to come into resonance (**more shielded**).
- Protons in **electron-poor environments** sense a **larger effective magnetic field** and, therefore, will require a **higher frequency** to come into resonance (**less shielded**).



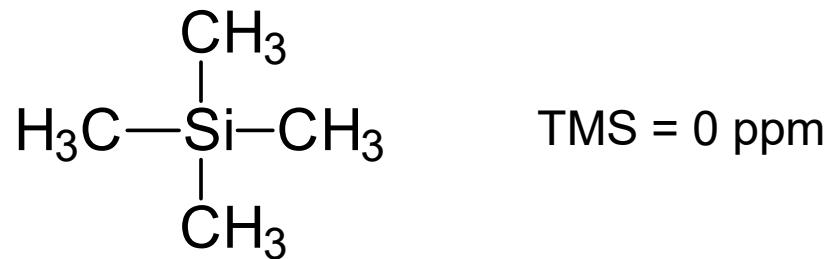
Protons in a Molecule

Depending on their chemical environment, protons in a molecule are shielded by different amounts.



NMR Signals

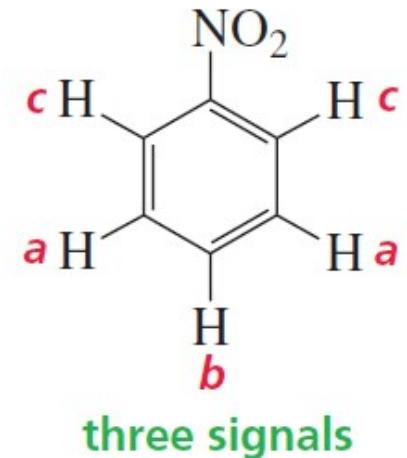
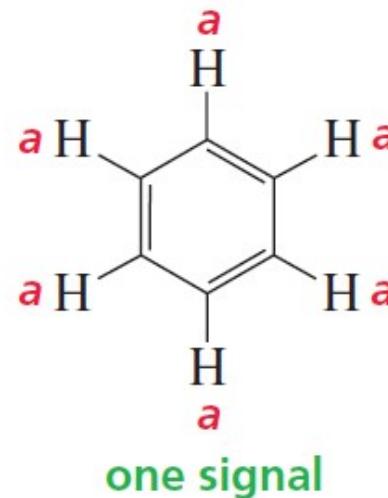
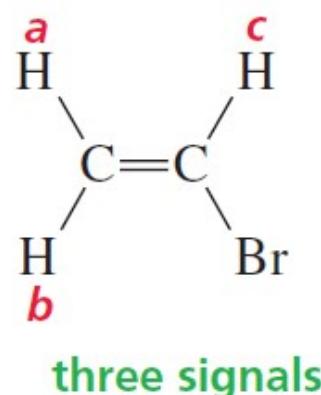
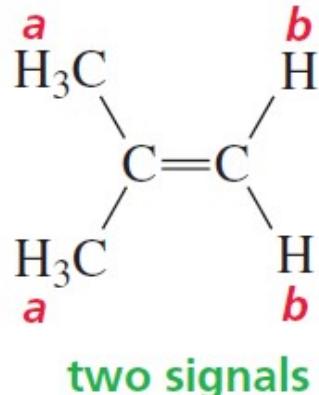
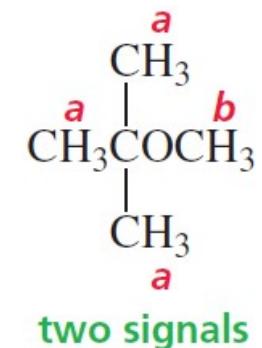
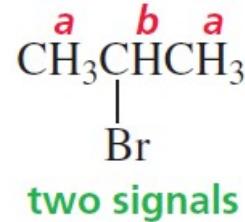
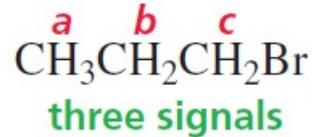
- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded the proton is.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on adjacent atoms.



The Number of Signals in the ^1H NMR Spectrum

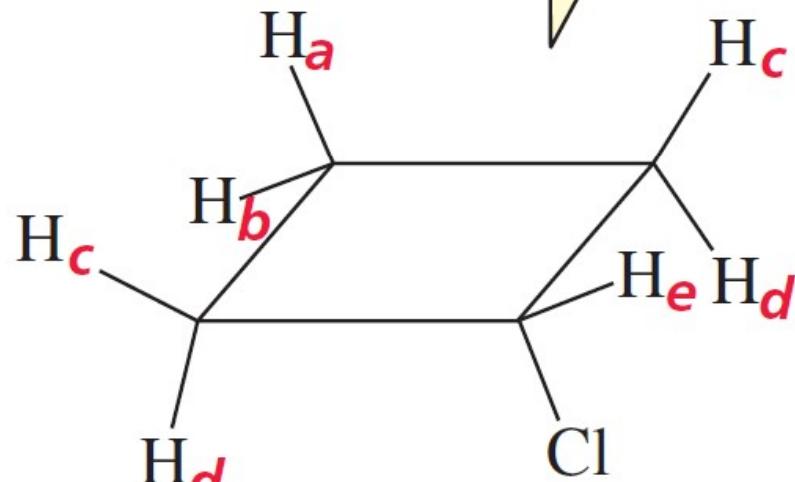
- Protons in the same environment are called chemically equivalent protons
- Each set of chemically equivalent protons in a compound gives rise to a signal in the ^1H NMR spectrum of that compound.

Counting chemically equivalent protons



chlorocyclobutane

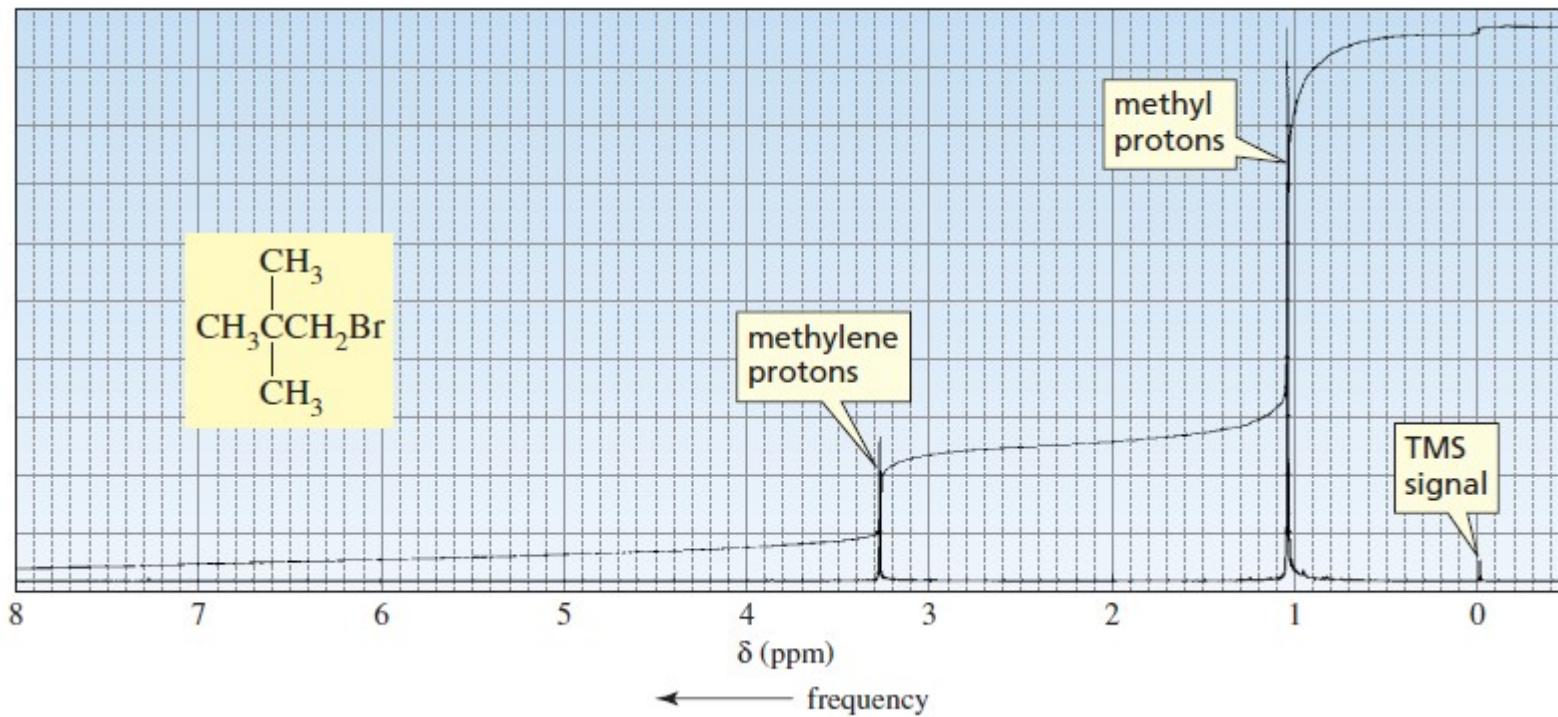
its ^1H NMR spectrum
has five signals



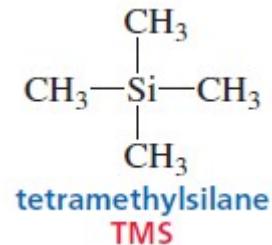
chlorocyclobutane

H_a and H_b are not equivalent
H_c and H_d are not equivalent

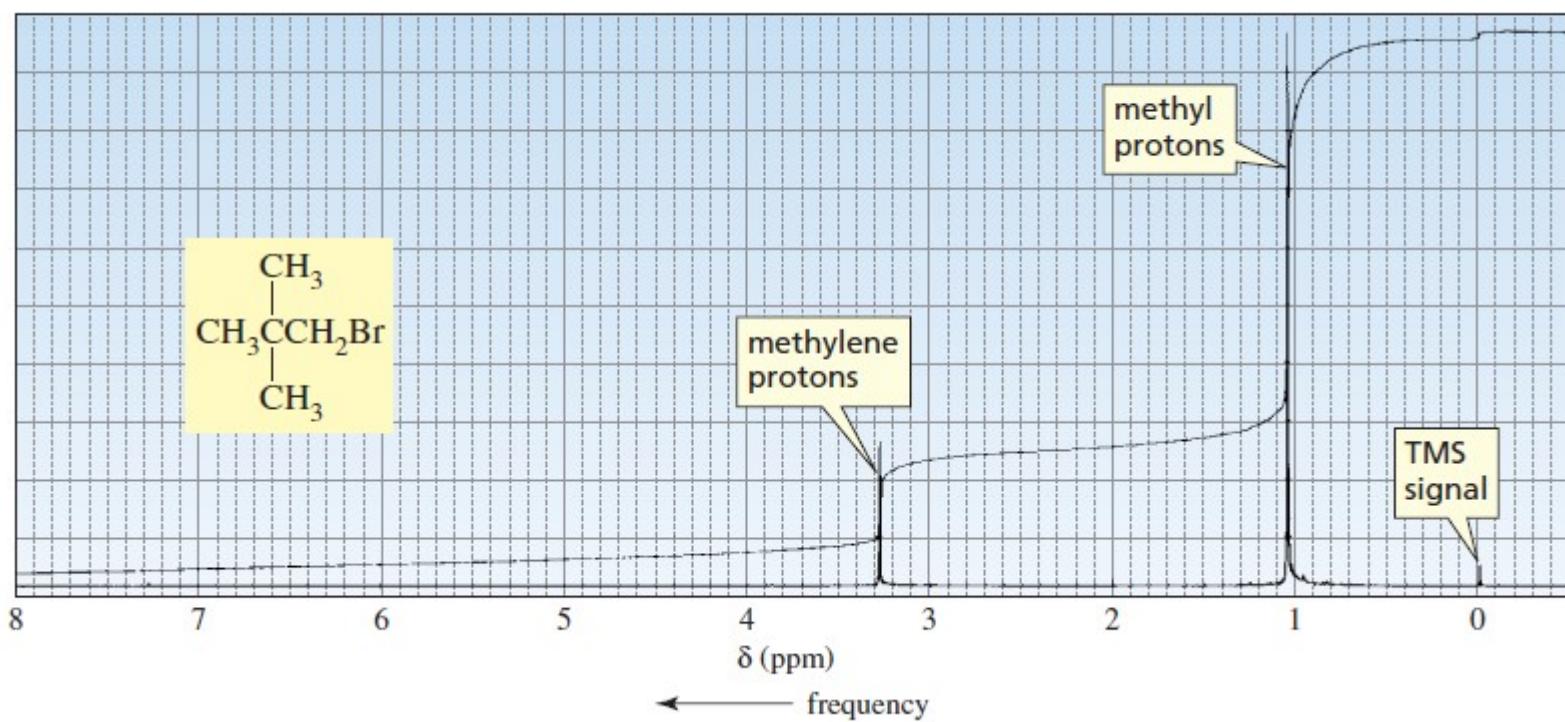
Chemical Shift



Chemical Shift



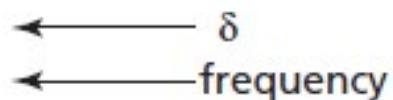
- The positions of the signals in an NMR spectrum are defined according to how far they are from the signal of the reference compound.
- The position at which a signal occurs in an NMR spectrum is called the **chemical shift**.
 - measure of how far the signal is from the reference TMS signal.



The Chemical Shift

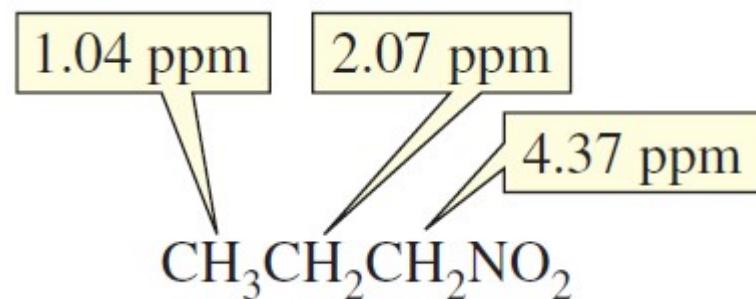
protons in electron-poor environments
deshielded protons
downfield
high frequency
large δ values

protons in electron-dense environments
shielded protons
upfield
low frequency
small δ values



The Relative Positions of NMR Signals

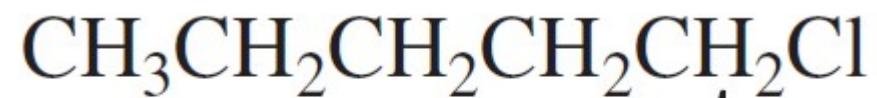
- the **right-hand side** of an NMR spectrum is the **low-frequency** side, where protons in **electron-dense environments** (more shielded) show a signal.
- The **left-hand side** is the **high-frequency side**, where **less shielded** protons show a signal.



The Relative Positions of NMR Signals



4.50 ppm



3.50 ppm



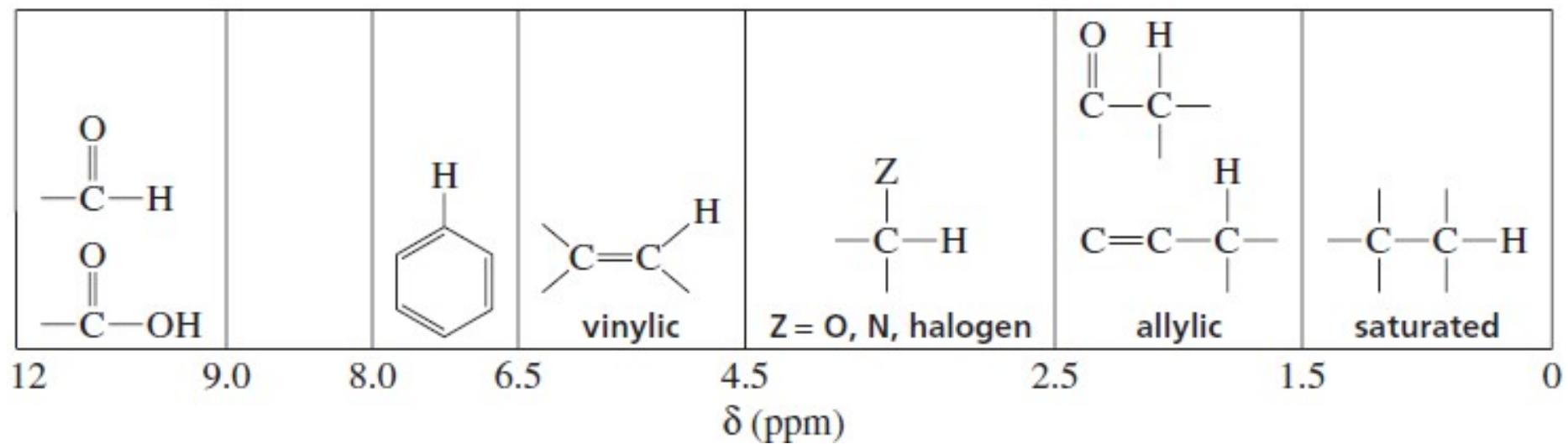
3.40 ppm



3.20 ppm

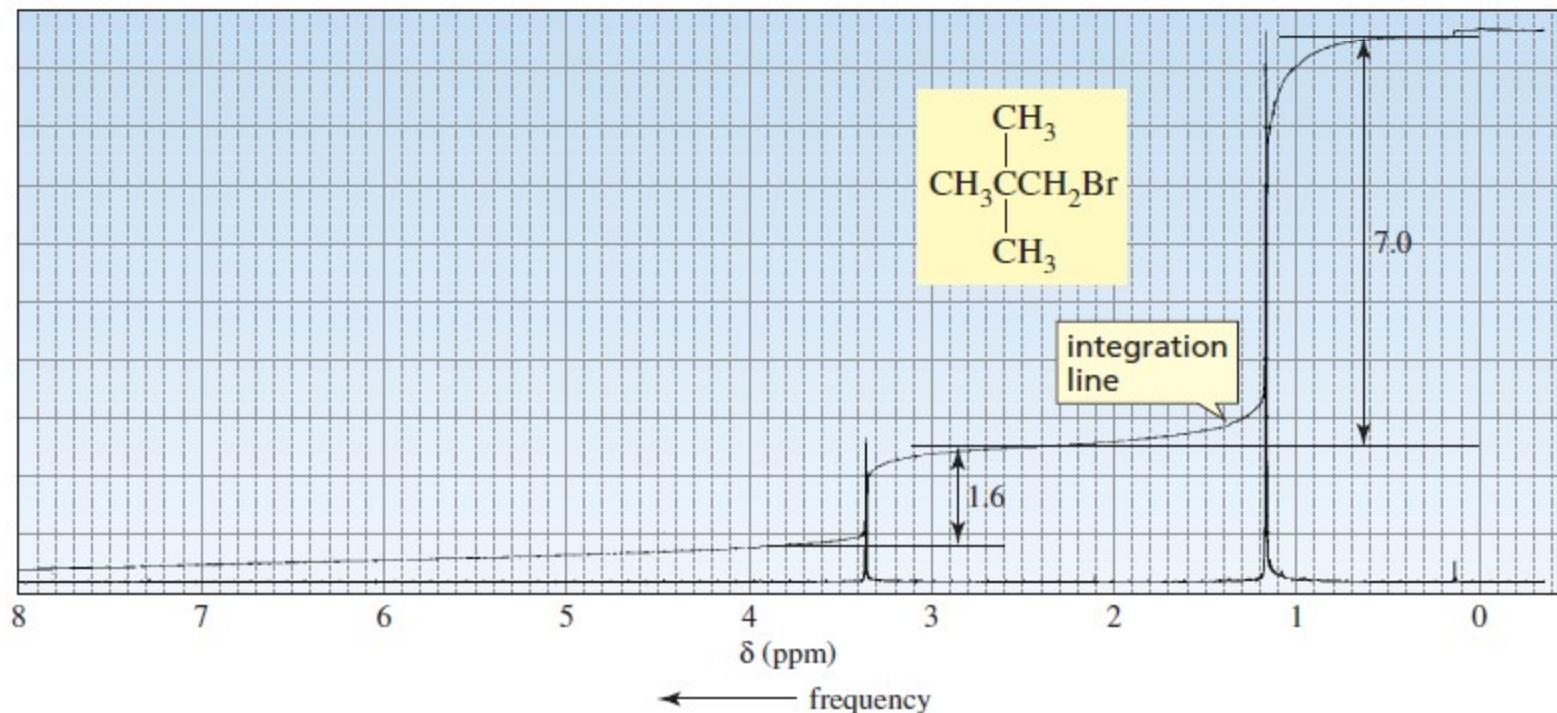
Electron withdrawal causes NMR signals to appear at higher frequencies

Characteristic Values of Chemical Shifts

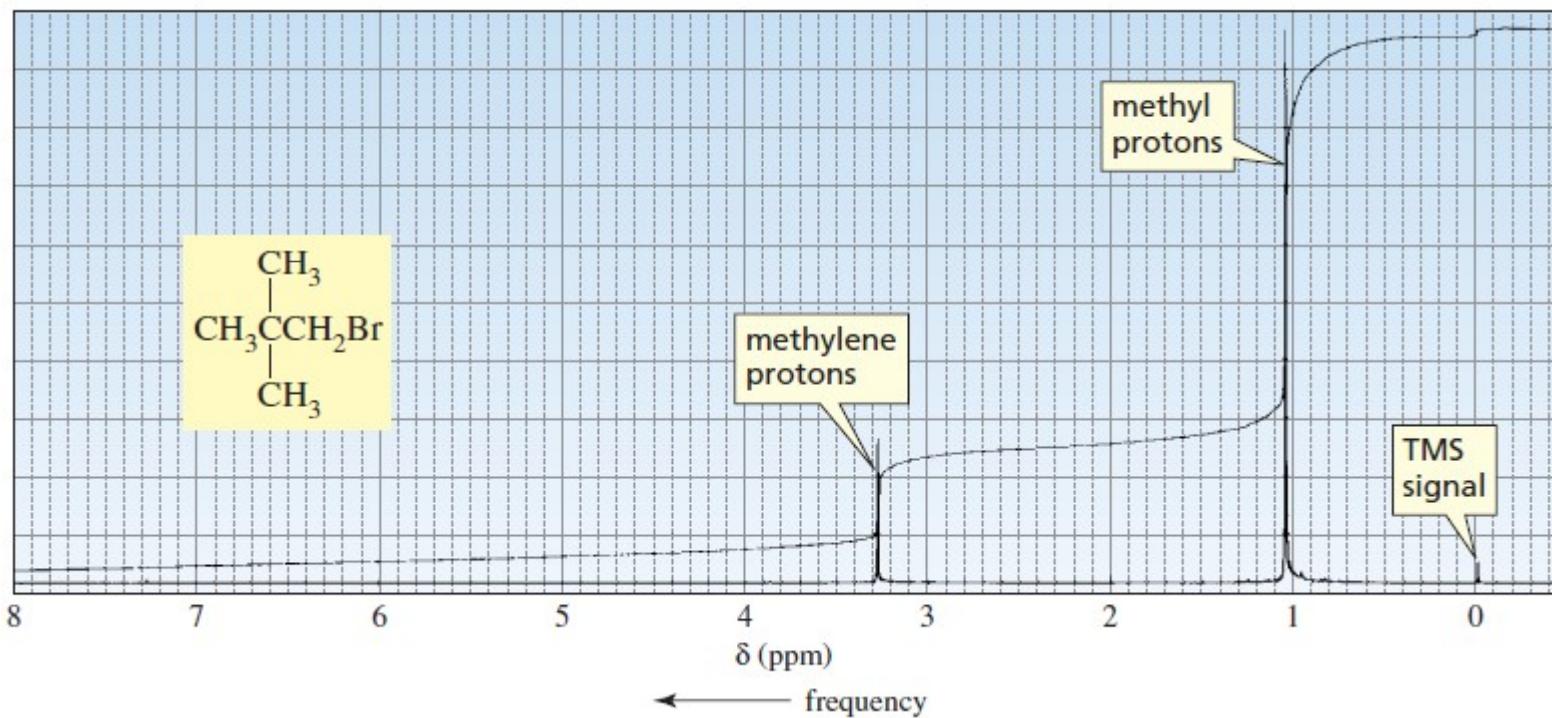


Integration of NMR Signals

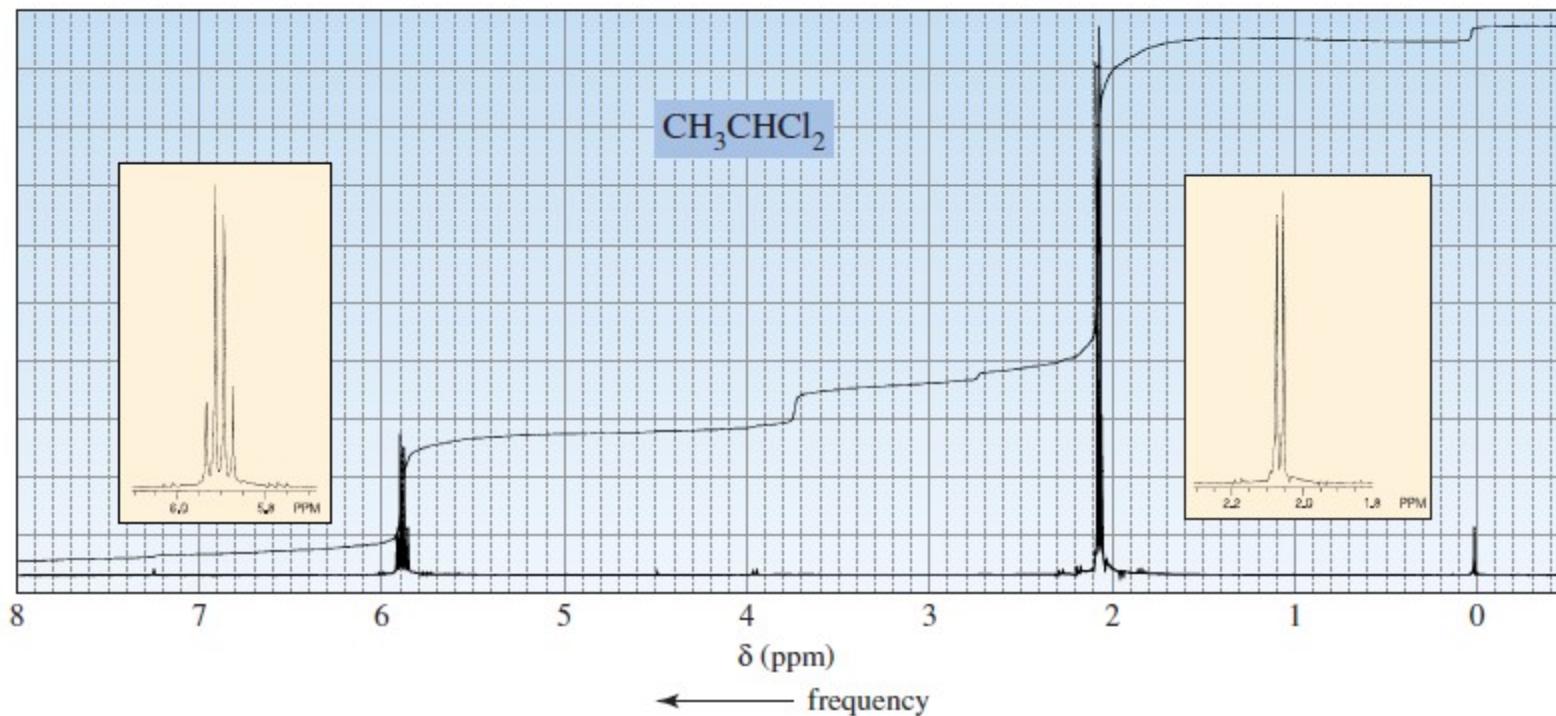
- the area under each signal is proportional to the number of protons that gives rise to the signal.



Splitting of the Signals

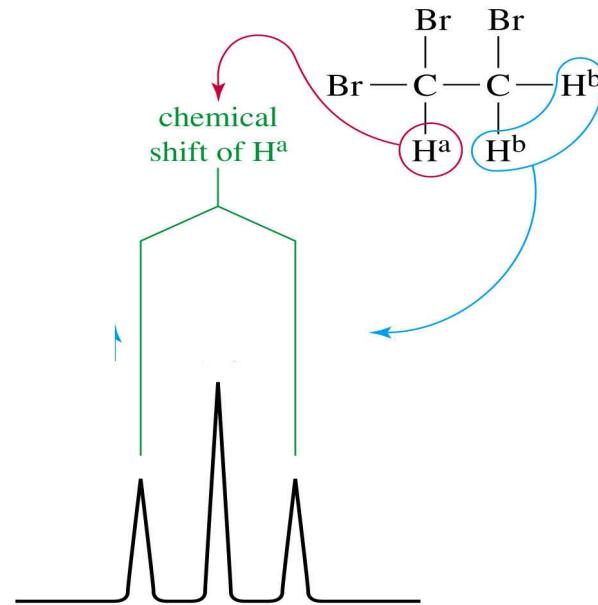


Splitting of the Signals



The $N + 1$ Rule

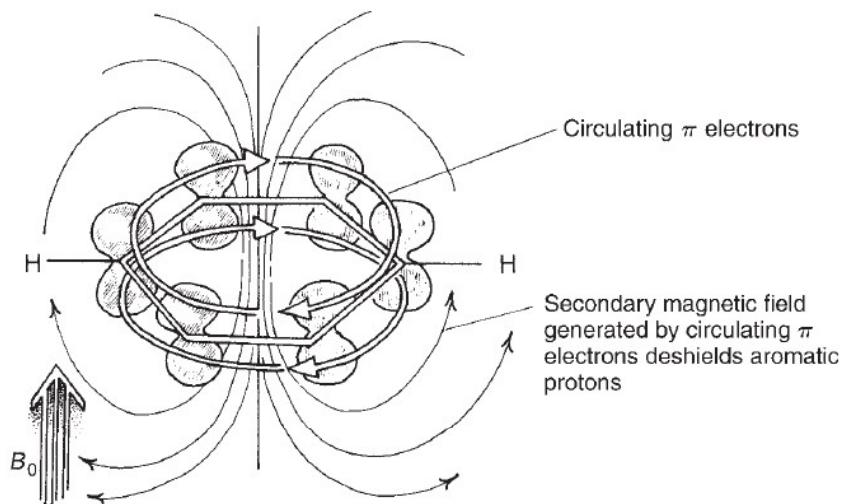
If a signal is split by N equivalent protons, it is split into $N + 1$ peaks.



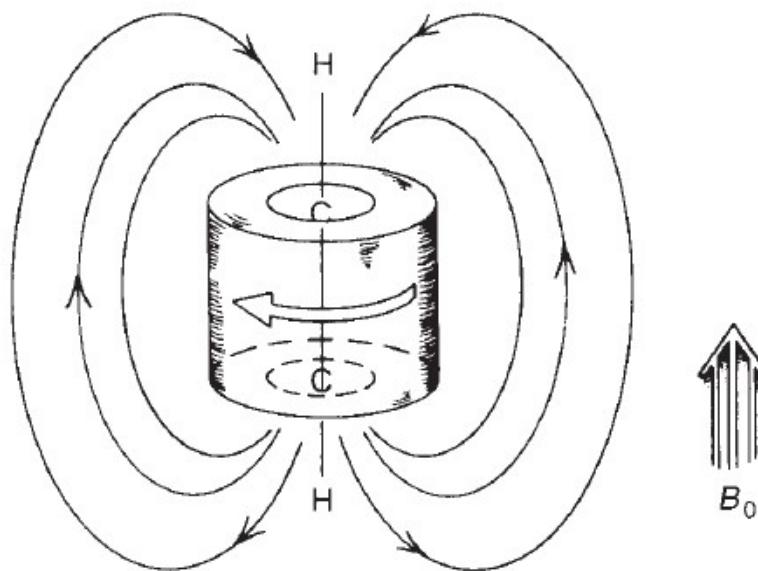
=
>

Relative Peak Intensities of Symmetric Multiplets		
<i>Number of Equivalent Protons Causing Splitting</i>	<i>Number of Peaks (multiplicity)</i>	<i>Area Ratios (Pascal's triangle)</i>
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

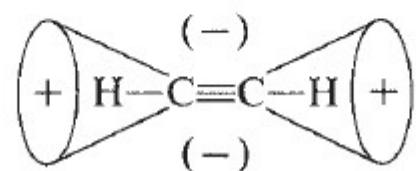
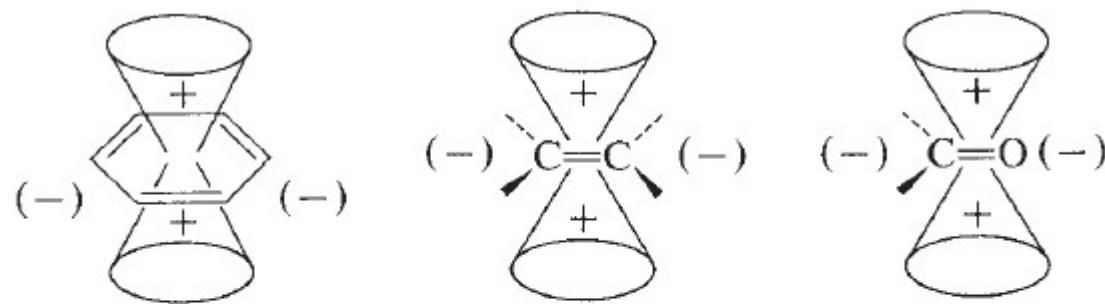
MAGNETIC ANISOTROPY

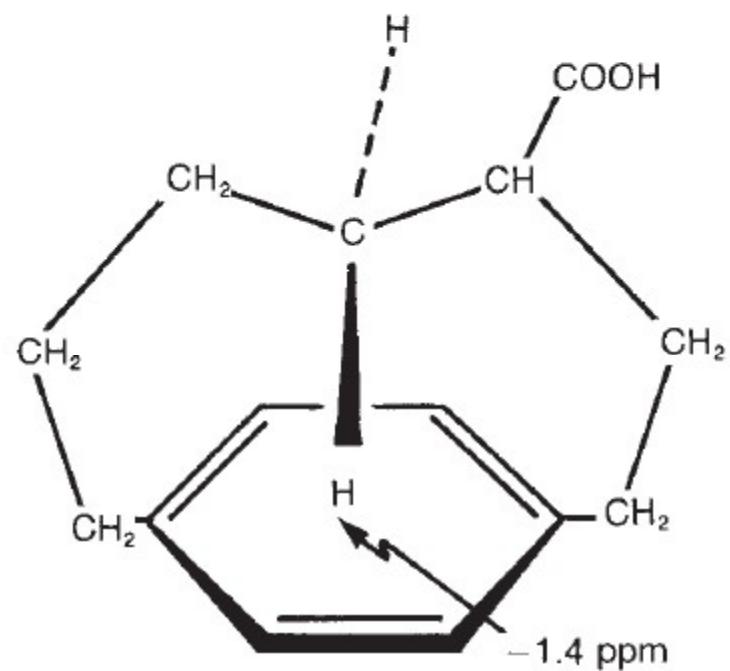
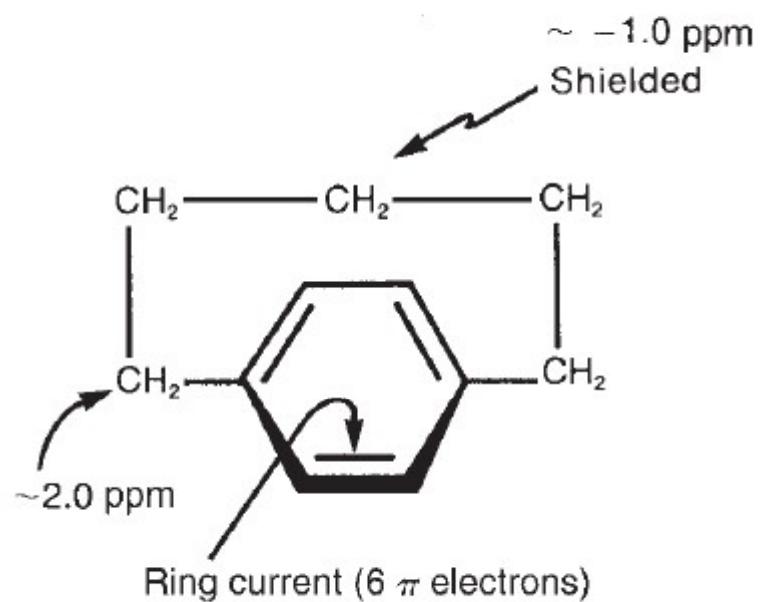


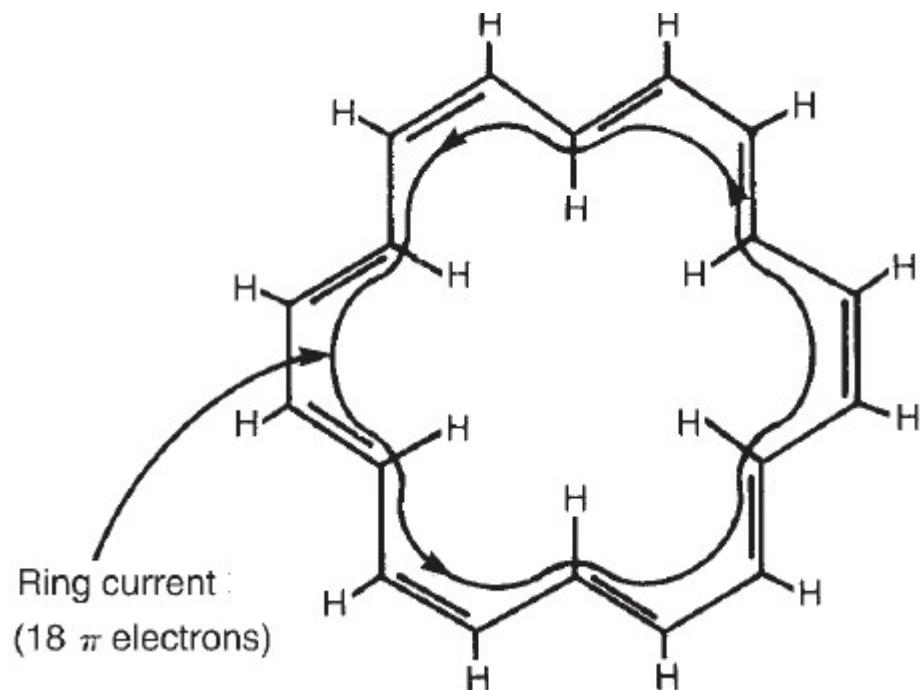
- The benzene hydrogens are said to be deshielded by the diamagnetic anisotropy of the ring
- A proton attached to a benzene ring is influenced by three magnetic fields: the strong magnetic field applied by the electromagnets of the NMR spectrometer and two weaker fields, one due to the usual shielding by the valence electrons around the proton, and the other due to the anisotropy generated by the ring-system p electrons. It is the anisotropic effect that gives the benzene protons a chemical shift that is greater than expected



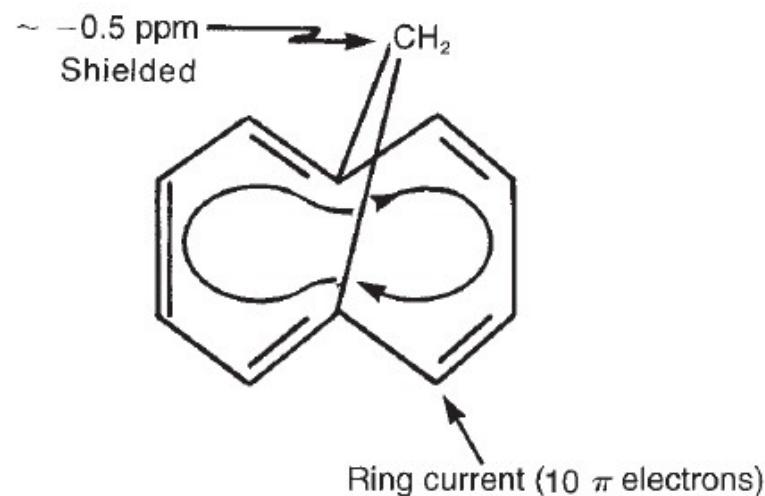
Diamagnetic anisotropy in acetylene.







Inner hydrogens ~ -1.8 ppm
Outer hydrogens ~ 8.9 ppm



SPECTRAL ANALYSIS BOX—Alcohols

CHEMICAL SHIFTS

$\text{C}-\text{OH}$ 0.5–5.0 ppm

The chemical shift of the $-\text{OH}$ hydrogen is highly variable, its position depending on concentration, solvent, and temperature. The peak may be broadened at its base by the same set of factors.

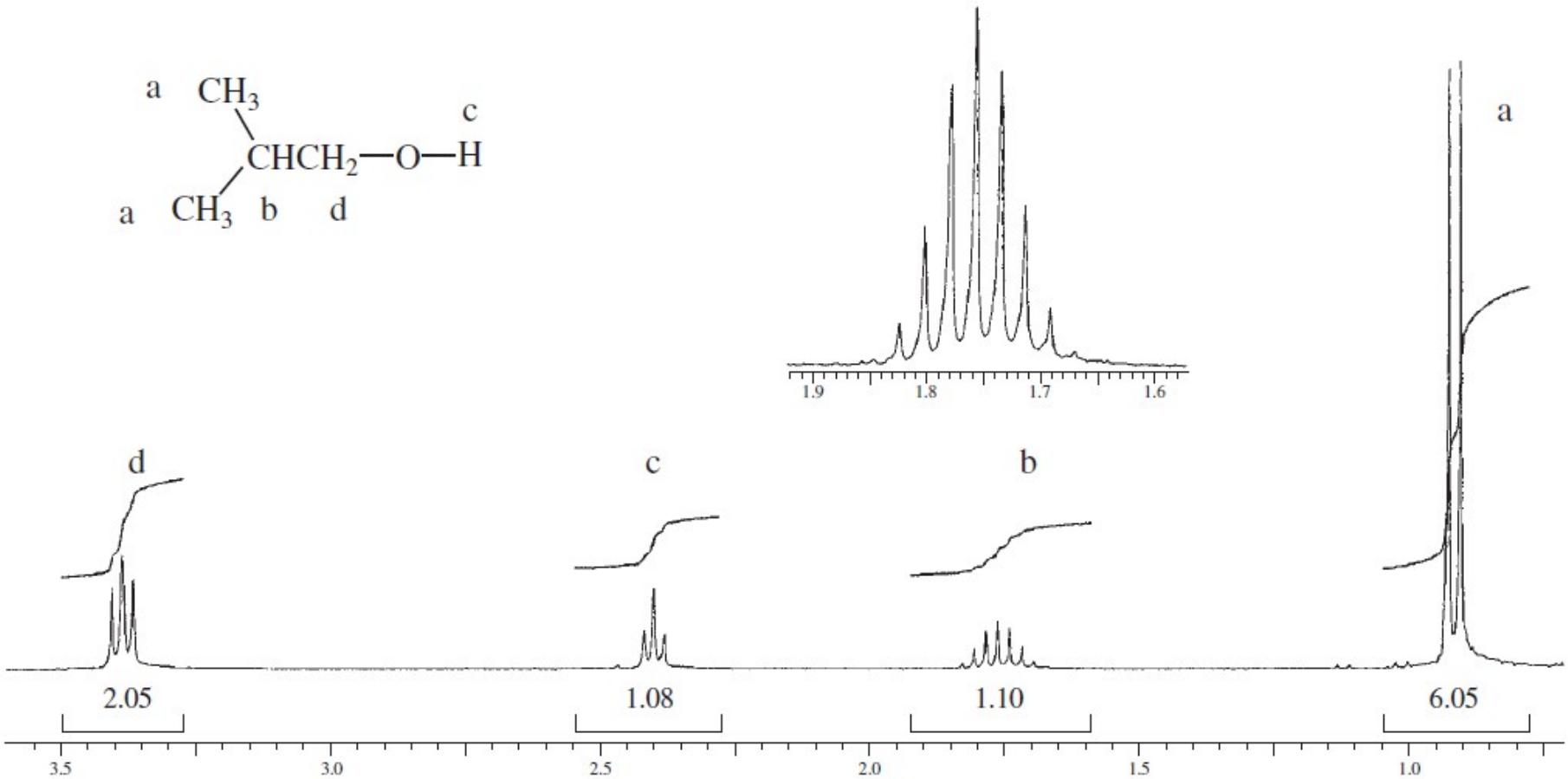
$\text{CH}-\text{O}-\text{H}$ 3.2–3.8 ppm

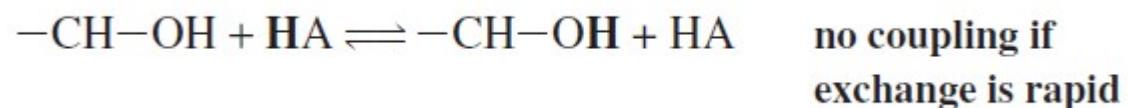
Protons on the α carbon are deshielded by the electronegative oxygen atom and are shifted downfield in the spectrum.

COUPLING BEHAVIOR

$\text{CH}-\text{OH}$ *No coupling (usually), or*
 $^3J = 5 \text{ Hz}$

Because of the rapid chemical exchange of the $-\text{OH}$ proton in many solutions, coupling is not usually observed between the $-\text{OH}$ proton and those hydrogens attached to the α carbon.



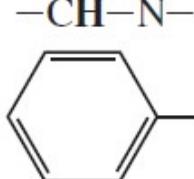


Temperature, acid impurities, water etc.

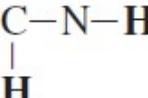


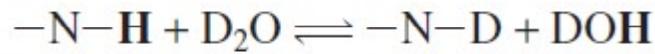
SPECTRAL ANALYSIS BOX—Amines

CHEMICAL SHIFTS

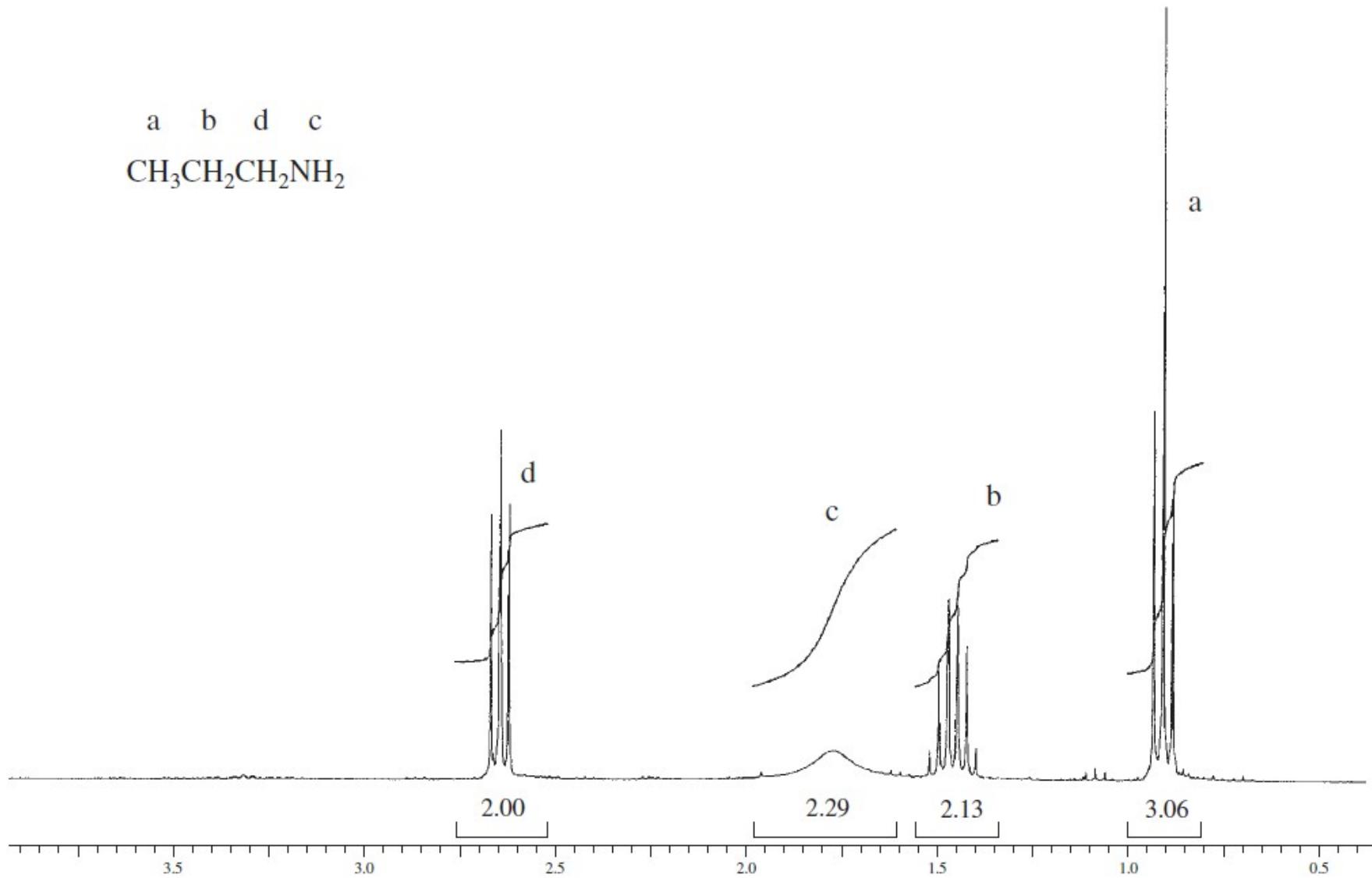
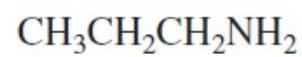
$\text{R}-\text{N}-\text{H}$	0.5–4.0 ppm	Hydrogens attached to a nitrogen have a variable chemical shift depending on the temperature, acidity, amount of hydrogen bonding, and solvent.
$-\text{CH}-\text{N}-$ 	2.2–2.9 ppm	The α hydrogen is slightly deshielded due to the electronegativity of the attached nitrogen.
$\text{C}_6\text{H}_5-\text{N}-\text{H}$	3.0–5.0 ppm	This hydrogen is deshielded due to the anisotropy of the ring and the resonance that removes electron density from nitrogen and changes its hybridization.

COUPLING BEHAVIOR

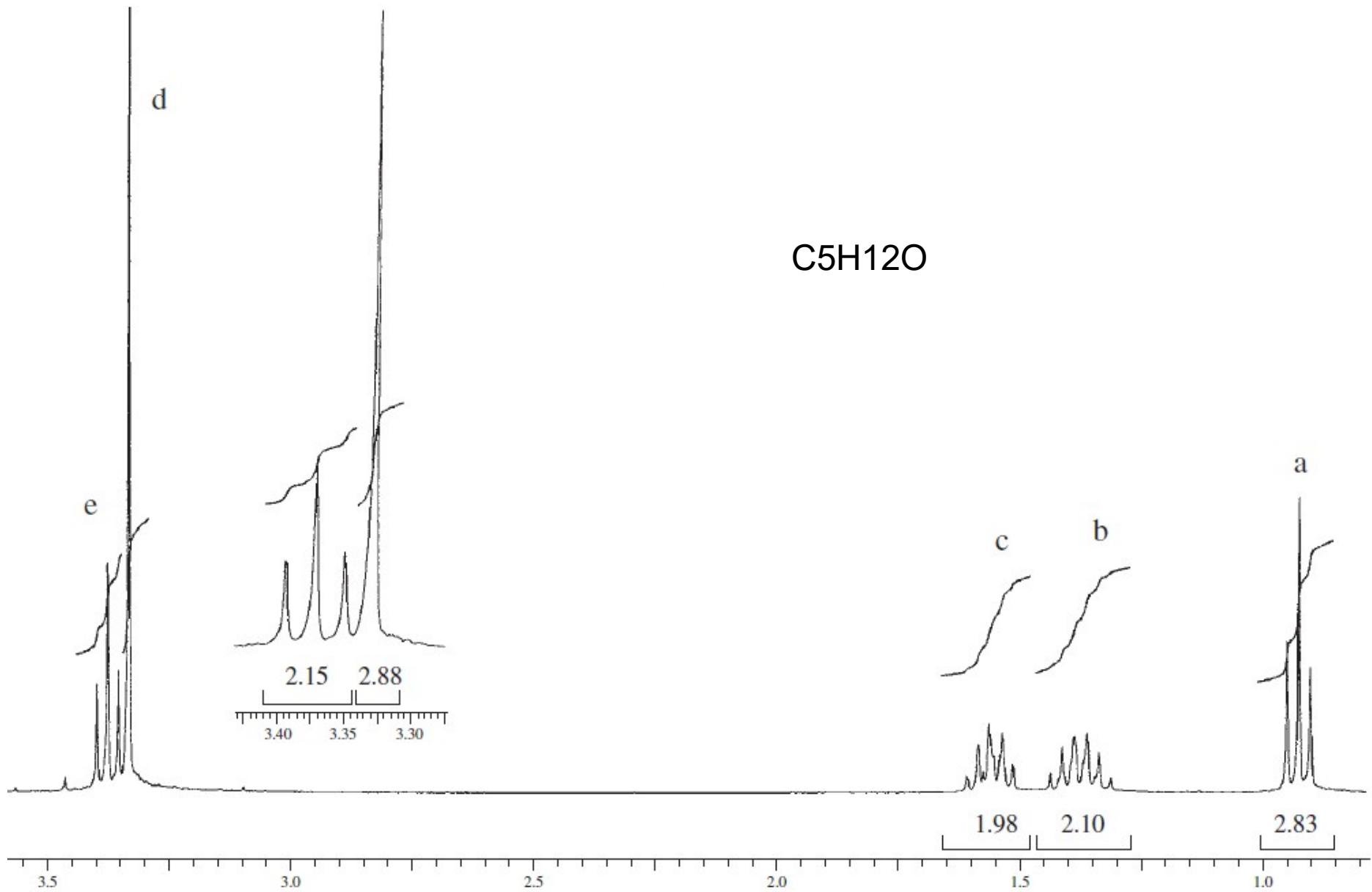
$-\text{N}-\text{H}$	$^1J \approx 50 \text{ Hz}$	Direct coupling between a nitrogen and an attached hydrogen is not usually observed but is quite large when it occurs. More commonly, this coupling is obscured by quadrupole broadening by nitrogen or by proton exchange. See Sections 8.4 and 8.5.
$-\text{N}-\text{CH}$	$^2J \approx 0 \text{ Hz}$	This coupling is usually not observed.
$\text{C}-\text{N}-\text{H}$ 	$^3J \approx 0 \text{ Hz}$	Due to chemical exchange, this coupling is usually not observed.



a b d c



C₅H₁₂O



SPECTRAL ANALYSIS BOX—Aldehydes

CHEMICAL SHIFTS

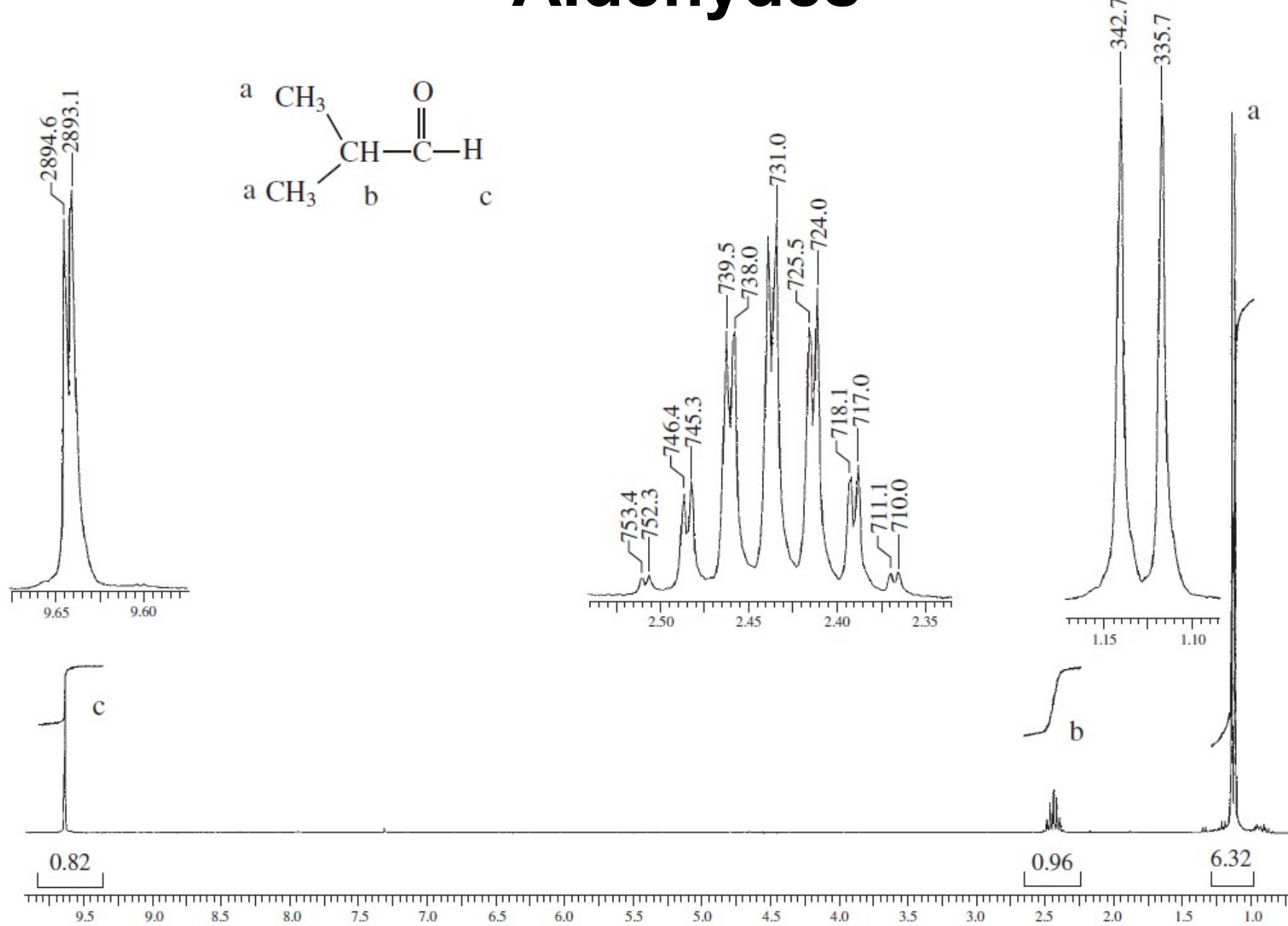
$\text{R}-\text{CHO}$ 9.0–10.0 ppm The aldehyde hydrogen is shifted far downfield due to the anisotropy of the carbonyl group ($\text{C}=\text{O}$).

$\text{R}-\text{CH}-\text{CH}=\text{O}$ 2.1–2.4 ppm Hydrogens on the carbon adjacent to the $\text{C}=\text{O}$ group are also deshielded due to the carbonyl group, but they are more distant, and the effect is smaller.

COUPLING BEHAVIOR

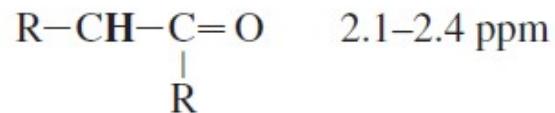
$-\text{CH}-\text{CHO}$ $^3J \approx 1\text{--}3 \text{ Hz}$ Coupling occurs between the aldehyde hydrogen and hydrogens on the adjacent carbon, but 3J is small.

Aldehydes



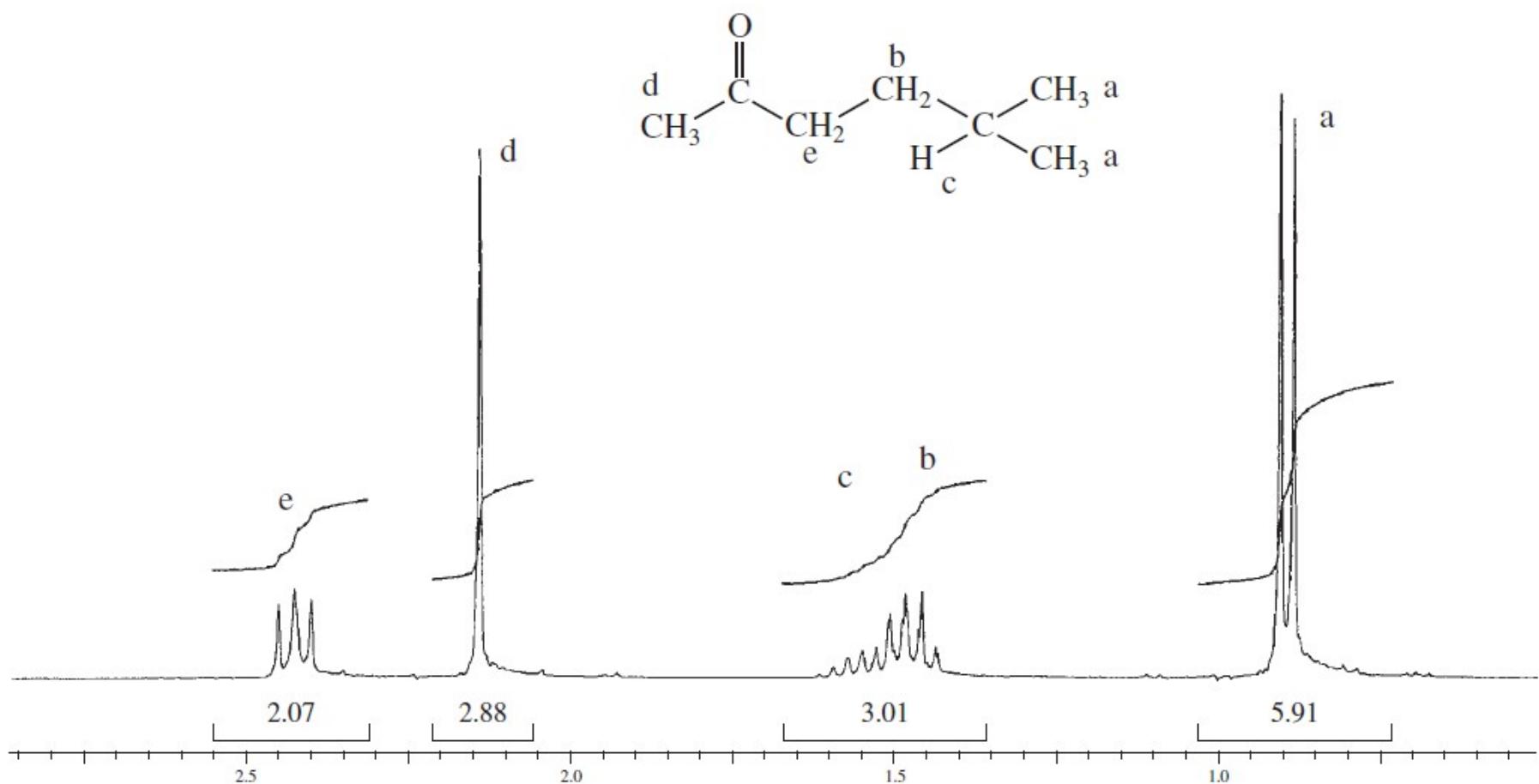
SPECTRAL ANALYSIS BOX—Ketones

CHEMICAL SHIFTS



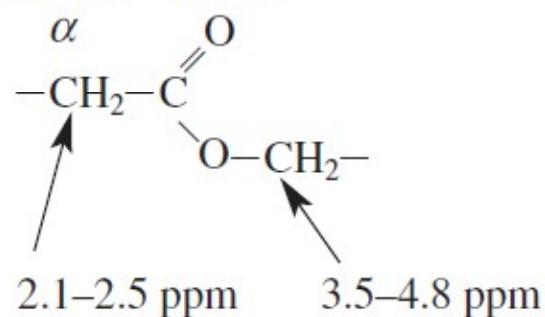
The α hydrogens in ketones are deshielded by the anisotropy of the adjacent C=O group.

Ketones



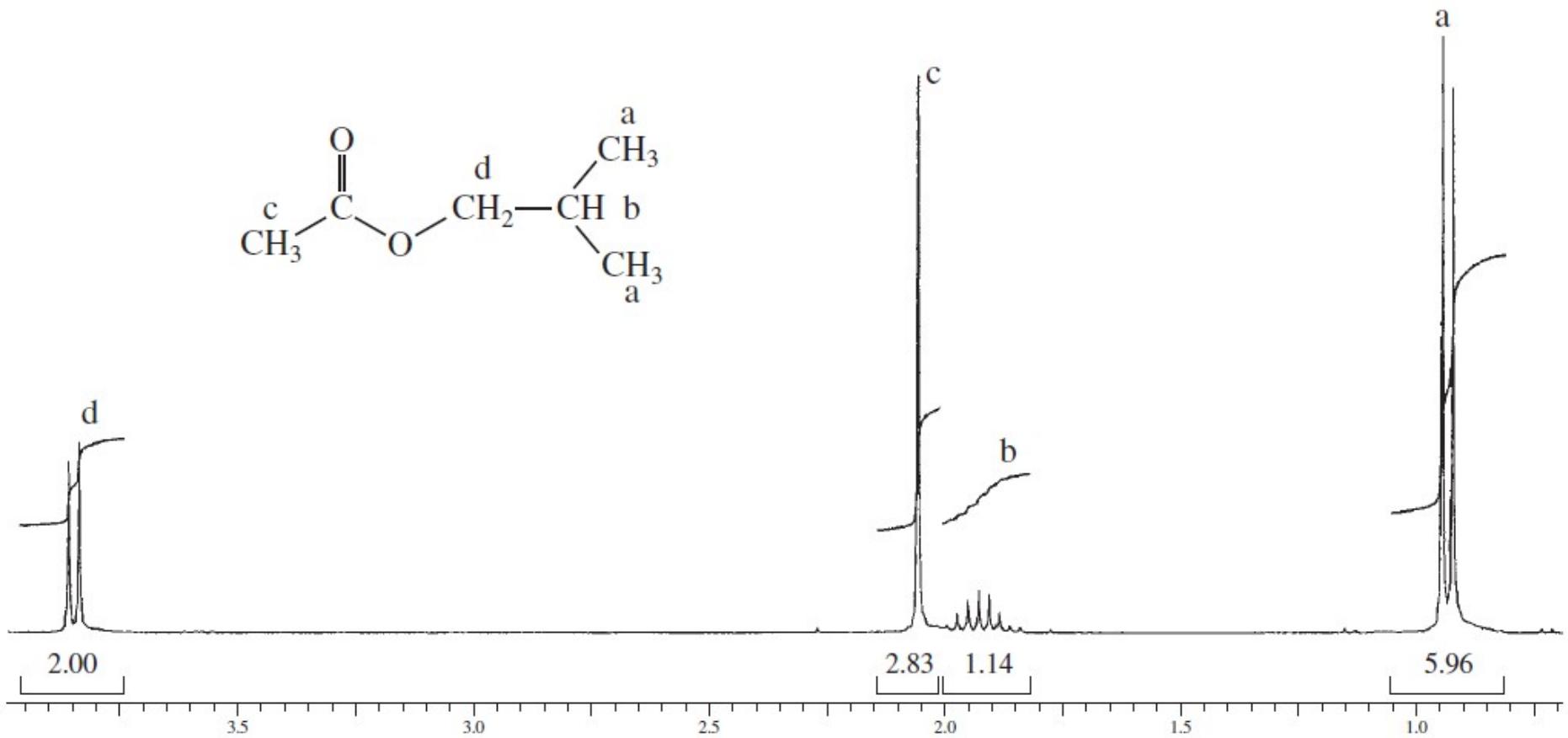
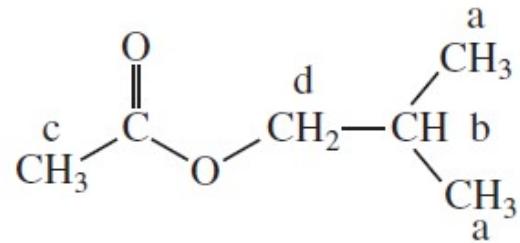
SPECTRAL ANALYSIS BOX—Esters

CHEMICAL SHIFTS



The α hydrogens in esters are deshielded by the anisotropy of the adjacent ($\text{C}=\text{O}$) group.

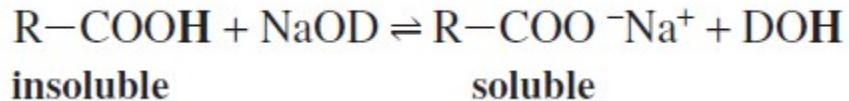
Hydrogens on the carbon attached to the single-bonded oxygen are deshielded due to the electronegativity of oxygen.

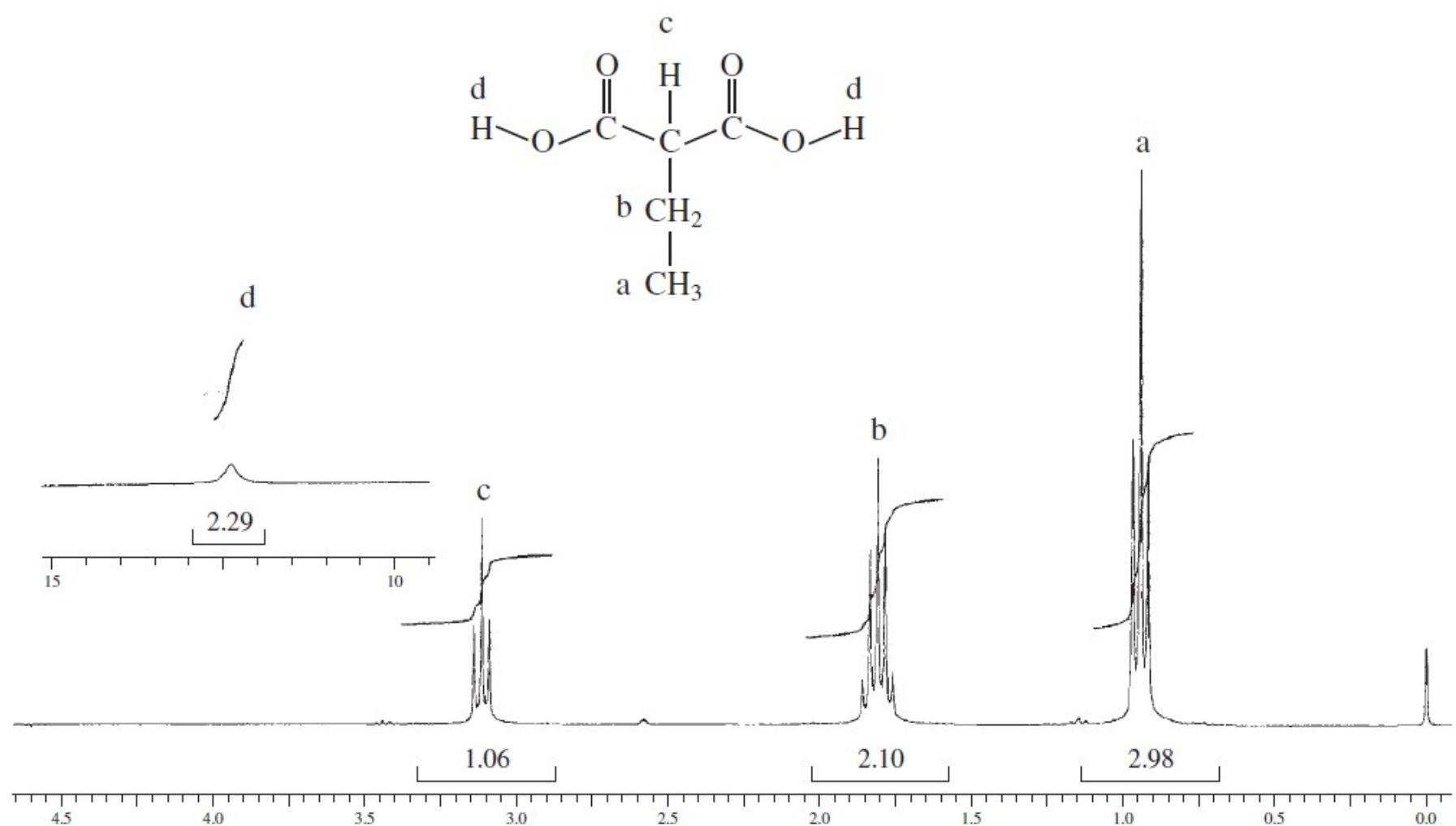


SPECTRAL ANALYSIS BOX—Carboxylic Acids

CHEMICAL SHIFTS

R-COOH	11.0–12.0 ppm	This hydrogen is deshielded by the attached oxygen, and it is highly acidic. This (usually broad) signal is a very characteristic peak for carboxylic acids. Note in some cases, however, due to factors discussed below, that this peak may be so broadened as to disappear into the baseline.
-CH-COOH	2.1–2.5 ppm	Hydrogens adjacent to the carbonyl group are slightly deshielded.





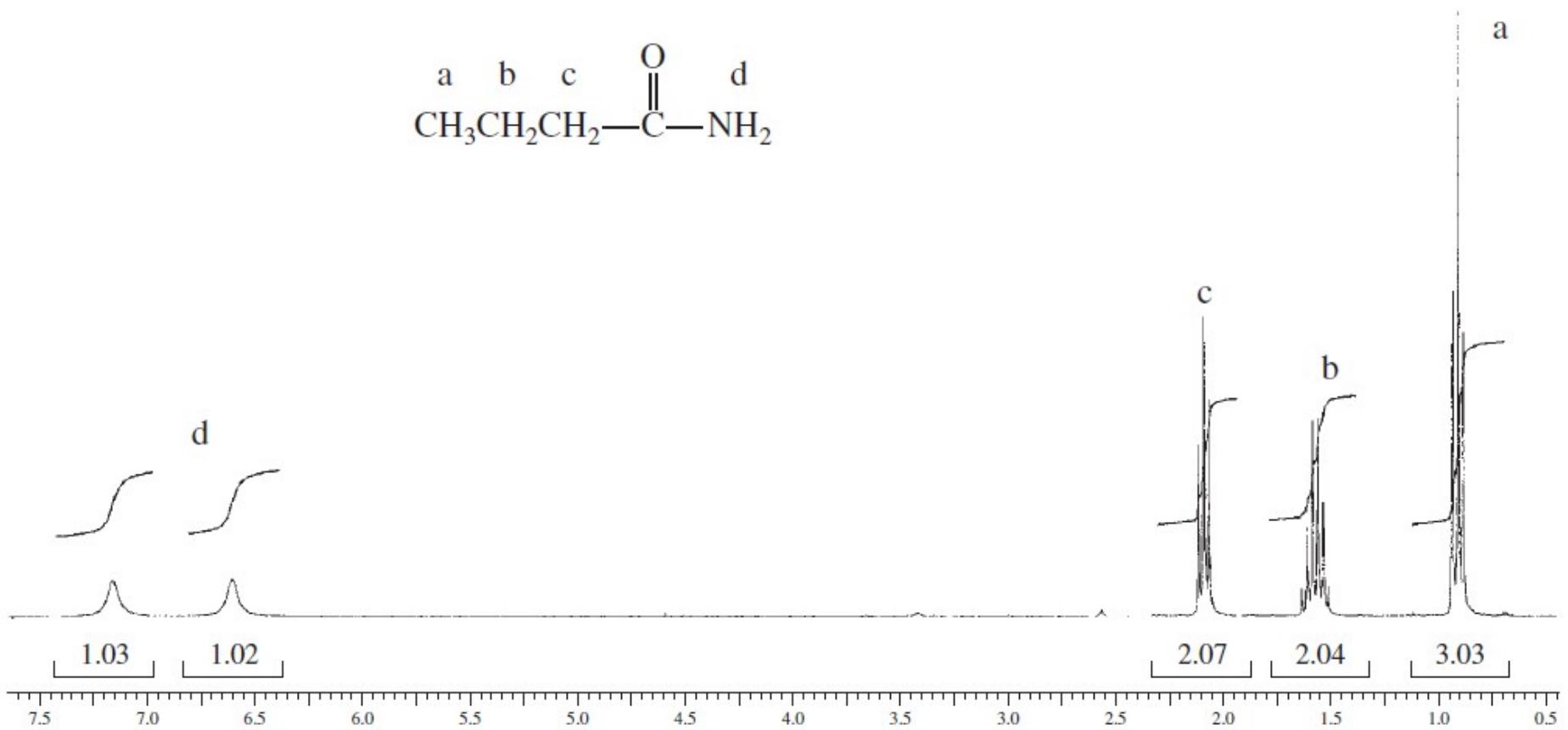
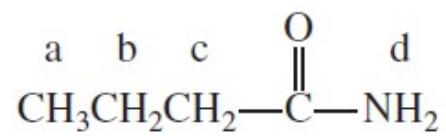
SPECTRAL ANALYSIS BOX—Amides

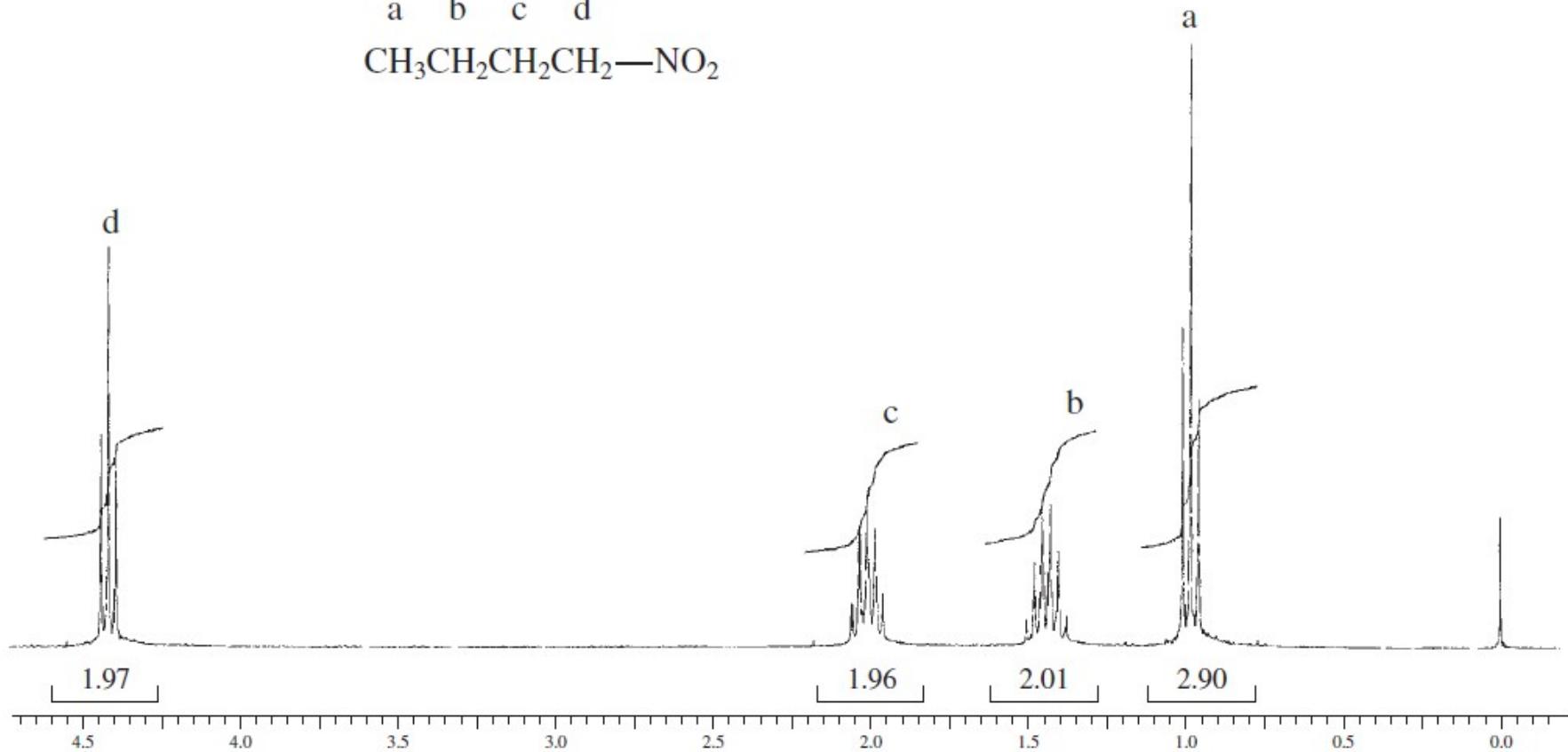
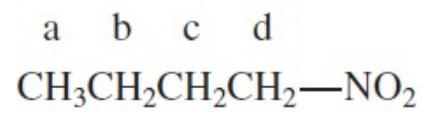
CHEMICAL SHIFTS

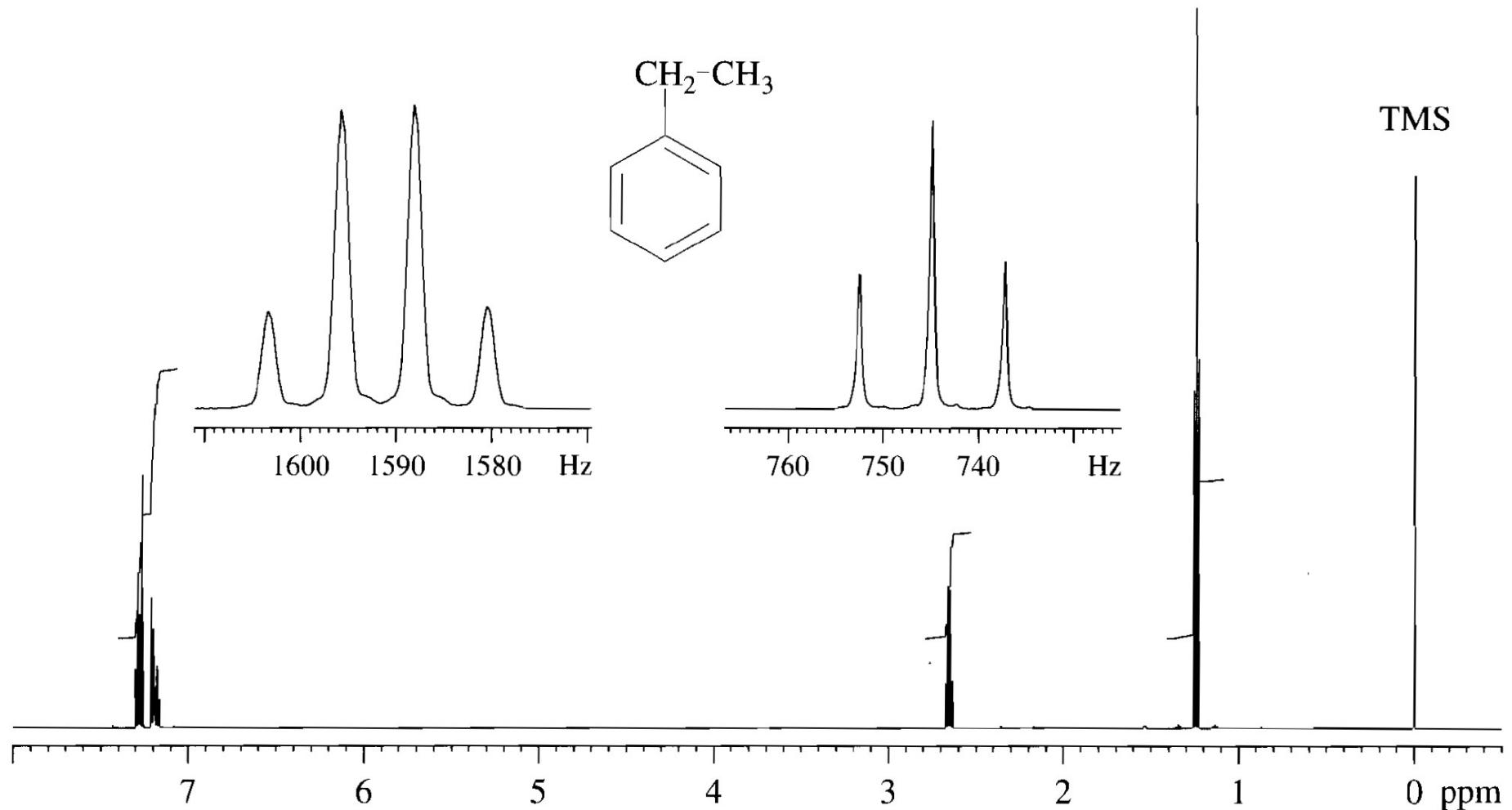
$\text{R}(\text{CO})-\text{N}-\text{H}$	5.0–9.0 ppm	Hydrogens attached to an amide nitrogen are variable in chemical shift, the value being dependent on the temperature, concentration, and solvent.
$-\text{CH}-\text{CONH}-$	2.1–2.5 ppm	The α hydrogens in amides absorb in the same range as other acyl (next to $\text{C}=\text{O}$) hydrogens. They are slightly deshielded by the carbonyl group.
$\text{R}(\text{CO})-\text{N}-\text{CH}_3$	2.2–2.9 ppm	Hydrogens on the carbon next to the nitrogen of an amide are slightly deshielded by the electronegativity of the attached nitrogen.

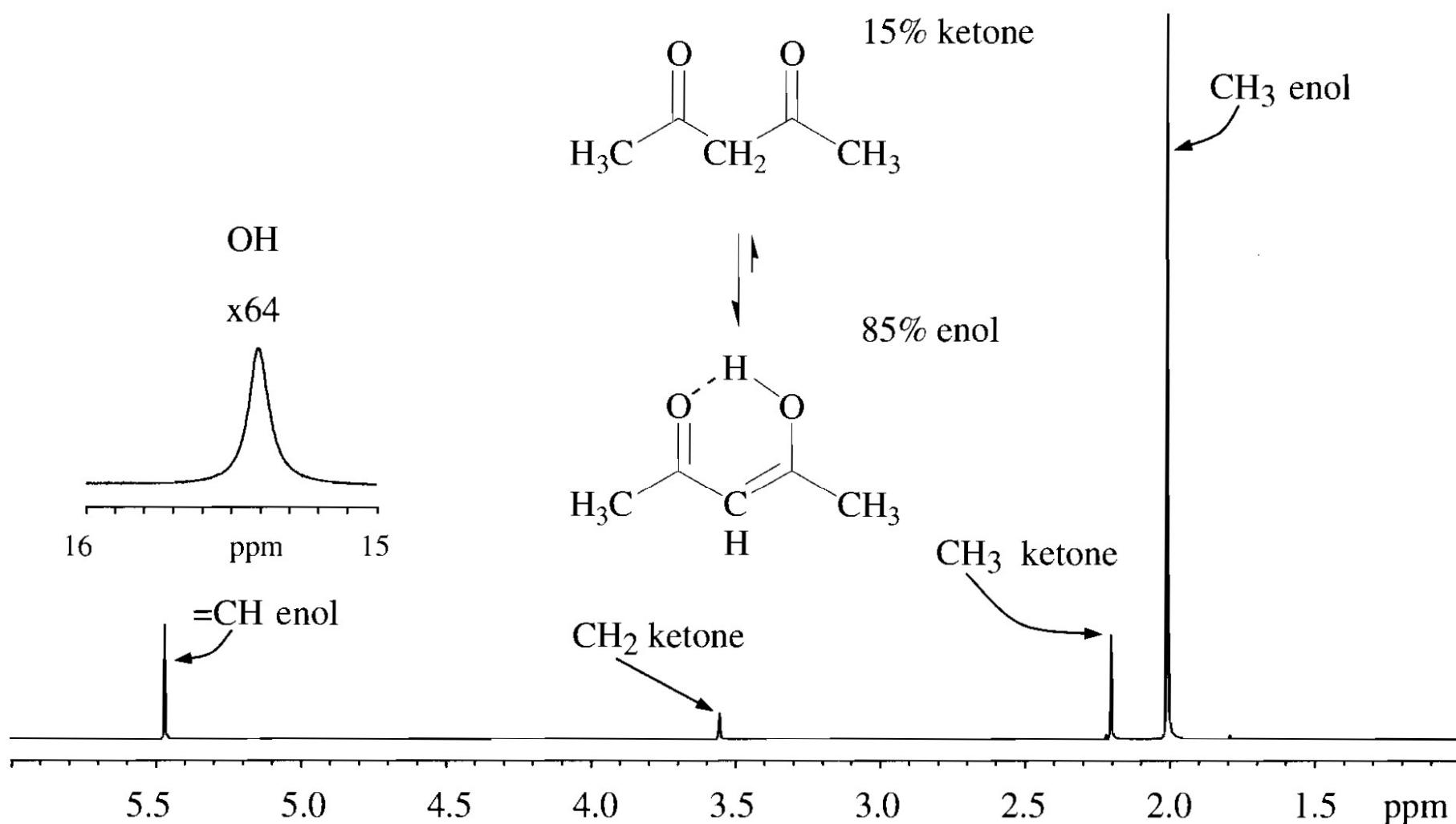
COUPLING BEHAVIOR

$-\text{N}-\text{H}$	$^1J \approx 50 \text{ Hz}$	In cases in which this coupling is seen (rare), it is quite large, typically 50 Hz or more. In most cases, either the quadrupole moment of the nitrogen atom or chemical exchange decouples this interaction.
$-\text{N}-\text{CH}-$	$^2J \approx 0 \text{ Hz}$	Usually not seen for the same reasons stated above.
$-\overset{\text{H}}{\underset{ }{\text{N}}}-\text{CH}-$	$^3J \approx 0-7 \text{ Hz}$	Exchange of the amide NH is slower than in amines, and splitting of the adjacent CH is observed even if the NH is broadened.



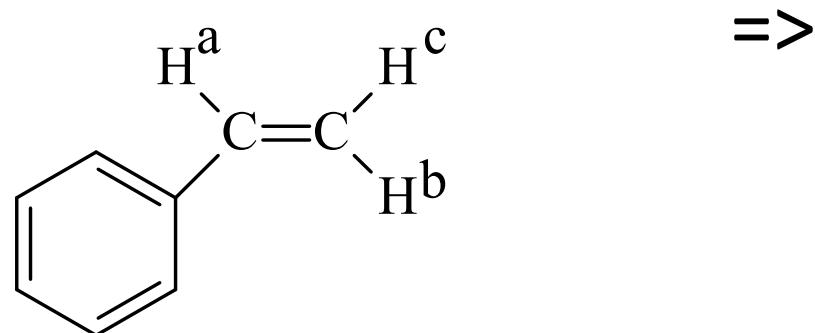




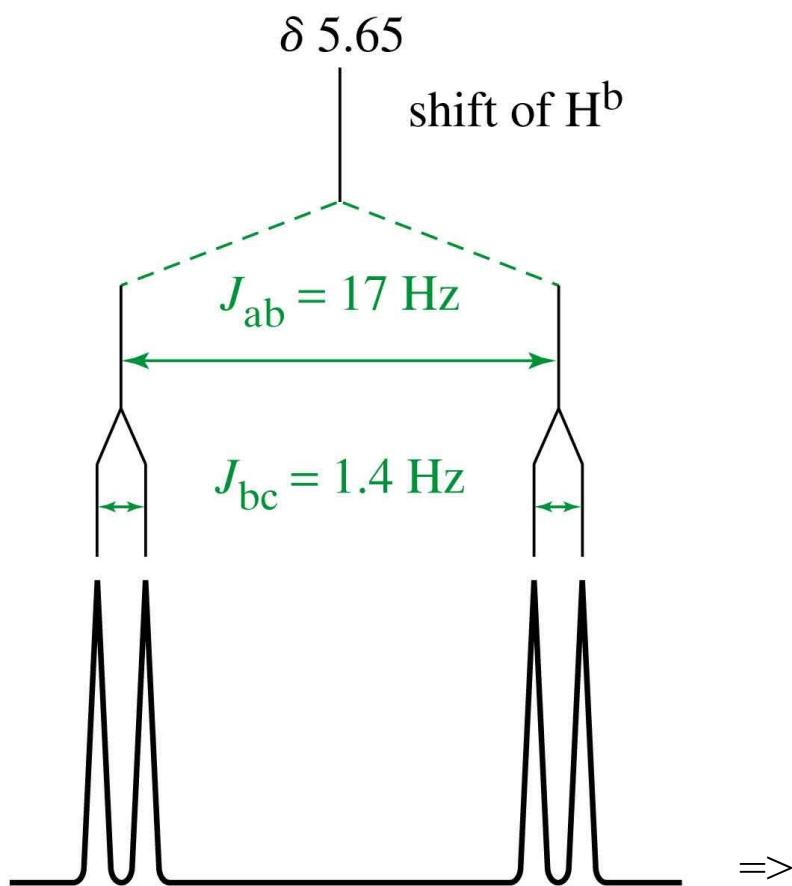
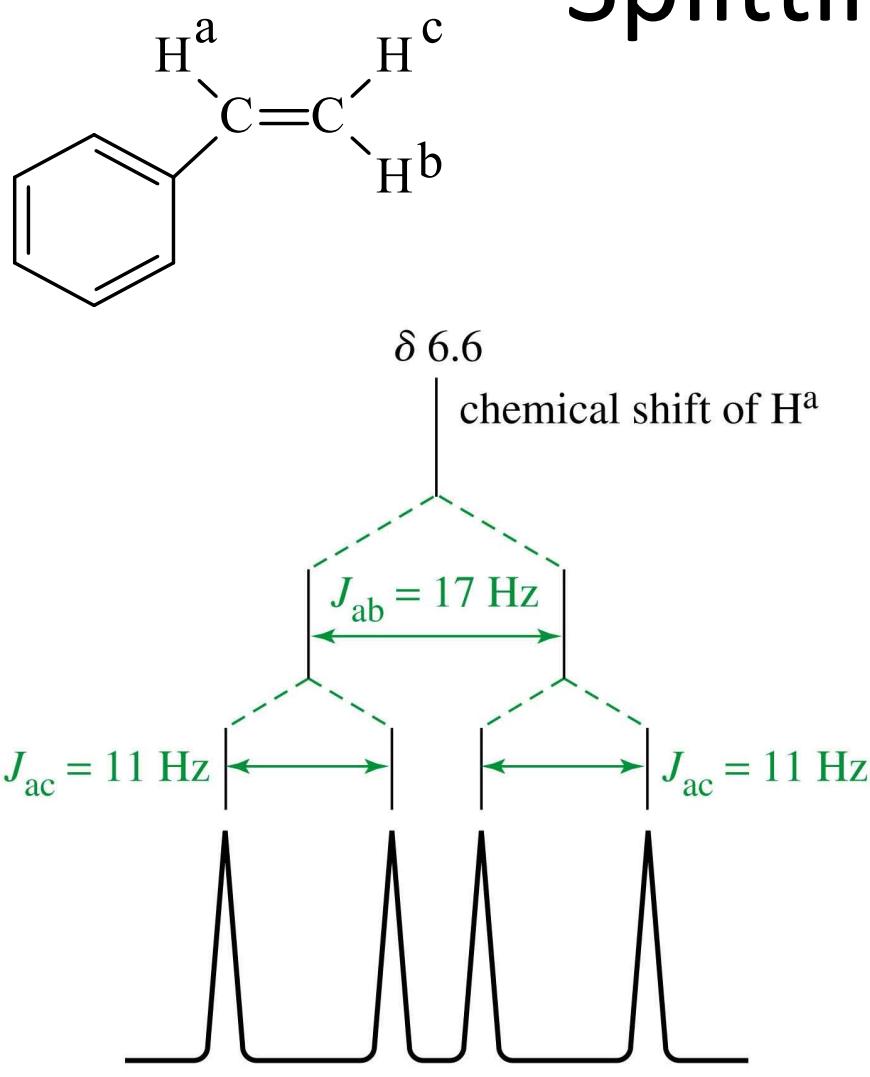


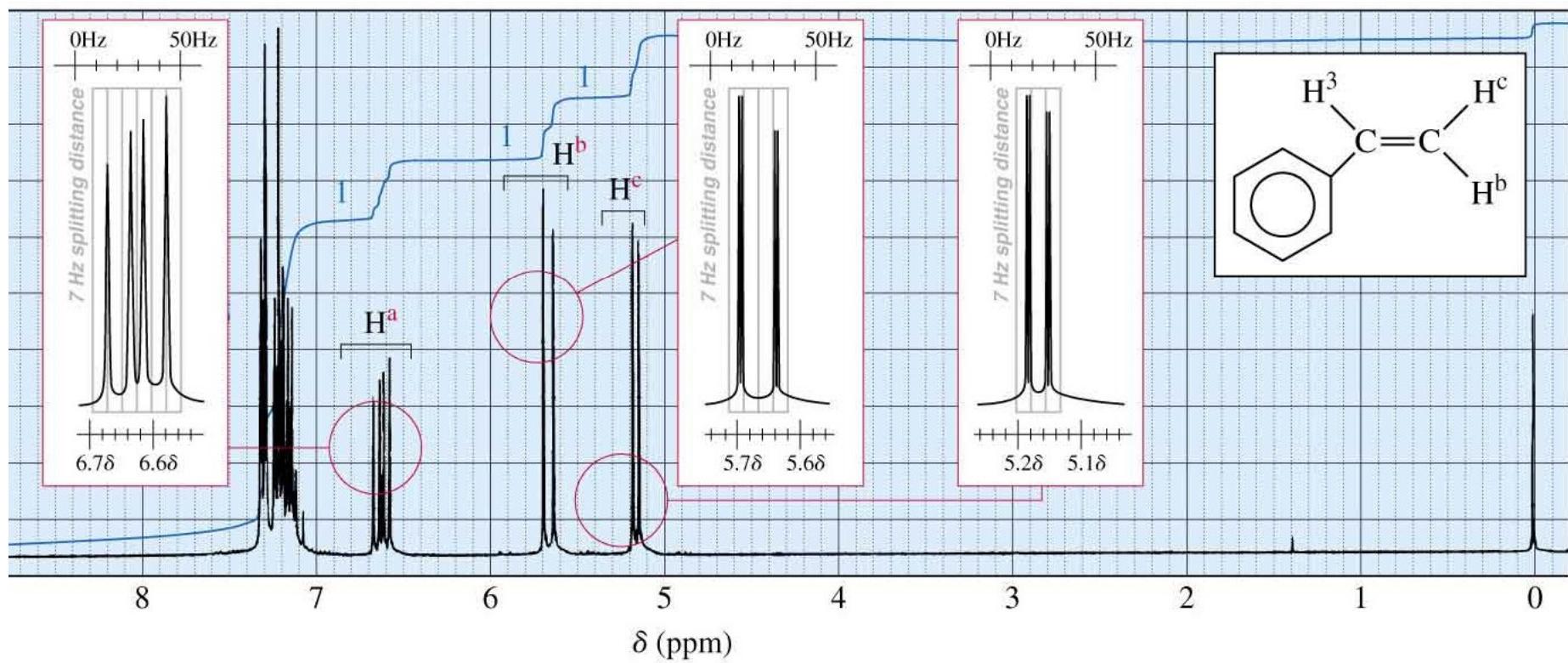
Complex Splitting

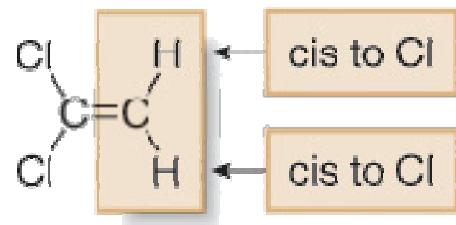
- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- Example: H^a of styrene which is split by an adjacent H *trans* to it ($J = 17$ Hz) and an adjacent H *cis* to it ($J = 11$ Hz).



Splitting Tree

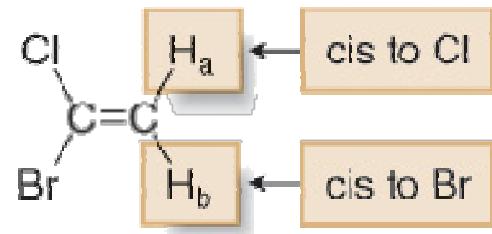






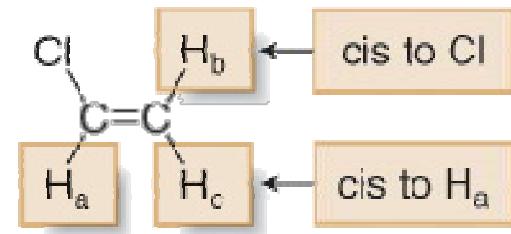
1,1-dichloroethylene

1 type of H
1 NMR signal



1-bromo-1-chloroethylene

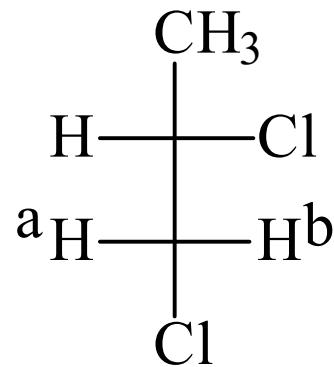
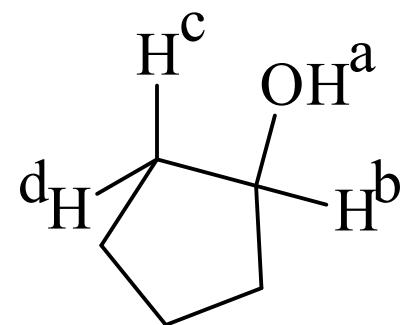
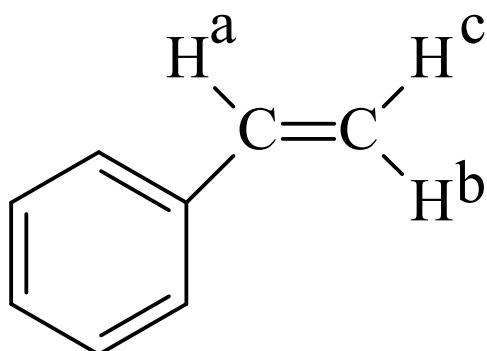
2 types of H's
2 NMR signals



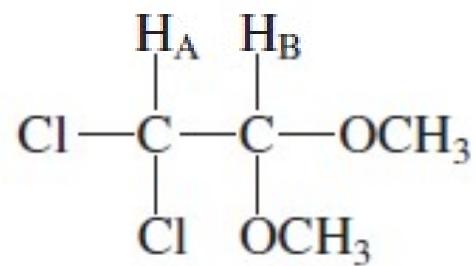
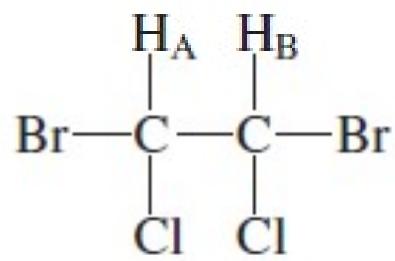
chloroethylene

3 types of H's
3 NMR signals

Some Nonequivalent Protons

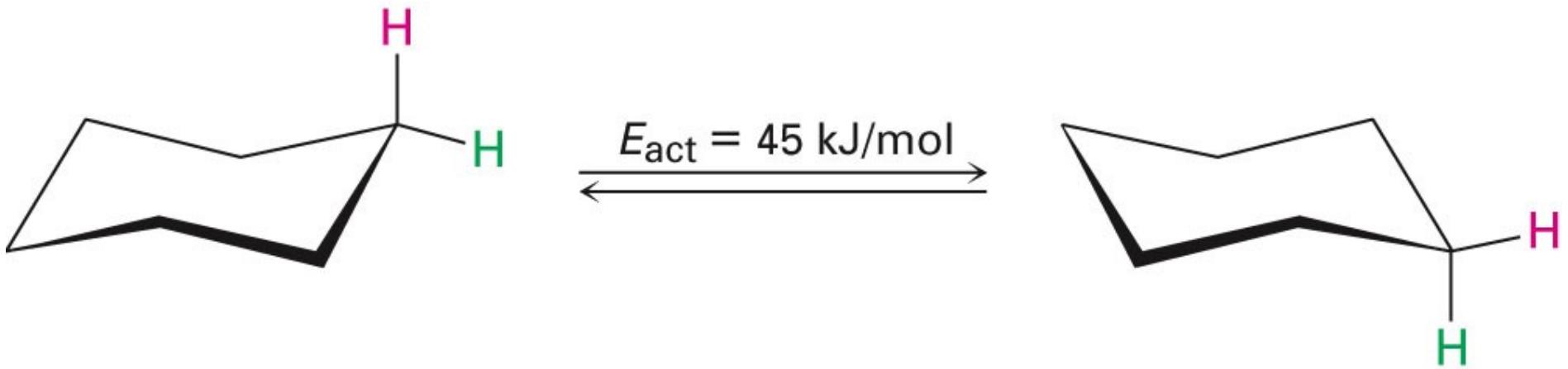


What is the expected difference in ^1H NMR ?

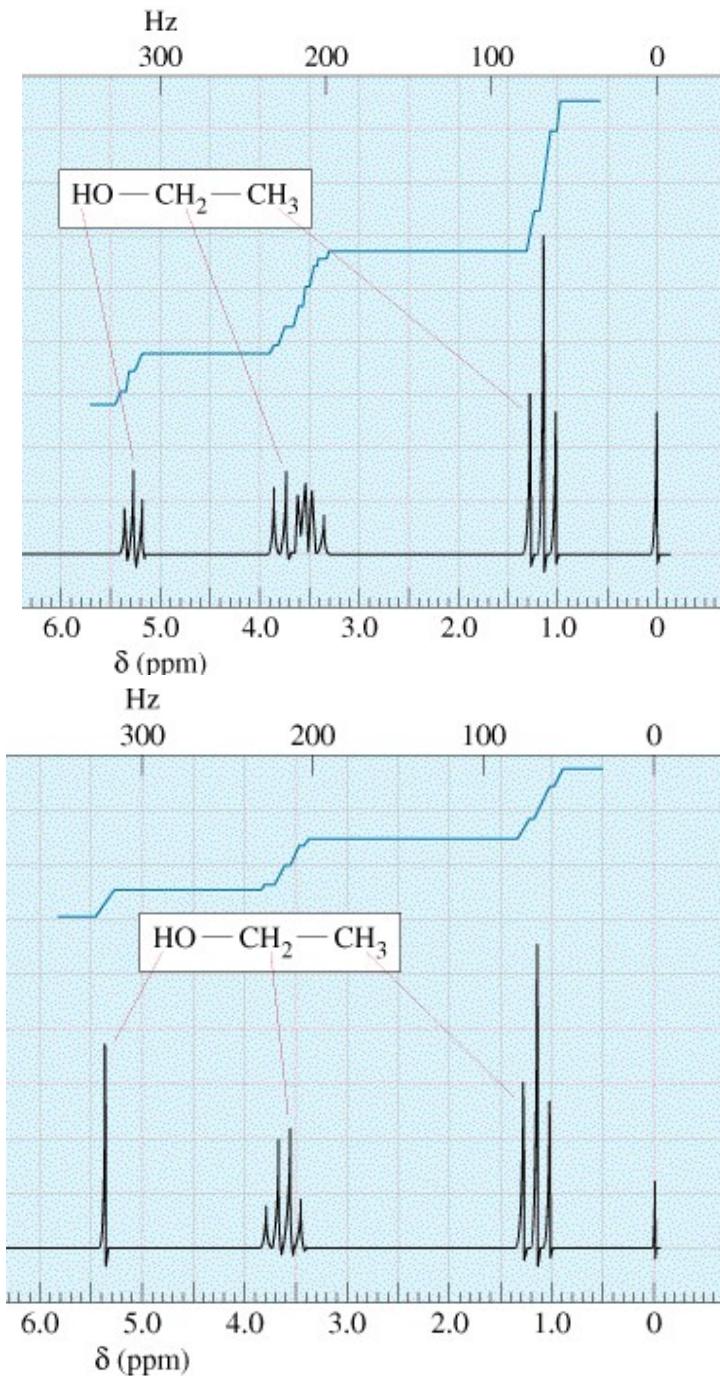


Time Dependence

- Molecules are tumbling relative to the magnetic field, so NMR is an averaged spectrum of all the orientations.
- Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal.
- Proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule.



^1H NMR: 1 peak at 25 °C
2 peaks at –90 °C



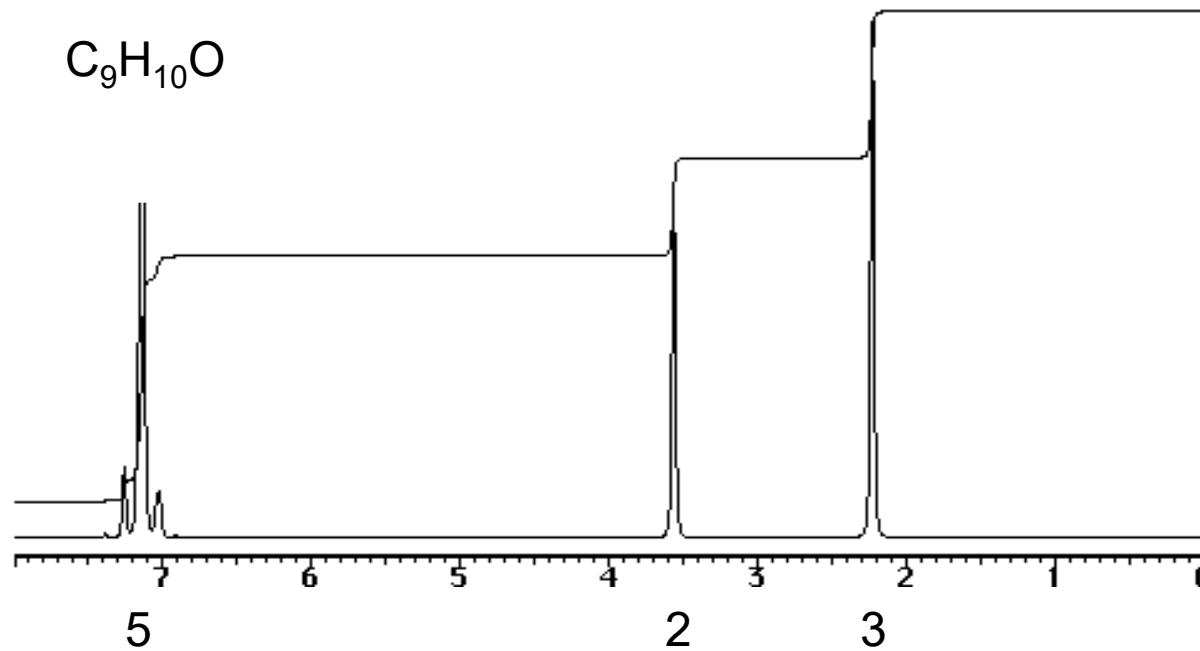
Hydroxyl Proton

- Ultrapure samples of ethanol show splitting.
- Ethanol with a small amount of acidic or basic impurities will not show splitting.

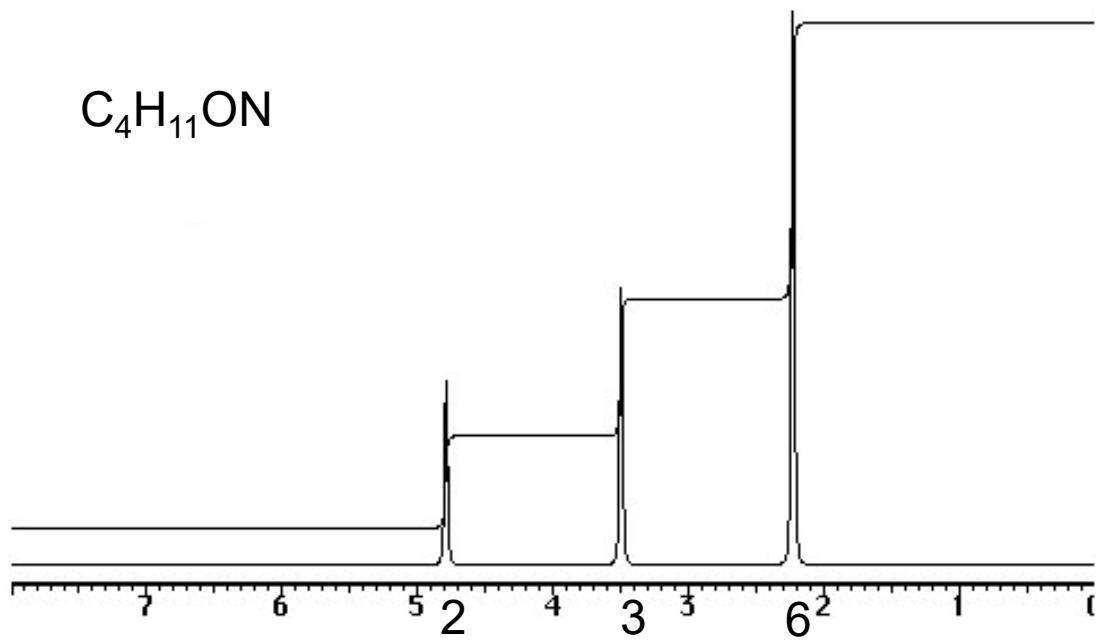
=>

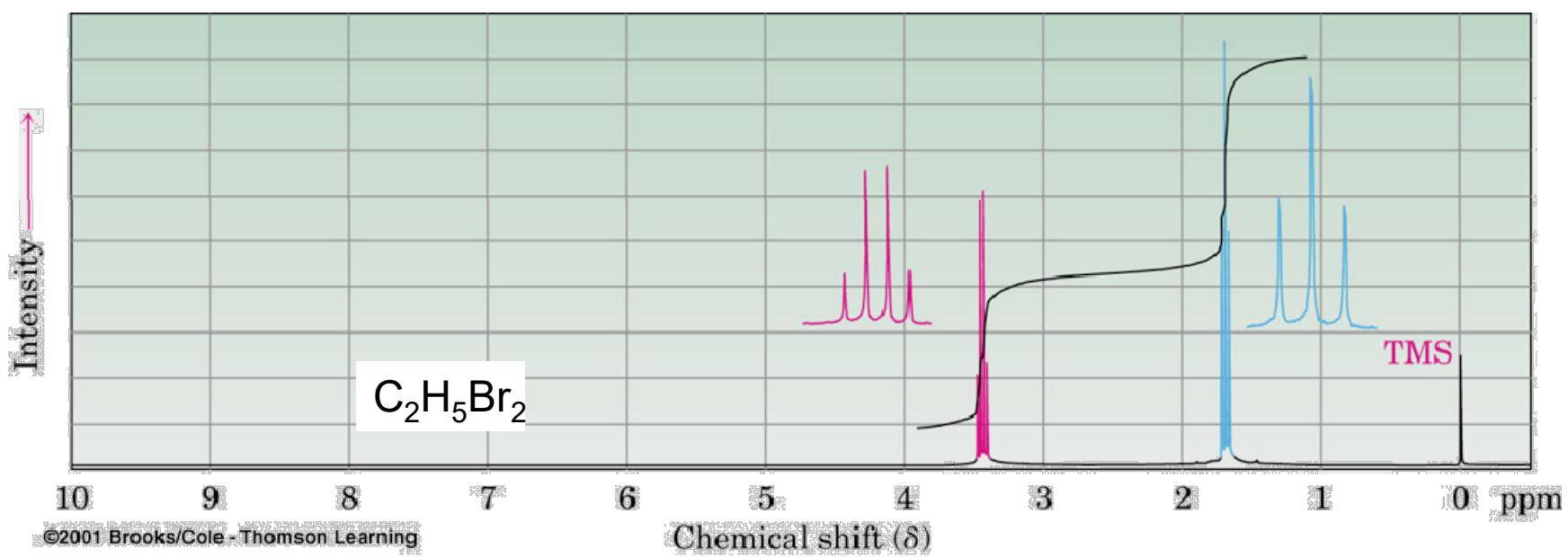
- Four different features of a ^1H NMR spectrum provide information about a compound's structure:
 - a. Number of signals
 - b. Position of signals
 - c. Intensity of signals.
 - d. Spin-spin splitting of signals.

$C_9H_{10}O$



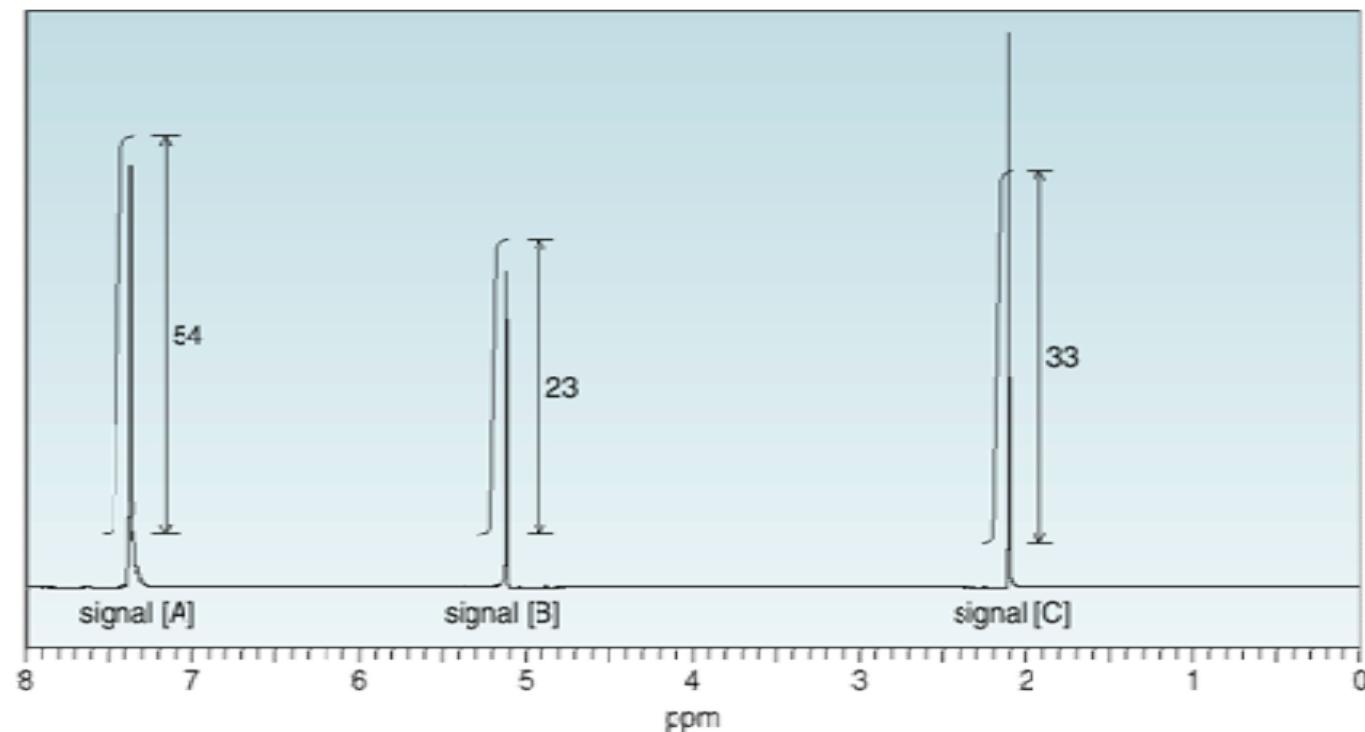
$C_4H_{11}ON$





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Example A compound of molecular formula $C_9H_{10}O_2$ gives the following integrated 1H NMR spectrum. How many protons give rise to each signal?

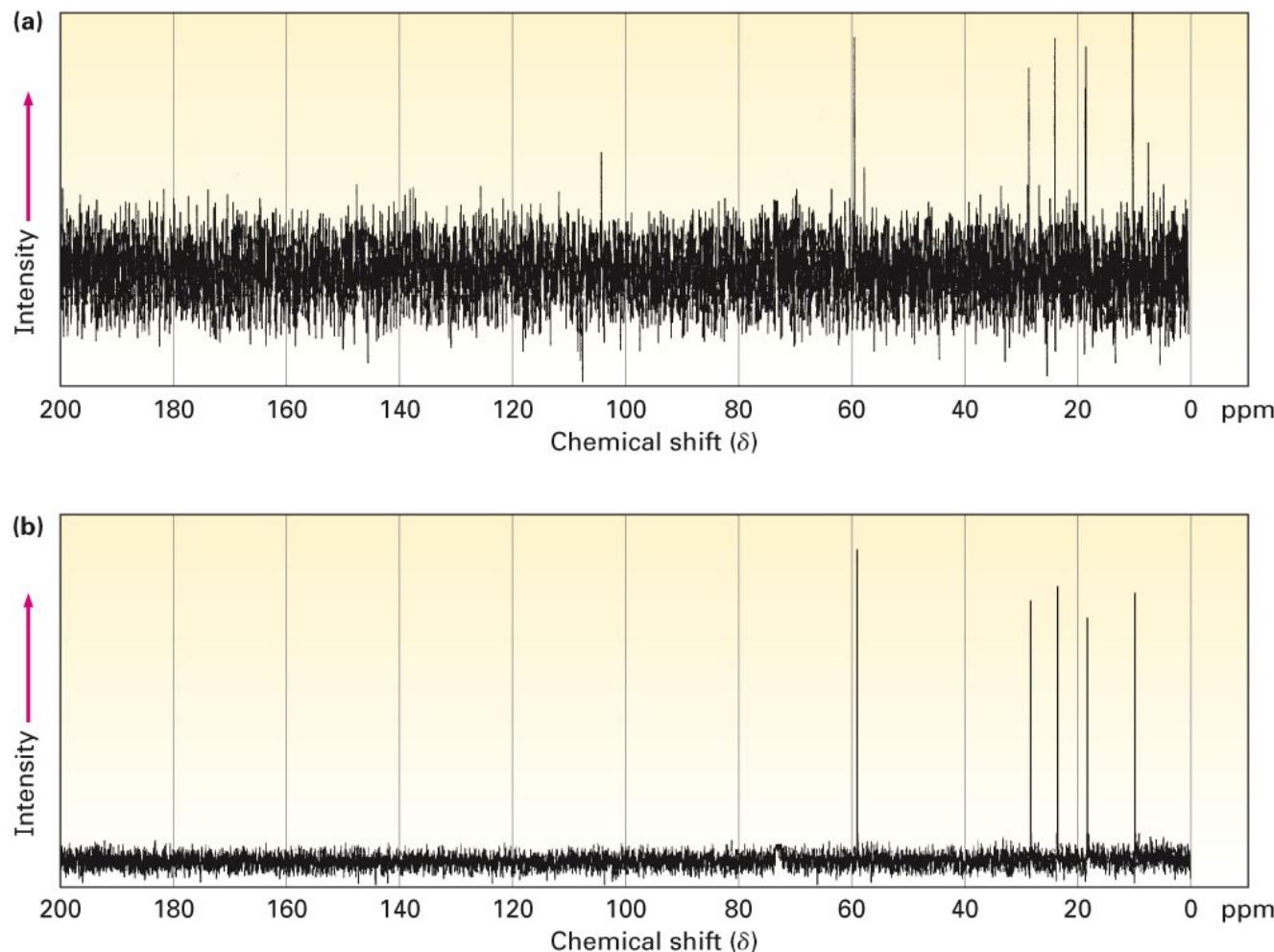


Differences in ^{13}C Technique

- Resonance frequency is \sim one-fourth, 15.1 MHz instead of 60 MHz.
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.

=>

^{13}C NMR Spectroscopy: Signal Averaging and FT-NMR



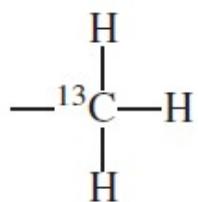
Carbon-13 NMR spectra of pentan-1-ol. Spectrum (a) is a single run, showing background noise. Spectrum (b) is an average of 200 runs

Spin-Spin Splitting

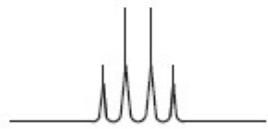
- It is unlikely that a ^{13}C would be adjacent to another ^{13}C , so splitting by carbon is negligible.
- ^{13}C will magnetically couple with attached protons and adjacent protons.
- These complex splitting patterns are difficult to interpret.

=>

3 protons

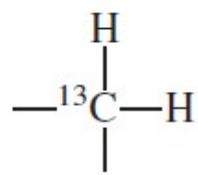


$$\begin{aligned}n + 1 &= 3 + 1 \\&= 4\end{aligned}$$

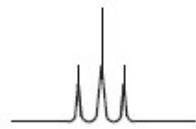


Methyl
carbon

2 protons

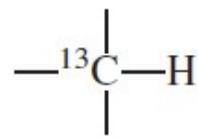


$$n + 1 = 3$$

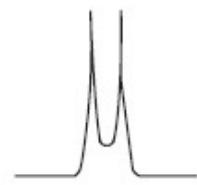


Methylene
carbon

1 proton

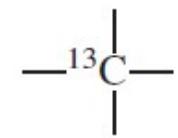


$$n + 1 = 2$$



Methine
carbon

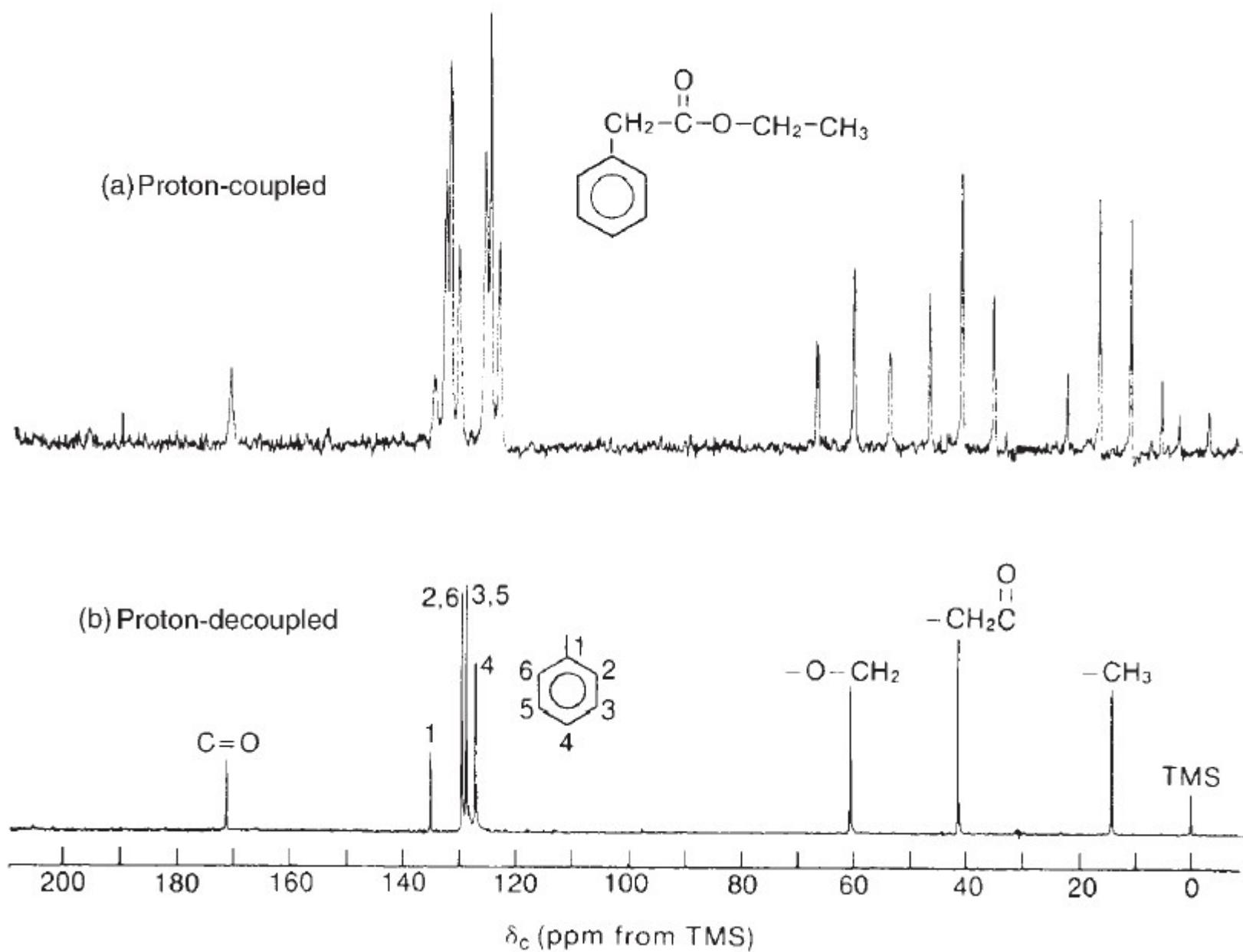
0 protons



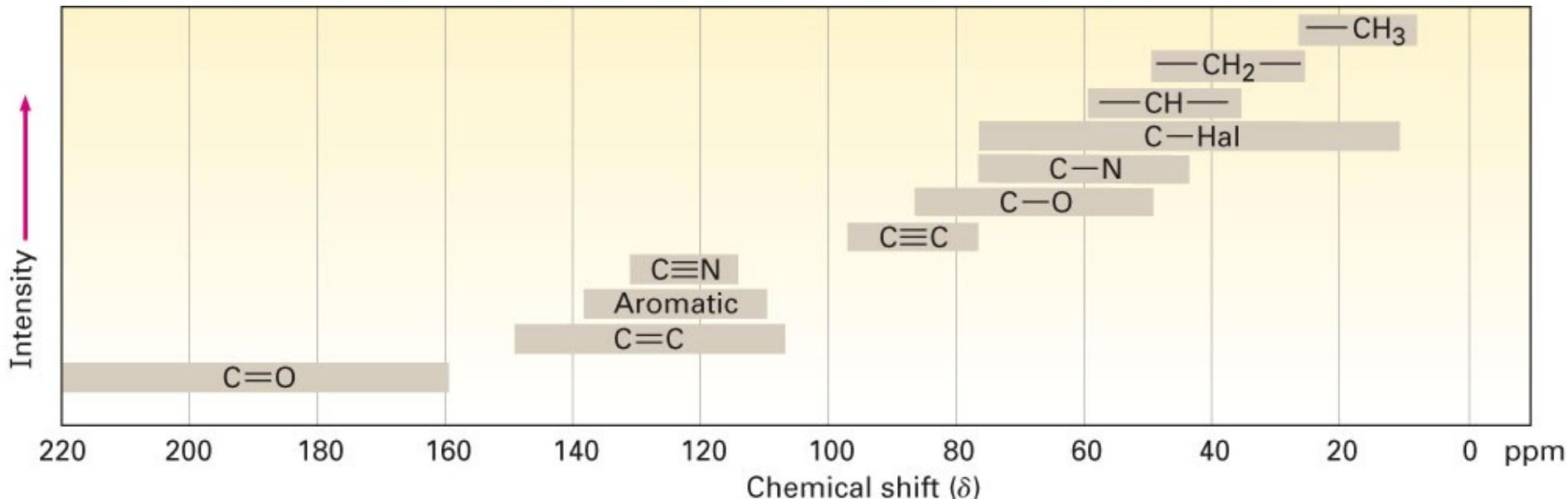
$$n + 1 = 1$$



Quaternary
carbon



11.5 Characteristics of ^{13}C NMR Spectroscopy



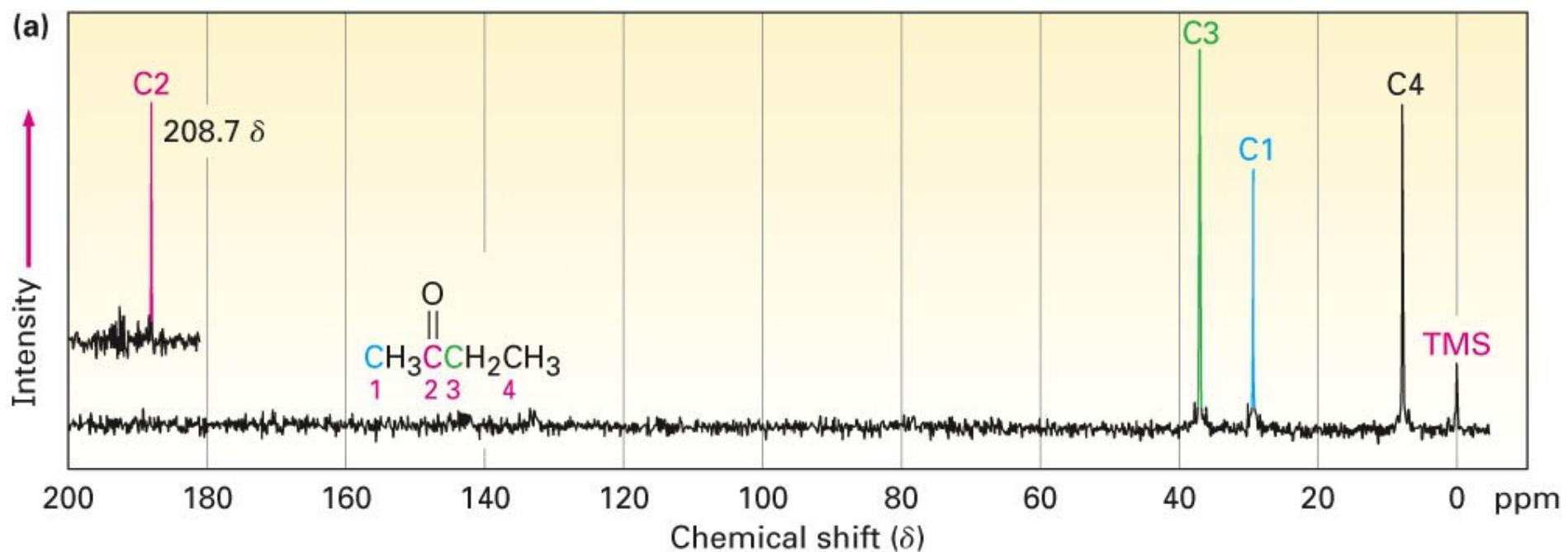
Factors that affect chemical shifts:

1. Chemical shift affected by nearby electronegative atoms
 - Carbons bonded to electronegative atoms absorb downfield from typical alkane carbons
2. Hybridization of carbon atoms
 - sp^3 -hybridized carbons generally absorb from 0 to 90 d
 - sp^2 -hybridized carbons generally absorb from 110 to 220 d
 - $\text{C}=\text{O}$ carbons absorb from 160 to 220 d

Characteristics of ^{13}C NMR Spectroscopy

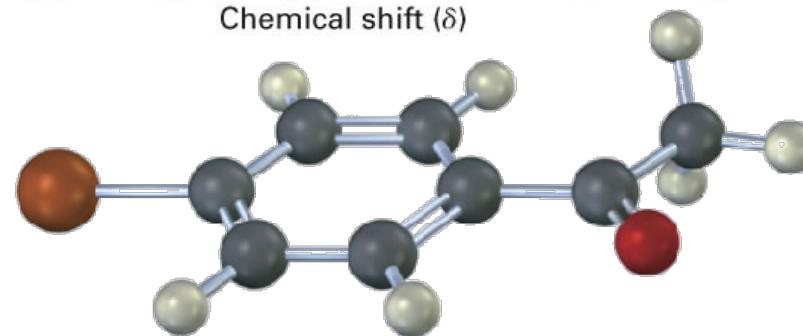
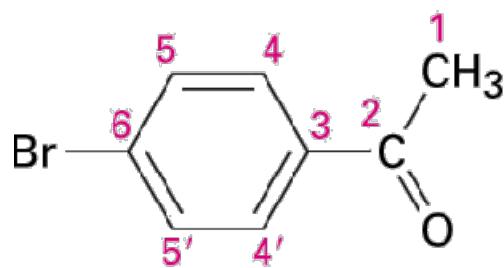
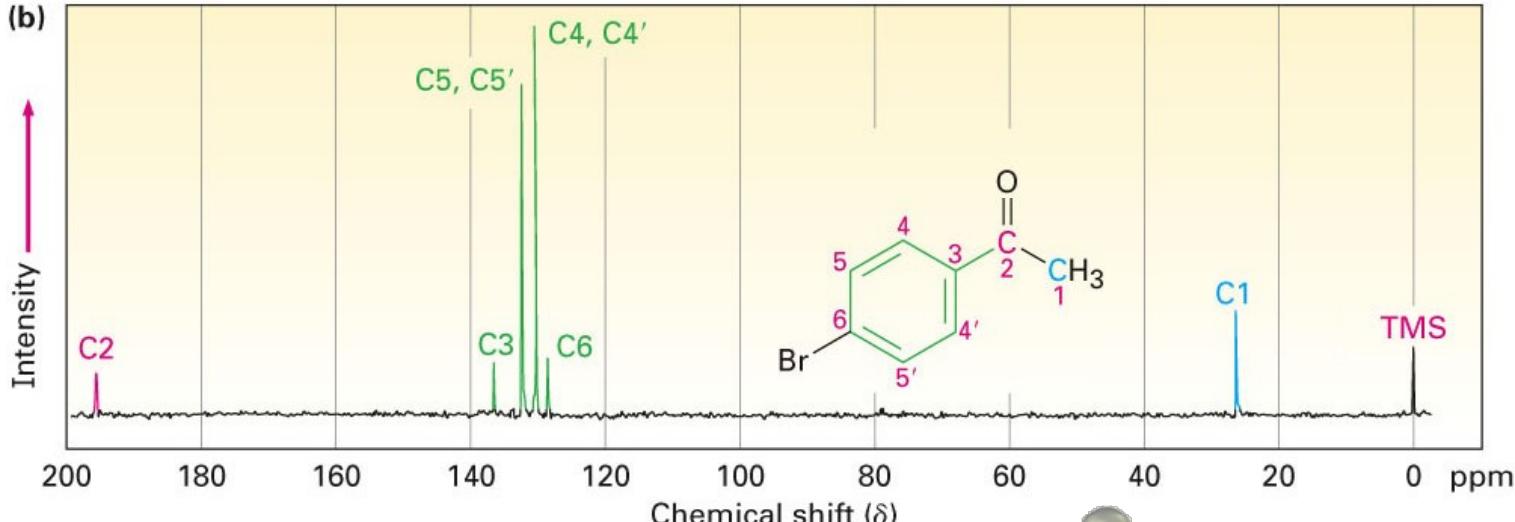
^{13}C spectrum for butan-2-one

- Butan-2-one contains 4 chemically nonequivalent carbon atoms
- Carbonyl carbons ($\text{C}=\text{O}$) are always found at the low-field end of the spectrum from 160 to 220 δ



Characteristics of ^{13}C NMR Spectroscopy

^{13}C NMR spectrum of *p*-bromoacetophenone shows only six absorptions, even though the molecule contains eight carbons. A molecular plane of symmetry makes ring carbons 4 and 4', and ring carbons 5 and 5' equivalent. Thus, six ring carbons show only four absorptions.

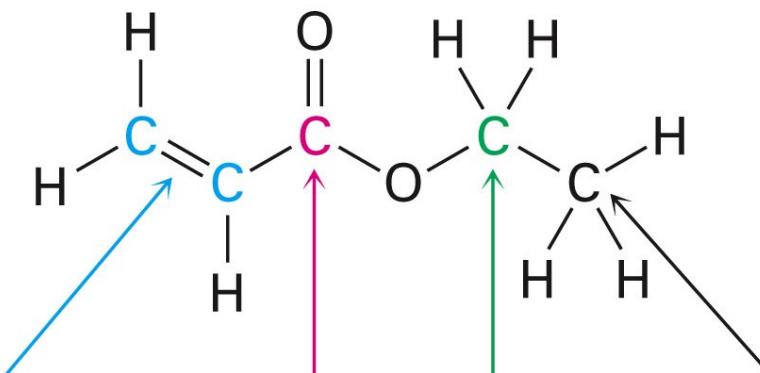


***para*-Bromoacetophenone**

At what approximate positions would you expect ethyl acrylate, $\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_2\text{CH}_3$, to show ^{13}C NMR absorptions?

Solution

- Ethyl acrylate has five distinct carbons: two different $\text{C}=\text{C}$, one $\text{C}=\text{O}$, one $\text{C}(\text{O})-\text{C}$, and one alkyl C. the likely absorptions are



- The actual absorptions are at 14.1, 60.5, 128.5, 130.3, and 166.0 δ