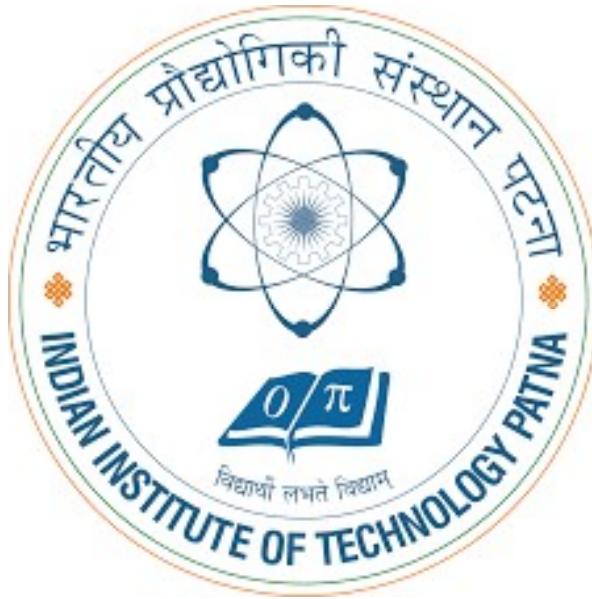
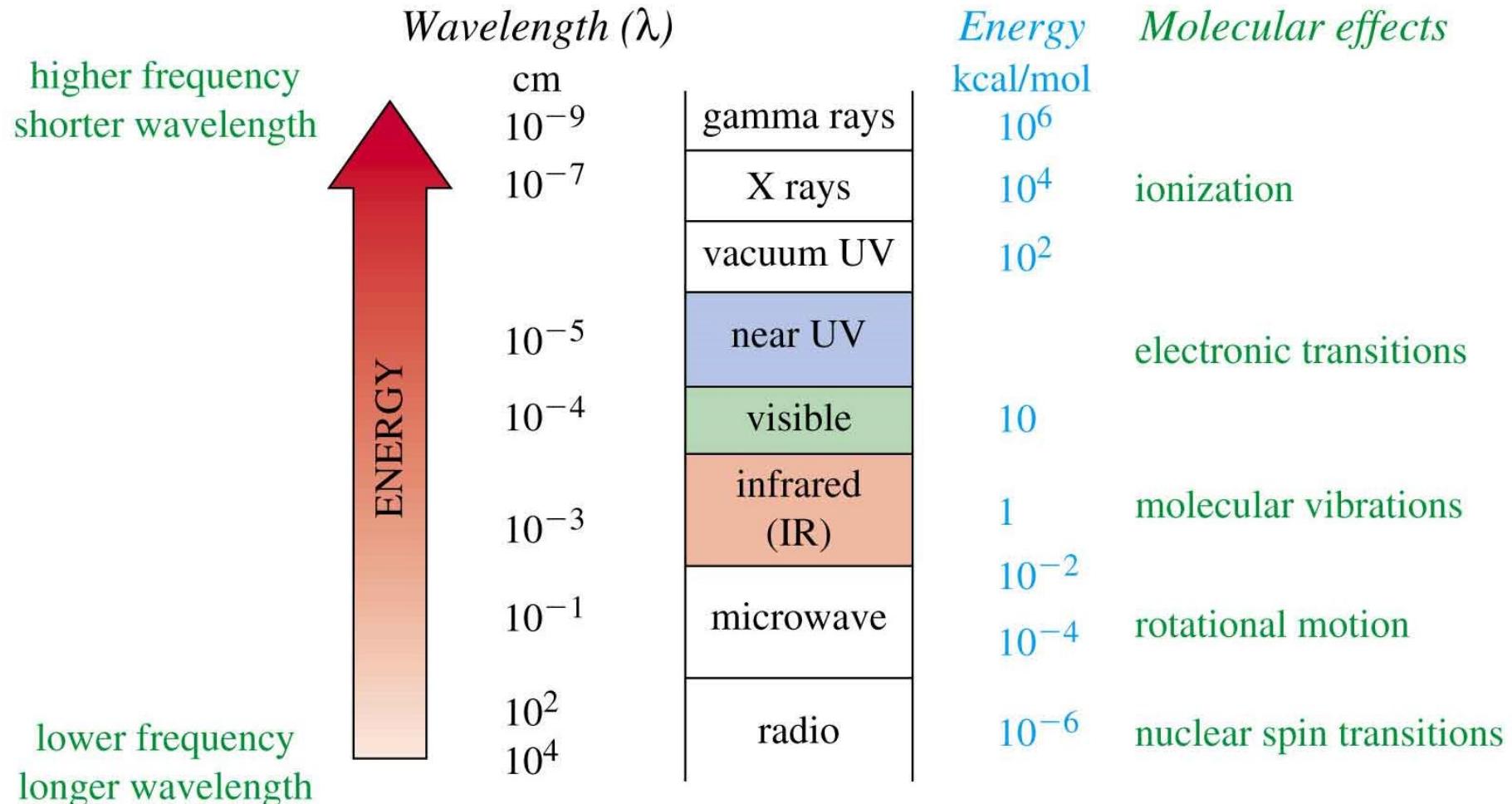


CH103: Introductory Chemistry



Modern techniques in structural elucidation
of compounds (UV – Vis, IR, NMR)

The Spectrum and Molecular Effects



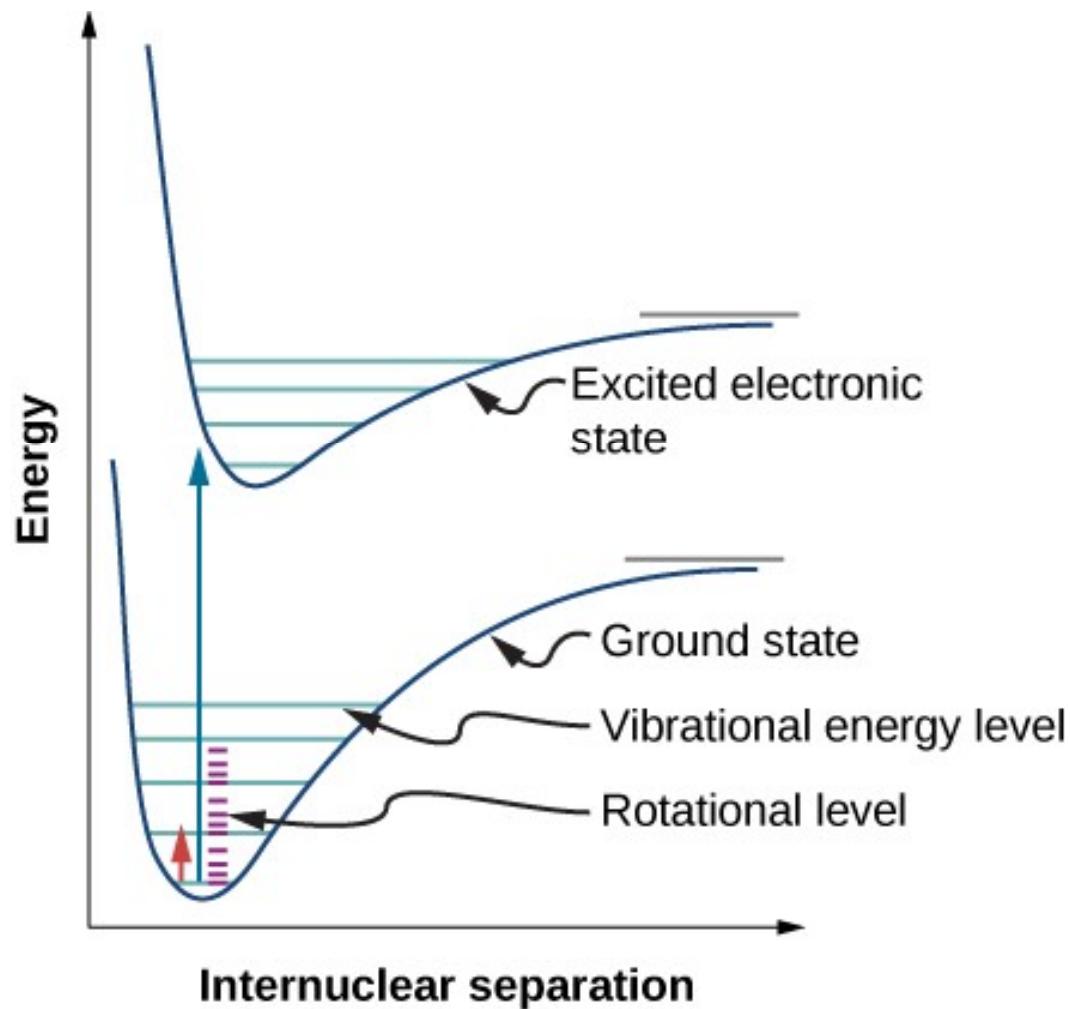
Spectroscopic Techniques and Chemistry they Probe

UV-Vis Spectroscopy	UV-vis region	bonding electrons
Atomic Absorption	UV-vis region	atomic transitions (val. e-)
FT-IR	IR/Microwave	vibrations, rotations
Raman	IR/UV	vibrations
FT-NMR	Radio waves	nuclear spin states
X-Ray Spectroscopy	X-rays	inner electrons, elemental
X-ray Crystallography	X-rays	3-D structure

Spectroscopy

- **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.

Spectroscopy



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 nm = 10^{-9} m or 10Å**

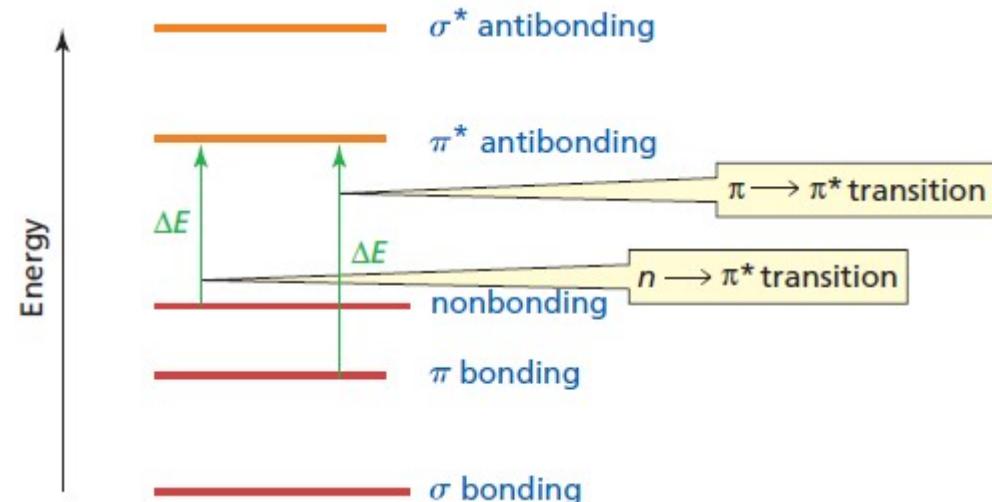
$$E = \frac{hc}{\lambda}$$

h = Planck's constant

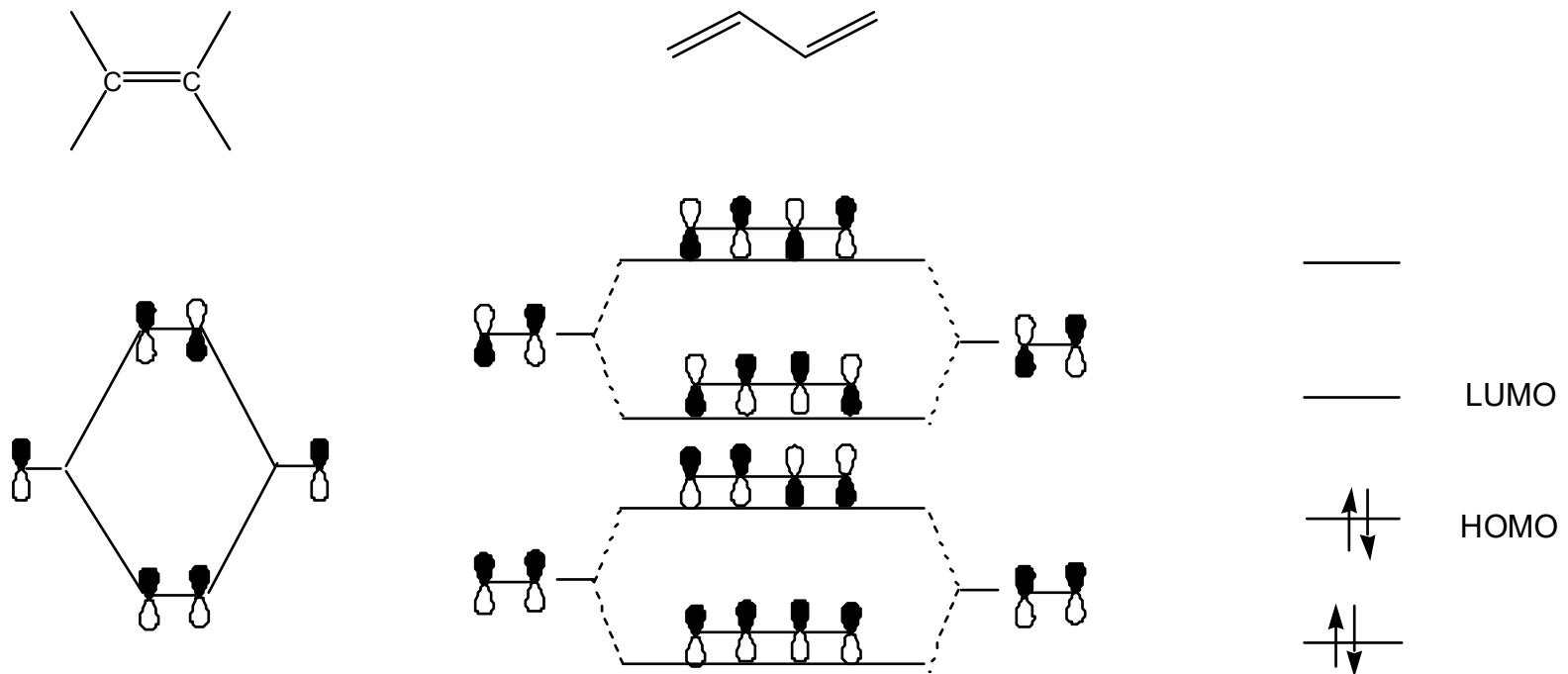
c = velocity of light

λ = wavelength

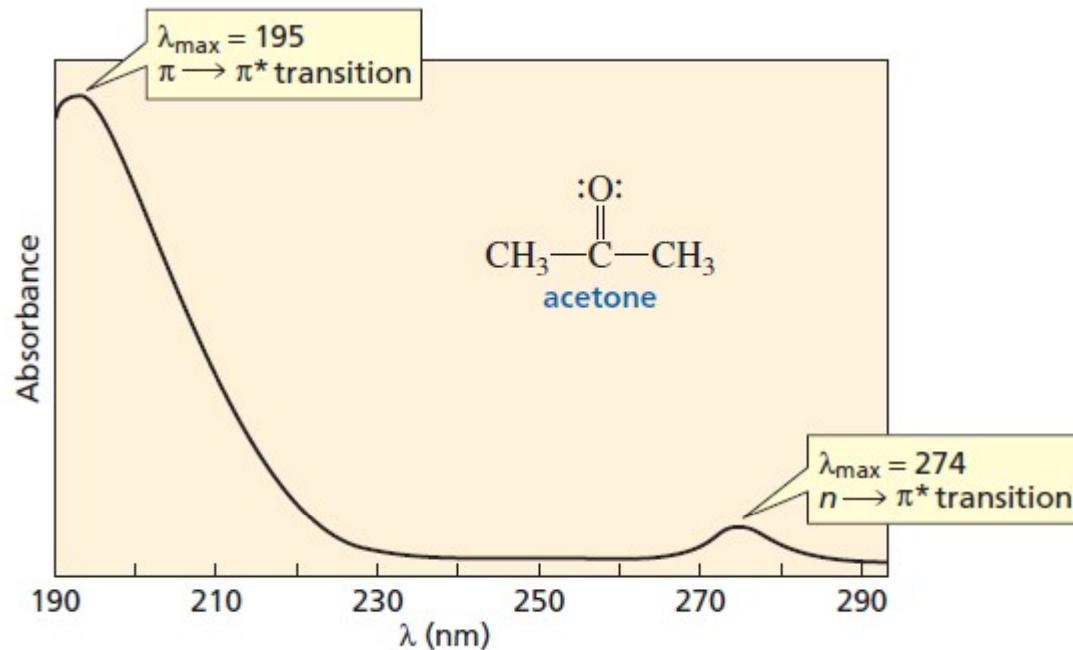
- normal electronic configuration of a molecule is known as its **ground state**
- When a molecule absorbs light of an appropriate wavelength and an electron is promoted to a higher energy molecular orbital, the molecule is then in an **excited state**.
- an electronic transition is the promotion of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



HOMO-LUMO



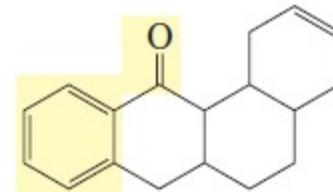
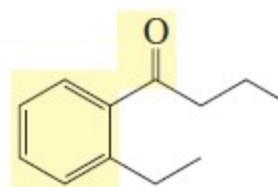
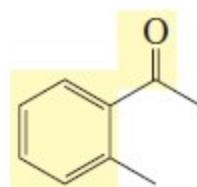
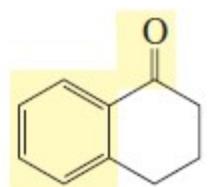
UV-Visible Spectroscopy



- 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

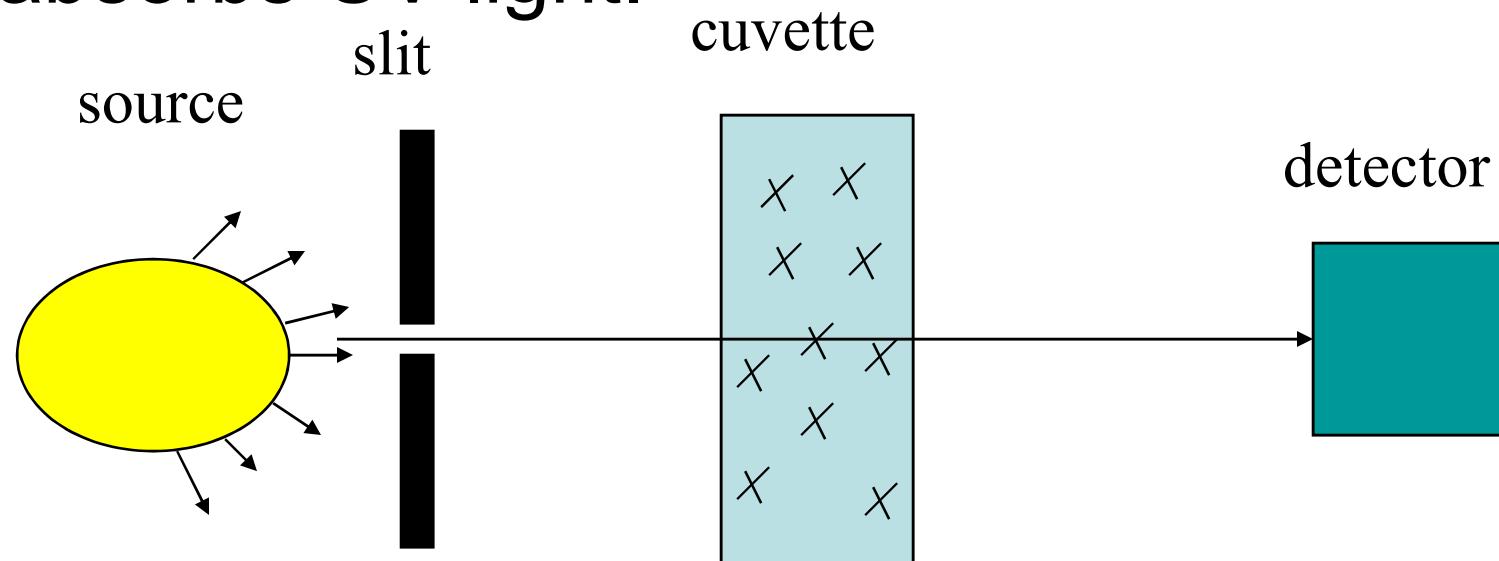
l = length of the light path through the sample, in centimeters

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.

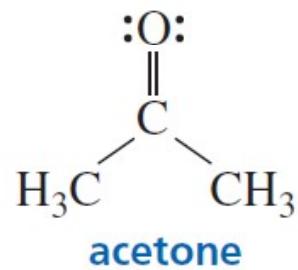
UV-Visible Spectroscopy

- 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.

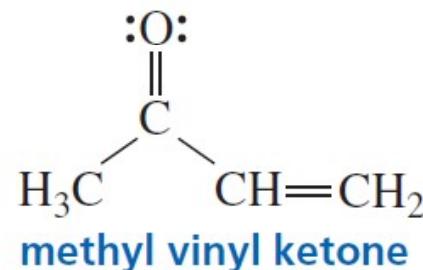


UV-Vis and conjugated double bonds

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



acetone



methyl vinyl ketone

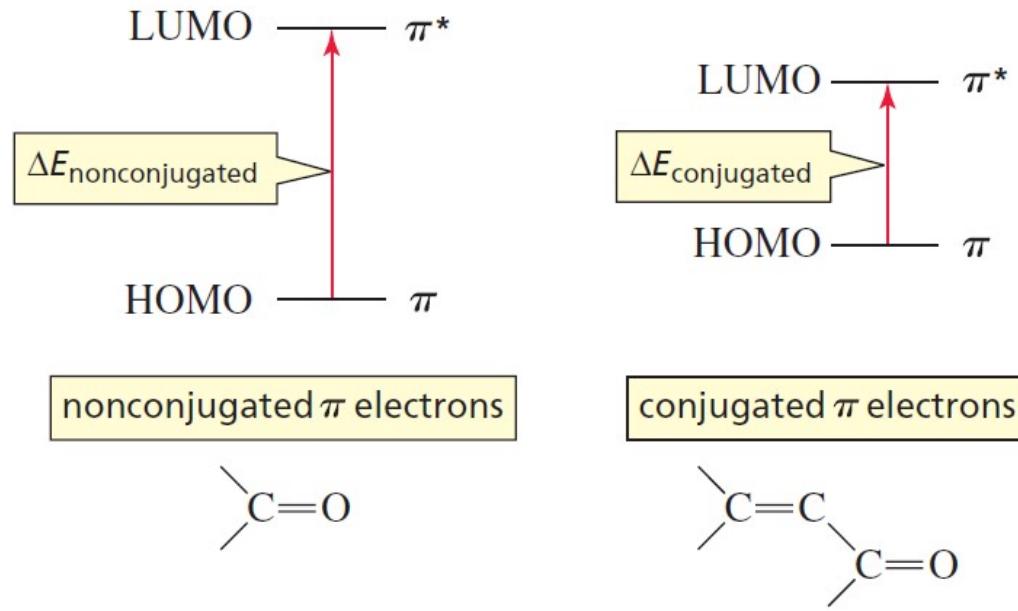
$n \longrightarrow \pi^*$ $\lambda_{\text{max}} = 274 \text{ nm } (\varepsilon_{\text{max}} = 13.6)$

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

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

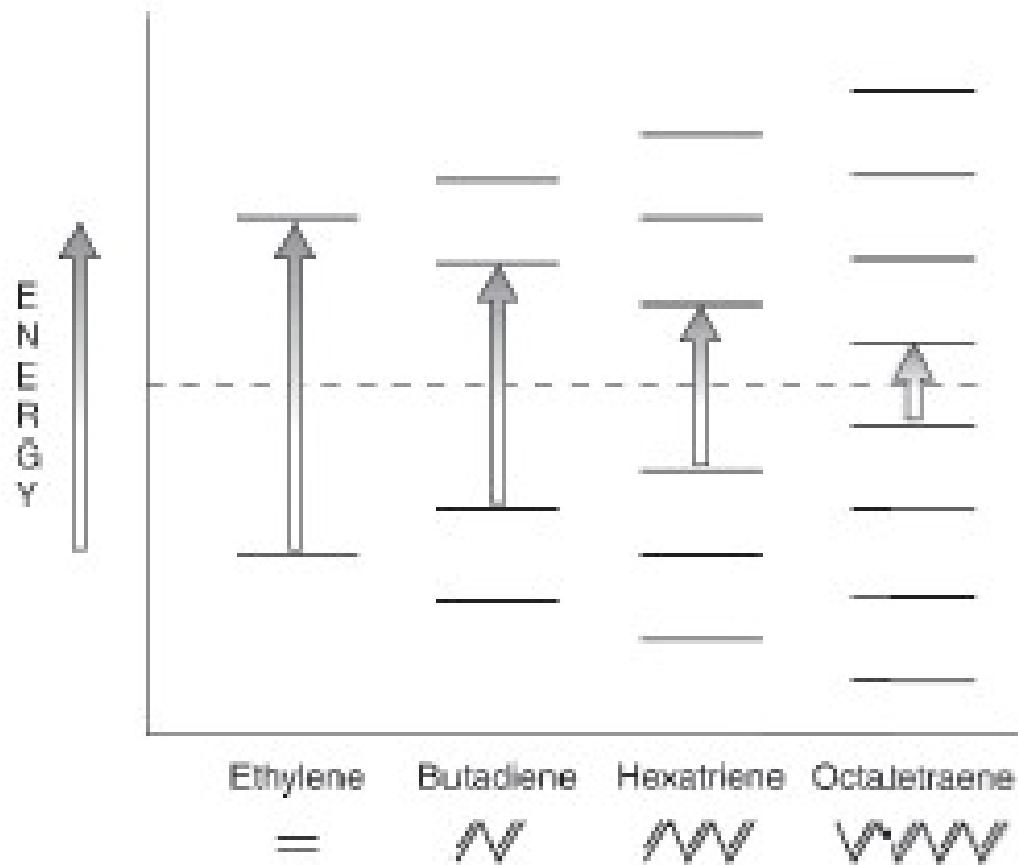
$\lambda_{\text{max}} = 203 \text{ nm } (\varepsilon_{\text{max}} = 9600)$

Effect of Conjugation on λ_{max}



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

Conjugation



Effect of Conjugation

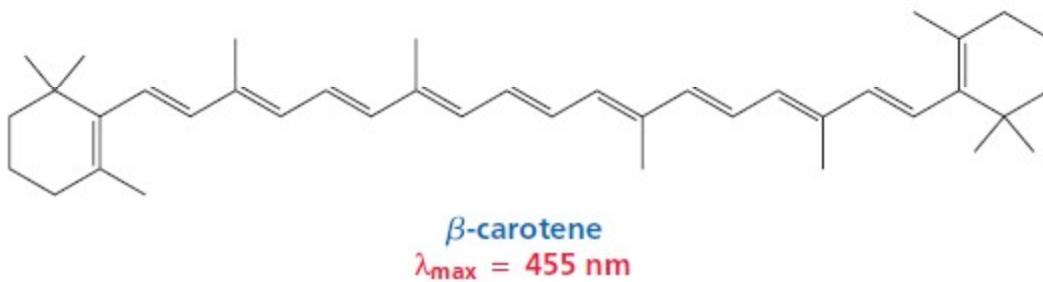
- both the λ_{\max} and the ϵ increase as the number of conjugated double bonds increases.

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

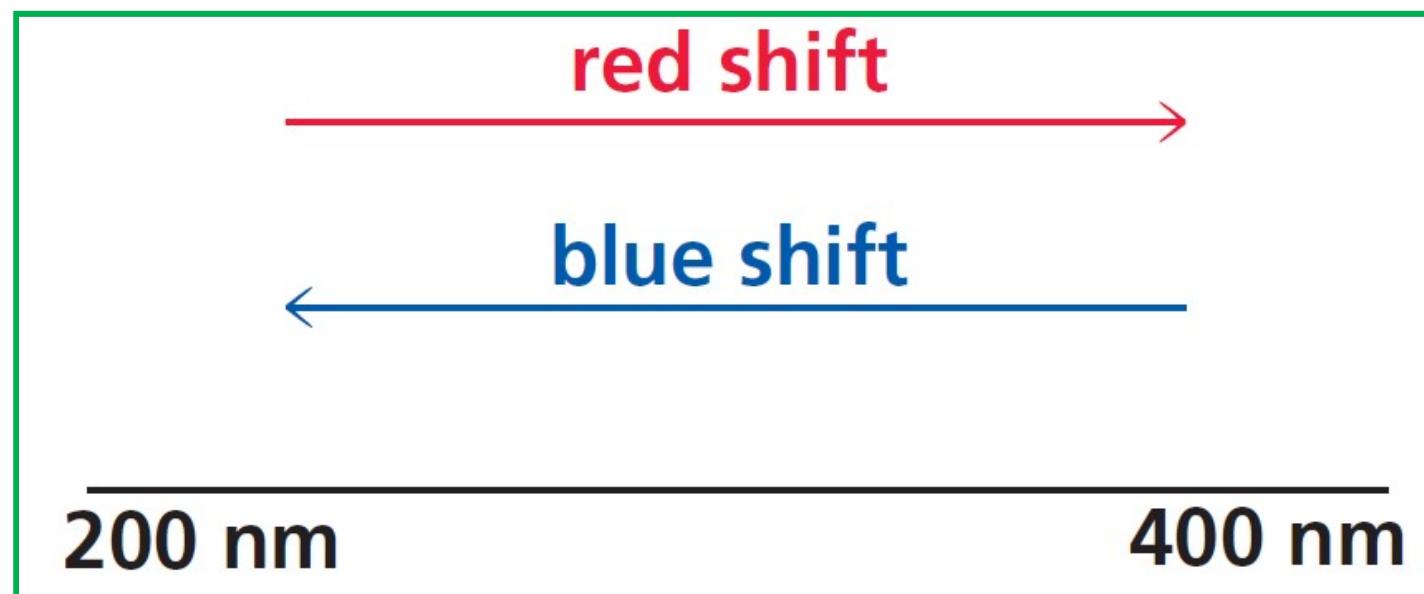
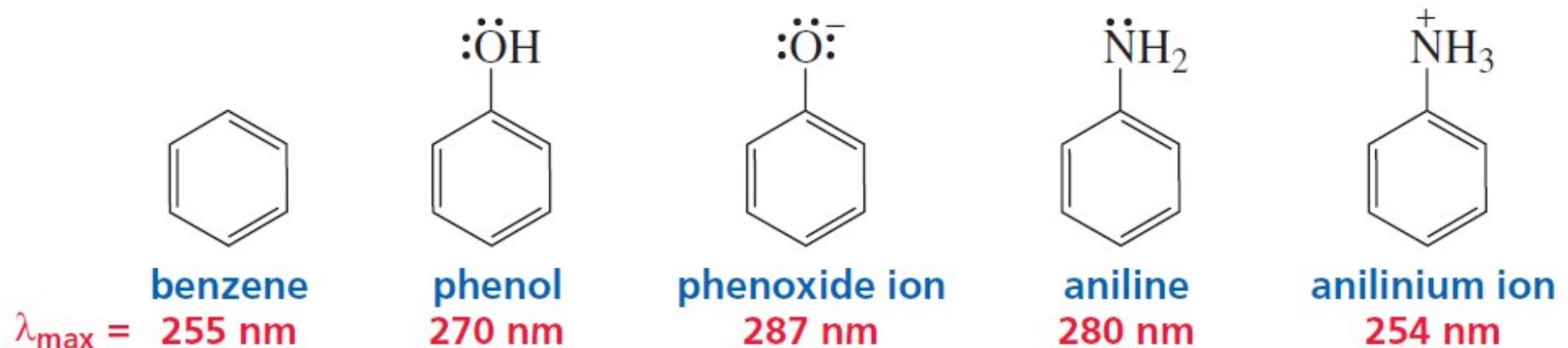
Effect of Conjugation

- 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**.

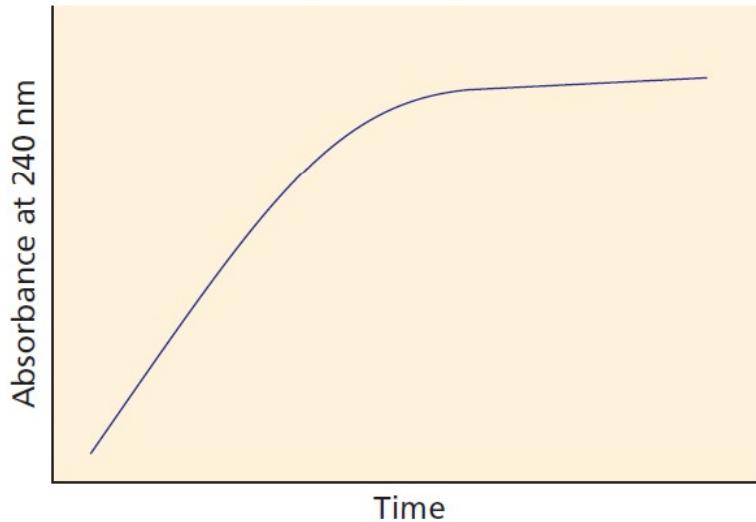
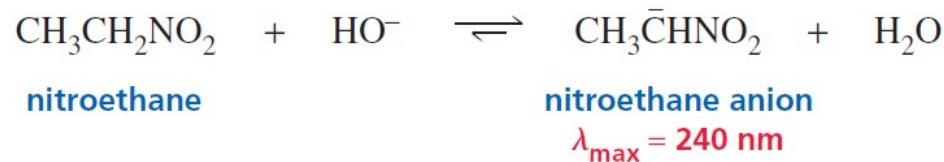


- **Auxochrome** : a substituent that when attached to a chromophore, alters the λ_{max} and the intensity of the absorption, usually increasing both.

Auxochrome

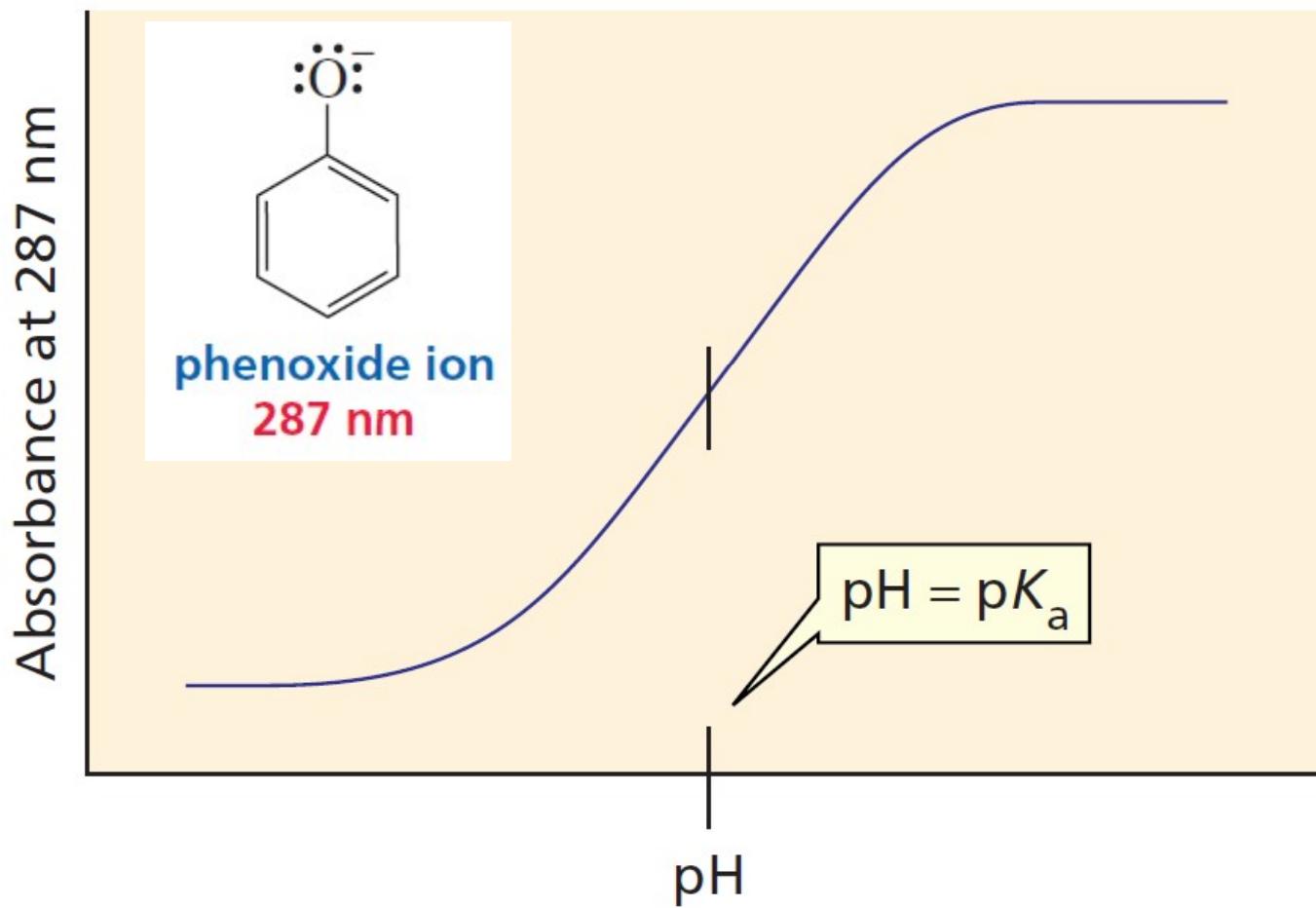


Uses of UV/VIS Spectroscopy

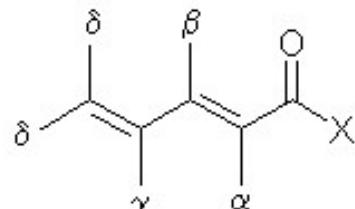
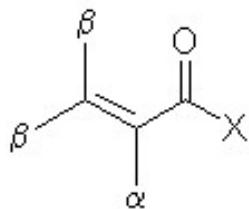


one of the reactants or one of the products absorbs UV or visible light at a wavelength at which the other reactants and products have little or no absorbance.

pK_a determination using UV/Vis spectroscopy



Woodward's Rules for Conjugated Carbonyl Compounds



Base values:

$X = R$

Six-membered ring or acyclic parent enone $\lambda = 215 \text{ nm}$

Five-membered ring parent enone $\lambda = 202 \text{ nm}$

$X = H$ $\lambda = 208 \text{ nm}$

$X = OH, OR$ $\lambda = 195 \text{ nm}$

Increments for:

Double bond extending conjugation 30

Exocyclic double bond 5

Endocyclic double bond in a 5- or 7-membered ring for $X = OH, OR$ 5

Homocyclic diene component 39

Alkyl substituent or ring residue α 10

β 12

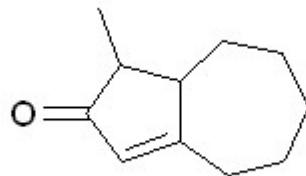
γ or higher 18

Polar groupings: α 35

-OH β 30

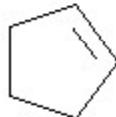
An example

Considering C = O
Bond as an exocyclic
bond

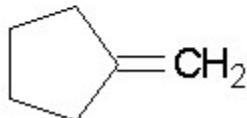


Five-membered ring parent enone:	202 nm
β -Alkyl groups or ring residues:	$2 \times 12 =$ 24 nm
Exocyclic double bond:	<u>5 nm</u>
Calculated:	231 nm
Observed:	226 nm

Cyclopentene is an example of an **endocyclic** double bond.



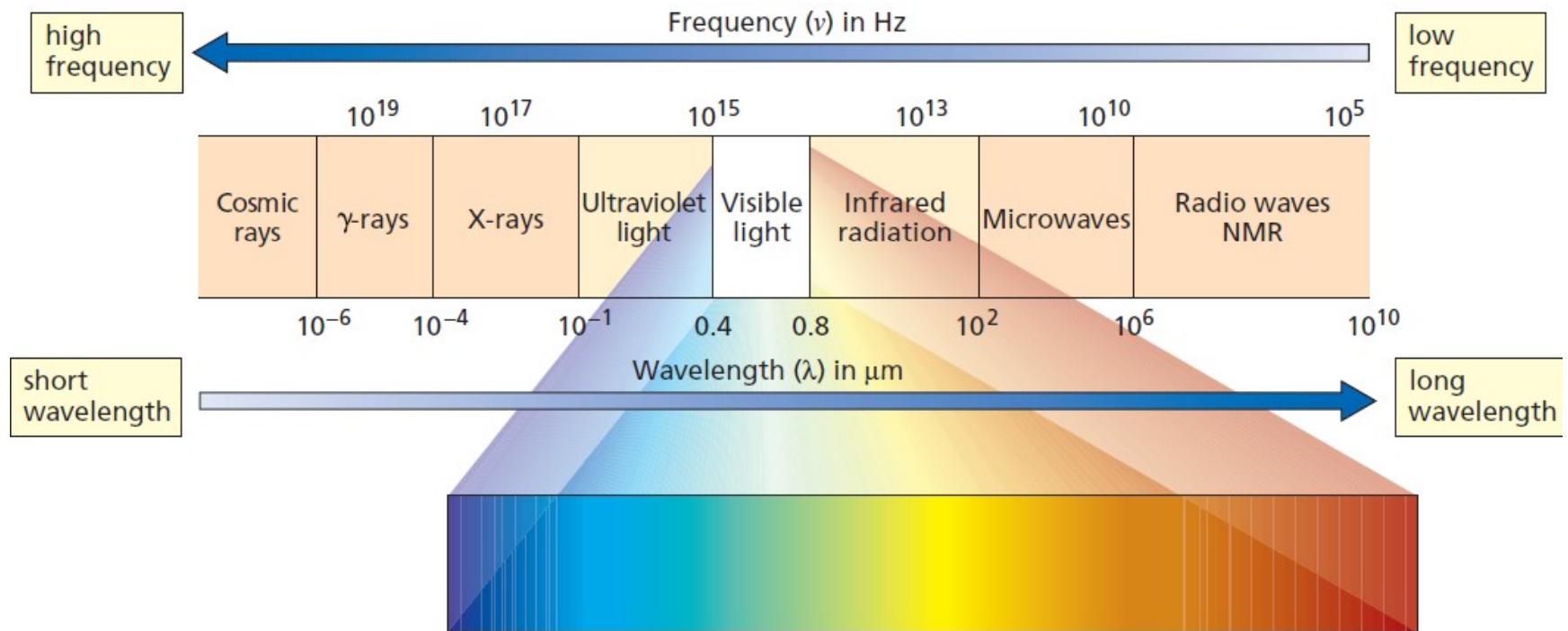
Methylenecyclopentane is an example of an **exocyclic** double bond.



Woodward-Fieser Rules for Dienes

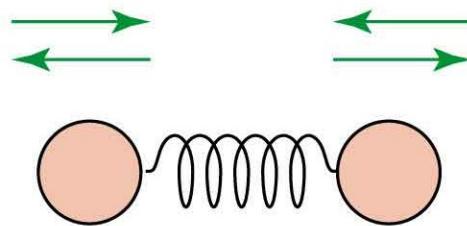
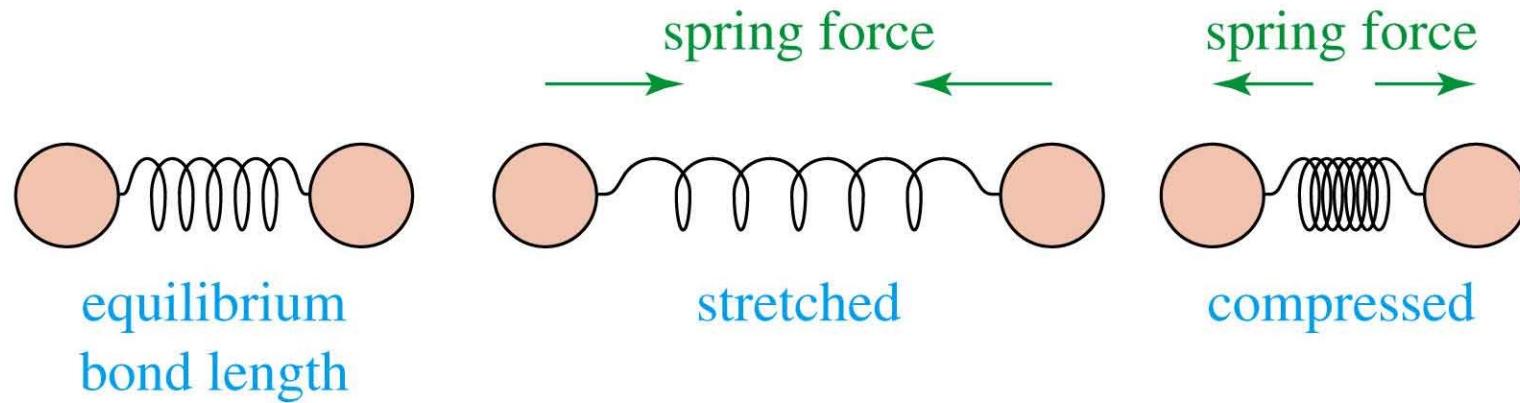
<http://www.chemistry.ccsu.edu/glagovich/teaching/316/uvvis/uvvis.html>

Infrared Spectroscopy



Molecular Vibrations

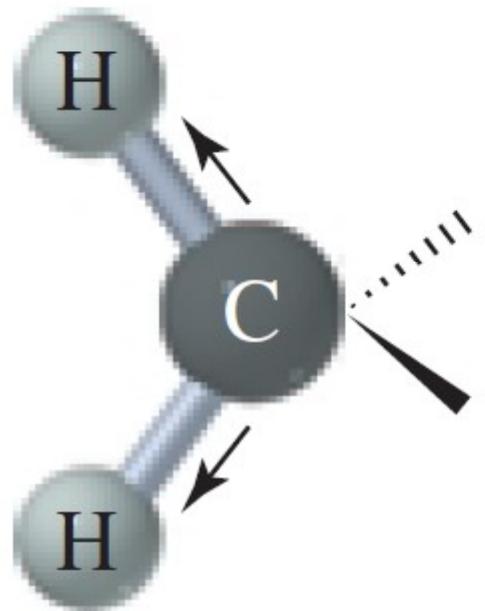
Covalent bonds vibrate at only certain allowable frequencies.



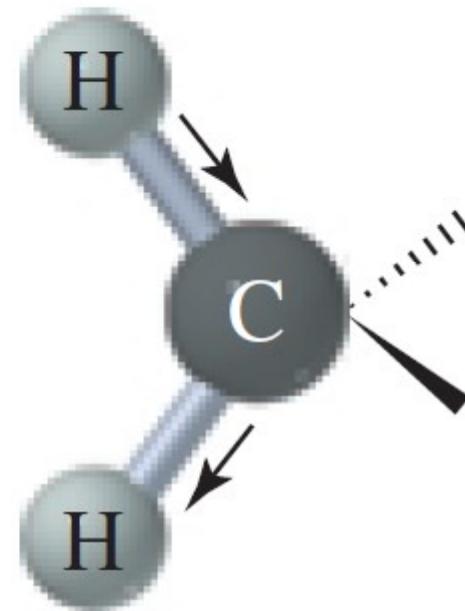
Infrared Spectroscopy

- 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

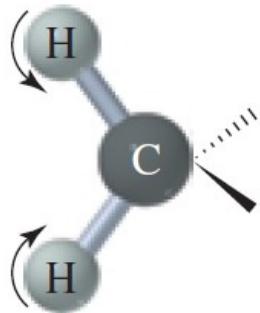


symmetric stretch

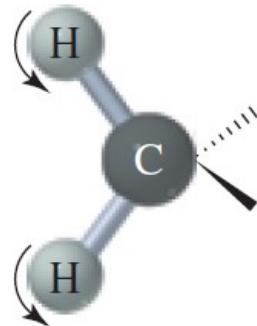


asymmetric stretch

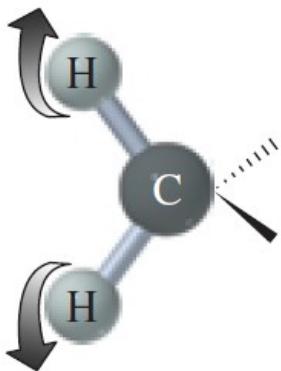
Bending Vibrations



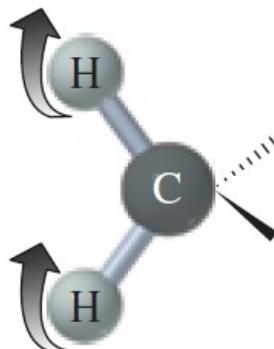
symmetric in-plane
bend (scissor)



asymmetric in-plane
bend (rock)

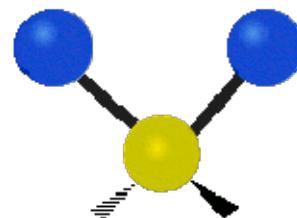
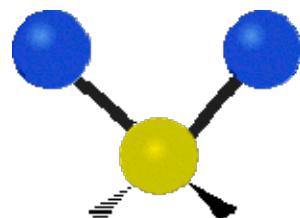
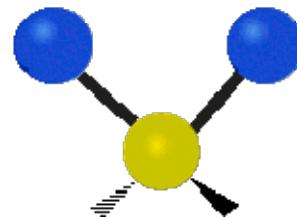
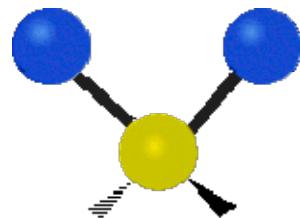
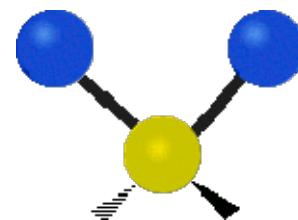
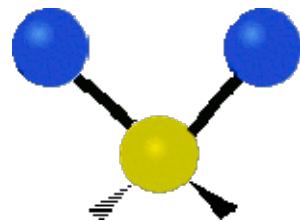


symmetric out-of-plane
bend (twist)



asymmetric out-of-plane
bend (wag)

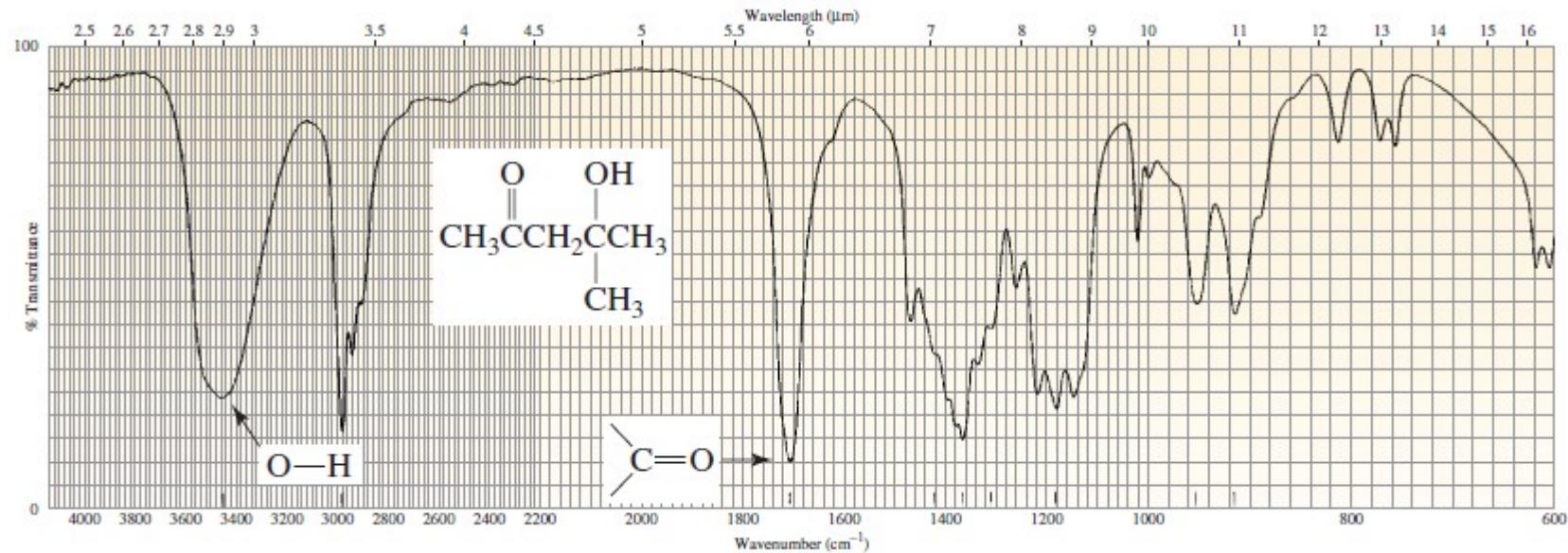
Vibrations



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.

IR Spectrum

- 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

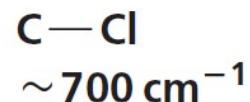
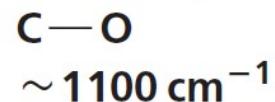
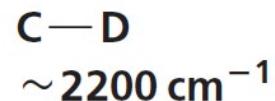
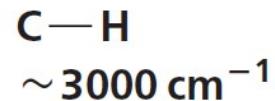
$$\tilde{\nu} = \frac{1}{2\pi c} \left[\frac{f(m_1 + m_2)}{m_1 m_2} \right]^{1/2}$$

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

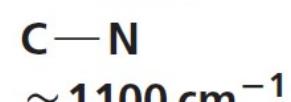
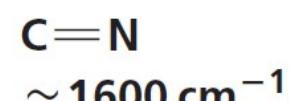
The Position of Absorption Bands

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

Lighter atoms show absorption bands at larger wavenumbers.



Stronger bonds show absorption bands at larger wavenumbers.



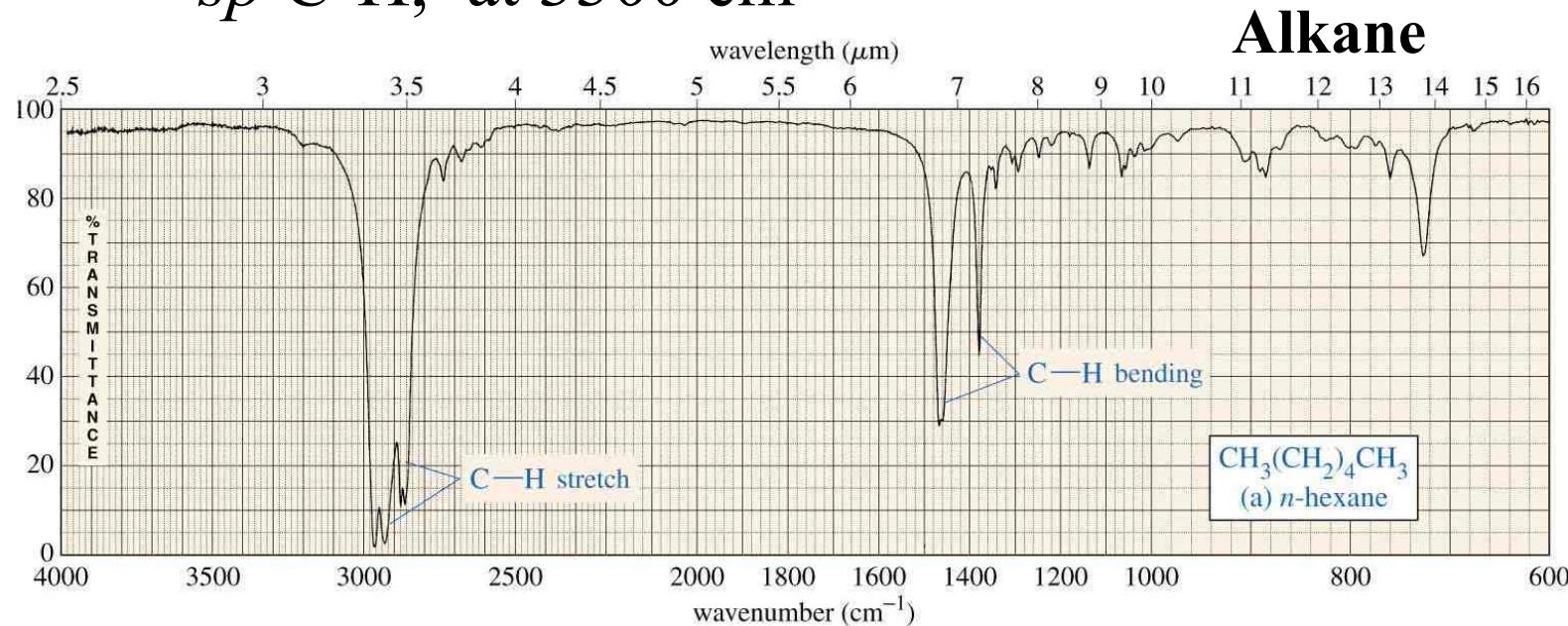
Carbon-Carbon Bond Stretching

- Stronger bonds absorb at higher frequencies:
 - C-C 1200 cm^{-1}
 - C=C 1660 cm^{-1}
 - C≡C 2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
 - isolated C=C $1640\text{-}1680\text{ cm}^{-1}$
 - conjugated C=C $1620\text{-}1640\text{ cm}^{-1}$
 - aromatic C=C approx. 1600 cm^{-1}

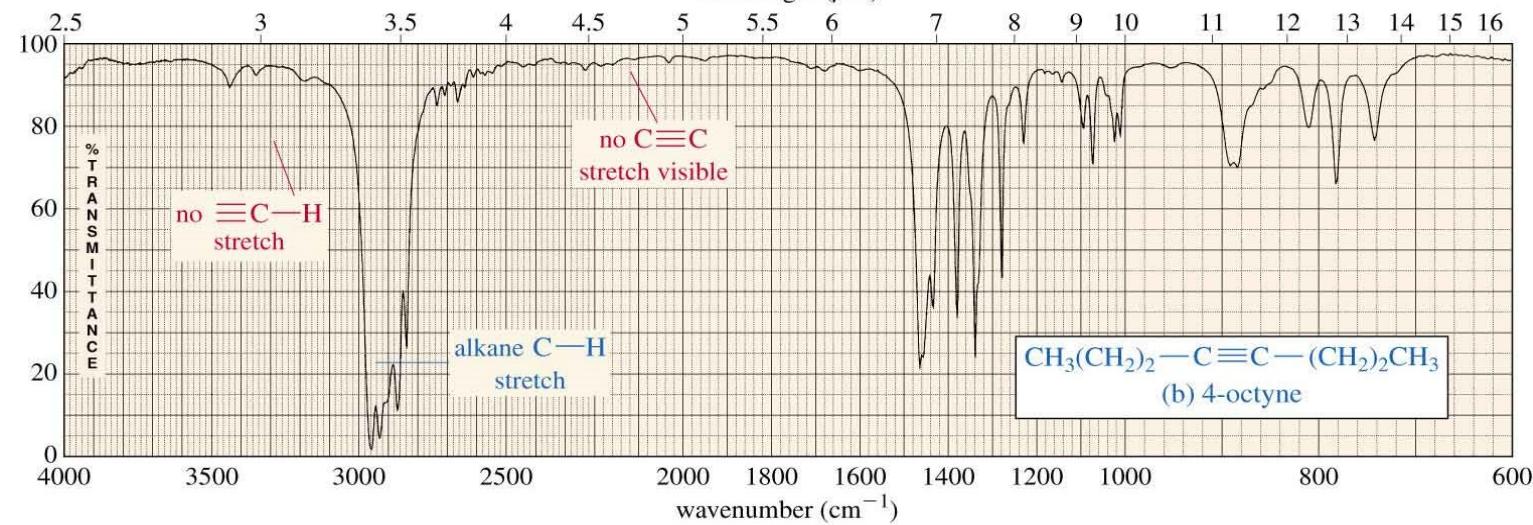
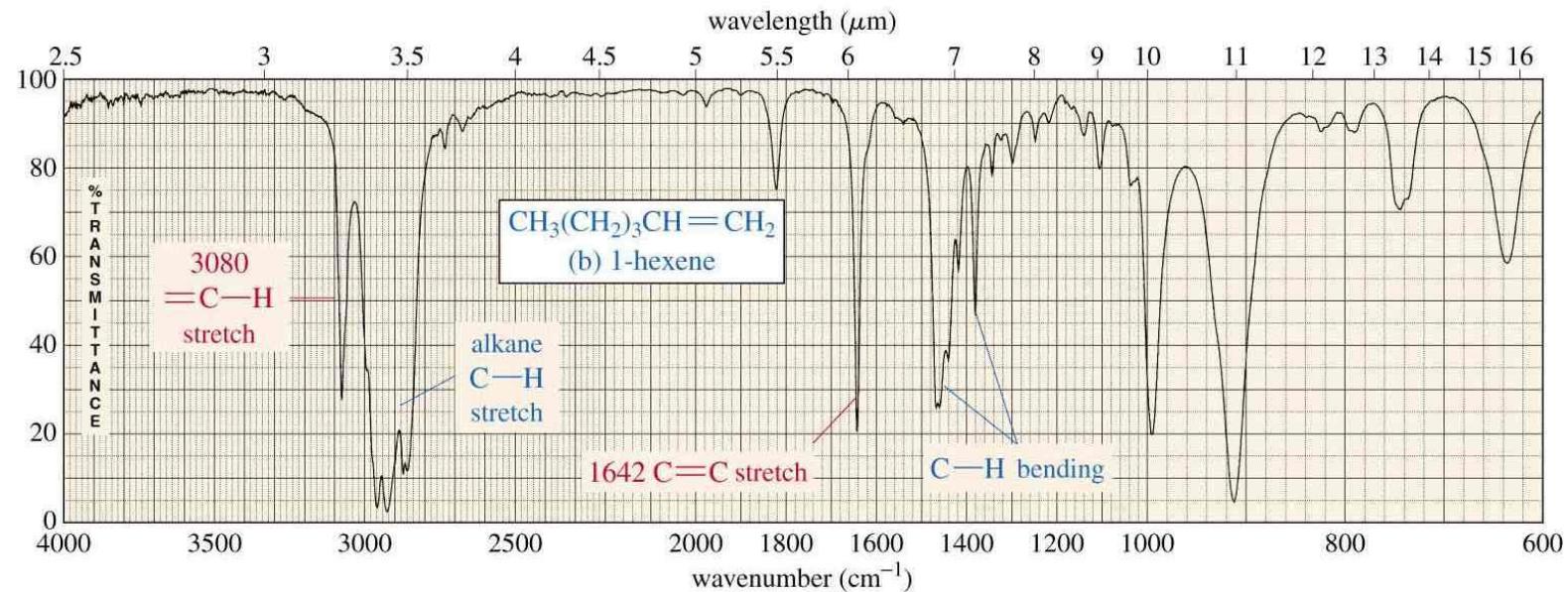
Carbon-Hydrogen Stretching

Bonds with more *s* character absorb at a higher frequency.

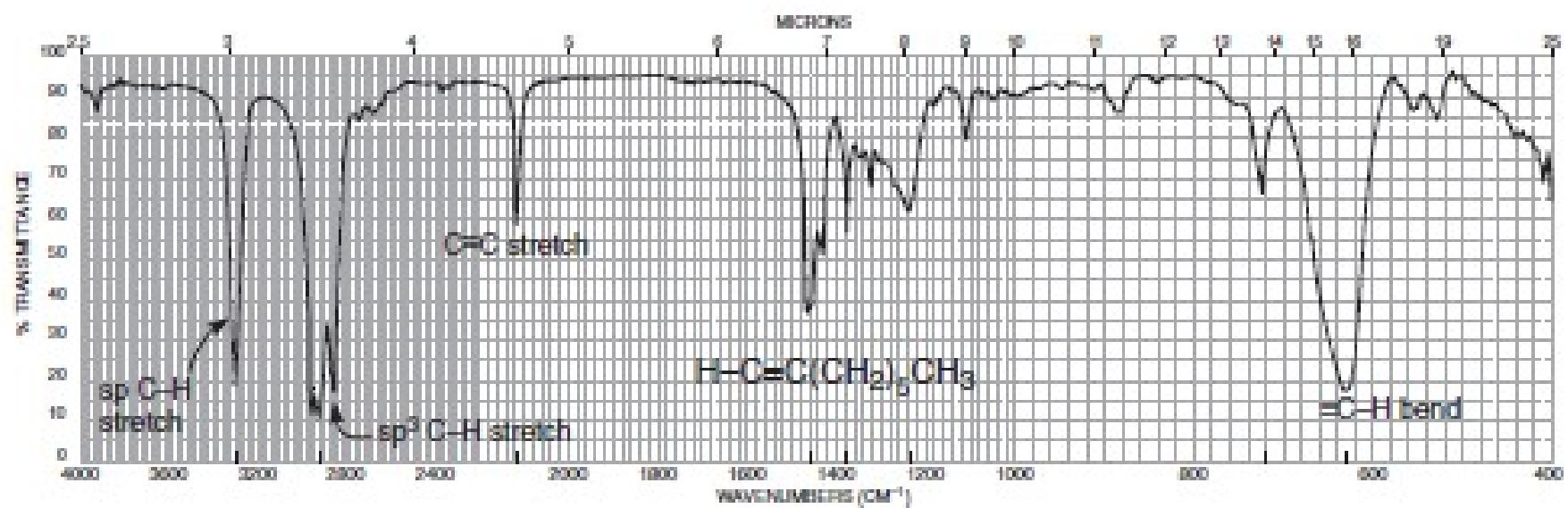
- sp^3 C-H, just below 3000 cm^{-1} (to the right)
- sp^2 C-H, just above 3000 cm^{-1} (to the left)
- sp C-H, at 3300 cm^{-1}



Alkene & Alkyne IR Spectrum

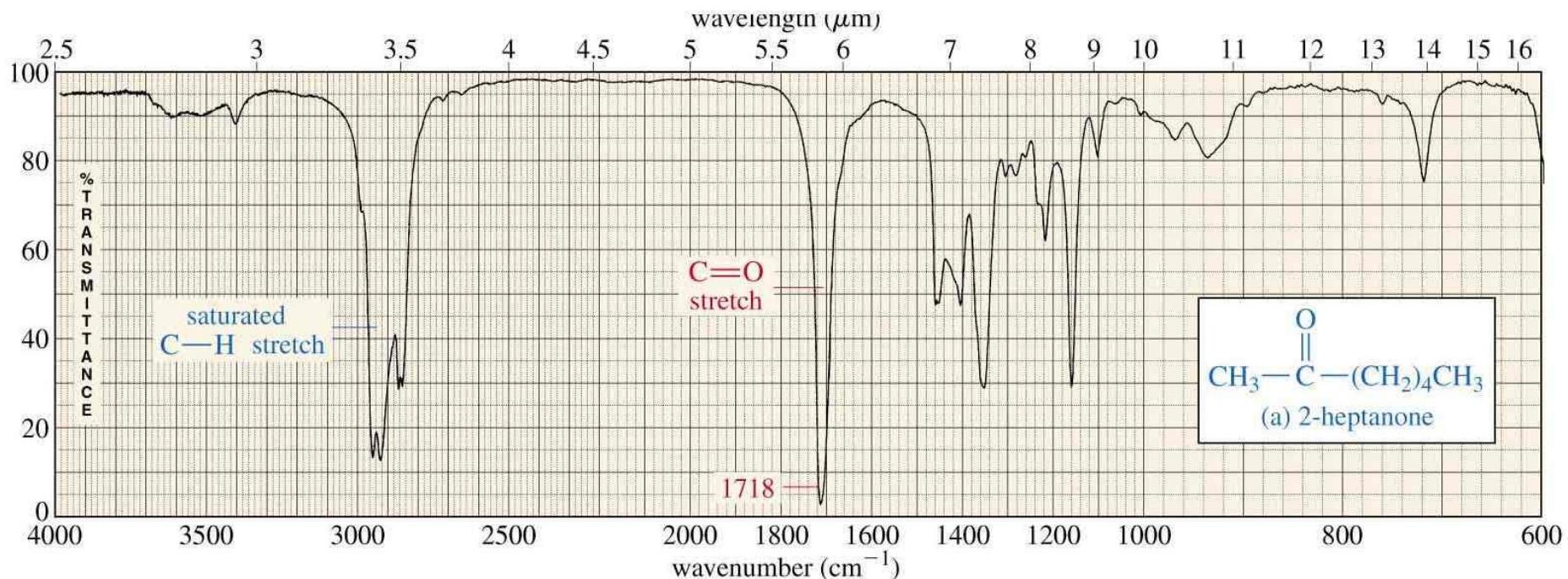


Alkene & Alkyne IR Spectrum

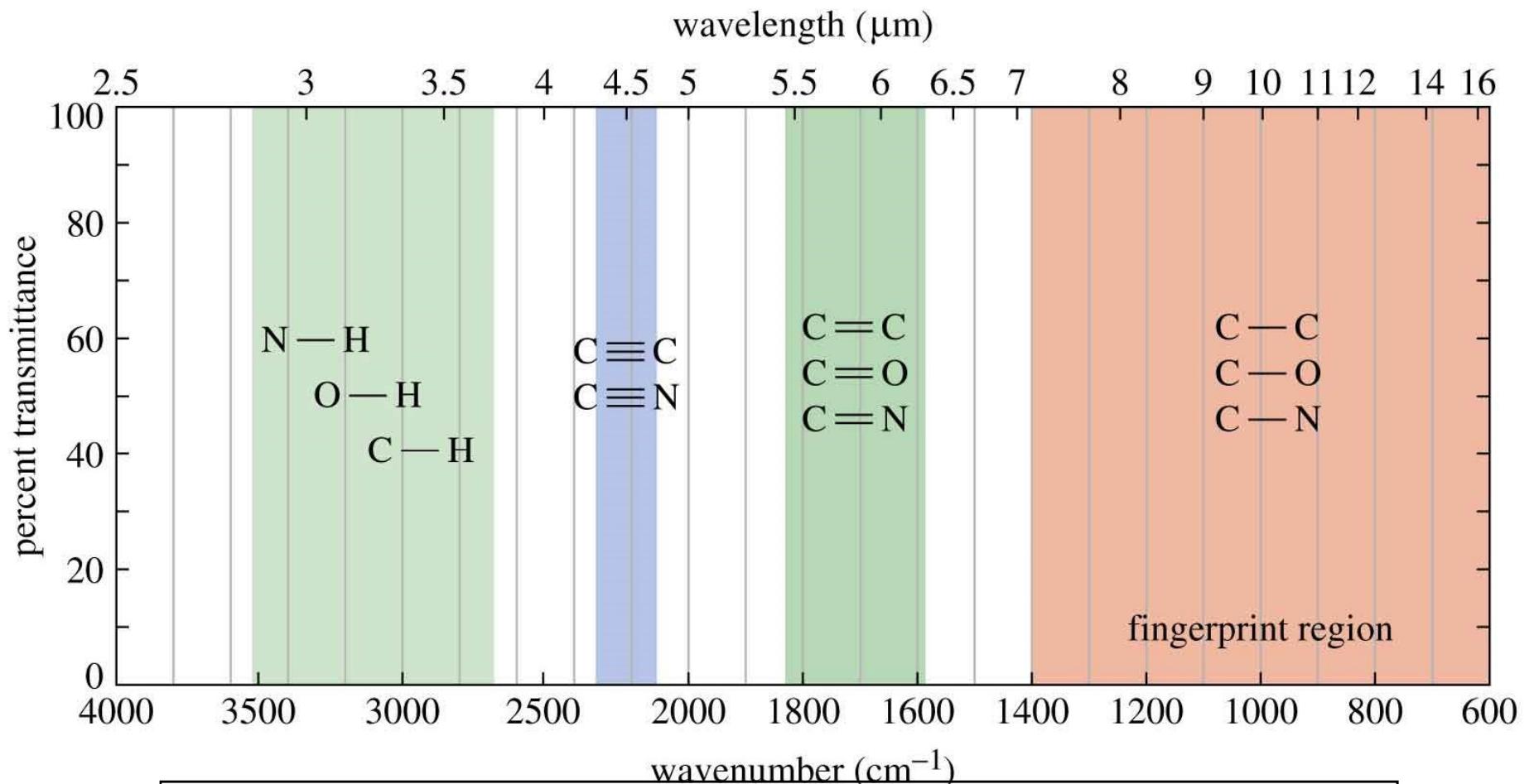


Carbonyl Stretching

- The C=O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1} .
- Usually, it's the strongest IR signal.
- Carboxylic acids will have O-H also.
- Aldehydes have two C-H signals around 2700 and 2800 cm^{-1} .



Summary of IR Absorptions



Alcohol and amine peaks are broad at around 3300-3500

Strengths and Limitations

- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The functional group is usually indicated.
- The *absence* of a signal is definite proof that the functional group is absent.
- Correspondence with a known sample's IR spectrum confirms the identity of the compound.

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 .

NMR Spectroscopy

- 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

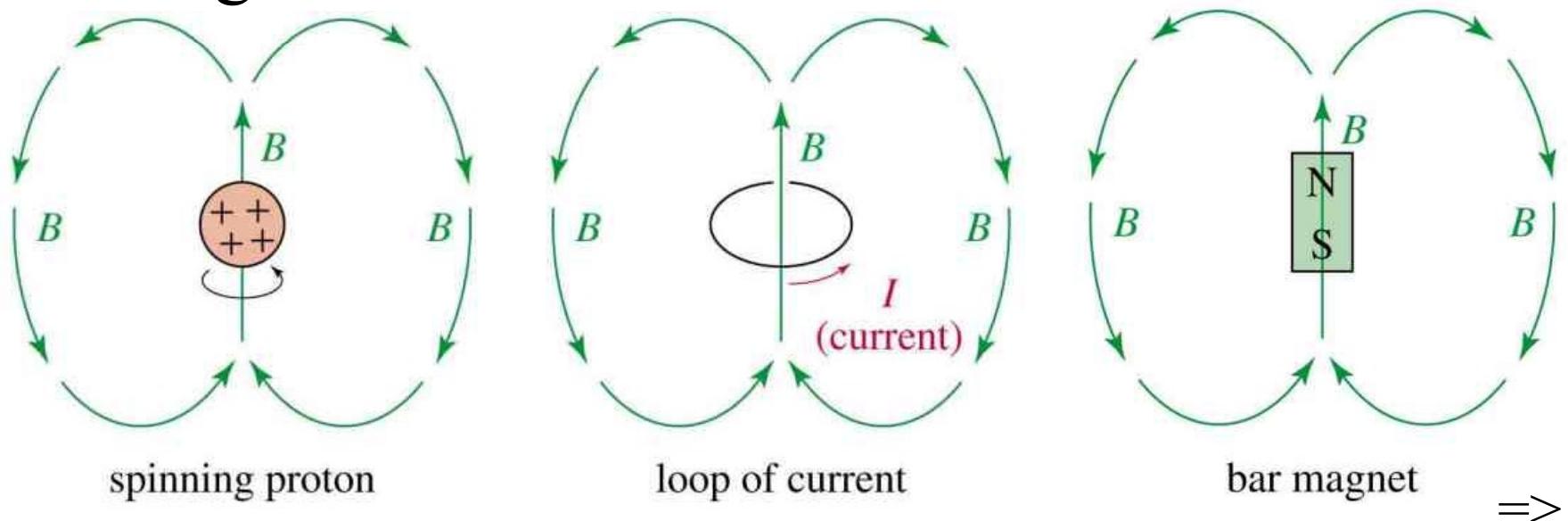
- NMR is one of the most powerful tool available for organic structure determination.
- It is used to study a wide variety of nuclei:
 - ^1H
 - ^{13}C
 - ^{15}N
 - ^{19}F
 - ^{31}P



Magnetic shielding of nucleus by surrounding electron cloud

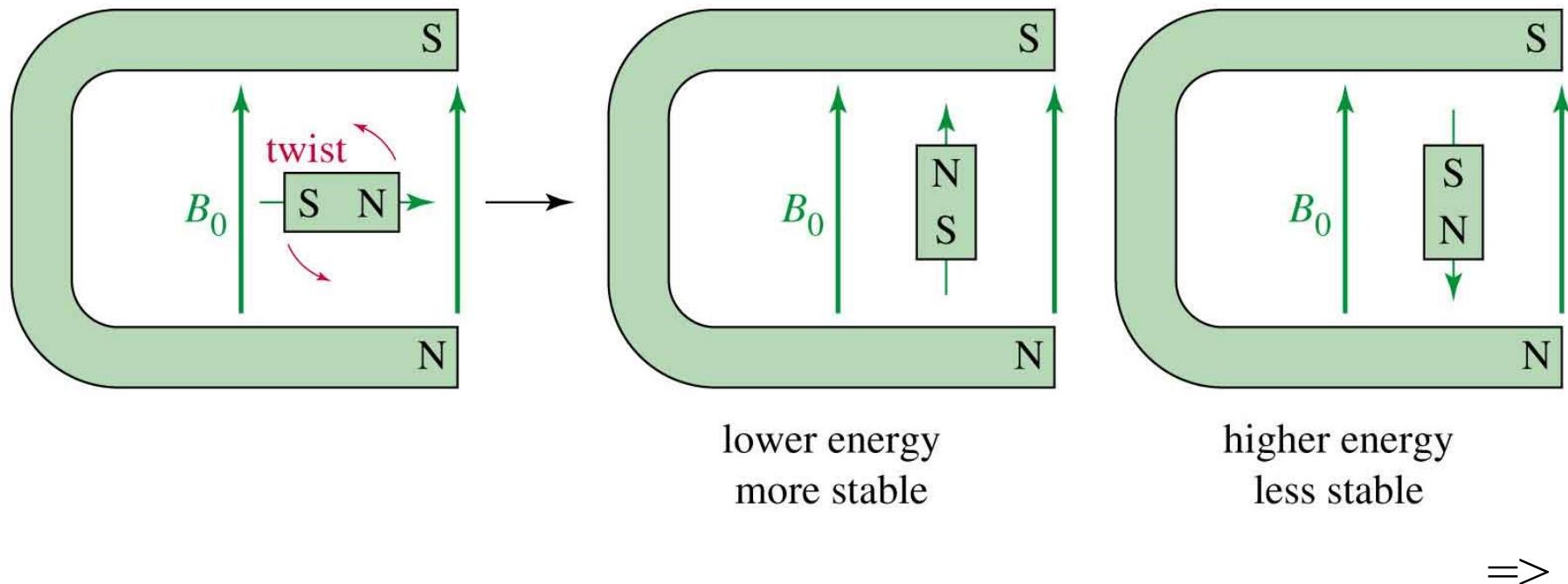
Nuclear Spin

- 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.

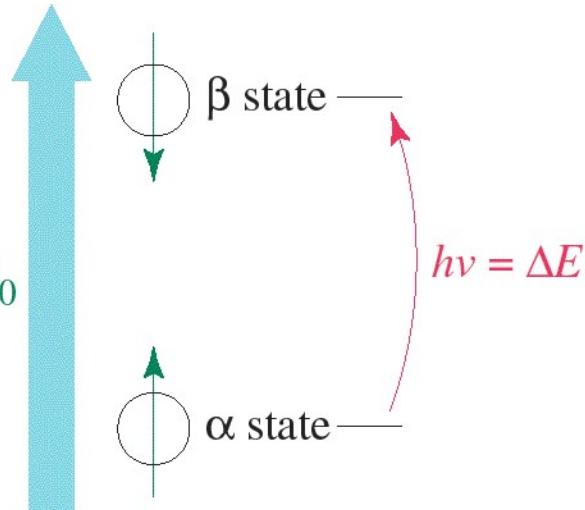


Two Energy States

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, B_0
 - $\Delta E \propto B_0$



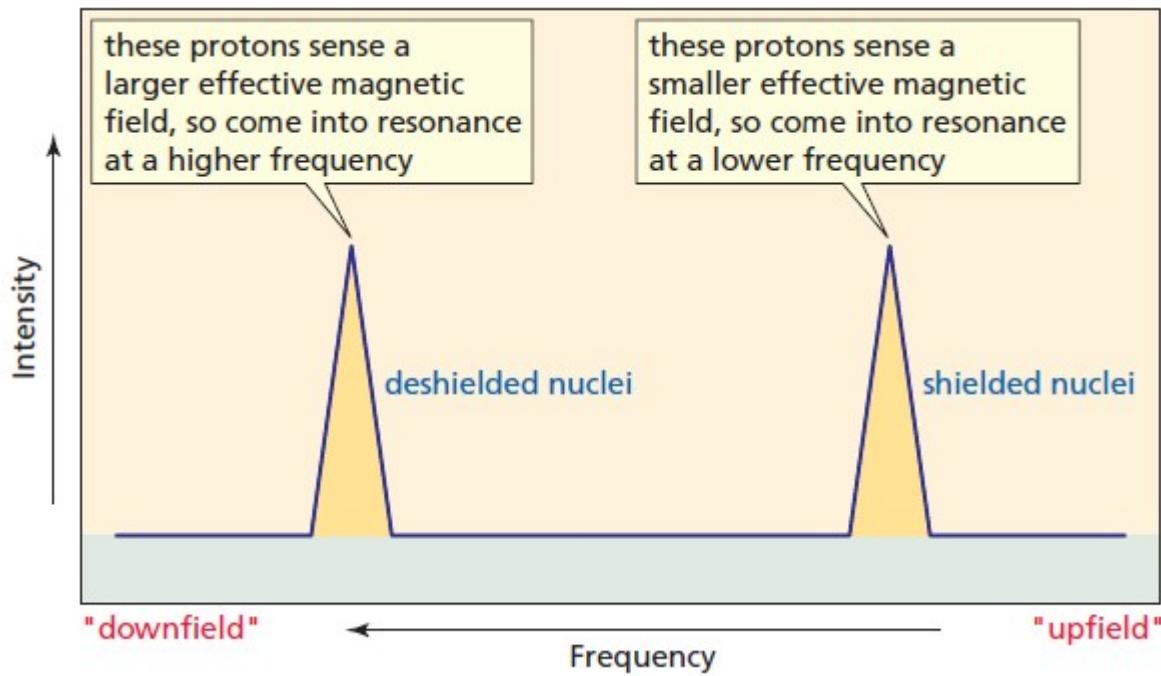
Magnetic Shielding

- 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.

Magnetic Shielding

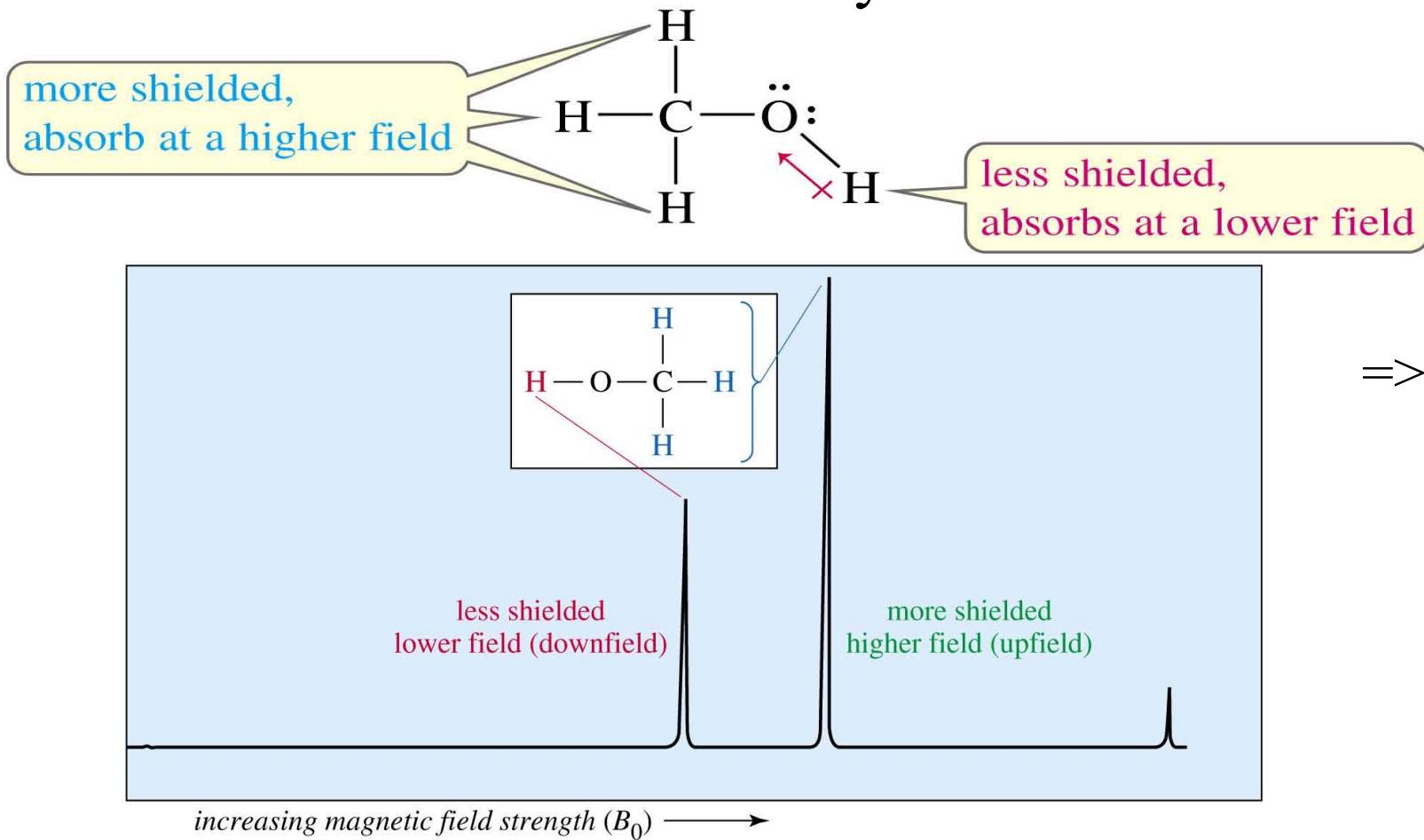
- Protons in **electron-dense environments** sense a **smaller effective magnetic field**. They, therefore, will require a **lower frequency** to come into resonance (**more shielded**).
- Protons in **electron-poor environments** sense a **larger effective magnetic field** and, therefore, will require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

Magnetic Shielding



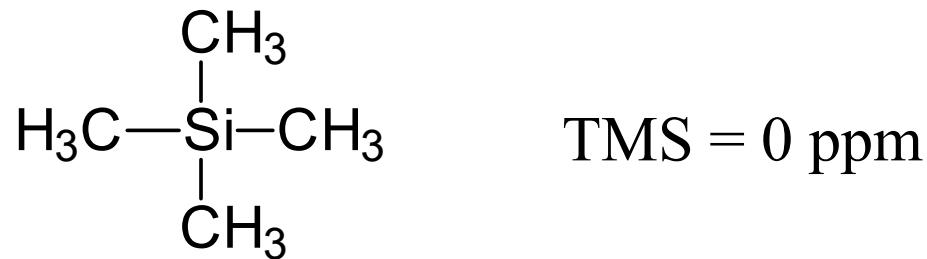
Protons in a Molecule

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



NMR Signals

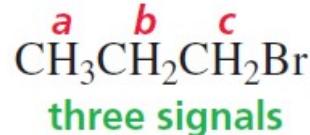
- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded the proton is.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on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



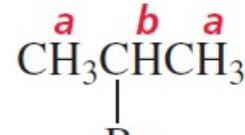
The Number of Signals in the ^1H NMR Spectrum

- 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.

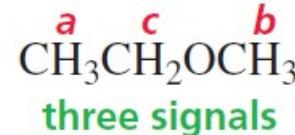
Counting chemically equivalent protons



three signals



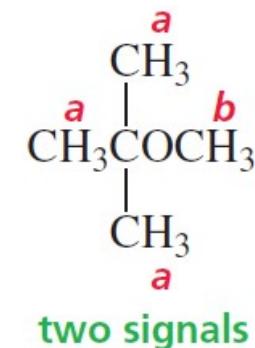
two signals



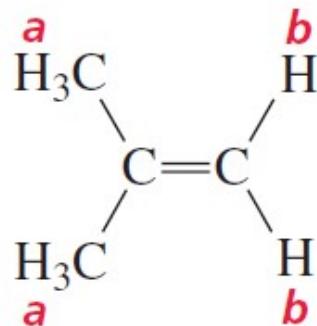
three signals



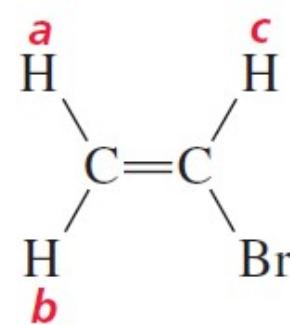
one signal



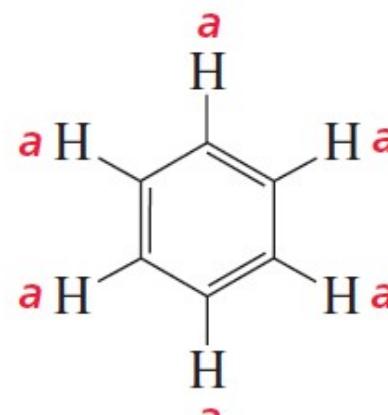
two signals



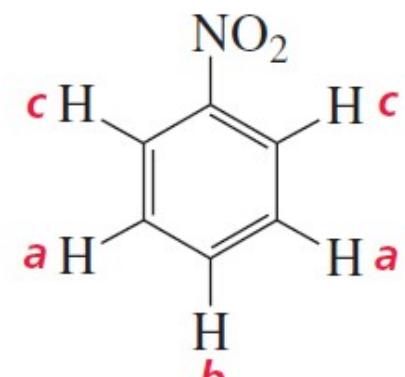
two signals



three signals



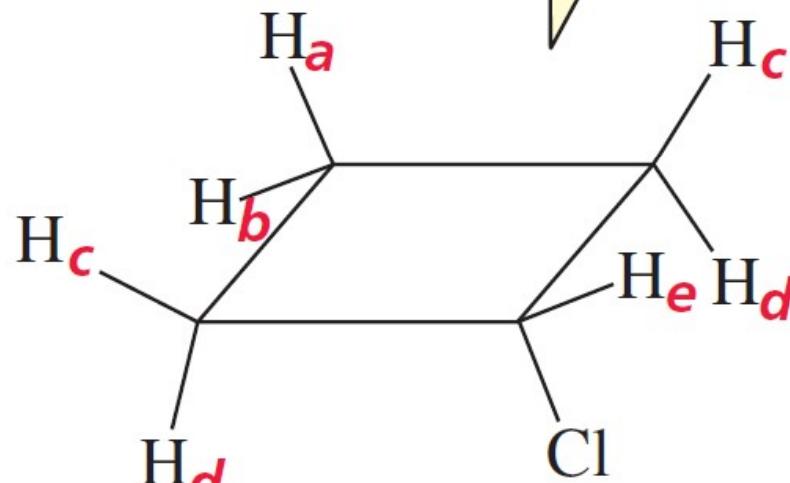
one signal



three signals

Chlorocyclobutane

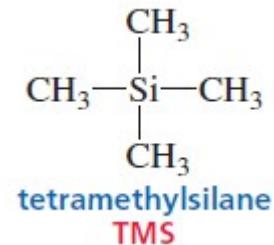
its ^1H NMR spectrum
has five signals



chlorocyclobutane

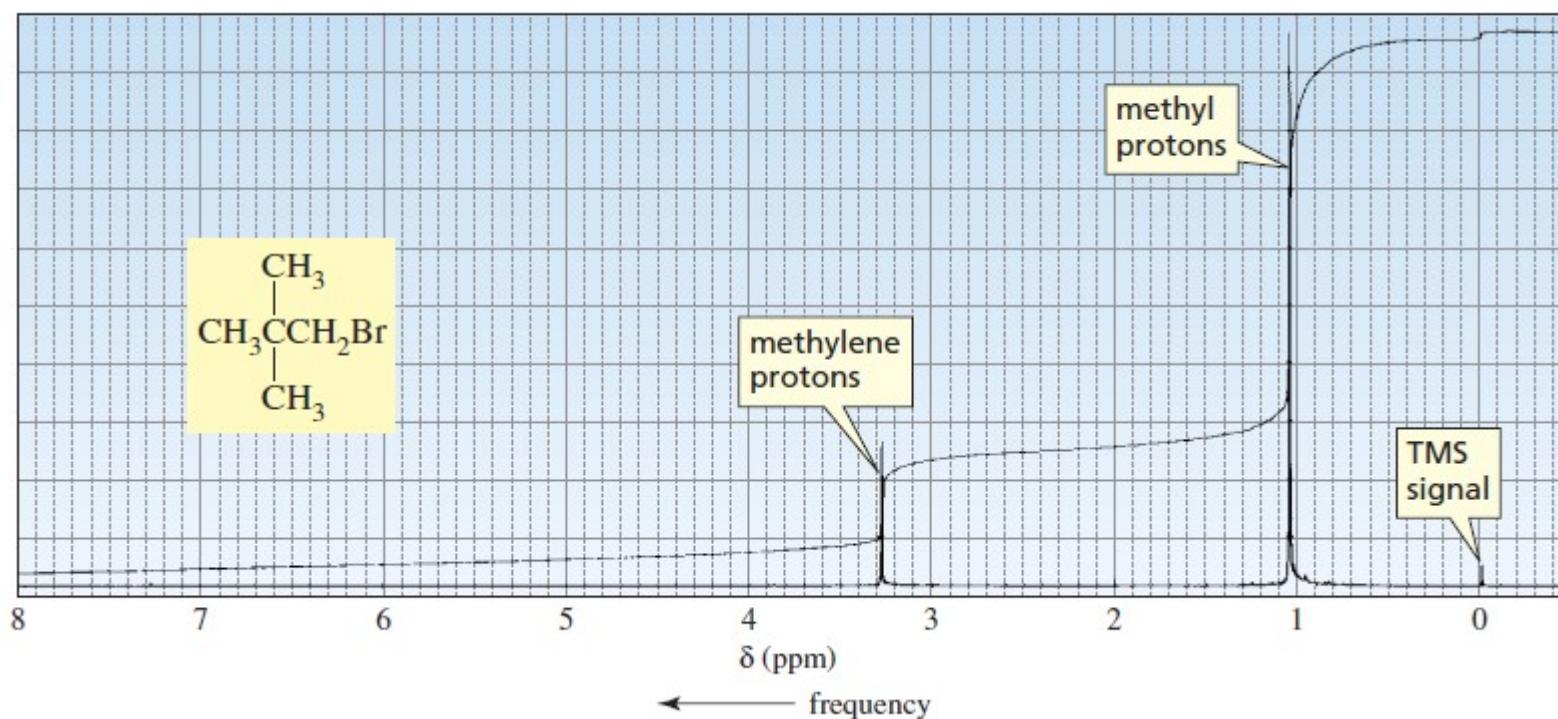
H_a and **H_b** are not equivalent
H_c and **H_d** are not equivalent

The 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



The Chemical Shift

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

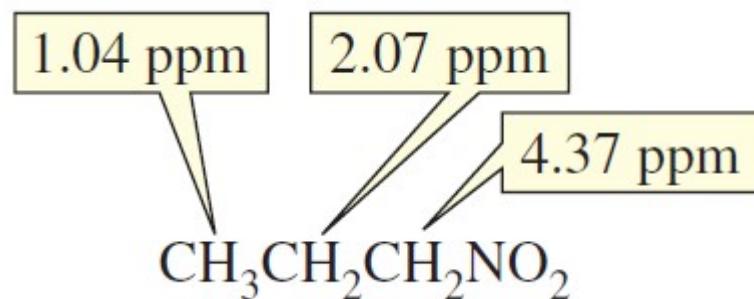
protons in electron-dense environments
shielded protons
upfield
low frequency
small δ values

← δ
← frequency

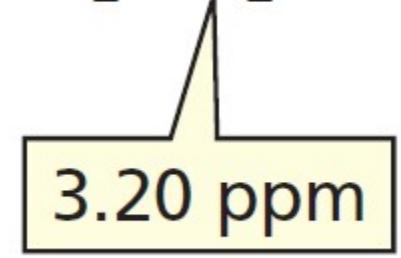
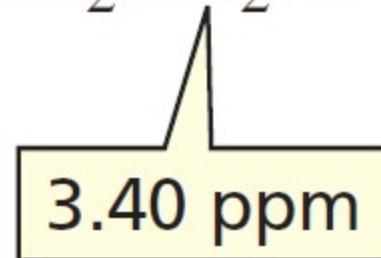
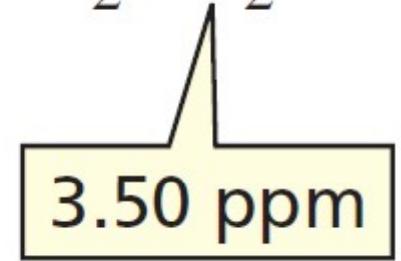
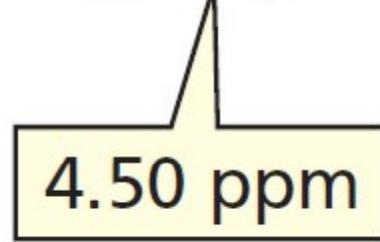
$$\delta = \frac{\text{(shift in Hz)}}{\text{(spectrometer frequency in MHz)}}$$

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.



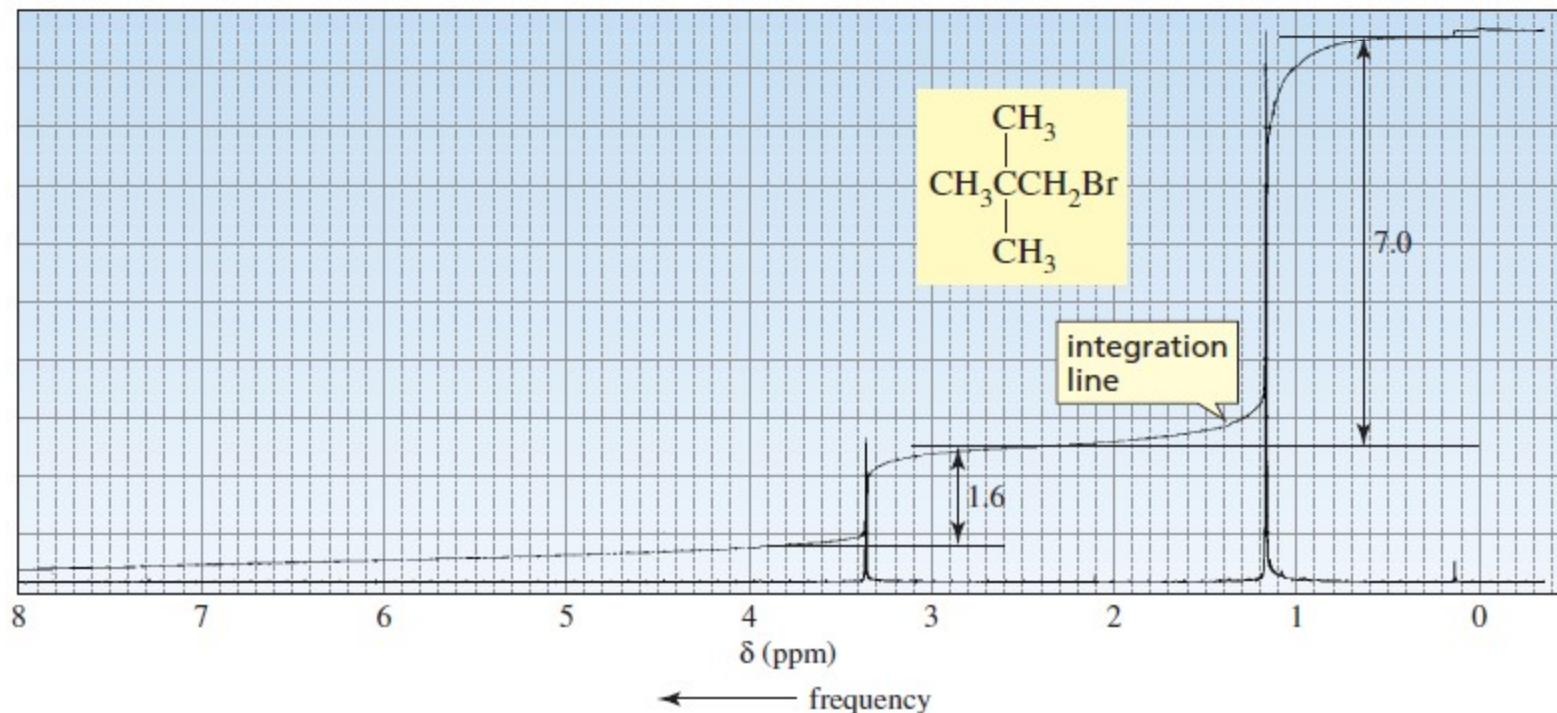
The Relative Positions of NMR Signals



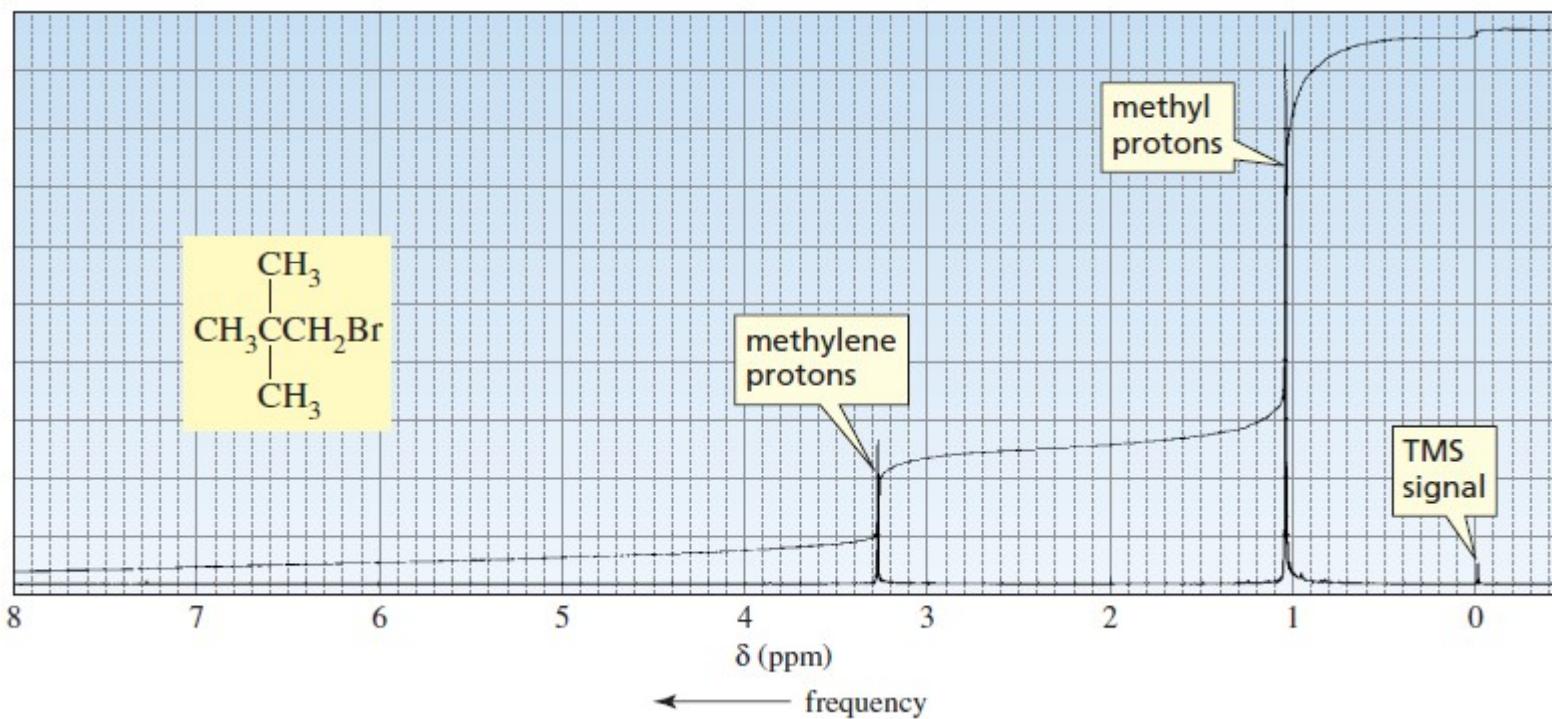
Electron withdrawal causes NMR signals to appear at higher frequencies

Integration of NMR Signals

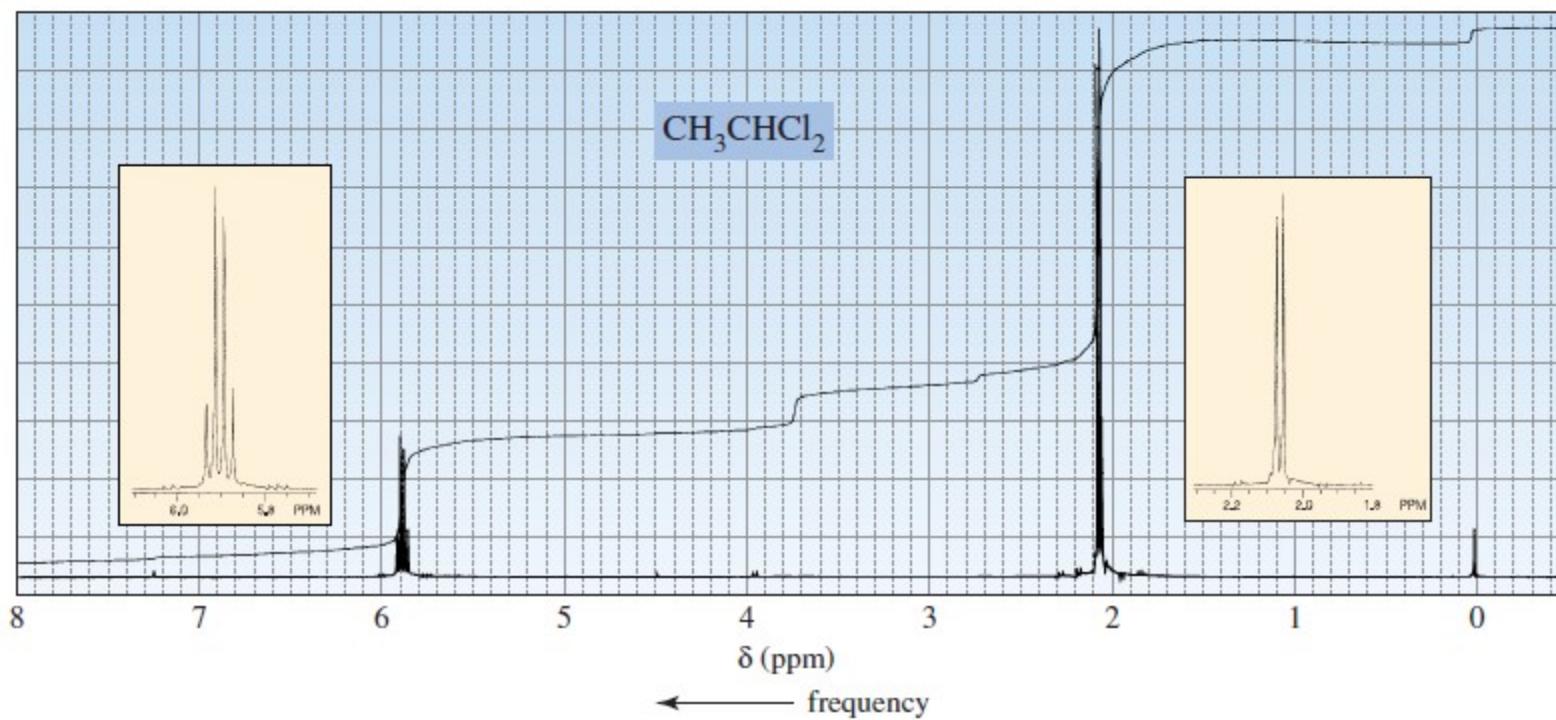
- the area under each signal is proportional to the number of protons that gives rise to the signal.



Splitting of the Signals

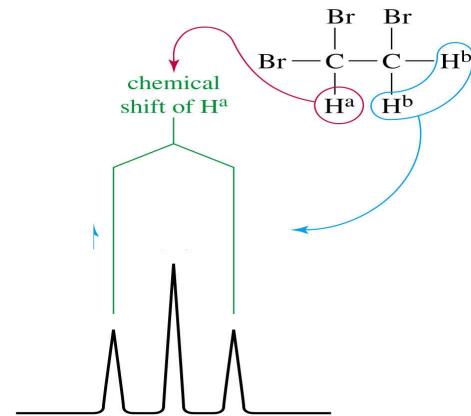


Splitting of the Signals



The $N + 1$ Rule

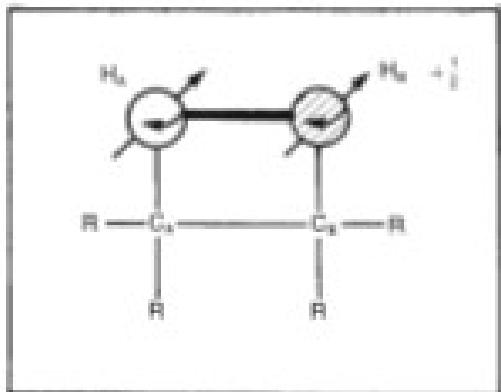
If a signal is split by N equivalent protons, it is split into $N + 1$ peaks.



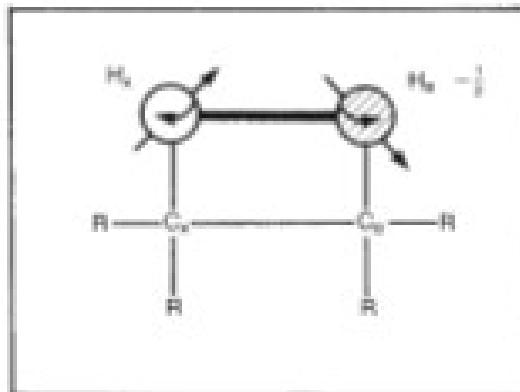
=
>

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

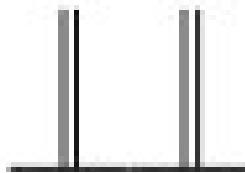
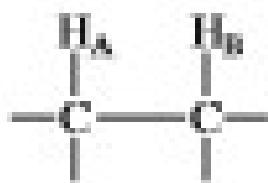
THE ORIGIN OF SPIN-SPIN SPLITTING



X-type molecule

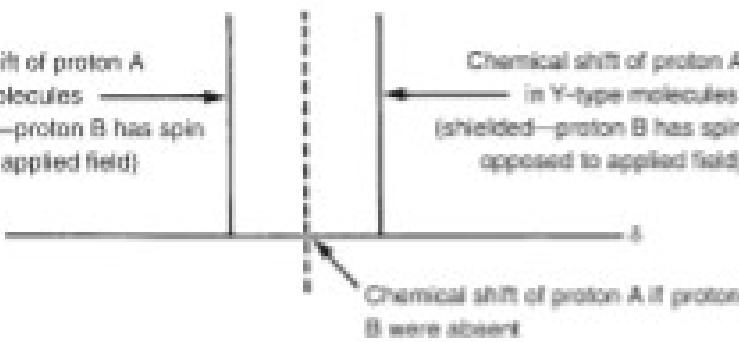


Y-type molecule



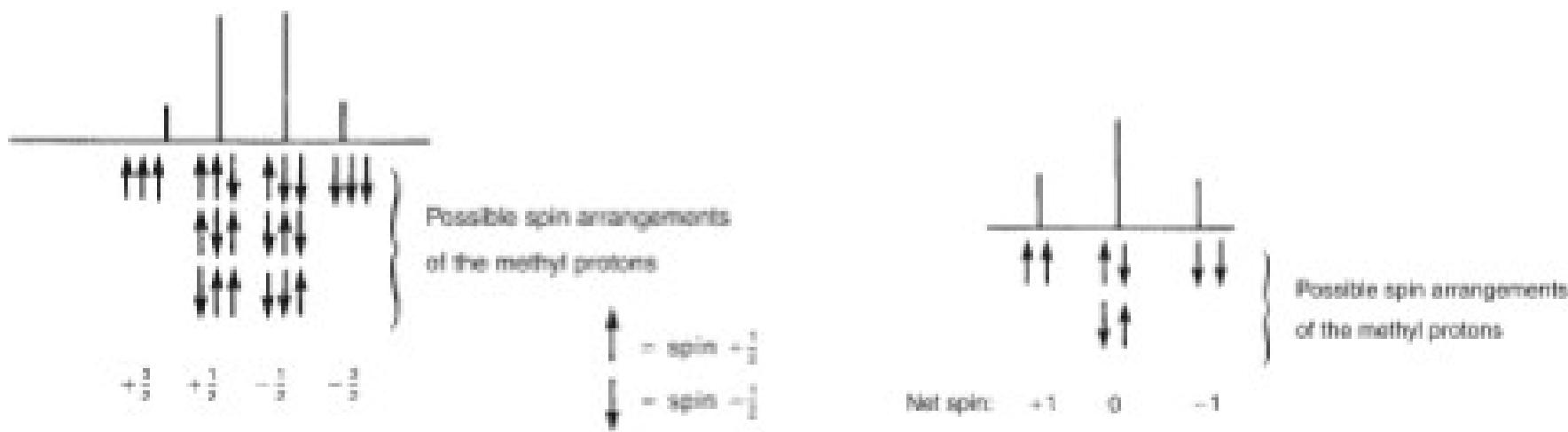
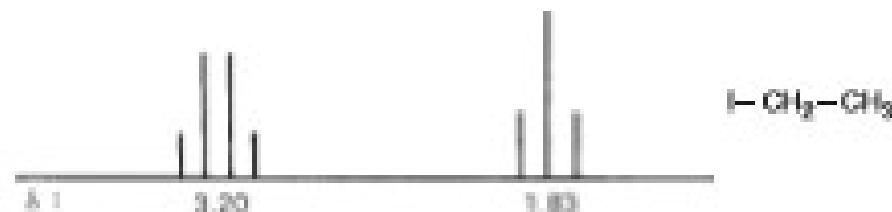
Chemical shift of proton A
in X-type molecules →
(deshielded—proton B has spin
aligned with applied field)

Chemical shift of proton A
in Y-type molecules →
(shielded—proton B has spin
opposed to applied field)



THE ORIGIN OF SPIN-SPIN SPLITTING

THE ETHYL GROUP (CH_3CH_2-)



Magnetic Anisotropy

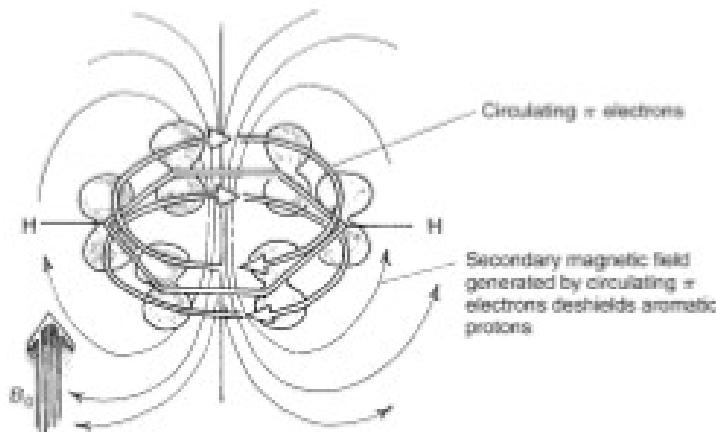
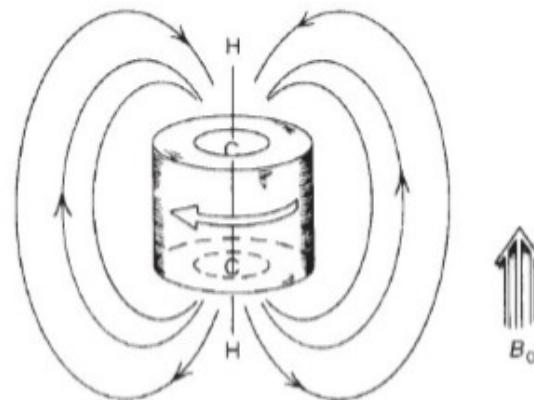


FIGURE 5.21 Diamagnetic anisotropy in benzene.

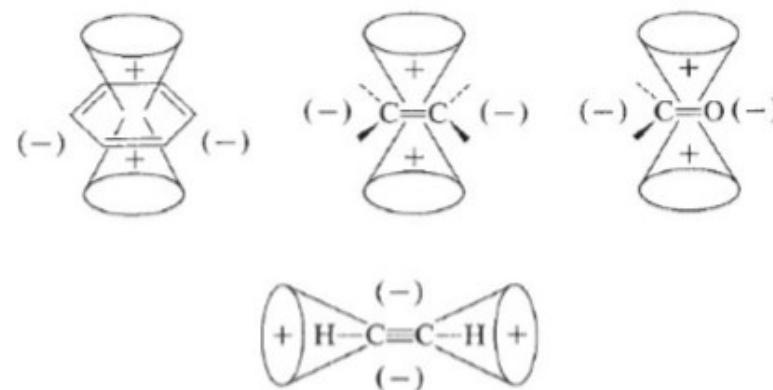
The benzene hydrogens are said to be deshielded by the diamagnetic anisotropy of the ring

- 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

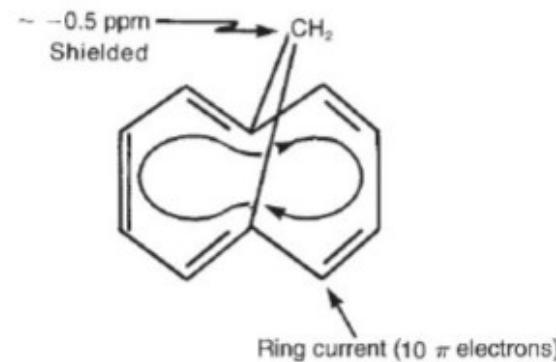
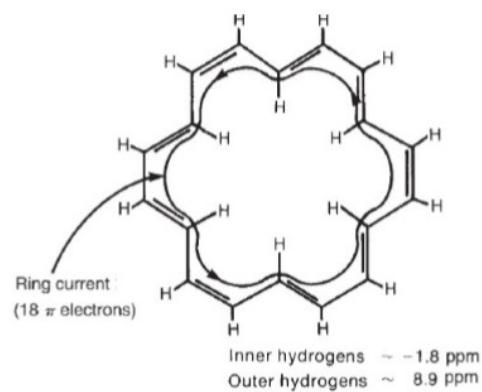
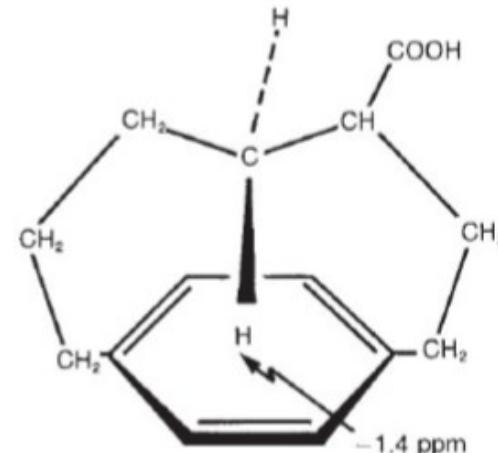
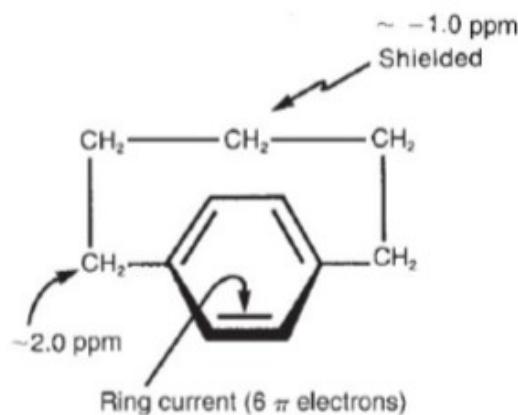
Magnetic Anisotropy



Diamagnetic anisotropy in acetylene.



Magnetic Anisotropy



Alkanes

SPECTRAL ANALYSIS BOX-Alkynes

CHEMICAL SHIFTS

$\text{R}-\text{CH}_3$	0.7–1.3 ppm	Methyl groups are often recognizable as a tall singlet, doublet, or triplet even when overlapping other CH absorptions.
$\text{R}-\text{CH}_2-\text{R}$	1.2–1.4 ppm	In long chains, all of the methylene (CH_2) absorptions may be overlapped in an unresolvable group.
R_2CH	1.4–1.7 ppm	Note that methine hydrogens (CH) have a larger chemical shift than those in methylene or methyl groups.

COUPLING BEHAVIOR

$-\text{CH}-\text{CH}-$ $\delta \approx 7-8 \text{ Hz}$ In hydrocarbon chains, adjacent hydrogens will generally couple, with the spin-spin splitting following the $n+1$ Rule.

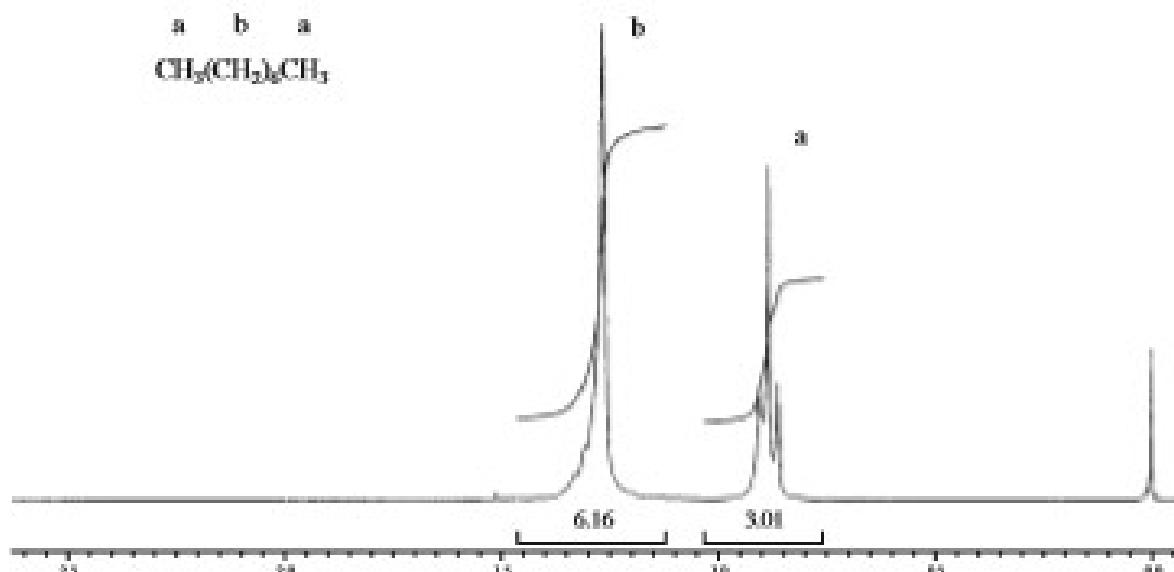


FIGURE 5.37 ^1H spectrum of octane (300 MHz).

Alkenes

SPECTRAL ANALYSIS BOX—Alkenes

CHEMICAL SHIFTS



Hydrogens attached to a double bond (vinyl hydrogens) are deshielded by the anisotropy of the adjacent double bond.



Hydrogens attached to a carbon adjacent to a double bond (allylic hydrogens) are also deshielded by the anisotropy of the double bond, but because the double bond is more distant, the effect is smaller.

COUPLING BEHAVIOR



The splitting patterns of vinyl protons may be complicated by the fact that they may not be equivalent even when located on the same carbon of the double

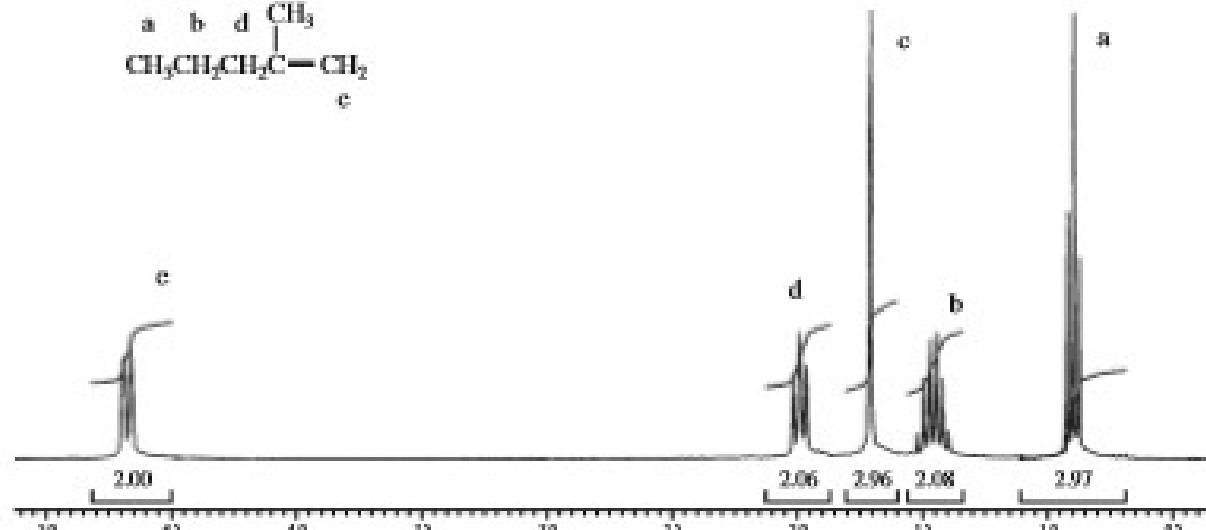


FIGURE 5.38 ^1H spectrum of 2-methyl-1-pentene (300 MHz).

Alkynes

SPECTRAL ANALYSIS BOX—Alkynes

CHEMICAL SHIFTS

$\text{C}\equiv\text{C}-\text{H}$ 1.7–2.7 ppm The terminal or acetylenic hydrogen has a chemical shift near 1.9 ppm due to anisotropic shielding by the adjacent π bonds.

$\text{C}\equiv\text{C}-\text{CH}-$ 1.6–2.6 ppm Protons on a carbon next to the triple bond are also affected by the π system.

COUPLING BEHAVIOR

$\text{H}-\text{C}\equiv\text{C}-\text{C}-\text{H}$ $^4J = 2-3$ Hz “Allylic coupling” is often observed in alkynes, but is relatively small.

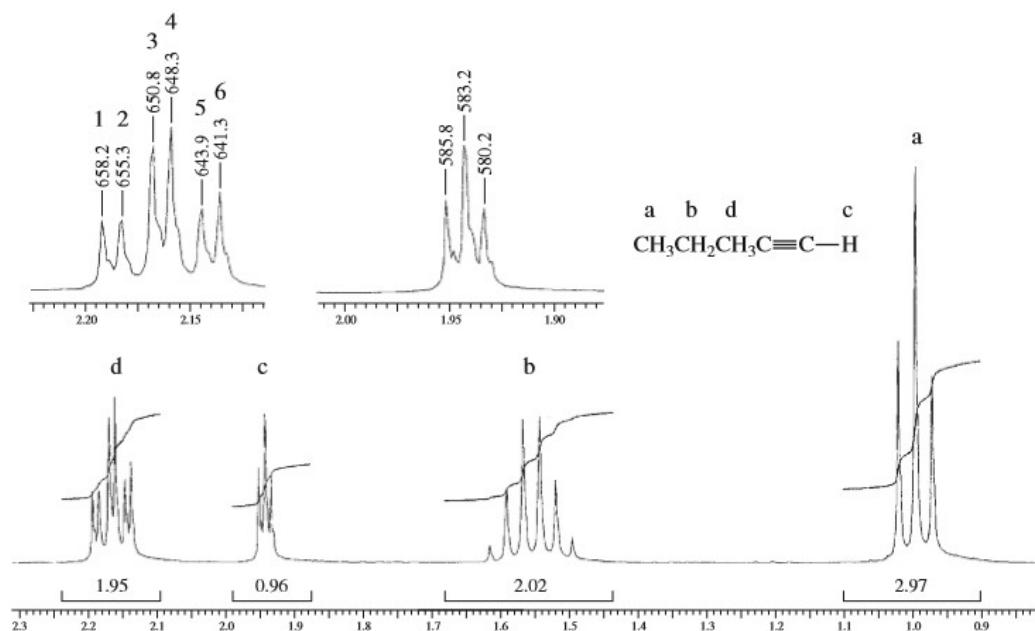


FIGURE 5.40 ^1H spectrum of 1-pentyne (300 MHz).

Aromatic Compounds

SPECTRAL ANALYSIS BOX—Aromatic Compounds

CHEMICAL SHIFTS



6.5–8.0 ppm

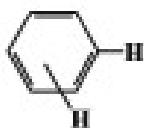
Hydrogens attached to an aromatic (benzenoid) ring have a large chemical shift, usually near 7.0 ppm. They are deshielded by the large anisotropic field generated by the electrons in the ring's π system.



2.3–2.7 ppm

Benzylic hydrogens are also deshielded by the anisotropic field of the ring, but they are more distant from the ring, and the effect is smaller.

COUPLING BEHAVIOR



$^3J_{ortho} = 7\text{--}10 \text{ Hz}$
 $^4J_{meta} = 2\text{--}3 \text{ Hz}$
 $^5J_{para} = 0\text{--}1 \text{ Hz}$

Splitting patterns for the protons on a benzene ring are discussed in Section 7.10. It is often possible to determine the positions of the substituents on the ring from these splitting patterns and the magnitudes of the coupling constants.

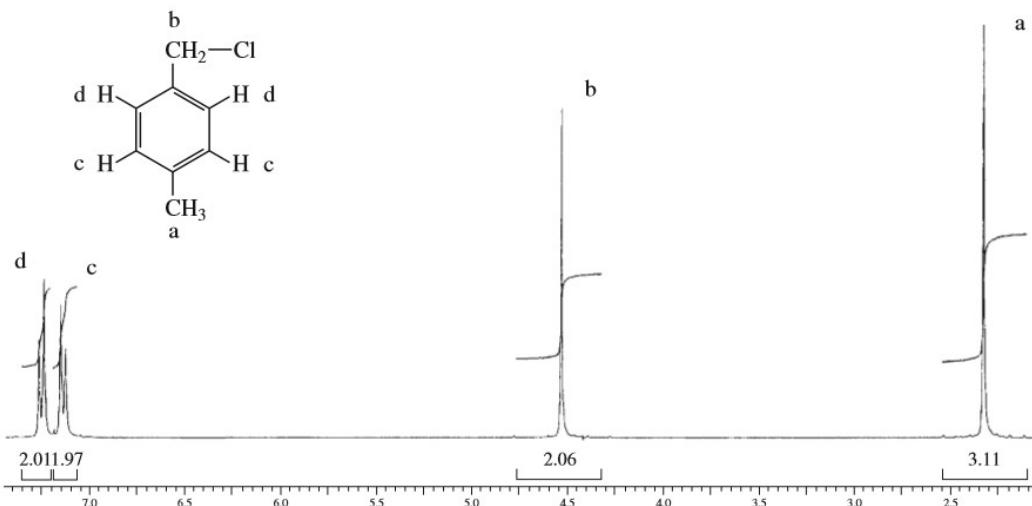


FIGURE 5.39 ^1H spectrum of α -chloro-*p*-xylene (300 MHz).

Alkyl Halides

SPECTRAL ANALYSIS BOX—Alkyl Halides

CHEMICAL SHIFTS

—CH—I	2.0–4.0 ppm	The chemical shift of a hydrogen atom attached to the same carbon as a halide atom will increase (move further downfield).
—CH—Br	2.7–4.1 ppm	This deshielding effect is due to the electronegativity of the attached halogen atom. The extent of the shift is increased as the electronegativity of the attached atom increases, with the largest shift found in compounds containing fluorine.
—CH—Cl	3.1–4.1 ppm	
—CH—F	4.2–4.8 ppm	

COUPLING BEHAVIOR

—CH—F	$^2J \approx 50$ Hz	Compounds containing fluorine will show spin–spin splitting due to coupling between the fluorine and the hydrogens on either the same or the adjacent carbon atom. ^{19}F has a spin of $\frac{1}{2}$. The other halogens (I, Cl, Br) do not show any coupling.
—CH—CF—	$^3J \approx 20$ Hz	

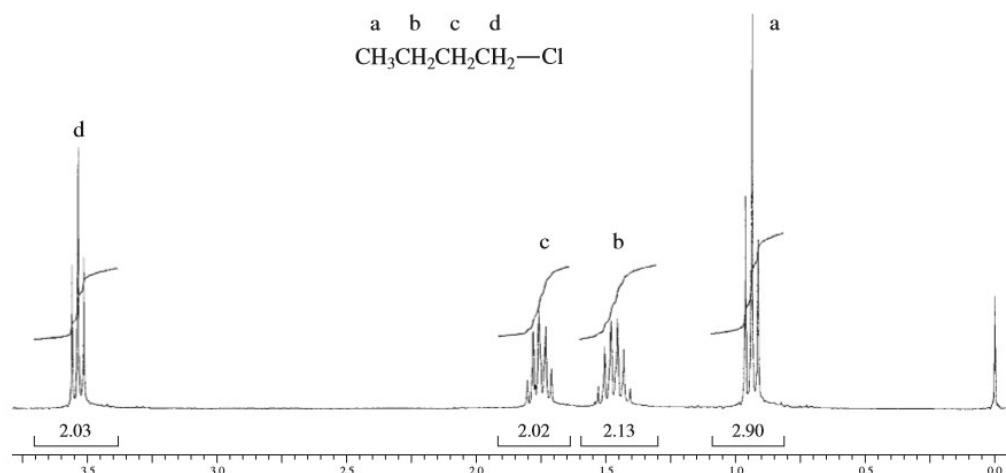


FIGURE 5.41 ^1H spectrum of 1-chlorobutane (300 MHz).

Alcohols

SPECTRAL ANALYSIS BOX—Alcohols

CHEMICAL SHIFTS

C—OH 0.5–5.0 ppm The chemical shift of the —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.

CH—O—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

CH—OH *No coupling (usually), or* Because of the rapid chemical exchange of the —OH proton in many solutions, coupling is not usually observed between the —OH proton and those hydrogens attached to the α carbon.
 $^3J = 5$ Hz

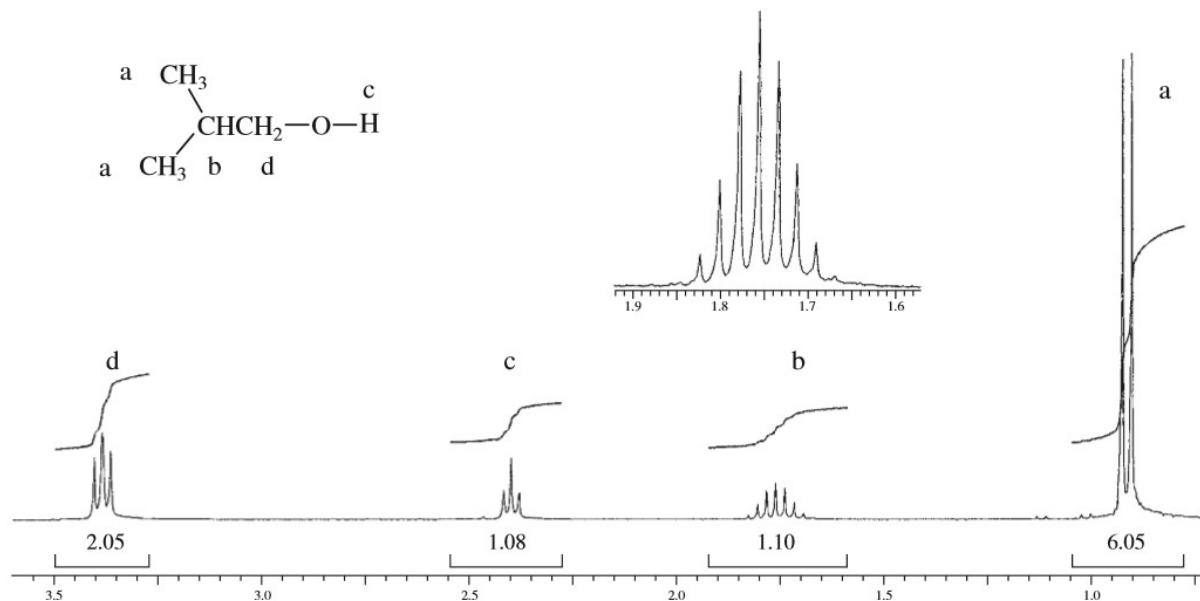
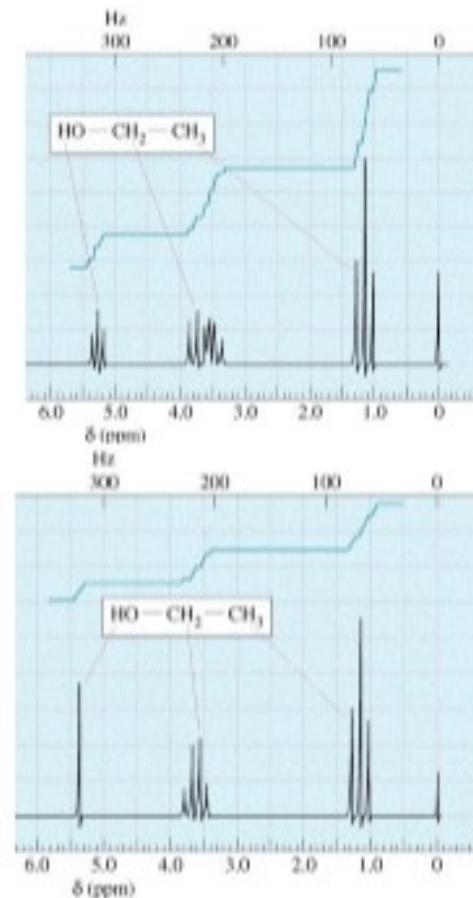


FIGURE 5.42 ^1H spectrum of 2-methyl-1-propanol (300 MHz).

Hydroxyl Proton

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



Ethers

SPECTRAL ANALYSIS BOX—Ethers

CHEMICAL SHIFTS



The hydrogens on the carbons attached to the oxygen are deshielded due to the electronegativity of the oxygen.

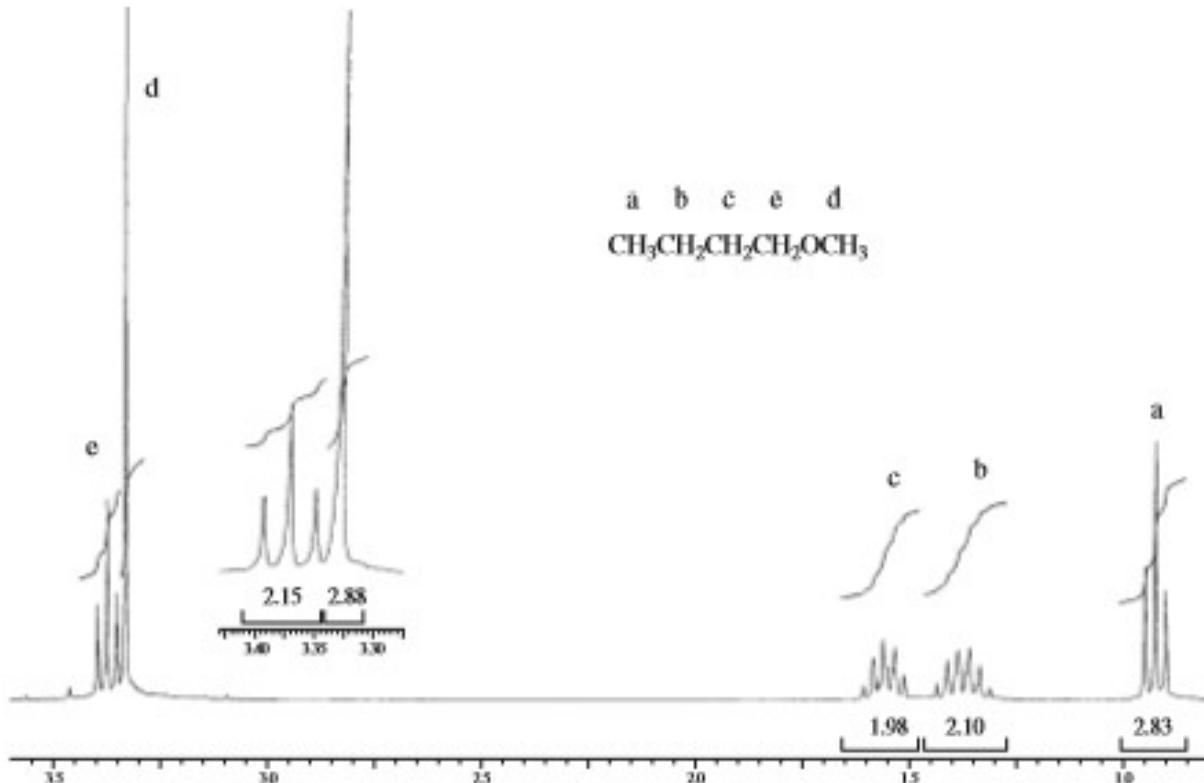


FIGURE 5.43 ^1H spectrum of butyl methyl ether (300 MHz).

Amines

SPECTRAL ANALYSIS BOX—Amines

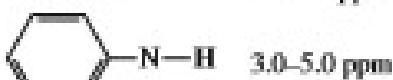
CHEMICAL SHIFTS



Hydrogens attached to a nitrogen have a variable chemical shift depending on the temperature, acidity, amount of hydrogen bonding, and solvent.



The α hydrogen is slightly deshielded due to the electronegativity of the attached nitrogen.



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



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

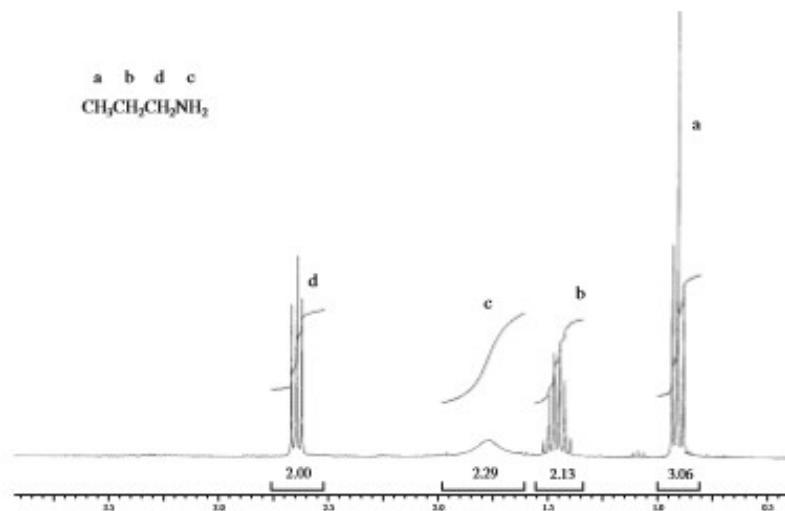


FIGURE 5.44 ^1H spectrum of propylamine (300 MHz).

Nitriles

SPECTRAL ANALYSIS BOX—Nitriles

CHEMICAL SHIFTS

$-\text{CH}_2\text{C}\equiv\text{N}$ 2.1–3.0 ppm The α hydrogens are slightly deshielded by the cyano group.

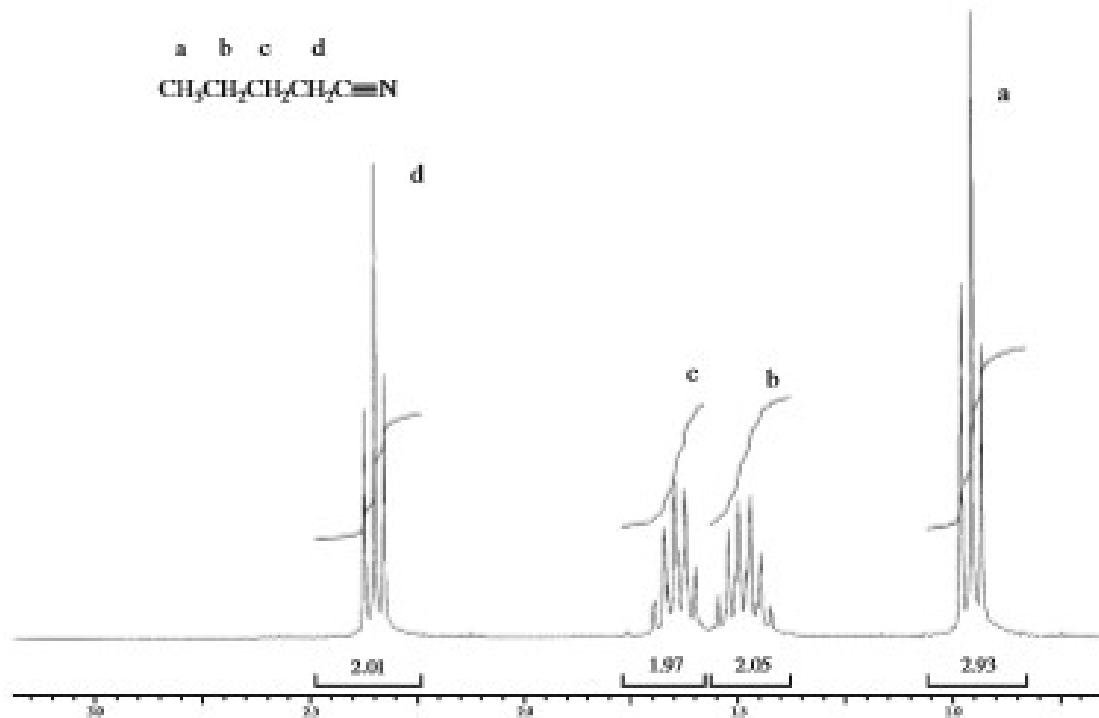


FIGURE 5.45 ^1H spectrum of valeronitrile (300 MHz).

Aldehydes

SPECTRAL ANALYSIS BOX—Aldehydes

CHEMICAL SHIFTS

R—CHO 9.0–10.0 ppm The aldehyde hydrogen is shifted far downfield due to the anisotropy of the carbonyl group (C=O).

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

COUPLING BEHAVIOR

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

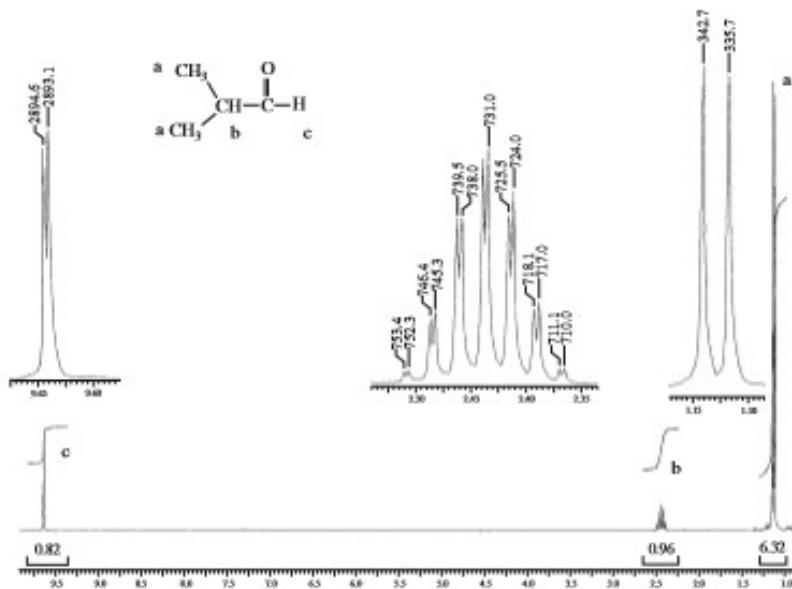


FIGURE 5.46 ^1H spectrum of 2-methylpropanal (isobutyraldehyde) at 300 MHz.

Ketones

SPECTRAL ANALYSIS BOX—Ketones

CHEMICAL SHIFTS



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

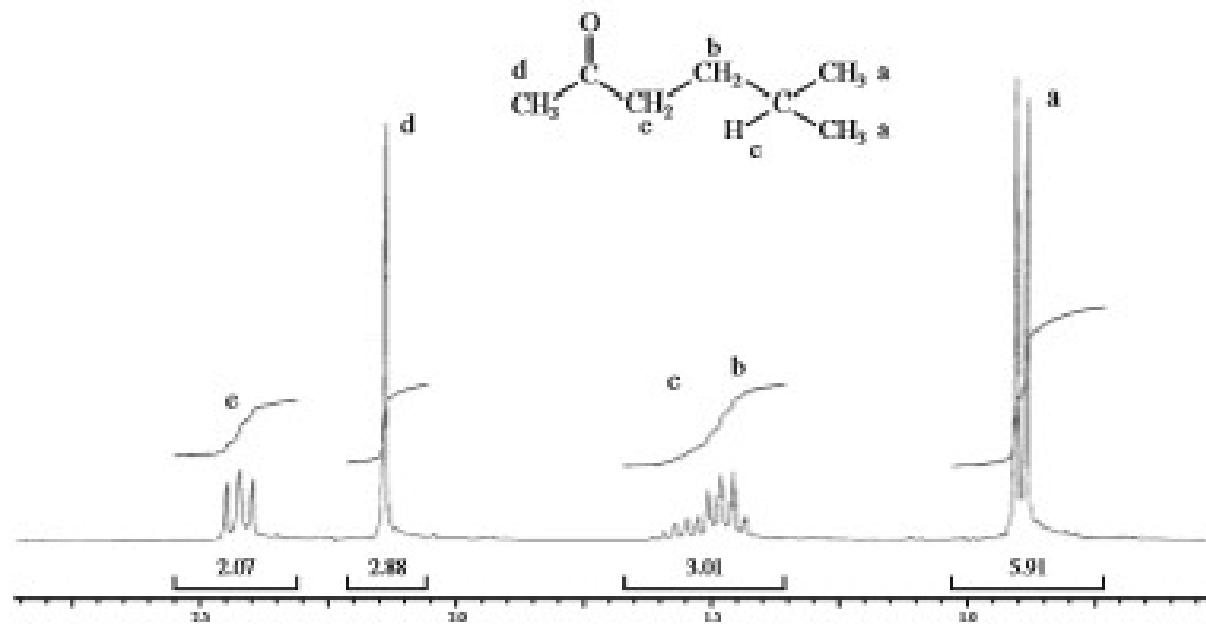
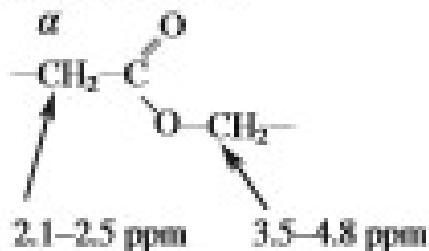


FIGURE 5.47 ^1H spectrum of 5-methyl-2-hexanone (300 MHz).

Esters

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.

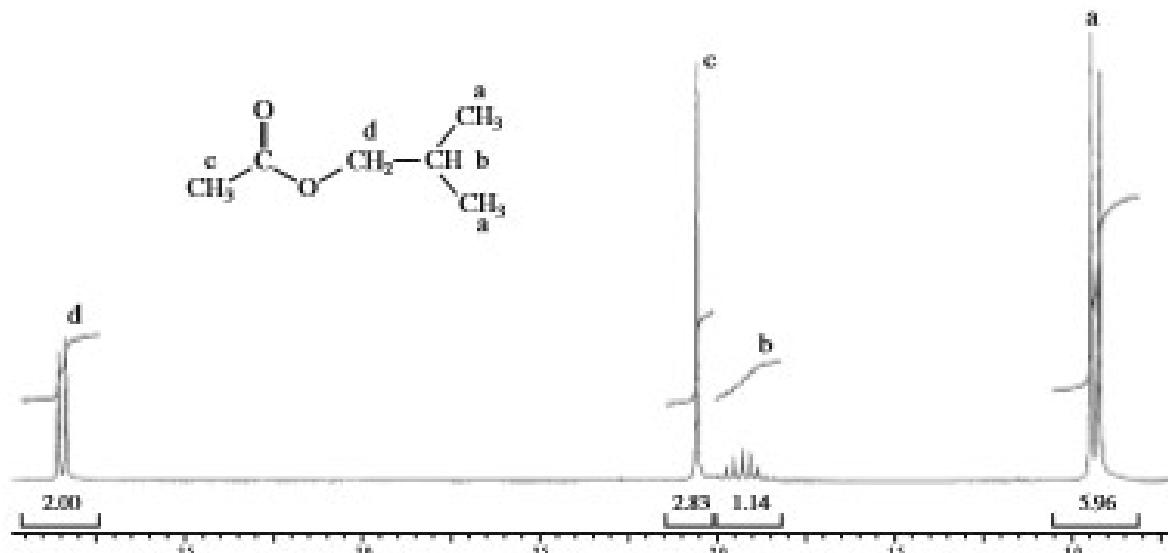


FIGURE 5.48 ^1H spectrum of isobutyl acetate (300 MHz).

Carboxylic Acids

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.

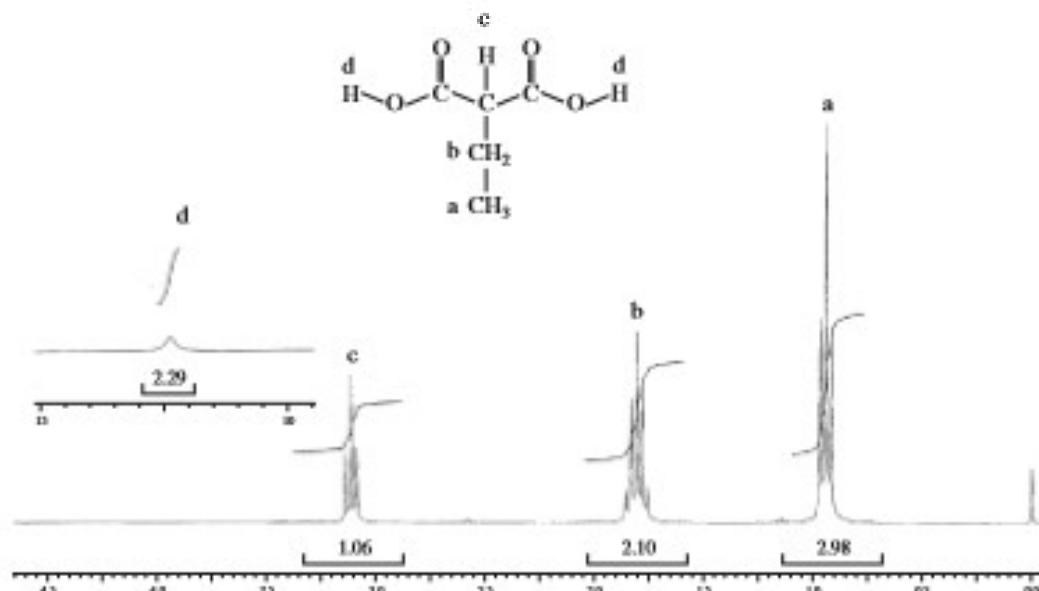


FIGURE 5.49 ^1H spectrum of ethylmalonic acid (300 MHz).

Amides

SPECTRAL ANALYSIS BOX—Amides

CHEMICAL SHIFTS

R(CO)–N–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.
–CH–CONH–	2.1–2.5 ppm	The α hydrogens in amides absorb in the same range as other acyl (next to C=O) hydrogens. They are slightly deshielded by the carbonyl group.
R(CO)–N–CH	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.

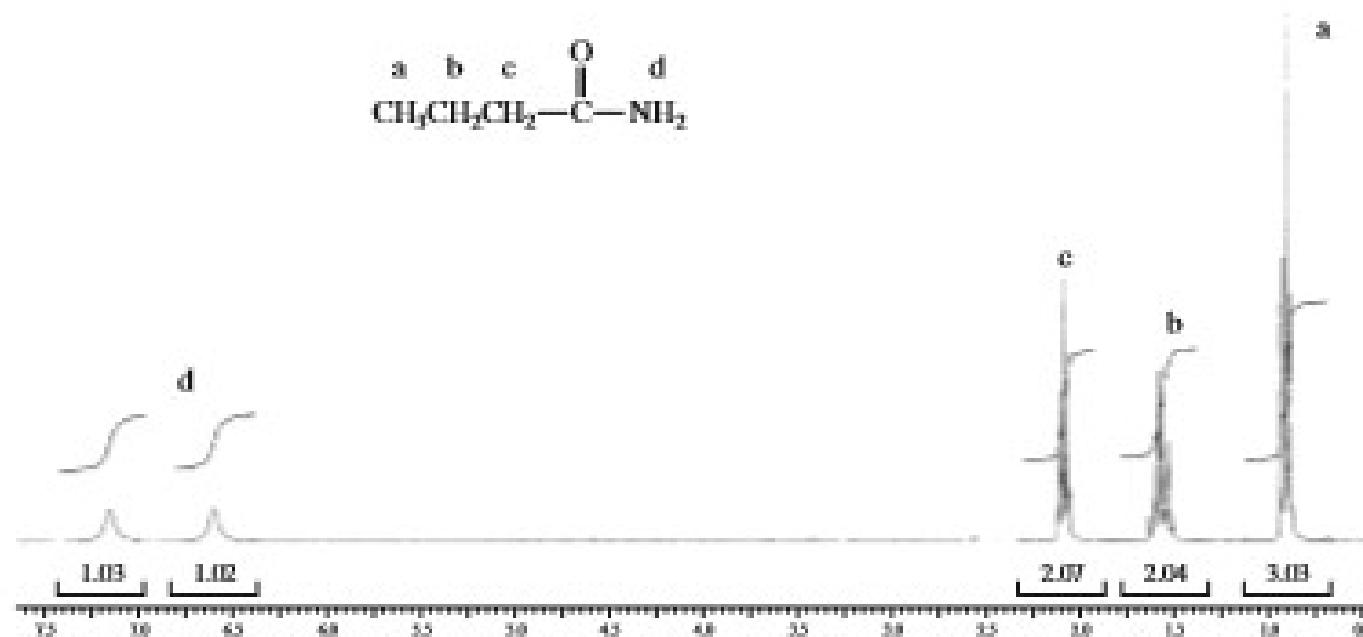


FIGURE 5.50 ^1H spectrum of butyramide (300 MHz).

Nitroalkanes

SPECTRAL ANALYSIS BOX—Nitroalkanes

$-\text{CH}_2\text{NO}_2$ 4.1–4.4 ppm Deshielded by the nitro group.

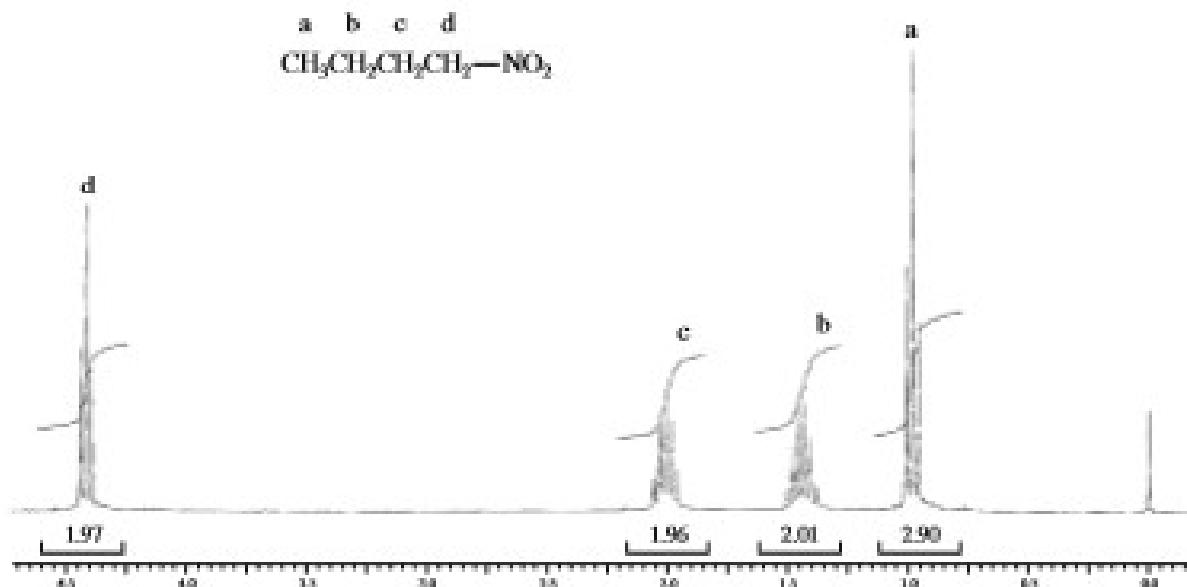
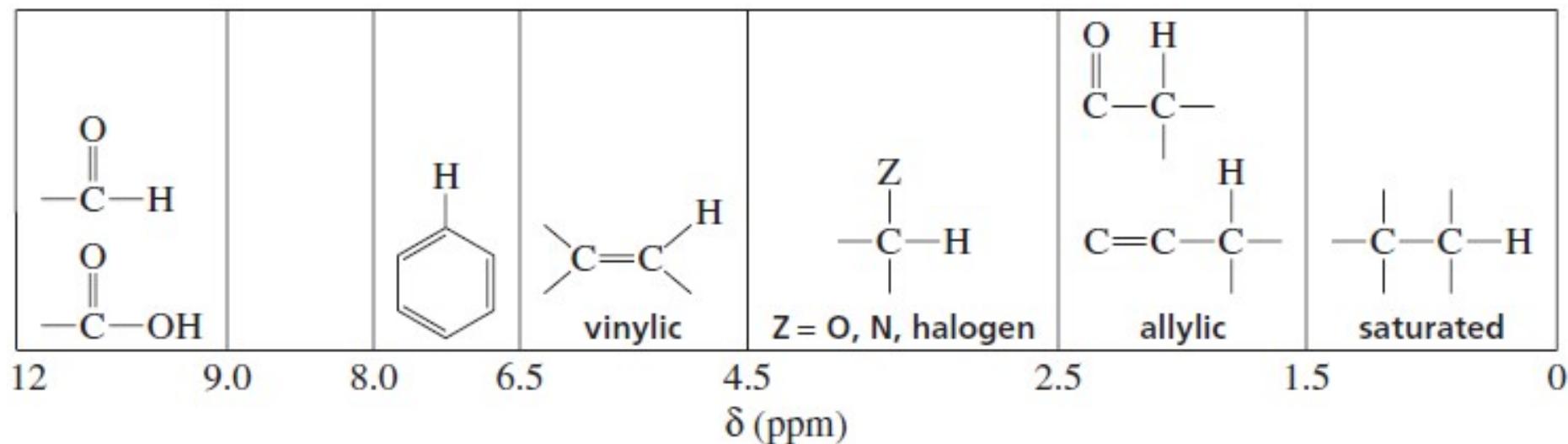
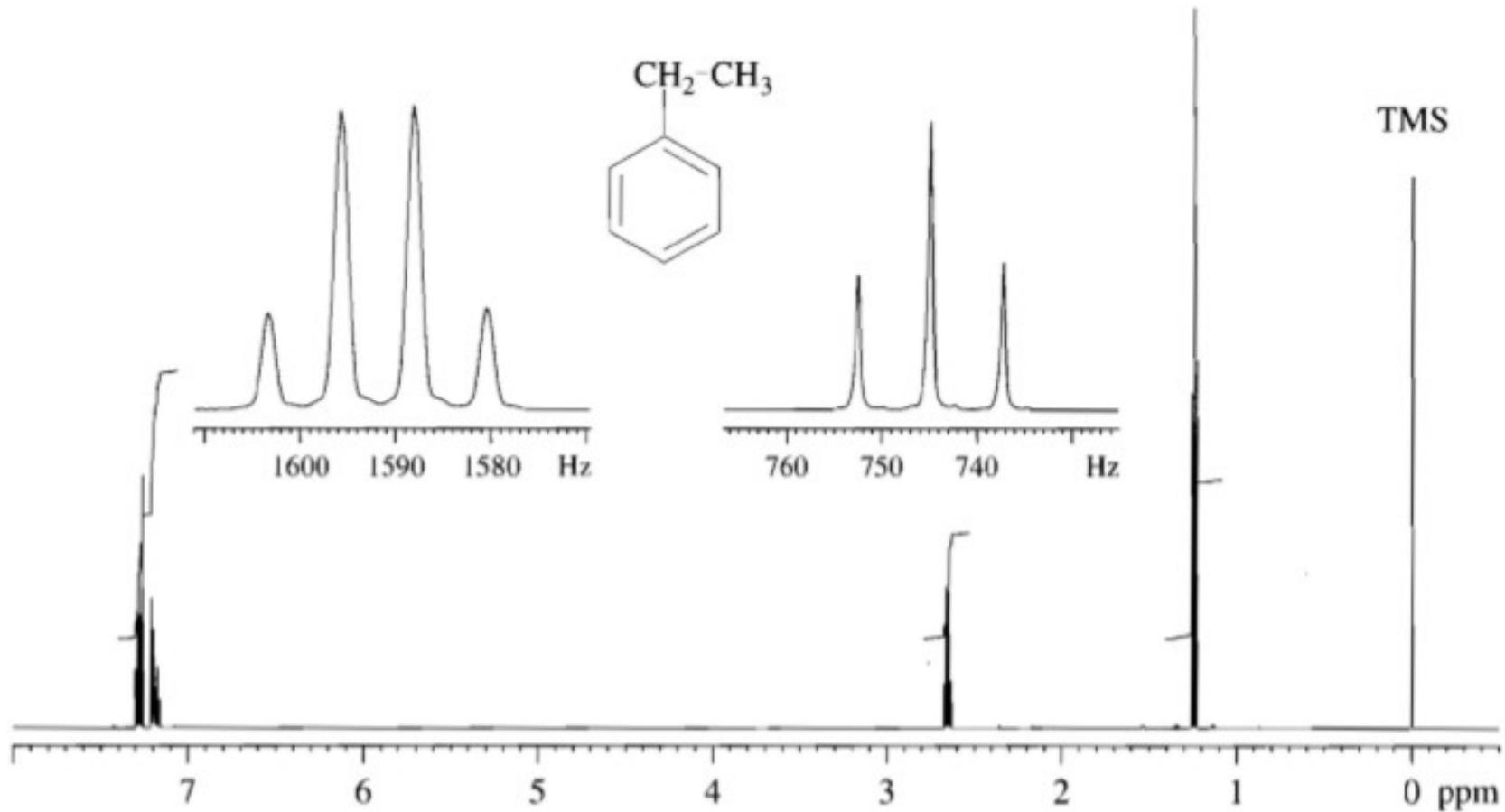


FIGURE 5.51 ^1H spectrum of 1-nitrobutane (300 MHz).

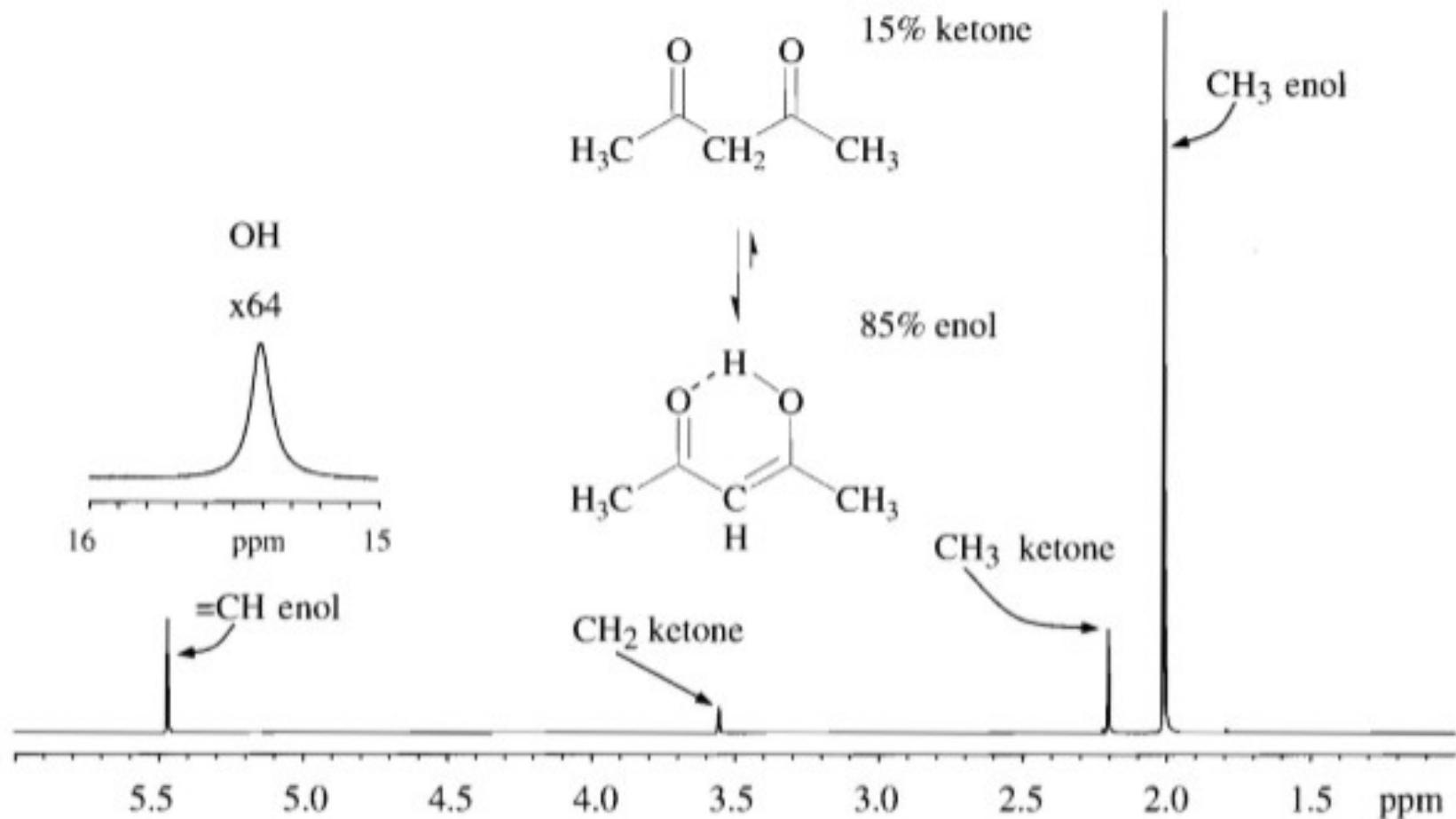
Characteristic Values of Chemical Shifts



NMR

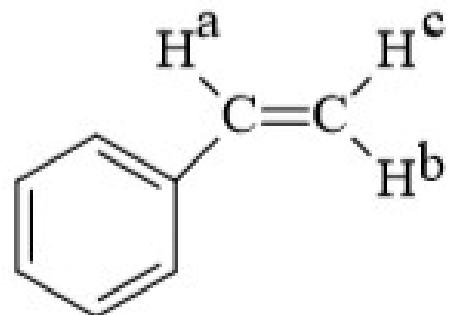


Keto-Enol



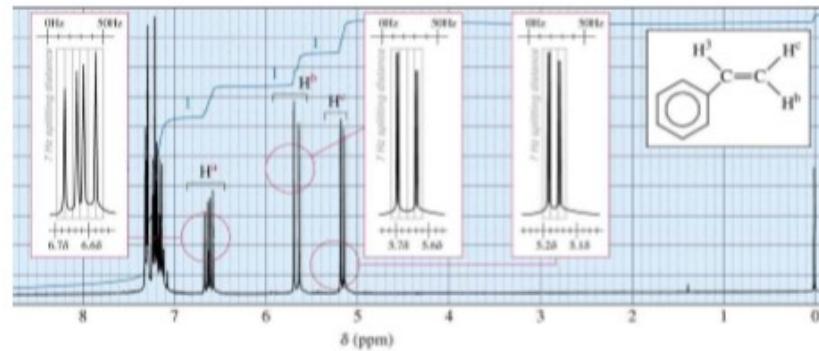
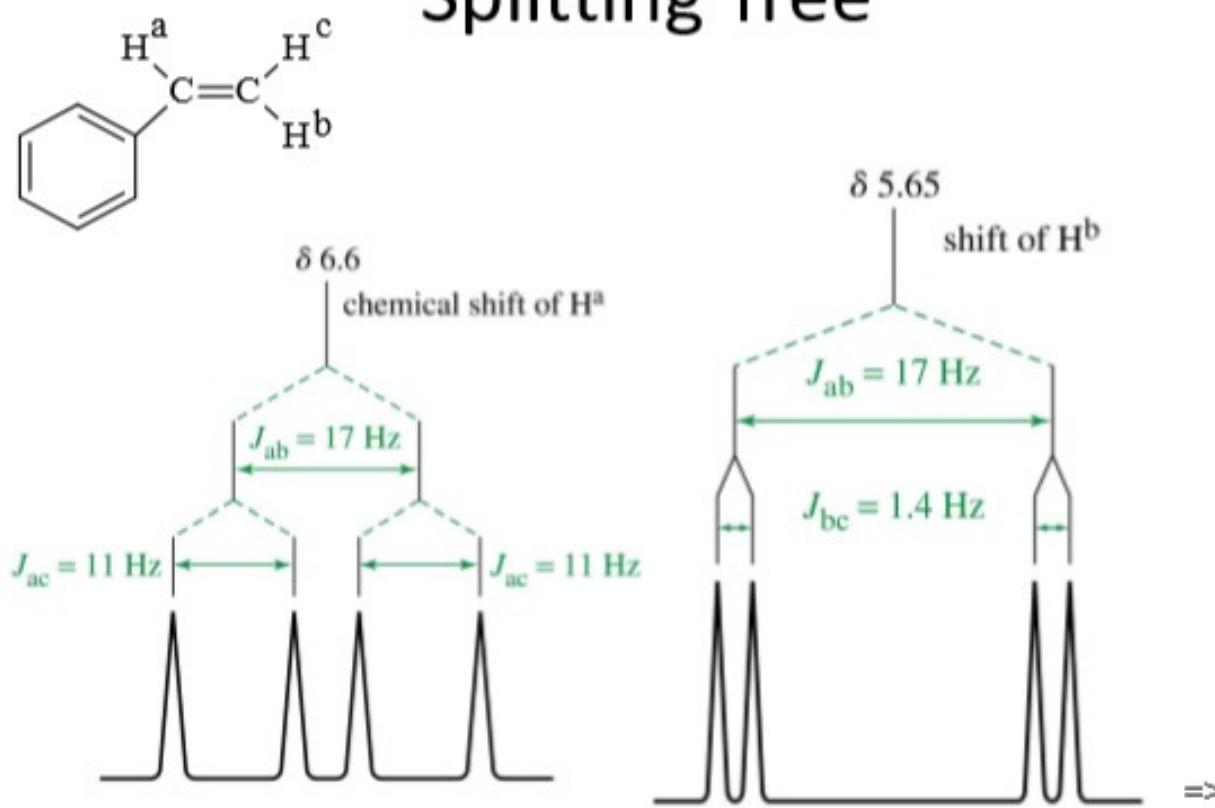
Complex Splitting

- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- 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).



Complex Splitting

Splitting Tree



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.

