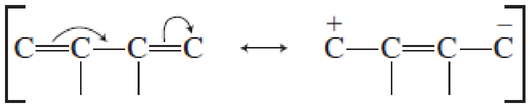
Lecture # 4

C=C Stretching Vibrations

Simple Alkyl-Substituted Alkenes. The C=C stretching frequency usually appears between 1670 and 1640 cm^{-1} for simple noncyclic (acyclic) alkenes. The C=C frequencies increase as alkyl groups are added to a double bond. For example, simple monosubstituted alkenes yield values near 1640 cm^{-1}, 1,1-disubstituted alkenes absorb at about 1650 cm^{-1}, and tri- and tetrasubstituted alkenes absorb near 1670 cm^{-1}. *Trans*-Disubstituted alkenes absorb at higher frequencies (1670 cm^{-1})

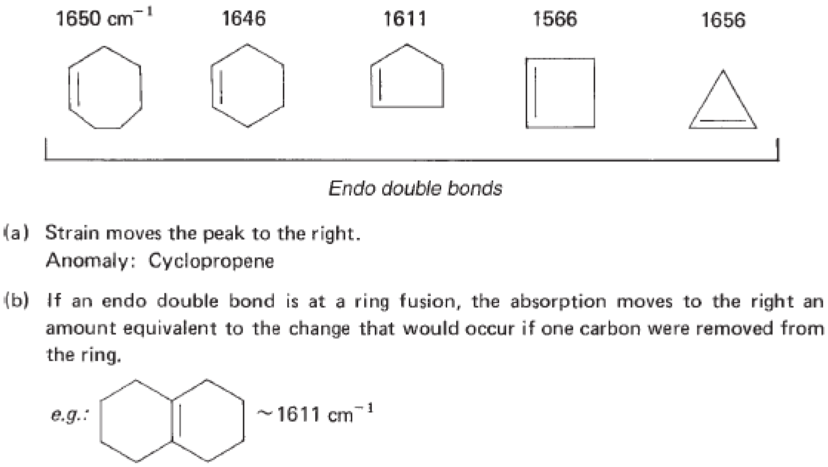
than *cis*-disubstituted alkenes (1658 cm^{-1}).

Conjugation Effects. Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single-bond character (through resonance, as the following example shows), a lower force constant *K*, and thus a lower frequency of vibration. For example, the vinyl double bond in styrene gives an absorption at 1630 cm^{-1}.



With several double bonds, the number of C=C absorptions often corresponds to the number of conjugated double bonds. An example of this correspondence is found in 1,3-pentadiene, where absorptions are observed at 1600 and 1650 cm^{-1}. In the exception to the rule, butadiene gives only one band near 1600 cm^{-1}. If the double bond is conjugated with a carbonyl group, the C=C absorption shifts to a lower frequency and is also intensified by the strong dipole of the carbonyl group.

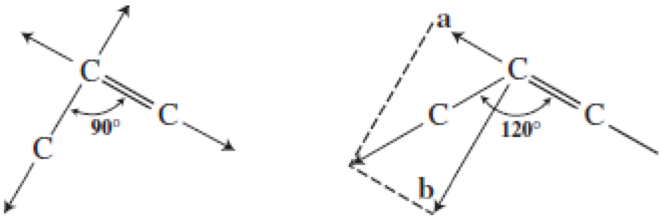
Ring-Size Effects with Internal Double Bonds.



(a) Strain moves the peak to the right.
Anomaly: Cyclopropene

(b) If an endo double bond is at a ring fusion, the absorption moves to the right an amount equivalent to the change that would occur if one carbon were removed from the ring.

FIGURE 2.19 C=C stretching vibrations in endocyclic systems.



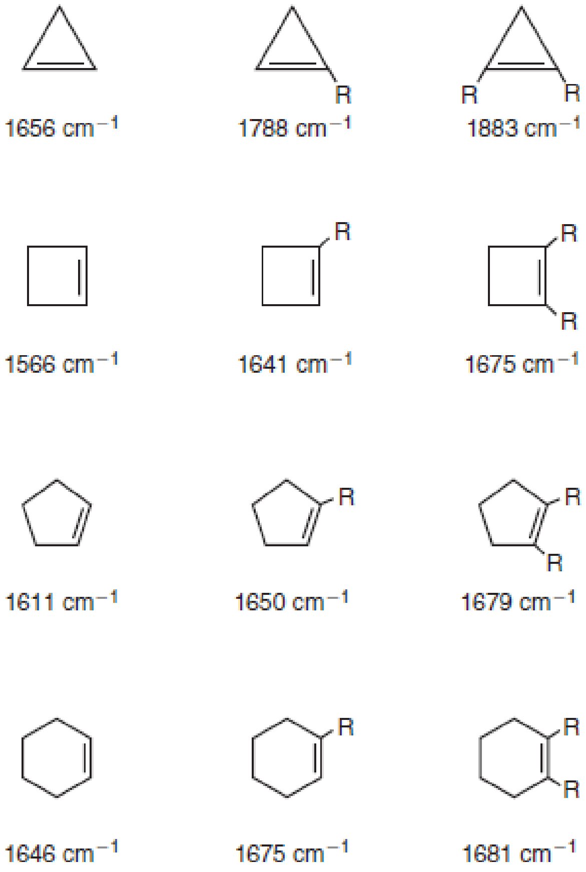


FIGURE 2.20 The effect of alkyl substitution on the frequency of a C=C bond in a ring.

Ring-Size Effects with External Double Bonds. *External (exocyclic)* double bonds give an increase in absorption frequency with decreasing ring size, as shown in Figure 2.21. Allene is included in the figure because it is an extreme example of an *exo* double-bond absorption.

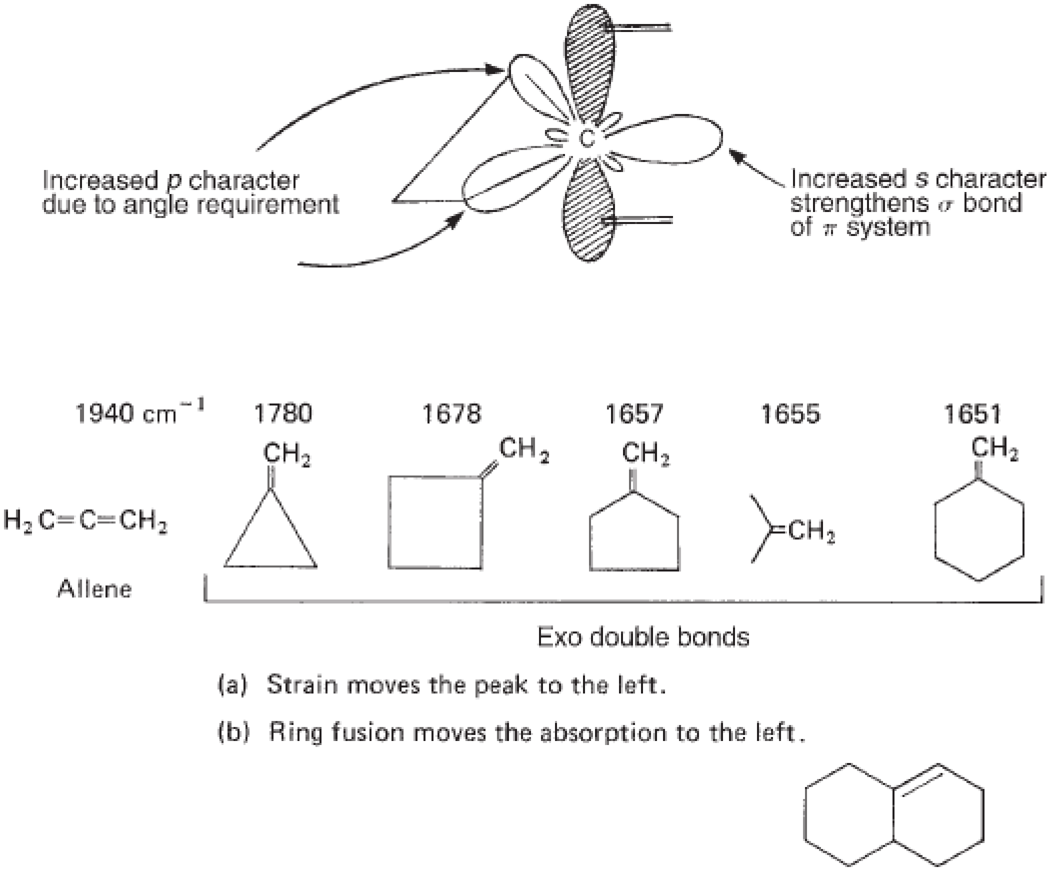


FIGURE 2.21 C=C stretching vibrations in exocyclic systems.

The most valuable information for alkenes is obtained from analysis of the C—H out-of-plane region of the spectrum, which extends from 1000 to 650 cm^{-1}. These bands are frequently the strongest peaks in the spectrum. The number of absorptions and their positions in the spectrum can be used to indicate the substitution pattern on the double bond.

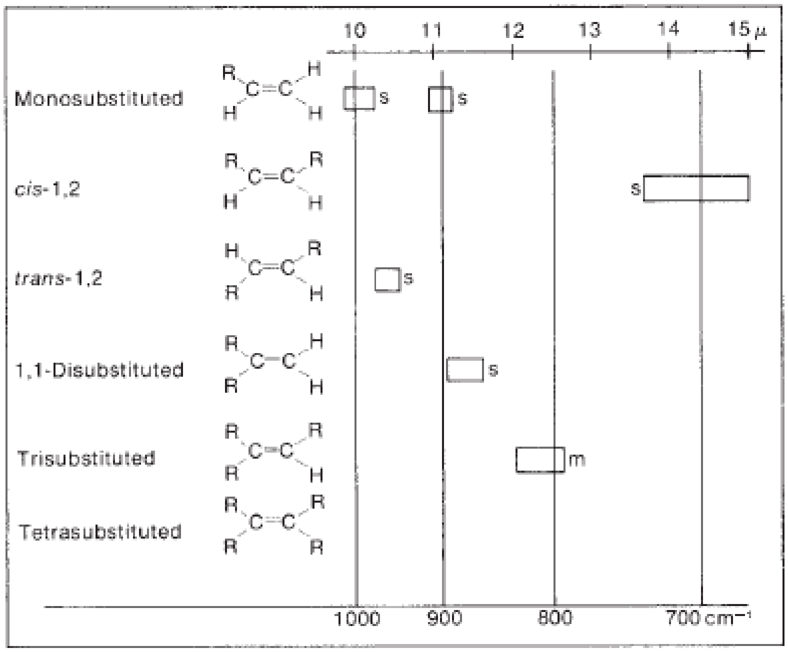


FIGURE 2.22 The C—H out-of-plane bending vibrations for substituted alkenes.

2.11 AROMATIC RINGS

SPECTRAL ANALYSIS BOX

AROMATIC RINGS

=C—H	Stretch for *sp*^{2} C—H occurs at values greater than 3000 cm^{-1} (3050–3010 cm^{-1}).
=C—H	Out-of-plane (oop) bending occurs at 900–690 cm^{-1}. These bands can be used with great utility to assign the ring substitution pattern (see discussion).
C=C	Ring stretch absorptions often occur in pairs at 1600 cm^{-1} and 1475 cm^{-1}.

Overtone/combination bands appear between 2000 and 1667 cm^{-1}. These *weak* absorptions can be used to assign the ring substitution pattern (see discussion).

Examples: toluene (Fig. 2.23), *ortho*-diethylbenzene (Fig. 2.24), *meta*-diethylbenzene (Fig. 2.25), *para*-diethylbenzene (Fig. 2.26), and styrene (Fig. 2.27).

The in-plane C—H bending vibrations occur between 1300 and 1000 cm^{-1}. However, these bands are rarely useful because they overlap other, stronger absorptions that occur in this region.

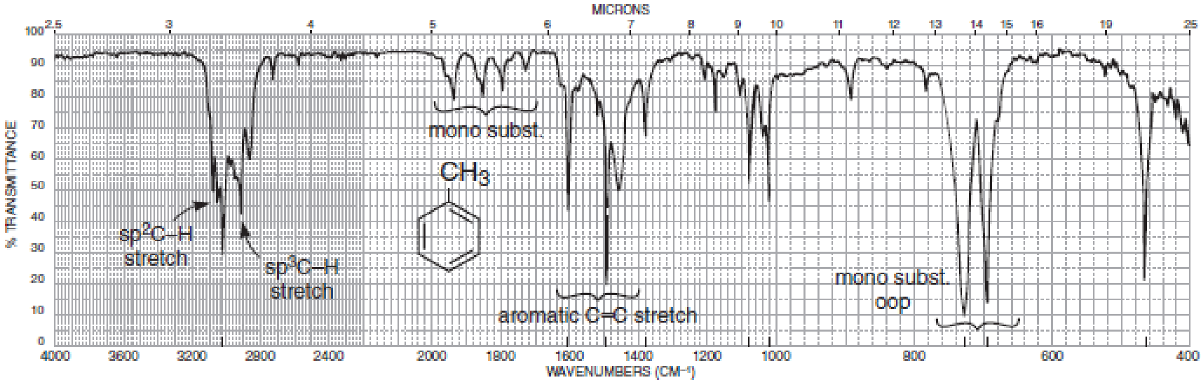


FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

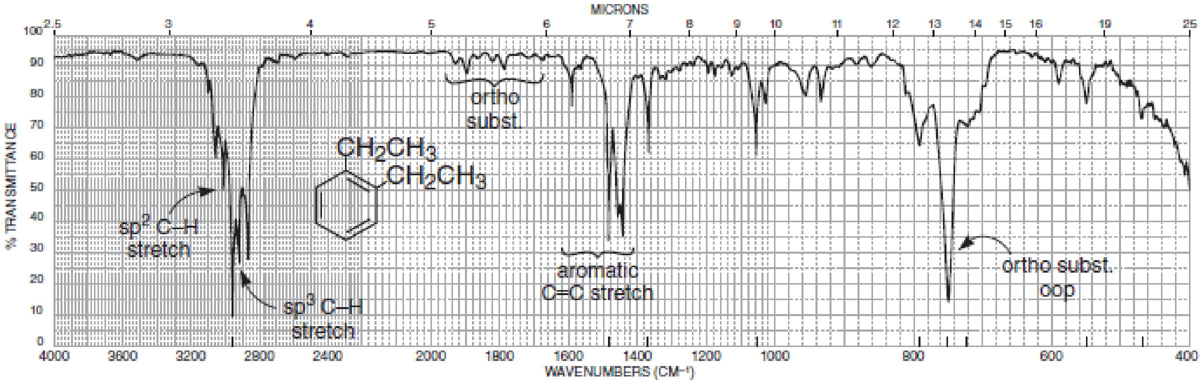


FIGURE 2.24 The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).

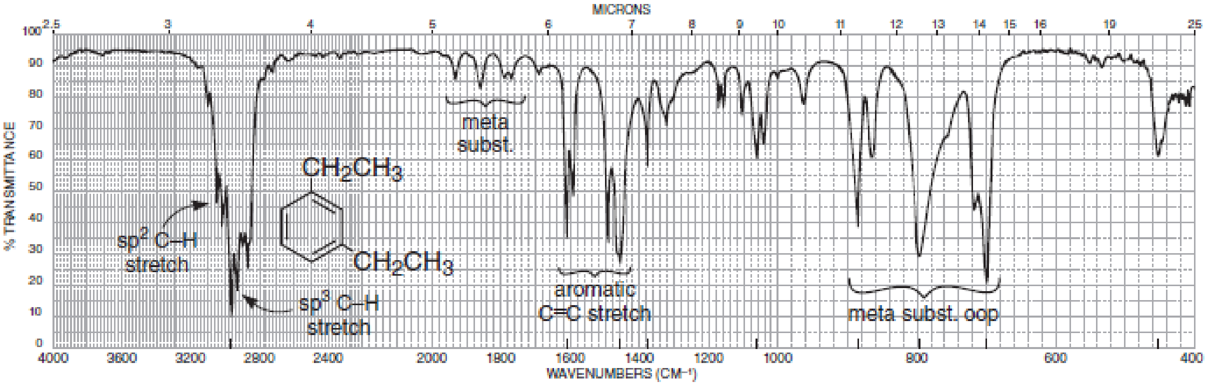


FIGURE 2.25 The infrared spectrum of *meta*-diethylbenzene (neat liquid, KBr plates).

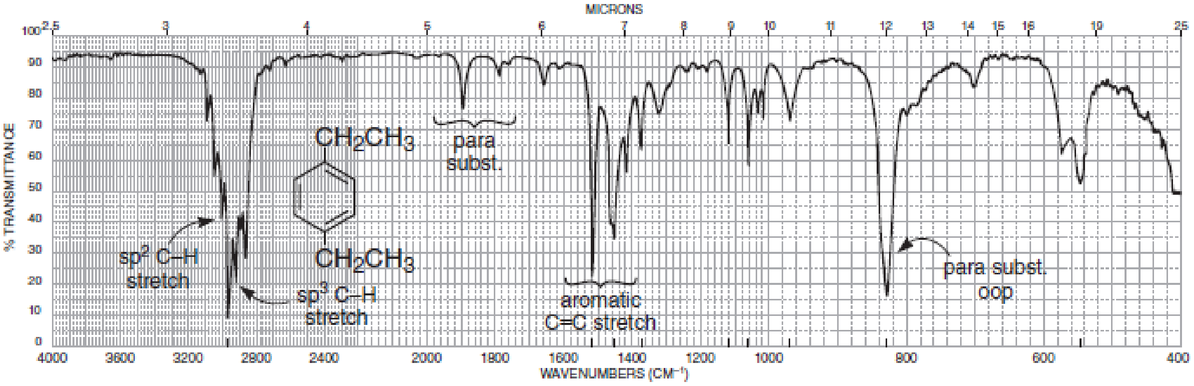


FIGURE 2.26 The infrared spectrum of *para*-diethylbenzene (neat liquid, KBr plates).

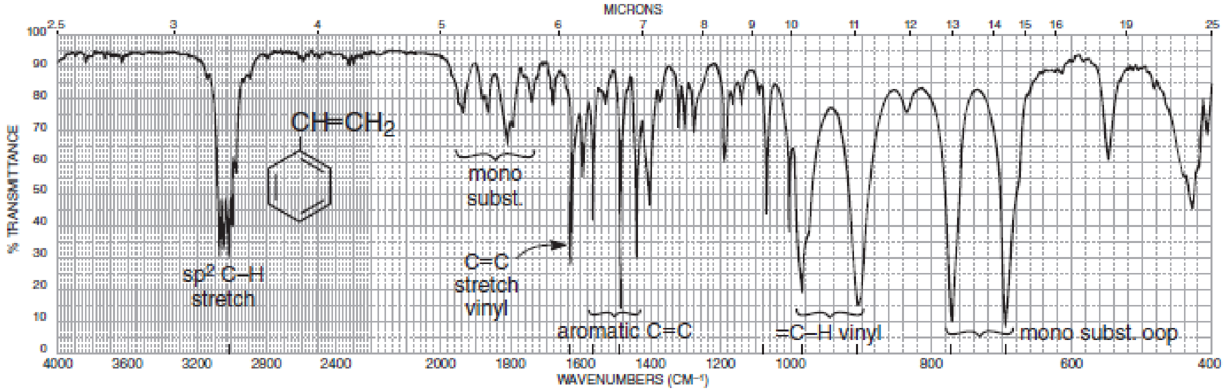
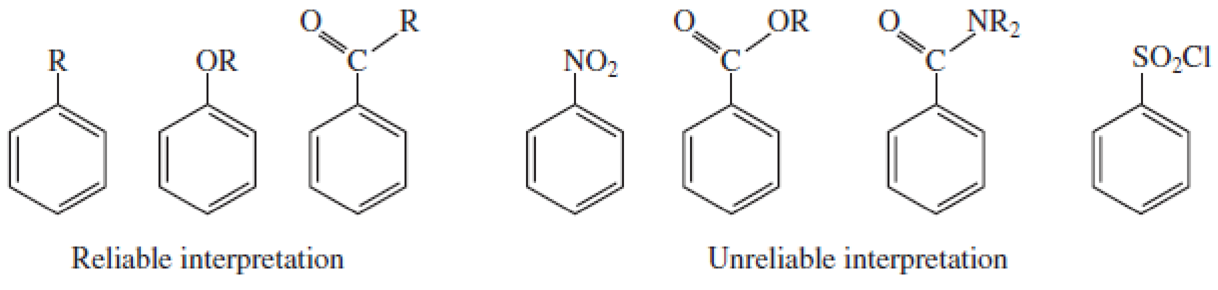


FIGURE 2.27 The infrared spectrum of styrene (neat liquid, KBr plates).

aromatic ring. The assignment of structure based on these out-of-plane bending vibrations is most reliable for alkyl-, alkoxy-, halo-, amino-, or carbonyl-substituted aromatic compounds. Aromatic nitro compounds, derivatives of aromatic carboxylic acids, and derivatives of sulfonic acids sometimes lead to unsatisfactory interpretation.



Combinations and Overtone Bands

Many *weak* combination and overtone absorptions appear between 2000 and 1667 cm^{-1}. The relative shapes and number of these peaks can be used to tell whether an aromatic ring is mono-, di-, tri-, tetra-, penta-, or hexasubstituted. Positional isomers can also be distinguished. Since the absorptions are weak, these bands are best observed by using neat liquids or concentrated solutions. If the compound has a high-frequency carbonyl group, this absorption will overlap the weak overtone bands so that no useful information can be obtained from the analysis of the region.

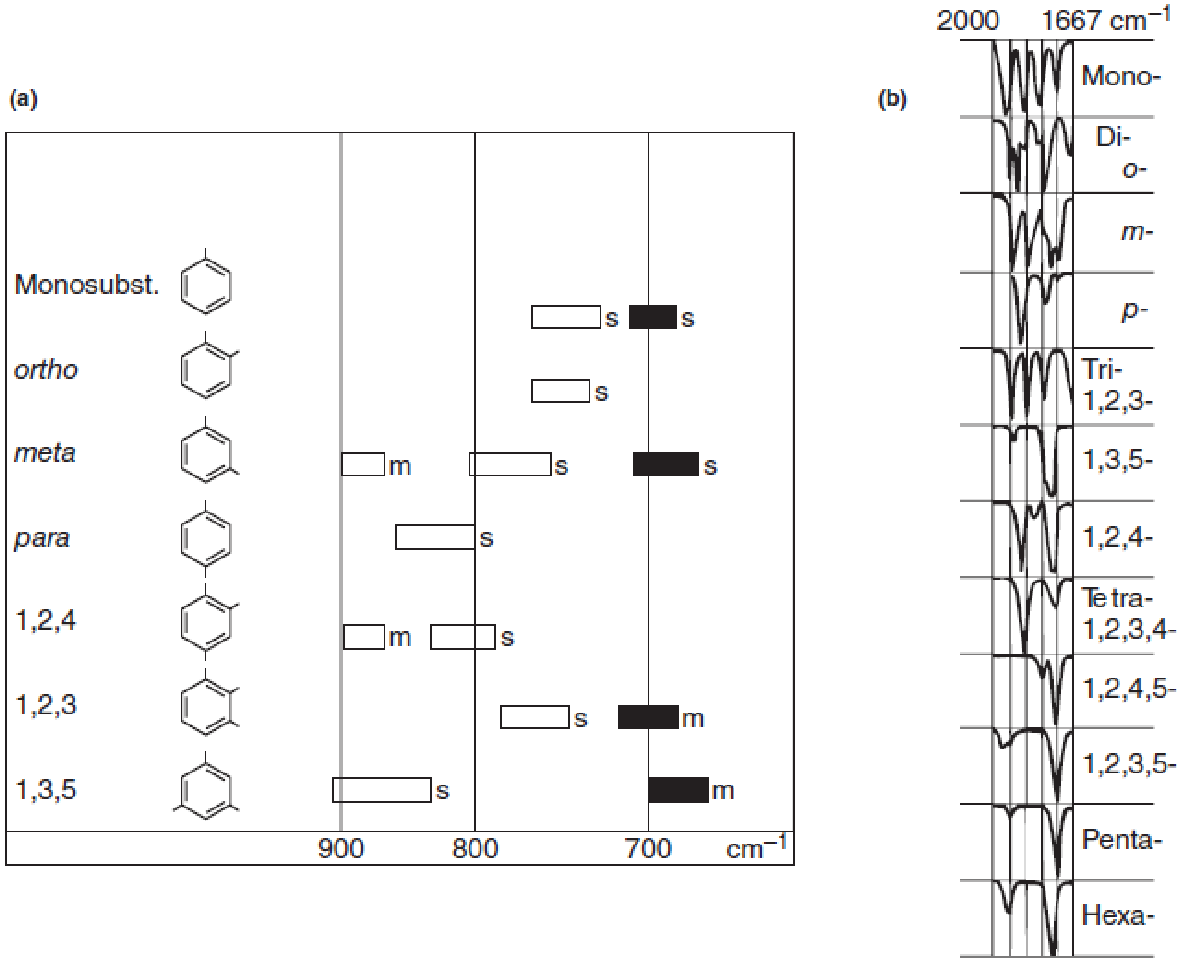


FIGURE 2.28 (a) The C—H out-of-plane bending vibrations for substituted benzenoid compounds. (*s* = *strong*, *m* = *medium*) (b) The 2000- to 1667-cm^{-1} region for substituted benzenoid compounds (from Dyer, John R., *Applications of Absorption Spectroscopy of Organic Compounds,* Prentice–Hall, Englewood Cliffs, N.J., 1965).

2.12 ALCOHOLS AND PHENOLS

SPECTRAL ANALYSIS BOX

ALCOHOLS AND PHENOLS

O—H	The free O—H stretch is a *sharp* peak at 3650–3600 cm^{-1}. This band appears in combination with the hydrogen-bonded O—H peak when the alcohol is dissolved in a solvent (see discussion). The hydrogen-bonded O—H band is a *broad* peak at 3400–3300 cm^{-1}. This band is usually the only one present in an alcohol that has not been dissolved in a solvent (neat liquid). When the alcohol is dissolved in a solvent, the free O—H and hydrogen-bonded O—H bands are present together, with the relatively weak free O—H on the left (see discussion).
C—O—H	Bending appears as a broad and weak peak at 1440–1220 cm^{-1}, often obscured by the CH_3 bendings.
C—O	Stretching vibration usually occurs in the range 1260–1000 cm^{-1}. This band can be used to assign a primary, secondary, or tertiary structure to an alcohol (see discussion).

Examples: The hydrogen-bonded O—H stretch is present in the pure liquid (neat) samples of 1-hexanol (Fig. 2.29), 2-butanol (Fig. 2.30), and *para*-cresol (Fig. 2.31).

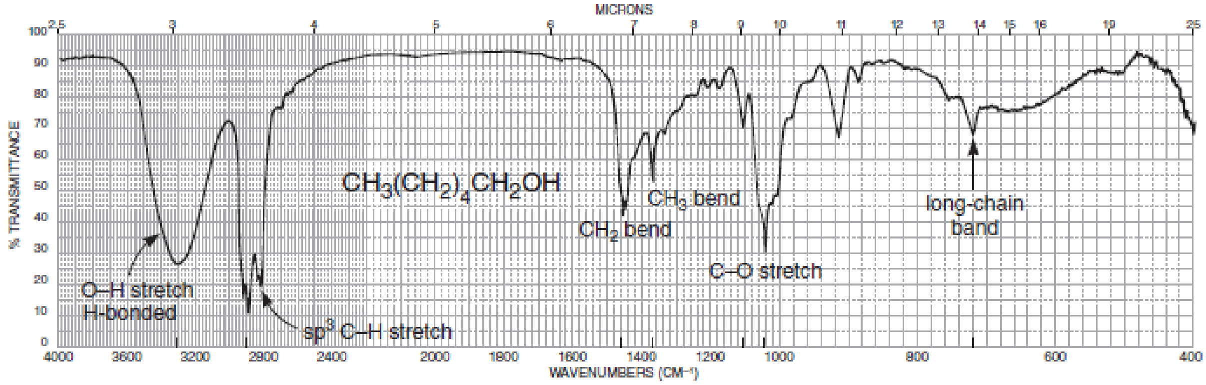


FIGURE 2.29 The infrared spectrum of 1-hexanol (neat liquid, KBr plates).

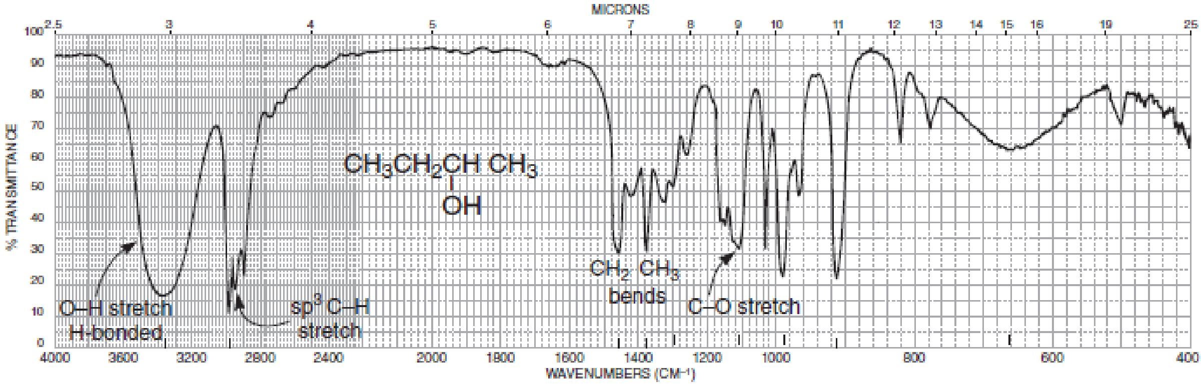


FIGURE 2.30 The infrared spectrum of 2-butanol (neat liquid, KBr plates).

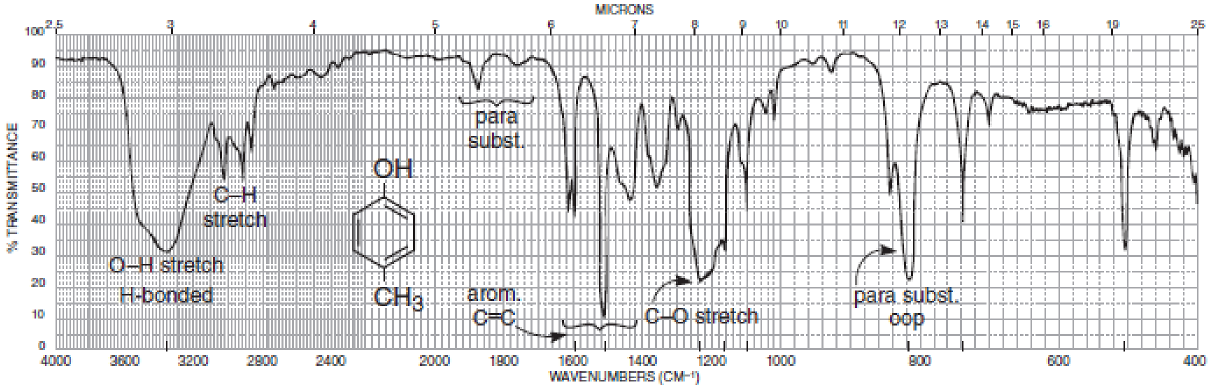
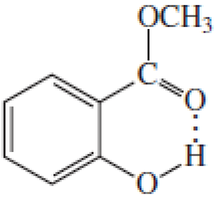


FIGURE 2.31 The infrared spectrum of *para*-cresol (neat liquid, KBr plates).

Intramolecular hydrogen bonding, present in *ortho*-carbonyl-substituted phenols, usually shifts the broad O—H band to a lower frequency. For example, the O—H band is centered at about 3200 cm^{-1} in the neat spectrum of methyl salicylate, while O—H bands from normal phenols are centered at about 3350 cm^{-1}. The intramolecular hydrogen-bonded band does not change its position significantly even at high dilution because the internal bonding is not altered by a change in concentration.



Methyl salicylate

Although phenols often have broader O—H bands than alcohols, it is difficult to assign a structure based on this absorption; use the aromatic C=C region and the C—O stretching vibration (to be discussed shortly) to assign a phenolic structure. Finally, the O—H stretching vibrations in carboxylic acids also occur in this region. They may easily be distinguished from alcohols and phenols by the presence of a *very broad* band extending from 3400 to 2400 cm^{-1} *and* the presence of a carbonyl absorption (see Section 2.14D).

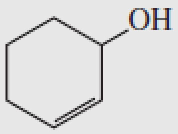
C—O—H Bending Vibrations

This bending vibration is coupled to H—C—H bending vibrations to yield some weak and broad peaks in the 1440 to 1220-cm^{-1} region. These broad peaks are difficult to observe because they are usually located under the more strongly absorbing CH_3 bending peaks at 1375 cm^{-1} (see Fig. 2.29).

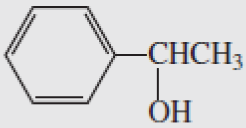
TABLE 2.7
C—O AND O—H STRETCHING VIBRATIONS IN ALCOHOLS AND PHENOLS

Compound	C—O Stretch (cm^{-1})	O—H Stretch (cm^{-1})
Phenols	1220	3610
3° Alcohols (saturated)	Decrease 1150	Increase 3620
2° Alcohols (saturated)	1100	3630
1° Alcohols (saturated)	↓ 1050	↓ 3640

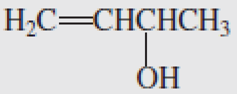
Unsaturation on adjacent carbons or a cyclic structure lowers the frequency of C—O absorption.
2° examples:



1100 → 1070 cm^{-1}



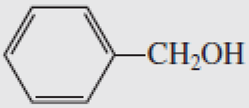
1100 → 1070 cm^{-1}



$H_2C{=}CH\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

1100 → 1060 cm^{-1}

1° examples:



1050 → 1017 cm^{-1}

$HC{\equiv}CCH_2OH$

1050 → 1030 cm^{-}

2.13 ETHERS

SPECTRAL ANALYSIS BOX

ETHERS

C—O The most prominent band is that due to C—O stretch, 1300–1000 cm^{-1}. Absence of C=O and O—H is required to ensure that C—O stretch is not due to an ester or an alcohol. Phenyl alkyl ethers give two strong bands at about 1250 and 1040 cm^{-1}, while aliphatic ethers give one strong band at about 1120 cm^{-1}.

Examples: dibutyl ether (Fig. 2.33) and anisole (Fig. 2.34).

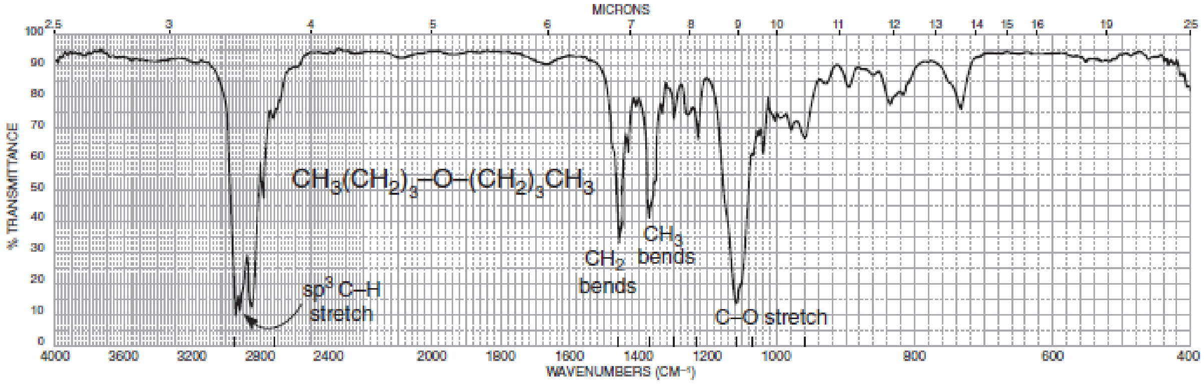


FIGURE 2.33 The infrared spectrum of dibutyl ether (neat liquid, KBr plates).

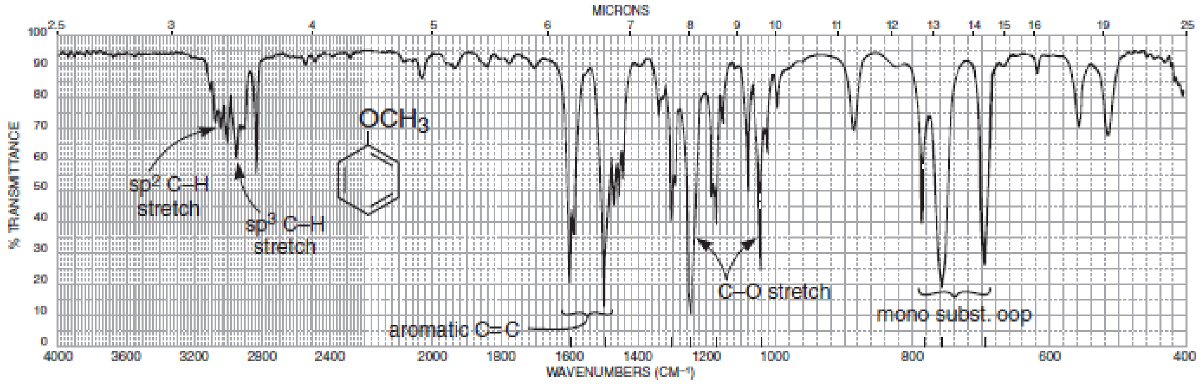
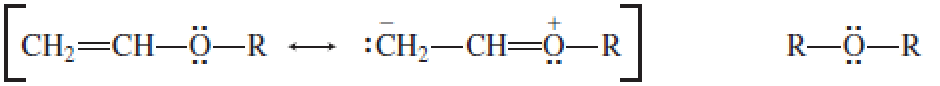


FIGURE 2.34 The infrared spectrum of anisole (neat liquid, KBr plates).



$$\left[CH_2{=}CH{-}\ddot{\underset{..}{O}}{-}R \longleftrightarrow :\overset{-}{C}H_2{-}CH{=}\overset{+}{\underset{..}{O}}{-}R \right] \qquad R{-}\ddot{\underset{..}{O}}{-}R$$

Resonance
1220 cm^{-1}

No resonance
1120 cm^{-1}

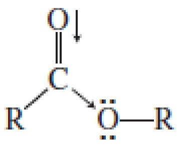
2.14 CARBONYL COMPOUNDS

← cm^{-1} →

1810	1800	1760	1735	1725	1715	1710	1675
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

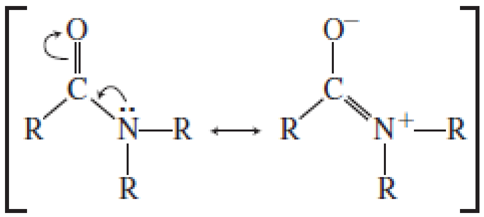
FIGURE 2.35 Normal base values for the C=O stretching vibrations for carbonyl groups.

Ester



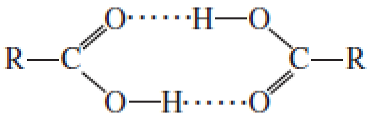
Electron-withdrawing effect raises C=O frequency

Amide

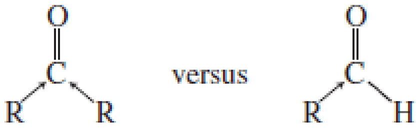


Resonance effect lowers C=O frequency

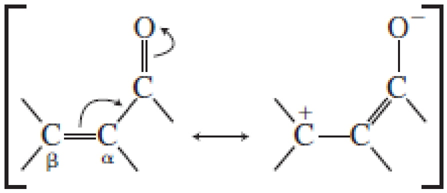
A carboxylic acid exists in monomeric form *only* in very dilute solution, and it absorbs at about 1760 cm^{-1} because of the electron-withdrawing effect just discussed. However, acids in concentrated solution, in the form of neat liquid, or in the solid state (KBr pellet and Nujol) tend to dimerize via hydrogen bonding. This dimerization weakens the C=O bond and lowers the stretching force constant K, resulting in a lowering of the carbonyl frequency of saturated acids to about 1710 cm^{-1}.

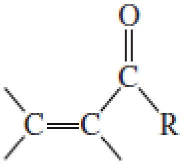


Ketones absorb at a lower frequency than aldehydes because of their additional alkyl group, which is electron donating (compared to H) and supplies electrons to the C=O bond. This electron-releasing effect weakens the C=O bond in the ketone and lowers the force constant and the absorption frequency.

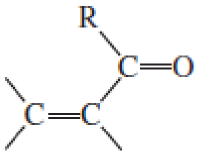


Factors That Influence the C=O Stretching Vibration





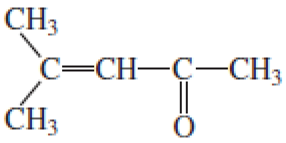
s-cis



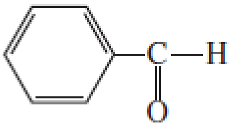
s-trans

Often, two closely spaced C=O absorption peaks are observed for these conjugated systems, resulting from two possible conformations, the *s-cis* and *s-trans*. The *s-cis* conformation absorbs at a frequency higher than the *s-trans* conformation. In some cases, the C=O absorption is broadened rather than split into the doublet.

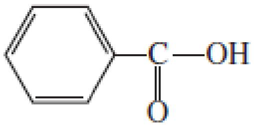
The following examples show the effects of conjugation on the C=O frequency.



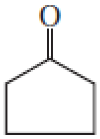
α,β-Unsaturated ketone
1715 → 1690 cm^{-1}



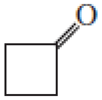
Aryl-substituted aldehyde
1725 → 1700 cm^{-1}



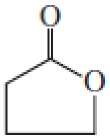
Aryl-substituted acid
1710 → 1680 cm^{-1}



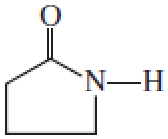
Cyclic ketone
1715 → 1745 cm^{-1}



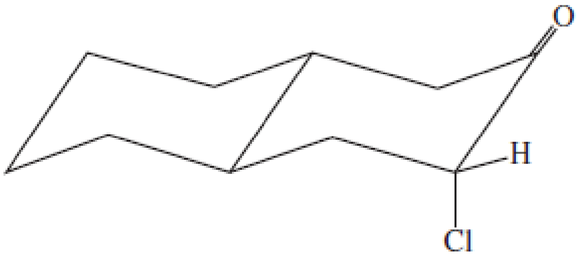
Cyclic ketone
1715 → 1780 cm^{-1}



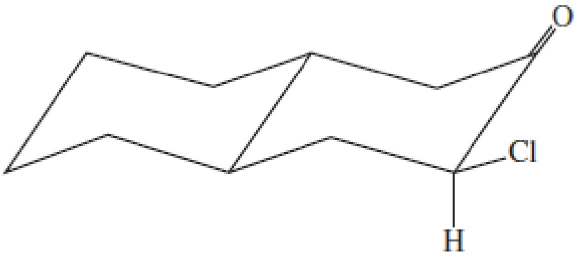
Cyclic ester
(lactone)
1735 → 1770 cm^{-1}



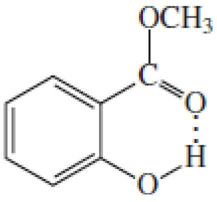
Cyclic amide
(lactam)
1690 → 1705 cm^{-1}



Axial chlorine
~1725 cm^{-1}



Equatorial chlorine
~1750 cm^{-1}



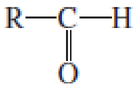
Methyl salicylate
1680 cm^{-1}

Aldehydes

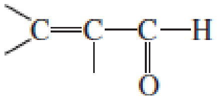
SPECTRAL ANALYSIS BOX

ALDEHYDES

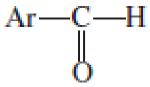
C=O


$R{-}\underset{\overset{\|}{O}}{C}{-}H$

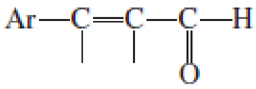
C=O stretch appears in the range 1740–1725 cm^{-1} for normal aliphatic aldehydes.


$>C{=}\underset{|}{C}{-}\underset{\overset{\|}{O}}{C}{-}H$

Conjugation of C=O with α,β C=C; 1700–1680 cm^{-1} for C=O and 1640 cm^{-1} for C=C.


$Ar{-}\underset{\overset{\|}{O}}{C}{-}H$

Conjugation of C=O with phenyl; 1700–1660 cm^{-1} for C=O and 1600–1450 cm^{-1} for ring.


$Ar{-}\underset{|}{C}{=}\underset{|}{C}{-}\underset{\overset{\|}{O}}{C}{-}H$

Longer conjugated system; 1680 cm^{-1} for C=O.

C—H

Stretch, aldehyde hydrogen (—CHO), consists of a pair of *weak* bands, one at 2860–2800 cm^{-1} and the other at 2760–2700 cm^{-1}. It is easier to see the band at the lower frequency because it is not obscured by the usual C—H bands from the alkyl chain. The higher-frequency aldehyde C—H stretch is often buried in the aliphatic C—H bands.

Examples: nonanal (Fig. 2.36), crotonaldehyde (Fig. 2.37), and benzaldehyde (Fig. 2.38).

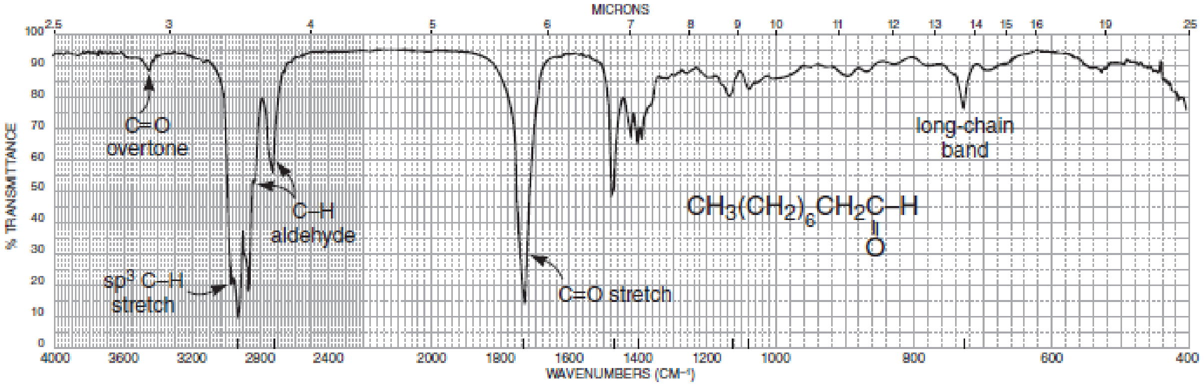


FIGURE 2.36 The infrared spectrum of nonanal (neat liquid, KBr plates).

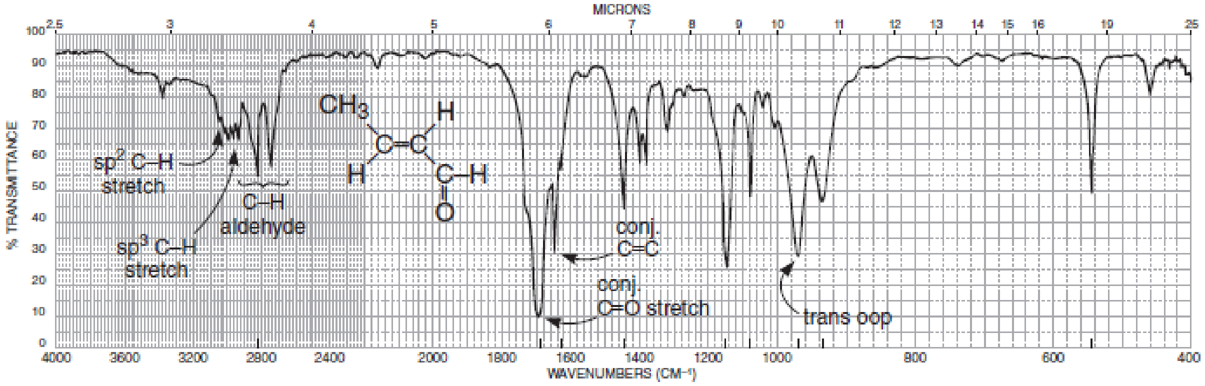
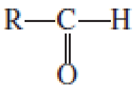
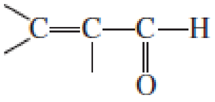
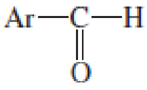


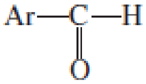
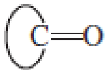
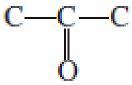
FIGURE 2.37 The infrared spectrum of crotonaldehyde (neat liquid, KBr plates).

C. Ketones

SPECTRAL ANALYSIS BOX

KETONES

C=O	
 $R-\underset{\underset{O}{\|}}{C}-H$	C=O stretch appears in the range 1720–1708 cm⁻¹ for normal aliphatic ketones.
	Conjugation of C=O with *α*,*β* C=C; 1700–1675 cm⁻¹ for C=O and 1644–1617 cm⁻¹ for C=C.
 $Ar-\underset{\underset{O}{\|}}{C}-H$	Conjugation of C=O with phenyl; 1700–1680 cm⁻¹ for C=O and 1600–1450 cm⁻¹ for ring.

 $Ar-C(=O)-H$	Conjugation with two aromatic rings; 1670–1600 cm^{-1} for C=O.
	Cyclic ketones; C=O frequency increases with decreasing ring size.
 $C-C(=O)-C$	Bending appears as a medium-intensity peak in the range 1300–1100 cm^{-1}.

Examples: 3-methyl-2-butanone (Fig. 2.4), mesityl oxide (Fig. 2.39), acetophenone (Fig. 2.40), cyclopentanone (Fig. 2.41), and 2,4-pentanedione (Fig. 2.42).

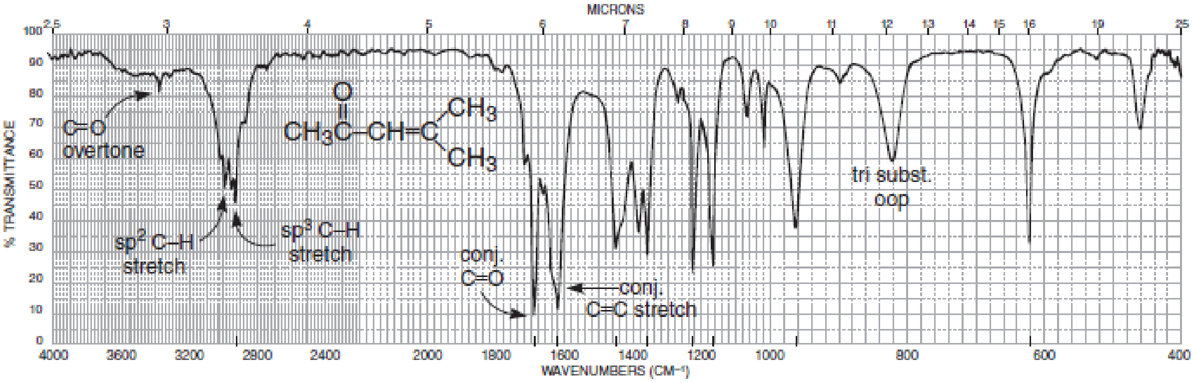


FIGURE 2.39 The infrared spectrum of mesityl oxide (neat liquid, KBr plates).

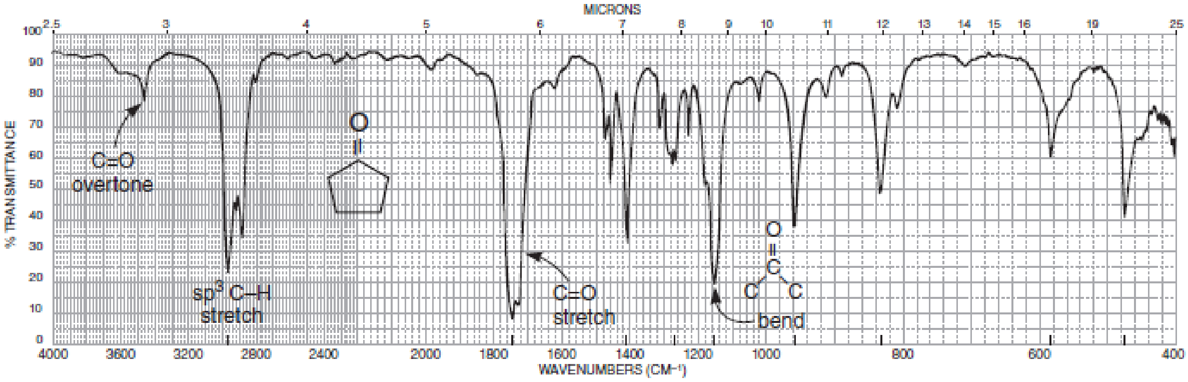


FIGURE 2.41 The infrared spectrum of cyclopentanone (neat liquid, KBr plates).

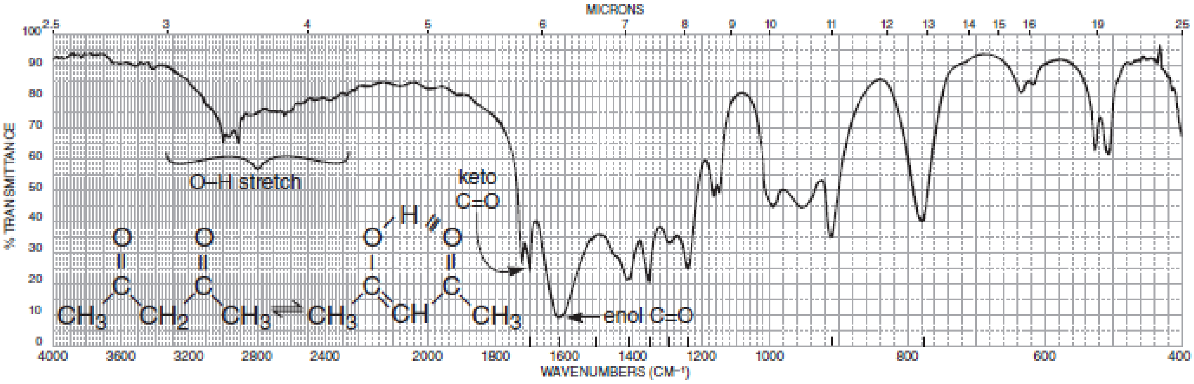
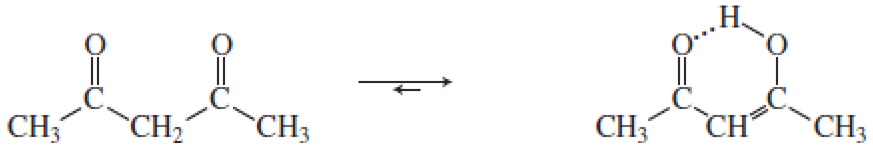


FIGURE 2.42 The infrared spectrum of 2,4-pentanedione (neat liquid, KBr plates).



Keto tautomer	Enol tautomer
C═O doublet	C═O (hydrogen bonded), 1622 cm^{-1}
1723 cm^{-1} (symmetric stretch)	O—H (hydrogen bonded), 3200–2400 cm^{-1}
1706 cm^{-1} (asymmetric stretch)	

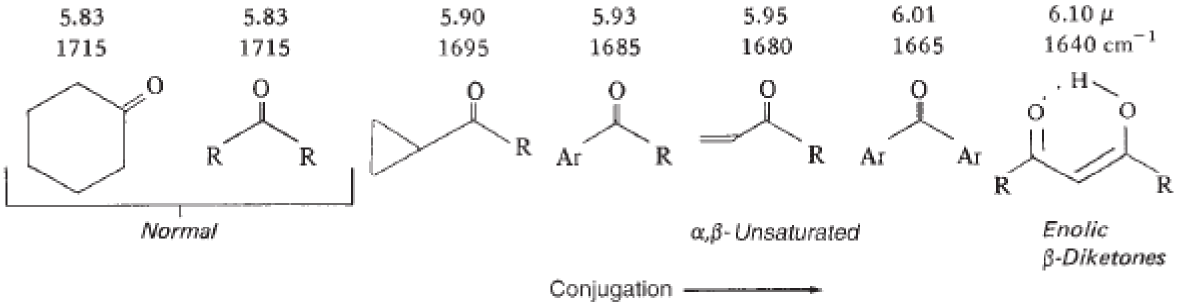


FIGURE 2.43 The C=O stretching vibrations in conjugated ketones.

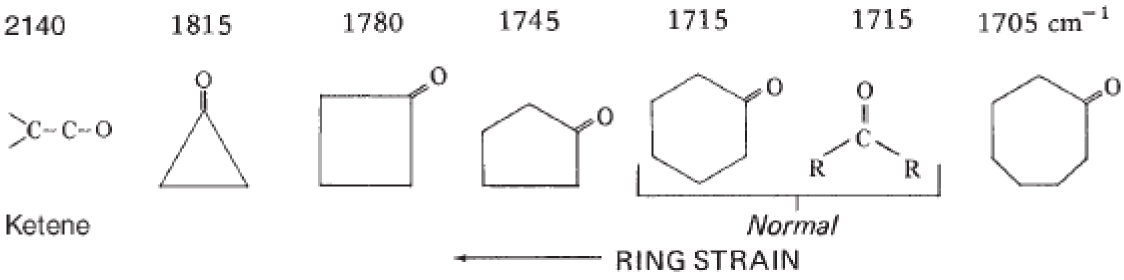
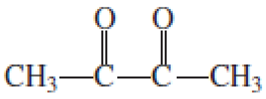
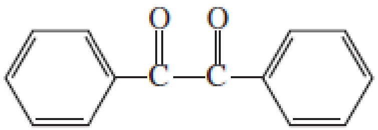


FIGURE 2.44 The C=O stretching vibrations for cyclic ketones and ketene.



$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

1716 cm^{-1}



1680 cm^{-1}

D. Carboxylic Acids

SPECTRAL ANALYSIS BOX

CARBOXYLIC ACIDS

O—H	Stretch, usually *very broad* (strongly H-bonded), occurs at 3400–2400 cm^{-1} and often overlaps the C—H absorptions.
C=O	Stretch, broad, occurs at 1730 –1700 cm^{-1}. Conjugation moves the absorption to a lower frequency.
C—O	Stretch occurs in the range 1320 –1210 cm^{-1}, medium intensity.

Examples: isobutyric acid (Fig. 2.45) and benzoic acid (Fig. 2.46).

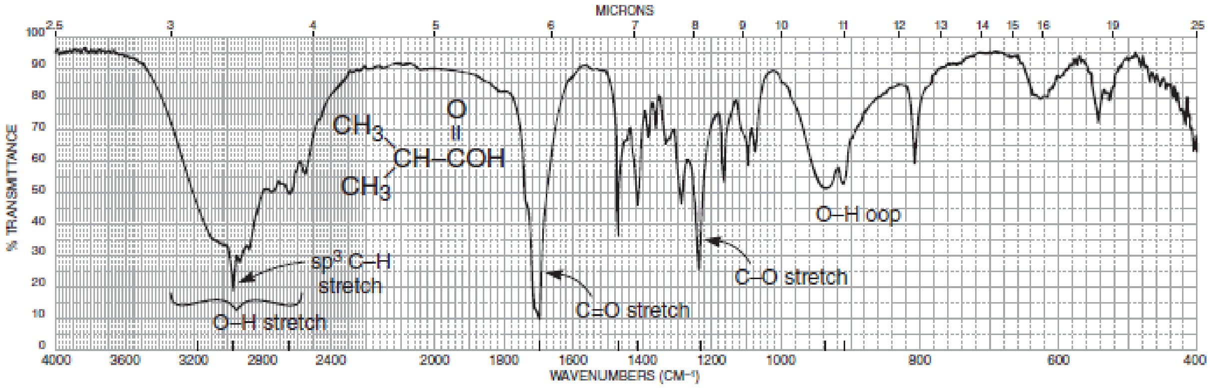


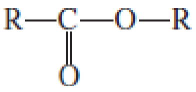
FIGURE 2.45 The infrared spectrum of isobutyric acid (neat liquid, KBr plates).

E. Esters

SPECTRAL ANALYSIS BOX

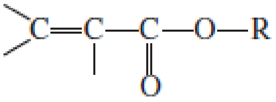
ESTERS

C=O

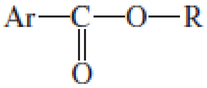


$R-\underset{\underset{O}{\|}}{C}-O-R$

C=O stretch appears in the range 1750–1735 cm^{-1} for normal aliphatic esters.

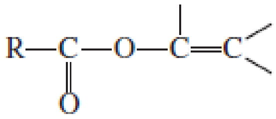


Conjugation of C=O with α,β C=C; 1740–1715 cm^{-1} for C=O and 1640–1625 cm^{-1} for C=C (two bands for some C=C, *cis* and *trans*.

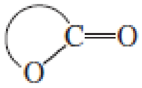


$Ar-\underset{\underset{O}{\|}}{C}-O-R$

Conjugation of C=O with phenyl; 1740–1715 cm^{-1} for C=O and 1600–1450 cm^{-1} for ring.



Conjugation of a single-bonded oxygen atom with C=C or phenyl; 1765–1762 cm^{-1} for C=O.



Cyclic esters (lactones); C=O frequency increases with decreasing ring size.

C–O

Stretch in two or more bands, one stronger and broader than the other, occurs in the range 1300–1000 cm^{-1}.

Examples: ethyl butyrate (Fig. 2.47), methyl methacrylate (Fig. 2.48), vinyl acetate (Fig. 2.49), methyl benzoate (Fig. 2.50), and methyl salicylate (Fig. 2.51).

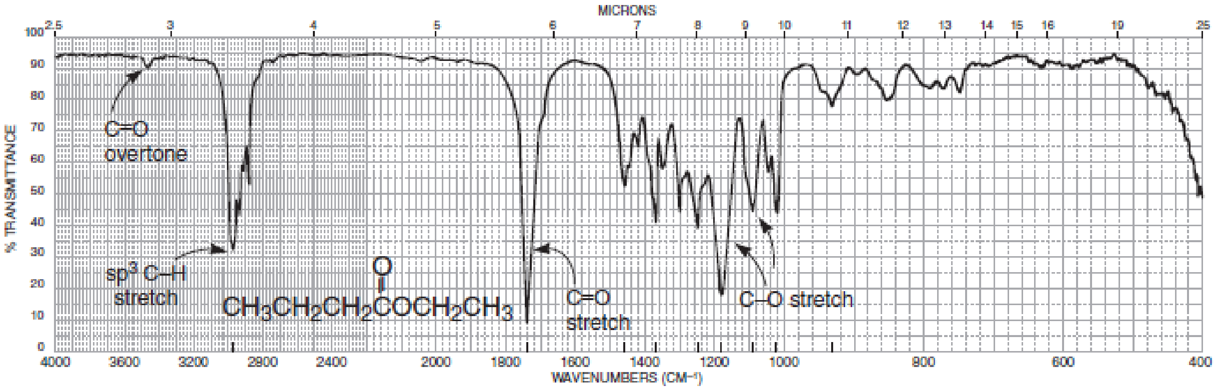
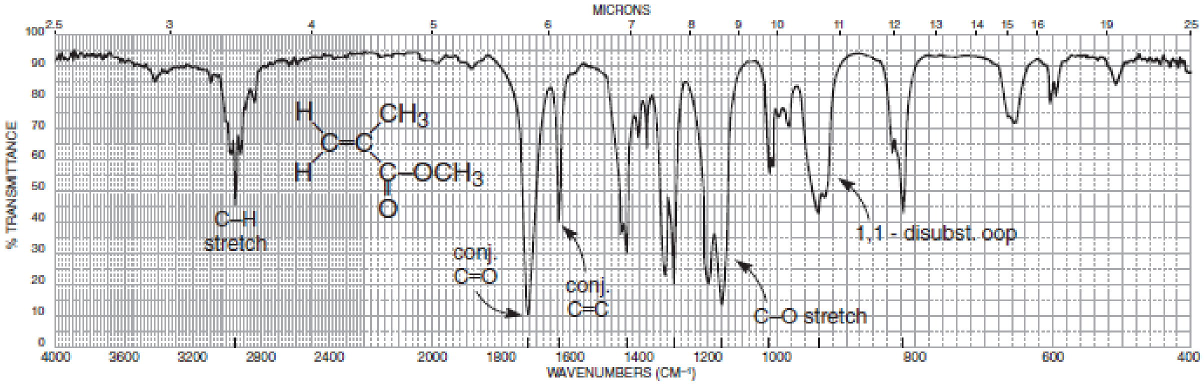
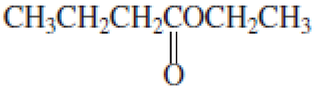


FIGURE 2.47 The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).

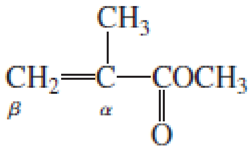


F I G U R E 2.48 The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).



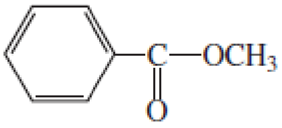
$CH_3CH_2CH_2\overset{}{\underset{\underset{O}{\|}}{C}}OCH_2CH_3$

Ethyl butyrate
1738 cm^{-1}



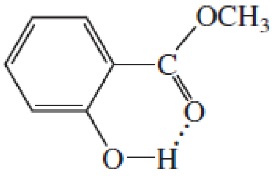
$\overset{\beta}{CH_2}=\overset{CH_3}{\underset{\alpha}{C}}-\underset{\underset{O}{\|}}{C}OCH_3$

Methyl methacrylate
1725 cm^{-1}



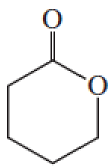
Methyl benzoate
1724 cm^{-1}

Hydrogen-Bonding Effects. When intramolecular (internal) hydrogen bonding is present, the C=O is shifted to a lower frequency, as predicted in Section 2.14A and shown in the spectrum of methyl salicylate (Fig. 2.51).

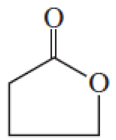


Methyl salicylate
1680 cm^{-1}

Cyclic Esters (Lactones). The C=O vibrations are shifted to higher frequencies with decreasing ring size, as predicted in Section 2.14A. The unstrained, six-membered cyclic ester δ-valerolactone absorbs at about the same value as a noncyclic ester (1735 cm^{-1}). Because of increased angle strain, γ-butyrolactone absorbs at about 35 cm^{-1} higher than δ-valerolactone.



δ-Valerolactone
1735 cm^{-1}



γ-Butyrolactone
1770 cm^{-1}

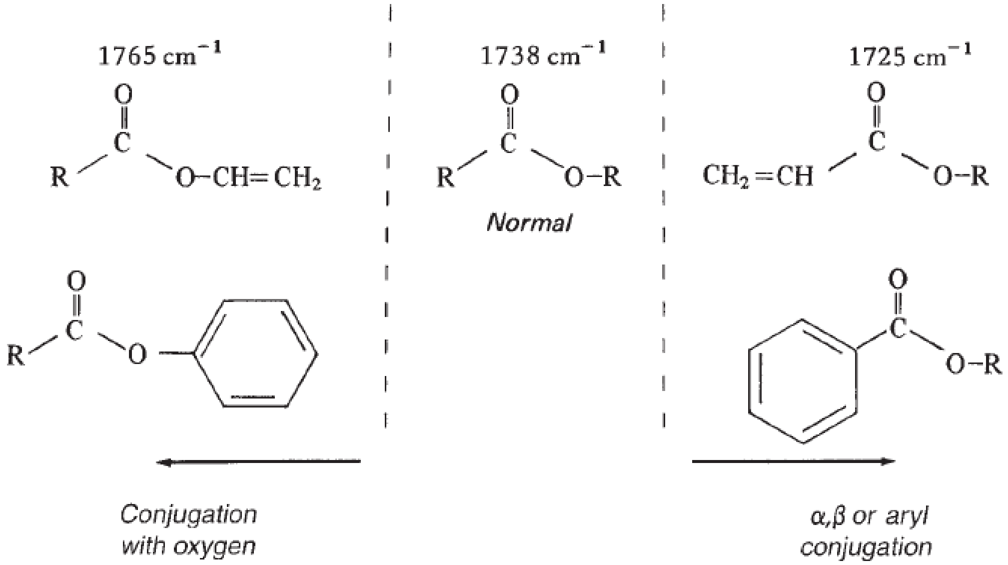


FIGURE 2.52 The effect of *α,β* unsaturation or aryl substitution and conjugation with oxygen on the C=O vibrations in noncyclic (acyclic) esters.