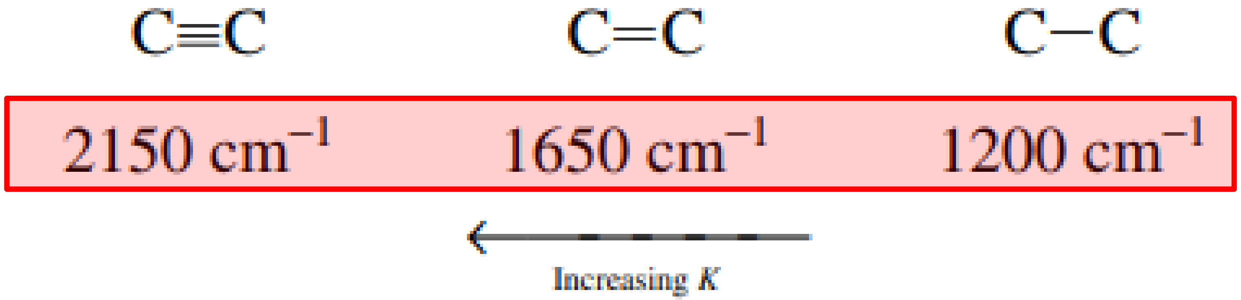
Infra-Red (IR)
&
Fourier Transform Infra-Red (FT-IR) Spectroscopy-
3rd Session

IR Absorption Wavenumber (Values) for Various Types of C-C Bonds: Stretching

- Due to dipole moment (DM) of carbon-carbon bonds: weak intensity
- Symmetry provides less DM in stretching



$C\equiv C$	$C=C$	$C-C$
$2150\ cm^{-1}$	$1650\ cm^{-1}$	$1200\ cm^{-1}$

← Increasing *K*

- Various double bond carbons:
- ✓ Aliphatic chain
- ✓ aliphatic cyclic: more symmetric; less DM; less intensity
- cis comparing to trans: less symmetry: more strongly absorption
- Terminal double bond: stronger absorption

IR Absorption Wavenumber (Values) for -C-H in Alkenes: OOP Bending

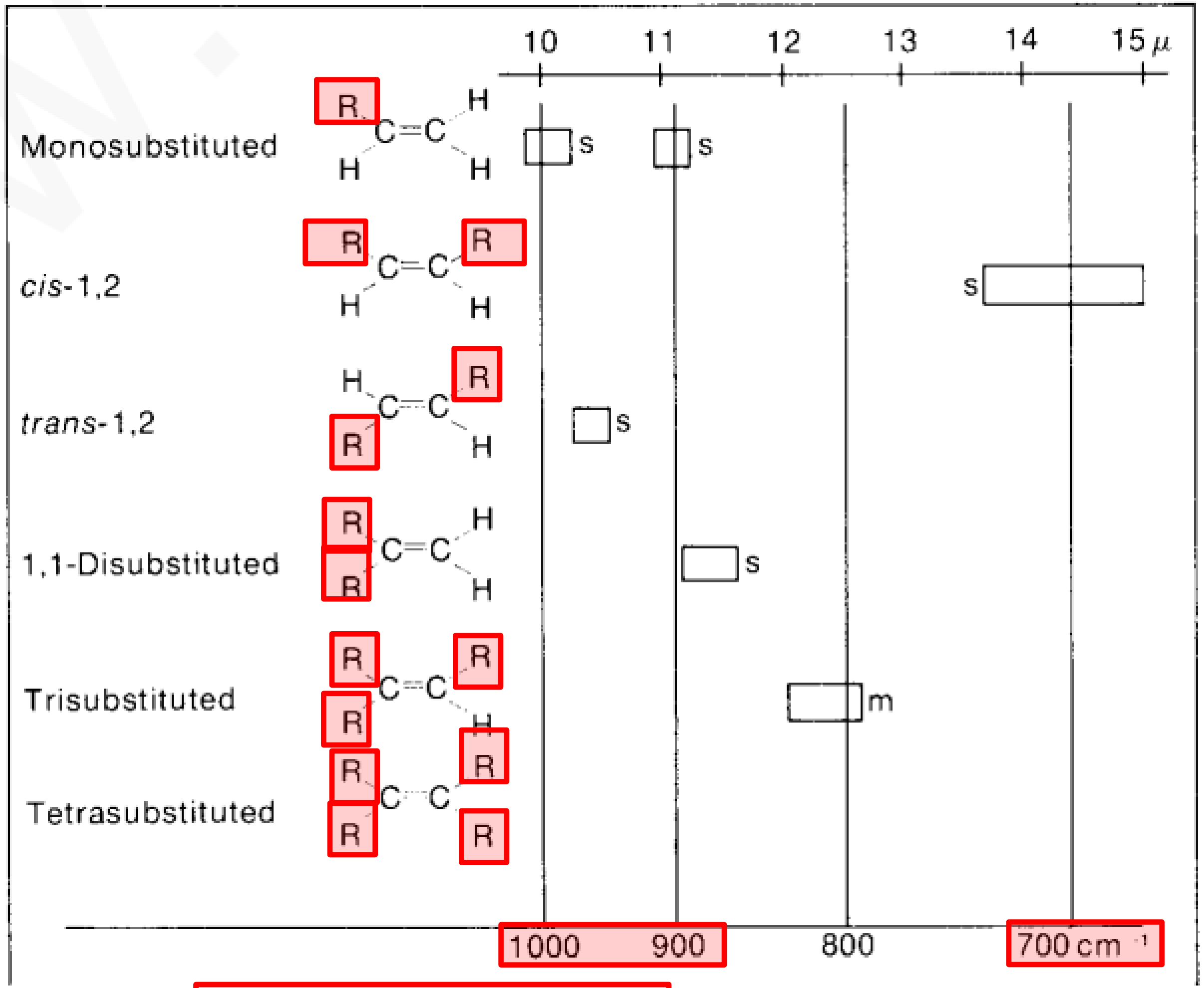


FIGURE 2.22 The C–H out-of-plane bending vibrations for substituted alkenes.

Example of IR Spectrum: Infrared Spectroscopy for 2-Pentene

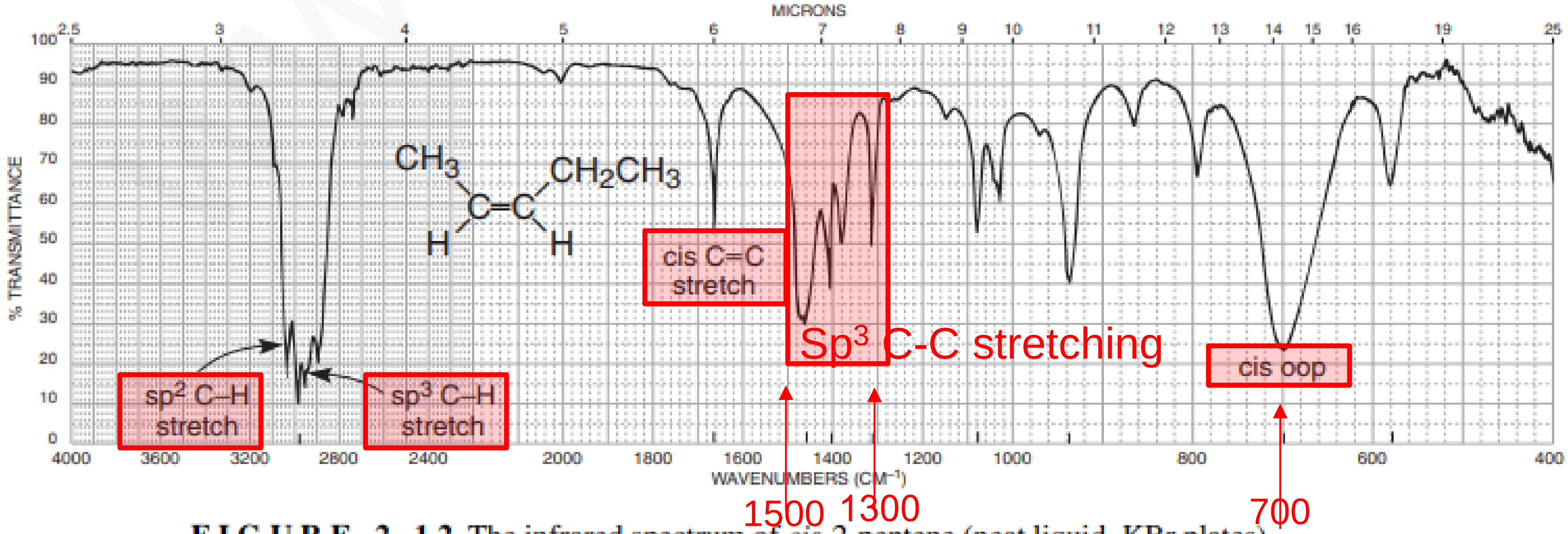


FIGURE 2.12 The infrared spectrum of *cis*-2-pentene (neat liquid, KBr plates).

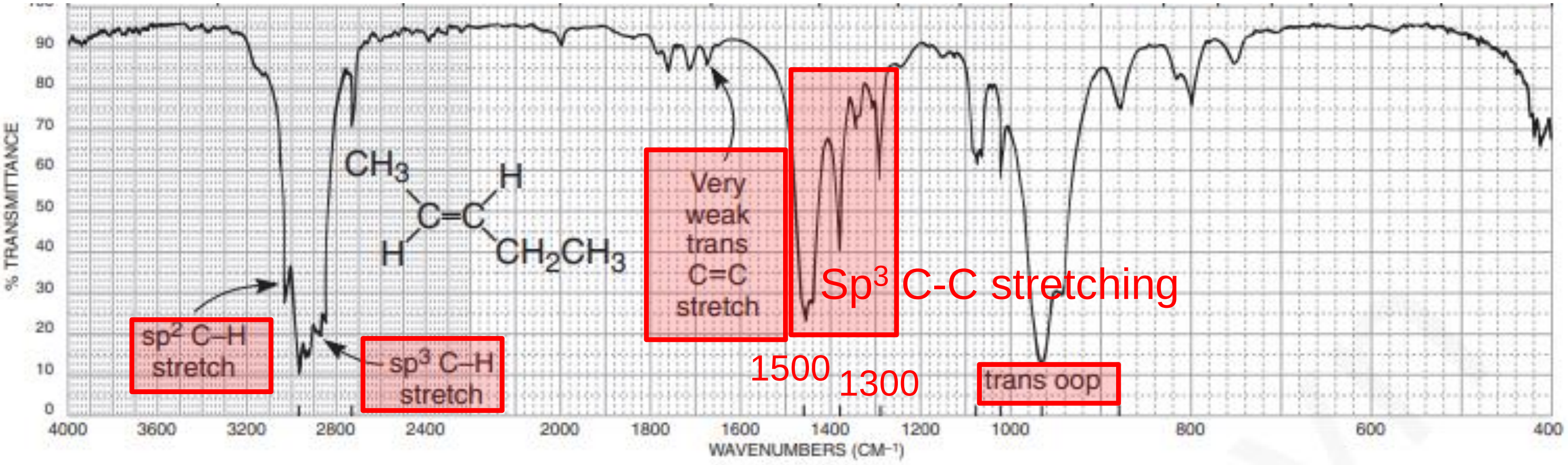


FIGURE 2.13 The infrared spectrum of *trans*-2-pentene (neat liquid, KBr plates).

Example of IR Spectrum: Infrared Spectroscopy for 1-Hexene

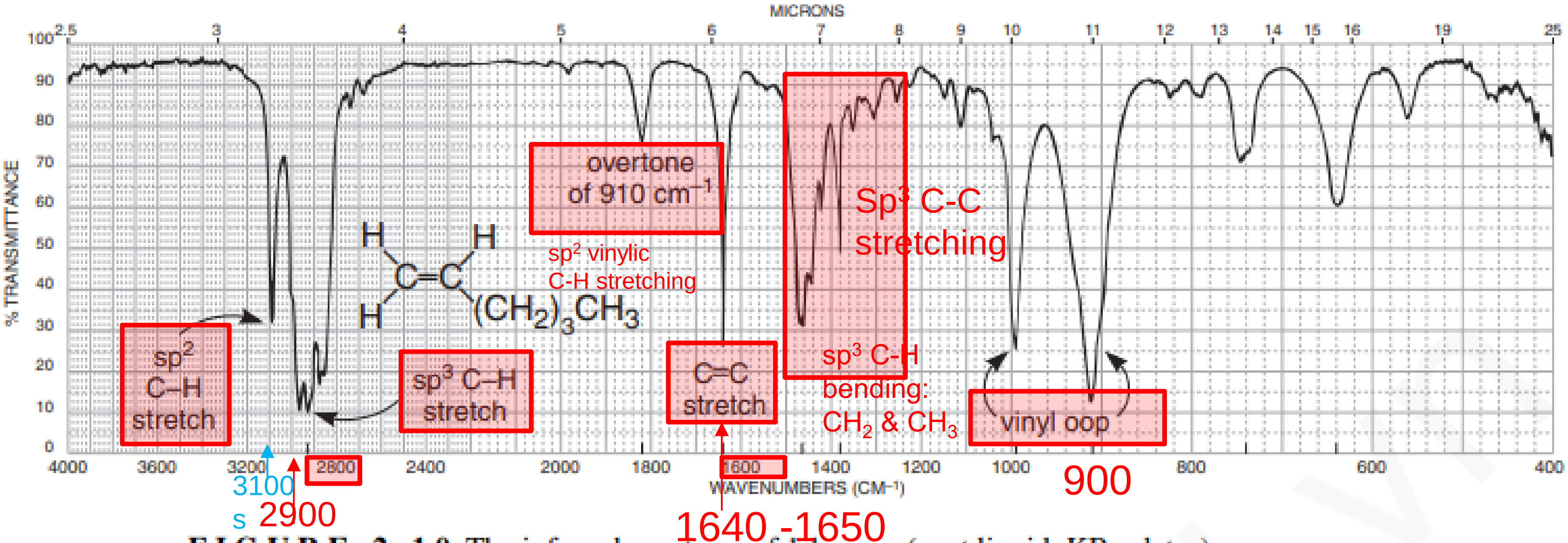
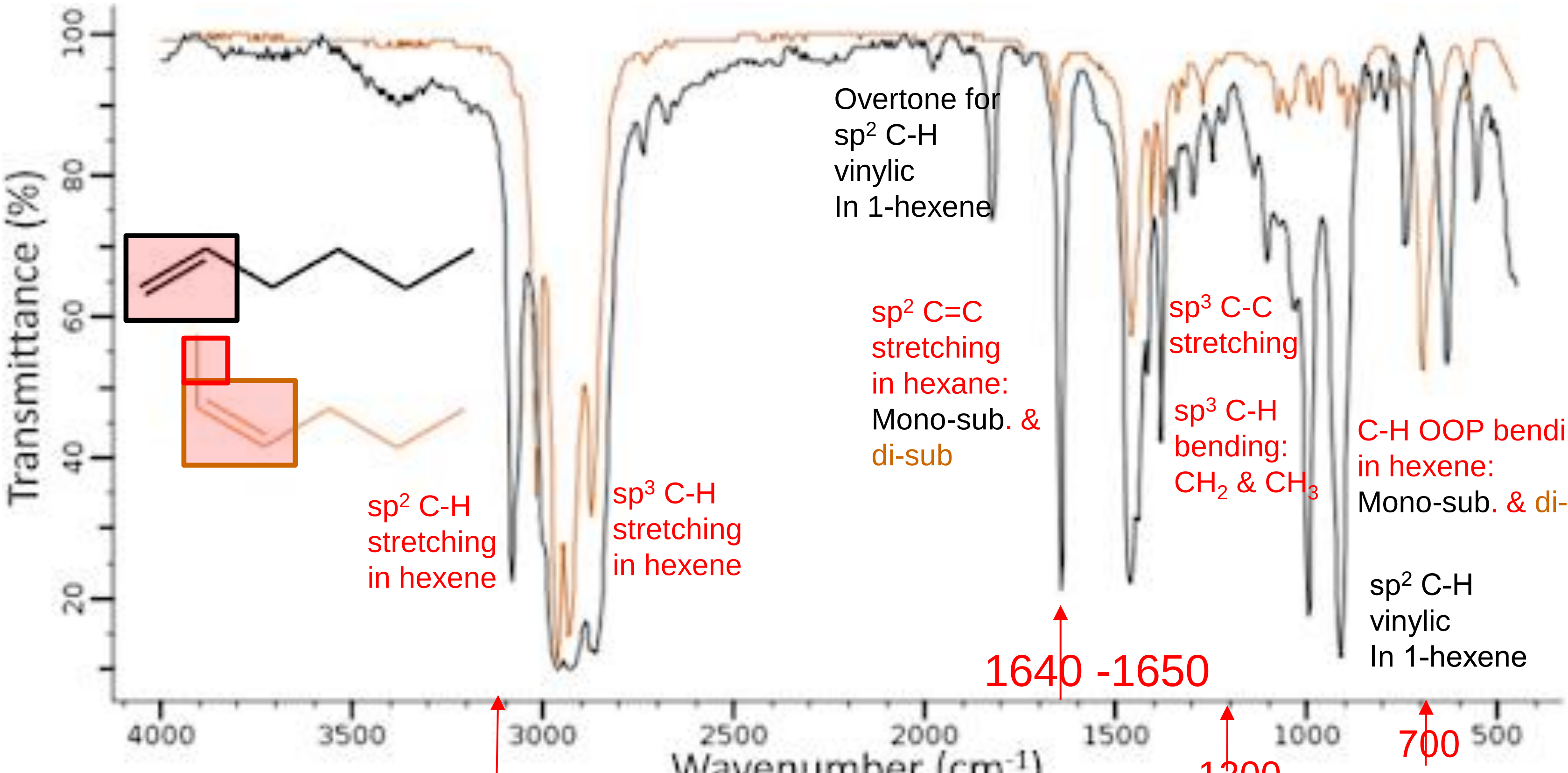


FIGURE 2.10 The infrared spectrum of 1-hexene (neat liquid, KBr plates).

IR for Identification of Isomers:
1-Hexene (in Black) & 2-Hexene (in Brown): C_6H_{11}



Overtone for sp^2 C-H vinylic In 1-hexene

sp^2 C-H stretching in hexene

sp^3 C-H stretching in hexene

sp^2 C=C stretching in hexane: Mono-sub. & di-sub

sp^3 C-C stretching

sp^3 C-H bending: CH_2 & CH_3

C-H OOP bending in hexene: Mono-sub. & di-sub.

sp^2 C-H vinylic In 1-hexene

1640 -1650

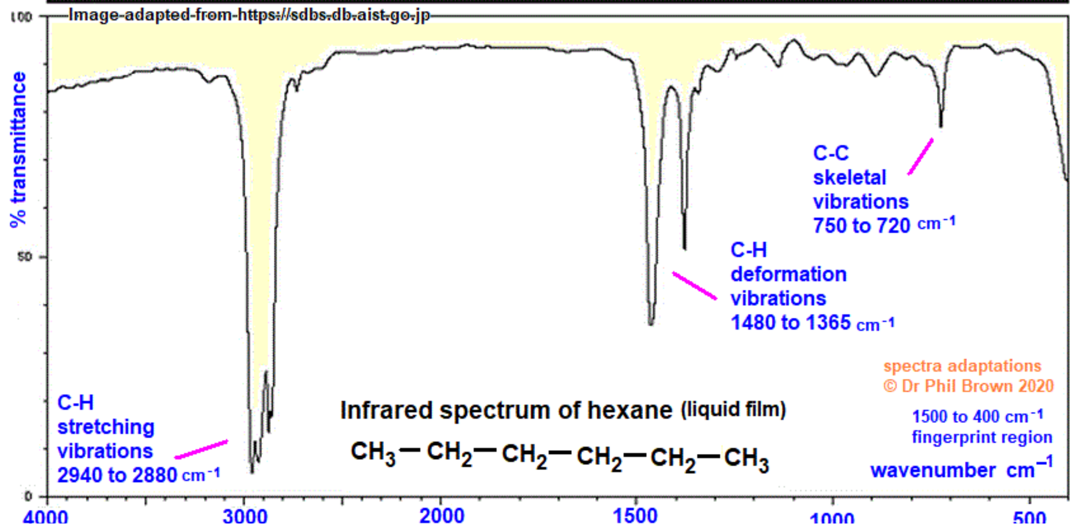
3100

1200

700

C-H OOP bending in 1-hexane (mono-substituted alkene)

Compare IR Spectrum for n-Hexane, 1-Hexene & 1-Hexyne



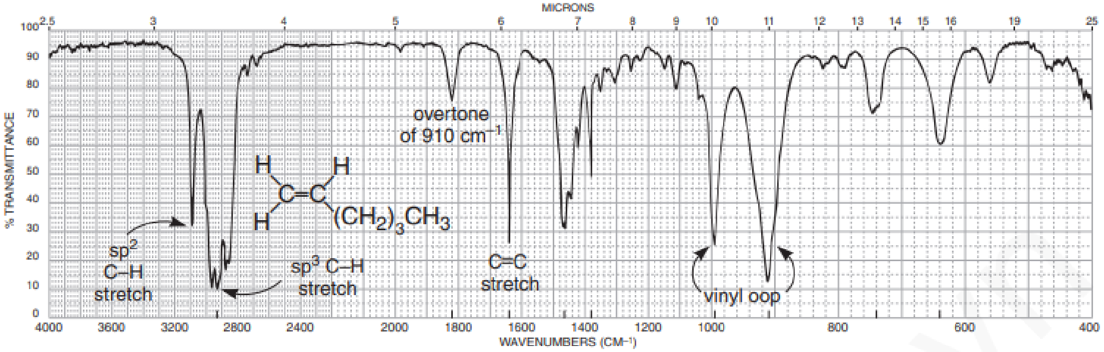
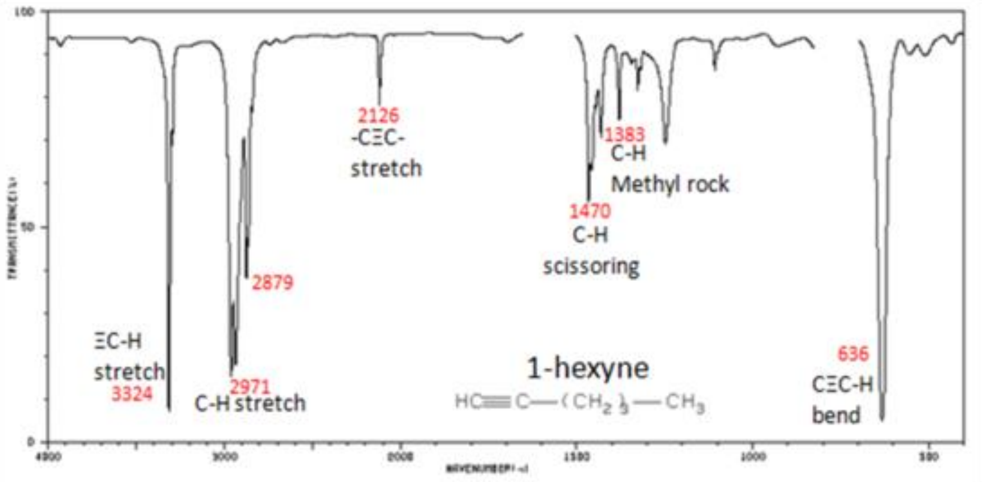
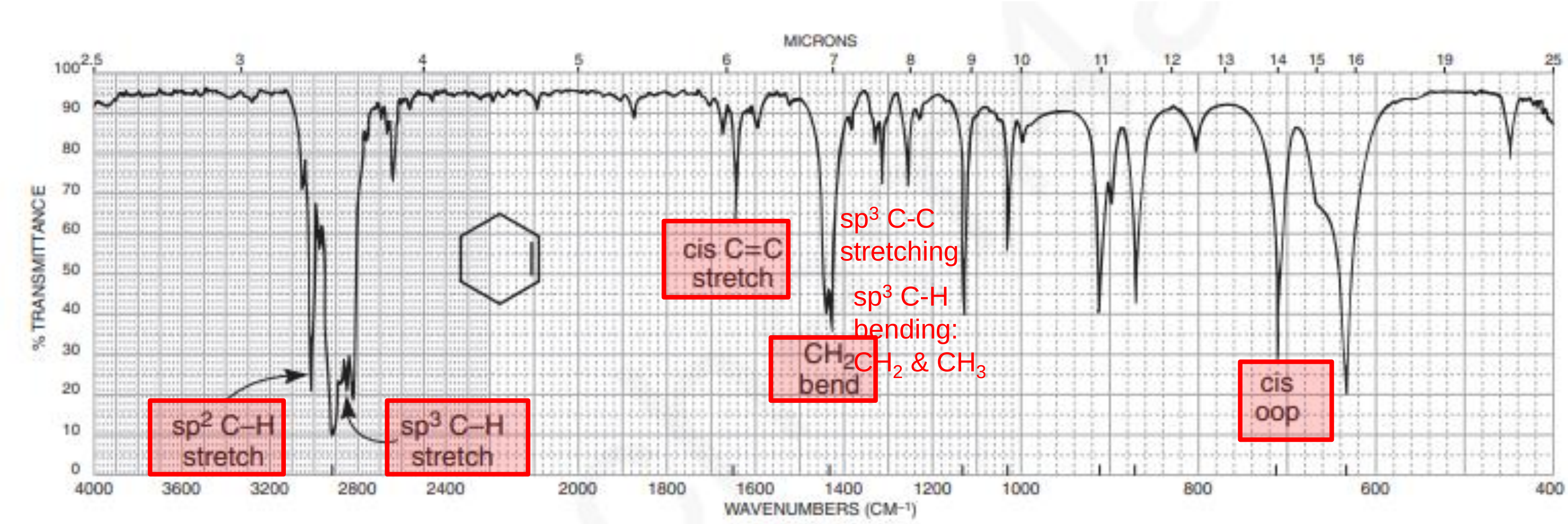


FIGURE 2.10 The infrared spectrum of 1-hexene (neat liquid, KBr plates).



SRA

Example of IR Spectrum: Infrared Spectroscopy for Cyclohexene: C_6H_{10}

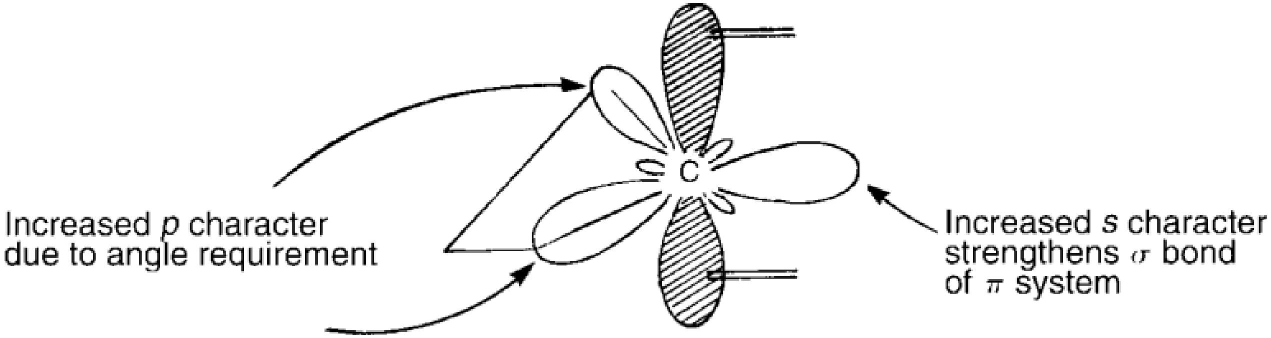


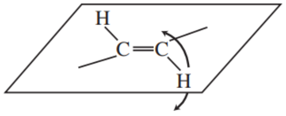
sp^3 C-C stretching

sp^3 C-H bending: CH_2 & CH_3

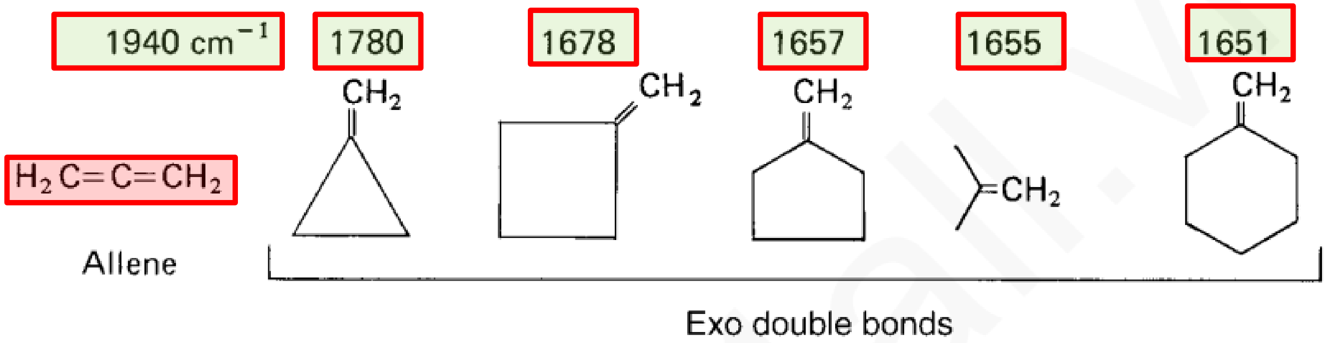
FIGURE 2.11 The infrared spectrum of cyclohexene (neat liquid, KBr plates).

IR Absorption Wavenumber (Values) for -C=C- in Exocyclic Systems: Stretching





C—H out-of-plane bending



(a) Strain moves the peak to the left.

(b) Ring fusion moves the absorption to the left.

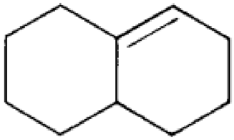
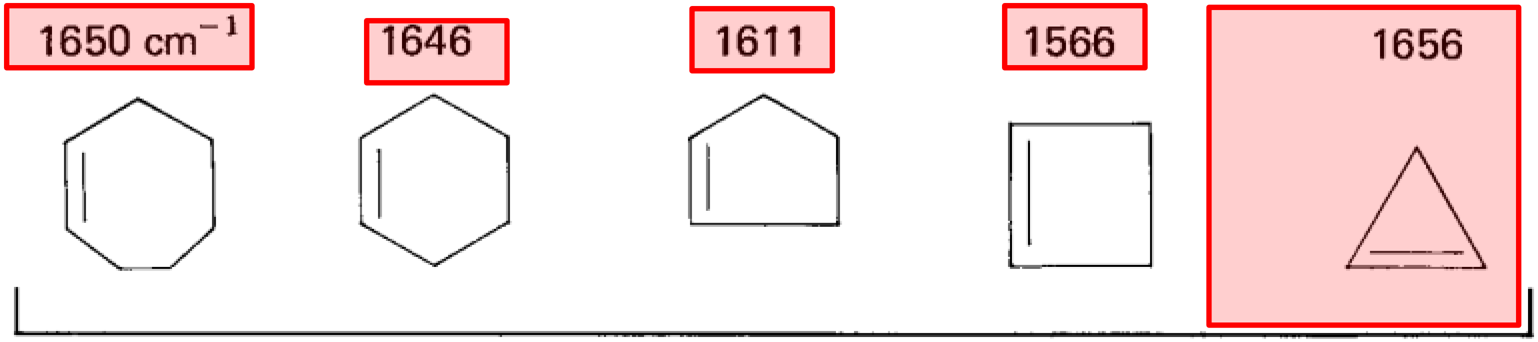
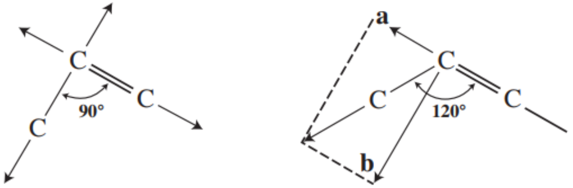


FIGURE 2.21 C=C stretching vibrations in exocyclic systems.

IR Absorption Wavenumber (Values) for -C=C- Vibrations in Endocyclic Systems: Stretching



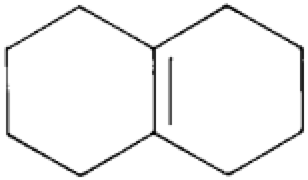
Endo double bonds



(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.

e.g.:



~1611 cm^{-1}

FIGURE 2.19 C=C stretching vibrations in endocyclic systems.

IR Absorption Wavenumber (Values) for -C=C- Vibrations in Endocyclic Systems Possessing Substitutes: Stretching

- Consider difference in Wavenumbe Due to substitute

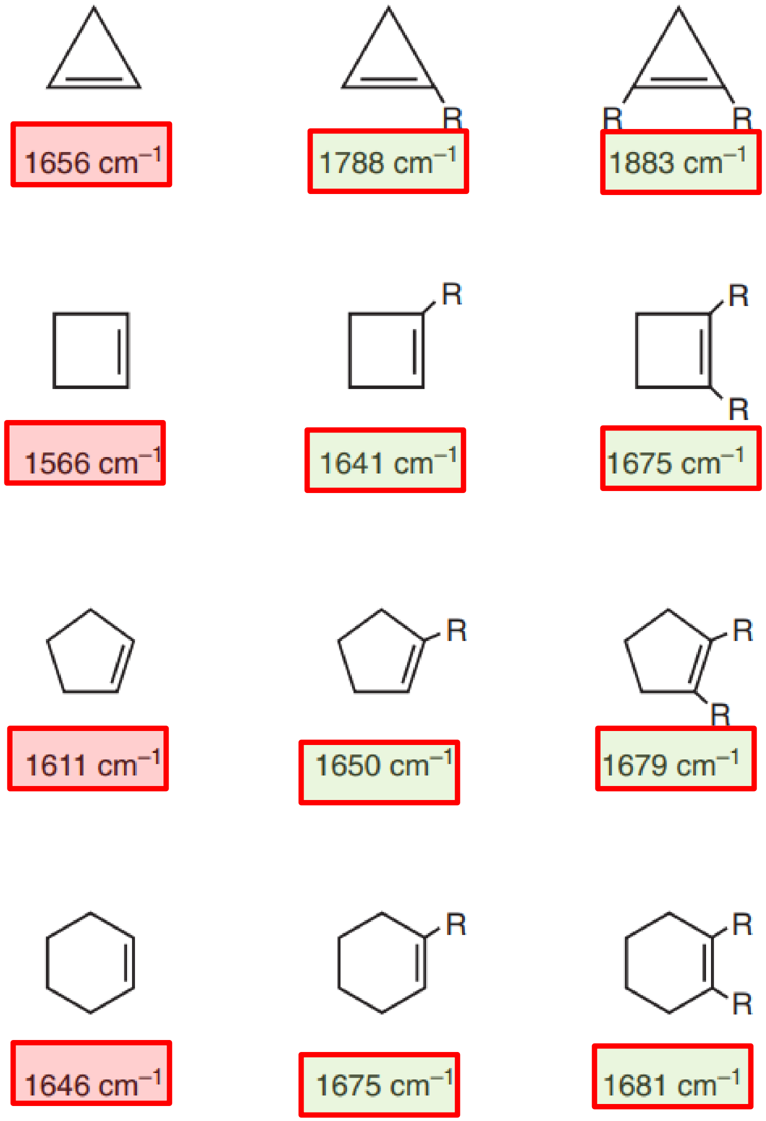


FIGURE 2.20 The effect of alkyl substitution on the frequency of a C=C bond in a ring.

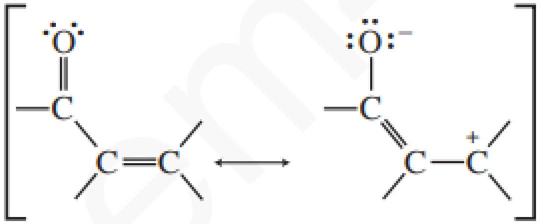
Resonance Effects in Single & Double Bond Carbon-Carbon: Stretching

- Alkene: 1650 cm^{-1}
- Conjugated alkene: 1610, 1590, 1500

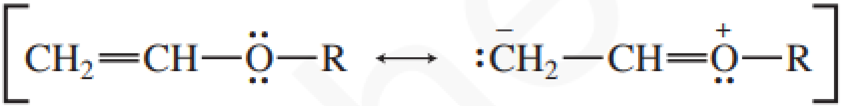
$C=C$

1650 cm^{-1}

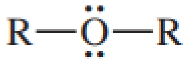
- Carbonyl: 1715 cm^{-1}
- Conjugated carbonyl: 1675-1680 cm^{-1}



- Ether: 1120 cm^{-1}
- Conjugated ether: 1220 cm^{-1}

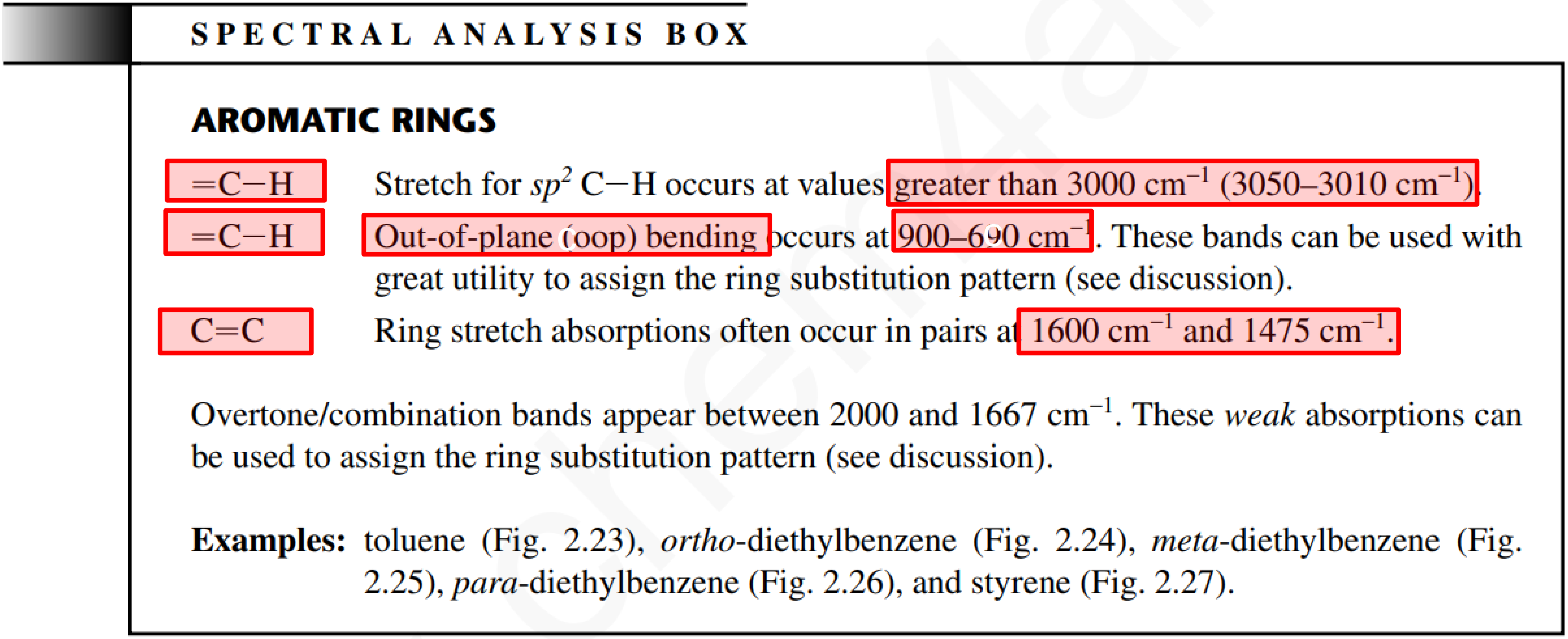


Resonance
1220 cm^{-1}



No resonance
1120 cm^{-1}

IR Absorption Wavenumber (Values) for =C-H & -C=C- Vibrations in Benzene & 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).

IR Absorption Wavenumber (Values) for C-H in Benzene: OOP Bending

C-H OOP bending:

650-1000 cm^{-1}

C-H OOP bending overtones:

1667-2000 cm^{-1}

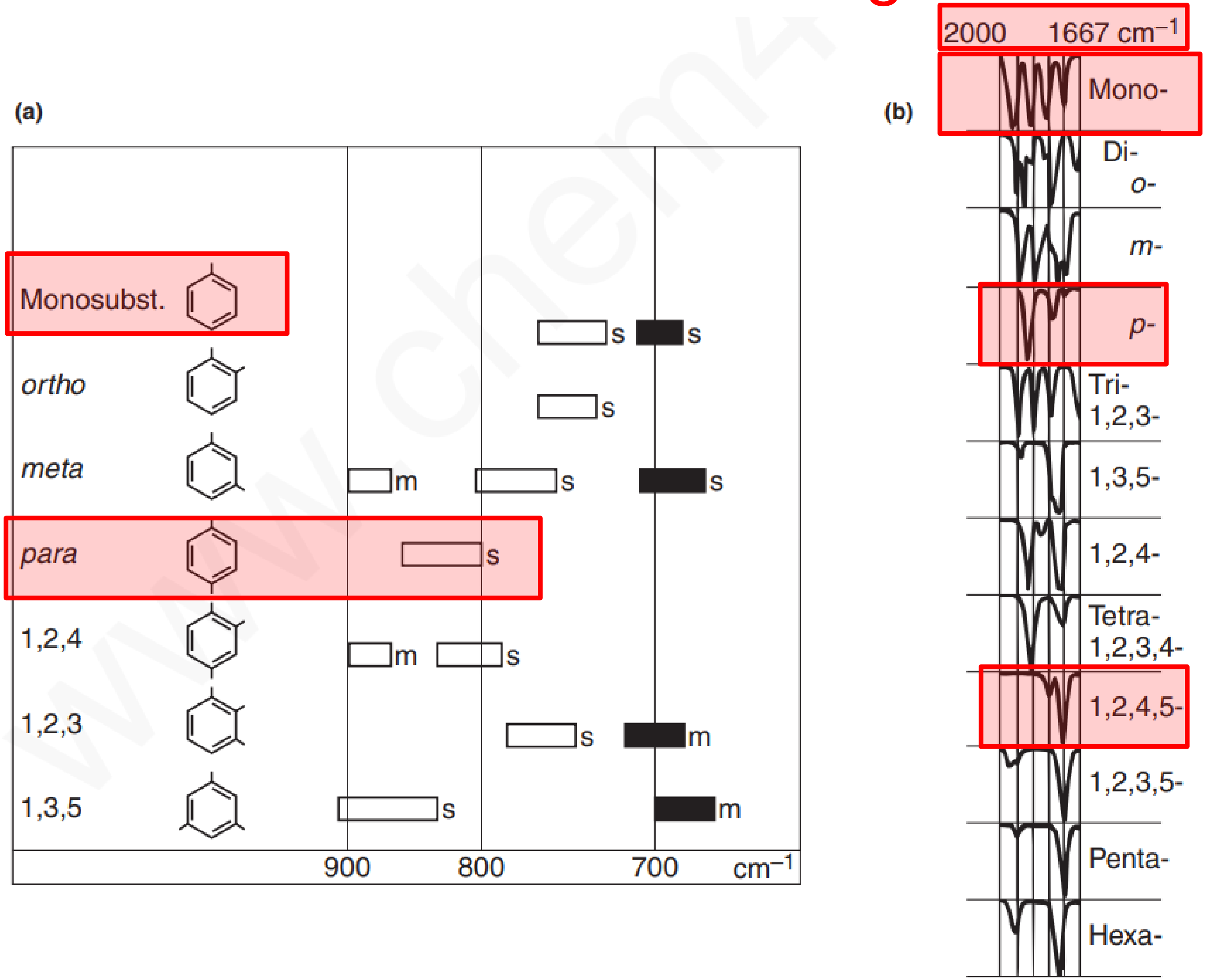


FIGURE 2.28 (a) The C−H out-of-plane bending vibrations for substituted benzenoid compounds. (*s = strong, m = medium*) (b) The 2000- to 1667-cm^{-1} region for substituted benzenoid compounds (from

Example of IR Spectrum: Infrared Spectroscopy for Toluene

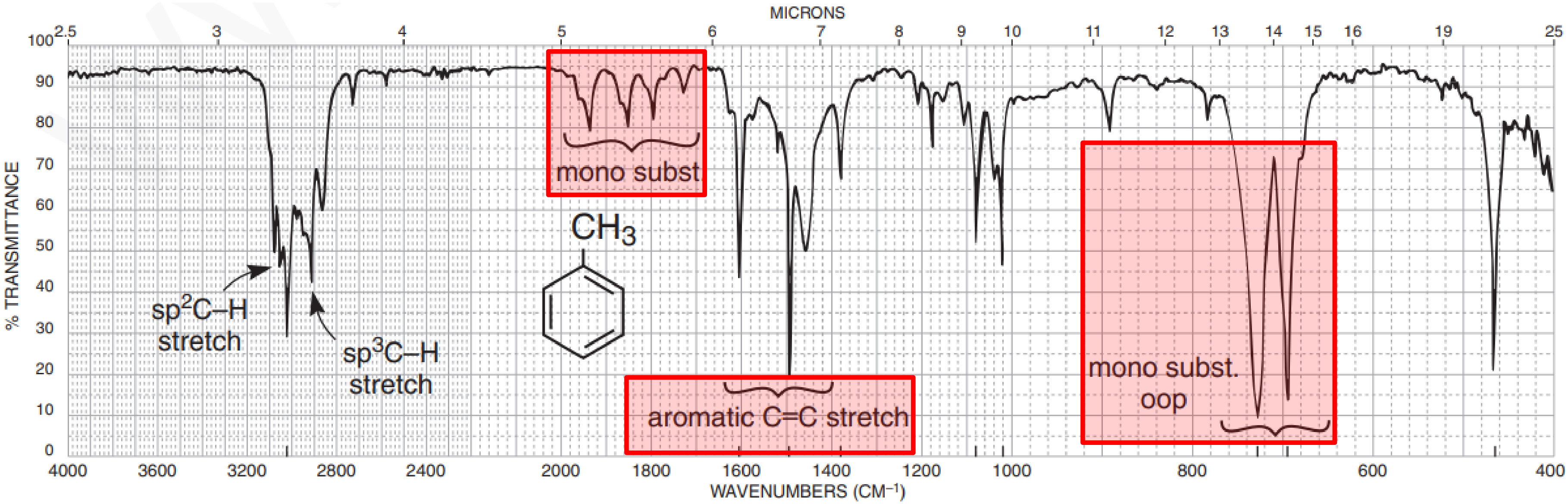


FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for o-Di-Ethyl-Benzene

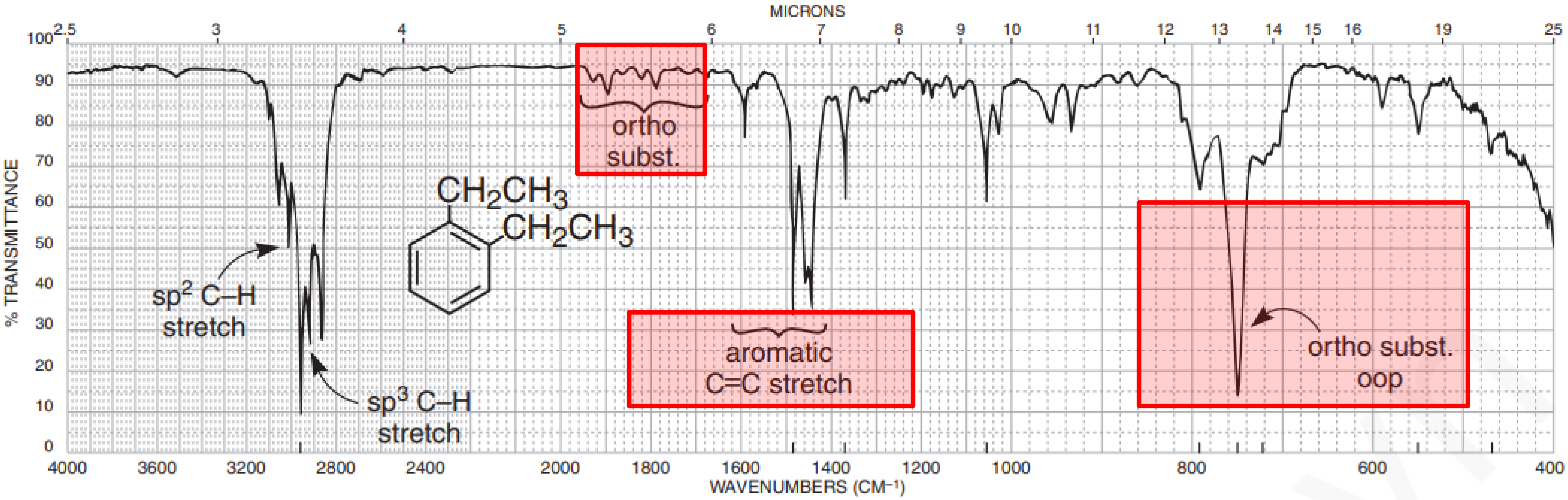


FIGURE 2.24 The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for m-Di-Ethyl-Benzene

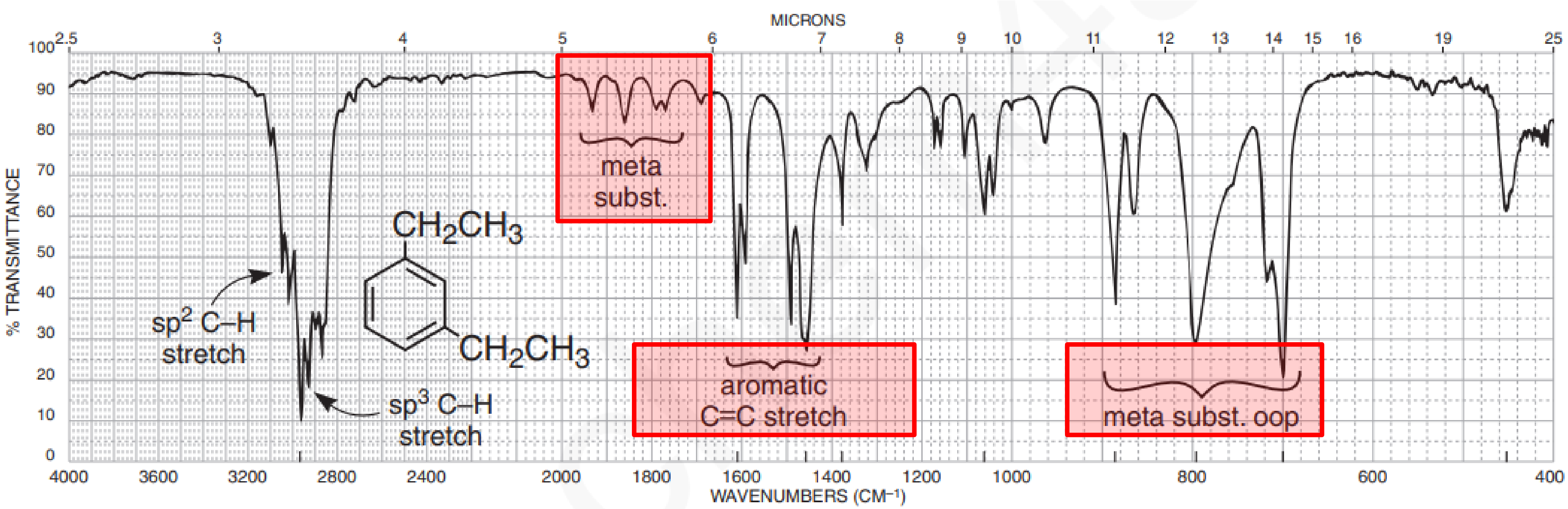
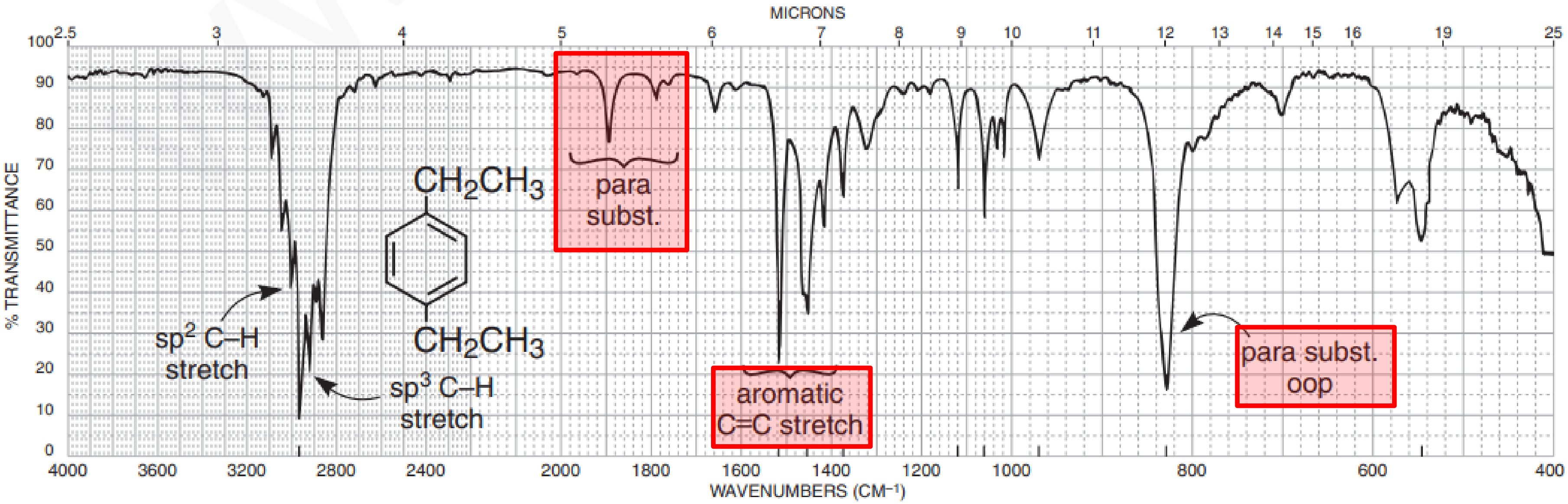


FIGURE 2.25 The infrared spectrum of *meta*-diethylbenzene (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for p-Di-Ethyl-Benzene



F I G U R E 2 . 2 6 The infrared spectrum of *para*-diethylbenzene (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for Vinyl-Benzene

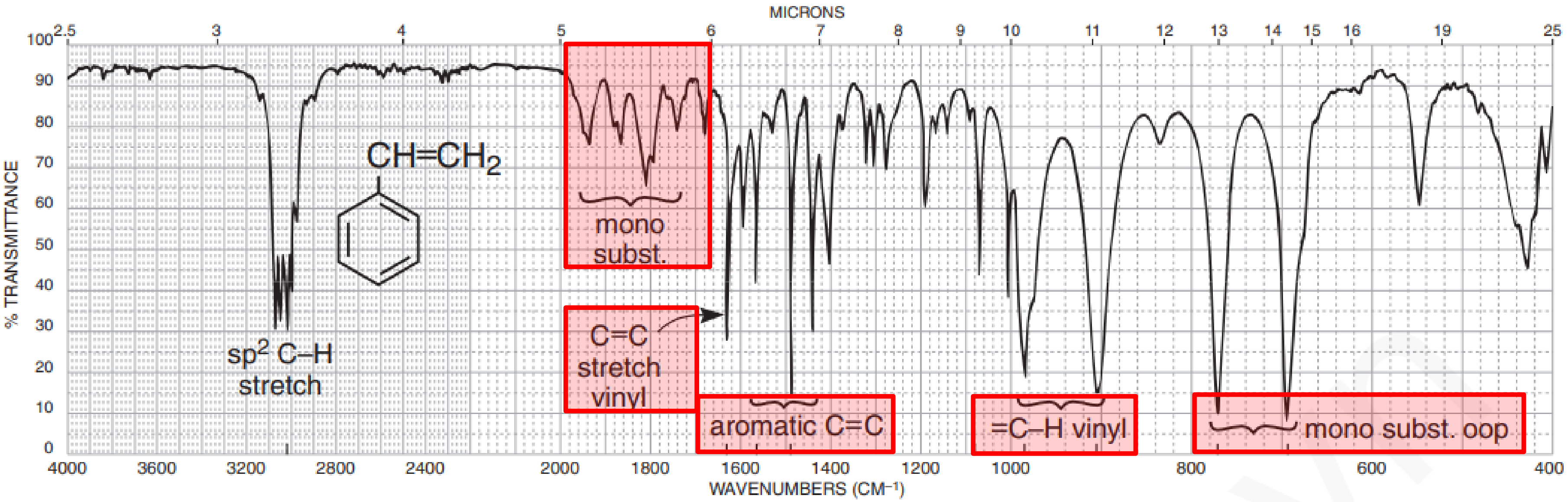
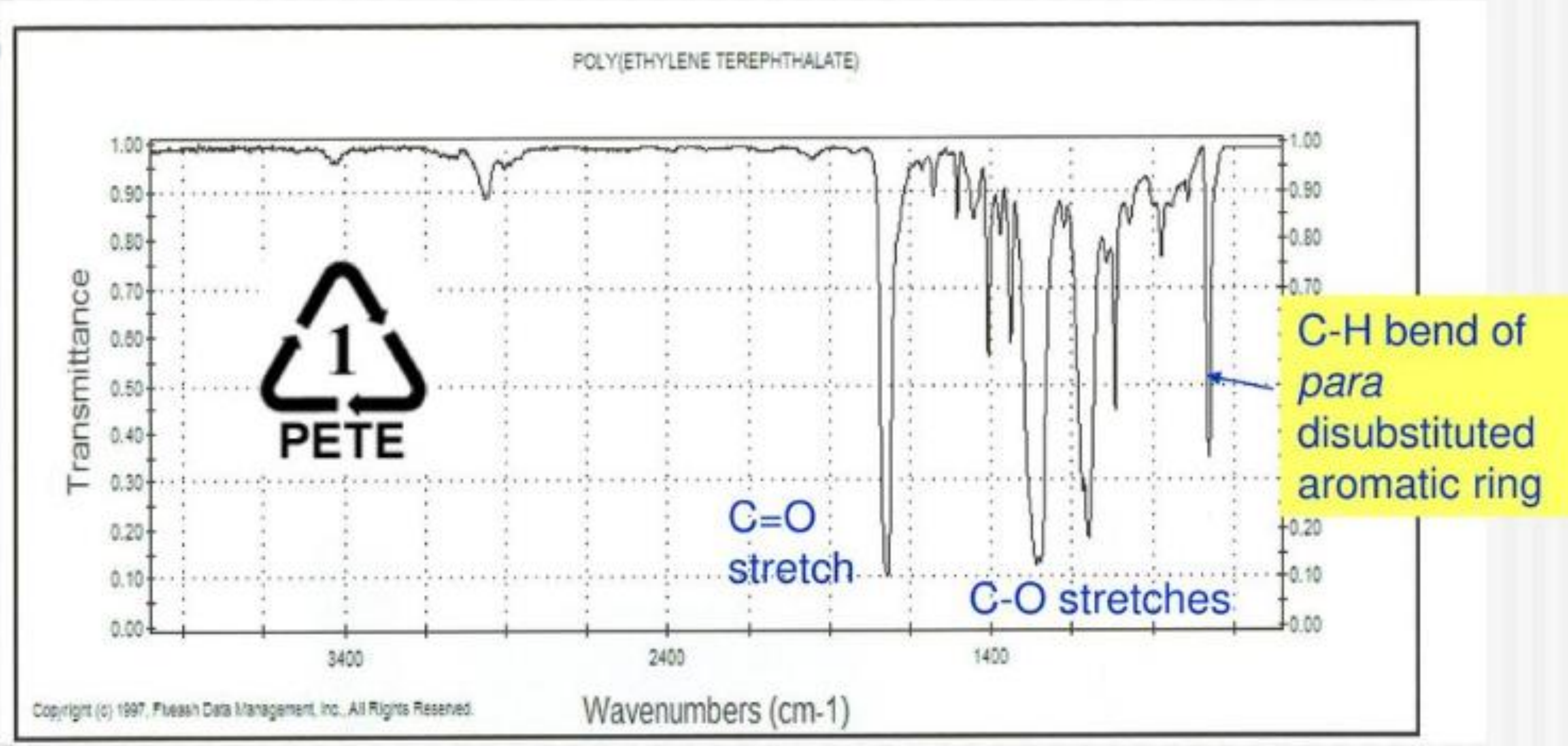


FIGURE 2.27 The infrared spectrum of styrene (neat liquid, KBr plates).

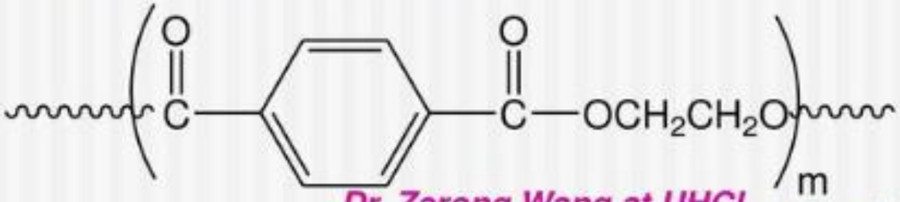
Infrared Spectrum of Poly(ethylene terephthalate)



C=O stretch

C-O stretches

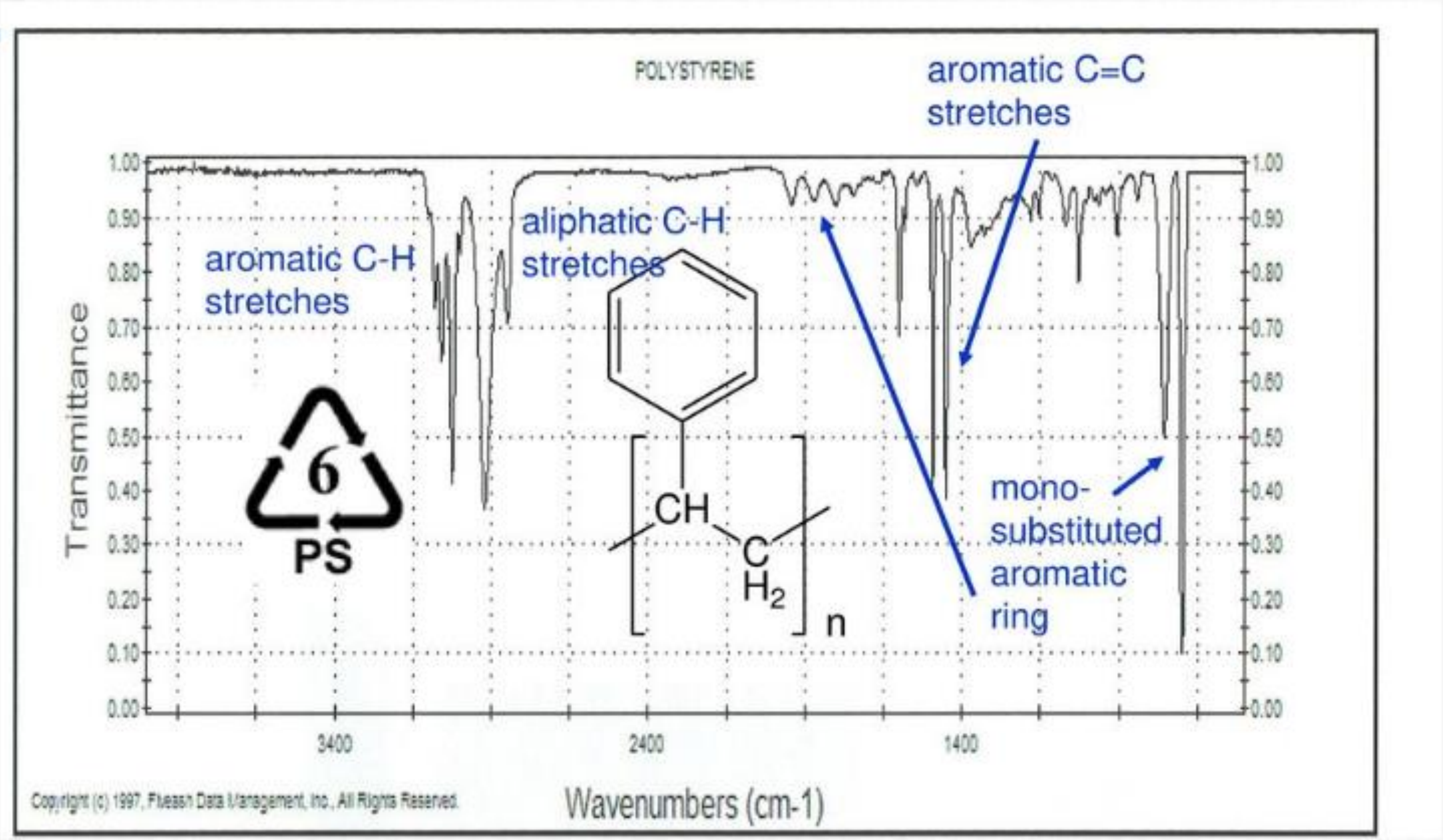
C-H bend of *para* disubstituted aromatic ring



Dr. Zerong Wang at UHCL

http://www.fdmspectra.com/

Infrared Spectrum of Polystyrene



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Example of IR Spectrum: Infrared Spectroscopy for 1-Octyne & 4-Octyne

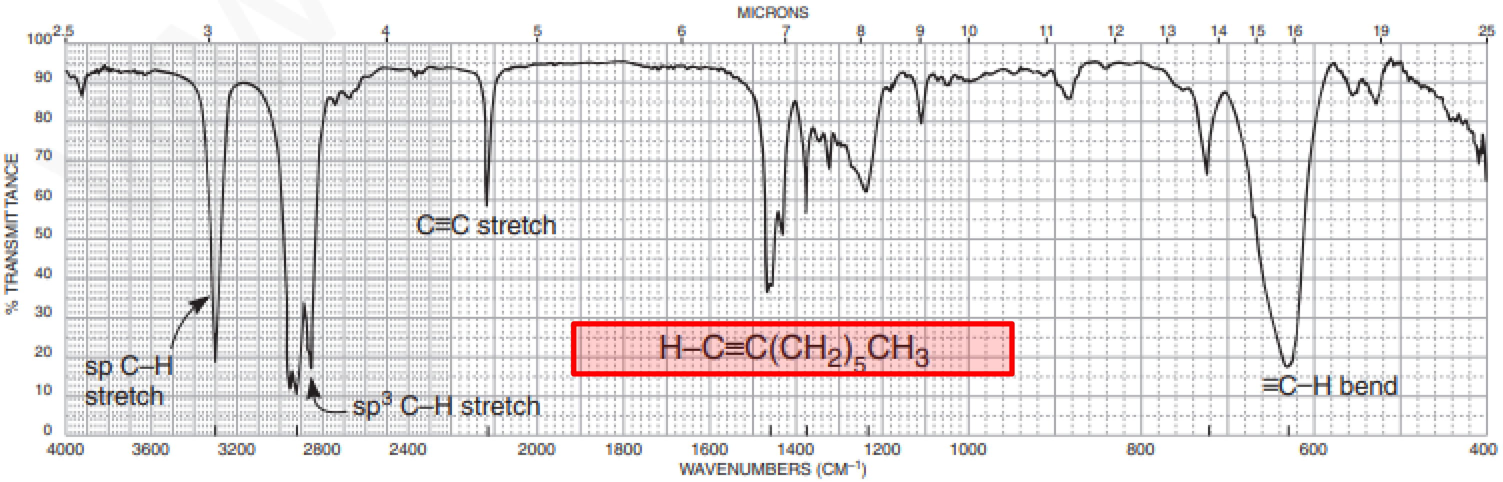


FIGURE 2.14 The infrared spectrum of 1-octyne (neat liquid, KBr plates).

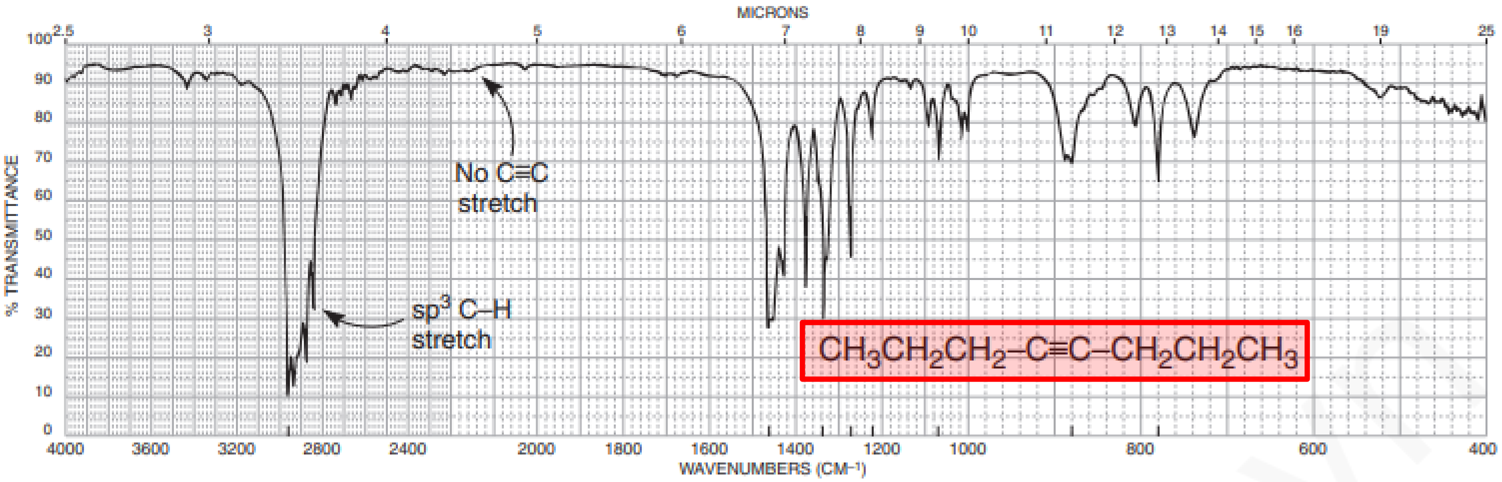


FIGURE 2.15 The infrared spectrum of 4-octyne (neat liquid, KBr plates).

IR Absorption Wavenumber (Values) for C-O & O-H in Alcohols & Phenol: Stretching

- Hydrogen bond:

✓ intramolecular

✓ intermolecular

✓ affects sharpness & width

✓ correlation to concentratic

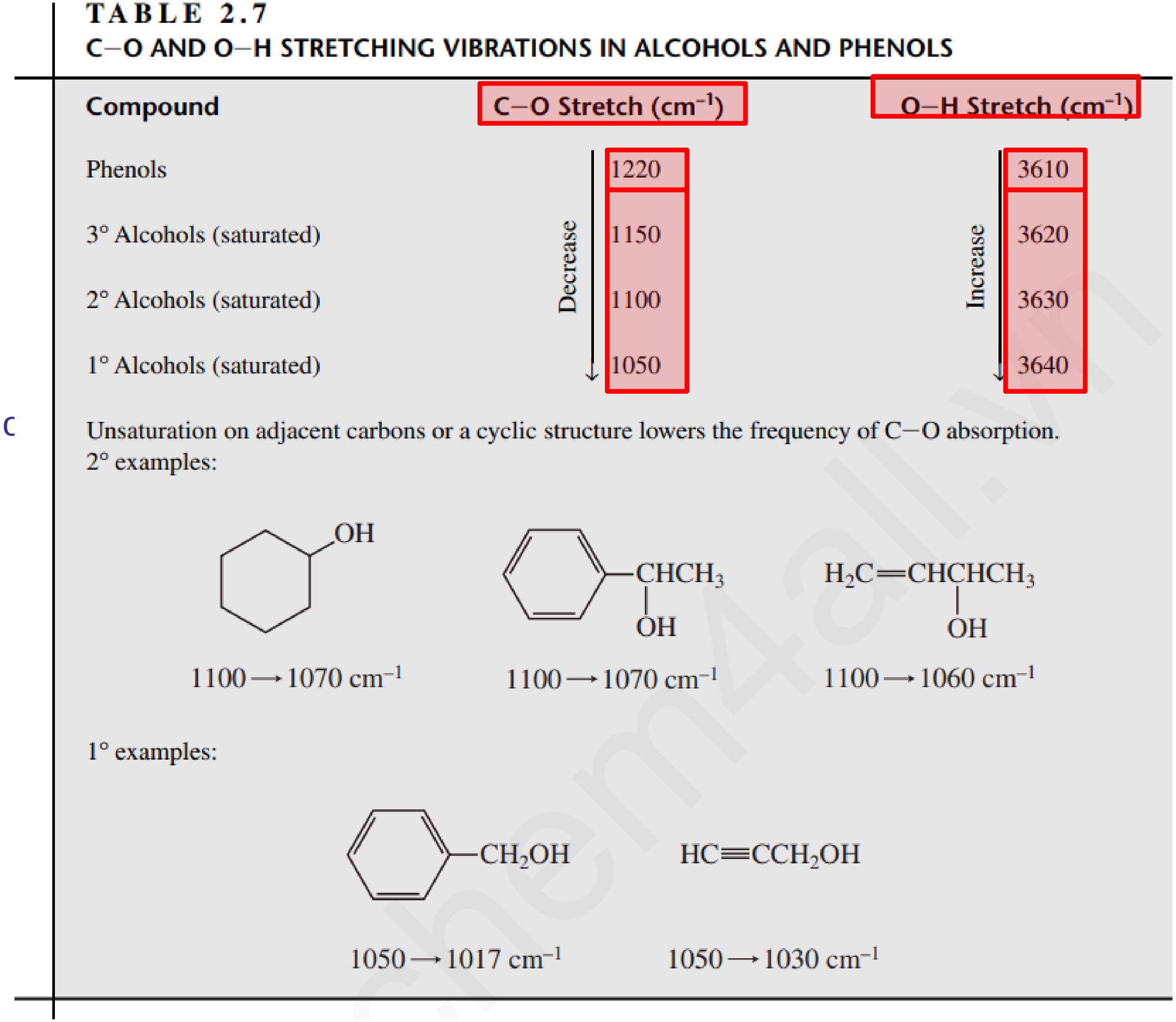


TABLE 2.7

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

Compound		**C—O Stretch (cm^{-1})**		**O—H Stretch (cm^{-1})**
Phenols	Decrease ↓	1220	Increase ↓	3610
3° Alcohols (saturated)		1150		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:

OH

1100 → 1070 cm^{-1}

$CHCH_3$ / OH

1100 → 1070 cm^{-1}

$H_2C{=}CHCHCH_3$ / OH

1100 → 1060 cm^{-1}

1° examples:

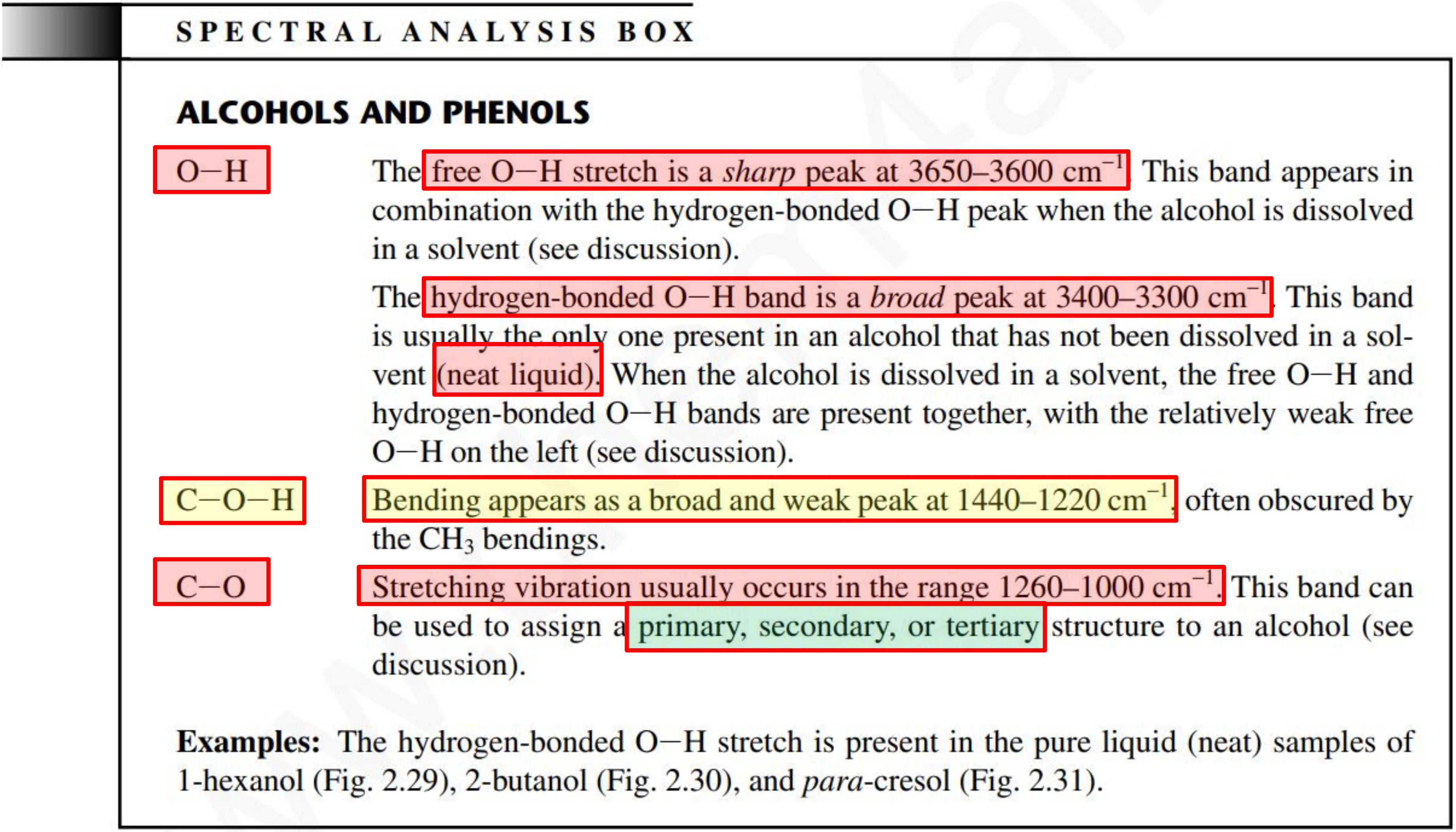
CH_2OH

1050 → 1017 cm^{-1}

$HC{\equiv}CCH_2OH$

1050 → 1030 cm^{-1}

IR Absorption Wavenumber (Values) for C-O & O-H in Alcohols & Phenol: Stretching (& C-O-H Bending)



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).

IR Absorption Wavenumber (Values) for Free & Hydrogen Bonded O-H in Alcohols & Phenol: Stretching

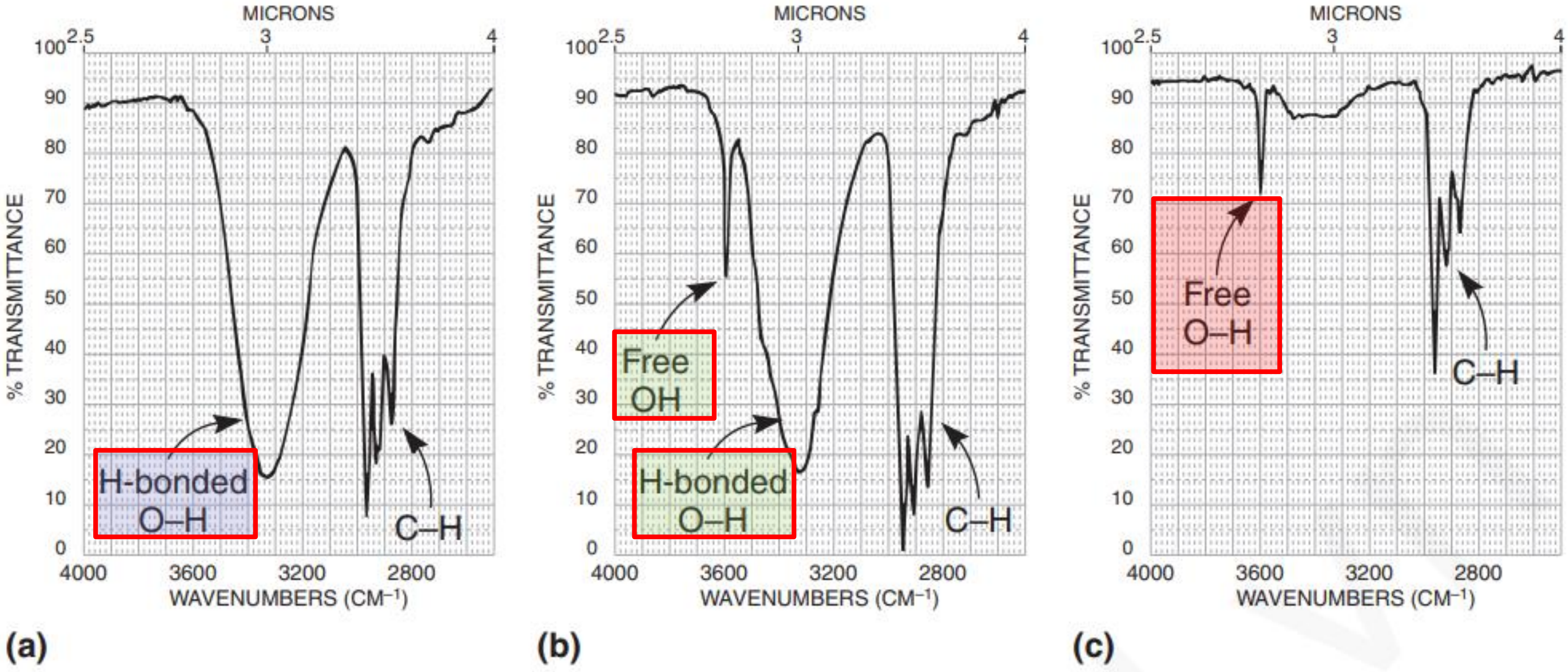
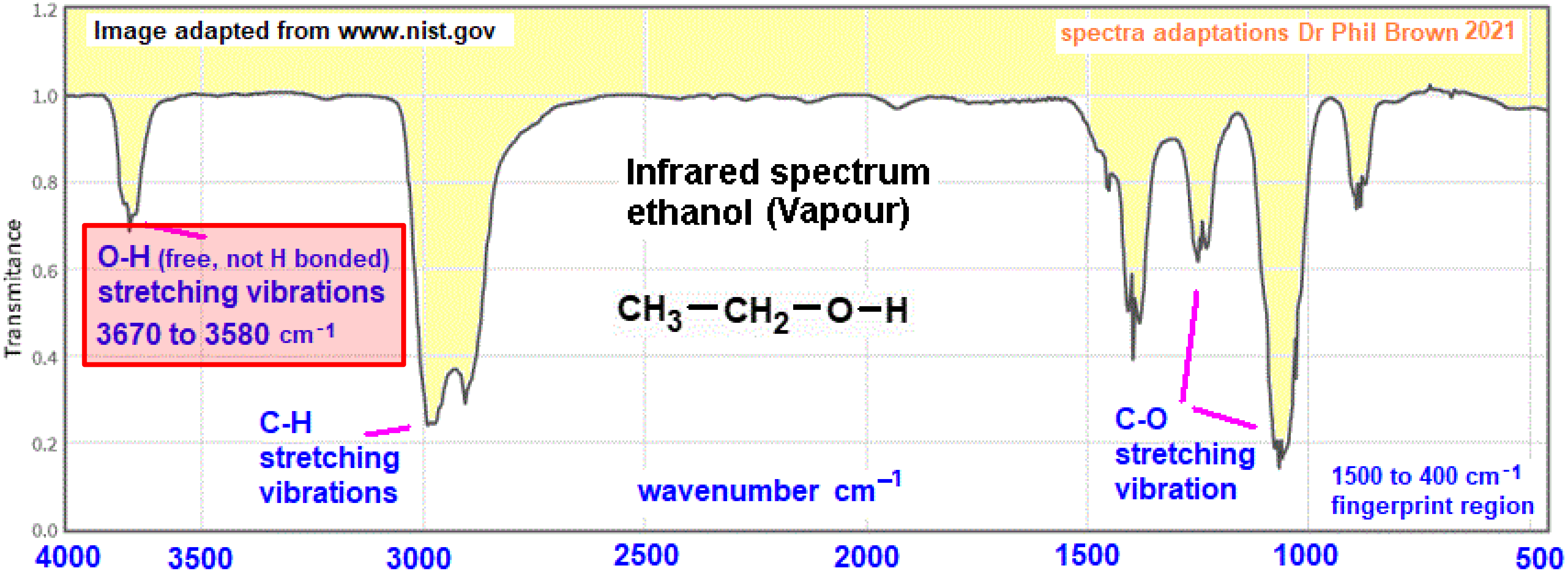


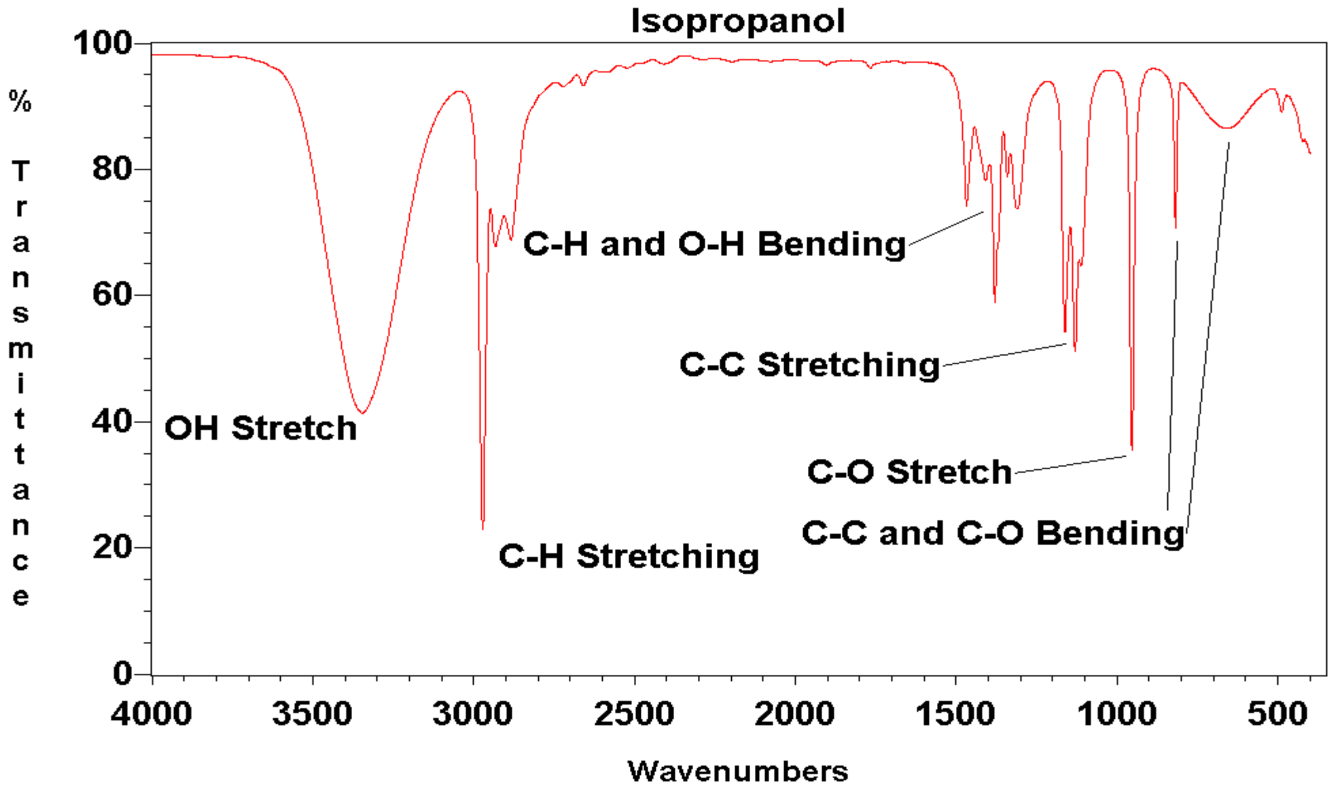
FIGURE 2.32 The O—H stretch region. (a) Hydrogen-bonded O—H only (neat liquid). (b) Free and hydrogen-bonded O—H (dilute solution). (c) Free and hydrogen-bonded O—H (very dilute solution).

Example of IR Spectrum: Infrared Spectroscopy for Ethanol

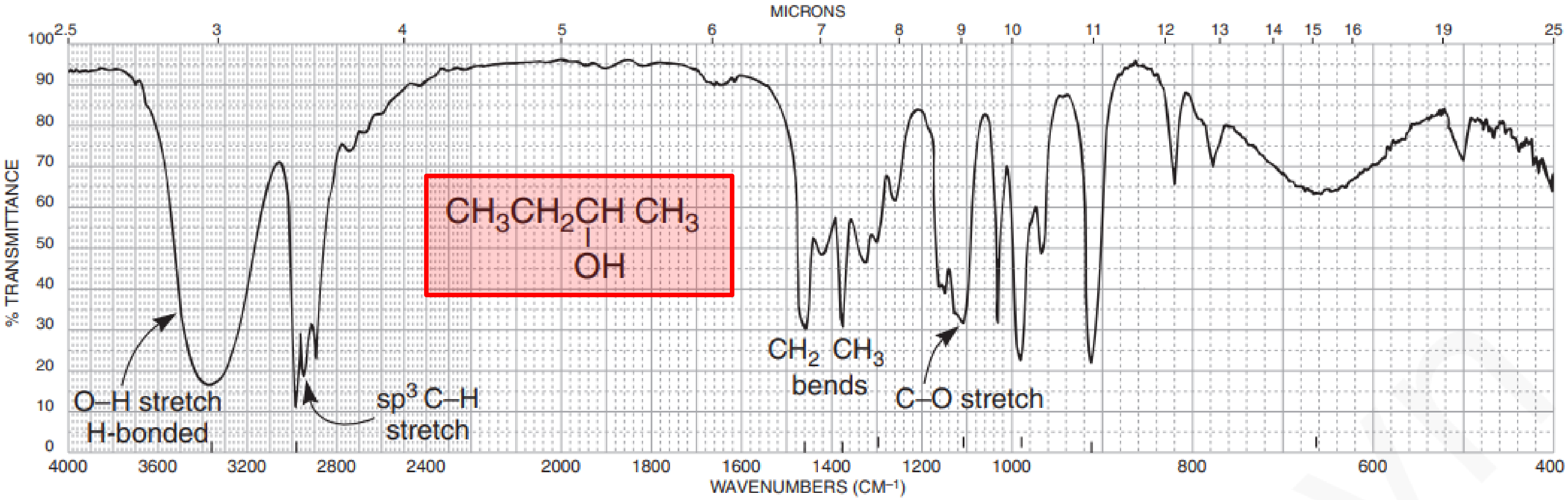


IR Spectrum Sample: Infrared Spectroscopy for Isopropyl Alcohol

- The infrared absorption bands for isopropyl alcohol ($CH(CH_3)_2OH$) to identify the various functional groups of the molecule.



Example of IR Spectrum: Infrared Spectroscopy for 2-Butanol



$CH_3CH_2CH(OH)CH_3$

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

Example of IR Spectrum: Infrared Spectroscopy for Hexanol

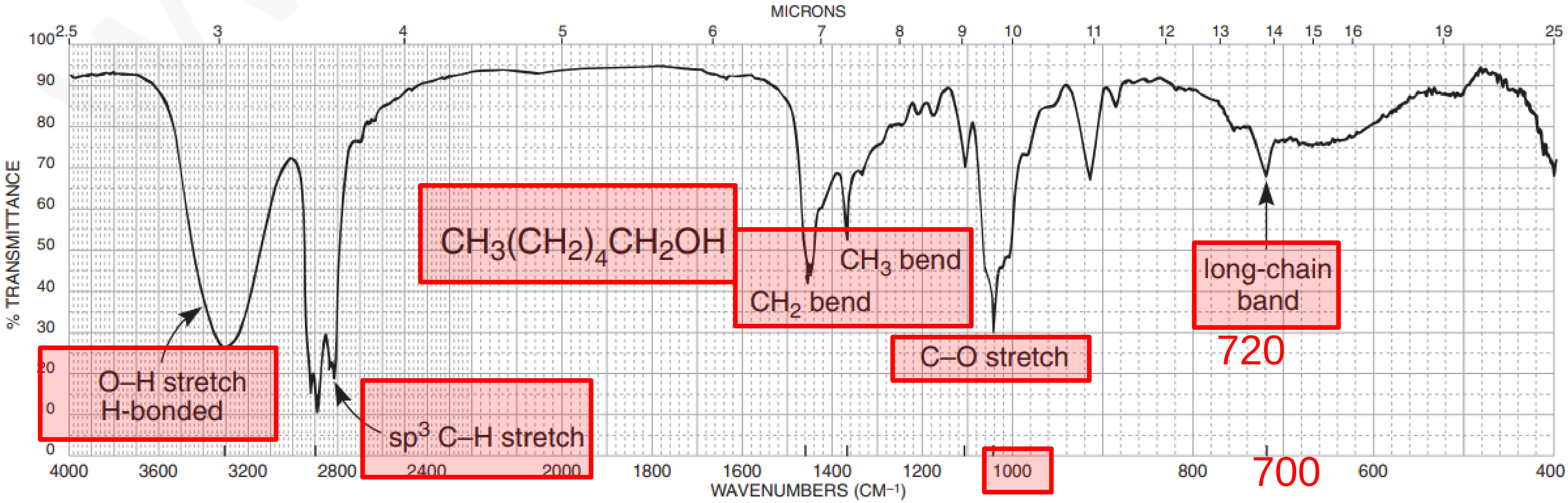
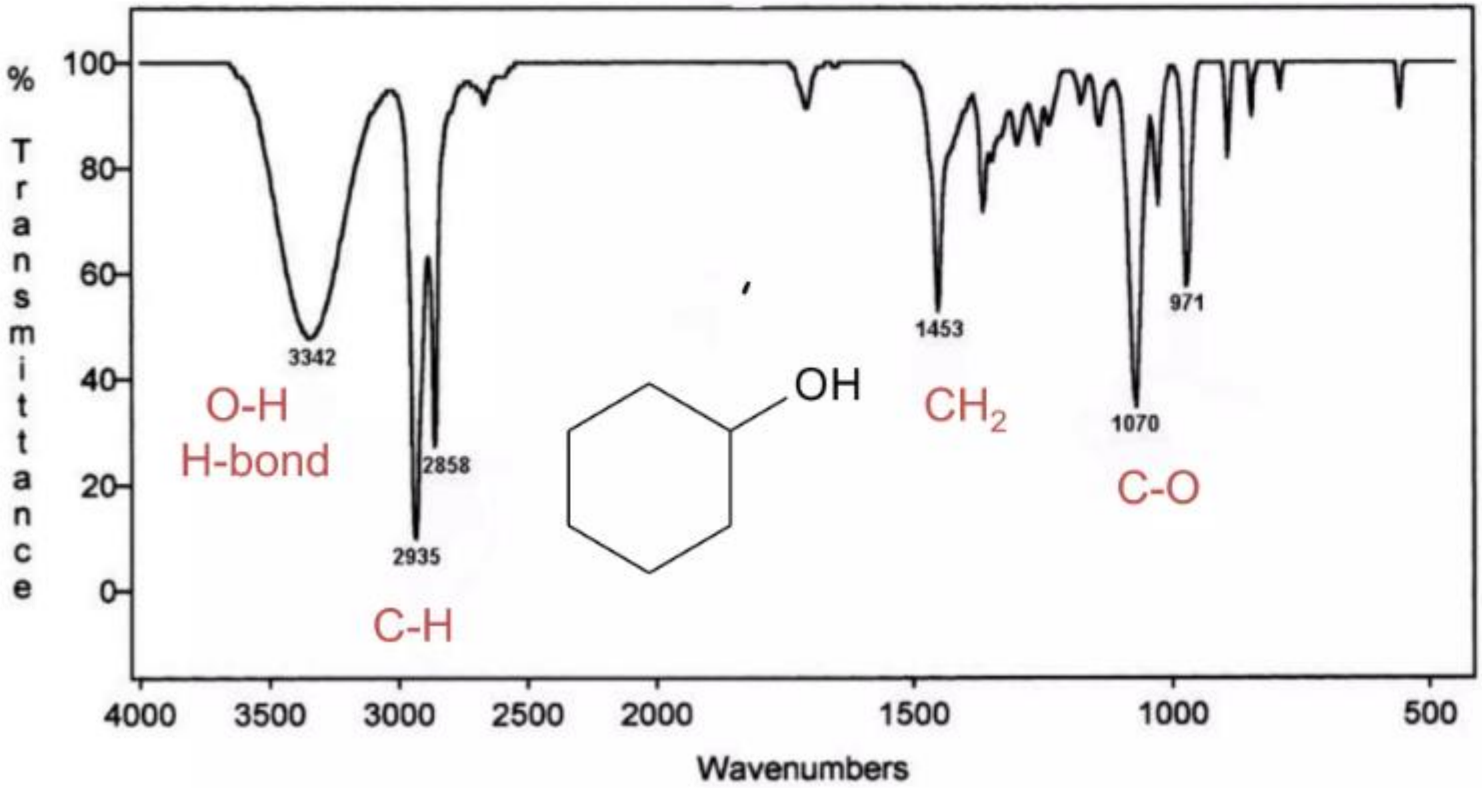


FIGURE 2.29 The infrared spectrum of 1-hexanol (neat liquid, KBr plates).

Example of IR Spectrum: Infrared Spectroscopy for Cyclohexanol



Example of IR Spectrum: Infrared Spectroscopy for Phenol

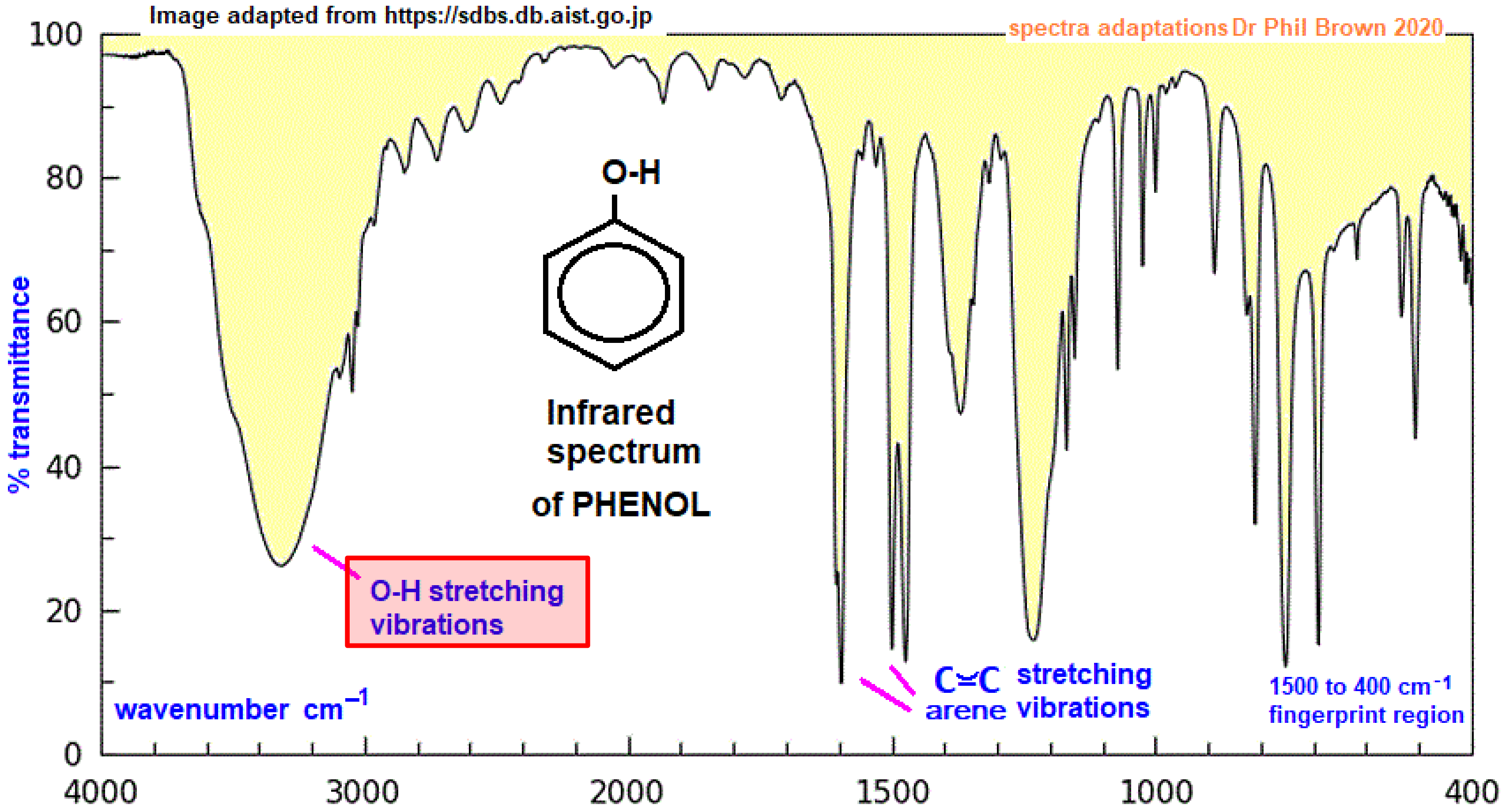


Image adapted from https://sdbs.db.aist.go.jp

spectra adaptations Dr Phil Brown 2020

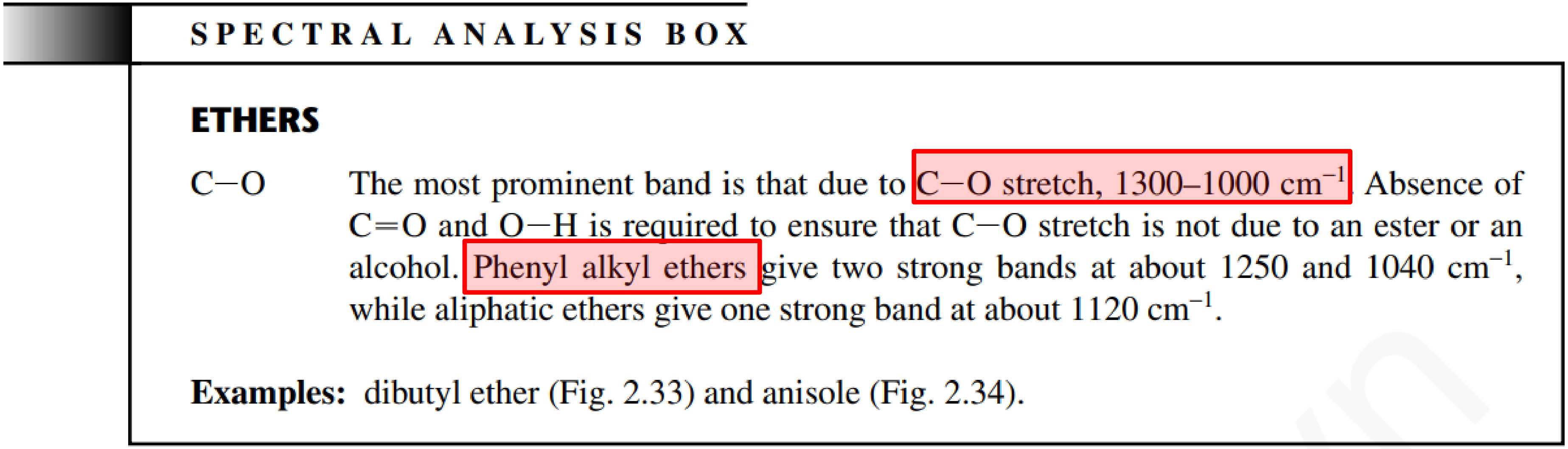
Infrared spectrum of PHENOL

O-H stretching vibrations

C≃C stretching arene vibrations

1500 to 400 cm^{-1} fingerprint region

IR Absorption Wavenumber (Values) for C-O in Ethers: Stretching



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).

Example of IR Spectrum: Infrared Spectroscopy for Methoxy-Benzene

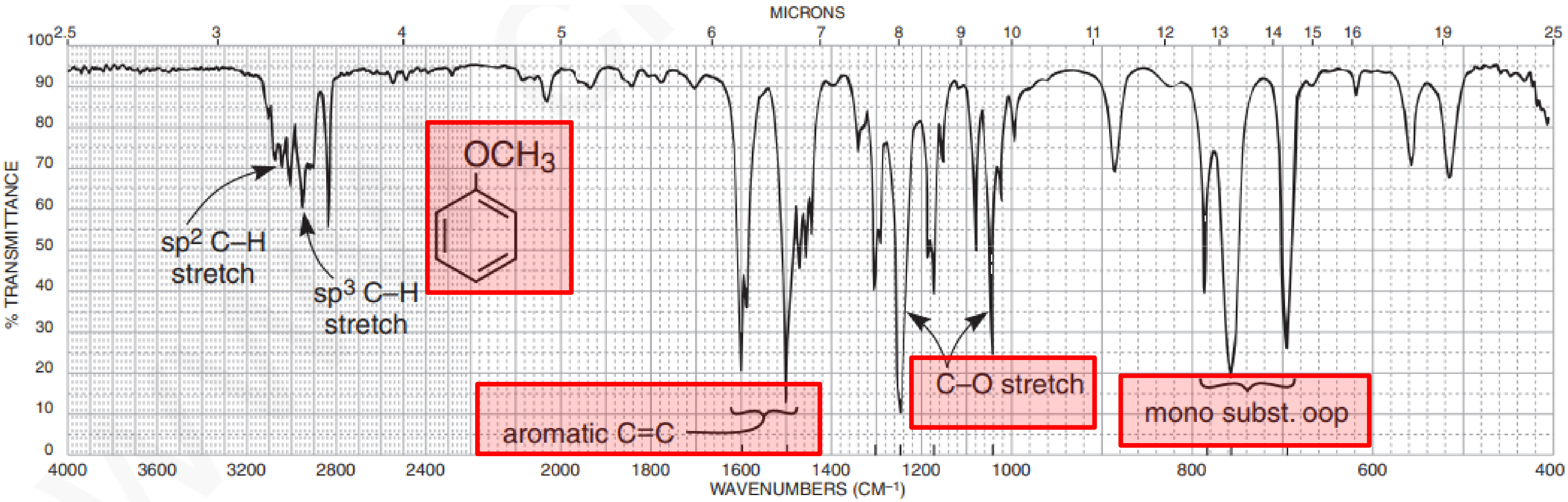
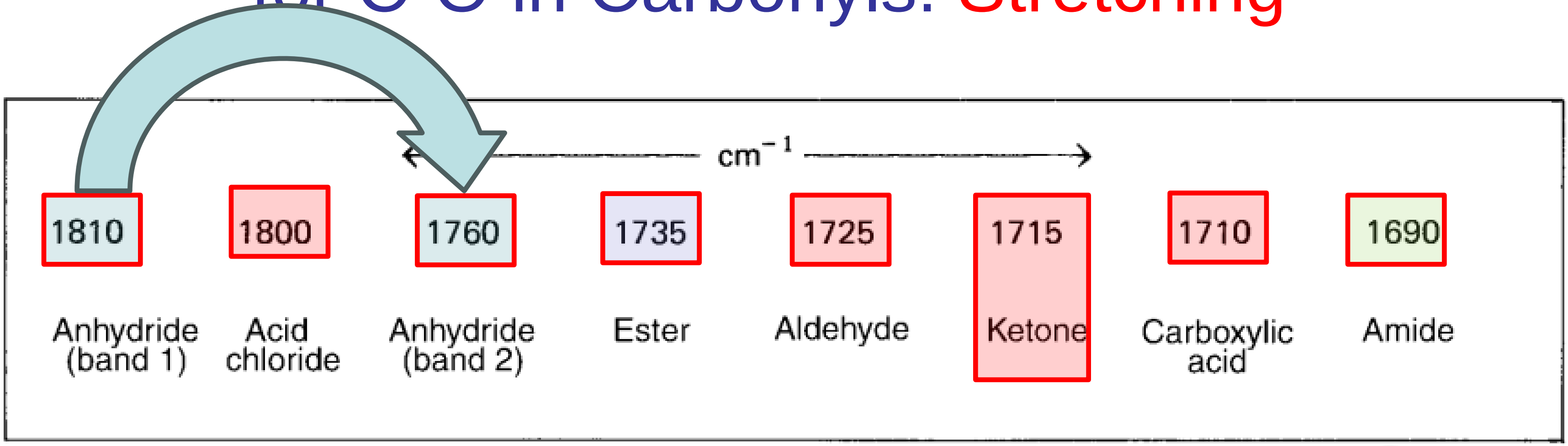


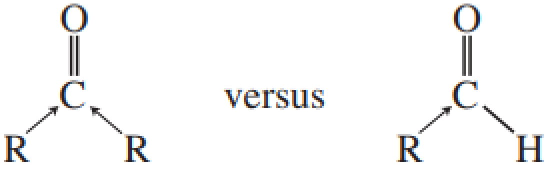
FIGURE 2.34 The infrared spectrum of anisole (neat liquid, KBr plates).

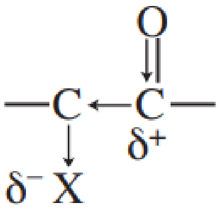
IR Absorption Wavenumber (Values) for C-O in Carbonyls: Stretching



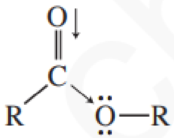
1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

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



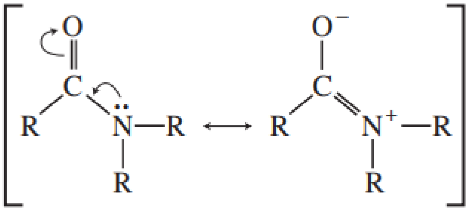


Ester



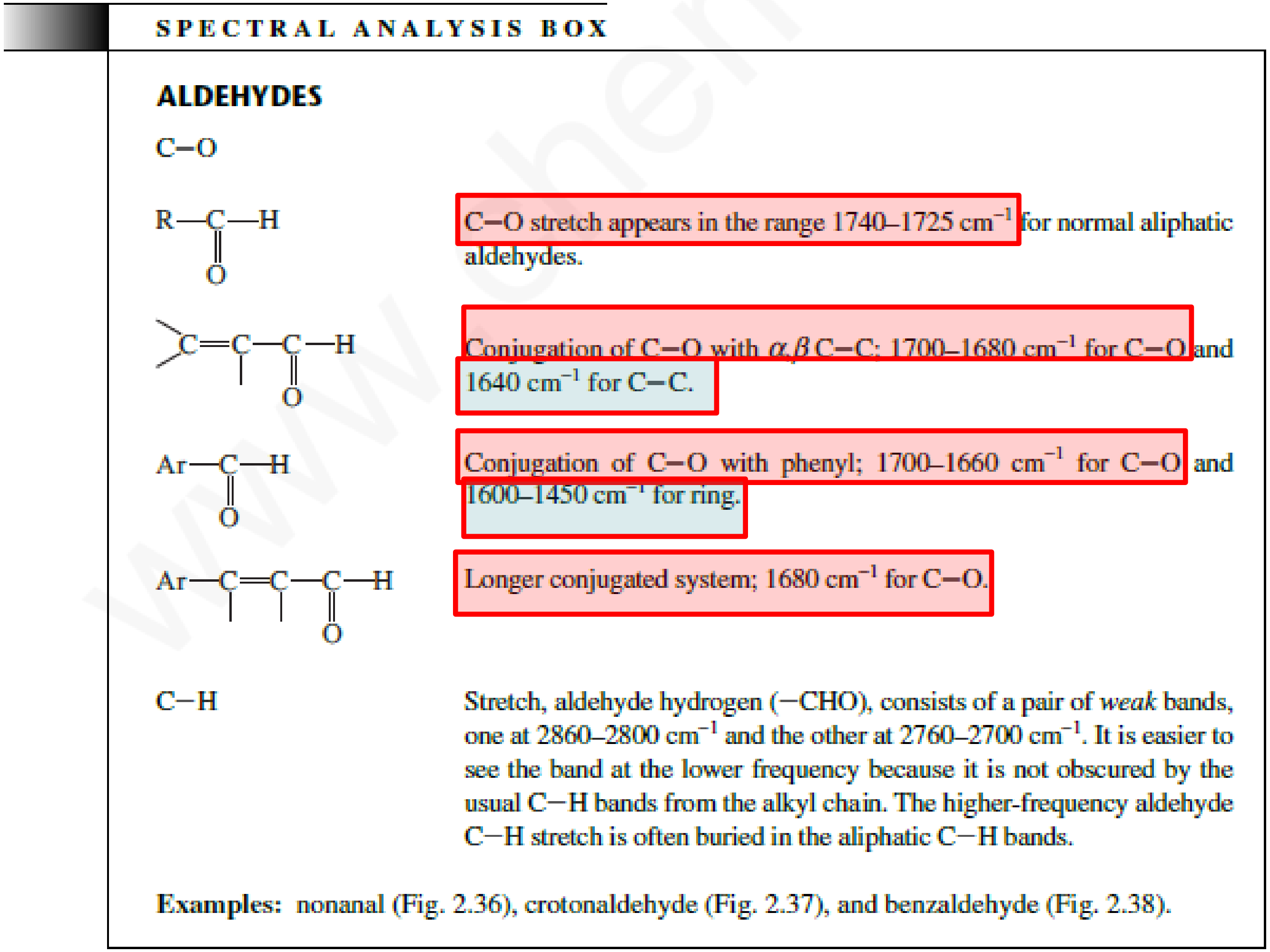
Electron-withdrawing effect raises C=O frequency

Amide



Resonance effect lowers C=O frequency

IR Absorption Wavenumber (Values) for C-O in Aldehydes: Stretching



SPECTRAL ANALYSIS BOX

ALDEHYDES

C=O

$R-C(=O)-H$	C=O stretch appears in the range 1740–1725 cm^{-1} for normal aliphatic aldehydes.
$>C=C(-)-C(=O)-H$	Conjugation of C=O with α,β C=C; 1700–1680 cm^{-1} for C=O and 1640 cm^{-1} for C=C.
$Ar-C(=O)-H$	Conjugation of C=O with phenyl; 1700–1660 cm^{-1} for C=O and 1600–1450 cm^{-1} for ring.
$Ar-C(-)=C(-)-C(=O)-H$	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).

Example of IR Spectrum: Infrared Spectroscopy for Nonanal

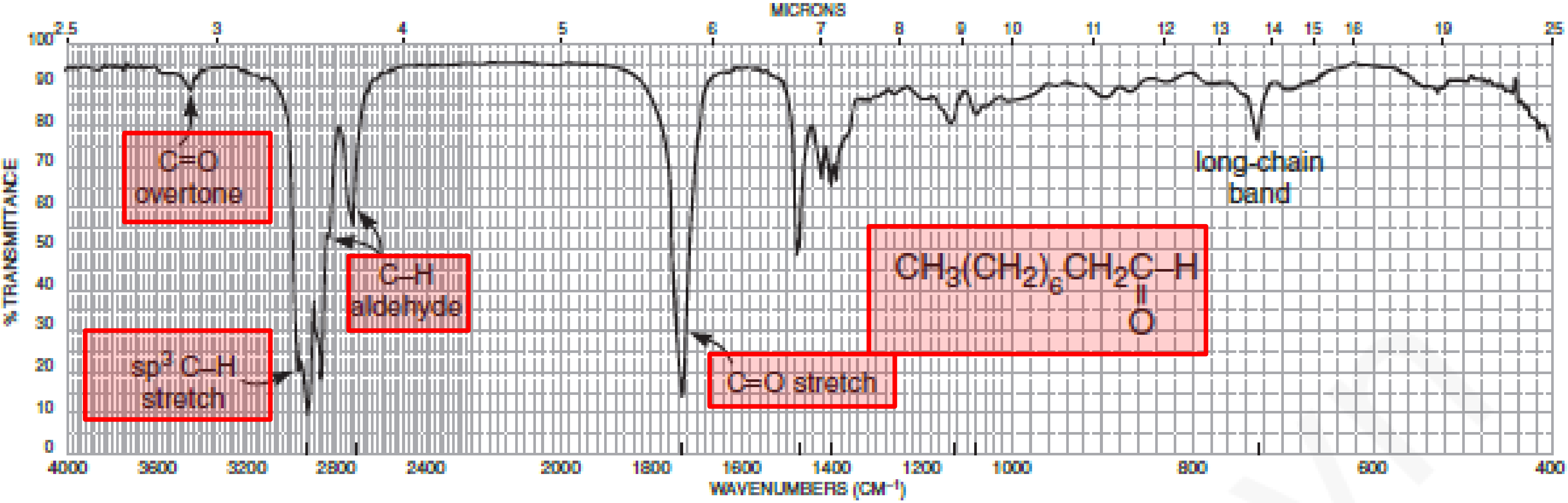


FIGURE 2.36 The infrared spectrum of nonanal (neat liquid, KBr plates).

Example of IR Spectrum: Infrared Spectroscopy for 2-butenal

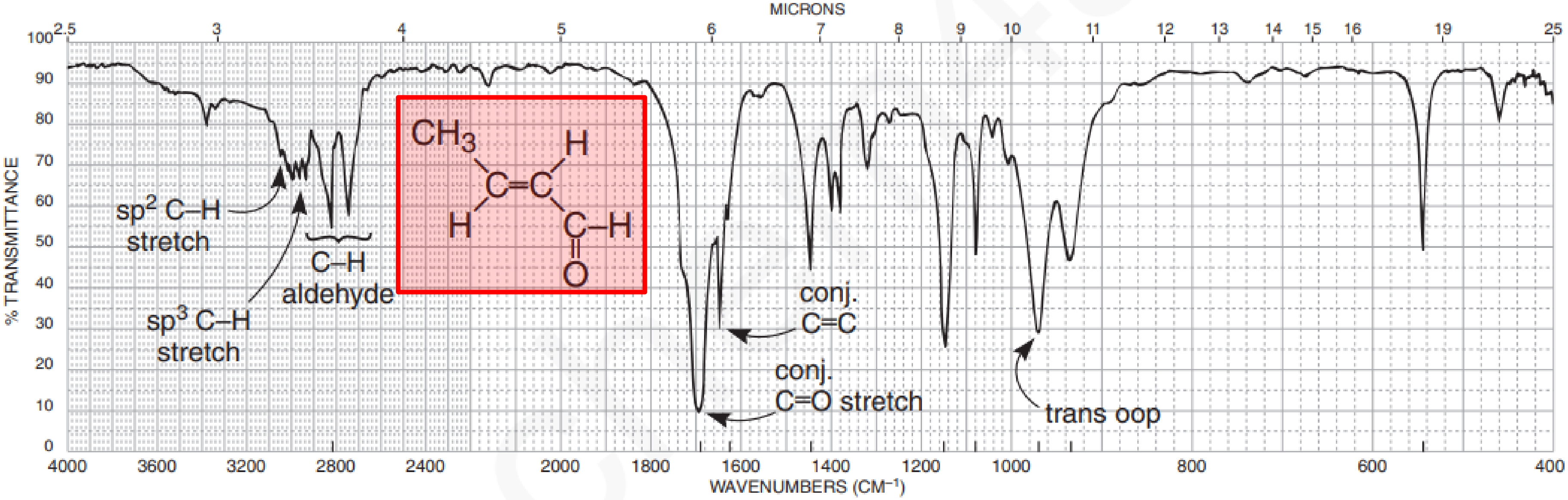


FIGURE 2.37 The infrared spectrum of crotonaldehyde (neat liquid, KBr plates).

Example of IR Spectrum: Infrared Spectroscopy for Benzaldehyde

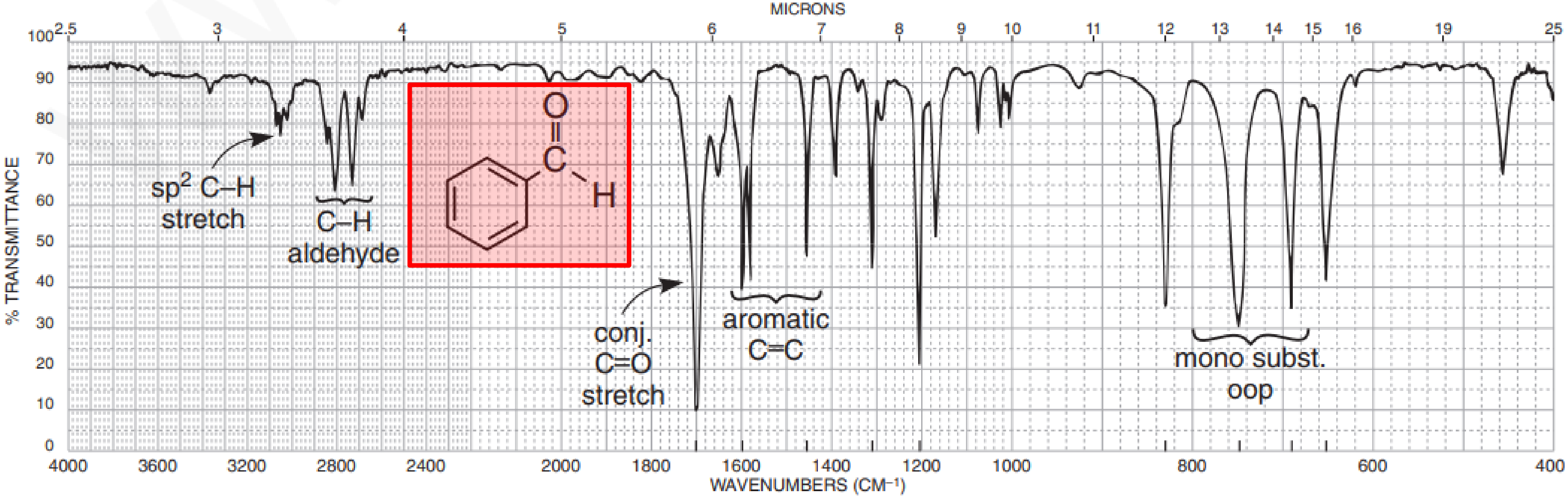
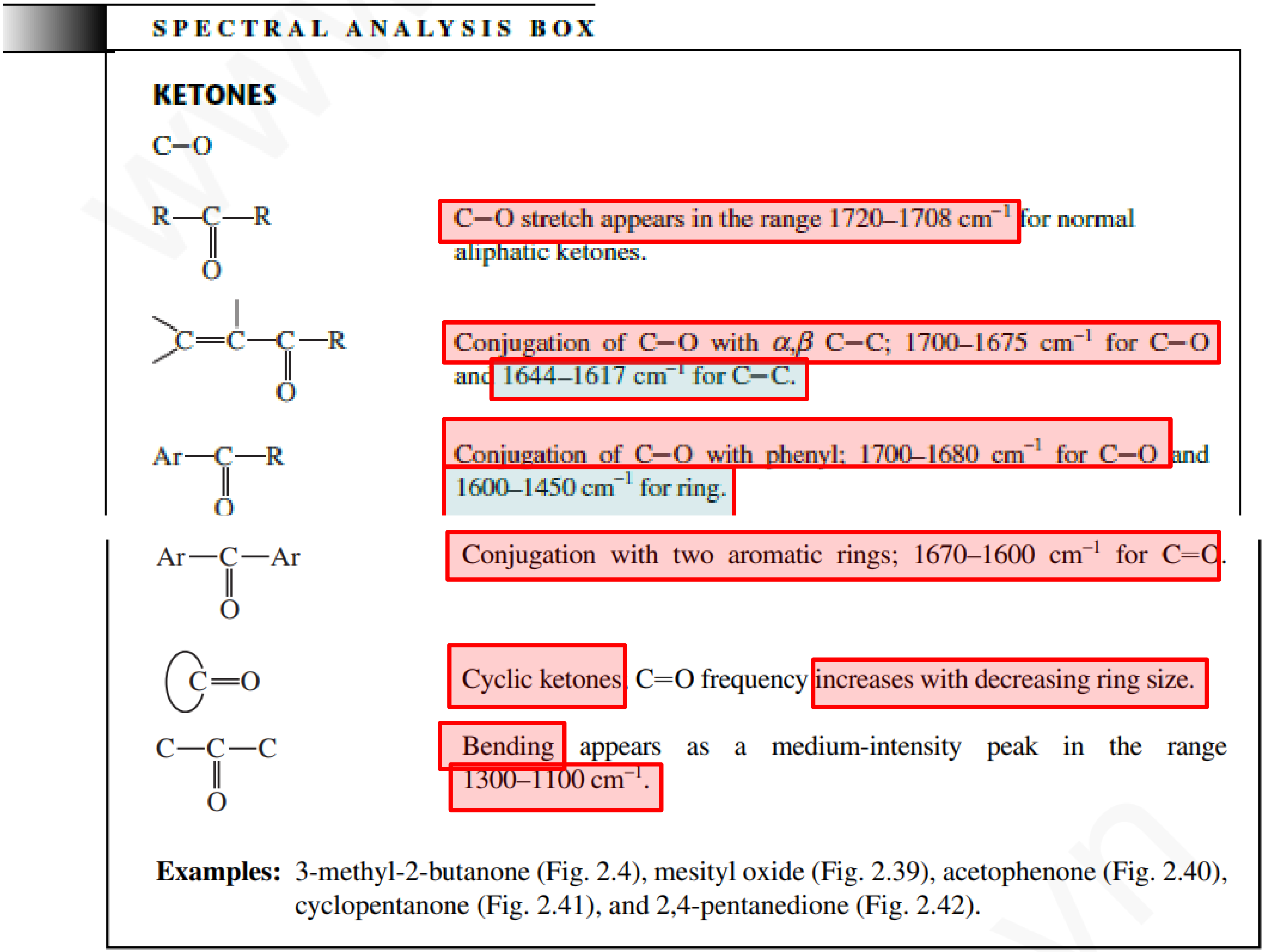


FIGURE 2.38 The infrared spectrum of benzaldehyde (neat liquid, KBr plates).

IR Absorption Wavenumber (Values) for C-O in Ketones: Stretching & Bending



SPECTRAL ANALYSIS BOX

KETONES

C–O

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.

Conjugation of C–O with phenyl; 1700–1680 cm^{-1} for C–O and 1600–1450 cm^{-1} for ring.

Conjugation with two aromatic rings; 1670–1600 cm^{-1} for C=O.

Cyclic ketones. C=O frequency increases with decreasing ring size.

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).

IR Absorption Wavenumber (Values) for C-O in Various Types of Ketones: Stretching

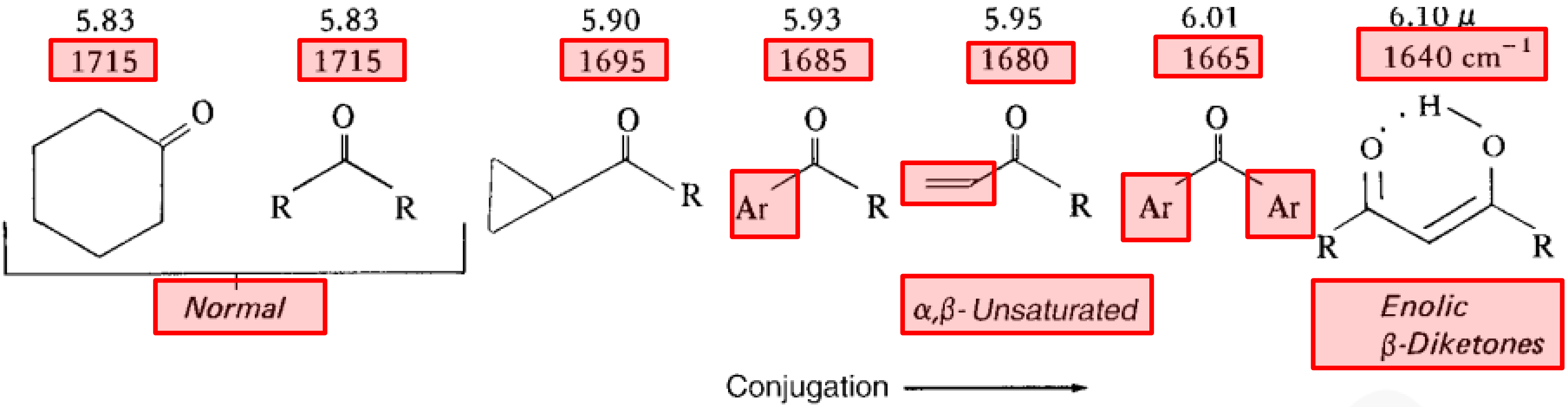
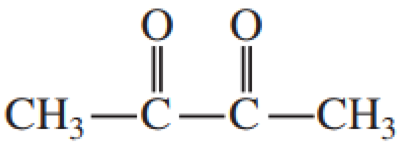
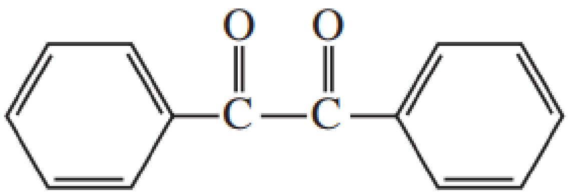


FIGURE 2.43 The C=O stretching vibrations in conjugated ketones.



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

$1716\ cm^{-1}$



$1680\ cm^{-1}$

IR Absorption Wavenumber (Values) for C-O in Cyclic Ketones & Ketenes: Stretching

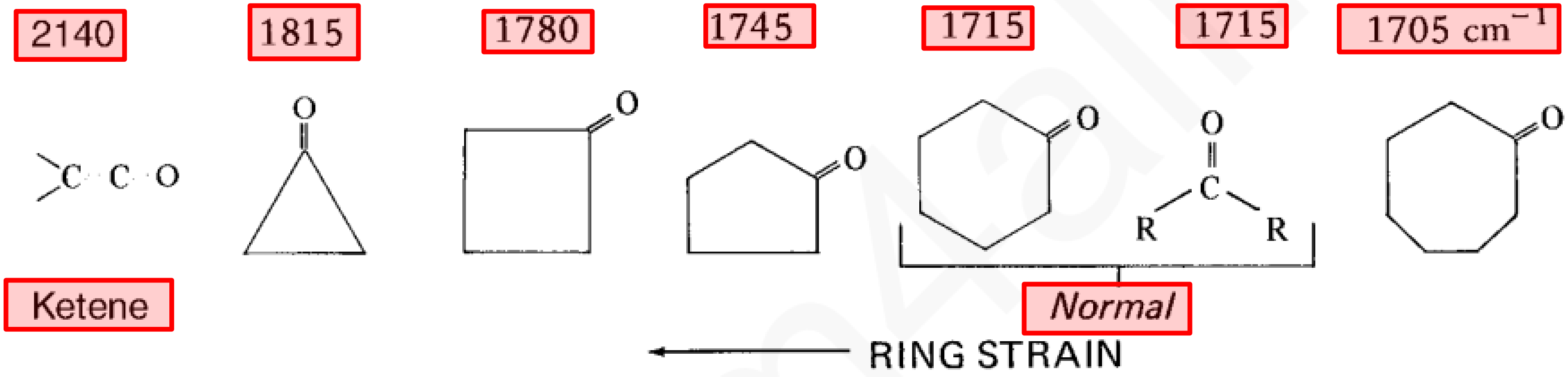


FIGURE 2.44 The C=O stretching vibrations for cyclic ketones and ketene.

Example of IR Spectrum:
Infrared Spectroscopy for Cyclopentanone

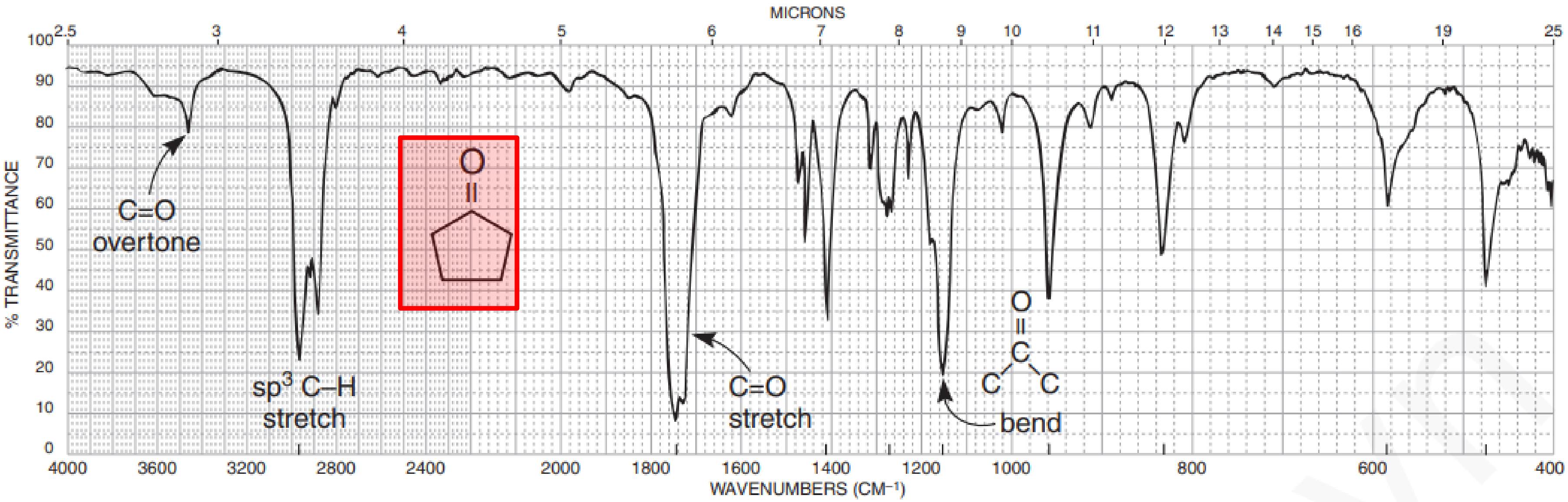
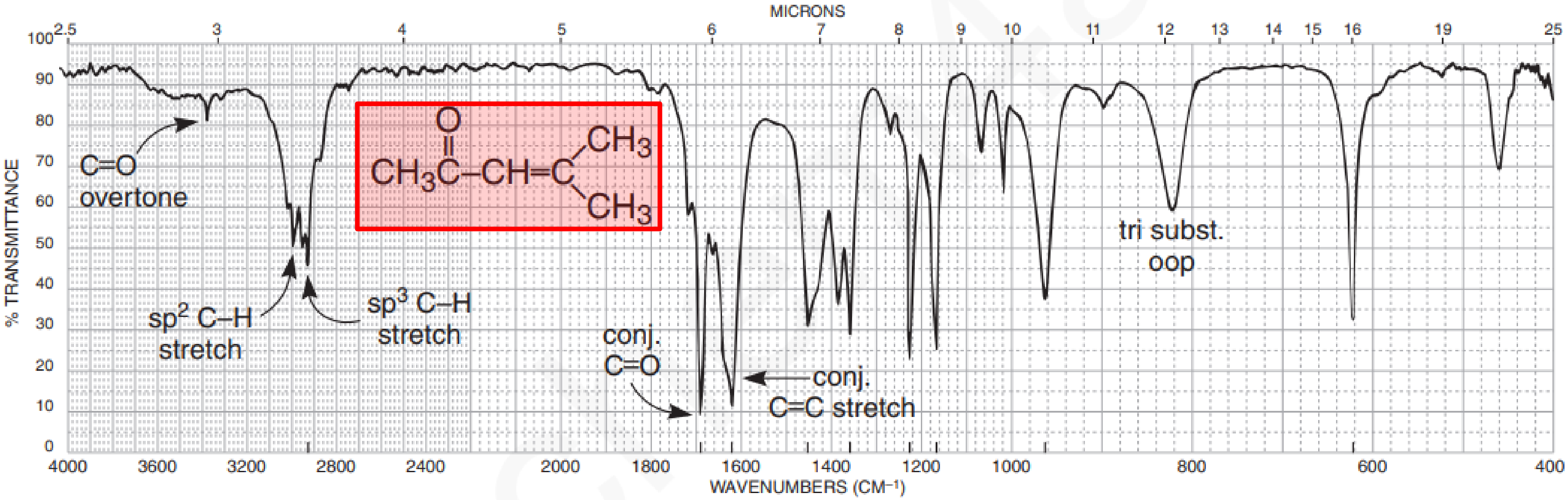


FIGURE 2.41 The infrared spectrum of cyclopentanone (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for Branched Derivative of Pent-3-en-2-one



F I G U R E 2 . 3 9 The infrared spectrum of mesityl oxide (neat liquid, KBr plates).

Example of IR Spectrum: Infrared Spectroscopy for Acetophenone

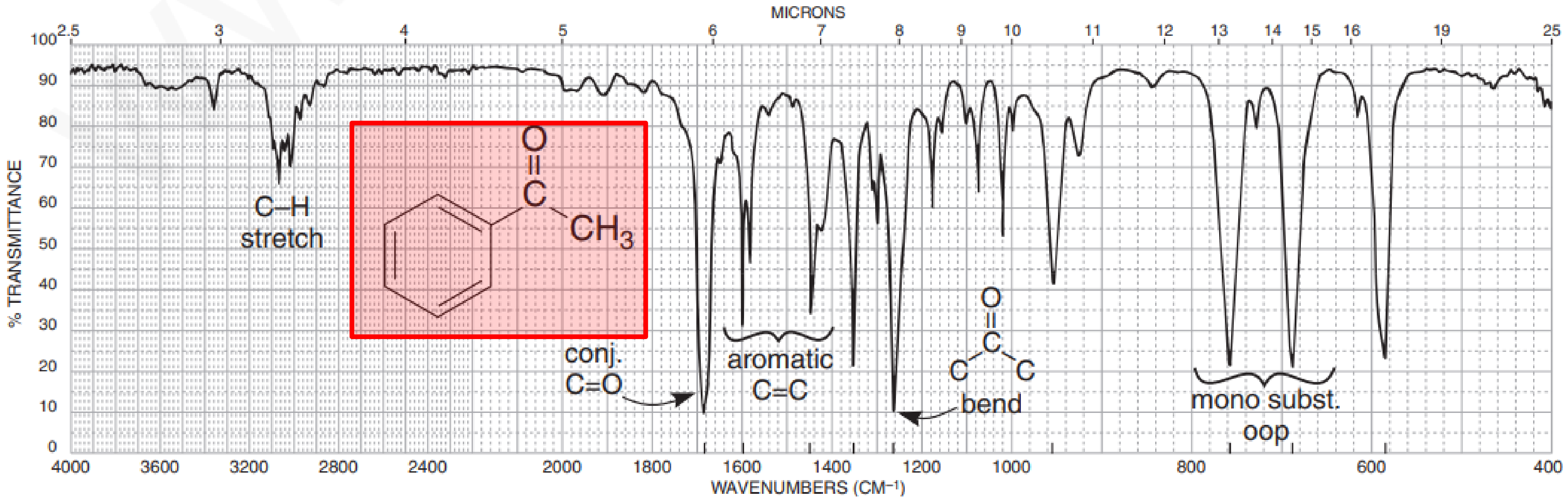
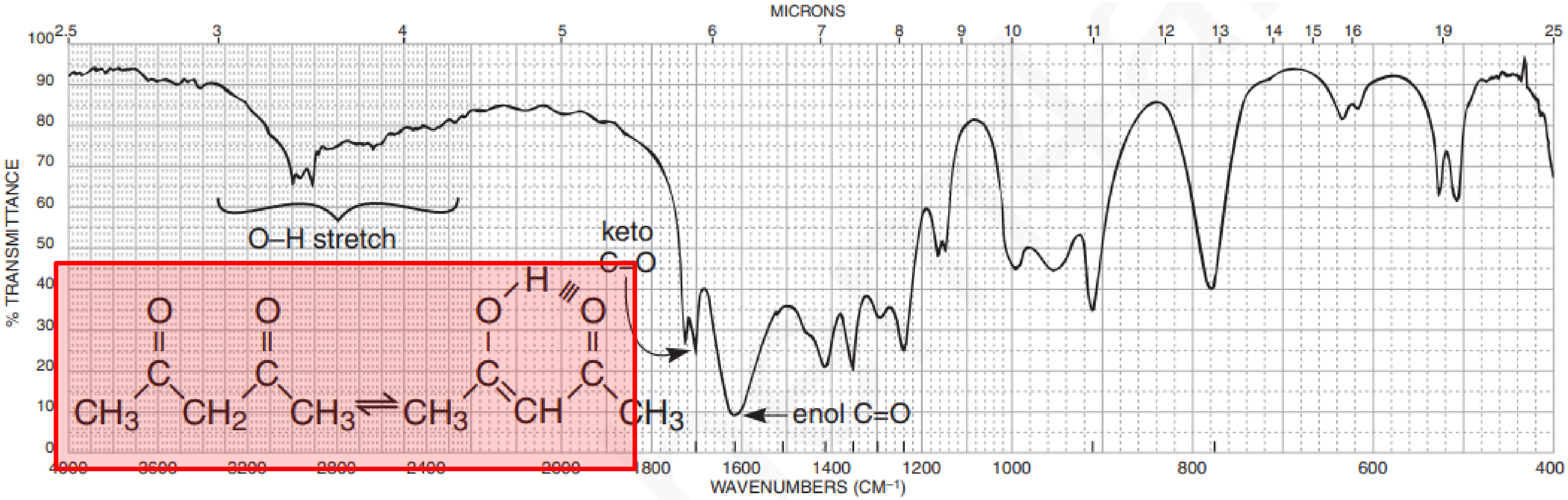


FIGURE 2.40 The infrared spectrum of acetophenone (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for Penta-1,3-dione



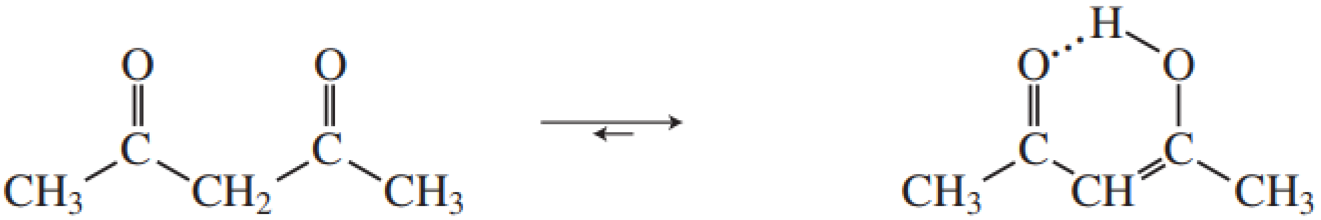
F I G U R E 2 . 4 2 The infrared spectrum of 2,4-pentanedione (neat liquid, KBr plates).

IR Absorption Wavenumber (Values) for C-O in ß-Keto-Enol Tautomerism: Stretching

- Intermolecular hydrogen bond

1715

Ketone



Keto tautomer

C=O doublet

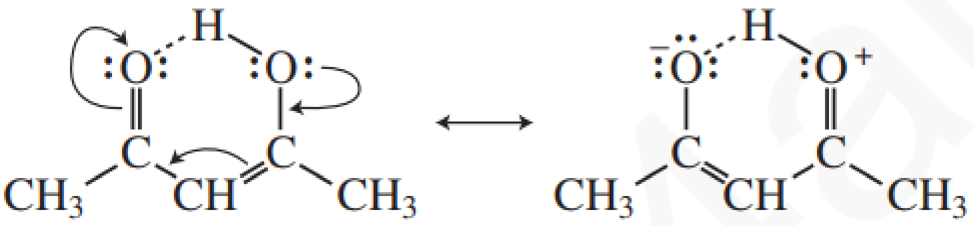
1723 cm^{-1} (symmetric stretch)

1706 cm^{-1} (asymmetric stretch)

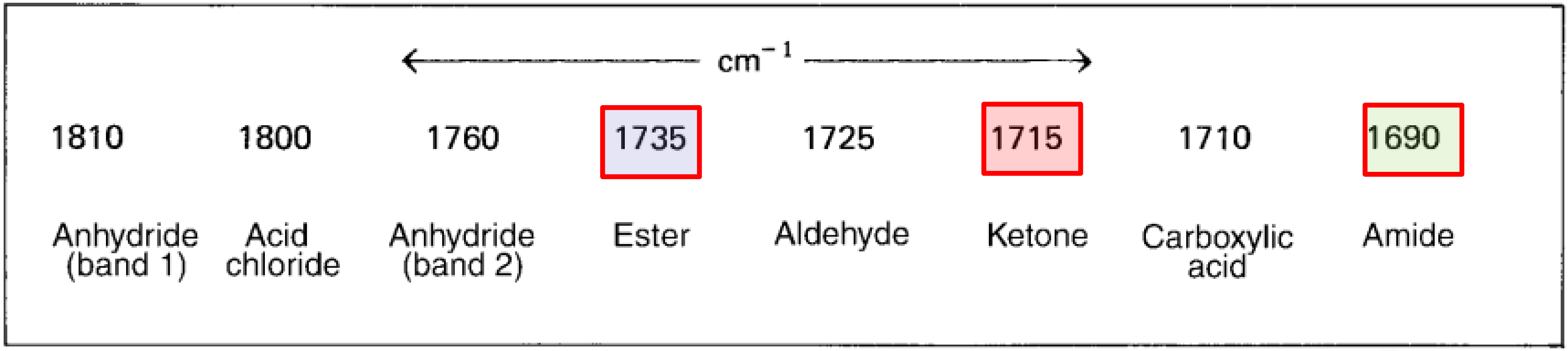
Enol tautomer

C=O (hydrogen bonded), 1622 cm^{-1}

O—H (hydrogen bonded), 3200–2400 cm^{-1}



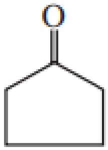
IR Absorption Wavenumber (Values) for C-O in Cyclic Carbonyls: Stretching



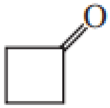
← cm^{-1} →

1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

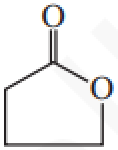
FIGURE 2.35 Normal base values for the C=O stretching vibrations for carbonyl groups.



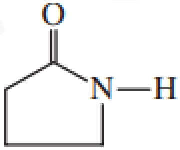
Cyclic ketone
1715 → 1745 cm^{-1}



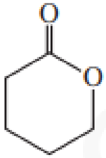
Cyclic ketone
1715 → 1780 cm^{-1}



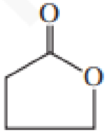
Cyclic ester
(lactone)
1735 → 1770 cm^{-1}



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



δ-Valerolactone
1735 cm^{-1}



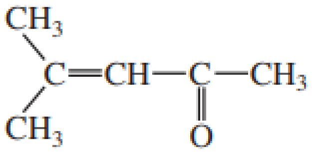
γ-Butyrolactone
1770 cm^{-1}

IR Absorption Wavenumber (Values) for C-O in Conjugated Carbonyls: Stretching

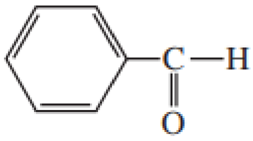
← cm^{-1} →

1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

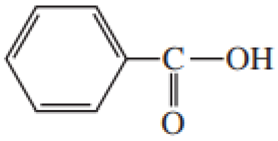
FIGURE 2.35 Normal base values for the C=O stretching vibrations for carbonyl groups.



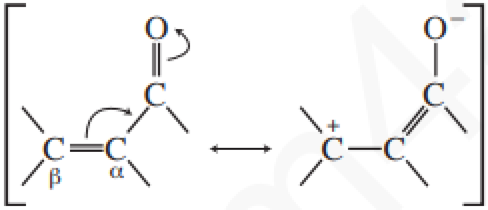
α,β-Unsaturated ketone
1715 ⟶ 1690 cm^{-1}

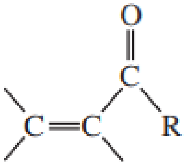


Aryl-substituted aldehyde
1725 ⟶ 1700 cm^{-1}

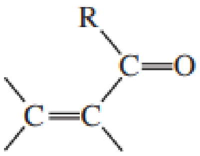


Aryl-substituted acid
1710 ⟶ 1680 cm^{-1}





s-cis



s-trans

IR Absorption Wavenumber (Values) for C=O in Cyclic Esters (Lactones): Stretching

1735

Ester

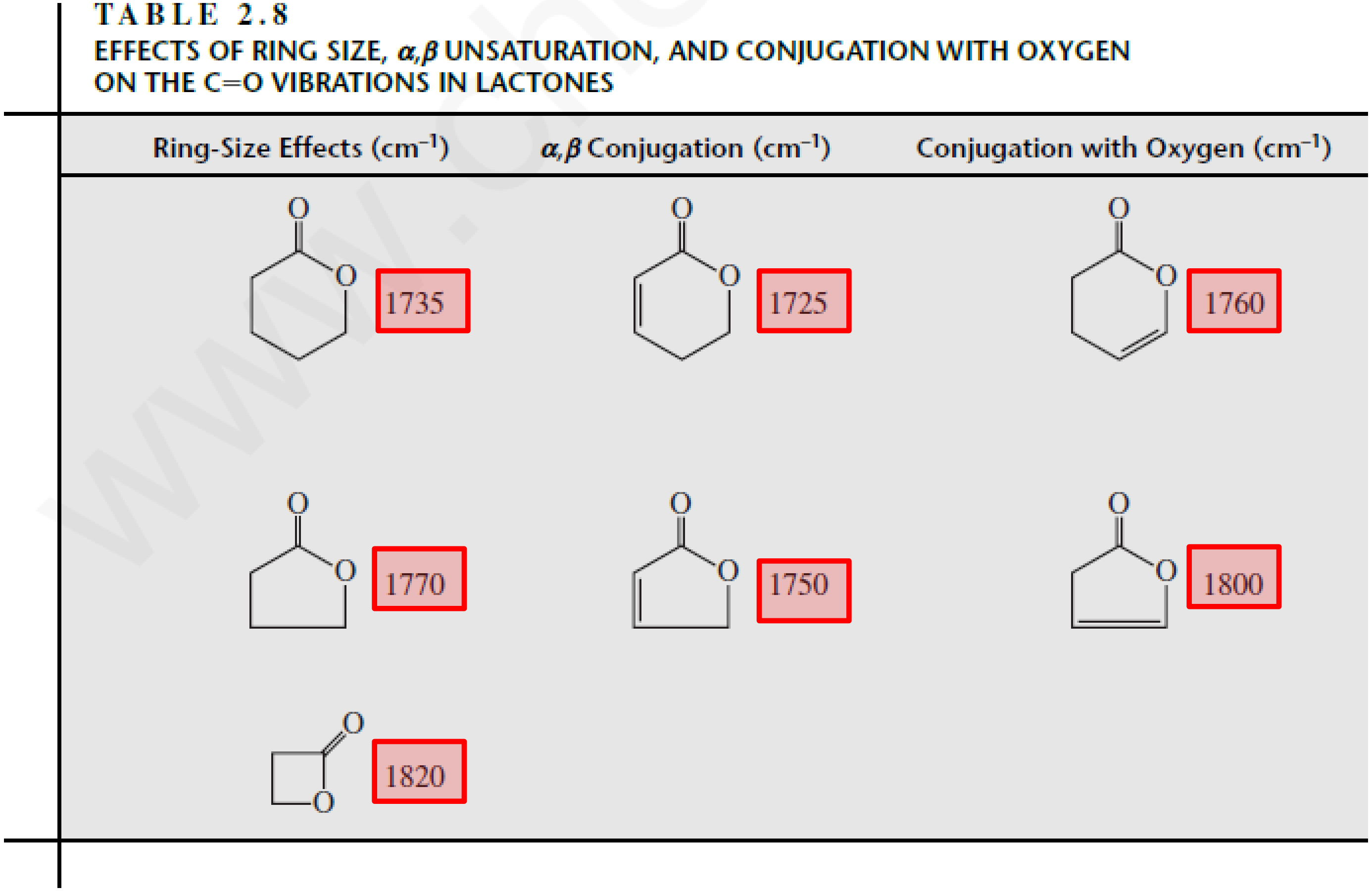
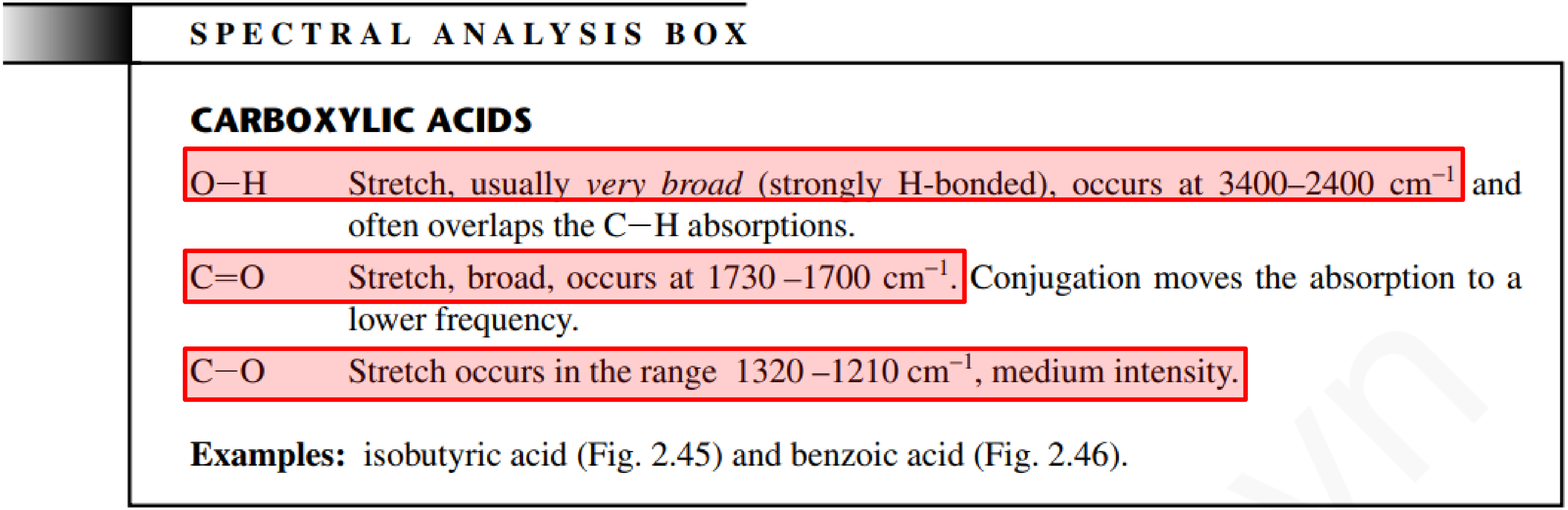


TABLE 2.8

EFFECTS OF RING SIZE, α,β UNSATURATION, AND CONJUGATION WITH OXYGEN ON THE C=O VIBRATIONS IN LACTONES

Ring-Size Effects (cm^{-1})	α,β Conjugation (cm^{-1})	Conjugation with Oxygen (cm^{-1})
1735	1725	1760
1770	1750	1800
1820		

IR Absorption Wavenumber (Values) for Carboxylic Acids: Stretching



SPECTRAL ANALYSIS BOX

CARBOXYLIC ACIDS

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

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

Example of IR Spectrum:
Infrared Spectroscopy for 2-Methyl Propanoic Acid

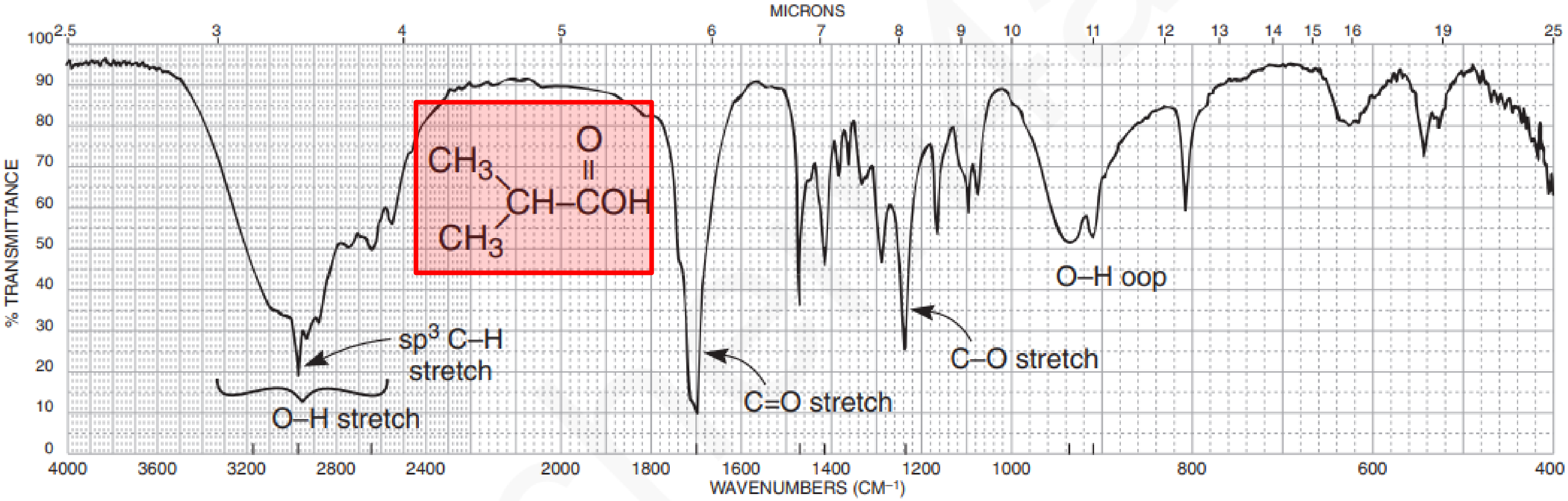


FIGURE 2.45 The infrared spectrum of isobutyric acid (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for Benzoic Acid

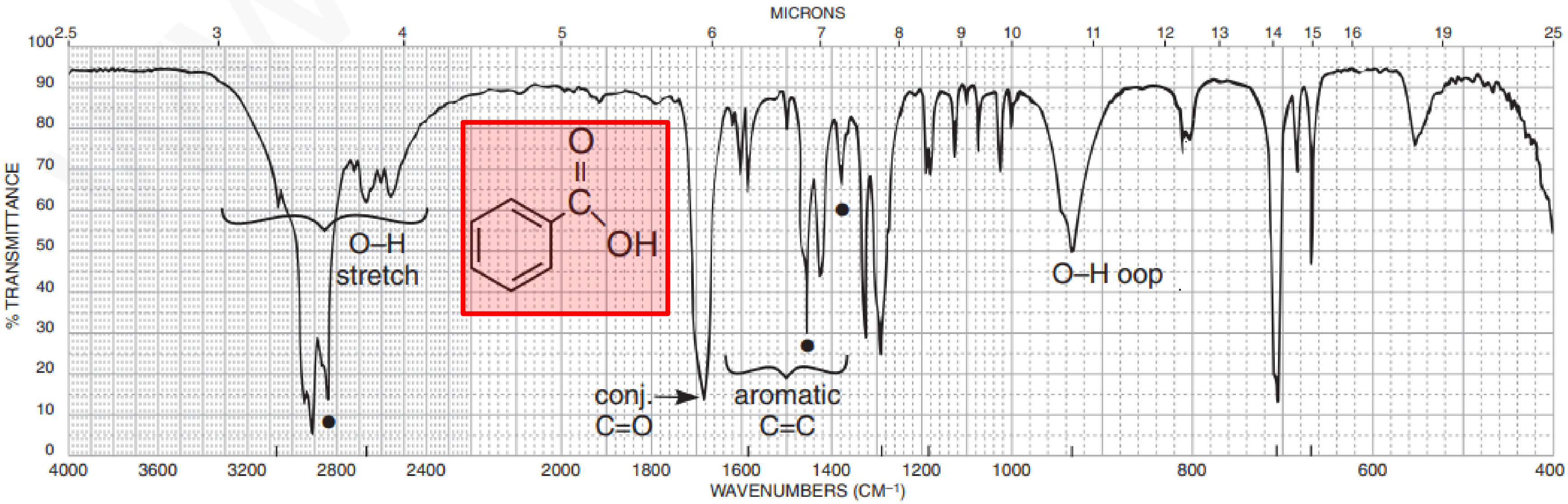
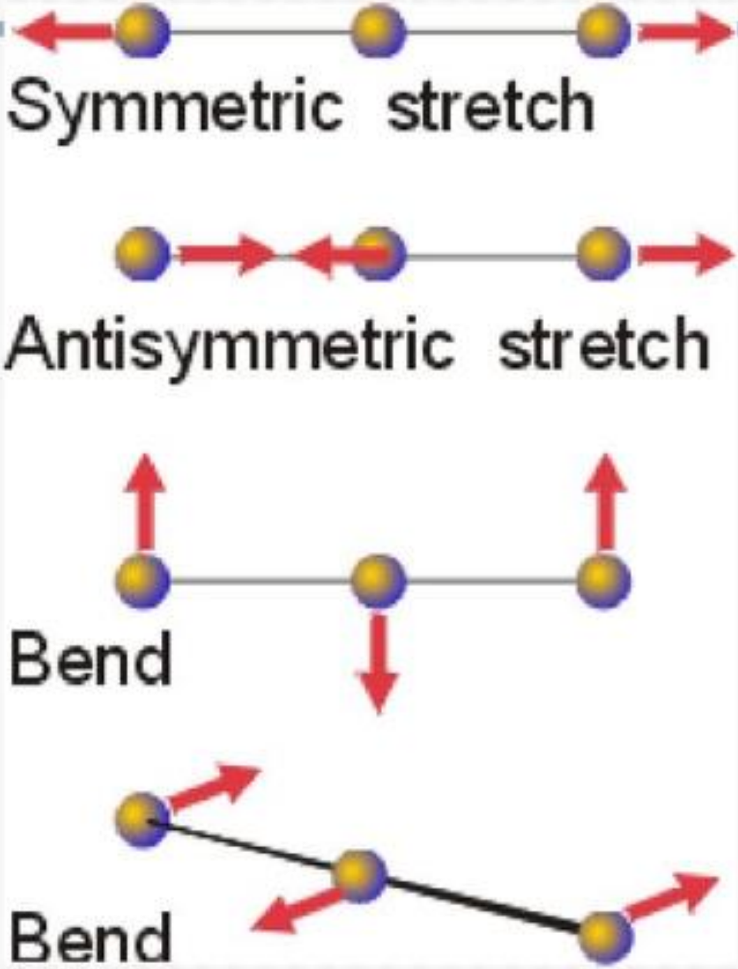


FIGURE 2.46 The infrared spectrum of benzoic acid (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

Infrared vibrations of CO_2



Infrared inactive

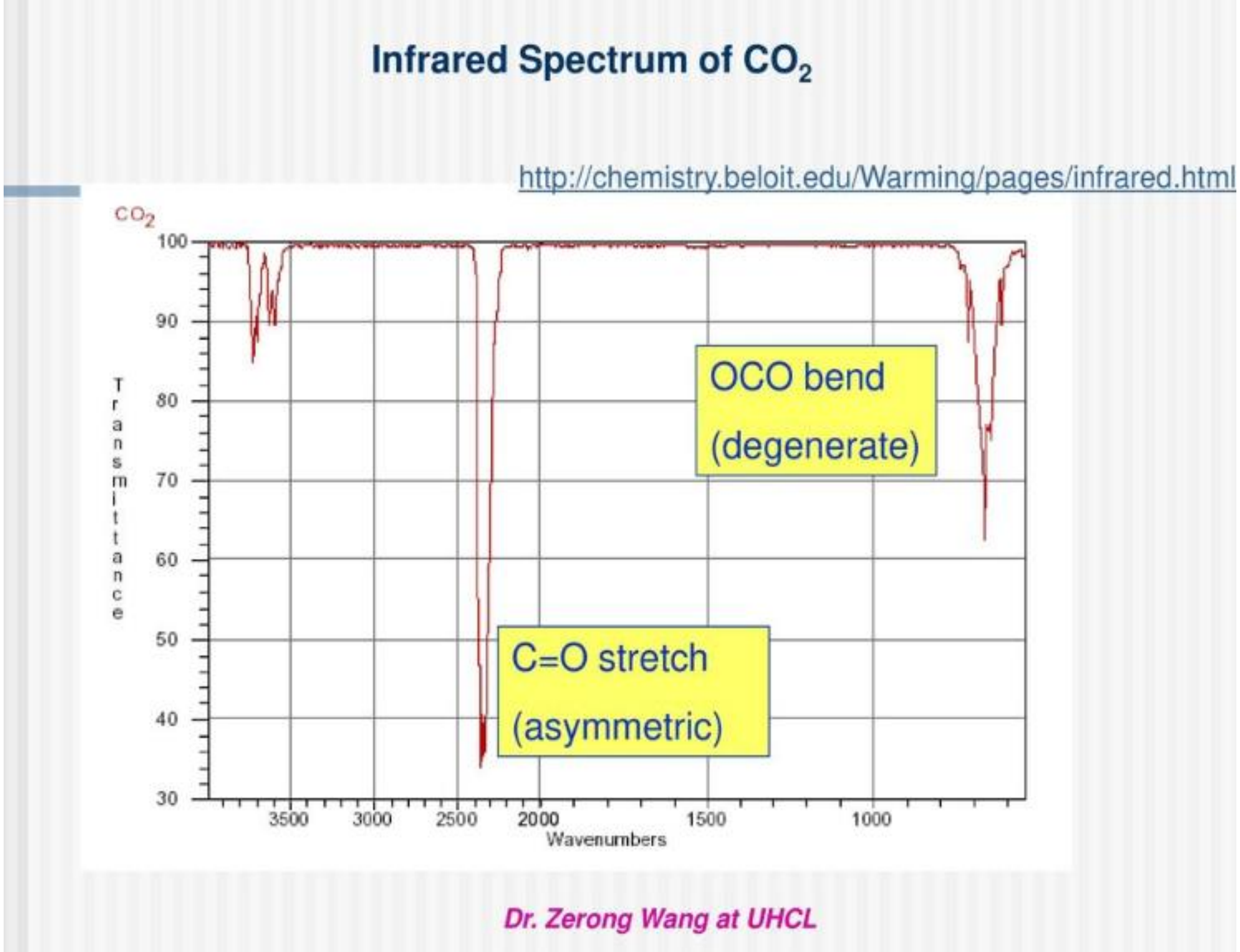
Infrared active

Degenerate bending modes

Dr. Zerong Wang at UHCL

Shriver & Atkins, *Inorganic Chemistry*, p. 134

IR Transmittance Spectrum for CO_2



Infrared Spectrum of CO_2

http://chemistry.beloit.edu/Warming/pages/infrared.html

OCO bend (degenerate)

C=O stretch (asymmetric)

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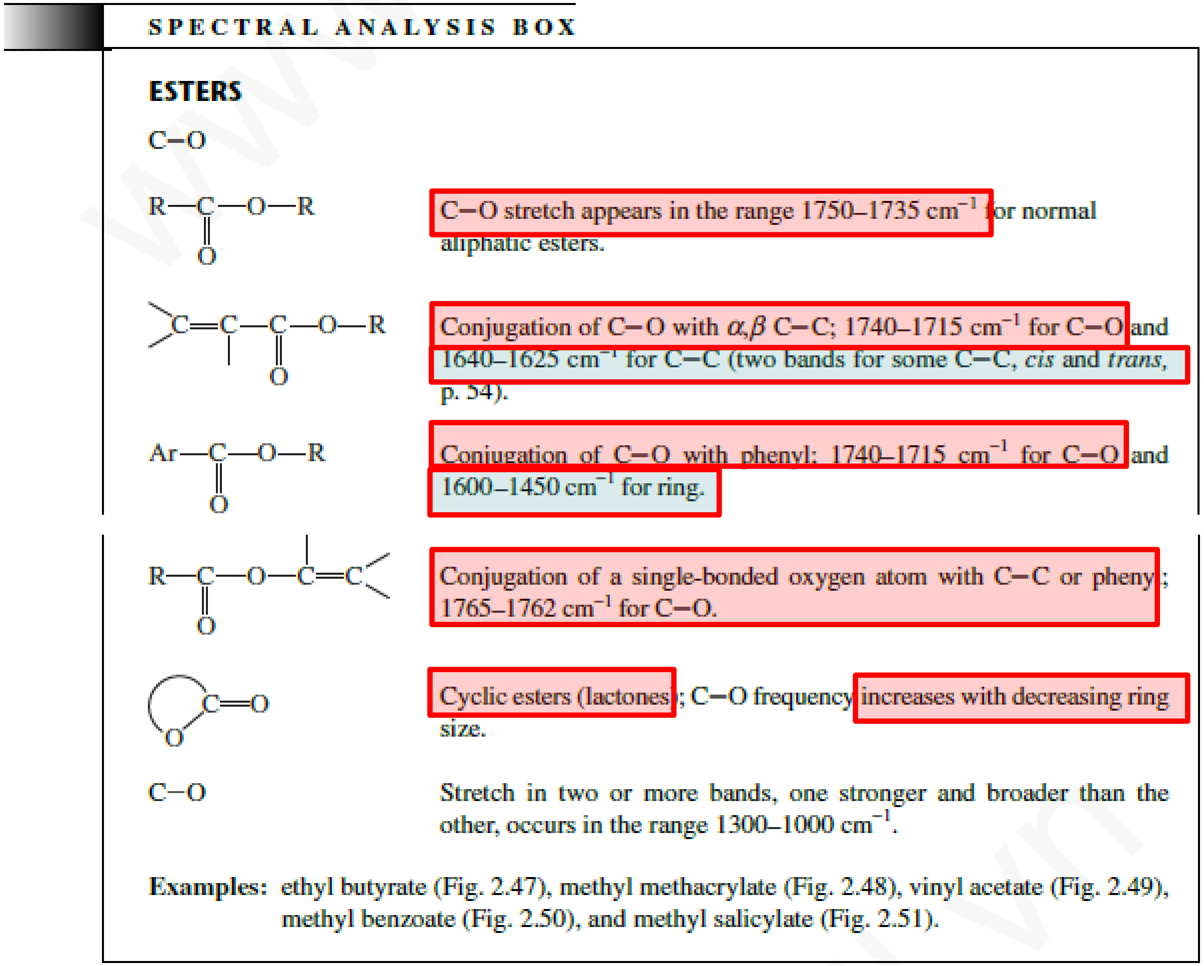
IR Absorption Wavenumber (Values) for C-O in Esters: Stretching



SPECTRAL ANALYSIS BOX

ESTERS

C–O

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

$C=C-C(=O)-O-R$ — 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*, p. 54).

$Ar-C(=O)-O-R$ — Conjugation of C–O with phenyl; 1740–1715 cm^{-1} for C–O and 1600–1450 cm^{-1} for ring.

$R-C(=O)-O-C=C$ — 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).

IR for Unsaturated Esters

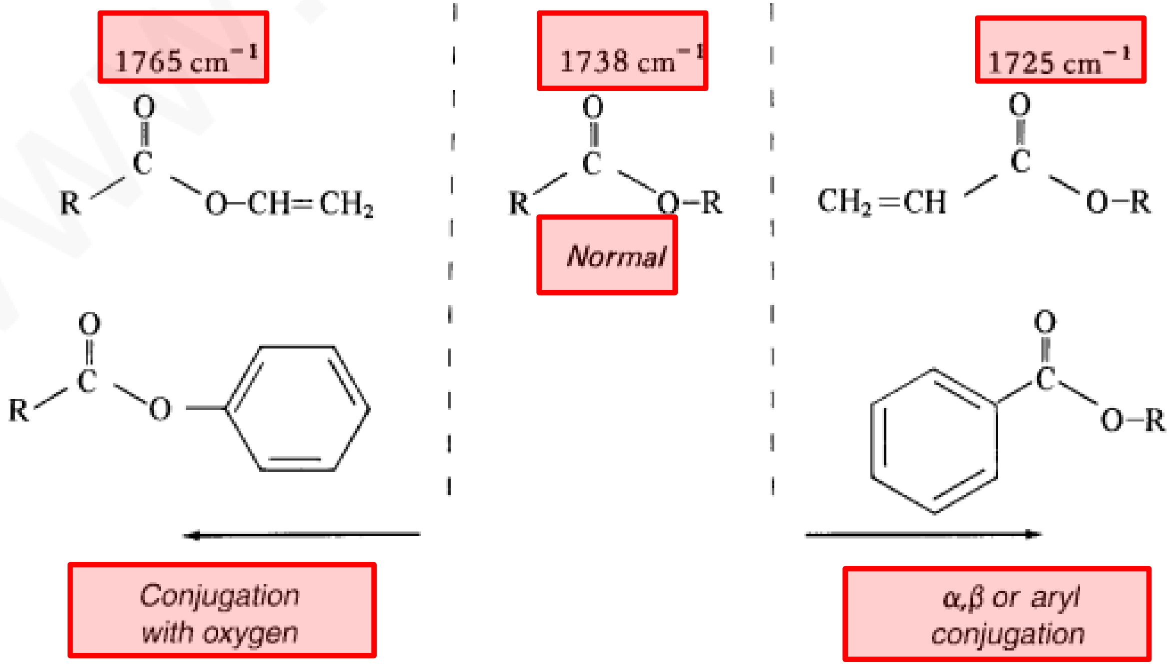


FIGURE 2.52 The effect of α,β unsaturation or aryl substitution and conjugation with oxygen on the C=O vibrations in noncyclic (acyclic) esters.

Example of IR Spectrum: Infrared Spectroscopy for 2-Ethyl Butanoate Ester

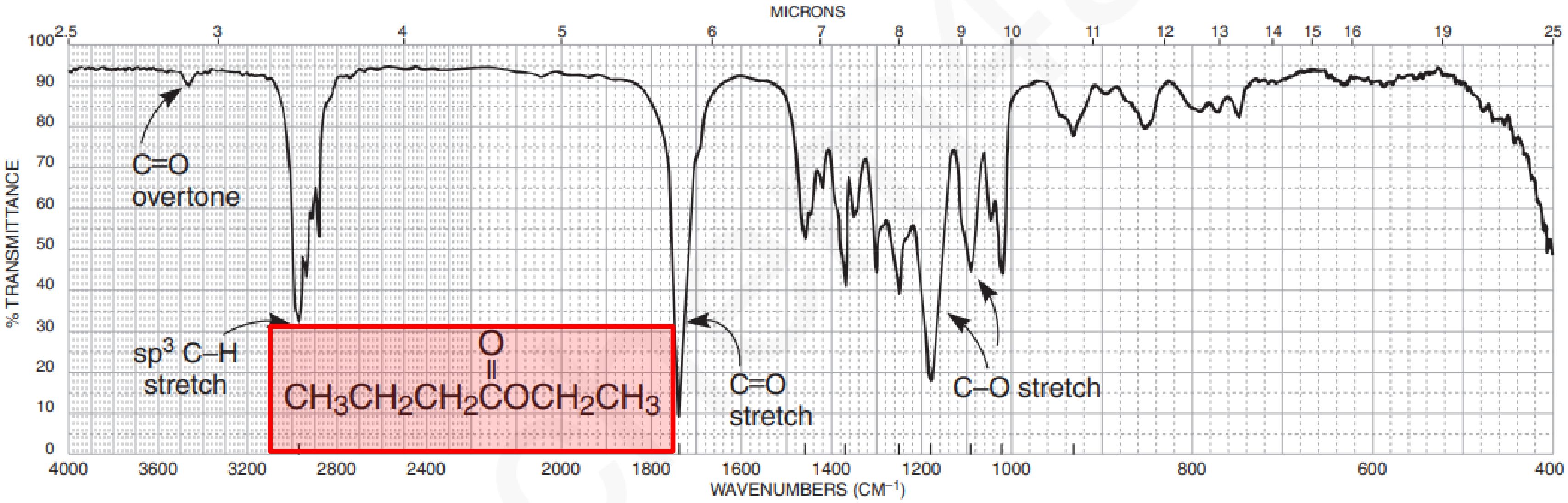


FIGURE 2.47 The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).

Example of IR Spectrum: Infrared Spectroscopy for 2-Methyl 2-Propenoate Ester

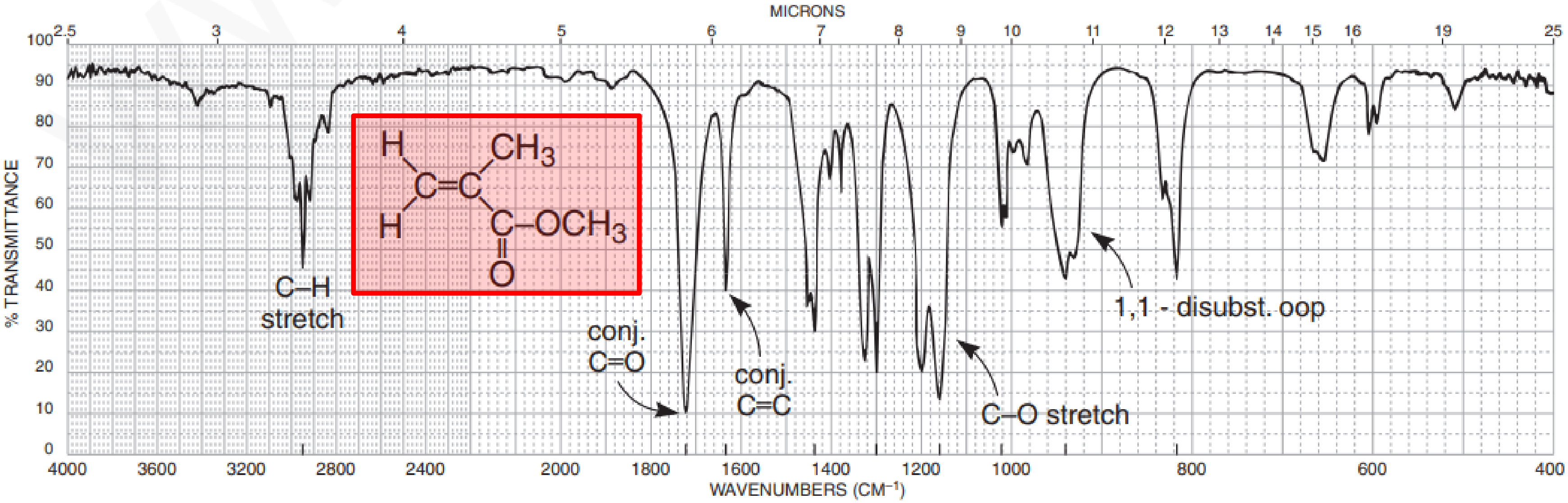


FIGURE 2.48 The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for Vinyl Acetate Ester

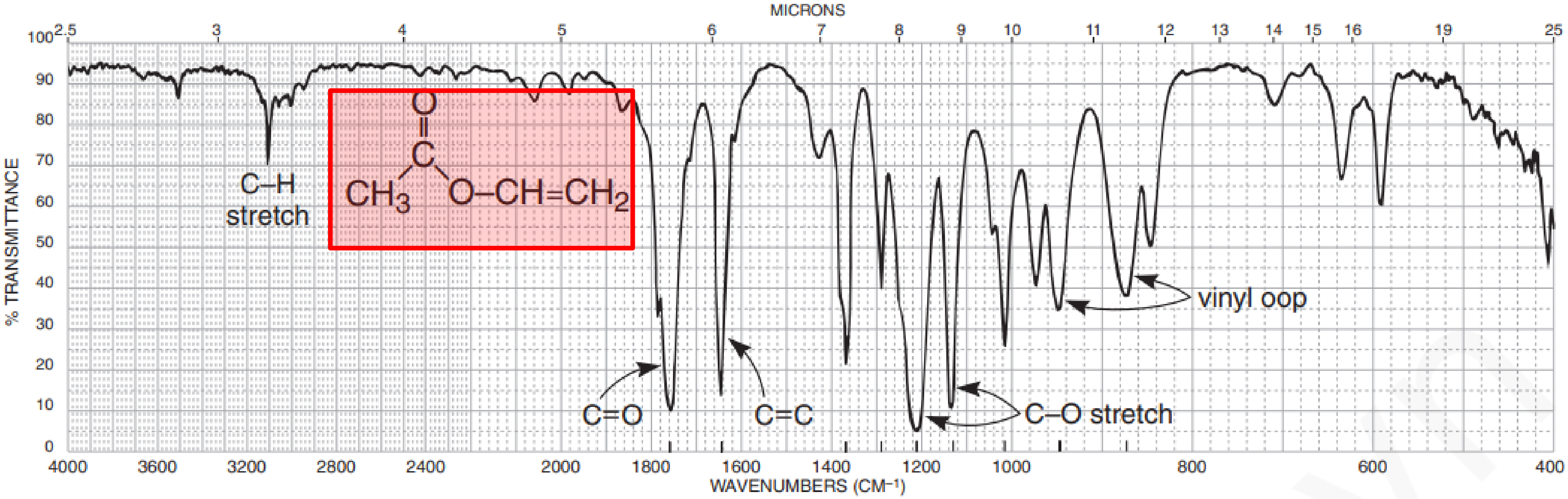


FIGURE 2.49 The infrared spectrum of vinyl acetate (neat liquid, KBr plates).

Example of IR Spectrum:
Infrared Spectroscopy for Methyl Benzoate Ester

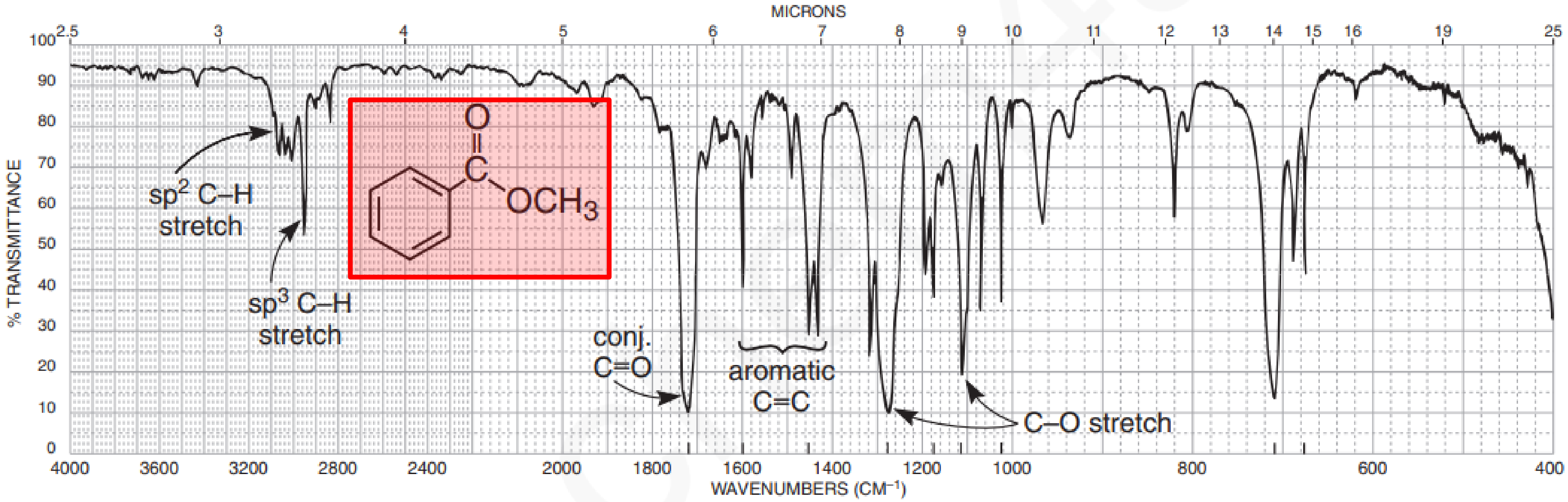


FIGURE 2.50 The infrared spectrum of methyl benzoate (neat liquid, KBr plates).

Example of IR Spectrum: Infrared Spectroscopy for Methyl Salicylate Ester

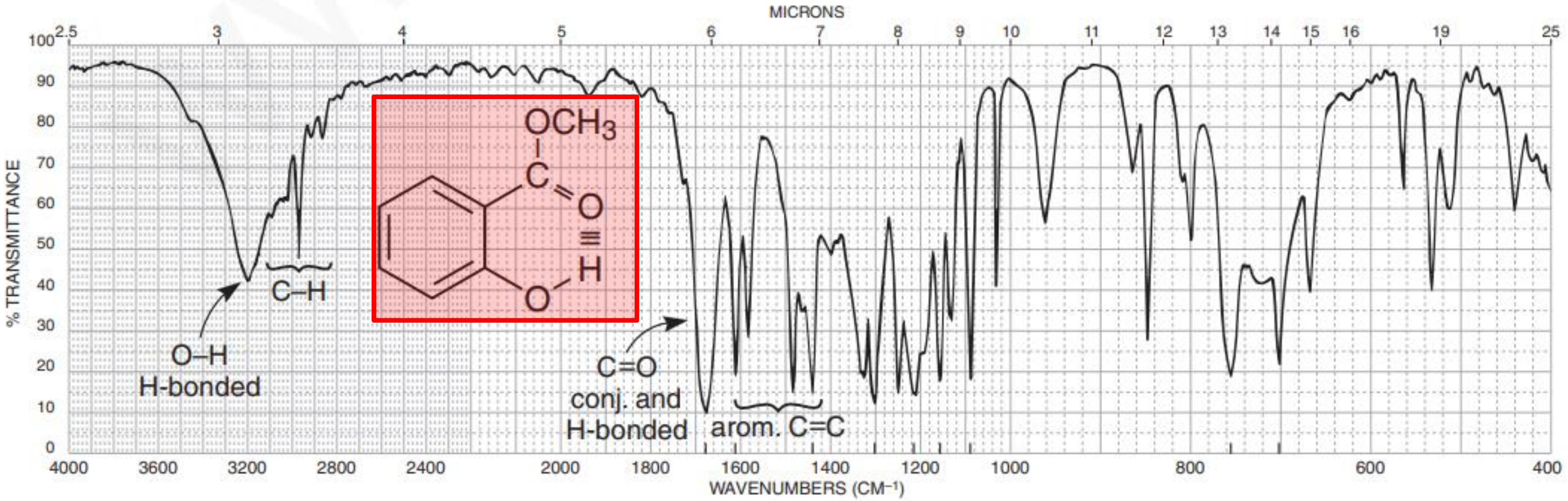
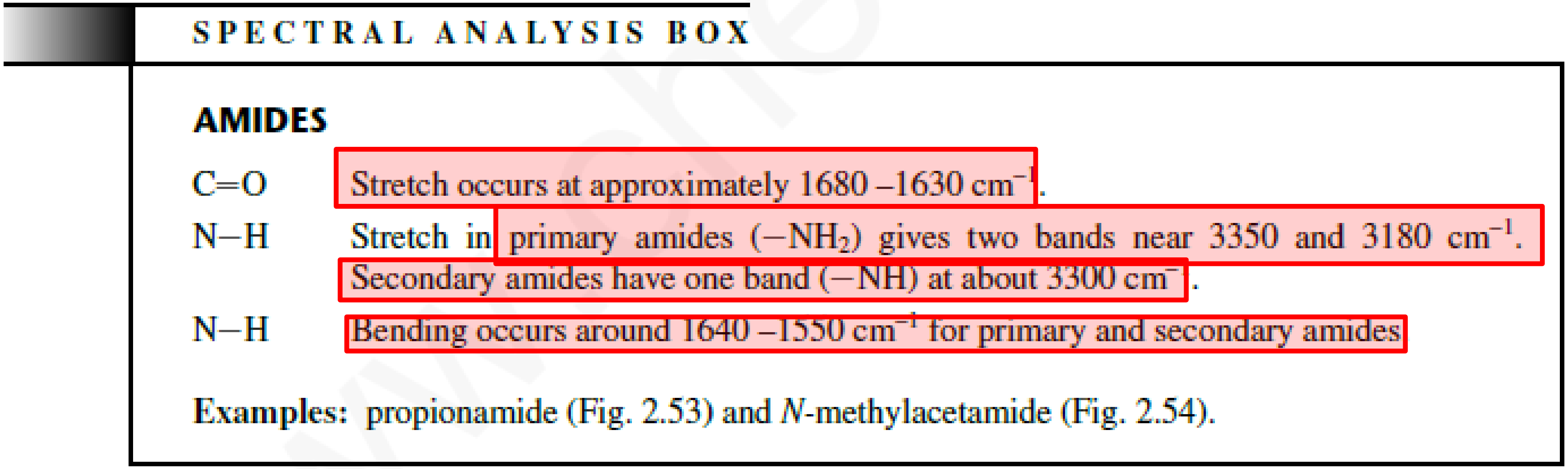


FIGURE 2.51 The infrared spectrum of methyl salicylate (neat liquid, KBr plates).

IR Absorption Wavenumber (Values) for C-O & N-H in Amides: Stretching



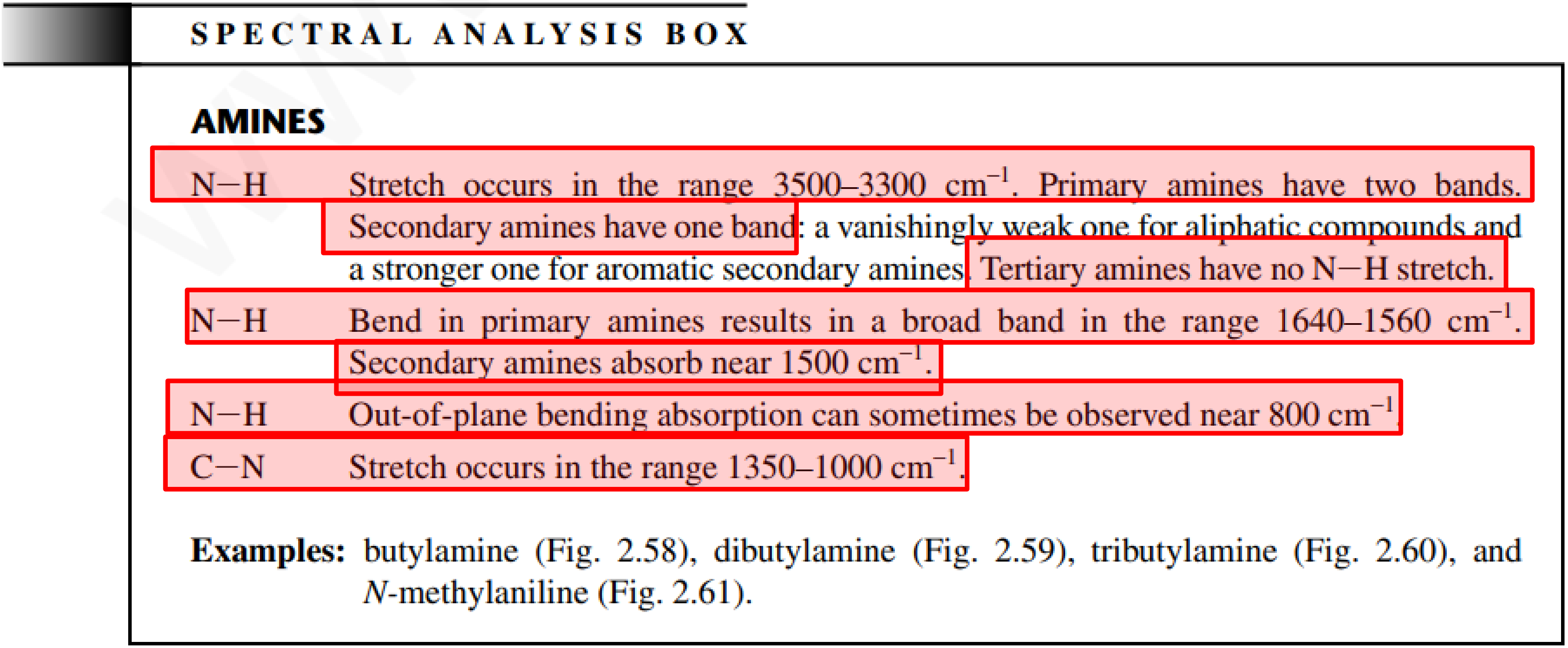
SPECTRAL ANALYSIS BOX

AMIDES

C=O	Stretch occurs at approximately 1680 –1630 cm^{-1}.
N–H	Stretch in primary amides (–NH_2) gives two bands near 3350 and 3180 cm^{-1}. Secondary amides have one band (–NH) at about 3300 cm^{-1}.
N–H	Bending occurs around 1640 –1550 cm^{-1} for primary and secondary amides

Examples: propionamide (Fig. 2.53) and *N*-methylacetamide (Fig. 2.54).

IR Absorption Wavenumber (Values) for C-N & N-H in Amines: Stretching & Bending



SPECTRAL ANALYSIS BOX

AMINES

N—H	Stretch occurs in the range 3500–3300 cm^{-1}. Primary amines have two bands. Secondary amines have one band: a vanishingly weak one for aliphatic compounds and a stronger one for aromatic secondary amines. Tertiary amines have no N—H stretch.
N—H	Bend in primary amines results in a broad band in the range 1640–1560 cm^{-1}. Secondary amines absorb near 1500 cm^{-1}.
N—H	Out-of-plane bending absorption can sometimes be observed near 800 cm^{-1}.
C—N	Stretch occurs in the range 1350–1000 cm^{-1}.

Examples: butylamine (Fig. 2.58), dibutylamine (Fig. 2.59), tributylamine (Fig. 2.60), and *N*-methylaniline (Fig. 2.61).

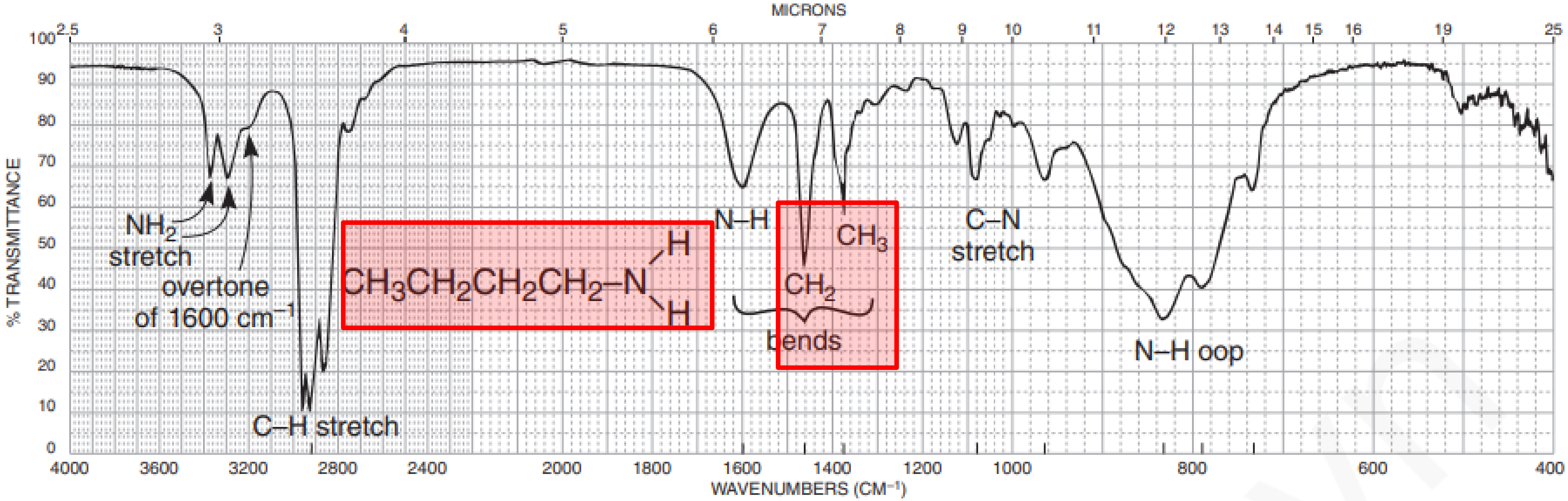


FIGURE 2.58 The infrared spectrum of butylamine (neat liquid, KBr plates).

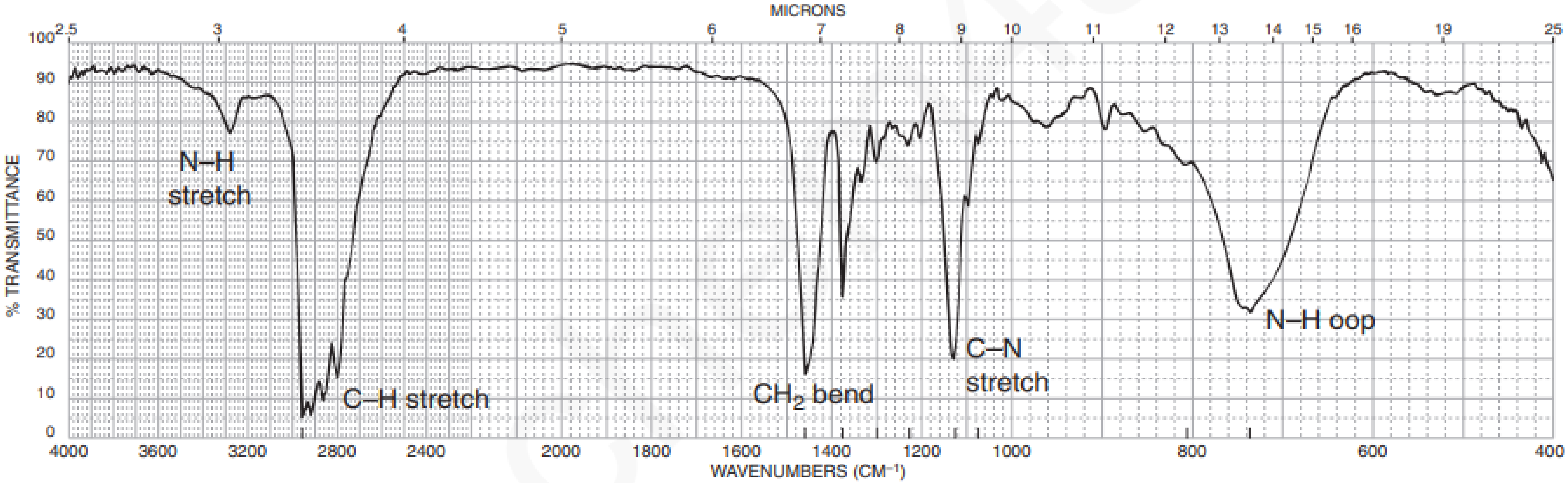
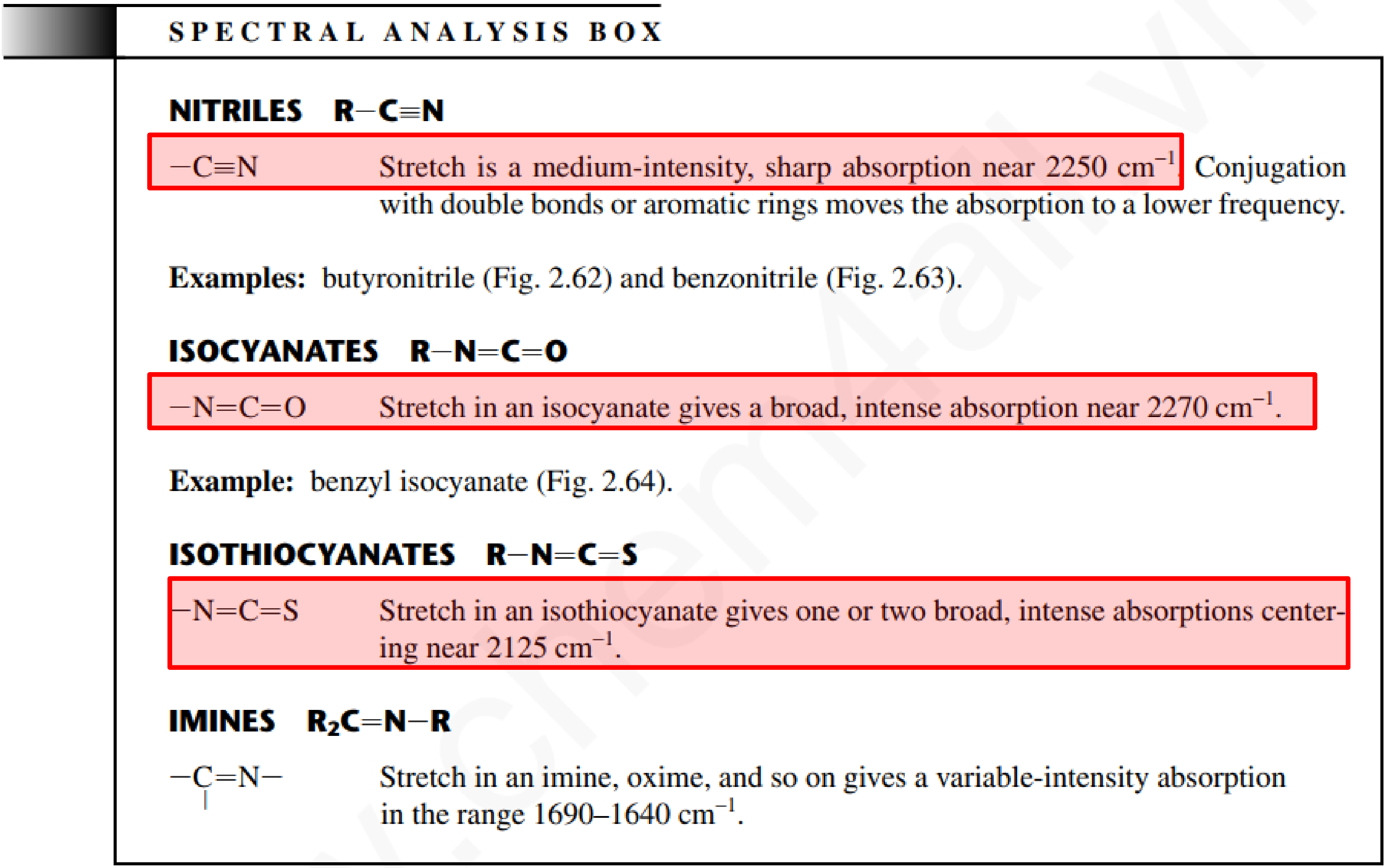


FIGURE 2.59 The infrared spectrum of dibutylamine (neat liquid, KBr plates).

IR Absorption Wavenumber (Values) for C-N in Nitril, Isocyanate & Isothiocyanate: Stretching



SPECTRAL ANALYSIS BOX

NITRILES $R-C\equiv N$

$-C\equiv N$ Stretch is a medium-intensity, sharp absorption near 2250 cm^{-1}. Conjugation with double bonds or aromatic rings moves the absorption to a lower frequency.

Examples: butyronitrile (Fig. 2.62) and benzonitrile (Fig. 2.63).

ISOCYANATES $R-N=C=O$

$-N=C=O$ Stretch in an isocyanate gives a broad, intense absorption near 2270 cm^{-1}.

Example: benzyl isocyanate (Fig. 2.64).

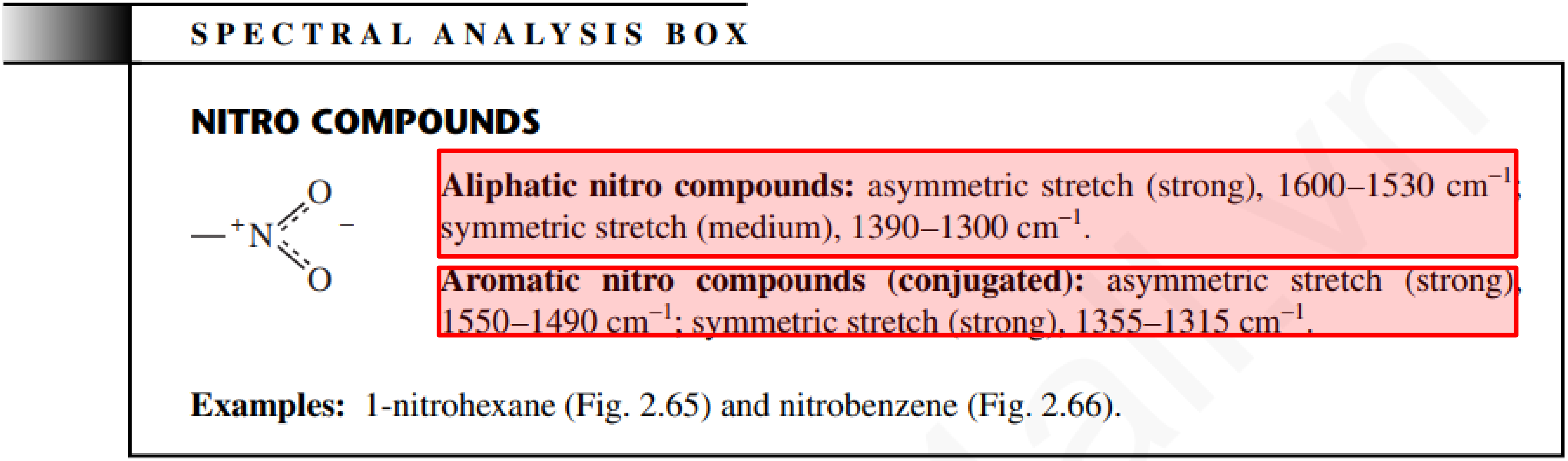
ISOTHIOCYANATES $R-N=C=S$

$-N=C=S$ Stretch in an isothiocyanate gives one or two broad, intense absorptions centering near 2125 cm^{-1}.

IMINES $R_2C=N-R$

$-\underset{|}{C}=N-$ Stretch in an imine, oxime, and so on gives a variable-intensity absorption in the range 1690–1640 cm^{-1}.

IR Absorption Wavenumber (Values) for C-N in Nitro & Nitroso Stretching



SPECTRAL ANALYSIS BOX

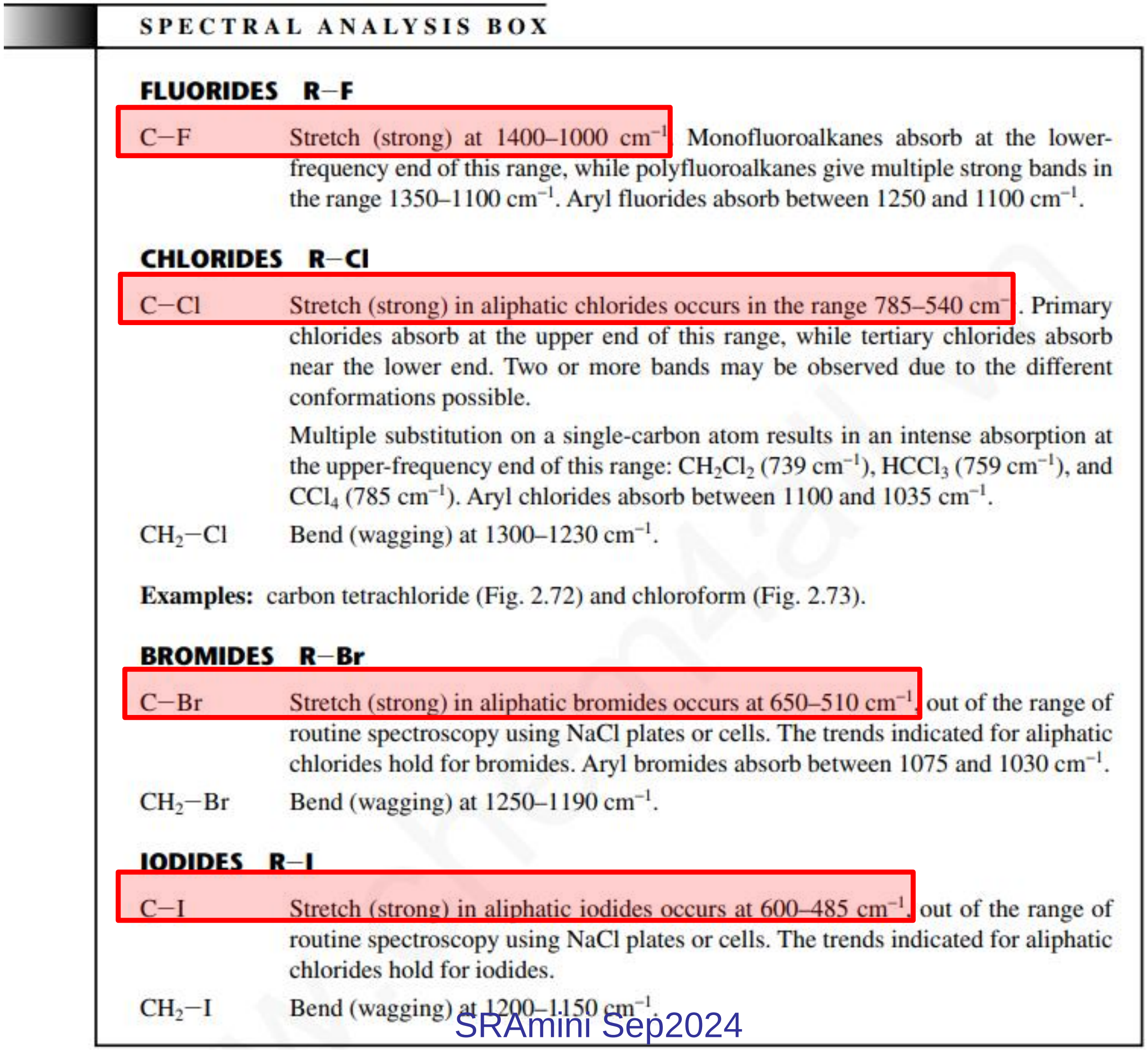
NITRO COMPOUNDS

Aliphatic nitro compounds: asymmetric stretch (strong), 1600–1530 cm^{-1}; symmetric stretch (medium), 1390–1300 cm^{-1}.

Aromatic nitro compounds (conjugated): asymmetric stretch (strong), 1550–1490 cm^{-1}; symmetric stretch (strong), 1355–1315 cm^{-1}.

Examples: 1-nitrohexane (Fig. 2.65) and nitrobenzene (Fig. 2.66).

IR Absorption Wavenumber (Values) for C-X in Halogens



SPECTRAL ANALYSIS BOX

FLUORIDES R—F

C—F	Stretch (strong) at 1400–1000 cm^{-1}. Monofluoroalkanes absorb at the lower-frequency end of this range, while polyfluoroalkanes give multiple strong bands in the range 1350–1100 cm^{-1}. Aryl fluorides absorb between 1250 and 1100 cm^{-1}.

CHLORIDES R—Cl

C—Cl	Stretch (strong) in aliphatic chlorides occurs in the range 785–540 cm^{-1}. Primary chlorides absorb at the upper end of this range, while tertiary chlorides absorb near the lower end. Two or more bands may be observed due to the different conformations possible. Multiple substitution on a single-carbon atom results in an intense absorption at the upper-frequency end of this range: CH_2Cl_2 (739 cm^{-1}), $HCCl_3$ (759 cm^{-1}), and CCl_4 (785 cm^{-1}). Aryl chlorides absorb between 1100 and 1035 cm^{-1}.
CH_2—Cl	Bend (wagging) at 1300–1230 cm^{-1}.

Examples: carbon tetrachloride (Fig. 2.72) and chloroform (Fig. 2.73).

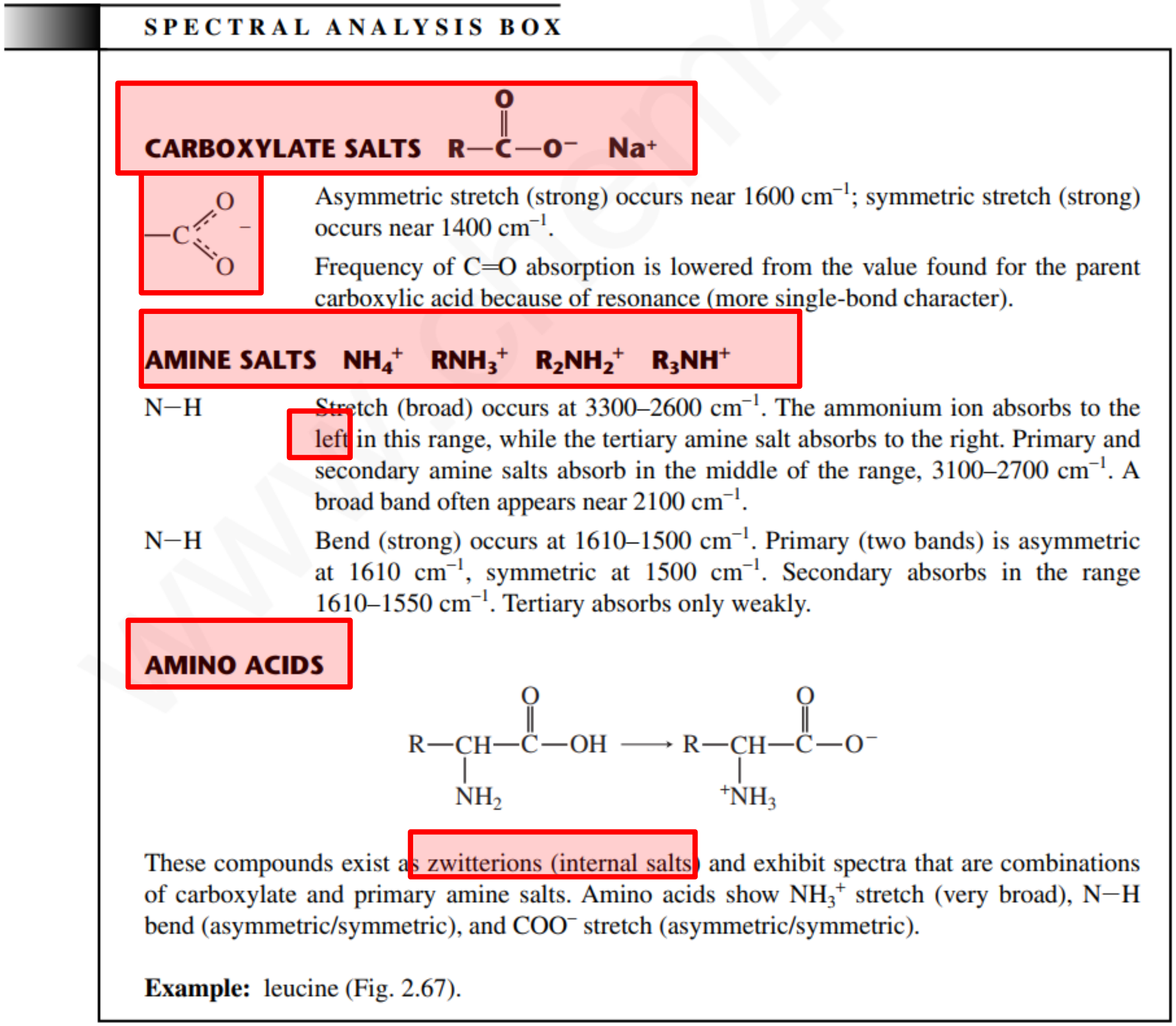
BROMIDES R—Br

C—Br	Stretch (strong) in aliphatic bromides occurs at 650–510 cm^{-1}, out of the range of routine spectroscopy using NaCl plates or cells. The trends indicated for aliphatic chlorides hold for bromides. Aryl bromides absorb between 1075 and 1030 cm^{-1}.
CH_2—Br	Bend (wagging) at 1250–1190 cm^{-1}.

IODIDES R—I

C—I	Stretch (strong) in aliphatic iodides occurs at 600–485 cm^{-1}, out of the range of routine spectroscopy using NaCl plates or cells. The trends indicated for aliphatic chlorides hold for iodides.
CH_2—I	Bend (wagging) at 1200–1150 cm^{-1}.

IR Absorption Wavenumber (Values) for Carboxylate & Ammonium Salts & Amino-Acids



SPECTRAL ANALYSIS BOX

CARBOXYLATE SALTS $R{-}\overset{O}{\overset{\|}{C}}{-}O^- \quad Na^+$

Asymmetric stretch (strong) occurs near 1600 cm^{-1}; symmetric stretch (strong) occurs near 1400 cm^{-1}.

Frequency of C=O absorption is lowered from the value found for the parent carboxylic acid because of resonance (more single-bond character).

AMINE SALTS NH_4^+ RNH_3^+ $R_2NH_2^+$ R_3NH^+

N—H Stretch (broad) occurs at 3300–2600 cm^{-1}. The ammonium ion absorbs to the left in this range, while the tertiary amine salt absorbs to the right. Primary and secondary amine salts absorb in the middle of the range, 3100–2700 cm^{-1}. A broad band often appears near 2100 cm^{-1}.

N—H Bend (strong) occurs at 1610–1500 cm^{-1}. Primary (two bands) is asymmetric at 1610 cm^{-1}, symmetric at 1500 cm^{-1}. Secondary absorbs in the range 1610–1550 cm^{-1}. Tertiary absorbs only weakly.

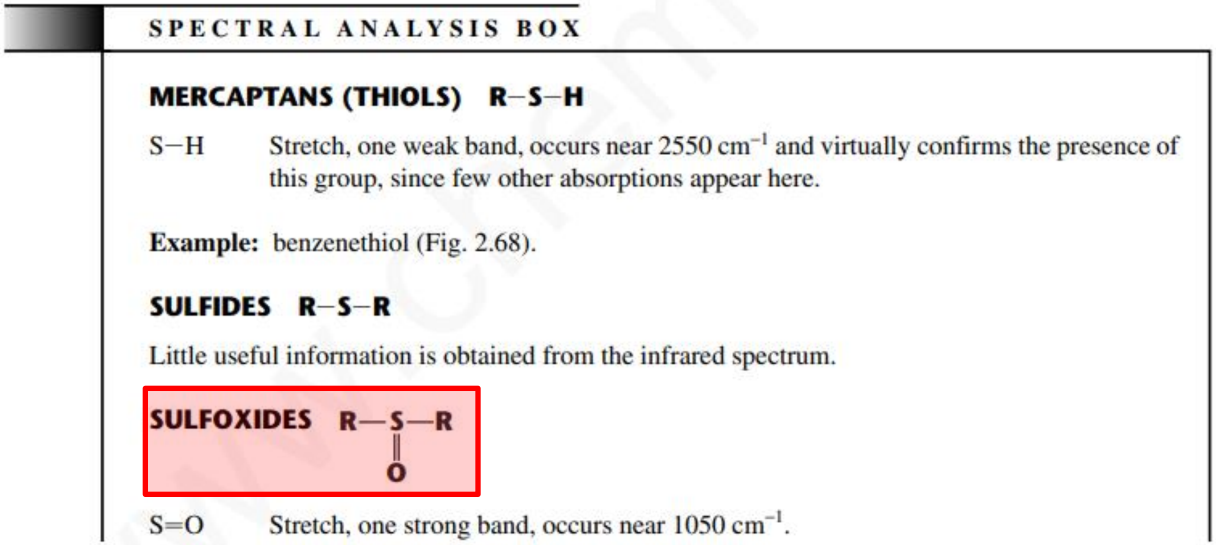
AMINO ACIDS

$$R{-}\underset{NH_2}{\underset{|}{CH}}{-}\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow R{-}\underset{^{+}NH_3}{\underset{|}{CH}}{-}\overset{O}{\overset{\|}{C}}{-}O^-$$

These compounds exist as zwitterions (internal salts) and exhibit spectra that are combinations of carboxylate and primary amine salts. Amino acids show NH_3^+ stretch (very broad), N—H bend (asymmetric/symmetric), and COO^- stretch (asymmetric/symmetric).

Example: leucine (Fig. 2.67).

IR Absorption Wavenumber (Values) for Sulfur Compounds-1



SPECTRAL ANALYSIS BOX

MERCAPTANS (THIOLS) R–S–H

S–H Stretch, one weak band, occurs near 2550 cm^{-1} and virtually confirms the presence of this group, since few other absorptions appear here.

Example: benzenethiol (Fig. 2.68).

SULFIDES R–S–R

Little useful information is obtained from the infrared spectrum.

SULFOXIDES $R{-}\underset{\underset{O}{\|}}{S}{-}R$

S=O Stretch, one strong band, occurs near 1050 cm^{-1}.

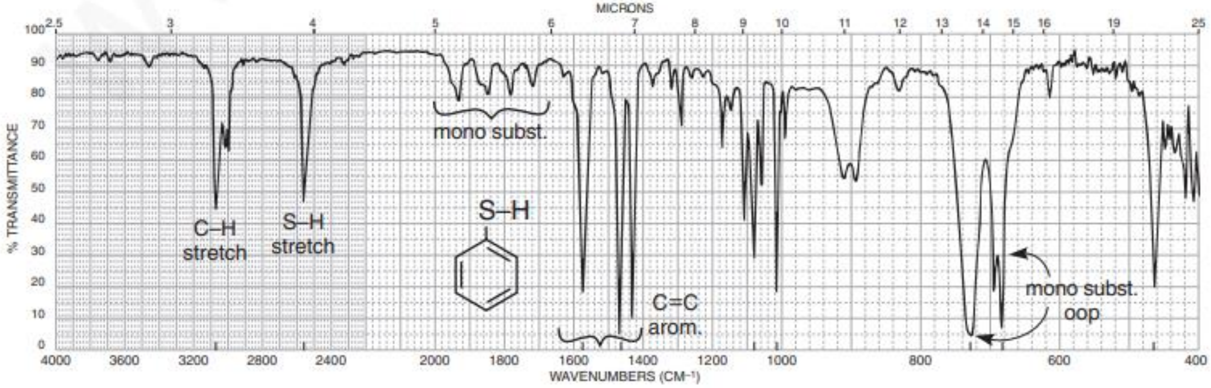
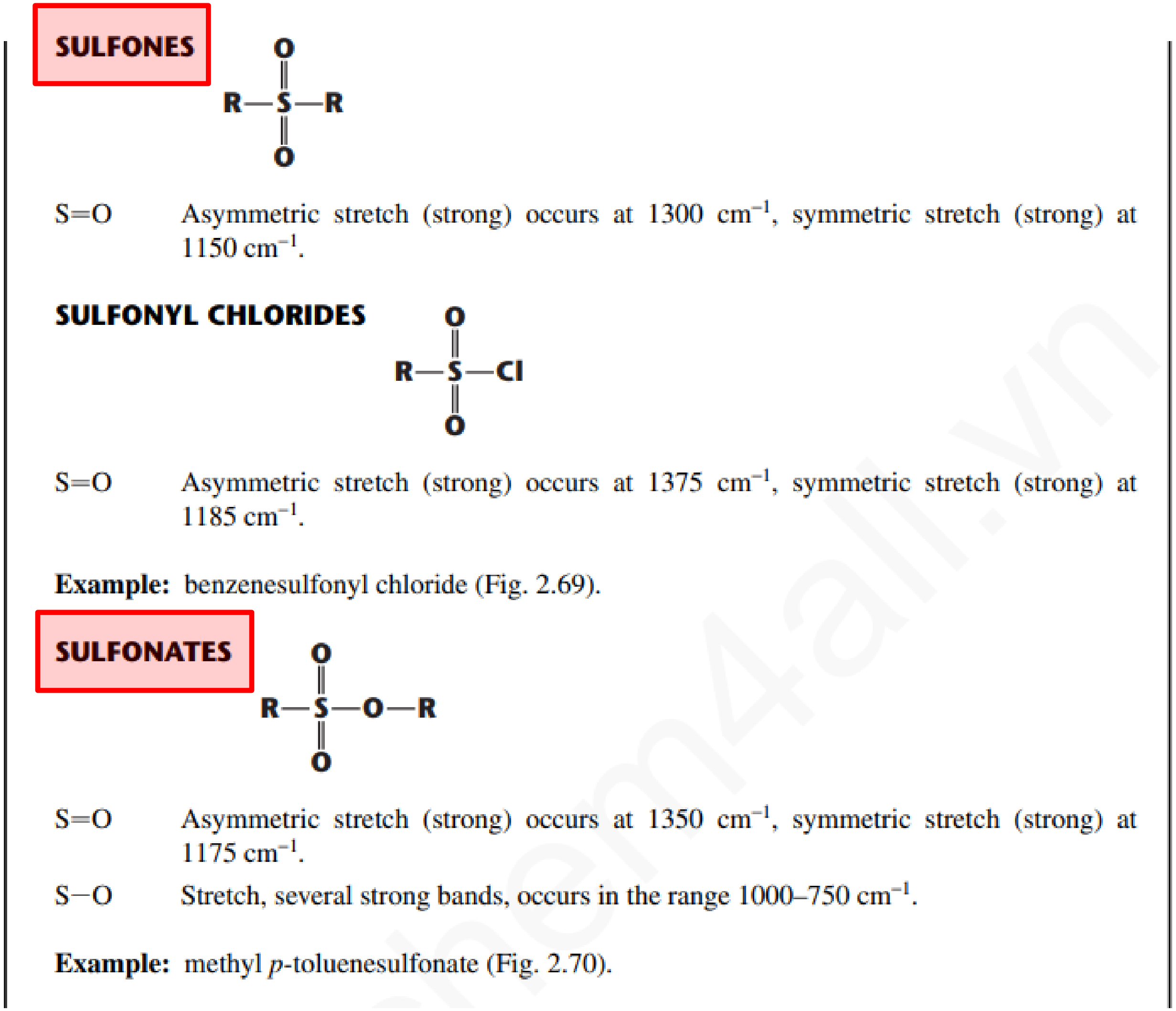


FIGURE 2.68 The infrared spectrum of benzenethiol (neat liquid, KBr plates).

IR Absorption Wavenumber (Values) for Sulfur Compounds-2



SULFONES

$R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-R$

S=O Asymmetric stretch (strong) occurs at 1300 cm^{-1}, symmetric stretch (strong) at 1150 cm^{-1}.

SULFONYL CHLORIDES

$R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-Cl$

S=O Asymmetric stretch (strong) occurs at 1375 cm^{-1}, symmetric stretch (strong) at 1185 cm^{-1}.

Example: benzenesulfonyl chloride (Fig. 2.69).

SULFONATES

$R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O-R$

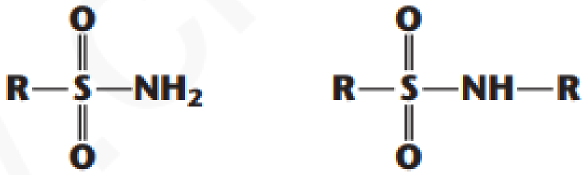
S=O Asymmetric stretch (strong) occurs at 1350 cm^{-1}, symmetric stretch (strong) at 1175 cm^{-1}.

S–O Stretch, several strong bands, occurs in the range 1000–750 cm^{-1}.

Example: methyl *p*-toluenesulfonate (Fig. 2.70).

IR Absorption Wavenumber (Values) for Sulfur Compounds-3

SULFONAMIDES (Solid State)

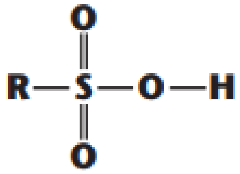


$\mathrm{R{-}S(=O)_2{-}NH_2}$ $\quad$ $\mathrm{R{-}S(=O)_2{-}NH{-}R}$

S=O	Asymmetric stretch (strong) occurs at 1325 cm^{-1}, symmetric stretch (strong) at 1140 cm^{-1}.
N—H	Primary stretch occurs at 3350 and 3250 cm^{-1}; secondary stretch occurs at 3250 cm^{-1}; bend occurs at 1550 cm^{-1}.

Example: benzenesulfonamide (Fig. 2.71).

SULFONIC ACIDS (Anhydrous)



$\mathrm{R{-}S(=O)_2{-}O{-}H}$

S=O	Asymmetric stretch (strong) occurs at 1350 cm^{-1}, symmetric stretch (strong) at 1150 cm^{-1}.
S—O	Stretch (strong) occurs at 650 cm^{-1}.