Organic Spectroscopy

IR Spectroscopy

Introduction; modes of molecular vibrations (fundamental and non-fundamental); IR active molecules; application of Hooke's law, force constant;

fingerprint region and its significance; effect of deuteration; overtone bands; vibrational coupling in IR; characteristic and diagnostic stretching frequencies of C-H, N-H, O-H, C-O, C-N, C-X, C=C (including skeletal vibrations of aromatic compounds), C=O, C=N, N=O, C≡C, C≡N; characteristic/diagnostic bending vibrations are included; factors affecting stretching frequencies: effect of conjugation, electronic effects, mass effect, bond multiplicity, ring-size, solvent effect, H-bonding on IR absorptions; application in functional group analysis.

Infrared Region

10,000 cm^{-1} to 100 cm^{-1}

Converted in Vibrational energy in molecules

Vibrational Spectra appears as bands instead of sharp lines => as it is accompanied by a number of rotational changes

Wave Number => $\bar{\nu}$ (cm^{-1}) => proportional to energy

$\bar{\nu}$ Depends on:

- Relative masses of atoms
- Force constant of bonds
- Geometry of atoms

The Units:

The frequency ν (s^{-1}) => # vibrations per second

For molecular vibrations, this number is very large (10^{13} s^{-1}) => inconvenient

More convenient : $\bar{\nu}$ Wavenumber

$$\bar{\nu} = \frac{\nu}{c}$$

(Frequency / Velocity)

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e.g. $\nu = 3 * 10^{13}\ s^{-1}$

$$\bar{\nu} = \frac{3 * 10^{13}\ s^{-1}}{3 * 10^{10}\ cm\ s^{-1}}$$

$$\bar{\nu} = 1000\ cm^{-1}$$

Wave Length : λ

$$\frac{1}{\lambda} = \bar{\nu}$$

Intensity in IR

Intensity: Transmittance (**T**) or **%T**

$$\mathbf{T} = \frac{I}{I_0}$$

Absorbance (**A**)

$$\mathbf{A} = \log \frac{I}{I_0}$$

IR : Plot of **%IR** that passes through a sample (**transmittance**) vs **Wavelenght**

Infrared

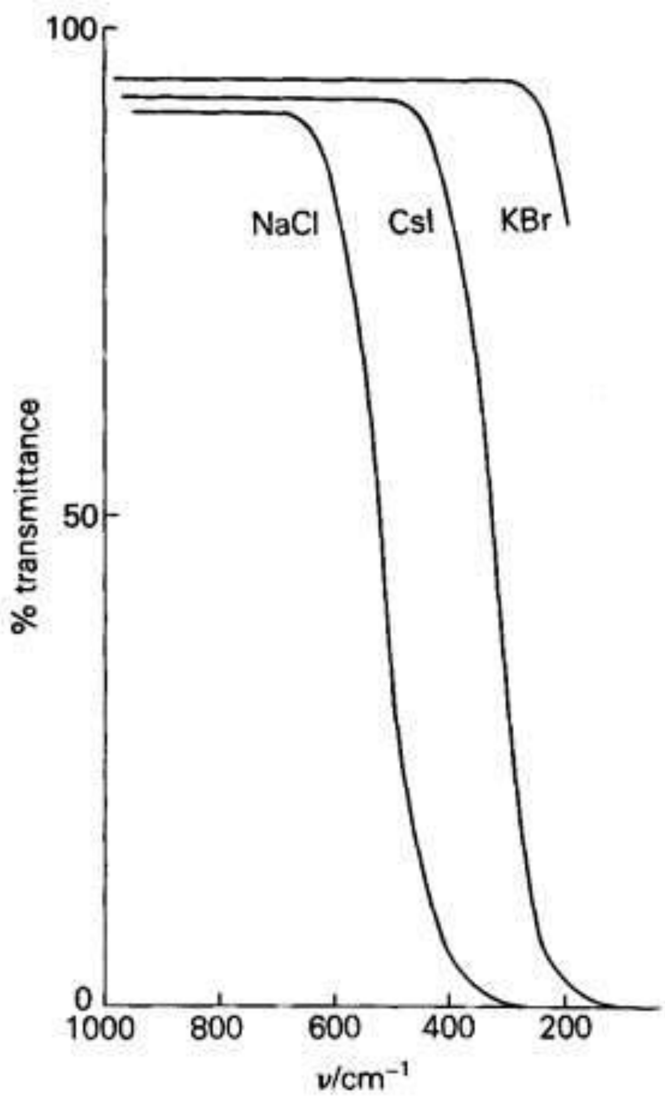
- **Position, Intensity and Shape of bands gives clues on Structure of molecules**
- **Modern IR uses Michelson Interferometer**
  => involves computer, and Fourier Transform

Sampling =>
plates, polished windows, Films Must be transparent in IR

NaCl, KCl : Cheap, easy to polish

NaCl transparent to **4000 - 650 cm^{-1}**
KCl transparent to **4000 - 500 cm^{-1}**
KBr transparent to **400 cm^{-1}**

Infrared: Low frequency spectra of window materials



Bond length and strength
vs
Stretching frequency

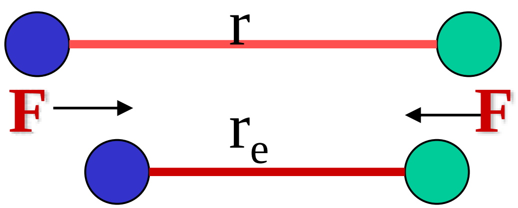
Bond	≡C-H	=C-H	-C-H
Length	1.08	1.10	1.12
Strenght	506 kJ	444 kJ	422 kJ
IR freq.	3300 cm^{-1}	3100 cm^{-1}	2900 cm^{-1}

Introduction

IR is one of the first technique inorganic chemists used (since 1940)

Molecular Vibration

Newton's law of motion is used classically to calculate force constant



The basic picture : atoms (mass) are connected with bonding electrons. R_e is the equilibrium distance and **F**: force to restore equilibrium

$F(x) = -kx$ where X is displacement from equilibrium

$$\omega_\iota = \frac{1}{2\pi}\sqrt{\frac{k_i}{\mu_i}}$$

Hook's Law

Where K_i is the force constant and μ_i is reduce mass of a particular motion

Because the energy is quantized: $E = h\,\omega_i$

Introduction

Displacement of atoms during vibration lead to distortion of electrical charge distribution of the molecule which can be resolve in dipole, quadrupole, octopole in various directions

=> Molecular vibration lead to oscillation of electric charge governed by vibration frequencies of the system

Oscillating molecular dipole can interact directly with oscillating electric vector of electromagnetic radiation of the same frequency

$$h\nu = h\omega$$

Vibrations are in the range 10^{11} to 10^{13} Hz => 30 - 3,000 cm^{-1}

Introduction: Symmetry selection rule

Stretching homonuclear diatomic molecule like N_2 does not generate oscillating dipole

⇒Direct interaction with oscillating electronic Dipole is not possible

⇒ inactive in IR

There is no place here to treat fundamentals of symmetry
In principle, the symmetry of a vibration need to be determined

Calculating stretching frequencies

Hooke's law :

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$\bar{\nu}$: Frequency in cm^{-1}

c : Velocity of light => $3 * 10^{10}$ cm/s

K : Force constant => dynes /cm

μ : masses of atoms in grams

$$\mu = \frac{m_1\, m_2}{m_1 + m_2} = \frac{M_1\, M_2}{M_1 + M_2\, (6.02 * 10^{23})}$$

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

C—C K = $5 * 10^5$ dynes/cm

C=C K = $10 * 10^5$ dynes/cm

C≡C K = $15 * 10^5$ dynes/cm

Calculating stretching frequencies

C=C K = 10* 10^5 dynes/cm

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

$$\mu = \frac{M_1 M_2}{M_1 + M_2} = \frac{(12)(12)}{12 + 12} = 6$$

$$\bar{\nu} = 4.12\sqrt{\frac{10 * 10^5}{6}} = 1682\ \mathrm{cm}^{-1}$$

$\bar{\nu}$ Experimental ➔ 1650 cm^{-1}

C—H K = 5* 10^5 dynes/cm

$$\bar{\nu} = 4.12\sqrt{\frac{5 * 10^5}{.923}} = 3032\ \mathrm{cm}^{-1}$$

$$\mu = \frac{M_1 M_2}{M_1 + M_2} = \frac{(12)(1)}{12 + 1} = 0.923$$

$\bar{\nu}$ Experimental ➔ 3000 cm^{-1}

C—D K = 5* 10^5 dynes/cm

$$\bar{\nu} = 4.12\sqrt{\frac{5 * 10^5}{.923}} = 2228\ \mathrm{cm}^{-1}$$

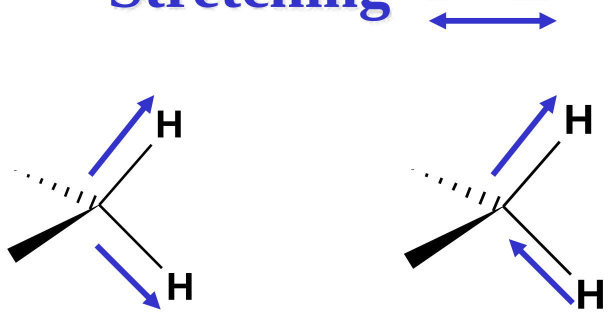
$$\mu = \frac{M_1 M_2}{M_1 + M_2} = \frac{(12)(2)}{12 + 2} = 1.71$$

$\bar{\nu}$ Experimental ➔ 2206 cm^{-1}

Types of Vibrations

Modes of vibration

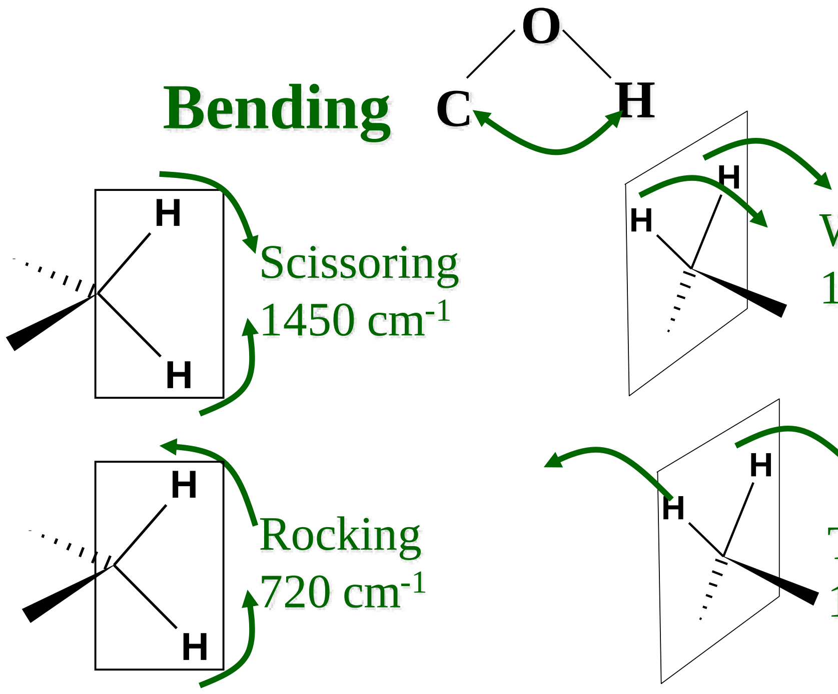
Stretching C—H



Symmetrical
2853 cm^{-1}

Asymmetrical
2926 cm^{-1}

Bending



Scissoring
1450 cm^{-1}

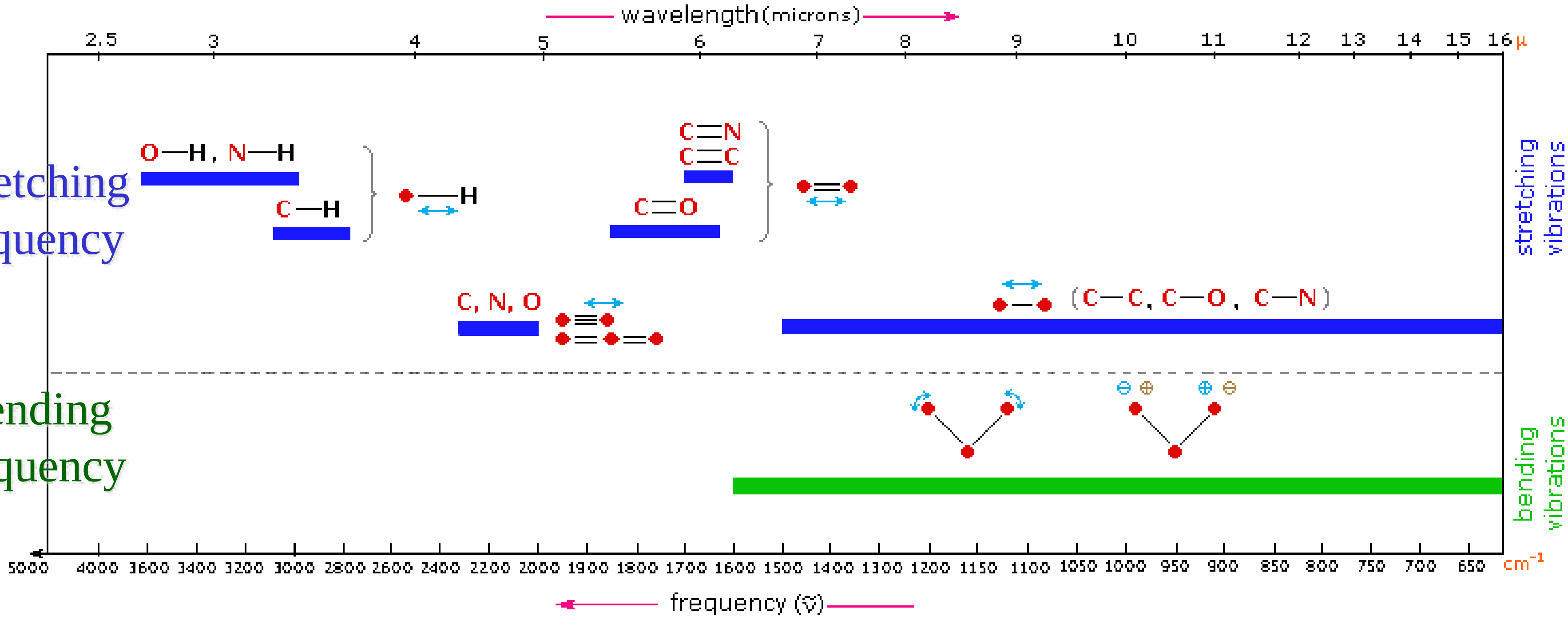
Wagging
1350 cm^{-1}

Rocking
720 cm^{-1}

Twisting
1250 cm^{-1}

Stretching frequency

Bending frequency



Vibrations

General trends:

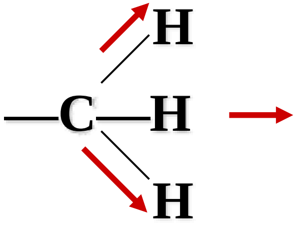
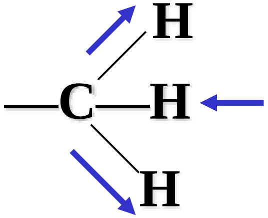
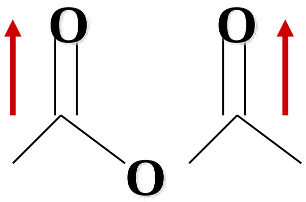
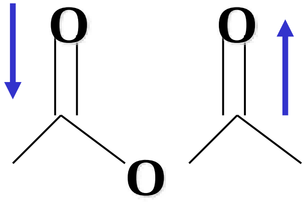
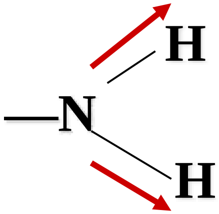
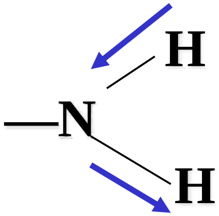
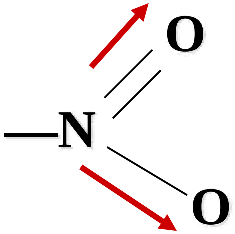
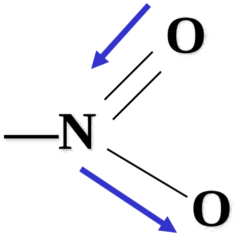
- Stretching frequencies are higher than bending frequencies

  (it is easier to bend a bond than stretching or compresing them)

- Bond involving Hydrogen are higher in freq. than with heavier atoms

- Triple bond have higher freq than double bond which has higher freq than single bond

Symmetrical and asymmetrical stretch

	Symmetrical Stretch		Asymmetrical Stretch	
Methyl		2872 cm^{-1}		2962 cm^{-1}
Anhydride		1760 cm^{-1}		1800 cm^{-1}
Amino		3300 cm^{-1}		3400 cm^{-1}
Nitro		1350 cm^{-1}		1550 cm^{-1}

Structural Information from Vibration Spectra

The symmetry of a molecule determines the number of bands expected

Number of bands can be used to decide on symmetry of a molecule

Tha task of assignment is complicated by presence of low intensity bands and presence of forbidden overtone and combination bands.
There are different levels at which information from IR can be analyzed to allow identification of samples:

- **Spectrum can be treated as finger print to recognize the product of a reaction as a known compound. (require access to a file of standard spectra)**
- **At another extreme , different bands observed can be used to deduce the symmetry of the molecule and force constants corresponding to vibrations.**
- **At intermediate levels, deductions may be drawn about the presence/absence of specific groups**

Methods of analyzing an IR spectrum

The effect of isotopic substitution on the observed spectrum Can give valuable information about the atoms involved in a particular vibration

1. **Comparison with standard spectra : traditional approach**
2. **Detection and Identification of impurities**

   if the compound have been characterized before, any bands that are not found in the pure sample can be assigned to the impurity

   (provided that the 2 spectrum are recorded with identical conditions: Phase, Temperature, Concentration)
3. **Quantitative Analysis of mixture**

   Transmittance spectra = I/I_0 x 100 => peak height is not lineraly related to intensity of absorption

   In Absorbance $A=\ln (I_o/I)$ => Direct measure of intensity

Analyzing an IR spectrum

In practice, there are similarities between frequencies of molecules containing similar groups.

Group - frequency correlations have been extensively developed for organic compounds and some have also been developed for inorganics

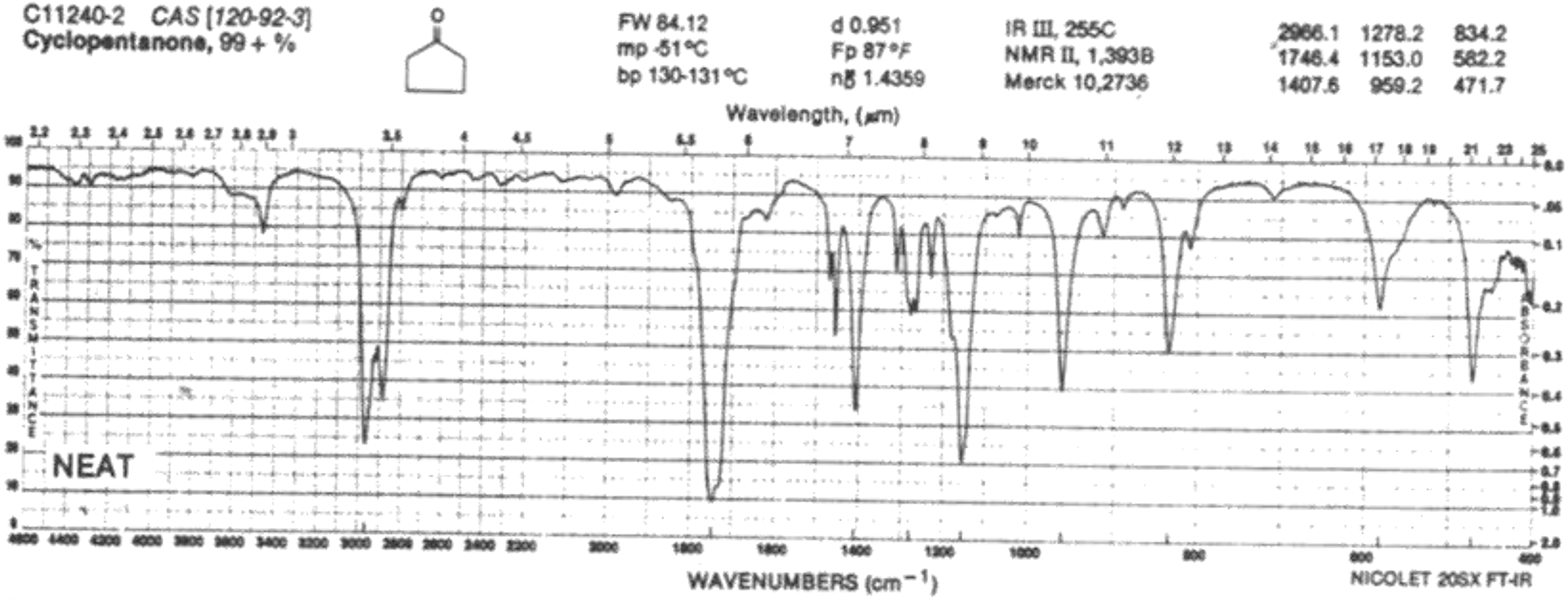


FIGURE 3.2. Cyclopentanone, thin film.

H-BonD

Vs. >C=O

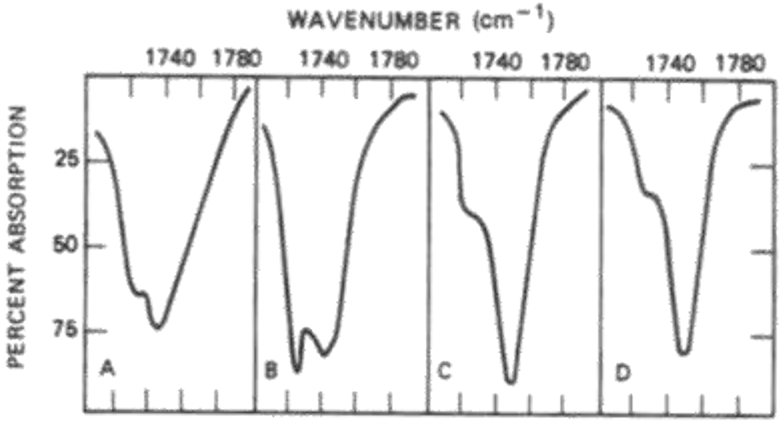


FIGURE 3.3. Infrared spectrum of cyclopentanone in various media. A. Carbon tetrachloride solution (0.15 *M*). B. Carbon disulfide solution (0.023 *M*). C. Chloroform solution (0.025 *M*). D. Liquid state (thin films). (Computed spectral slit width 2 cm⁻¹.)

Hydrogen bond and C=O

Intensity of C=O vs C=C

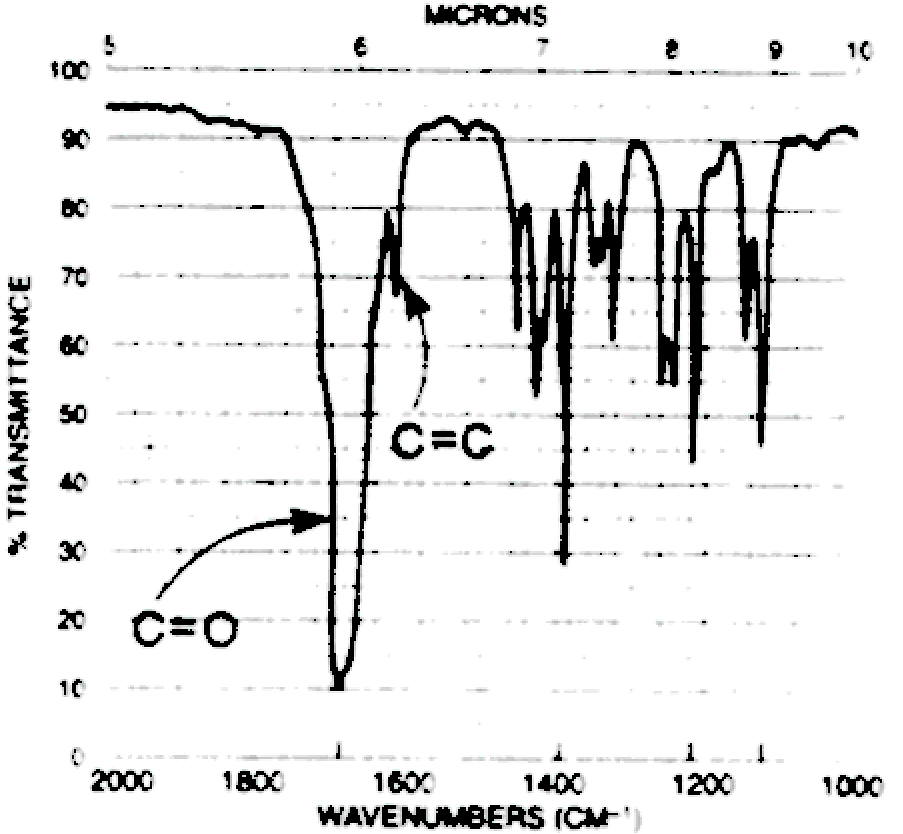
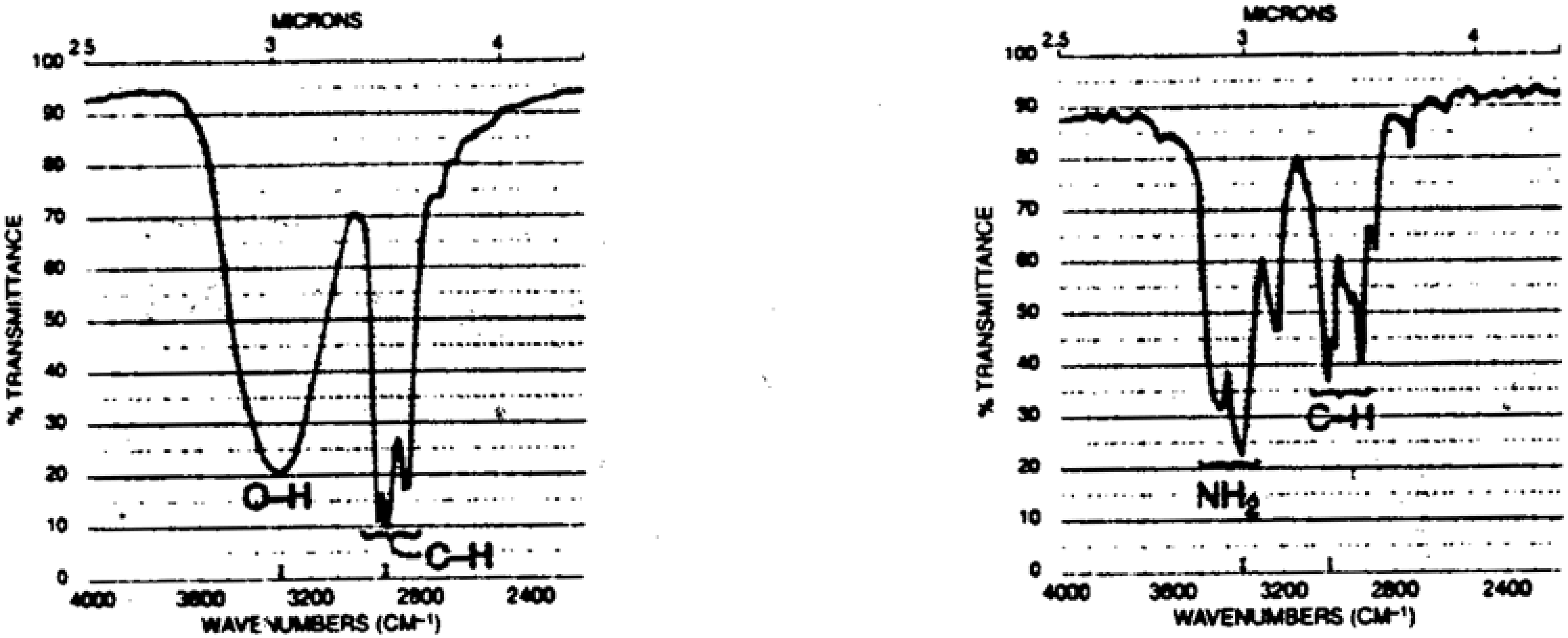


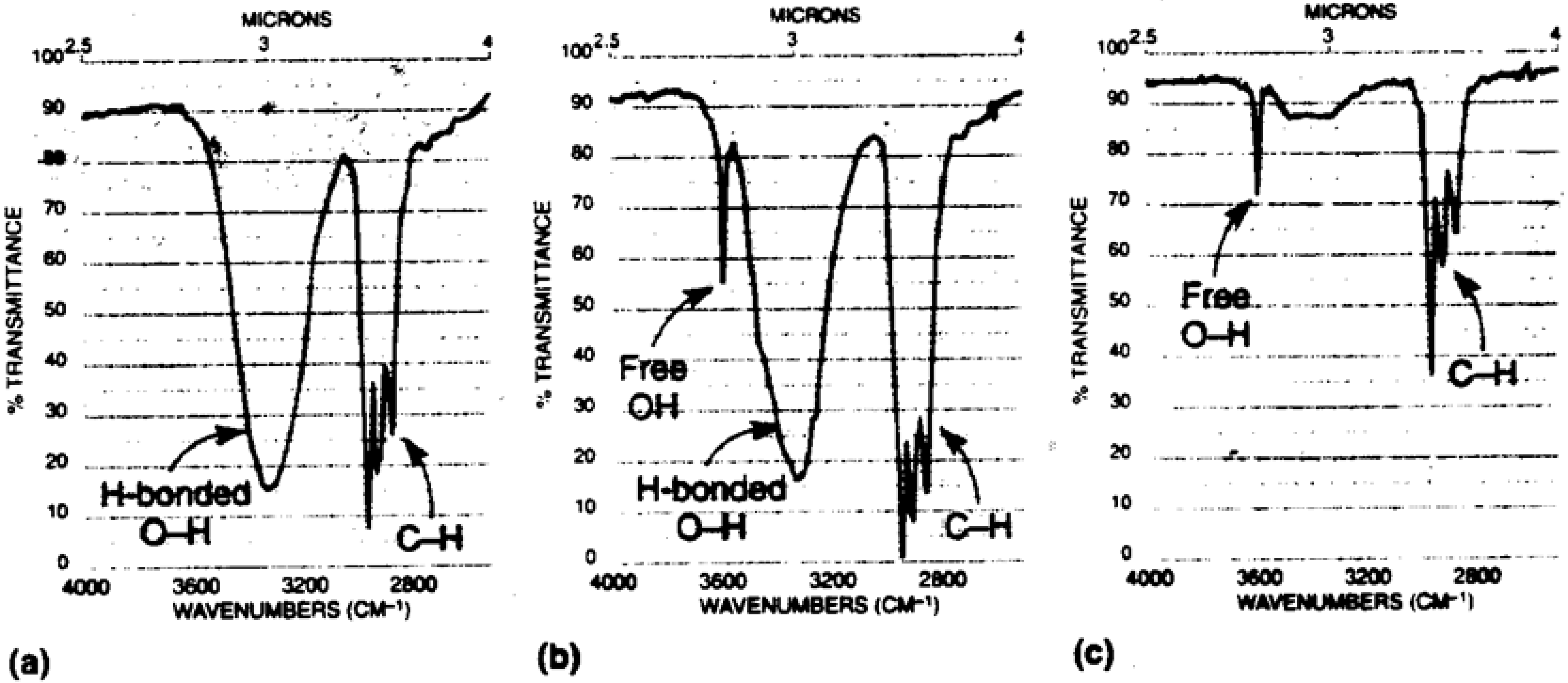
FIGURE 2.5 A comparison of the intensities of the C=O and C=C absorption bands

Band Shape: OH vs NH2 vs CH



▶ **FIGURE 2.6** A comparison of the shapes of the absorption bands for the O—H and N—H groups.

Free OH and Hydrogen bonded OH



► **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).

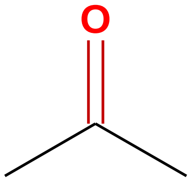
General IR comments

Precise treatment of vibrations in molecule is not feasible here
Some information from IR is also contained in MS and NMR

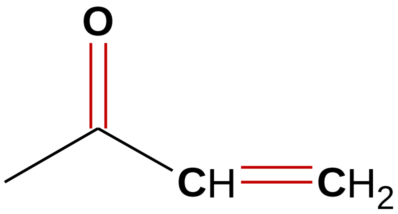
Certain bands occur in narrow regions : OH, CH, C=O

Detail of the structure is revealed by the exact position of the band

e.g. Ketones



1715 cm^{-1}



1680 cm^{-1}

Region 4000 – 1300 : Functional group

Absence of band in this region can be used to deduce absence of groups

Caution: some bands can be very broad because of hydrogen bonding

e.g. Enols v.broad OH, C=O absent!!

Weak bands in high frequency are extremely useful : S-H, $C\equiv C$, $C\equiv N$

Lack of strong bands in 900-650 means no aromatic

Stretch	**Alkanes,**	**Alkenes,**	**Alkynes**
C-H :	**<3000 cm^{-1}**	**>3000 cm^{-1}**	**3300 cm^{-1}** **sharp**
C-C	**Not useful**		
C=C		**1660-1600 cm^{-1}** conj. Moves to lower values Symmetrical : no band	
C≡C			**2150 cm^{-1}** conj. Moves to lower values Weak but very useful Symmetrical no band
Bending	**CH_2 Rocking** **720 cm^{-1} indicate** **Presence of 4-CH_2**	**1000-700 cm^{-1}** Indicate substitution pattern	**≡ C-H ~630 cm^{-1}** Strong and broad Confirm triple bond

D22110-4 *CAS [112-40-3]* $CH_3(CH_2)_{10}CH_3$
Dodecane, 99%

FW 170.34
mp -9.6 °C
bp 215-217 °C

d 0.749
Fp 160 °F
n$^{20}_{D}$ 1.4212

IR III, 4A
NMR II, 1,11A

2924.4 721.1
1467.3
1378.2

ALKANE

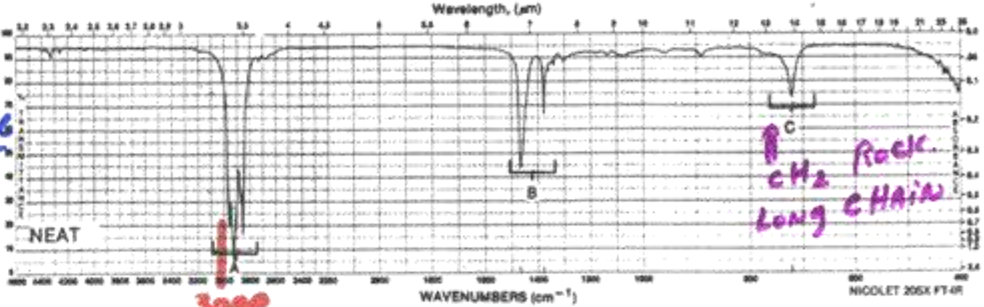


FIGURE 3.8. Dodecane. A. The C—H stretch: 2962 cm⁻¹ $\nu_{as}CH_3$, 2872 cm⁻¹ $\nu_s CH_3$, 2924 cm⁻¹ $\nu_{as}CH_2$, 2853 cm⁻¹ $\nu_s CH_2$. B. The C—H bend: 1467 cm⁻¹ $\delta_s CH_2$, 1450 cm⁻¹ $\delta_{as}CH_3$, 1378 cm⁻¹ $\delta_s CH_3$. C. The CH_2 rock: 721 cm⁻¹ ρ CH_2.

D180-7 *CAS [872-05-9]* $CH_2{=}CH(CH_2)_7CH_3$
1-Decene, 96%

FW 140.27
mp -66.3 °C
bp 166.5-173.5 °C

d 0.741
Fp 118 °F
n$^{20}_{D}$ 1.4195

IR III, 11A
NMR II, 1,21B

2925.7 1378.4 722.2
1641.7 991.2 634.1
1466.9 909.5

ALKENE

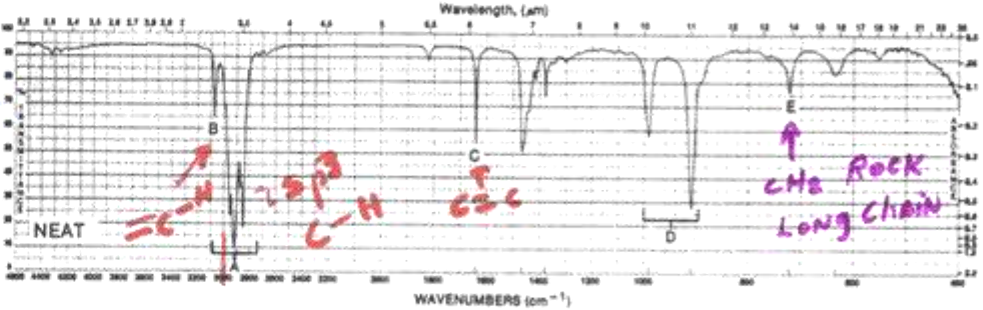


FIGURE 3.10. 1-Decene. A. The C—H stretch (see Fig. 3.8). Note alkene C—H stretch (B) at 3049 cm⁻¹. C. The C═C stretch, 1642 cm⁻¹, see Appendix Table D-1. D. Out-of-plane C—H bend: 991 cm⁻¹, (alkene) 909.5 cm⁻¹. E. Methylene rock: 722 cm⁻¹.

24442-2 *CAS [693-02-7]* $HC{\equiv}C(CH_2)_3CH_3$
1-Hexyne, 99%

FW 82.15
mp -132 °C
bp 71-72 °C

d 0.715
Fp -6 °F
n$^{20}_{D}$ 1.3974

NMR II, 2,949A

3310.6 1466.4 1249.7
2960.6 1379.8 729.8
2119.0 1327.0 630.0

ALKYNE

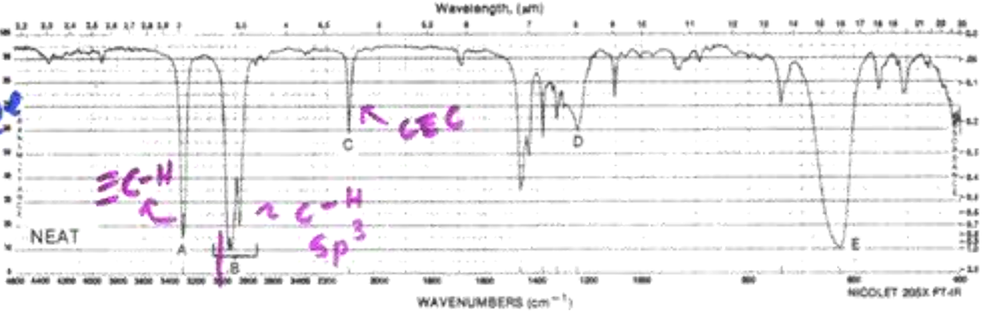
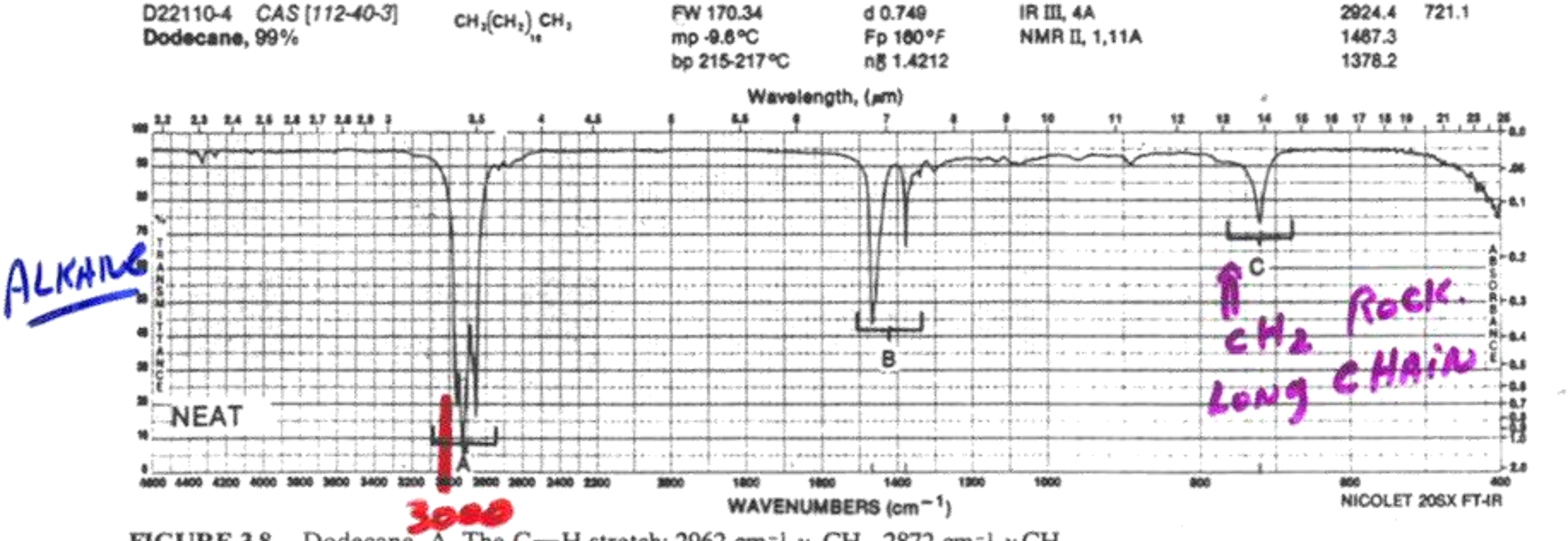


FIGURE 3.12. 1-Hexyne. A. The ≡C—H stretch, 3310 cm⁻¹. B. Alkyl C—H stretch (see Fig. 3.8), 2857–2941 cm⁻¹. C. The C≡C stretch, 2119 cm⁻¹. D. The ≡C—H bend overtone, 1250 cm⁻¹. E. The ≡C—H bend fundamental, 630 cm⁻¹.

Alkane



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Alkene : 1-Decene

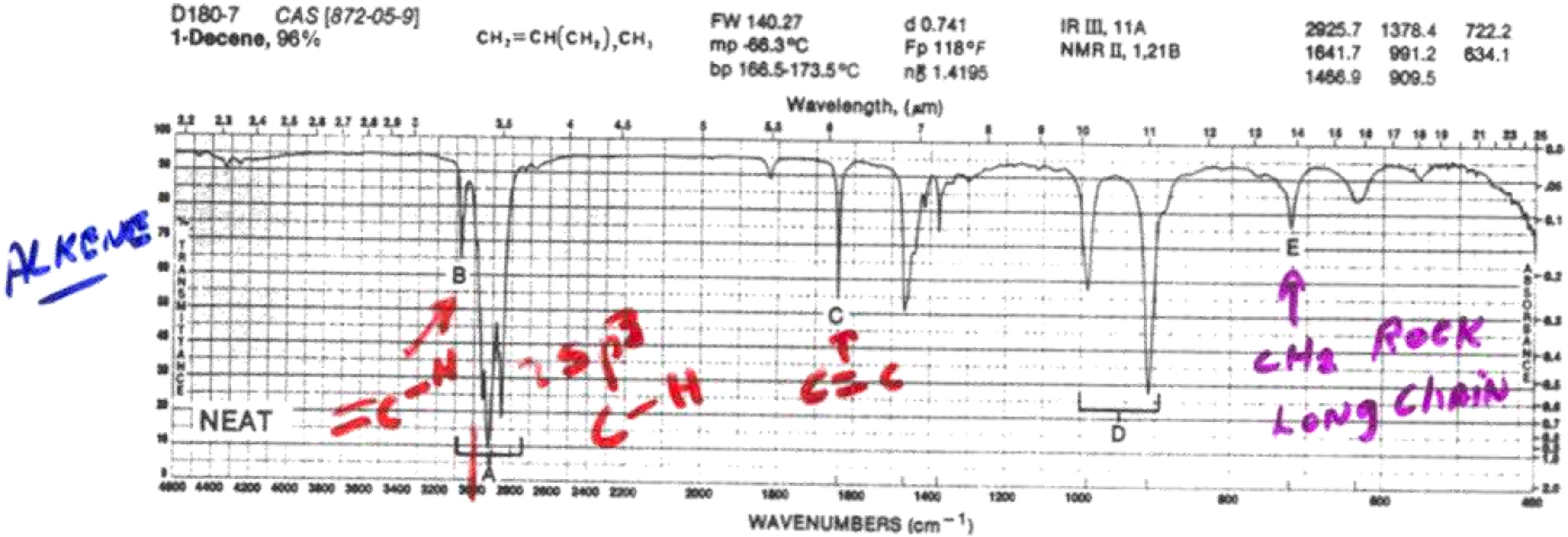


FIGURE 3.10. 1-Decene. A. The C—H stretch (see Fig. 3.8). Note alkene C—H stretch (B) at 3049 cm⁻¹. C. The C=C stretch, 1642 cm⁻¹, see Appendix Table D-1. D. Out-of-plane C—H bend: 991 cm⁻¹, (alkene) 909.5 cm⁻¹. E. Methylene rock: 722 cm⁻¹.

Symmetry

To give rise to absorption of IR => Oscillating Electric Dipole

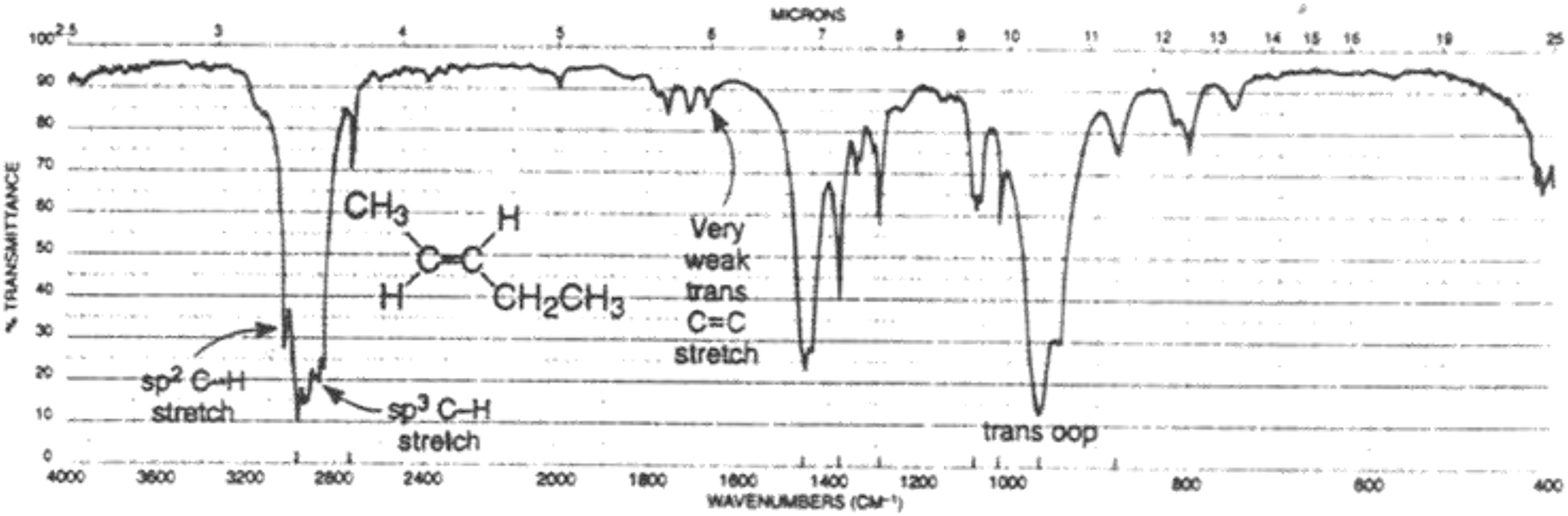
Molecules with Center of symmetry

Symmetric vibration => inactive

Antisymmetric vibration => active

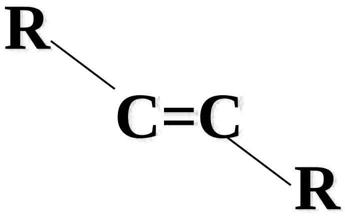
Alkene

INFRARED SPECTROSCOPY



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

In large molecule local symmetry produce weak or absent vibration

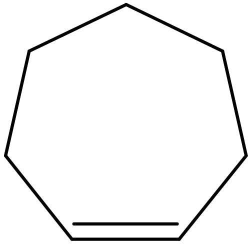


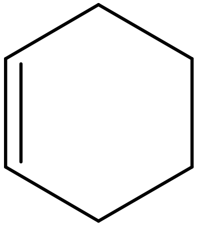
trans **C=C isomer -> weak in IR**

Observable in Raman

Alkene: Factors influencing vibration frequency

1- Strain move peak to right (decrease $\bar{\nu}$)


1650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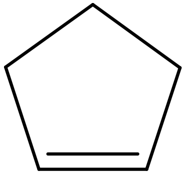
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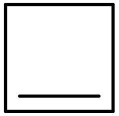
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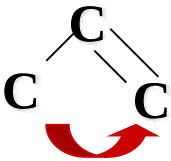
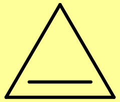
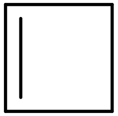


angle


1656 : exception

2- Substitution increase $\bar{\nu}$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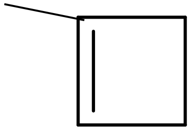
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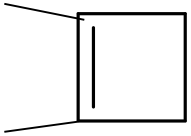
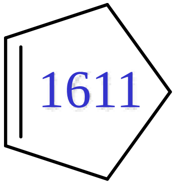

1675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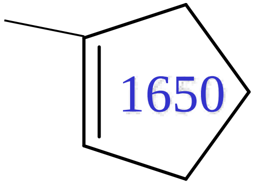
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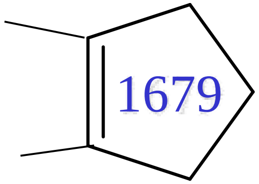
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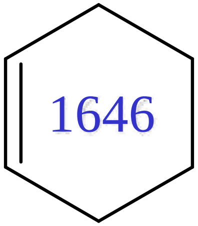
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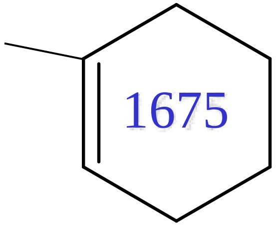
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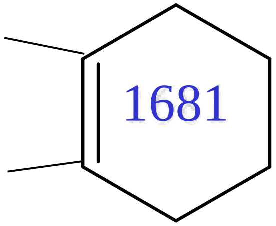

1681

3- conjugation decrease $\bar{\nu}$

C=C-Ph 1625 cm^{-1}

Alkene: Out-of-Plane bending

This region can be used to deduce substitution pattern

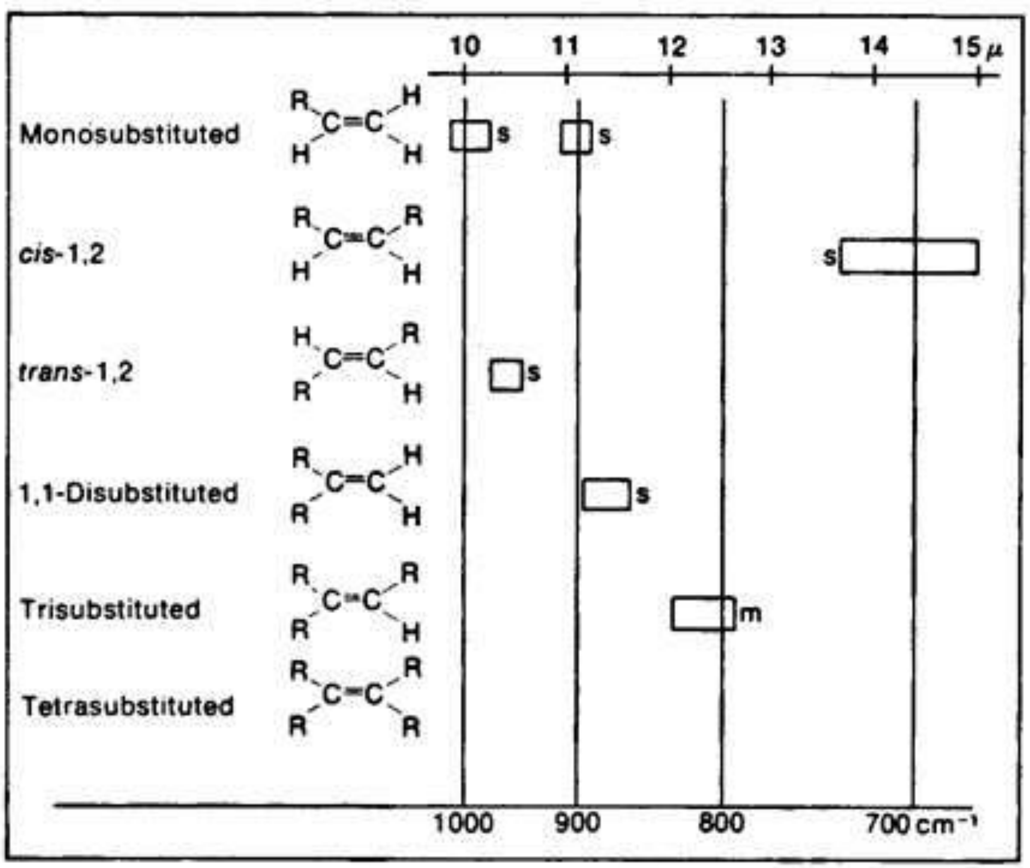


FIGURE 2.22 The C—H out-of-plane bending vibrations for substituted alkenes.

Alkyne: 1-Hexyne

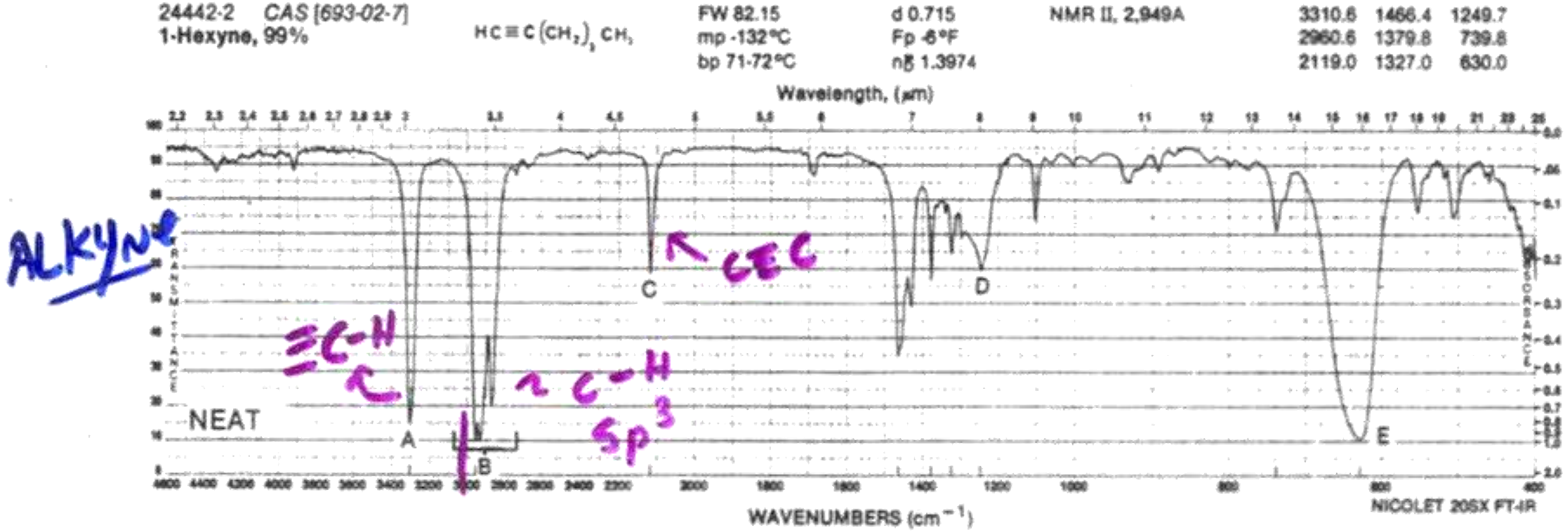
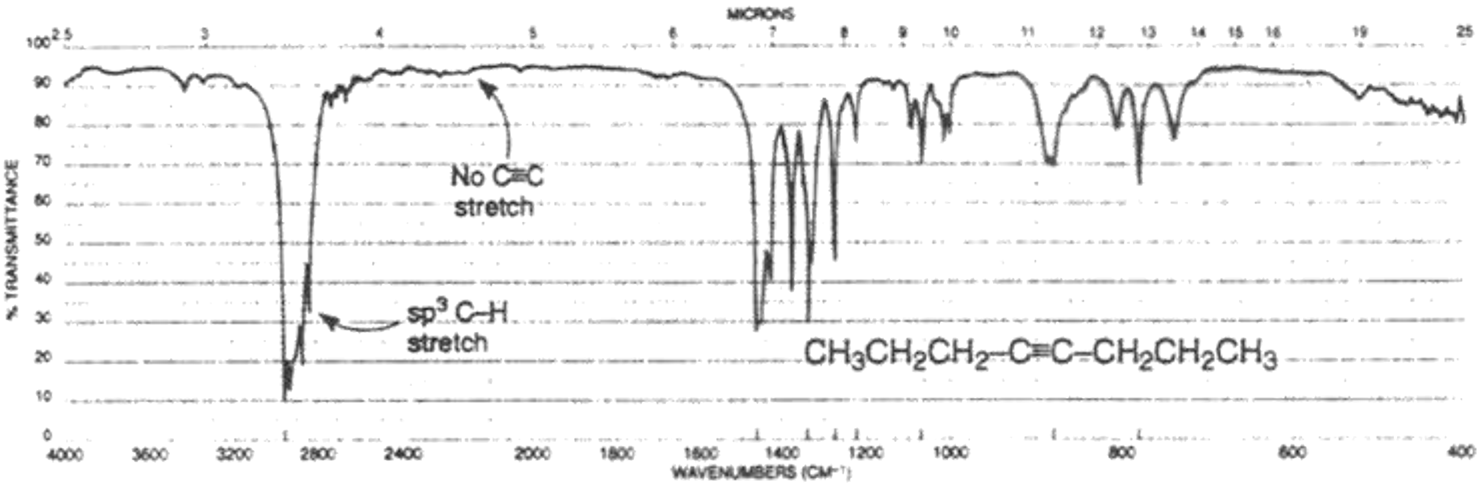
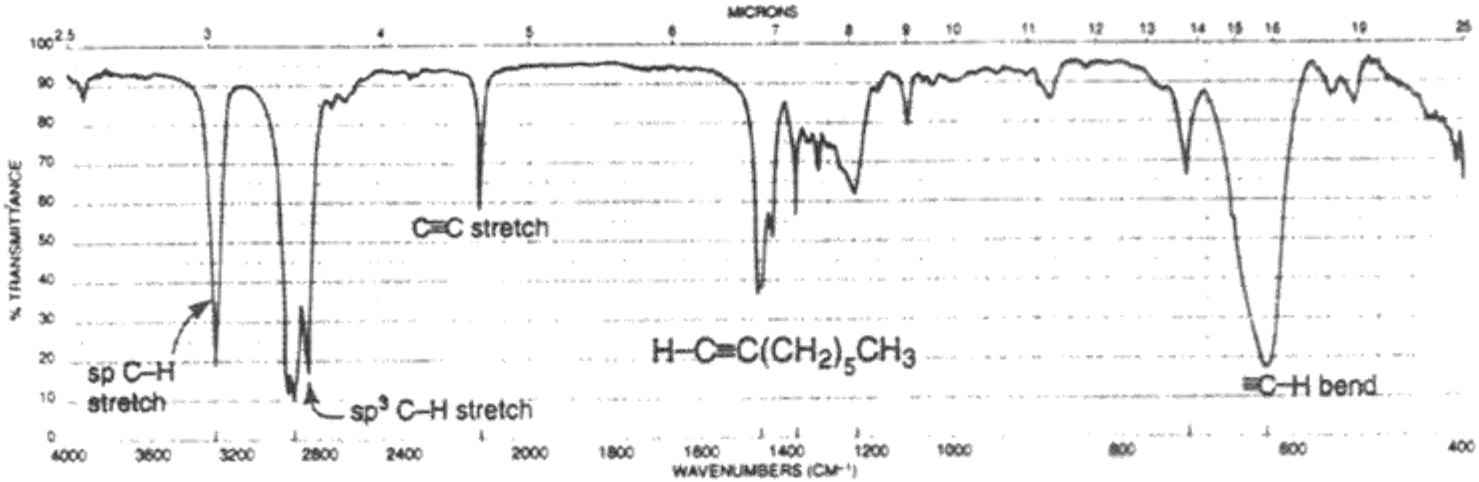


FIGURE 3.12. 1-Hexyne. A. The ≡C—H stretch, 3310 cm^{-1}. B. Alkyl C—H stretch (see Fig. 3.8), 2857–2941 cm^{-1}. C. The C≡C stretch, 2119 cm^{-1}. D. The ≡C—H bend overtone, 1250 cm^{-1}. E. The ≡C—H bend fundamental, 630 cm^{-1}.

Alkyne: Symmetry



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



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

In IR, Most important transition involve :

Ground State ($\nu_i = 0$) to First Excited State ($\nu i = 1$)

Transition ($\nu_i = 0$) to ($\nu_J = 2$) => Overtone

IR : Aromatic

=C-H > 3000 cm^{-1}

C=C 1600 and 1475 cm^{-1}

=C-H out of plane bending: great utility to assign ring substitution

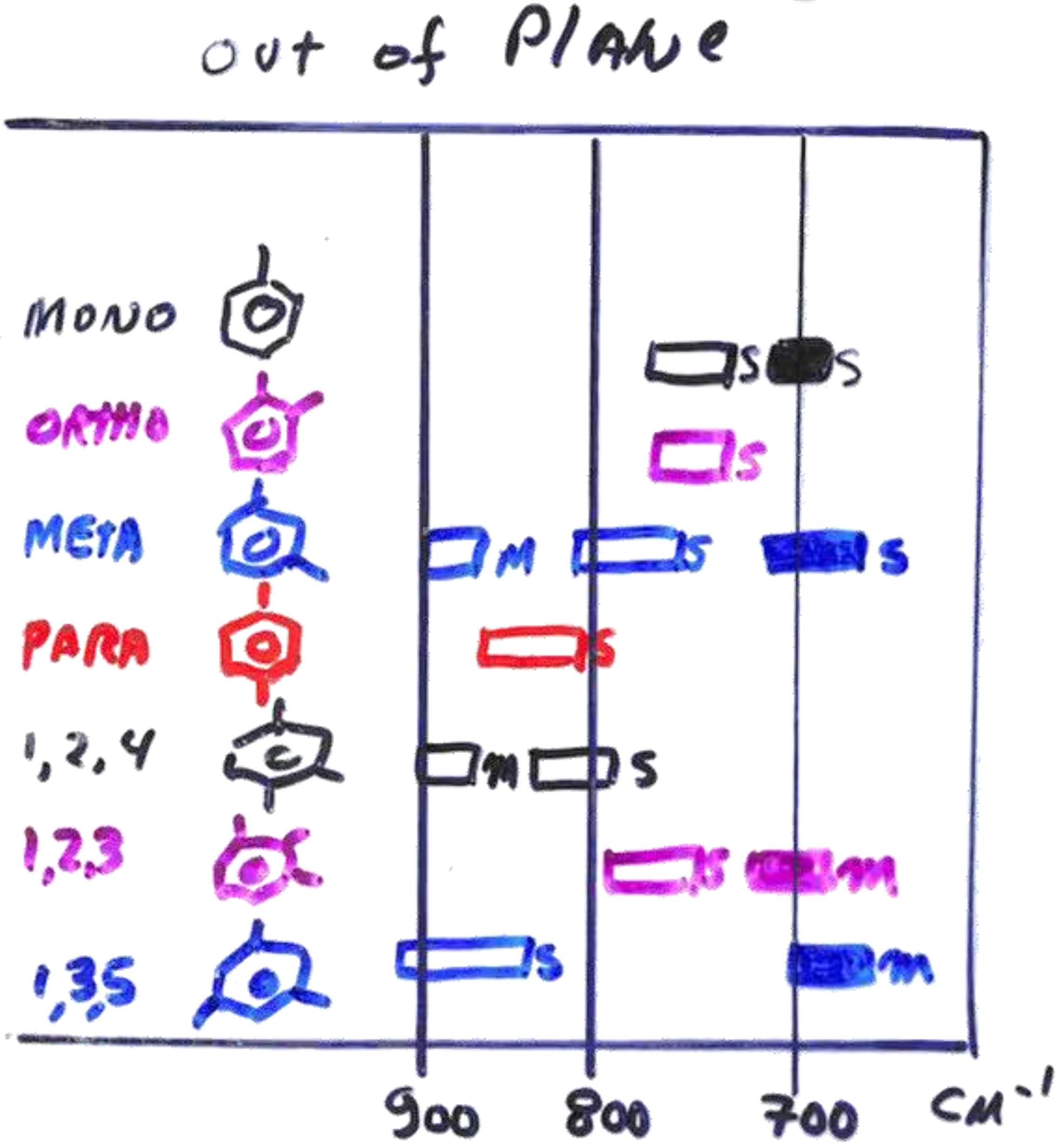
overtone 2000-1667: useful to assign ring substitution

e.g. Naphthalene:

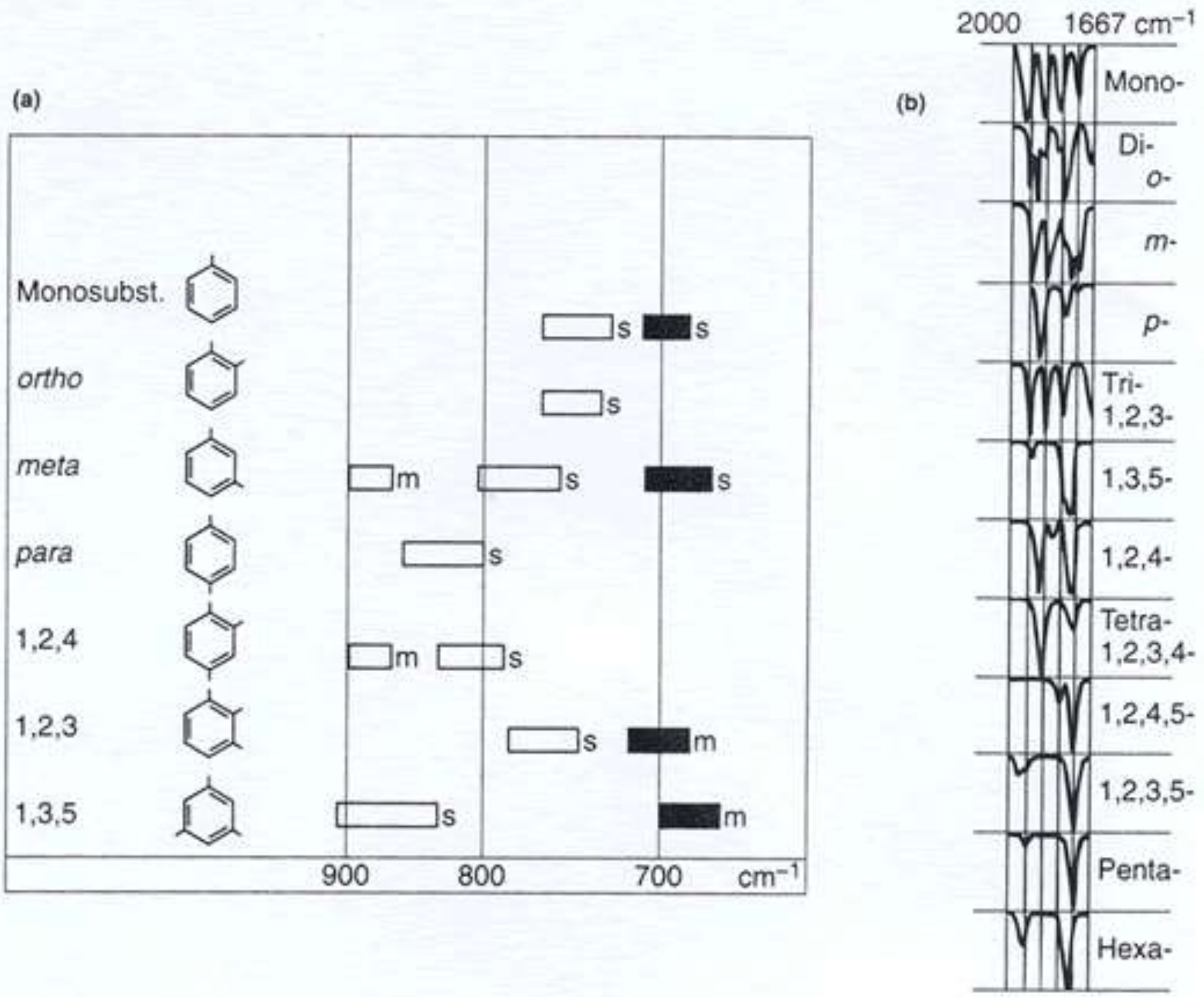
out of plane bending

Substitution pattern	$\bar{\nu}$
Isolated H	862-835
2 adjacent H	835-805
4 adjacent H	760-735

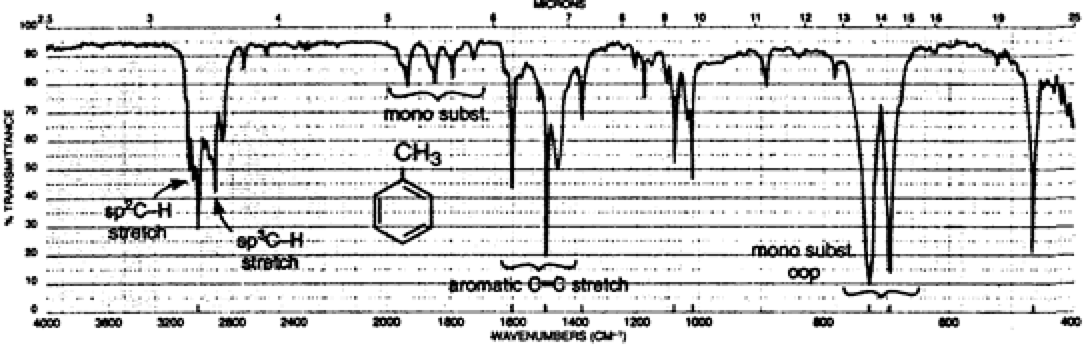
Aromatic substitution: Out of plane bending



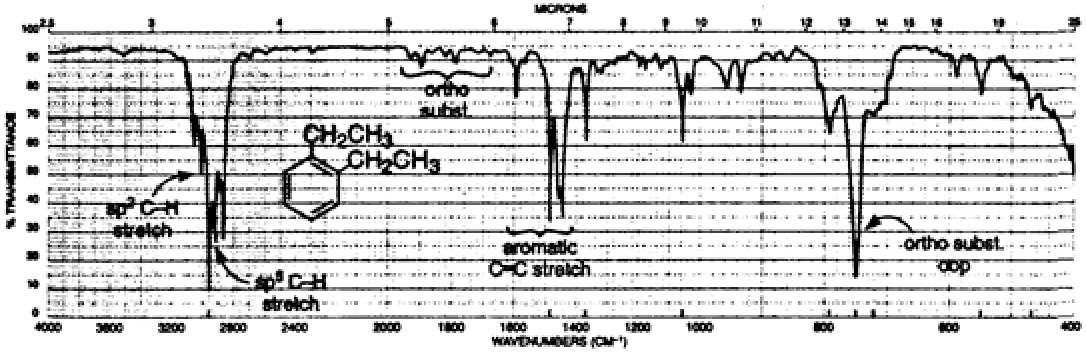
Aromatic substitution: Out of plane bending



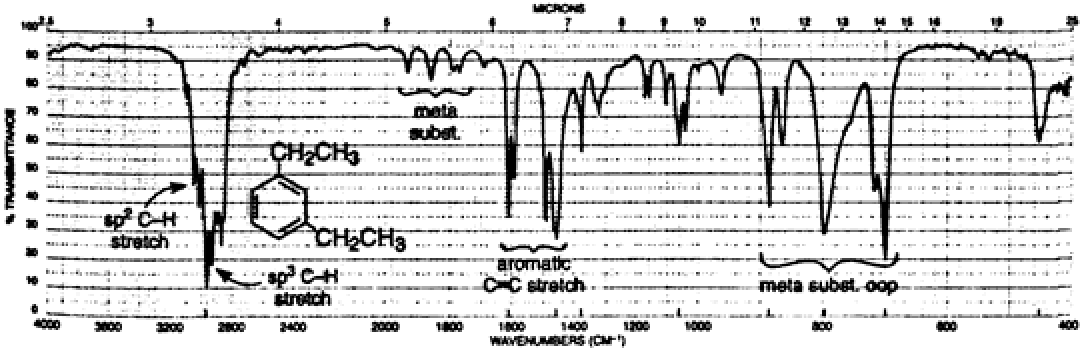
▸ **FIGURE 2.28** (a) The C—H out-of-plane bending vibrations for substituted benzenoid compounds. (b) The 2000-to-1667-cm^{-1} region for substituted benzenoid compounds (from Dyer, John R., *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice–Hall, Englewood Cliffs, N.J., 1965).



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

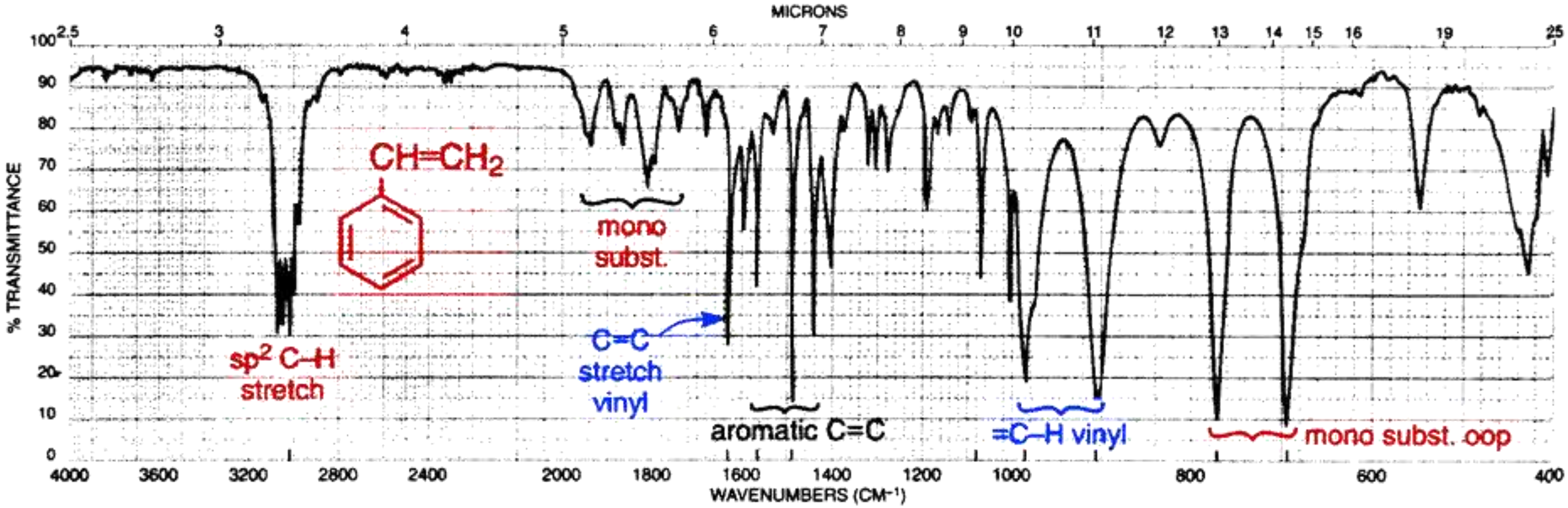


▶ **FIGURE 2.24** The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).



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

Aromatic and Alkene substitution



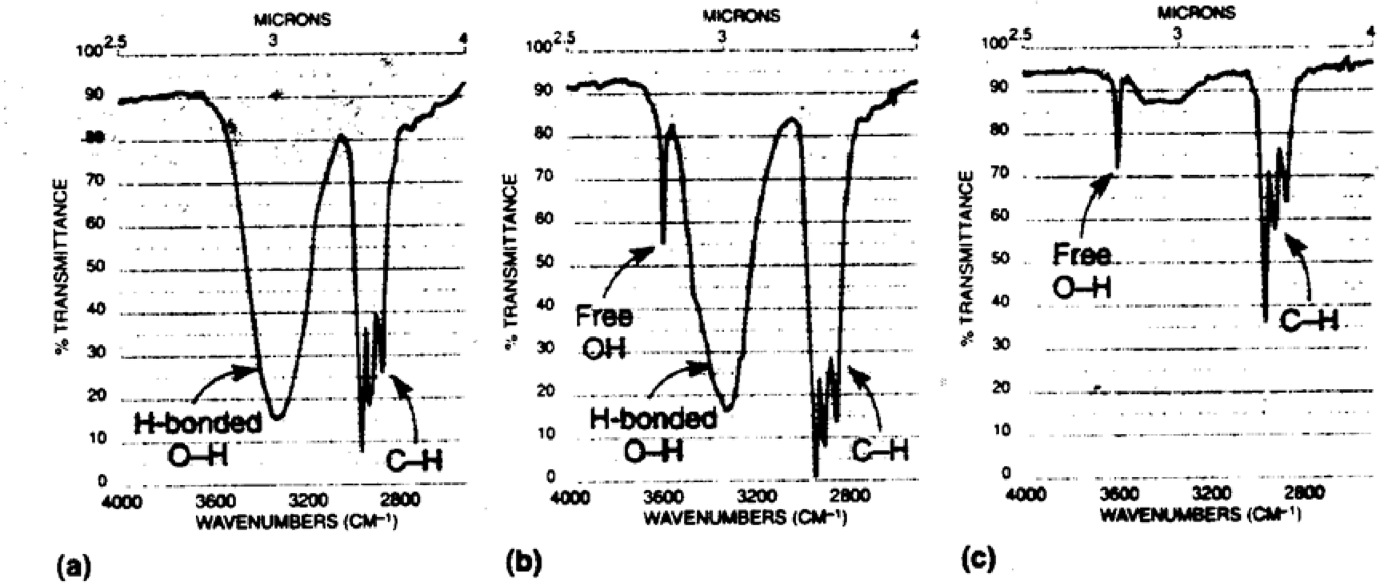
▶ **FIGURE 2.27** The infrared spectrum of styrene (neat liquid, KBr plates).

IR: Alcohols and Phenols

O-H Free : Sharp 3650-3600

O-H H-Bond : Broad 3400-3300

Intermolecular Hydrogen bonding Increases with concentration
=> **Less “Free” OH**



▶ **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).

IR: Alcohols and Phenols

C-O : 1260-1000 cm^{-1} (coupled to C-C => C-C-O)

C-O Vibration is sensitive to substitution:

Phenol	**1220**
3` Alcohols	**1150**
2` Alcohols	**1100**
1` Alcohols	**1050**

More complicated than above: shift to lower Wavenumber With unsaturation (Table 3.2)

Alcohol

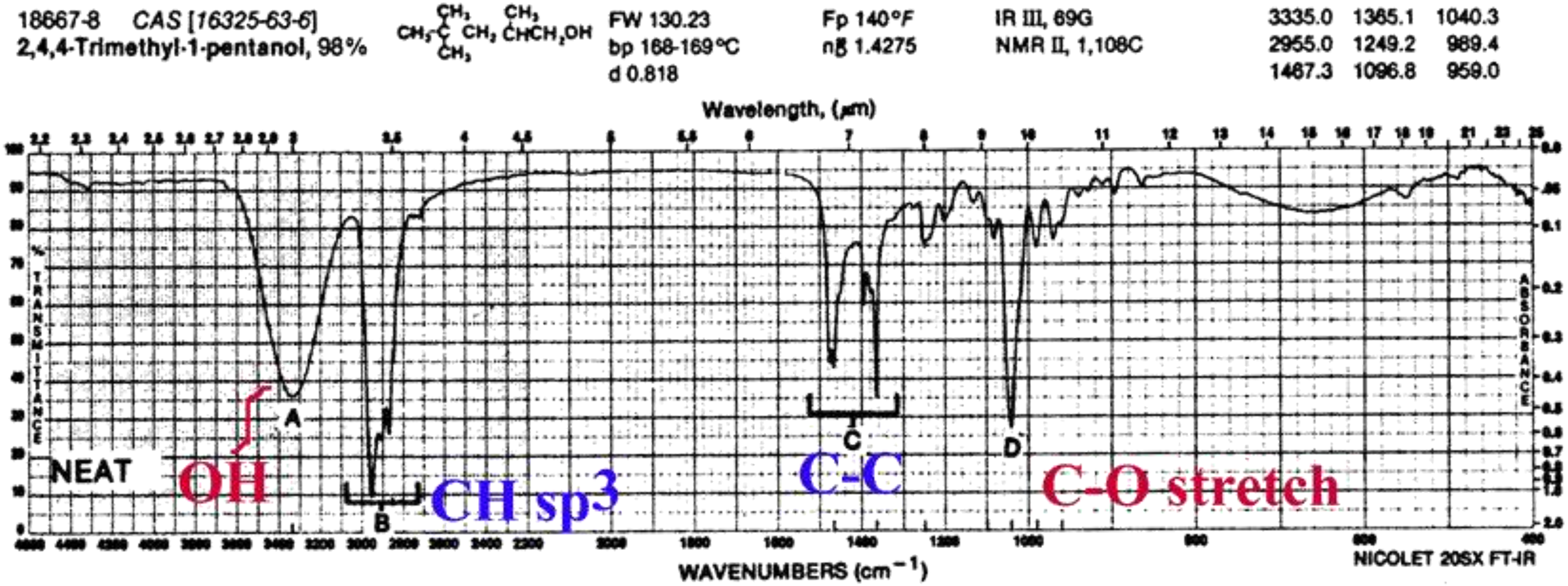
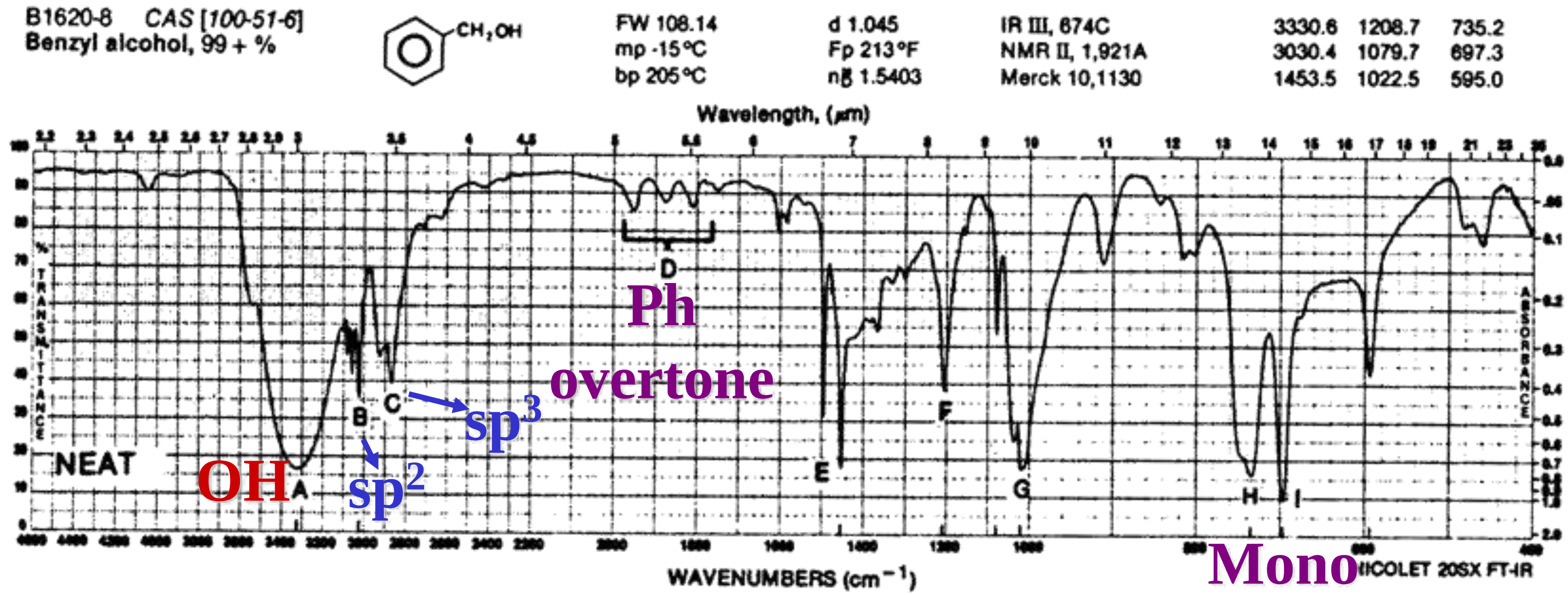


FIGURE 3.15. 24,4-Trimethyl-1-pentanol. A. The O—H stretch, intermolecular hydrogen bonding 3335 cm^{-1}. B. The C—H stretch (see Fig. 3.8, 3000–2800 cm^{-1}). C. The C—H bend (see Fig. 3.8). Note the pair of bands for the *gem*-dimethyl group at 1395 and 1365 cm^{-1}. D. The C—O stretch 1040 cm^{-1}.

C-O : 1040 cm^{-1} **indicate primary alcohol**

Benzyl Alcohol



B1620-8 *CAS* [*100-51-6*]
Benzyl alcohol, 99 + %

FW 108.14
mp -15 °C
bp 205 °C

d 1.045
Fp 213 °F
n_D^{20} 1.5403

IR III, 674C
NMR II, 1,921A
Merck 10,1130

3330.6	1208.7	735.2
3030.4	1079.7	697.3
1453.5	1022.5	595.0

OH

sp²

sp³

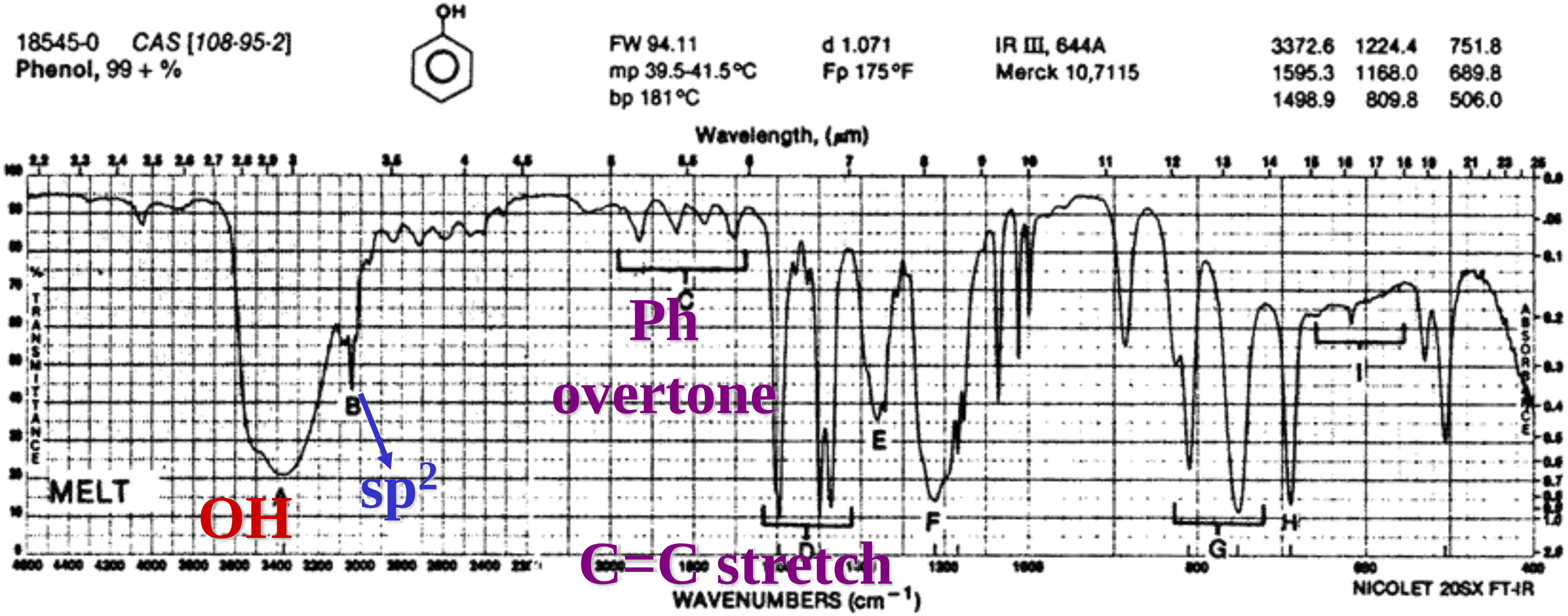
Ph overtone

Mono Subst. Ph
735 & 697 cm^{-1}

FIGURE 3.14. Benzyl alcohol. A. O—H stretch: intermolecular hydrogen bonded, 3331 cm^{-1}. B. The C—H stretch: aromatic 3100–3000 cm^{-1}. C. The C—H stretch: methylene, 2980–2840 cm^{-1}. D. Overtone or combination bands, 2000–1667 cm^{-1}. E. The C$\overset{\dots}{=}$C ring stretch, 1497, 1454 cm^{-1}, overlapped by CH_2 scissoring, about 1471 cm^{-1}. F. The

C-O : 1080, 1022 cm^{-1} : primary OH

Phenol



18545-0 CAS [108-95-2]
Phenol, 99 + %

FW 94.11
mp 39.5-41.5°C
bp 181°C

d 1.071
Fp 175°F

IR III, 644A
Merck 10,7115

3372.6	1224.4	751.8
1595.3	1168.0	689.8
1498.9	809.8	506.0

Ph overtone

OH

sp^2

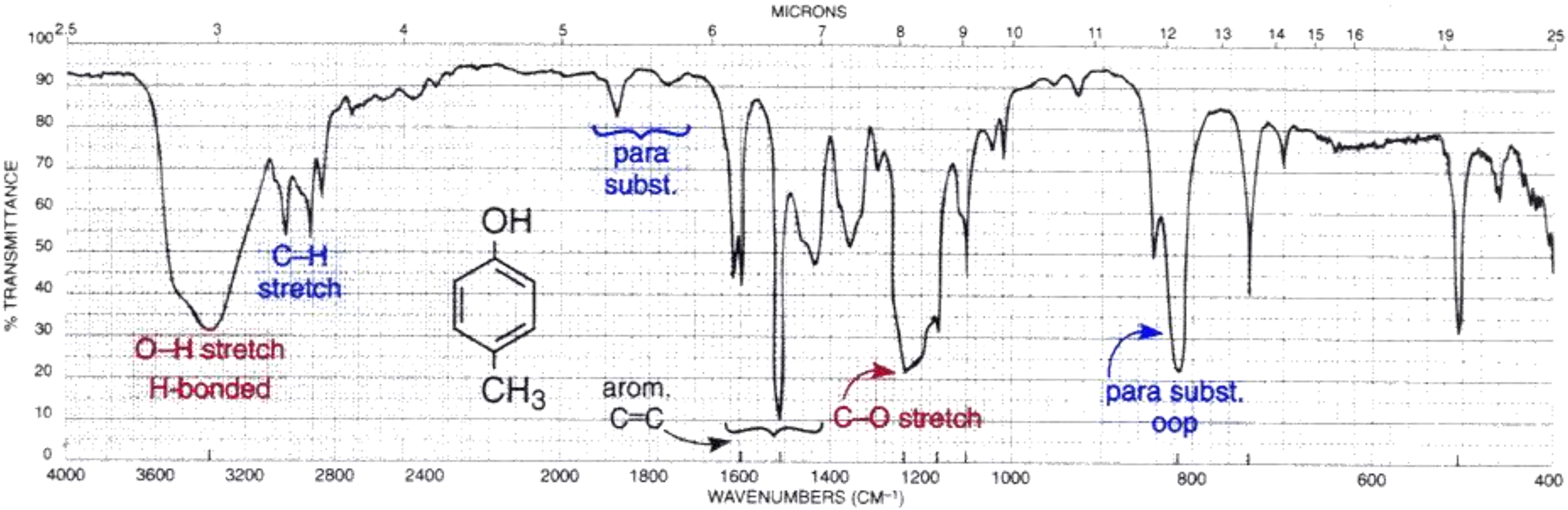
C=C stretch

FIGURE 3.16. Phenol. A. Broad intermolecular hydrogen bonded, O—H stretch, 3373 cm⁻¹. B. Aromatic C—H stretch, 3045 cm⁻¹. C. Overtone or combination bands, 2000–1667 cm⁻¹. D. The C═C ring stretch, 1595, 1499, 1470 cm⁻¹. E. In-plane O—H bend, 1360 cm⁻¹. F. The C—O stretch, 1224 cm⁻¹. G. Out-of-plane C—H bend, 810, 752 cm⁻¹. H. Out-of-plane ring C═C bend, 690 cm⁻¹. I. (Broad) hydrogen-bonded, out-of-plane O—H bend, about 650 cm⁻¹.

Mono Subst. Ph out-of plane 810 & 752 cm^{-1}

Ph-O : 1224 cm^{-1}

Phenol



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

IR: Ether

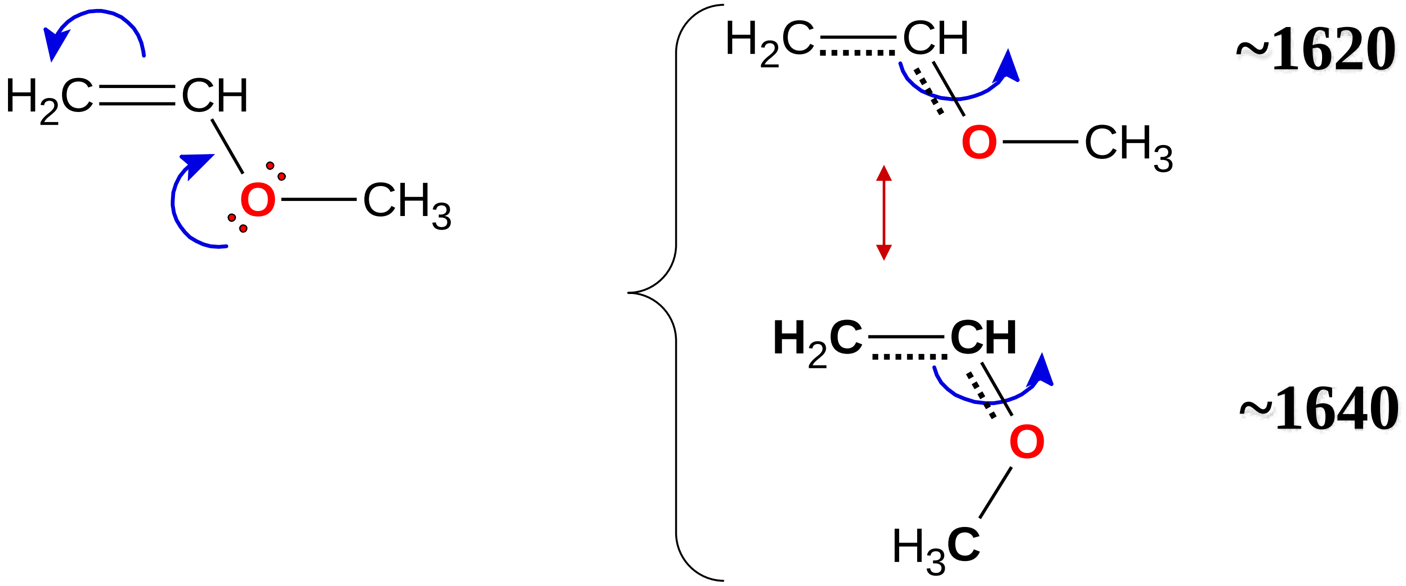
C-O-C => 1300-1000 cm^{-1}

Ph-O-C => 1250 and 1040 cm^{-1}

Aliphatic => 1120 cm^{-1}

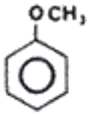
C=C in vinyl Ether => 1660-1610 cm^{-1}

appear as Doublet => rotational isomers



Ether

12322-6 *CAS [100-66-3]*
Anisole, 99%

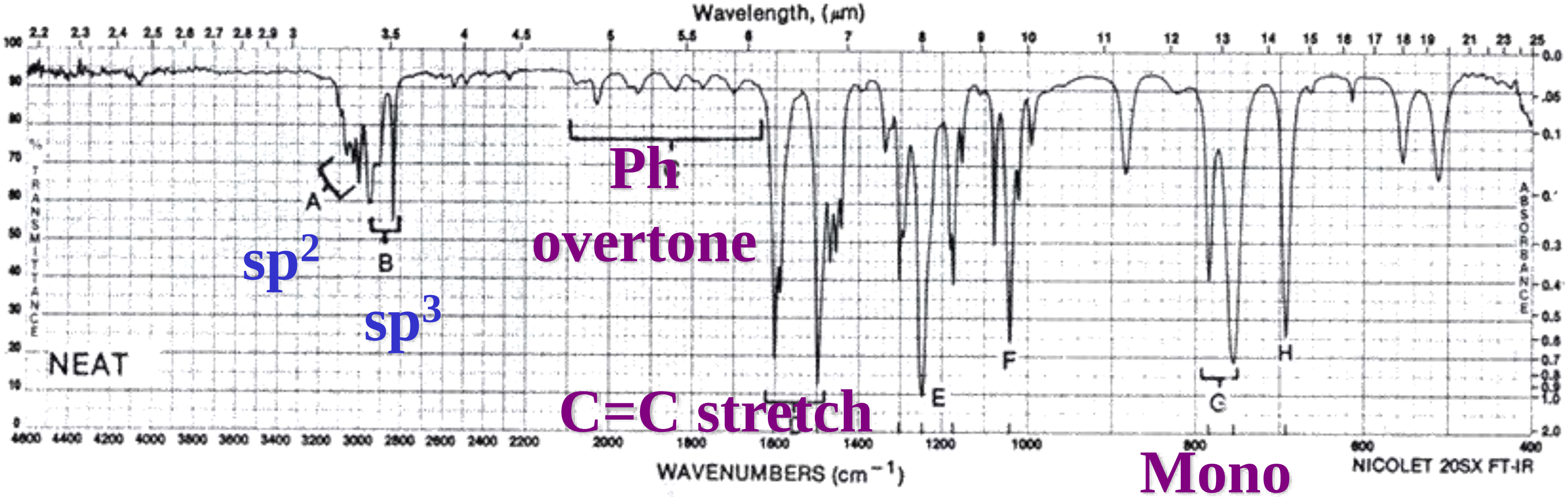


FW 108.14
mp -37°C
bp 154°C

d 0.995
Fp 125°F
n_D^{20} 1.5160

IR III, 624A
NMR II, 1,833A
Merck 10,691

1600.9	1247.3	784.1
1497.9	1172.6	754.4
1303.0	1040.5	692.0



sp^2

sp^3

Ph overtone

C=C stretch

FIGURE 3.19. Anisole. A. Aromatic C—H stretch, 3060, 3030, 3000 cm⁻¹. B. Methyl C—H stretch, 2950, 2835 cm⁻¹. C. Overtone-combination region, 2000–1650 cm⁻¹. D. The C═ ring stretch, 1600, 1498 cm⁻¹. E. Asymmetric C—O—C stretch, 1247 cm⁻¹. F. Symmetric C—O—C stretch, 1040 cm⁻¹. G. Out-of-plane C—H bend, 784, 754 cm⁻¹. H. Out-of-plane ring C═C bend, 692 cm⁻¹.

Mono Subst. Ph out-of plane 784, 754 & 692 cm^{-1}

Ph-O-C : 1247 cm^{-1} Asymmetric stretch
Ph-O-C : 1040 cm^{-1} Symmetric stretch

IR: Carbonyl

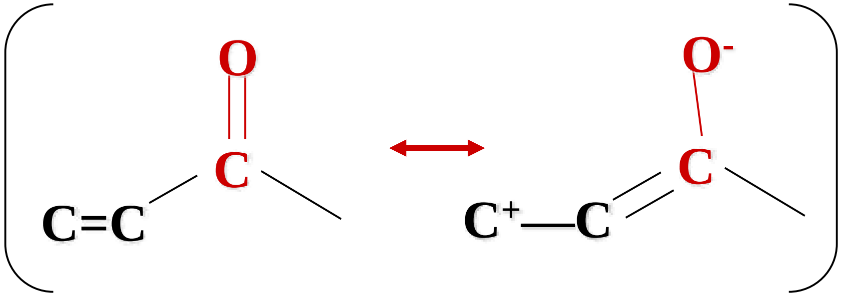
From 1850 – 1650 cm^{-1}

1810	1800	1760	1735	1725	1715	1710	1690
Anhydr Band	Acid Chloride	Anhydr Band 2	Ester	Aldehyde	Ketone	Acid	Amide

Ketone 1715 cm^{-1} is used as reference point for comparisons

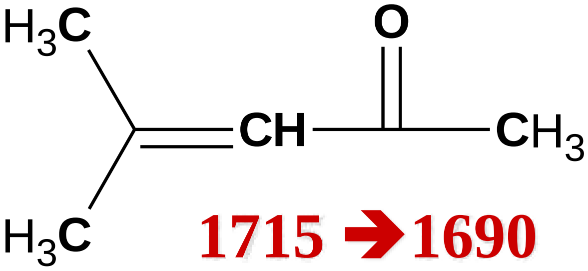
Factor influencing C=O

1) conjugation

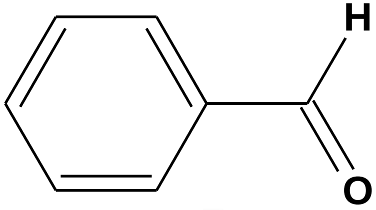


Conjugation increase single bond character of C=O

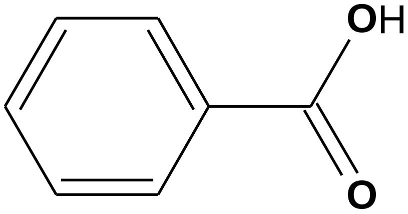
➔ Lower force constant ➔ lower frequency number



1715 ➔1690



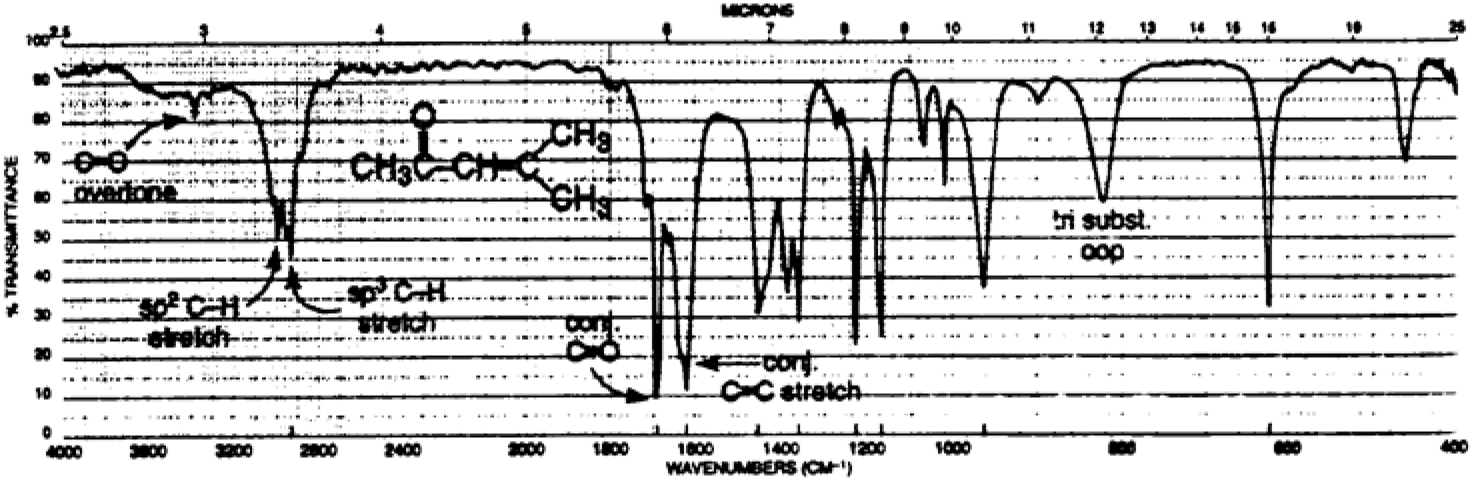
1725 ➔ 1700



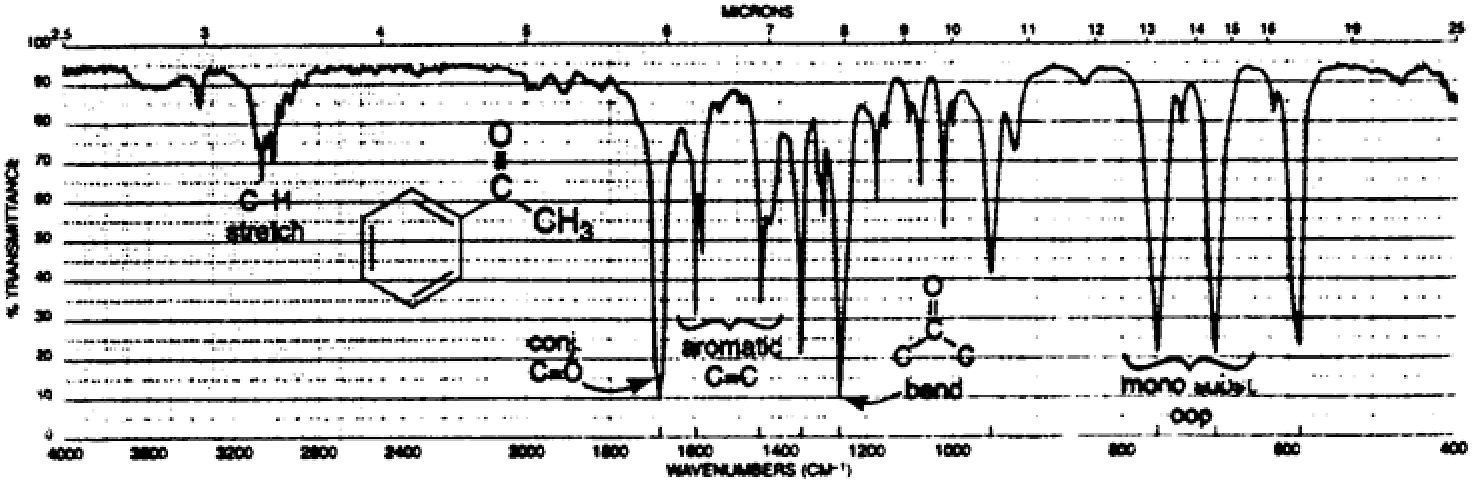
1710 ➔1680

Ketone and Conjugation

Conjugation: Lower $\bar{\nu}$



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

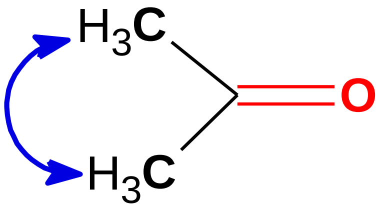


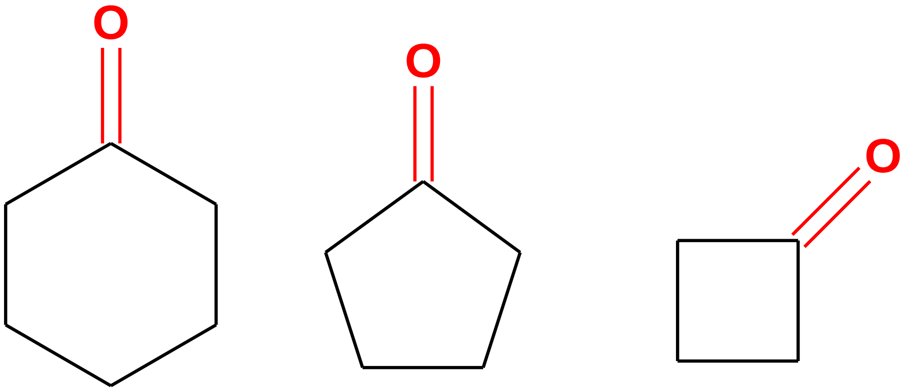
▸ **FIGURE 2.40** The infrared spectrum of acetophenone (neat liquid, KBr plates).

Ketone and Ring Strain

Factors influencing C=O

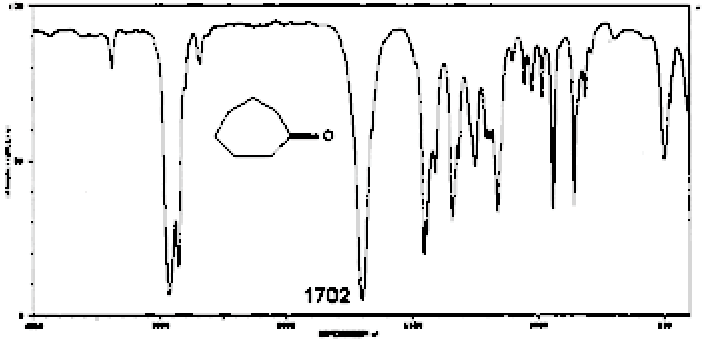
2) Ring size

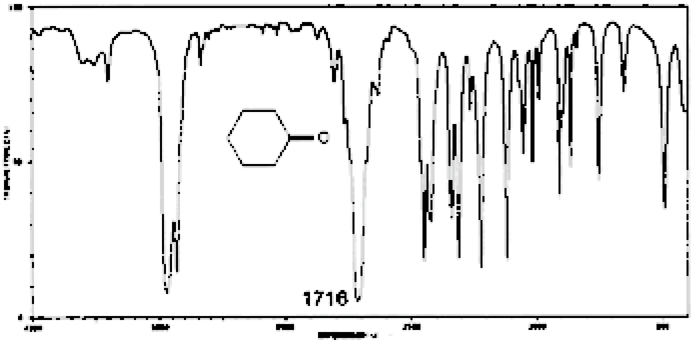


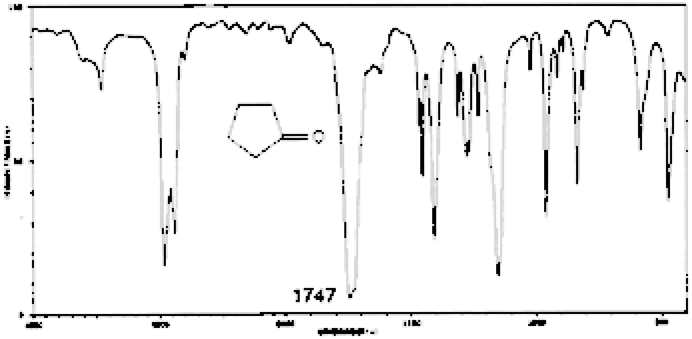


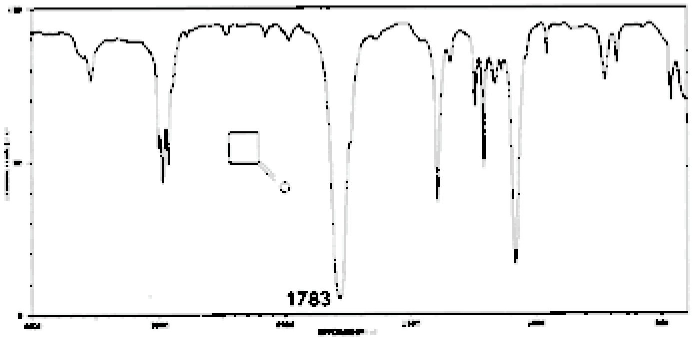
$1715\ \mathrm{cm^{-1}}$	$1751\ \mathrm{cm^{-1}}$	$1775\ \mathrm{cm^{-1}}$
Angle ~ 120º	< 120º	<< 120º

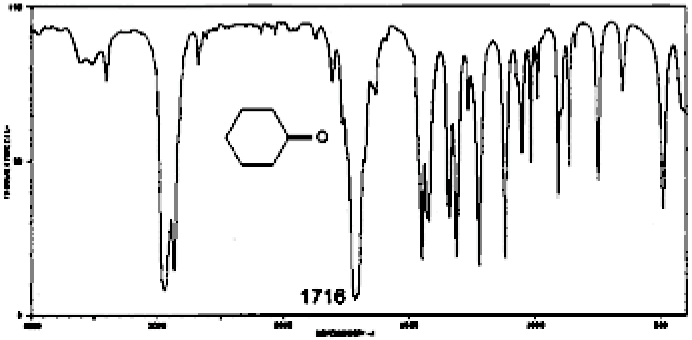
Ring Strain: Higher $\bar{\nu}$



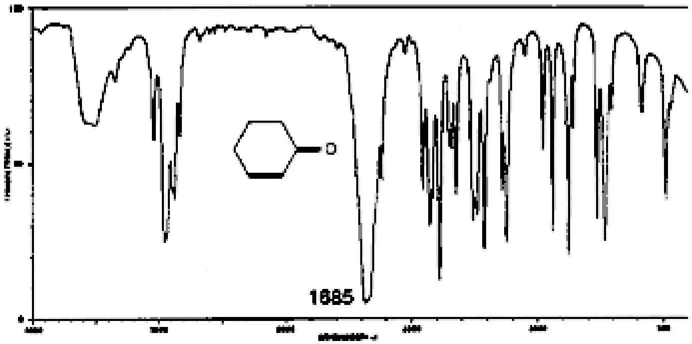






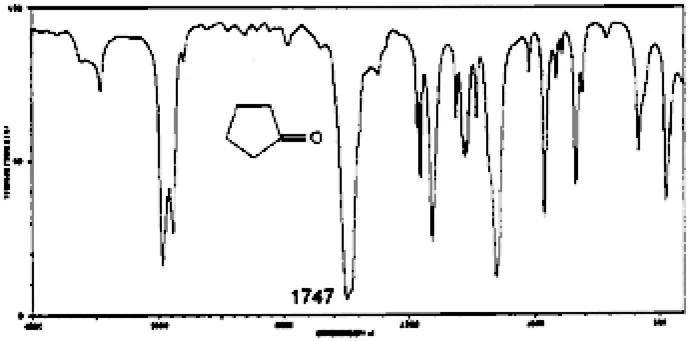


Ketone

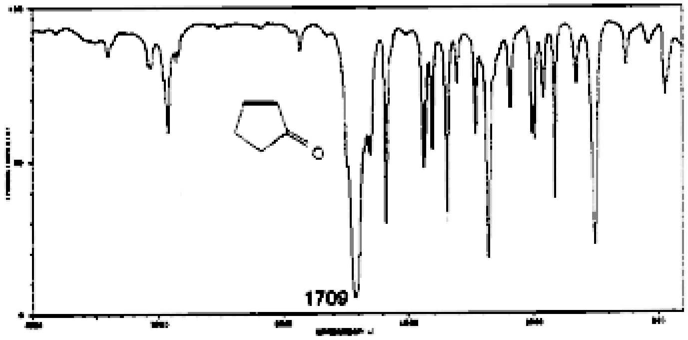


conj. Ketone

Ketone : Ring strain

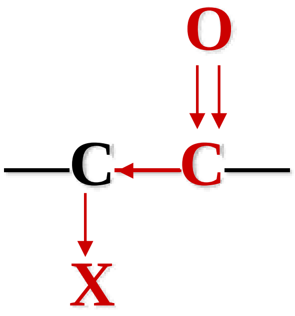


Ring strain + conj.

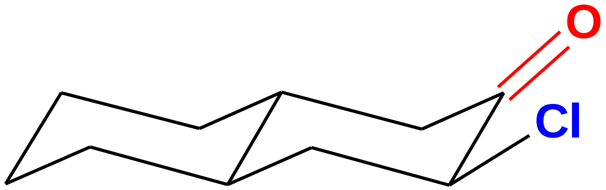


Factors influencing carbonyl: C=O

3) α substitution effect (Chlorine or other halogens)



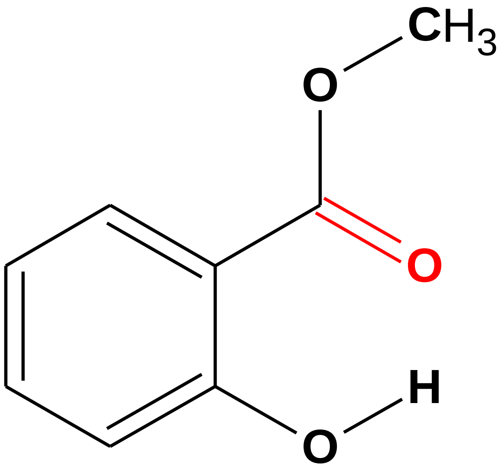
Result in stronger bound ➔ higher frequency $\bar{\nu}$



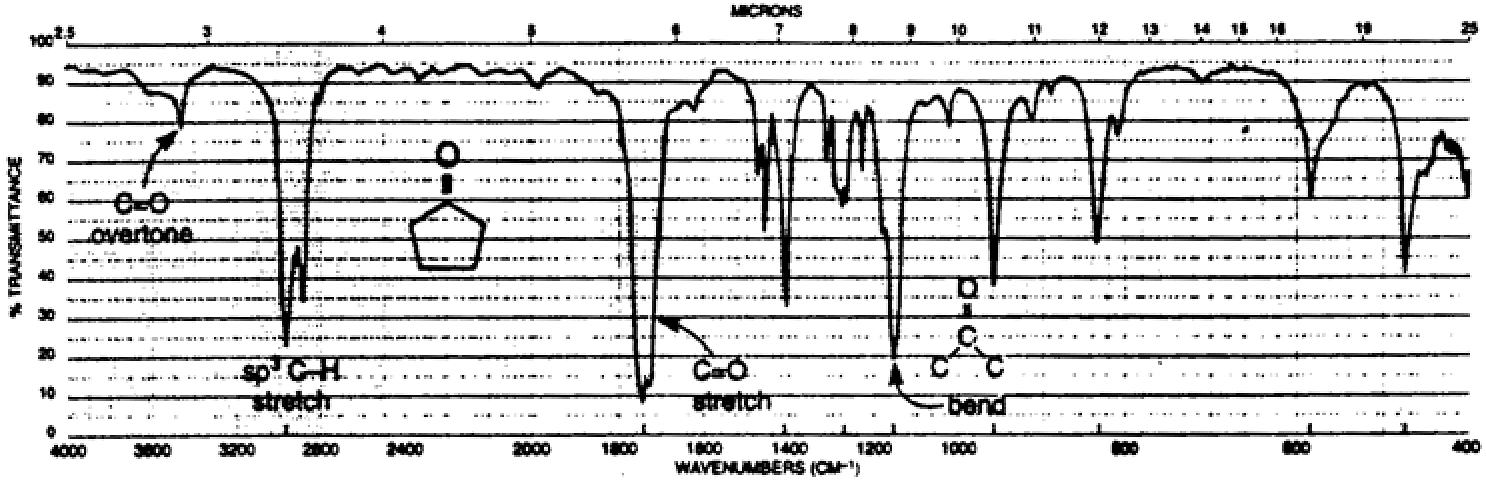
1750 cm^{-1}

4) Hydrogen bonding

Decrease C=O strenght→lower frequency

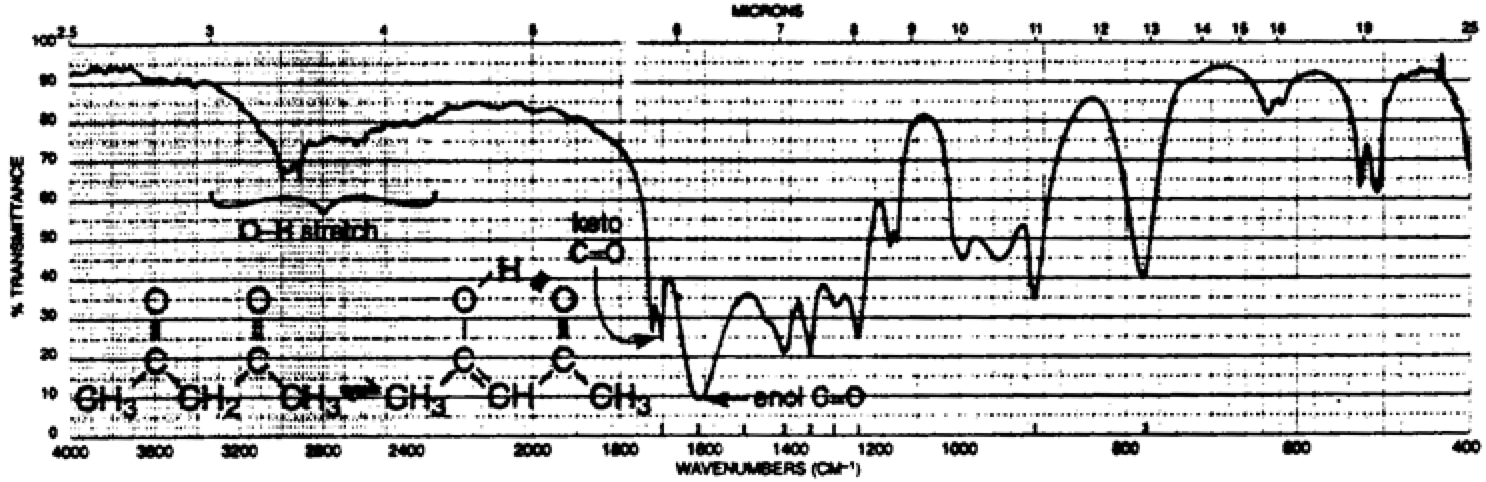


1680 cm^{-1}



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

Enol



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

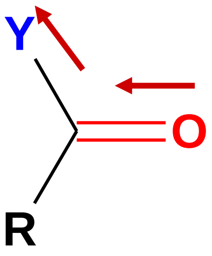
Factors influencing carbonyl: C=O

5) Heteroatom

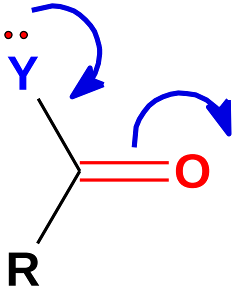
Inductive effect

Stronger bond

higher frequency



e.g. ester



e.g. amides

Resonance effect

Weaker bond

Lower frequence

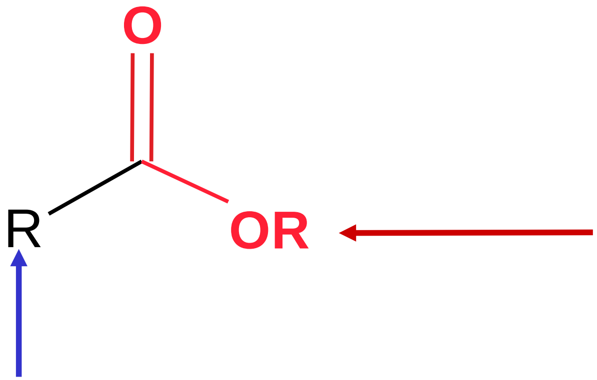
	Y	C=O
inductive	Cl	1815-1785
	Br	1812
	OH (monomer)	1760
	OR (Ester)	1705-1735
resonance	NH2	1695-1650
	SR	1720-1690

Ester Carbonyl

Esters **C=O** $\bar{\nu}$ **~ 1750 – 1735 cm^{-1}**

Conjugation => lower freq.

O-C : 1300 – 1000 2 or more bands

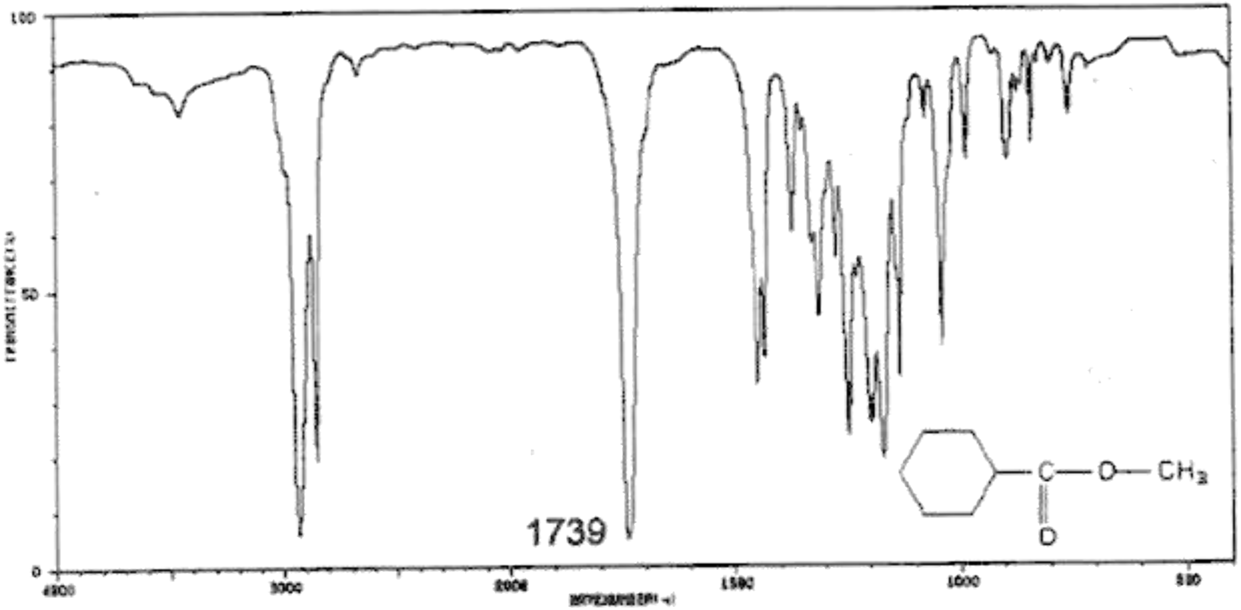


Inductive effect with O
reinforce carbonyl => **higher** $\bar{\nu}$

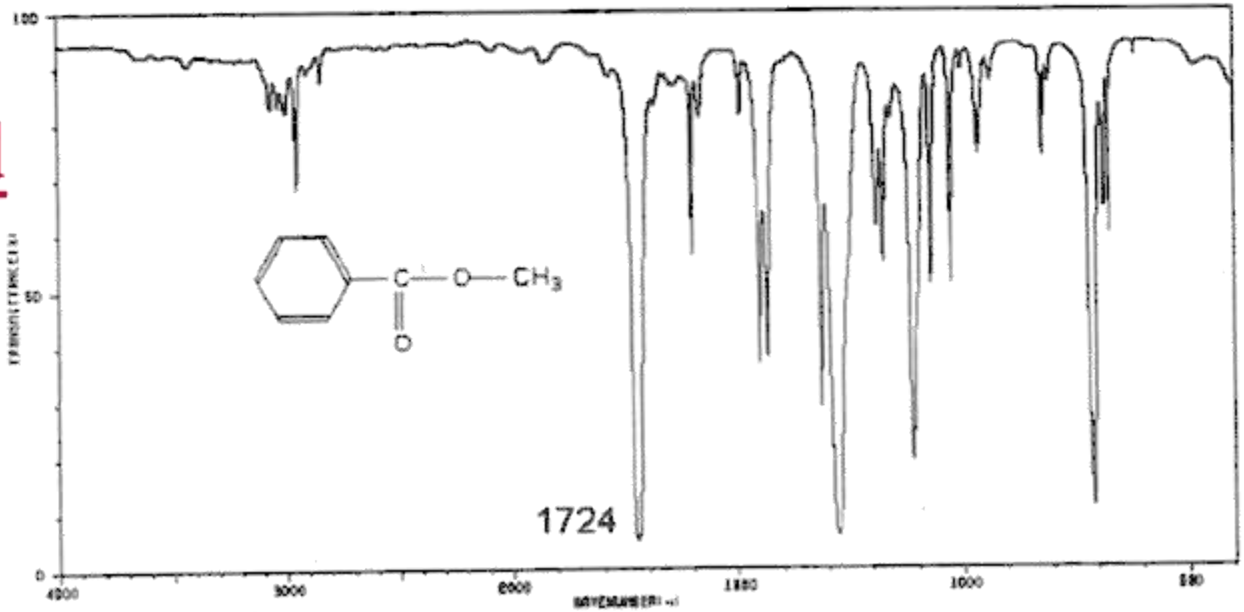
Conjugation with CO
weaken carbonyl => **Lower** $\bar{\nu}$

Ester carbonyl: C=O

ESTER



Conjugated ESTER



Ester carbonyl: C=O

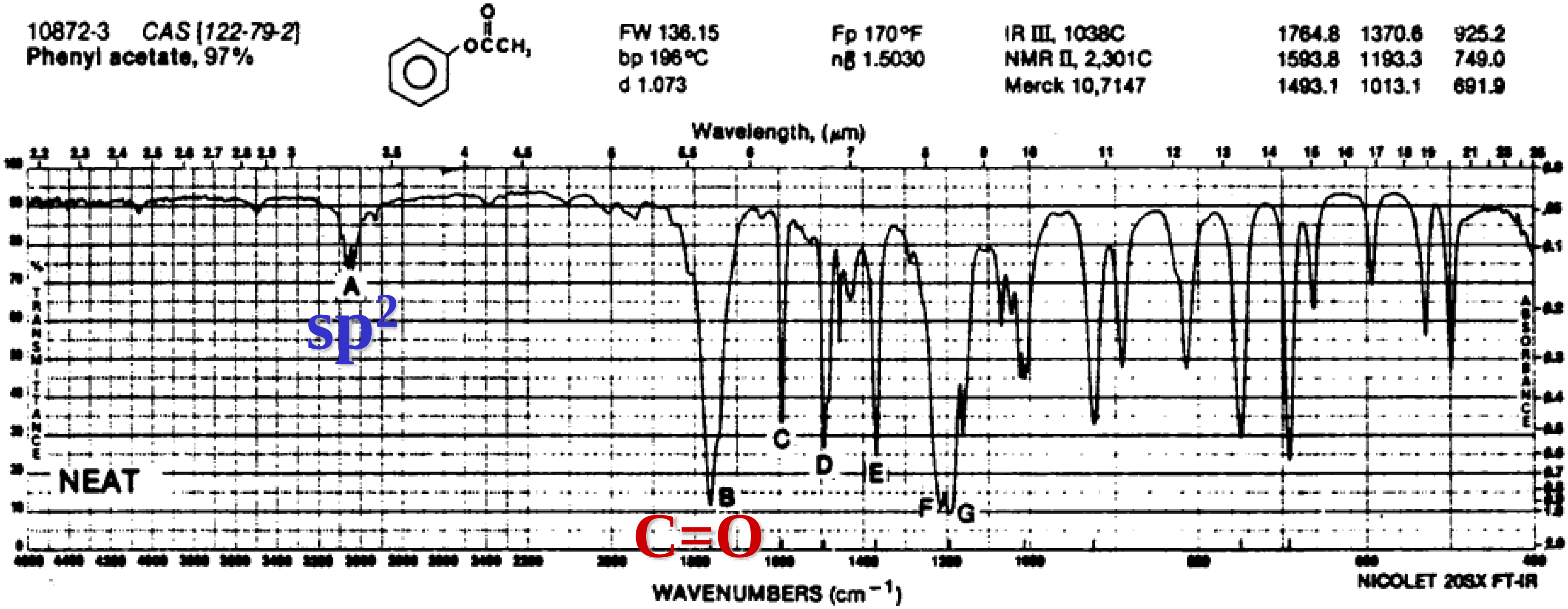


FIGURE 3.25. Phenyl acetate. A. Aromatic C—H stretch, 3070, 3040 cm^{-1}. B. The C═O stretch, 1765 cm^{-1}: this is higher frequency than that from a normal ester C═O stretch (~1740 cm^{-1}: see Table 3.3) because of phenyl conjugation with alcohol oxygen; conjugation of an aryl group or other unsaturation with the carbonyl group causes this C═O stretch to be at lower than normal frequency (e.g., benzoates absorb at about 1724 cm^{-1}). C. Ring C$\overset{...}{=}$C stretch, 1594 cm^{-1}. D. $\delta_{as}CH_3$, 1493 cm^{-1}. E. $\delta_{s}CH_3$, 1371 cm^{-1}. F. Acetate C(═O)—O stretch, 1215 cm^{-1}. G. The O—C$\overset{...}{=}$C asymmetrical stretch, 1193 cm^{-1}.

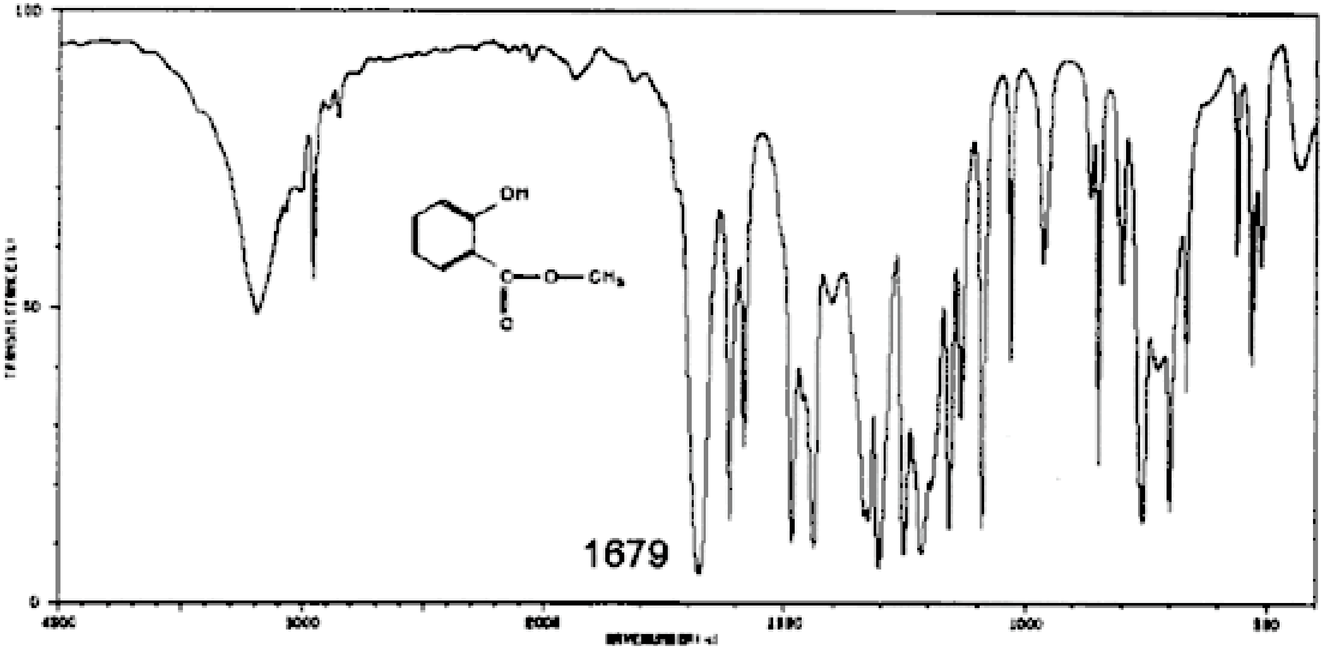
C=O : 1765 cm^{-1}

C-O 1215 cm^{-1}

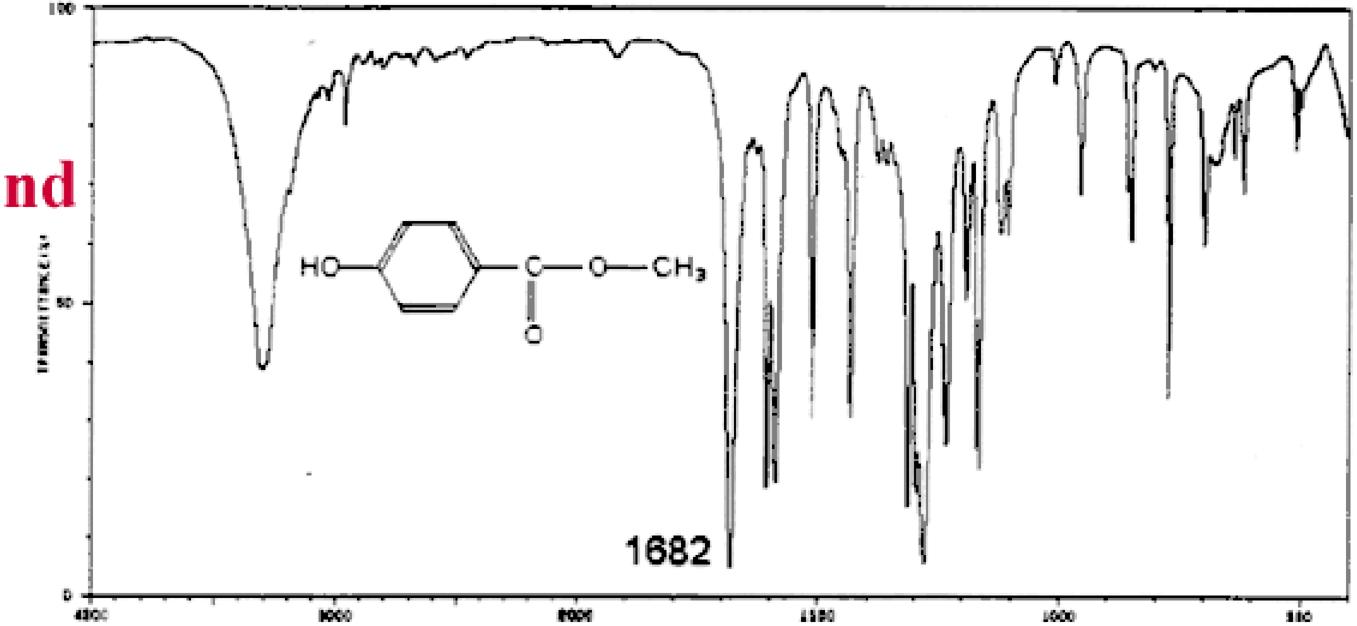
1193 cm^{-1}

Ester carbonyl: C=O

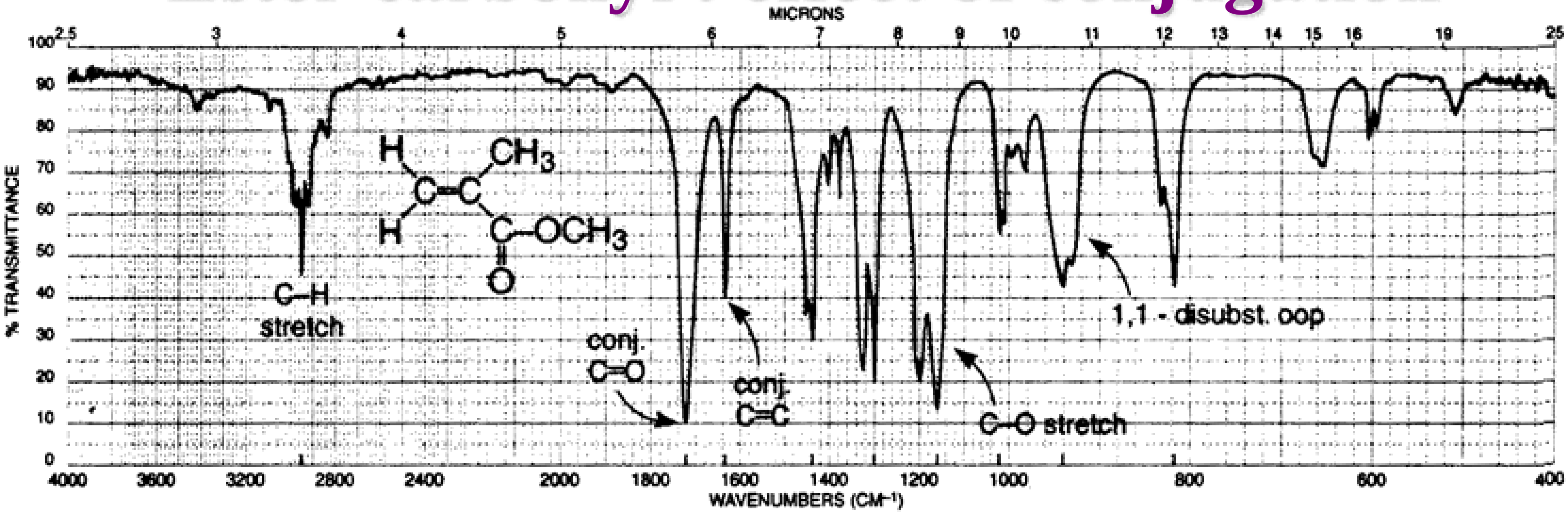
Conjugated Ester With H-Bond



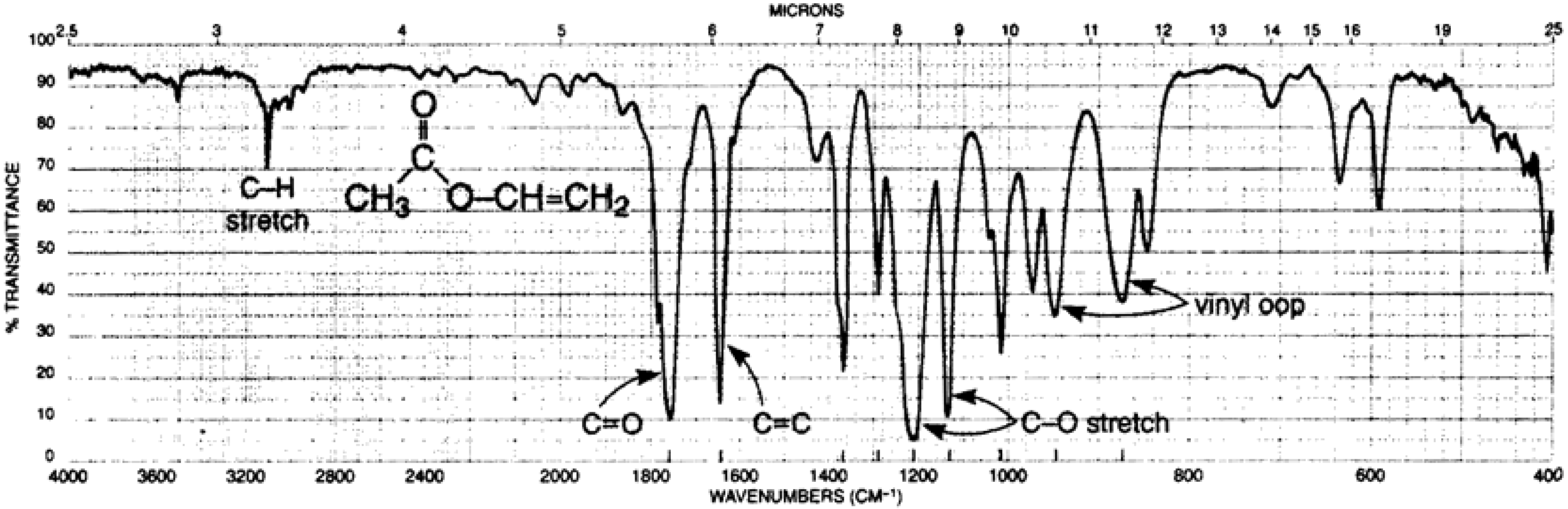
Conjugated Ester Without H-Bond



Ester carbonyl : effect of conjugation



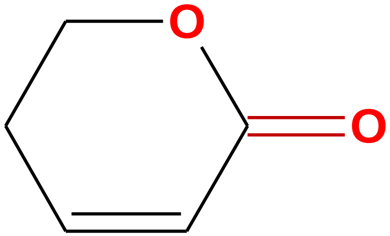
▶ **FIGURE 2.48** The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).



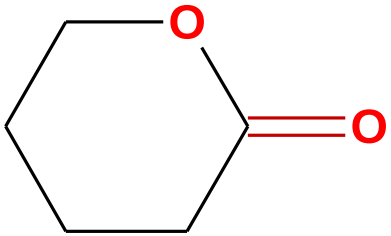
▶ **FIGURE 2.49** The infrared spectrum of vinyl acetate (neat liquid, KBr plates).

Lactone carbonyl: C=O

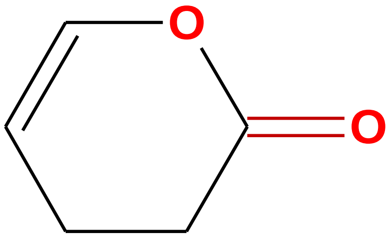
Lactones ➔ Cyclic Ester



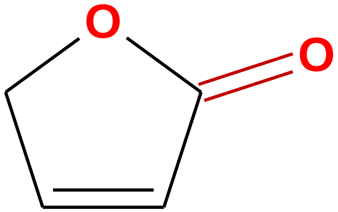
1720



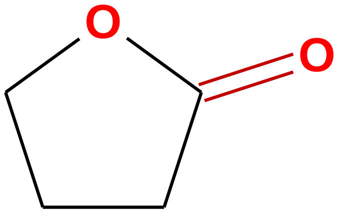
1735



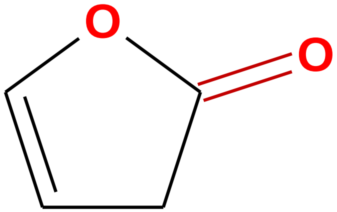
1760



1750



1770

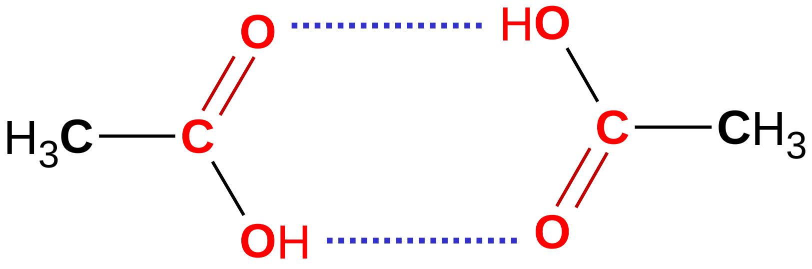


1800

Carbonyl compounds : Acids

Carboxylic acid

Exist as dimer :



Strong Hydrogen bond

OH : Very broad ➔ 3400 – 2400 cm^{-1}

C=O : broad ➔ 1730 – 1700 cm^{-1}

C—O : 1320 – 1210 cm^{-1} Medium intensity

Carbonyl compounds : Acids

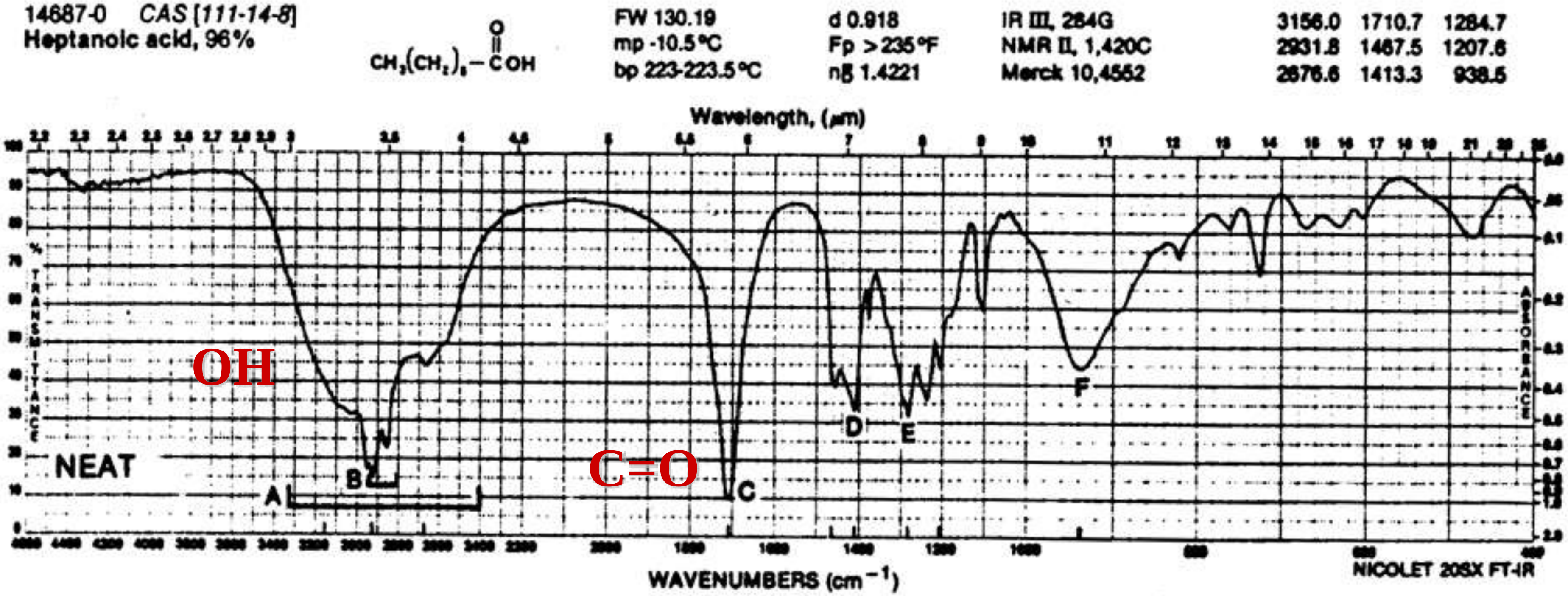


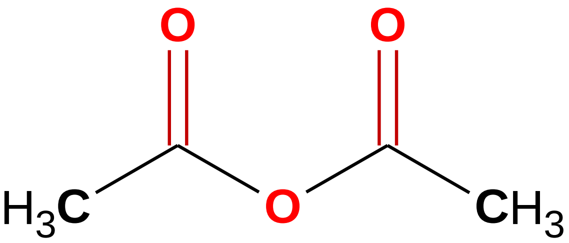
FIGURE 3.23. Heptanoic acid. A. Broad O—H stretch, 3300–2500 cm^{-1}. B. The C—H stretch (see Fig. 3.8), 2950, 2932, 2855 cm^{-1}. Superimposed upon O—H stretch. C. Normal, dimeric carboxylic C=O stretch, 1711 cm^{-1}. D. The C—O—H in-plane bend,* 1413 cm^{-1}. E. The C—O stretch,* dimer, 1285 cm^{-1}. F. The O—H out-of-plane bend, 939 cm^{-1}.
*Bands at D and E involve C—O—H interaction.

C=O : 1711 cm^{-1}

OH : Very Broad 3300 to 2500 cm^{-1}

C-O : 1285, 1207 cm^{-1}

Anhydrides



C=O always has 2 bands:

1830-1800 and 1775-1740 cm^{-1}

C—O multiple bands 1300 – 900 cm^{-1}

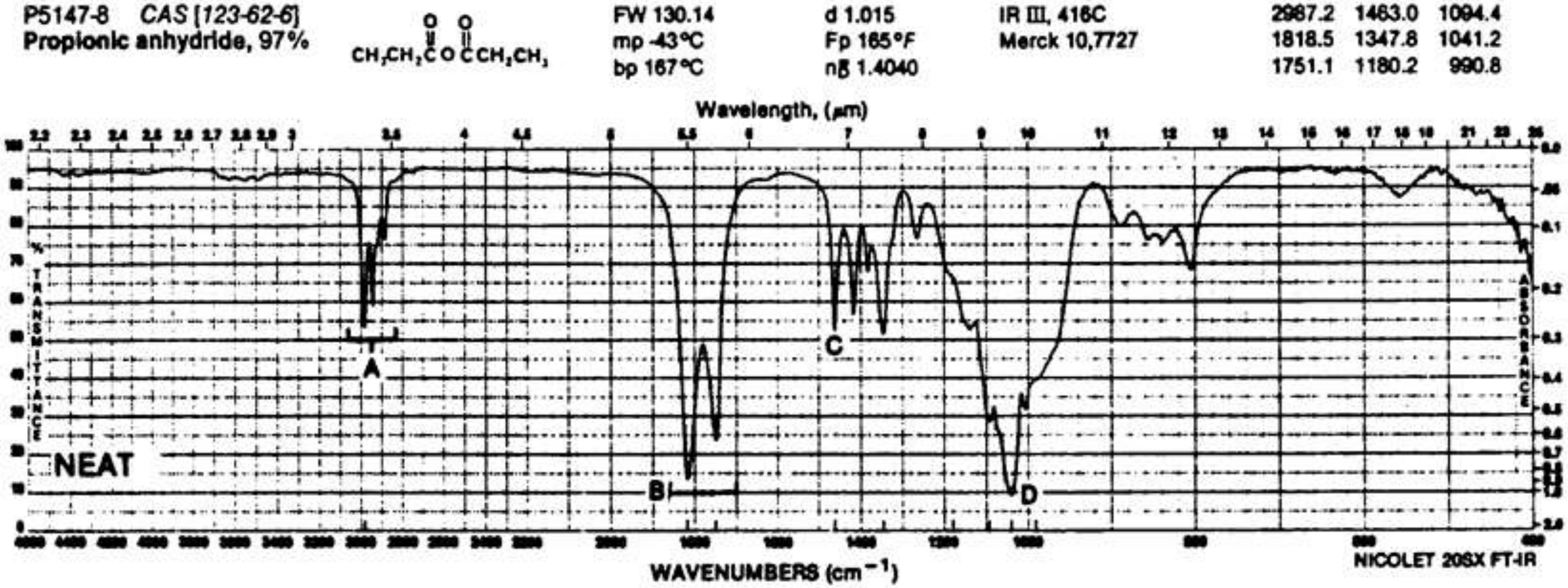


FIGURE 3.27. Propionic anhydride A. The C—H stretch, 2987, 2940, 2880 cm^{-1}. B. Asymetric and symmetric C═O coupled stretching, respectively: 1818, 1751 cm^{-1}. See Table 3.3. C. $\delta_s CH_2$ (scissoring), 1463 cm^{-1}. D. C—CO—O—CO—C stretch, 1041 cm^{-1}.

Carbonyl compounds : Aldehydes

Aldehydes **C=O** $\bar{\nu}$ **~ 1725 cm^{-1}**

Conjugation => lower freq.

O=C-H : 2 weak bands 2750, 2850 cm^{-1}

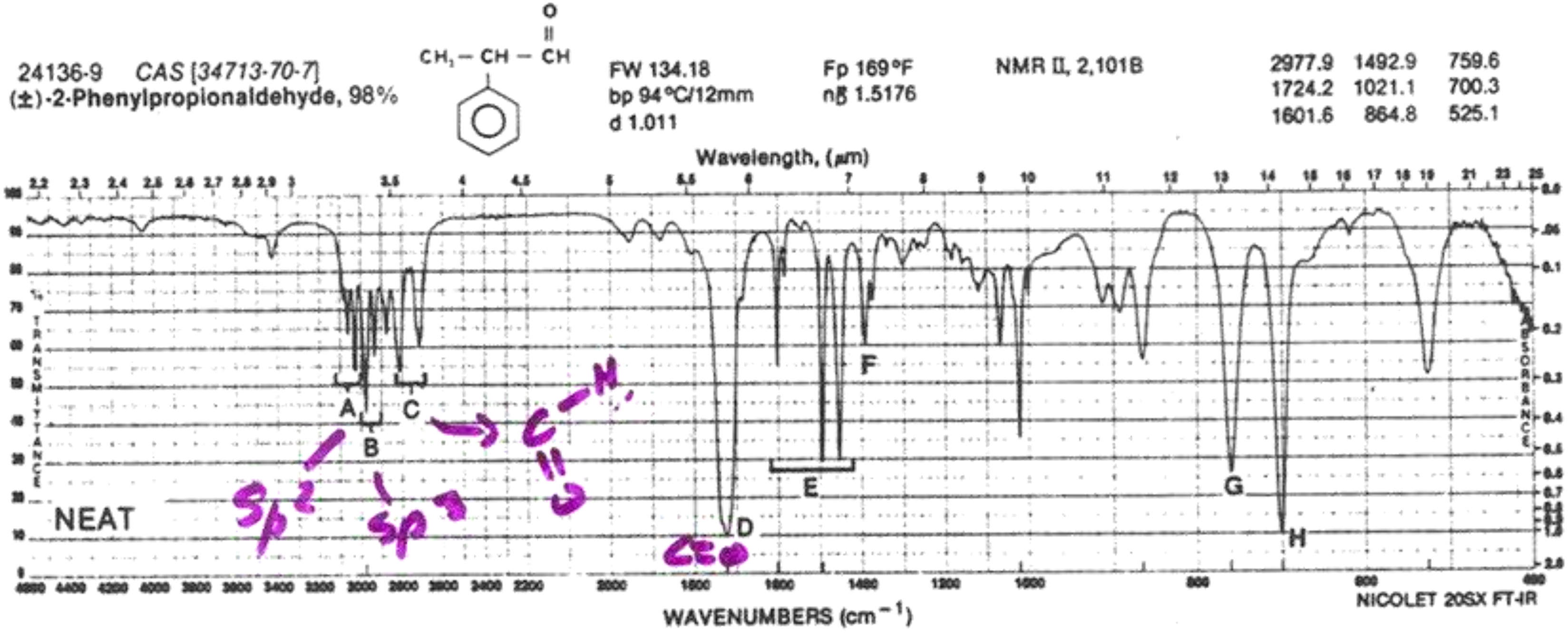


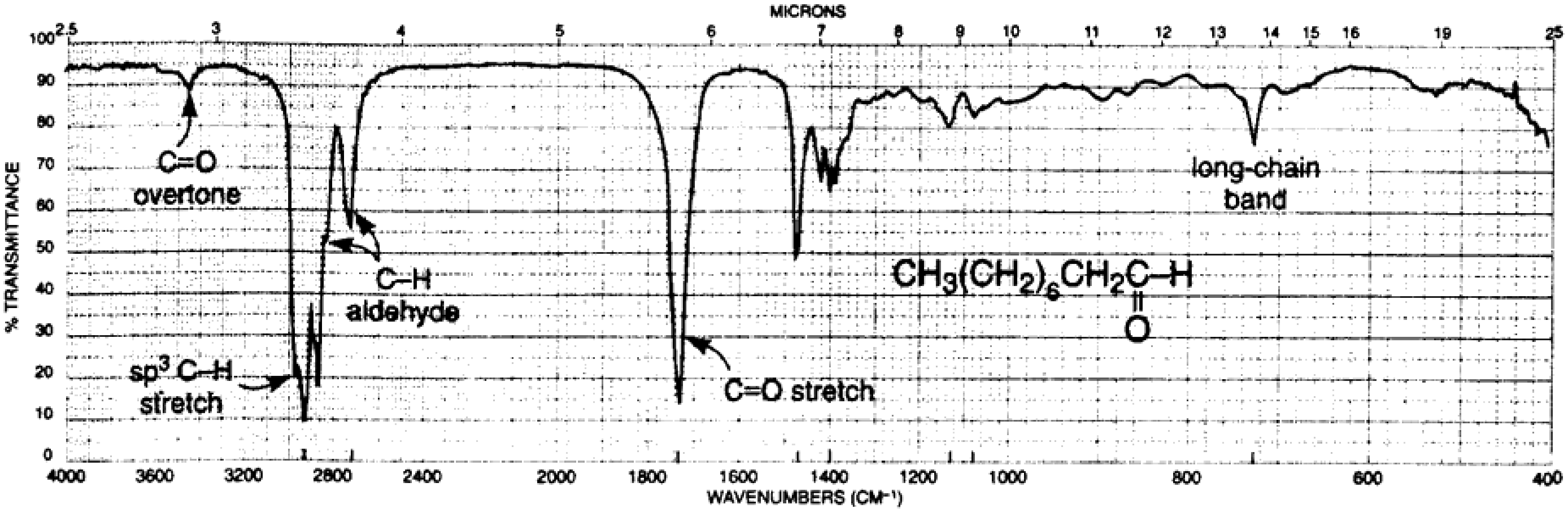
FIGURE 3.22. (±)-2-Phenylpropionaldehyde. A.* Aromatic, 3070, 3040 cm^{-1} (see Fig. 3.13). B.* Aliphatic, 2978, 2940, 2875 cm^{-1} (see Figs. 3.8 and 3.13). C.* Aldehydic, C—H stretch, 2825, 2720 cm^{-1}. Doublet from Fermi resonance with overtone of band at F. D. Normal aldehydic C=O stretch, 1724 cm^{-1}. Conjugated C=O stretch would be about 1700 cm^{-1}, for example, as for C_6H_5CHO. E. Ring C=C stretch, 1602, 1493, 1455 cm^{-1}. F. Aldehydic C—H bend, 1390 cm^{-1}. G. Out-of-plane C—H bend, 760 cm^{-1}. H. Out-of-plane C=C bend, 700 cm^{-1}.

*Bands A—C are C—H stretch absorptions

Source: Courtesy of Aldrich Chemical Company.

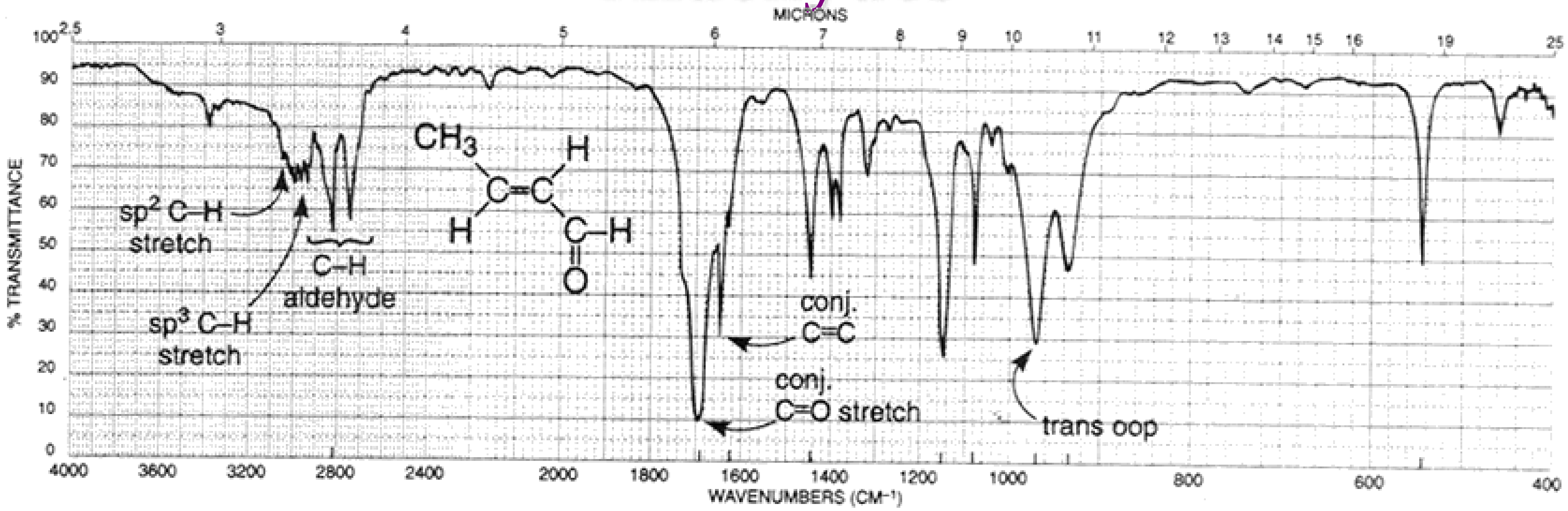
C=O : 1724 cm^{-1}

Carbonyl compounds : Aldehydes

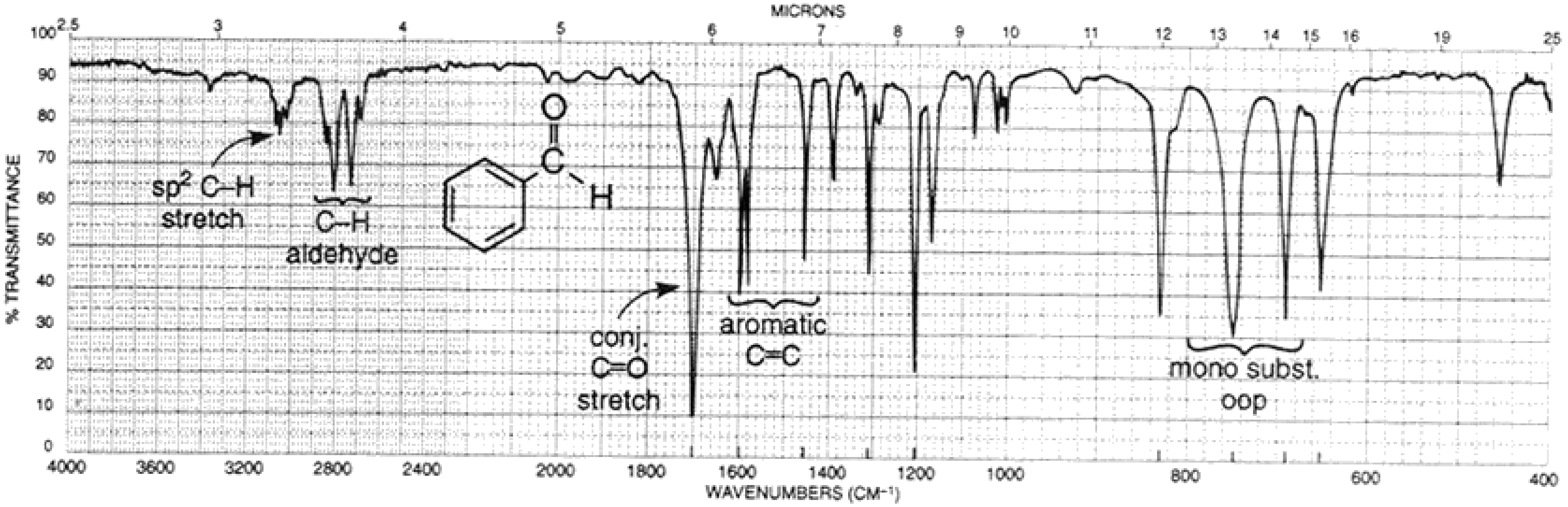


► **FIGURE 2.36** The infrared spectrum of nonanal (neat liquid, KBr plates).

Aldehydes



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



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

Other carbonyl

Amides

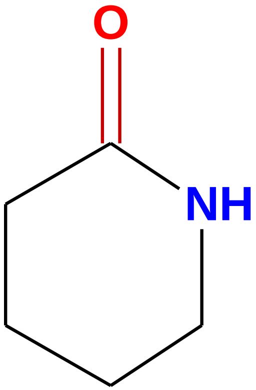
C=O ~1680-1630 cm^{-1} (band I)

NH_2 ~ 3350 and 3180 cm^{-1} (stretch)

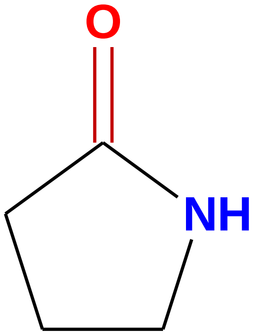
NH ~ 3300 cm^{-1} (stretch)

NH ~ 1640-1550 cm^{-1} (bending)

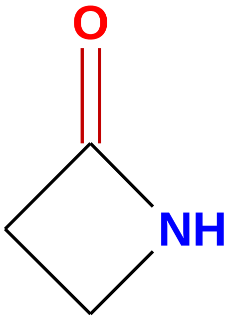
Lactams



~1660



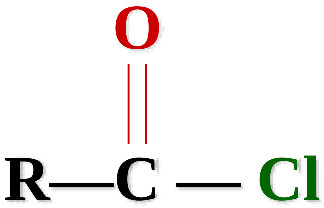
~1705



~1745

$\bar{\nu}$ Increase with strain

Acid Chlorides

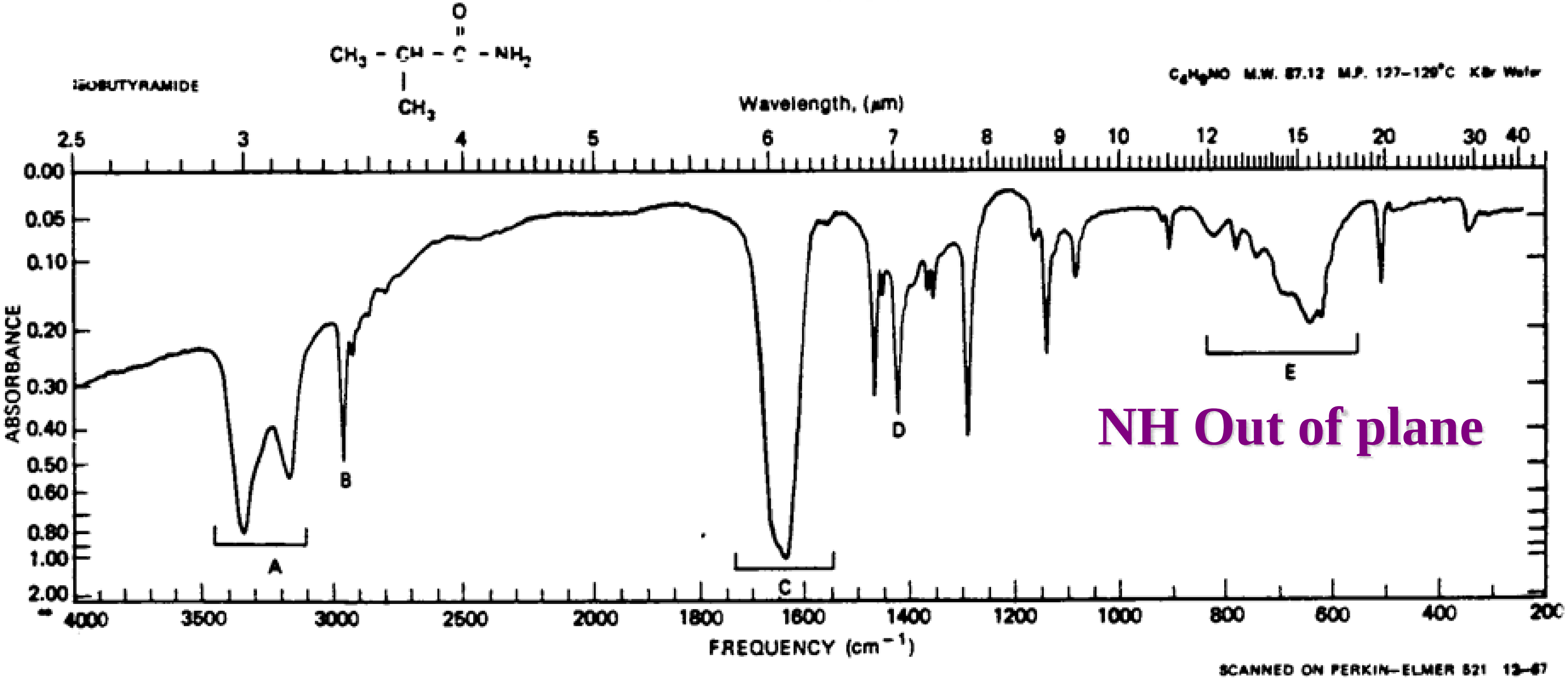


$R-C(=O)-Cl$

1810-1775 cm^{-1}

C — Cl 730 – 550 cm^{-1}

Amides



NH Out of plane

FIGURE 3.28. 2-methylpropanamide.* A. The N—H stretch, coupled, primary amide, hydrogen bonded; asymmetric, 3352 cm^{-1}; symmetric, 3170 cm^{-1}. B. Aliphatic C—H stretch, 2960 cm^{-1}. C. Overlap C=O stretch, amide I band, 1640 cm^{-1}; see Table 3.3. N—H bend, amide II band, 1640 cm^{-1}. D. The C—N stretch, 1425 cm^{-1}. E. Broad N—H out-or-plane bend 700–600 cm^{-1}.

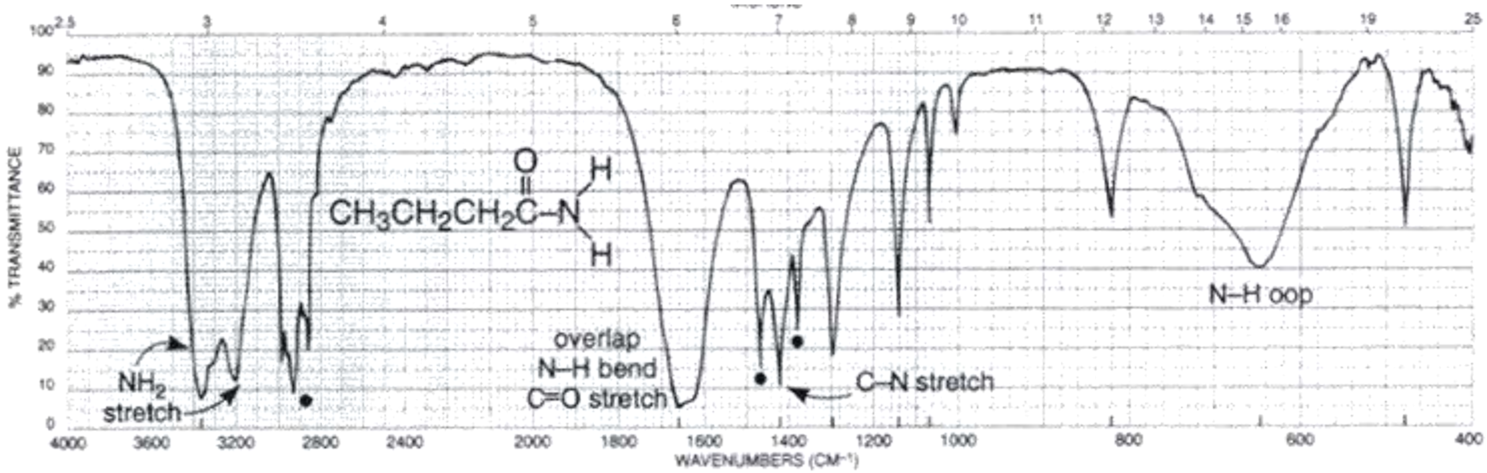
*The CA name for isobutyramide is 2-methylpropanamide.

NH_2 : Symmetrical stretch =>3170 cm^{-1}

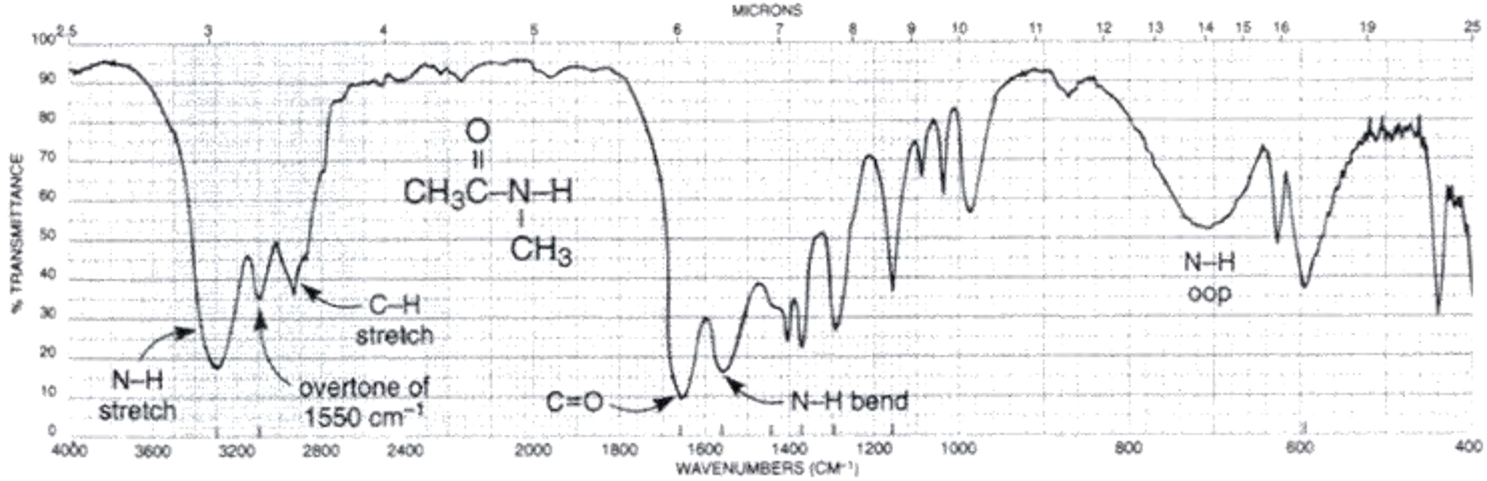
asymmetrical stretch => 3352 cm^{-1}

C=O : 1640 cm^{-1}

Amides

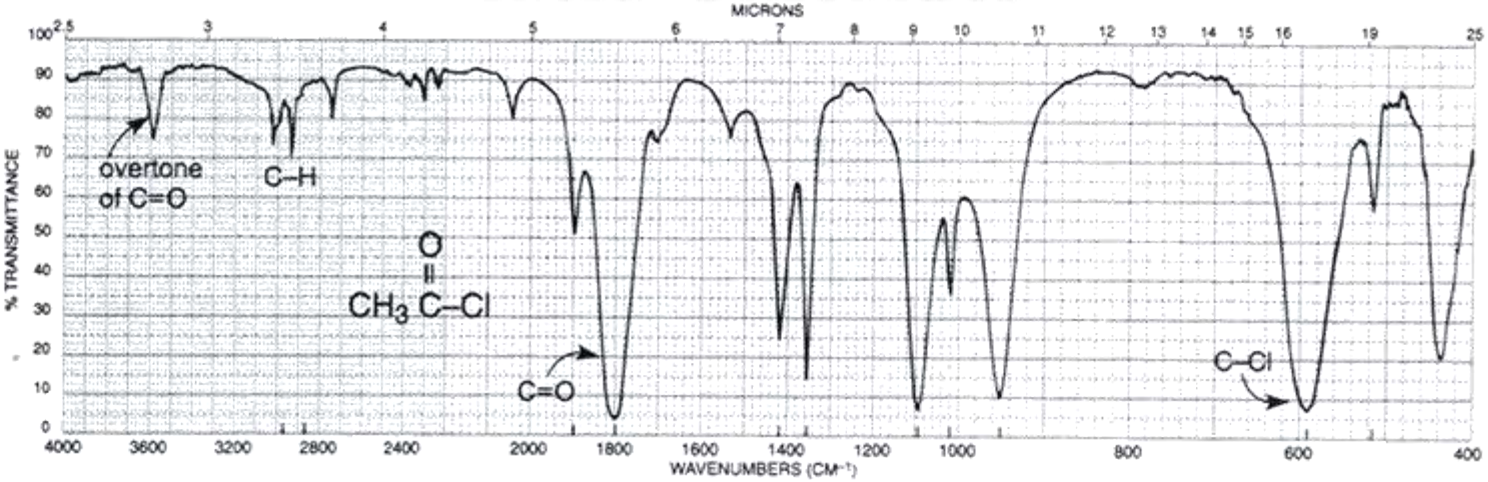


► **FIGURE 2.53** The infrared spectrum of propionamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

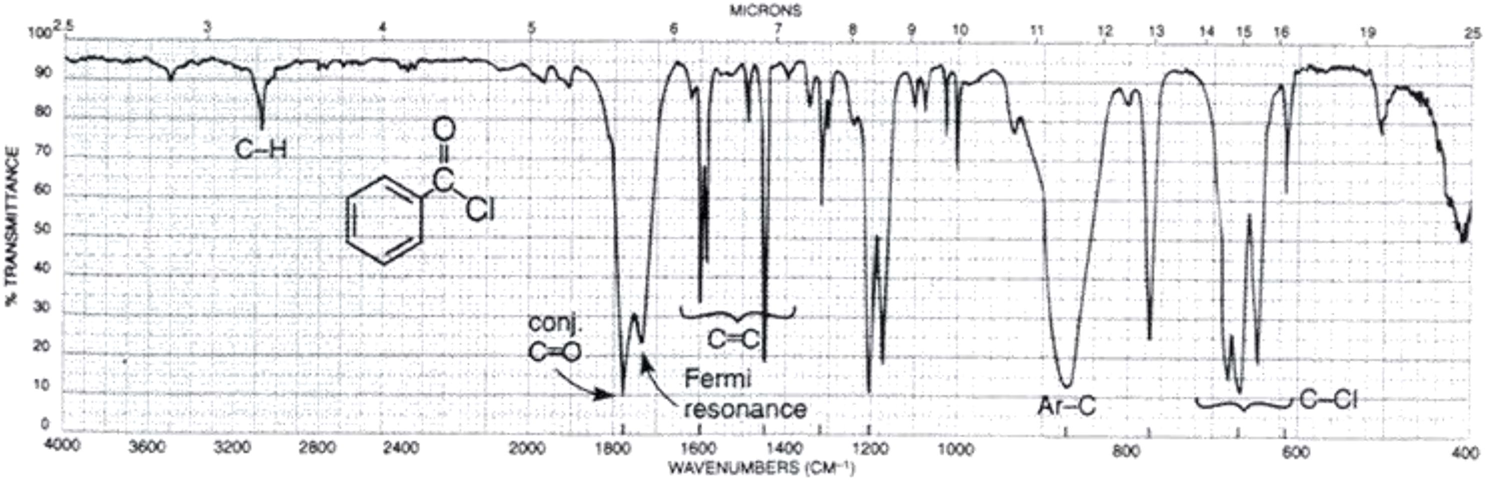


► **FIGURE 2.54** The infrared spectrum of *N*-methylacetamide (neat liquid, KBr plates).

Acid Chlorides



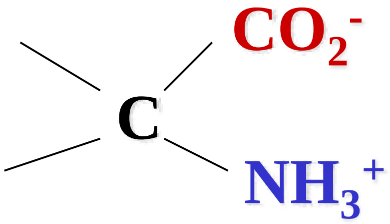
▶ **FIGURE 2.55** The infrared spectrum of acetyl chloride (neat liquid, KBr plates).



▶ **FIGURE 2.56** The infrared spectrum of benzoyl chloride (neat liquid, KBr plates).

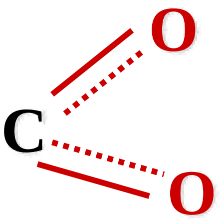
Amino acid

Exist as zwitterions



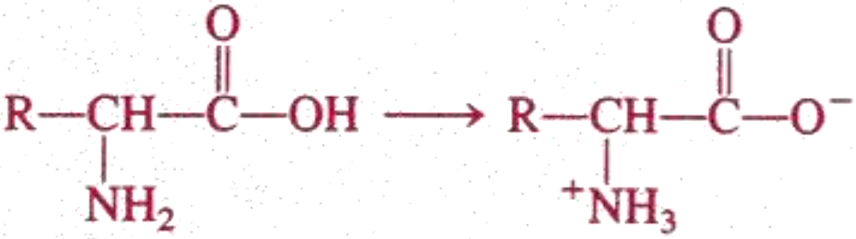
NH_3^+ : very broad 3330-2380

(OH + NH_3^+)



1600 – 1590 strong

Amino acid



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

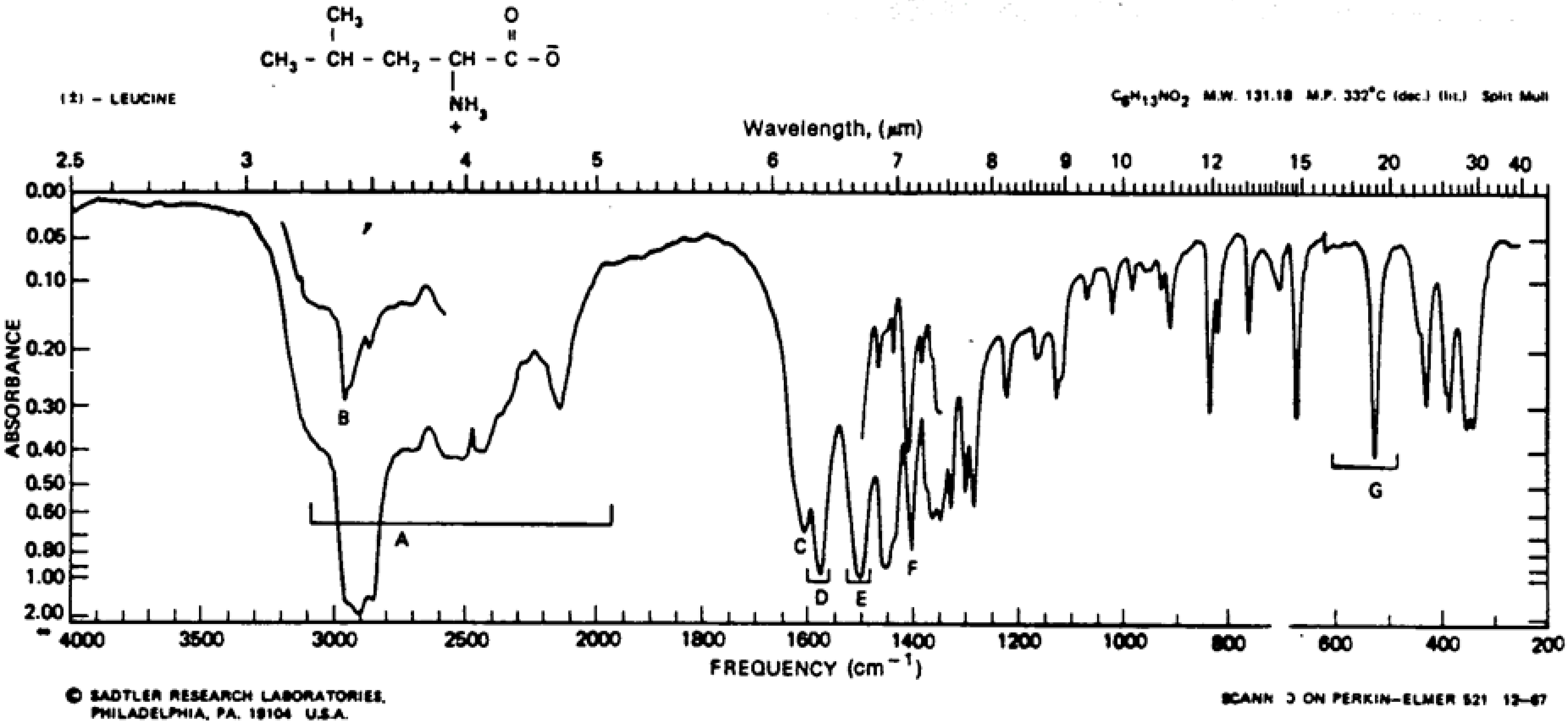


FIGURE 3.30. (±)-Leucine. A. Broad (—NH_3^+) N—H stretch, 3100–2000 cm^{-1}, extended by combination band at 2140 cm^{-1}, and other combination-overtone bands. B. Aliphatic C—H stretch (superimposed on N—H stretch), 2967 cm^{-1}. C. Asymmetric (—NH_3^+) N—H bend, 1610 cm^{-1}. D. Asymmetric carboxylate $(C\overset{\cdots}{=}O)_2$ stretch, 1580 cm^{-1}. E. Symmetric (—NH_3^+) N—H bend, 1505 cm^{-1}. F. Symmetric carboxylate $(C\overset{\cdots}{=}O)_2$ stretch, 1405 cm^{-1}. G. Torsional (—NH_3^+) N—H oscillation, 525 cm^{-1}.

Amine

NH 3500 – 3300 cm^{-1}

NH : 2 bands
NH : 1 band

NH bending : 1650 – 1500 cm^{-1}

C-N : 1350 – 1000 cm^{-1}

NH out-of-plane : ~ 800 cm^{-1}

Amine salt

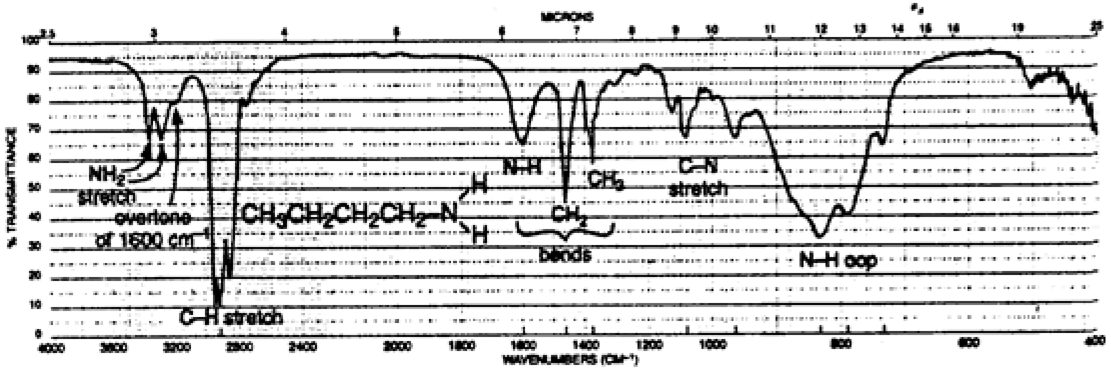
NH^+ 3500 – 3030 cm^{-1} broad / strong

Ammonium ➔ primary ➔ secomdary ➔ right $\bar{\nu}$

Left $\bar{\nu}$

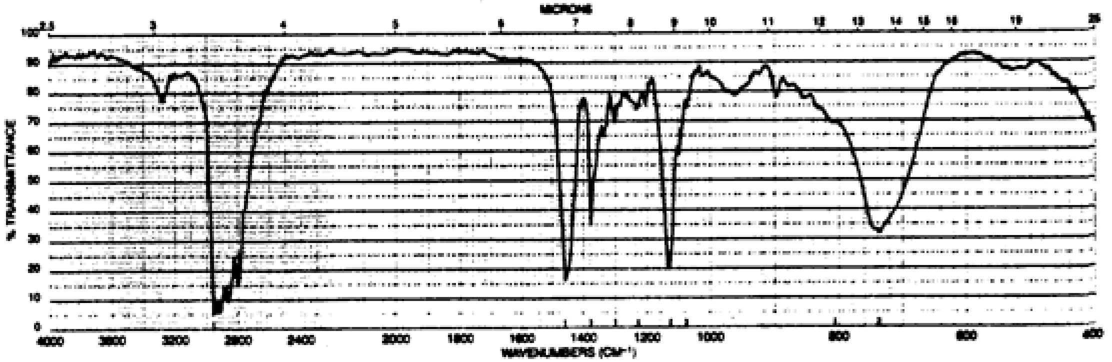
Amine

Primary Amine



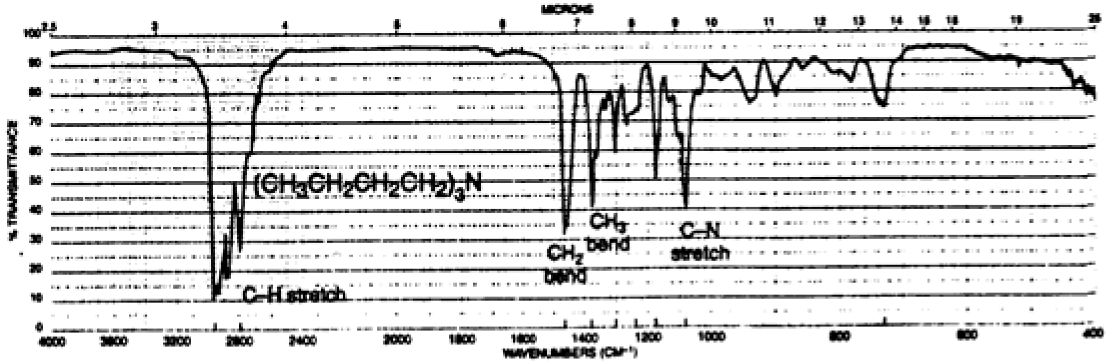
► FIGURE 2.58 The infrared spectrum of butylamine (neat liquid, KBr plates).

Secondary Amine



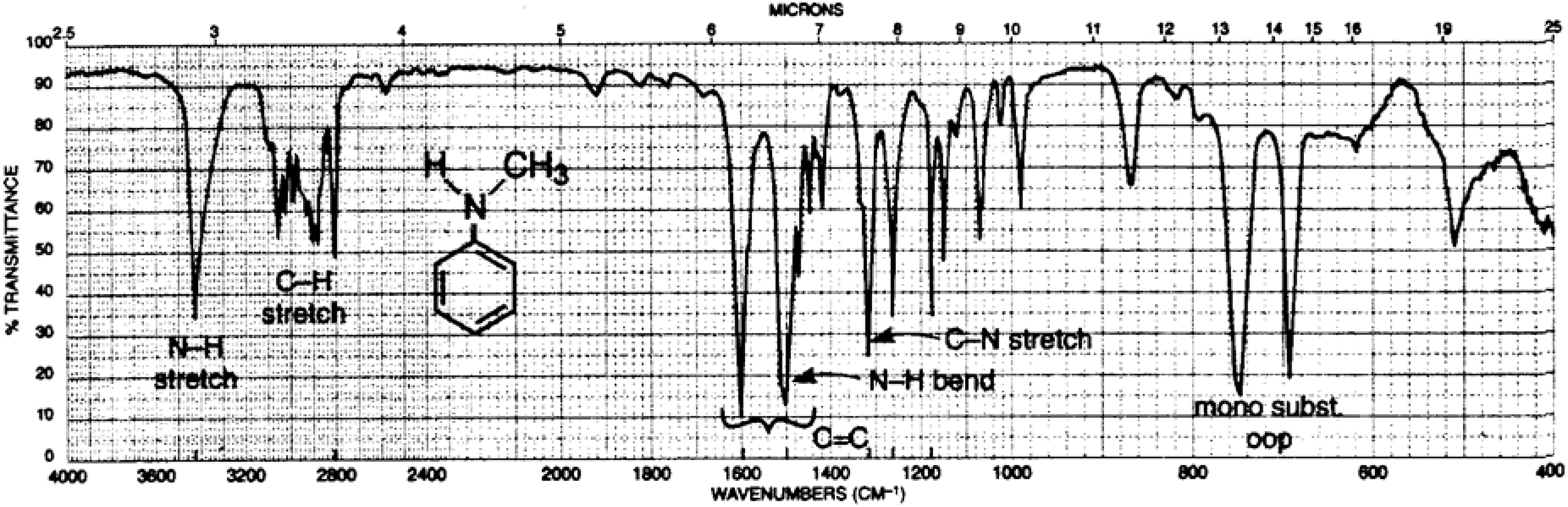
► FIGURE 2.59 The infrared spectrum of dibutylamine (neat liquid, KBr plates).

Tertiary Amine



► FIGURE 2.60 The infrared spectrum of tributylamine (neat liquid, KBr plates).

Aromatic Amine

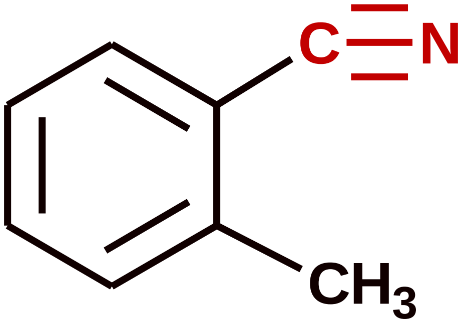


▶ **FIGURE 2.61** The infrared spectrum of *N*-methylaniline (neat liquid, KBr plates).

Other Nitrogen Compounds

Nitriles	**$R{-}C{\equiv}N$:**	**Sharp 2250 cm^{-1}** ***Conjugation moves to lower frequency***
Isocyanates	**$R{-}N{=}C{=}O$**	**Broad ~ 2270 cm^{-1}**
Isothiocyanates	**$R{-}N{=}C{=}S$**	**2 Broad peaks ~ 2125 cm^{-1}**
Imines / Oximes	**$R_2C{=}N{-}R$**	**1690 - 1640 cm^{-1}**

Nitrile



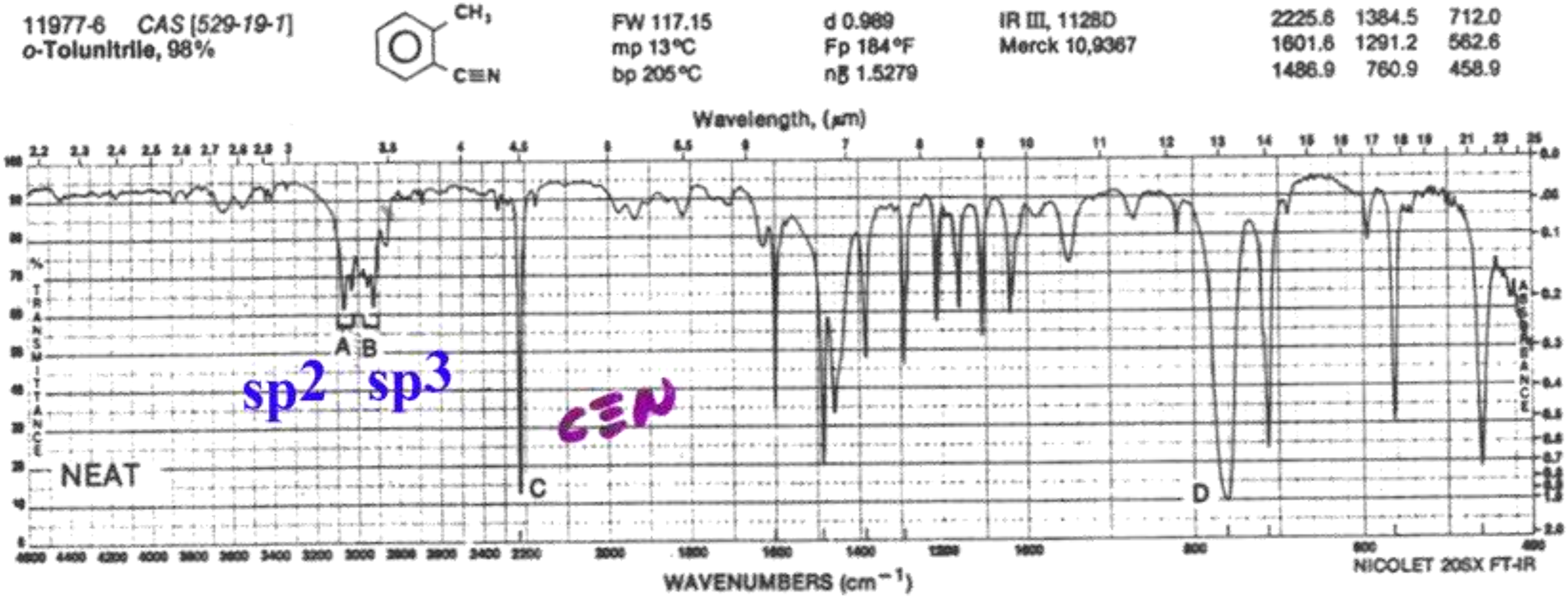
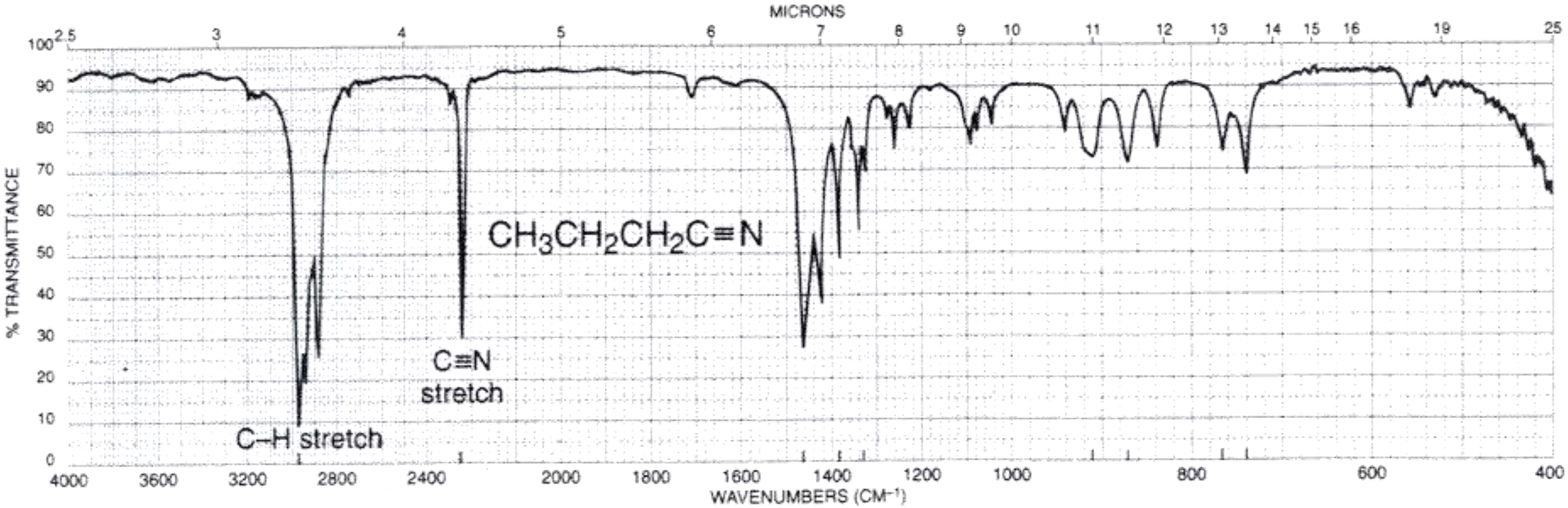


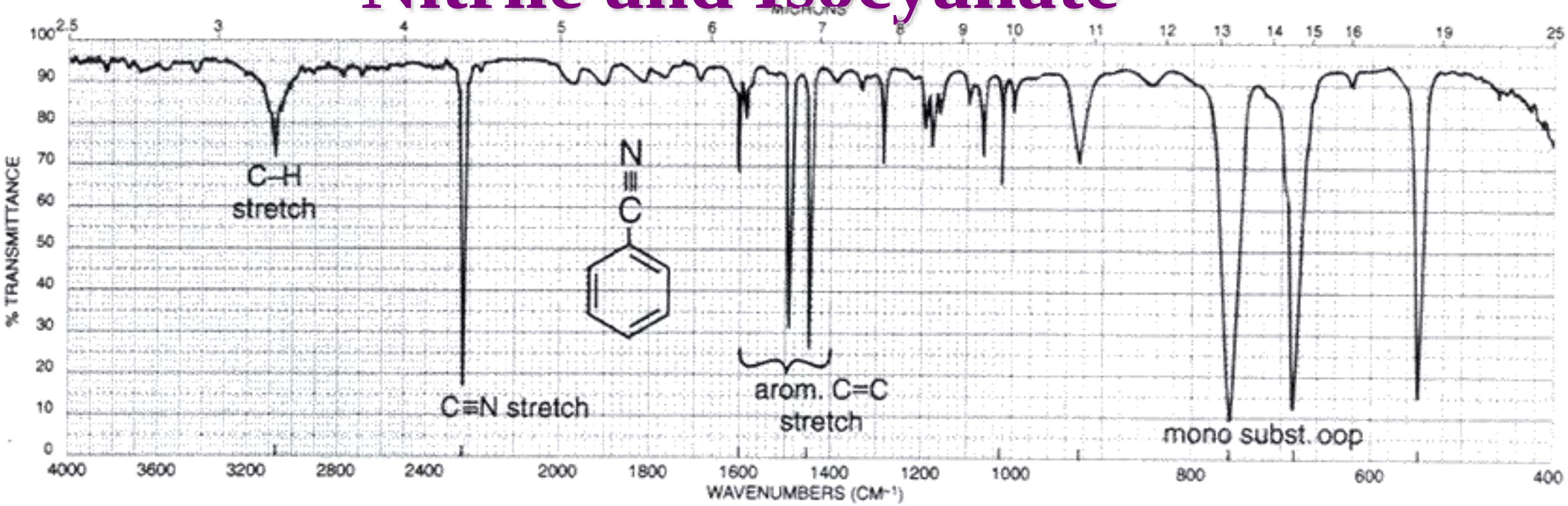
FIGURE 3.31. *o*-Tolunitrile. A. Aromatic C—H stretch, 3070, 3030 cm^{-1}. B. Aliphatic C—H stretch, 2960, 2930 cm^{-1}. C. The C≡N stretch, 2226 cm^{-1} (intensified by aryl conjugation; aliphatic nitriles absorb a higher frequency). D. Out-of-plane C—H bend (aromatic ring) D, 761 cm^{-1}.

Nitrile

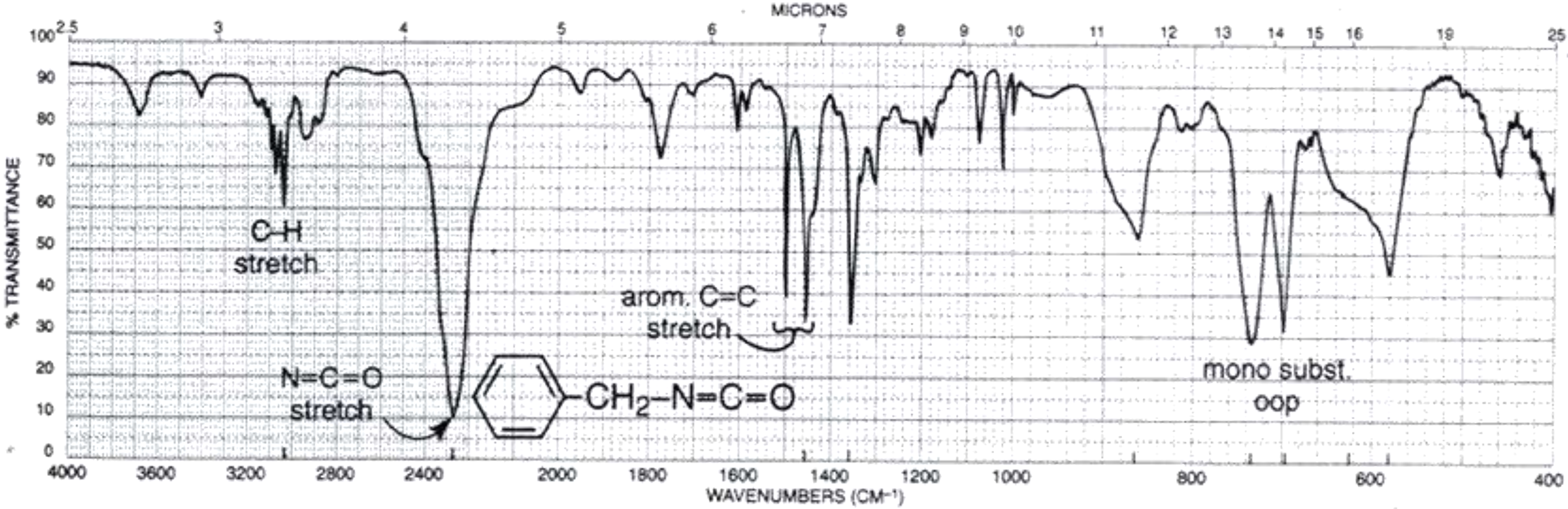


▶ **FIGURE 2.62** The infrared spectrum of butyronitrile (neat liquid, KBr plates).

Nitrile and Isocyanate

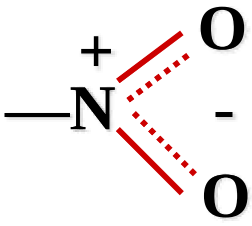


▶ **FIGURE 2.63** The infrared spectrum of benzonitrile (neat liquid, KBr plates).



▶ **FIGURE 2.64** The infrared spectrum of benzyl isocyanate (neat liquid, KBr plates).

Nitro



Aliphatic : Asymmetric : 1600-1530 cm^{-1}

Symmetric : 1390-1300 cm^{-1}

Aromatic : Asymmetric : 1550-1490 cm^{-1}

Symmetric : 1355-1315 cm^{-1}

Nitro

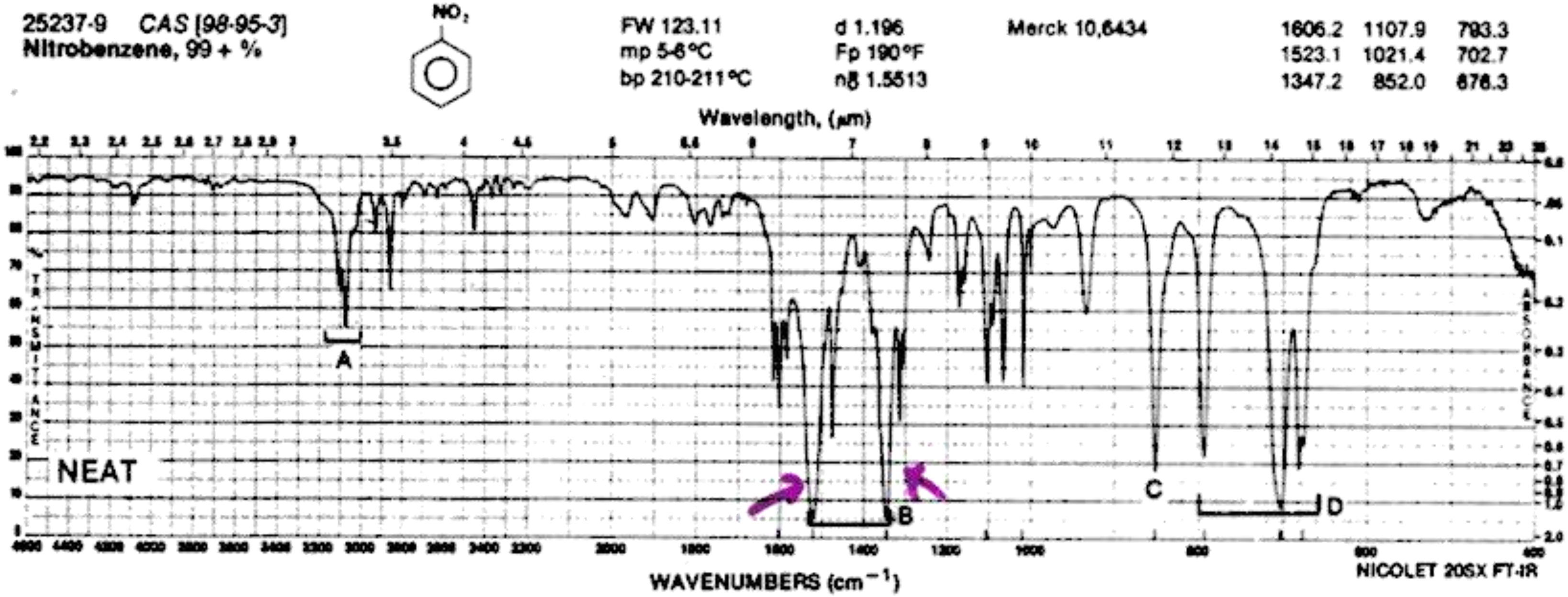
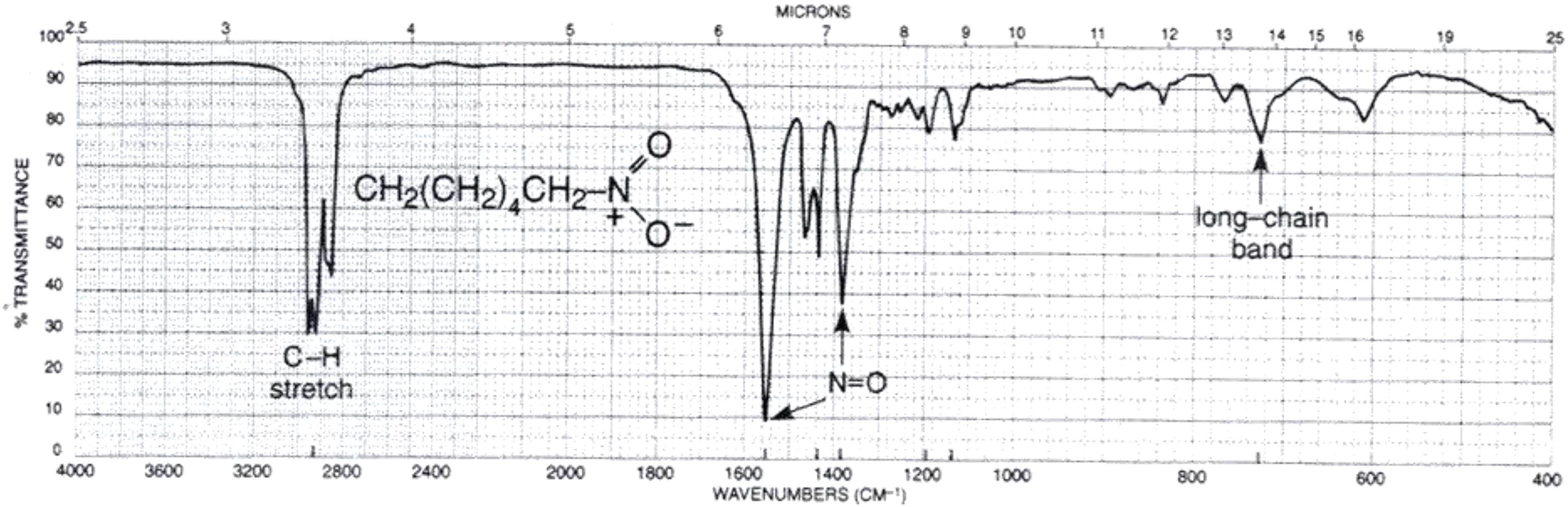


FIGURE 3.32. Nitrobenzene. A. Aromatic C—H stretch, 3100, 3080 cm^{-1}. B. Asymmetric ($ArNO_2$) $(N{=}O)_2$ stretch, 1523 cm^{-1}. Symmetric ($ArNO_2$) $(N{=}O)_2$ stretch 1347 cm^{-1}. C. C—N stretch for $ArNO_2$, 852 cm^{-1}. D. Low-frequency bands are of little use in determining the nature of ring substitution since these absorption patterns result from interaction of NO_2 and C—H out-of-plane bending frequencies. The inability of the "oop" region to reveal structural information is typical of aromatic compounds with highly polar substituents.

NO_2 : { 1523 Asym.
{ 1347 sym

Nitro



▶ **FIGURE 2.65** The infrared spectrum of 1-nitrohexane (neat liquid, KBr plates).

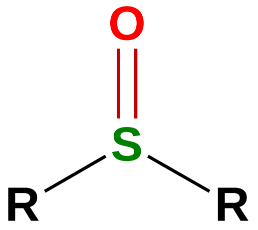
Sulfur

Mercaptans S – H : weak 2600-2550 cm^{-1}

Since only few absorption in that range it confirm its presence

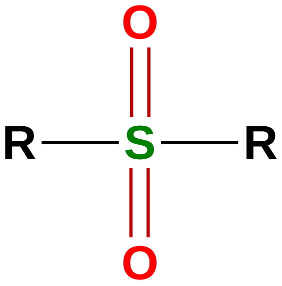
Sulfides,Disulfides : no useful information

Sulfoxides:



Strong ~ 1050 cm^{-1}

Sulfones:



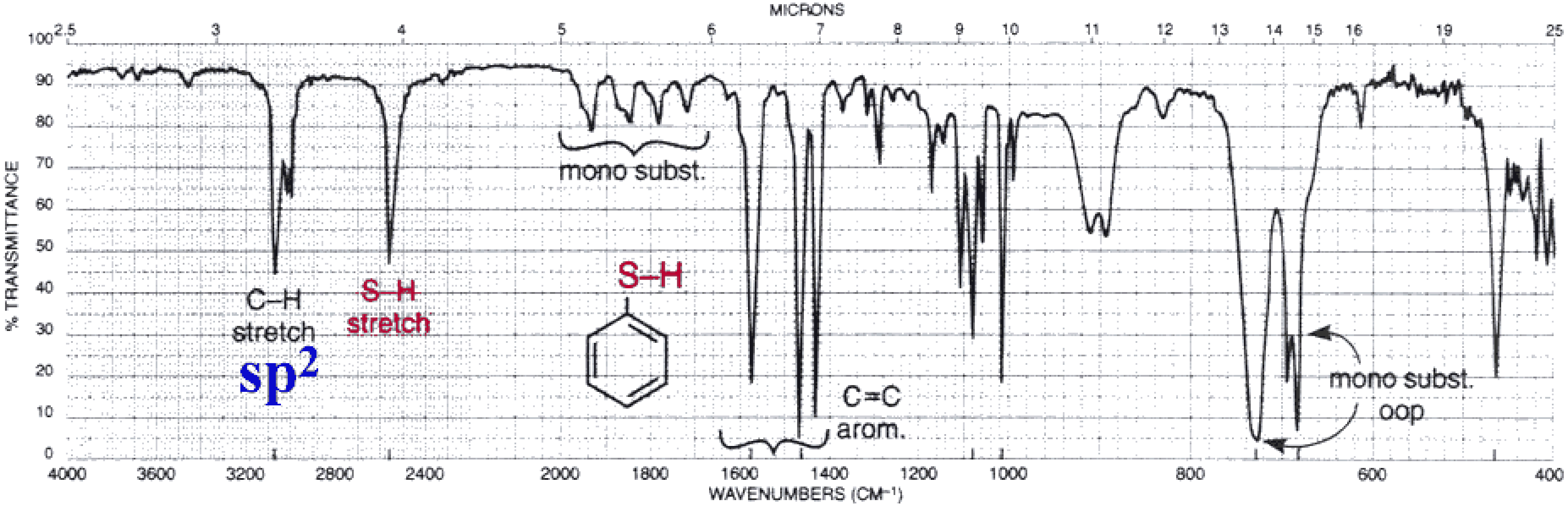
$$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R$$

2 bands :

Asymetrical ~ 1300 cm^{-1}

Symetrical ~ 1150 cm^{-1}

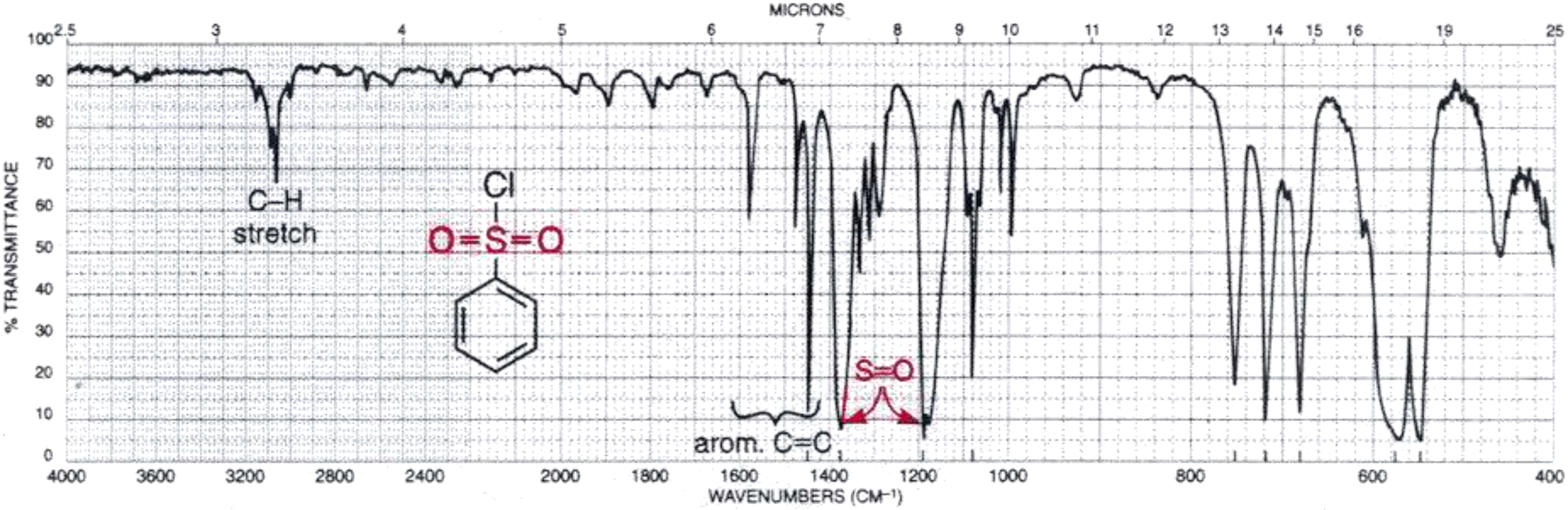
Sulfur: Mercaptan R-S-H



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

Sulfur: Sulfonyl Chloride

S=O : Asymmetrical stretch: 1375 cm-1
Symmetrical Stretch : 1185 cm-1

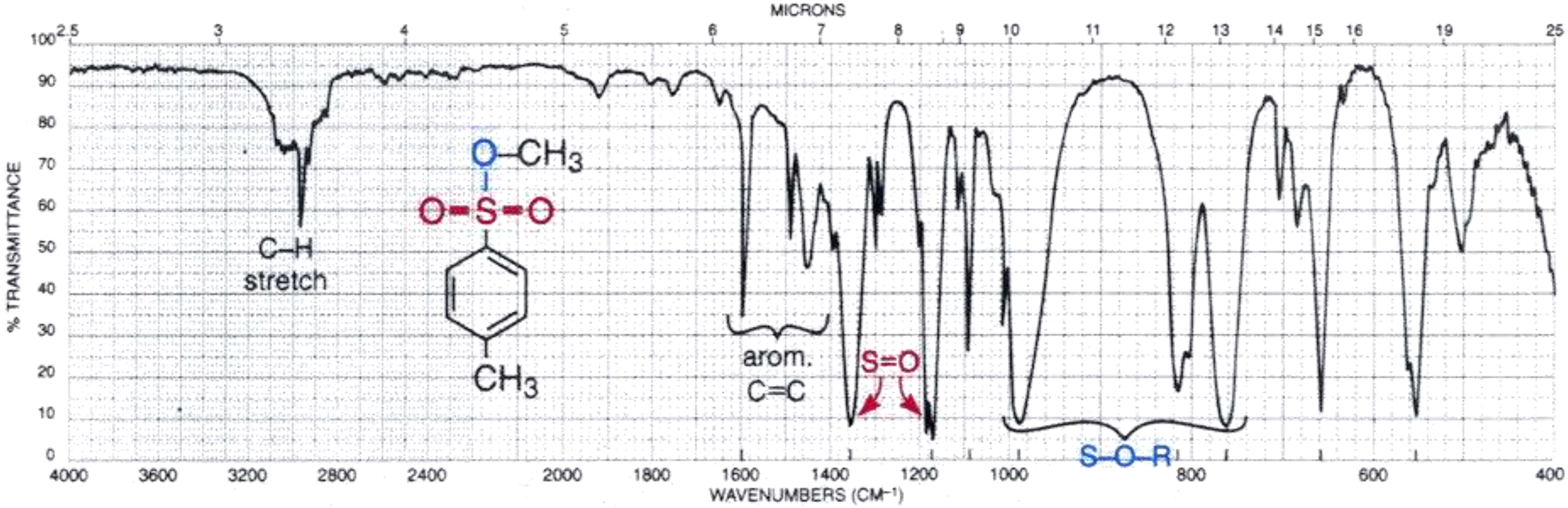


▶ **FIGURE 2.69** The infrared spectrum of benzenesulfonyl chloride (neat liquid, KBr plates).

Sulfur: Sulfonate

S=O : Asymmetrical stretch: 1350 cm-1
Symmetrical Stretch : 1175 cm-1

S-O : several bands between 1000 – 750 cm^{-1}



▶ **FIGURE 2.70** The infrared spectrum of methyl *p*-toluenesulfonate (neat liquid, KBr plates).

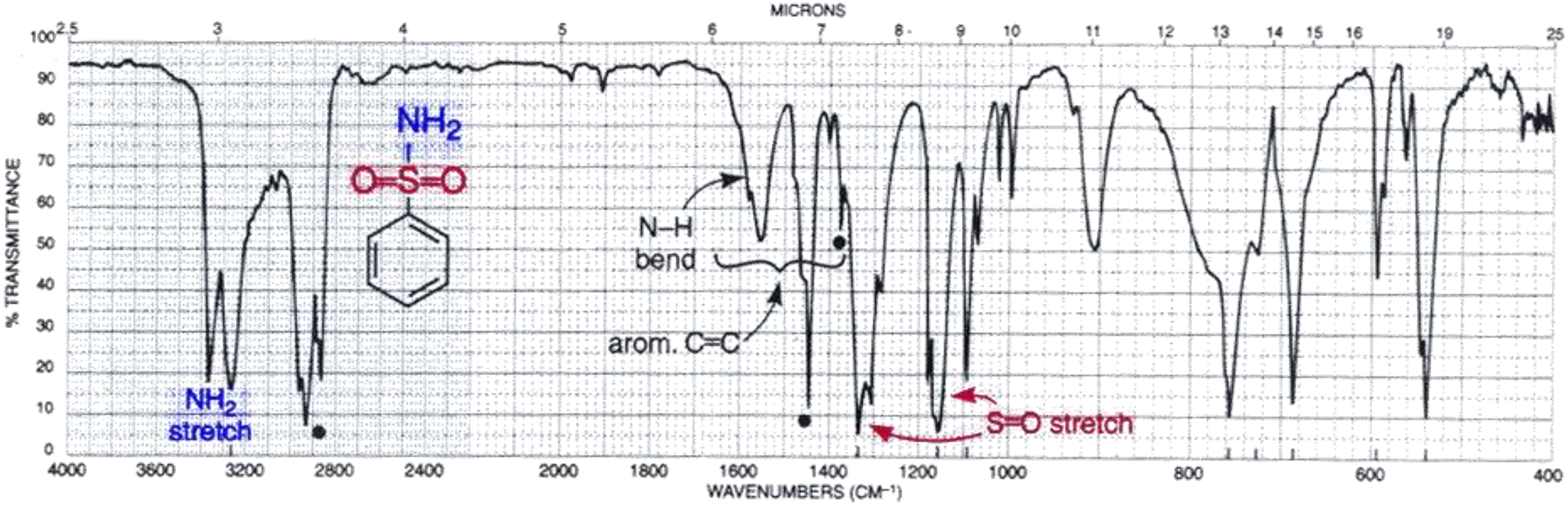
Sulfur: Sulfonamide

S=O : Asymmetrical stretch: 1325 cm-1

Symmetrical Stretch : 1140 cm-1

NH_2 stretch: 3350 and 3250 cm^{-1}

NH Bend: 1550 cm^{-1}



▶ **FIGURE 2.71** The infrared spectrum of benzenesulfonamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

Halogens

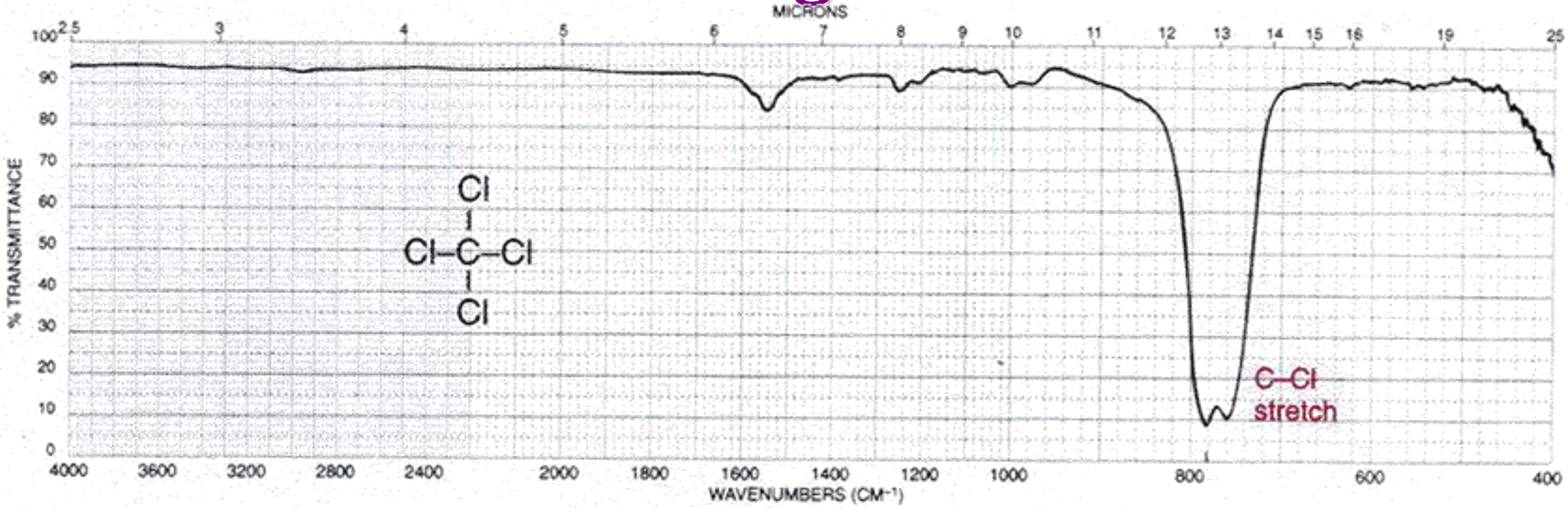
C—F : 1400 – 1000 cm^{-1}

C—Cl : strong 785 – 540 cm^{-1}

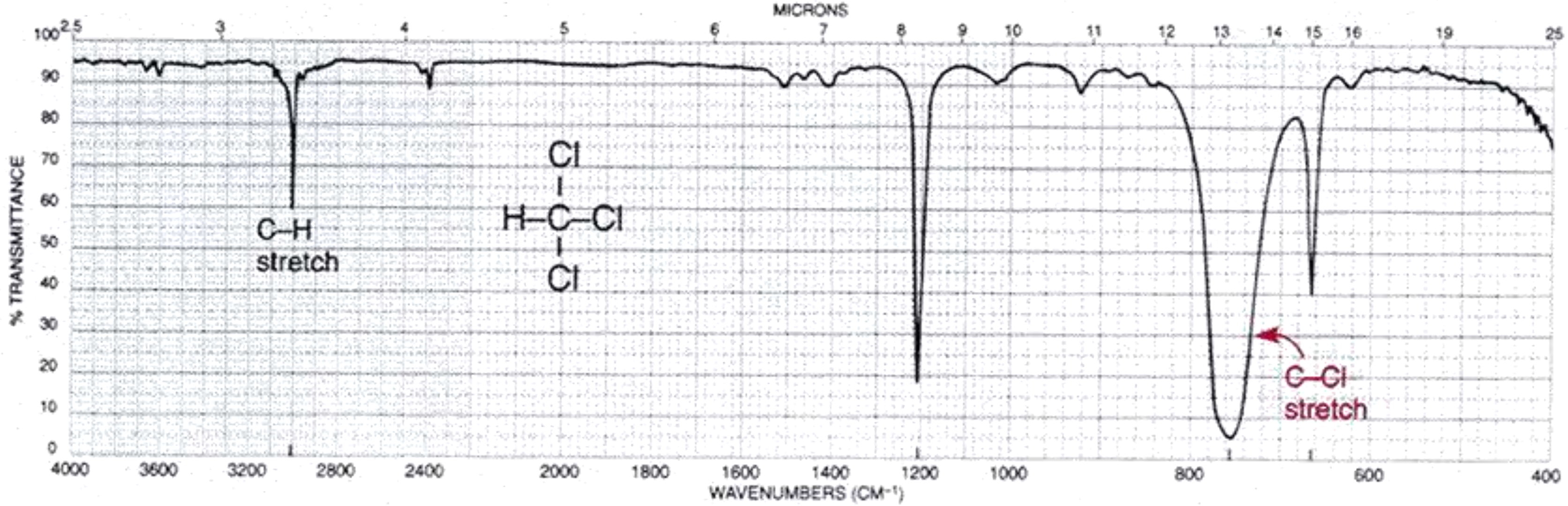
C—Br : 650 – 510 cm^{-1} (out of range with NaCl plates)

C—I : 600 – 485 cm^{-1} (out of range)

Halogens



▶ **FIGURE 2.72** The infrared spectrum of carbon tetrachloride (neat liquid, KBr plates).



▶ **FIGURE 2.73** The infrared spectrum of chloroform (neat liquid, KBr plates).