

# Chemistry

## 3<sup>rd</sup> Year

IR Spectroscopy

# Infrared

10,000  $\text{cm}^{-1}$  to 100  $\text{cm}^{-1}$

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

Older system uses the wavelenght  $\lambda$  ( $\mu\text{m}$  =>  $10^{-6}$  m)

$$\text{cm}^{-1} = 10^4 / \mu\text{m}$$

$\bar{\nu}$  Depends on:

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

# The Units:

The frequency  $\nu$  ( $\text{s}^{-1}$ )  $\Rightarrow$  # vibrations per second

For molecular vibrations, this number is very large ( $10^{13} \text{ s}^{-1}$ )  $\Rightarrow$  inconvenient

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

$$\bar{\nu} = \frac{\nu}{c} \quad (\text{Frequency} / \text{Velocity})$$

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

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

Wave Length :  $\lambda$

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

# Intensity in IR

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

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

Absorbance (**A**)

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

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

# 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

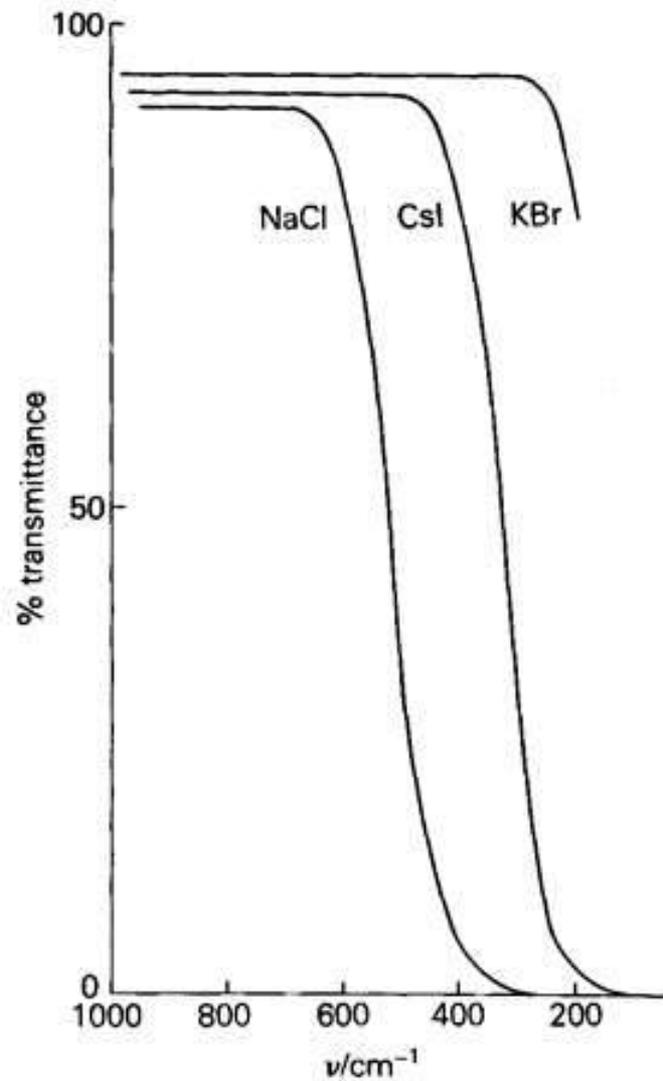
**NaCl, KCl : Cheap, easy to polish**

**NaCl** transparent to **4000 - 650 cm<sup>-1</sup>**

**KCl** transparent to **4000 - 500 cm<sup>-1</sup>**

**KBr** transparent to **400 cm<sup>-1</sup>**

# Infrared: Low frequency spectra of window materials



# Bond length and strength vs Stretching frequency

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

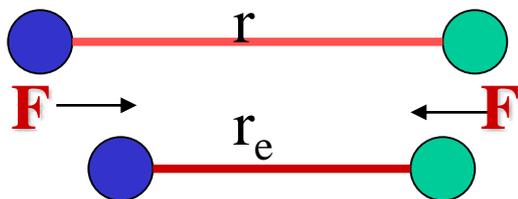
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# Introduction

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

$$F(x) = -kx \quad \text{where } X \text{ is displacement from equilibrium}$$

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

Where  $K_i$  is the force constant and  $\mu_i$  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  $\text{cm}^{-1}$**

# Introduction: Symmetry selection rule

**Stretching homonuclear diatomic molecule like  $\text{N}_2$  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  $\text{cm}^{-1}$

$c$  : Velocity of light  $\Rightarrow 3 * 10^{10} \text{ cm/s}$

$K$  : Force constant  $\Rightarrow \text{dynes /cm}$

$\mu$  : masses of atoms in grams

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

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

$\text{C—C}$      $K = 5 * 10^5 \text{ dynes/cm}$

$\text{C=C}$      $K = 10 * 10^5 \text{ dynes/cm}$

$\text{C}\equiv\text{C}$      $K = 15 * 10^5 \text{ dynes/cm}$

# Calculating stretching frequencies

**C=C**     **K = 10\* 10<sup>5</sup> dynes/cm**

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

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

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

$\bar{\nu}$  Experimental → 1650 cm<sup>-1</sup>

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**C—H**     **K = 5\* 10<sup>5</sup> dynes/cm**

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

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

$\bar{\nu}$  Experimental → 3000 cm<sup>-1</sup>

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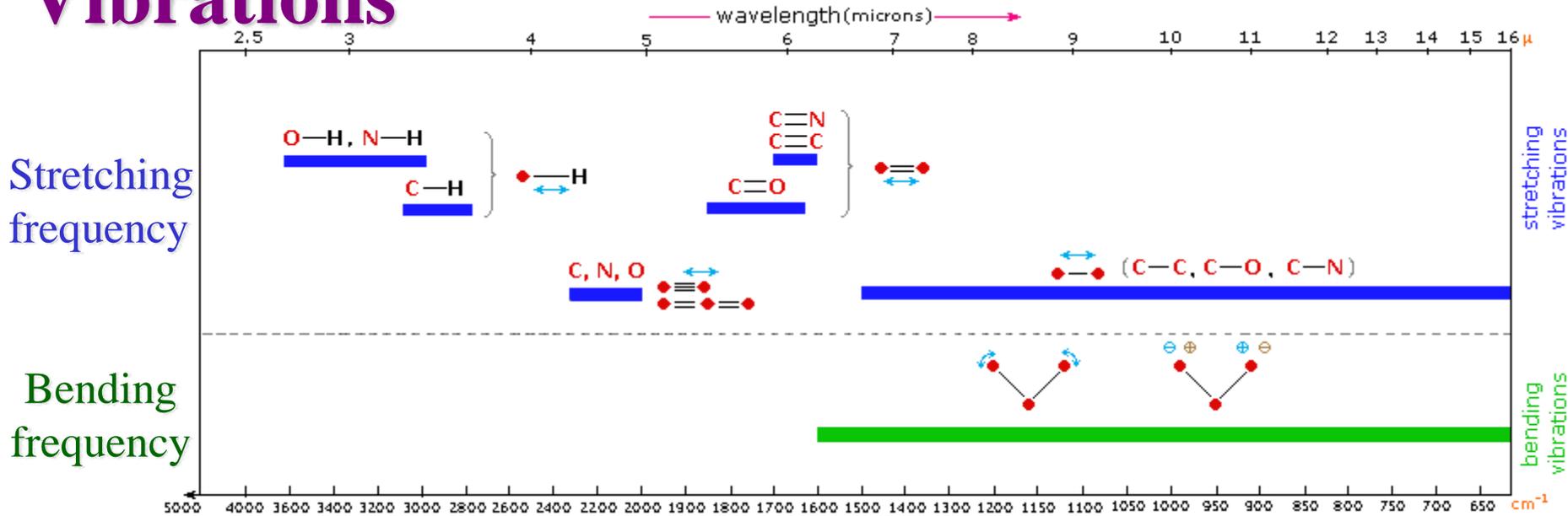
**C—D**     **K = 5\* 10<sup>5</sup> dynes/cm**

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

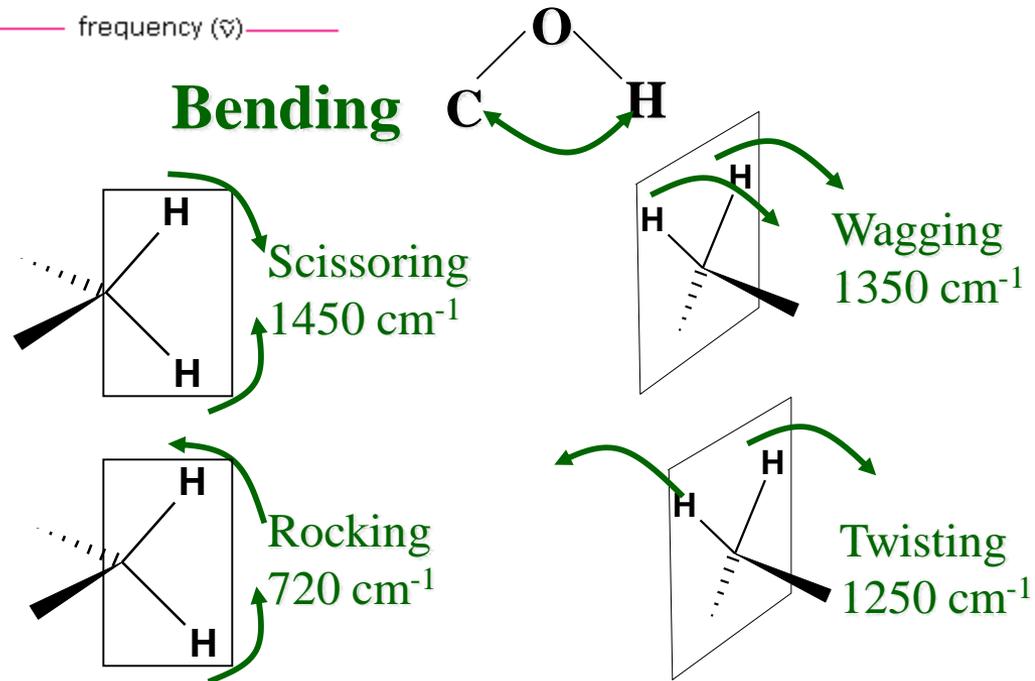
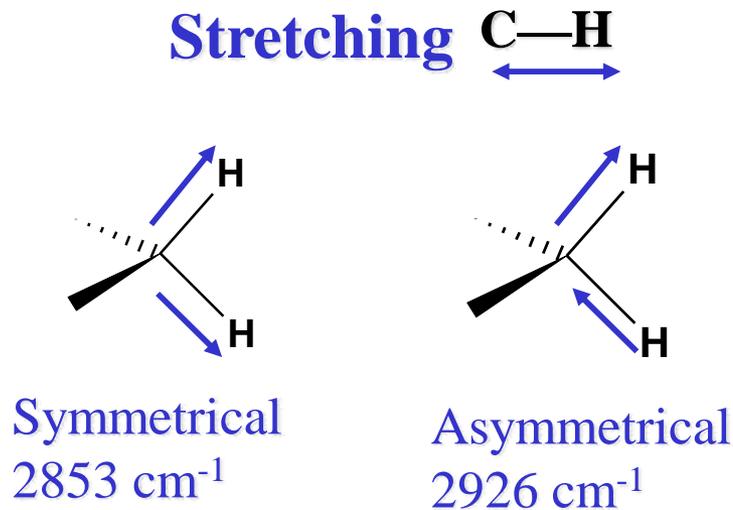
$$\mu = \frac{M_1 M_2}{M_1 + M_2} = \frac{(12)(2)}{12 + 2} = 1.71$$

$\bar{\nu}$  Experimental → 2206 cm<sup>-1</sup>

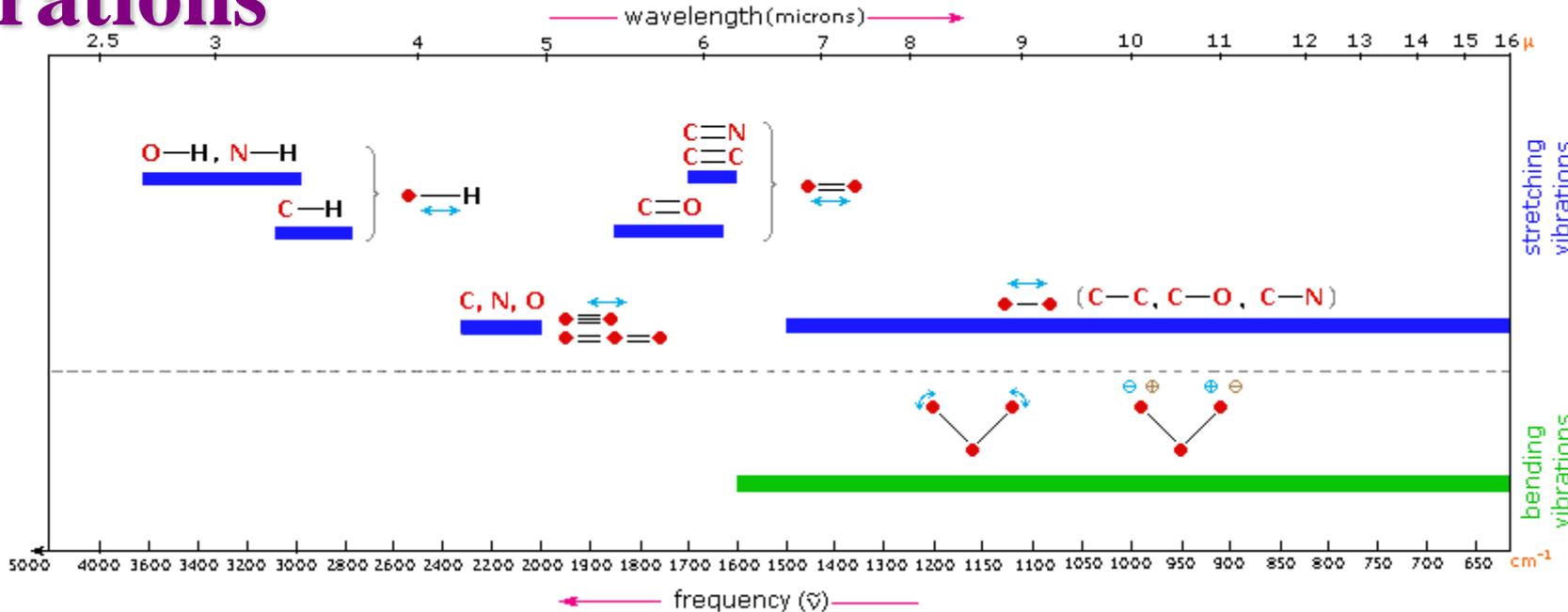
# Vibrations



## Modes of vibration



# Vibrations



## General trends:

- **Stretching frequencies** are higher than **bending frequencies**  
(it is easier to bend a bond than stretching or compressing 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**

# 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**

The 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 =  $I/I_0 \times 100$   $\Rightarrow$  peak height is not linearly related to intensity of absorption

In Absorbance  $A = \ln(I_0/I)$   $\Rightarrow$  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

C11240-2 CAS [120-92-3]  
Cyclopentanone, 99 + %



FW 84.12  
mp -51°C  
bp 130-131°C

d 0.951  
Fp 87°F  
n<sub>D</sub> 1.4359

IR III, 255C  
NMR II, 1,393B  
Merck 10,2736

2986.1	1278.2	834.2
1746.4	1153.0	582.2
1407.6	959.2	471.7

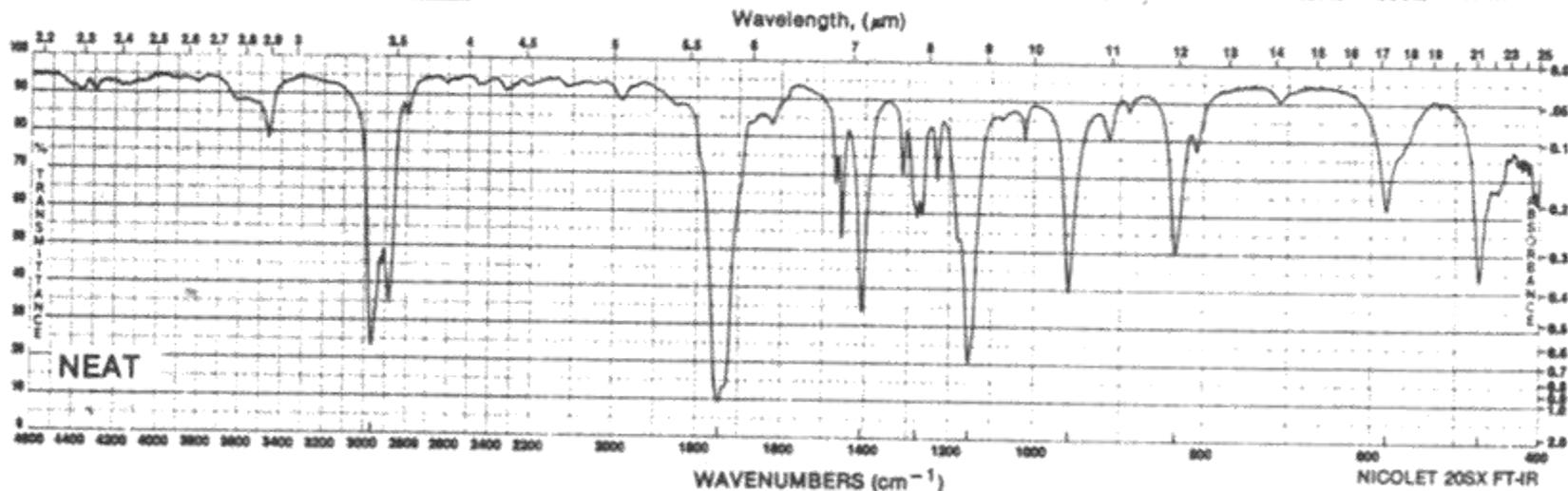


FIGURE 3.2. Cyclopentanone, thin film.

H-BOND  
vs.  $\text{C}=\text{O}$

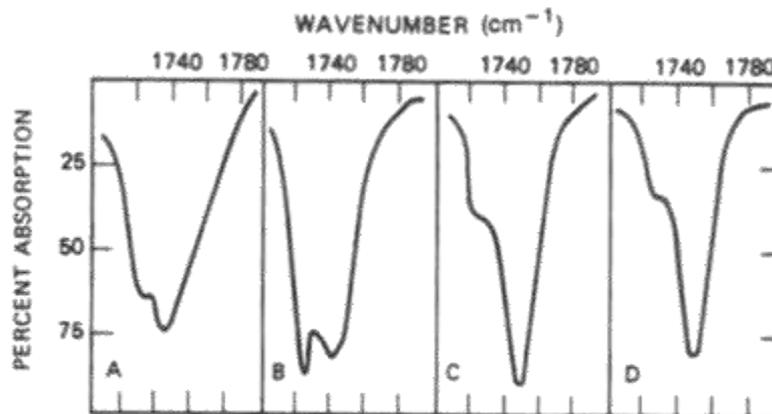
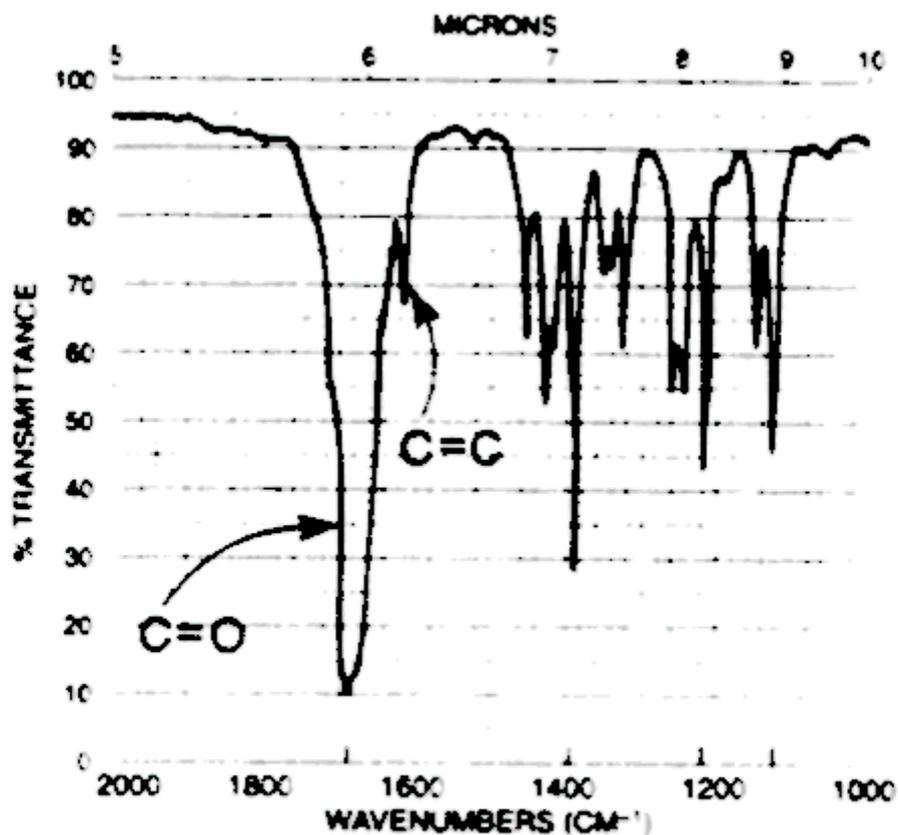


FIGURE 3.3. Infrared spectrum of cyclopentanone in various media. A. Carbon tetrachloride solution (0.15 M). B. Carbon disulfide solution (0.023 M). C. Chloroform solution (0.025 M). D. Liquid state (thin films). (Computed spectral slit width 2 cm<sup>-1</sup>.)

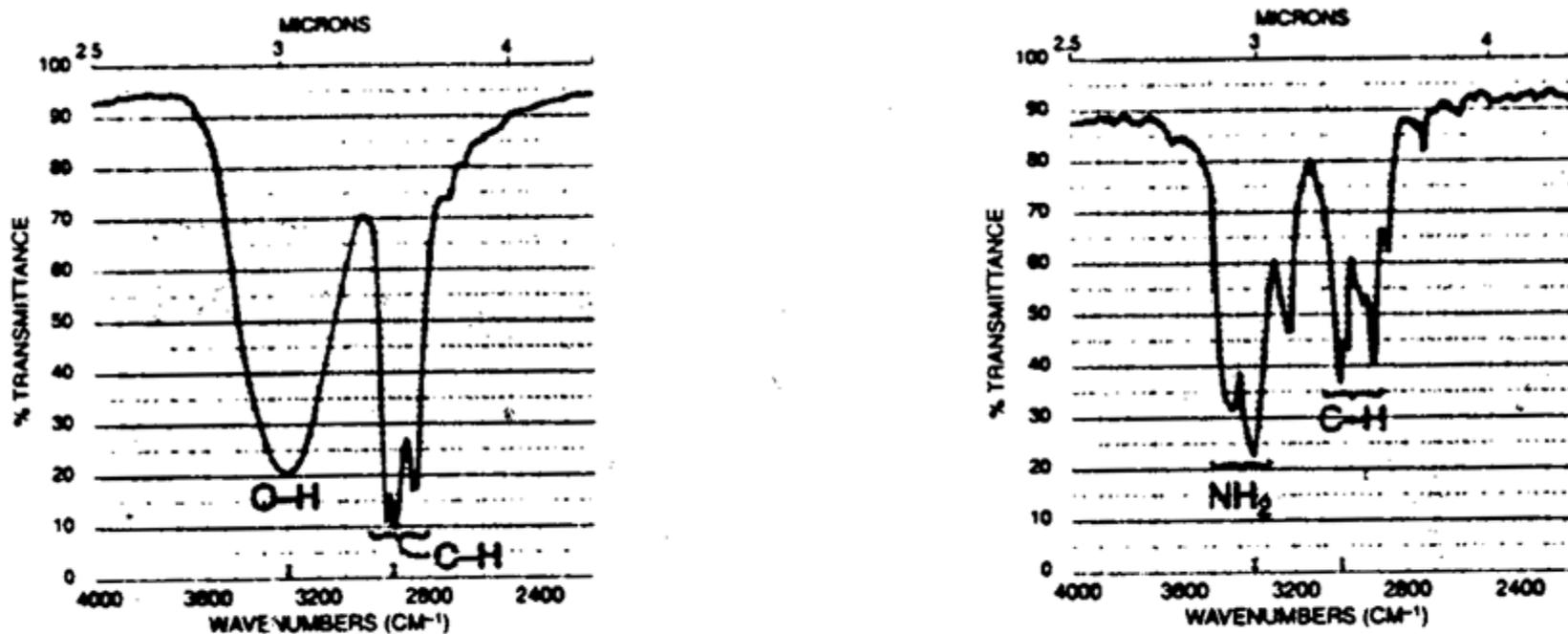
Hydrogen  
bond and  
C=O

# Intensity of C=O vs C=C



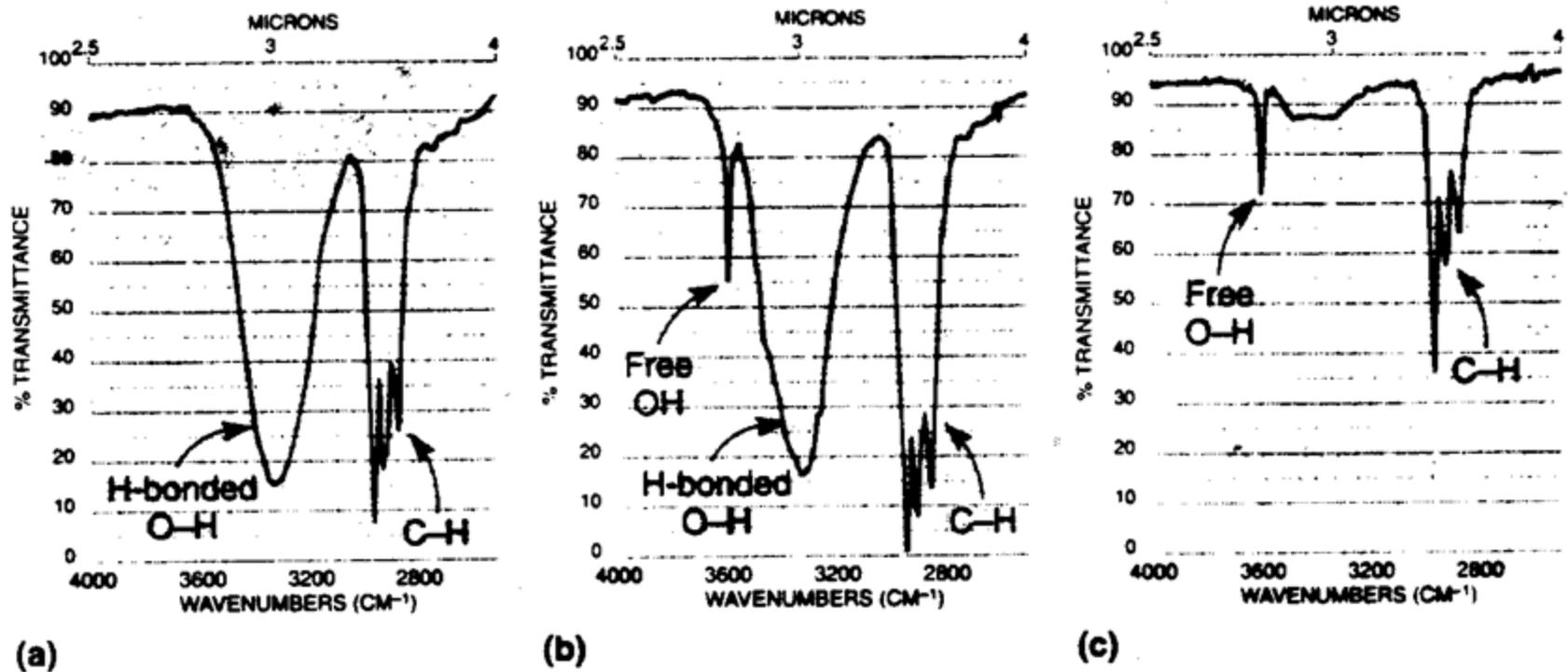
**FIGURE 2.5** A comparison of the intensities of the C=O and C=C absorption bands

# Band Shape: OH vs NH<sub>2</sub> 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



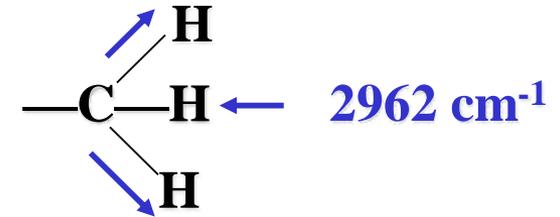
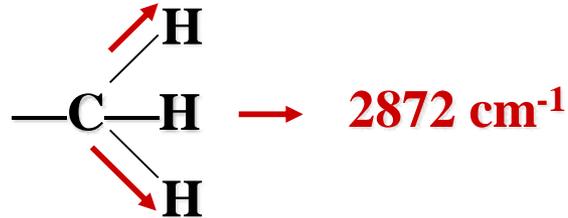
- **FIGURE 2.32** The O—H stretch region. (a) Hydrogen-bonded O—H only (neat liquid). (b) Free and hydrogen-bonded O—H (dilute solution). (c) Free and hydrogen-bonded O—H (very dilute solution).

# Symmetrical and asymmetrical stretch

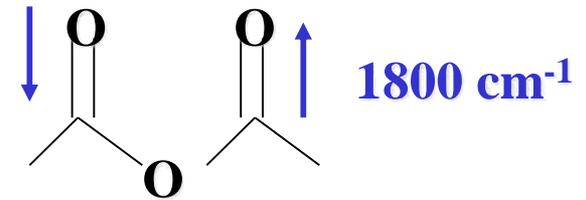
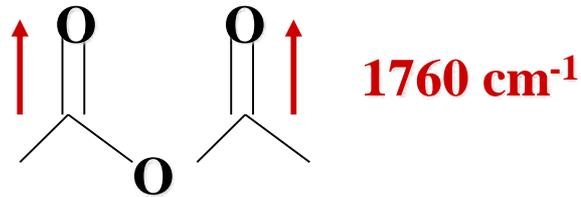
## Symmetrical Stretch

## Asymmetrical Stretch

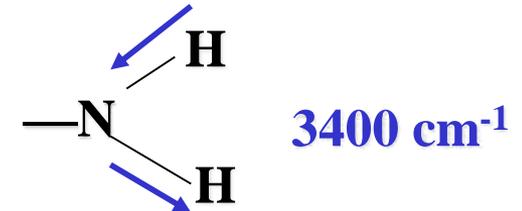
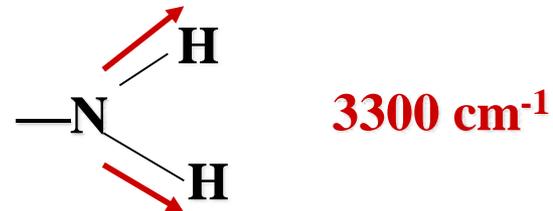
**Methyl**



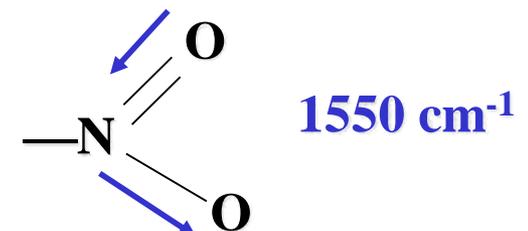
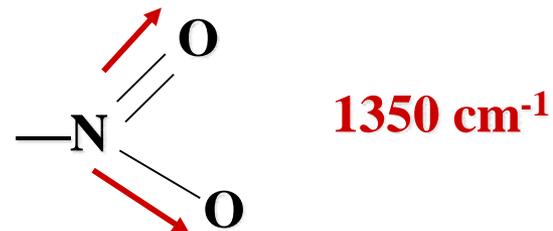
**Anhydride**



**Amino**



**Nitro**



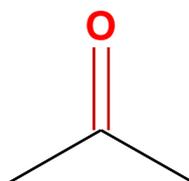
# General IR comments

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

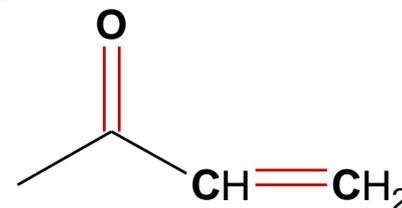
Certain bands occur in **narrow regions** : OH, CH, C=O

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

e.g. **Ketones**



**1715 cm<sup>-1</sup>**



**1680 cm<sup>-1</sup>**

## 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≡C, C≡N**

Lack of strong bands in 900-650 means no aromatic

Stretch	Alkanes,	Alkenes,	Alkynes
C-H :	<3000 cm <sup>-1</sup>	>3000 cm <sup>-1</sup>	3300 cm <sup>-1</sup> sharp
C-C	Not useful		
C=C		1660-1600 cm <sup>-1</sup> conj. Moves to lower values Symmetrical : no band	
C≡C			2150 cm <sup>-1</sup> conj. Moves to lower values Weak but very useful Symmetrical no band
Bending	CH <sub>2</sub> Rocking 720 cm <sup>-1</sup> indicate Presence of 4-CH <sub>2</sub>	1000-700 cm <sup>-1</sup> Indicate substitution pattern	≡ C-H ~630 cm <sup>-1</sup> Strong and broad Confirm triple bond

D22110-4 CAS [112-40-3] CH2(CH2)10CH3 FW 170.34 d 0.749 IR III, 4A 2924.4 721.1  
 Dodecane, 99% mp -9.8°C Fp 180°F nD 1.4212 NMR II, 1.11A 1487.3  
 bp 215-217°C nS 1.4212 1376.2

ALKANE

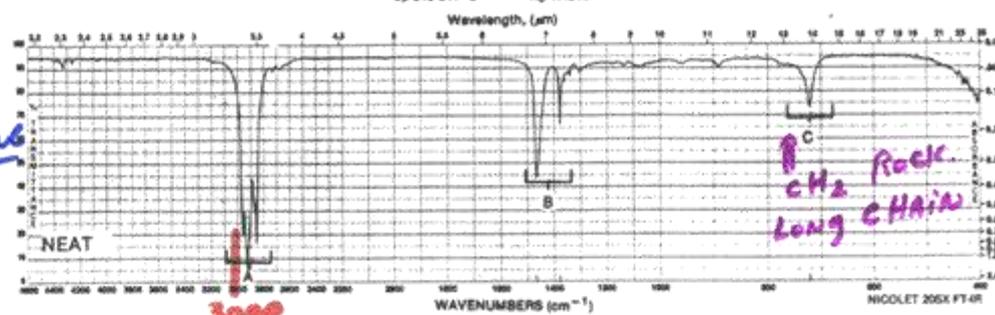


FIGURE 3.8. Dodecane. A. The C—H stretch:  $2962\text{ cm}^{-1}$   $\nu_{\text{as}}\text{CH}_2$ ,  $2872\text{ cm}^{-1}$   $\nu_{\text{s}}\text{CH}_2$ ,  $2924\text{ cm}^{-1}$   $\nu_{\text{as}}\text{CH}_3$ ,  $2853\text{ cm}^{-1}$   $\nu_{\text{s}}\text{CH}_3$ . B. The C—H bend:  $1467\text{ cm}^{-1}$   $\delta_{\text{as}}\text{CH}_2$ ,  $1450\text{ cm}^{-1}$   $\delta_{\text{s}}\text{CH}_2$ ,  $1378\text{ cm}^{-1}$   $\delta_{\text{s}}\text{CH}_3$ . C. The  $\text{CH}_2$  rock:  $721\text{ cm}^{-1}$   $\rho\text{CH}_2$ .

D180-7 CAS [872-05-9] CH2=CH(CH2)8CH3 FW 140.27 d 0.741 IR III, 11A 2925.7 1378.4 722.2  
 1-Decene, 99% mp -66.3°C Fp 118°F NMR II, 1.21B 1641.7 991.2 634.1  
 bp 166.5-173.5°C nD 1.4195 1466.9 909.5

ALKENE

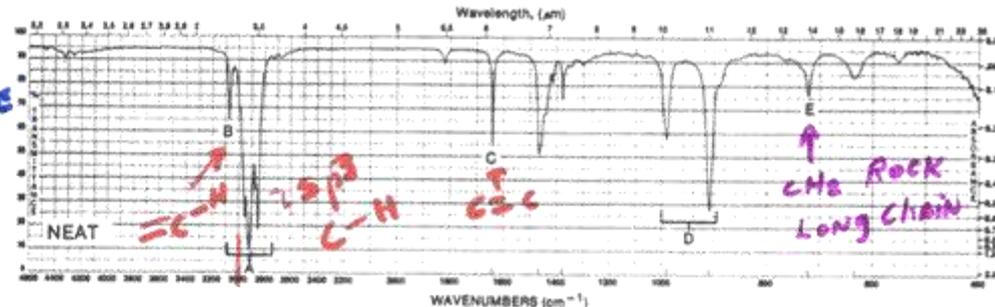


FIGURE 3.10. 1-Decene. A. The C—H stretch (see Fig. 3.8). Note alkene C—H stretch (B) at  $3049\text{ cm}^{-1}$ . C. The C=C stretch,  $1642\text{ cm}^{-1}$ , see Appendix Table D-1. D. Out-of-plane C—H bend:  $991\text{ cm}^{-1}$ , (alkene)  $909.5\text{ cm}^{-1}$ . E. Methylene rock:  $722\text{ cm}^{-1}$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

24442-2 CAS [693-02-7] HC#C(CH2)4CH3 FW 82.15 d 0.715 NMR II, 2.949A 3310.6 1466.4 1249.7  
 1-Hexyne, 99% mp -132°C Fp 6°F 2960.6 1376.8 738.6  
 bp 71-72°C nD 1.3974 2119.0 1327.0 630.0

ALKYNE

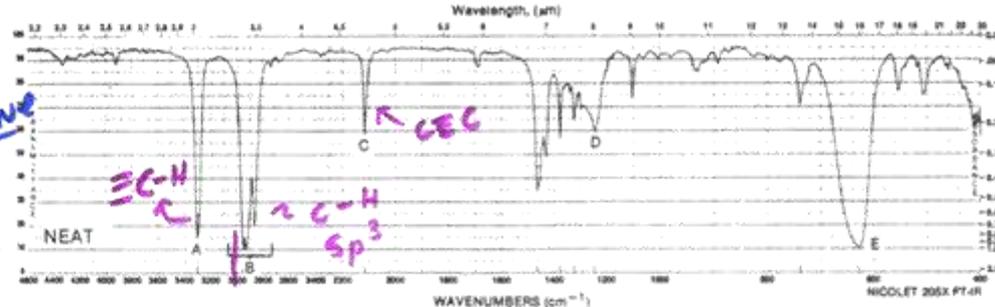
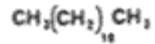


FIGURE 3.12. 1-Hexyne. A. The  $\equiv\text{C—H}$  stretch,  $3310\text{ cm}^{-1}$ . B. Alkyl C—H stretch (see Fig. 3.8),  $2857\text{--}2941\text{ cm}^{-1}$ . C. The C≡C stretch,  $2119\text{ cm}^{-1}$ . D. The  $\equiv\text{C—H}$  bend overtone,  $1250\text{ cm}^{-1}$ . E. The  $\equiv\text{C—H}$ 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

# Alkane

D22110-4 CAS [112-40-3]  
Dodecane, 99%



FW 170.34  
mp -9.8°C  
bp 215-217°C

d 0.749  
Fp 180°F  
n<sub>D</sub> 1.4212

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

2924.4 721.1  
1467.3  
1378.2

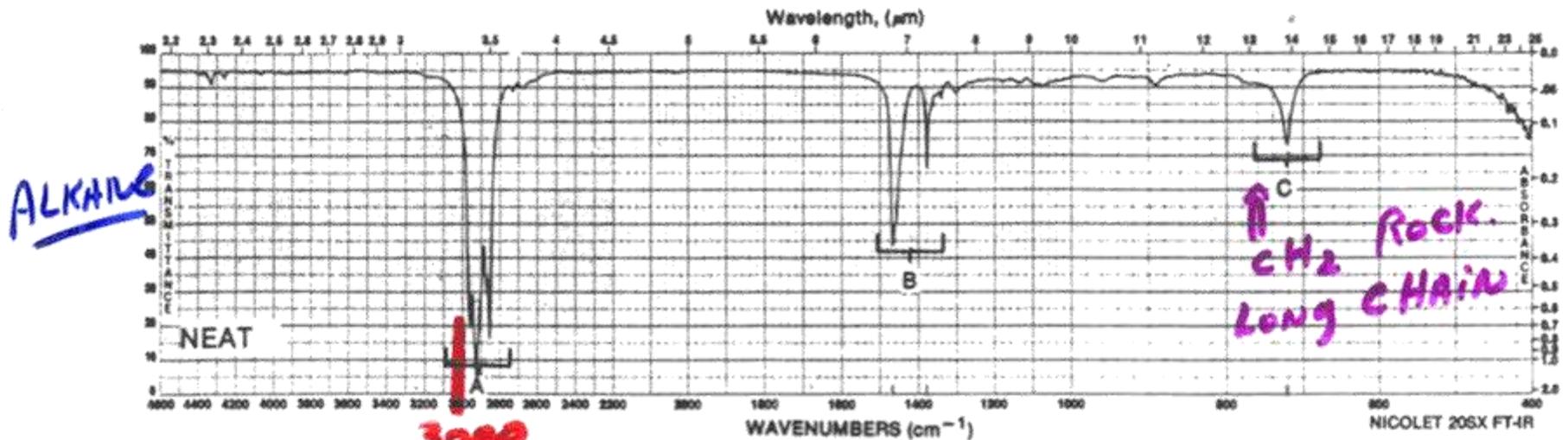


FIGURE 3.8. Dodecane. A. The C—H stretch:  $2962\text{ cm}^{-1}$   $\nu_{\text{as}}\text{CH}_3$ ,  $2872\text{ cm}^{-1}$   $\nu_s\text{CH}_3$ ,  $2924\text{ cm}^{-1}$   $\nu_{\text{as}}\text{CH}_2$ ,  $2853\text{ cm}^{-1}$   $\nu_s\text{CH}_2$ . B. The C—H bend:  $1467\text{ cm}^{-1}$   $\delta_s\text{CH}_2$ ,  $1450\text{ cm}^{-1}$   $\delta_{\text{as}}\text{CH}_3$ ,  $1378\text{ cm}^{-1}$   $\delta_s\text{CH}_3$ . C. The  $\text{CH}_2$  rock:  $721\text{ cm}^{-1}$   $\rho\text{CH}_2$ .

# Alkene : 1-Decene

D180-7 CAS [872-05-9]  
1-Decene, 96%



FW 140.27

mp -66.3°C

bp 166.5-173.5°C

d 0.741

Fp 118°F

n<sub>D</sub> 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

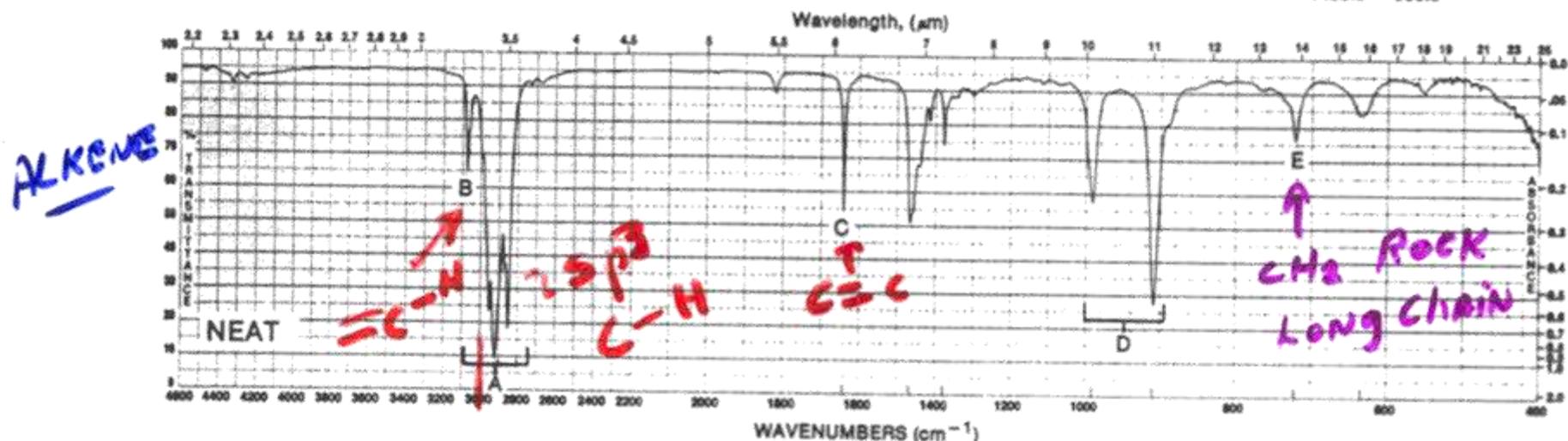


FIGURE 3.10. 1-Decene. A. The C—H stretch (see Fig. 3.8). Note alkene C—H stretch (B) at 3049  $\text{cm}^{-1}$ . C. The C=C stretch, 1642  $\text{cm}^{-1}$ , see Appendix Table D-1. D. Out-of-plane C—H bend: 991  $\text{cm}^{-1}$ , (alkene) 909.5  $\text{cm}^{-1}$ . E. Methylene rock: 722  $\text{cm}^{-1}$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

## Symmetry

To give rise to absorption of IR  $\Rightarrow$  Oscillating Electric Dipole

Molecules with Center of symmetry

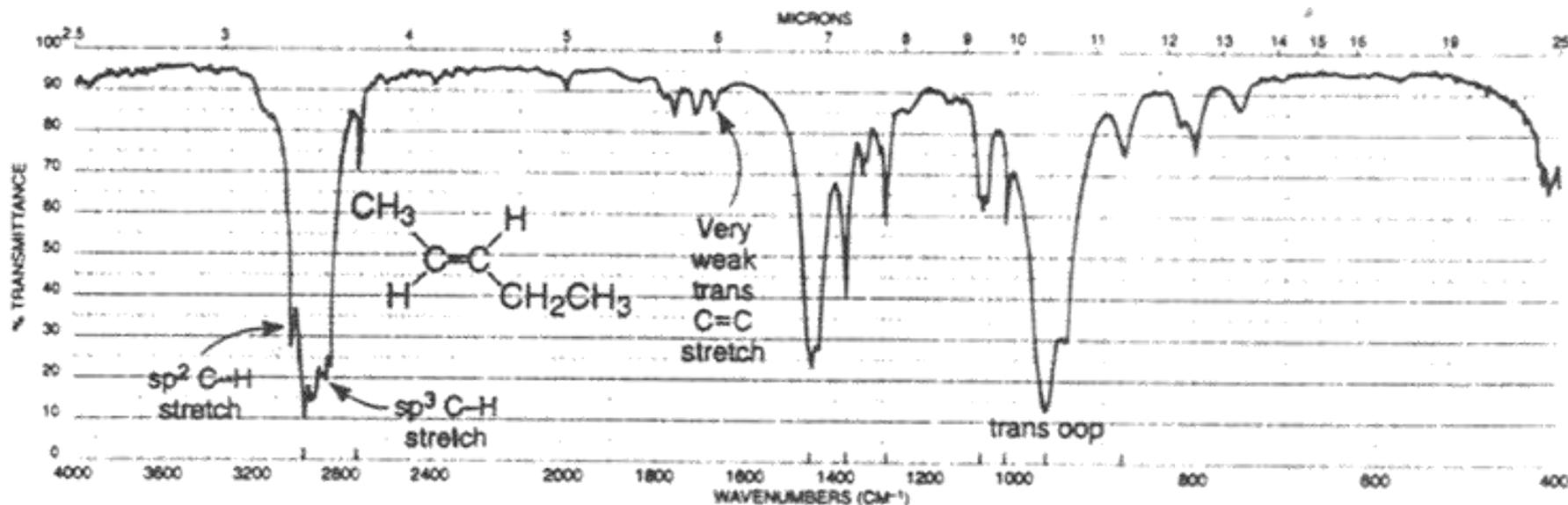
Symmetric vibration  $\Rightarrow$  inactive

Antisymmetric vibration  $\Rightarrow$  active



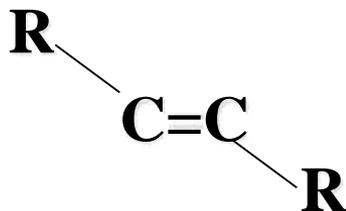
# Alkene

## 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**



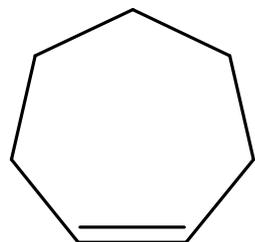
***trans* C=C isomer -> weak in IR**

**Observable in Raman**

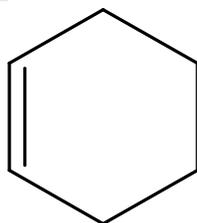


# Alkene: Factors influencing vibration frequency

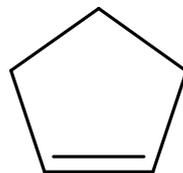
1- Strain move peak to right (decrease  $\bar{\nu}$ )



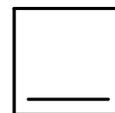
1650



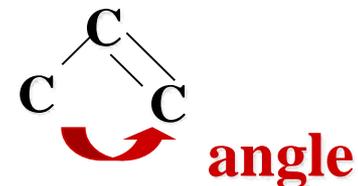
1646



1611



1566

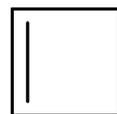


angle

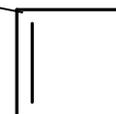


1656 : exception

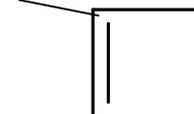
2- Substitution increase  $\bar{\nu}$



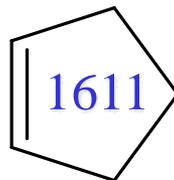
1566



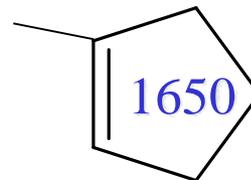
1641



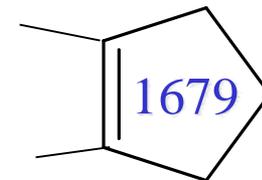
1675



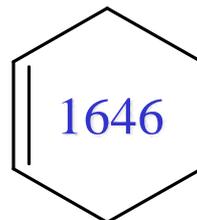
1611



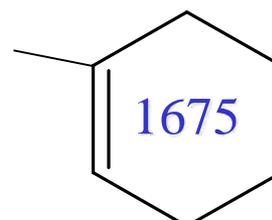
1650



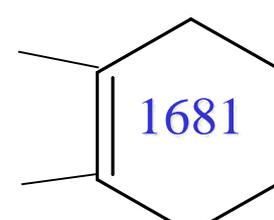
1679



1646



1675



1681

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

C=C-Ph 1625 cm<sup>-1</sup>

# Alkene: Out-of-Plane bending

This region can be used to deduce substitution pattern

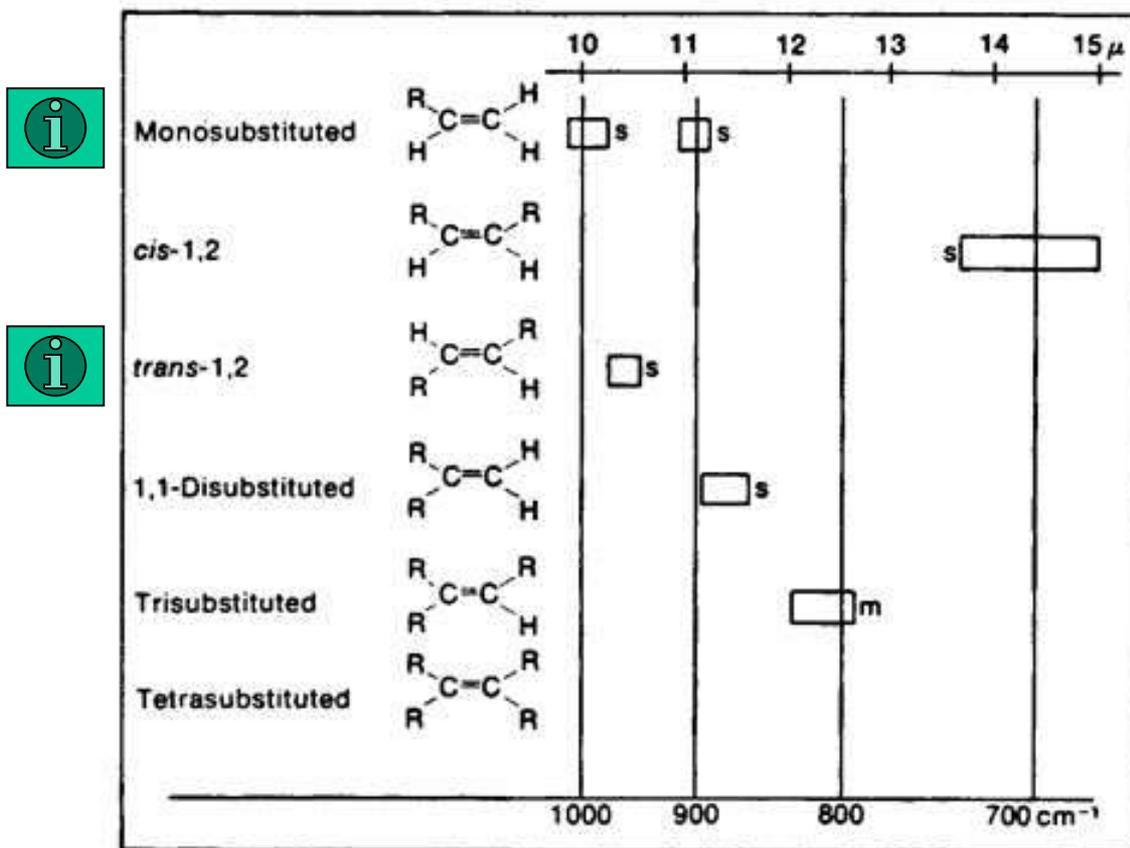


FIGURE 2.22 The C—H out-of-plane bending vibrations for substituted alkenes.



# Alkyne: 1-Hexyne

24442-2 CAS [693-02-7]  
1-Hexyne, 99%



FW 82.15  
mp -132°C  
bp 71-72°C

d 0.715  
Fp -6°F  
n<sub>D</sub> 1.3974

NMR II, 2.949A

3310.6	1466.4	1249.7
2960.6	1379.8	739.8
2119.0	1327.0	630.0

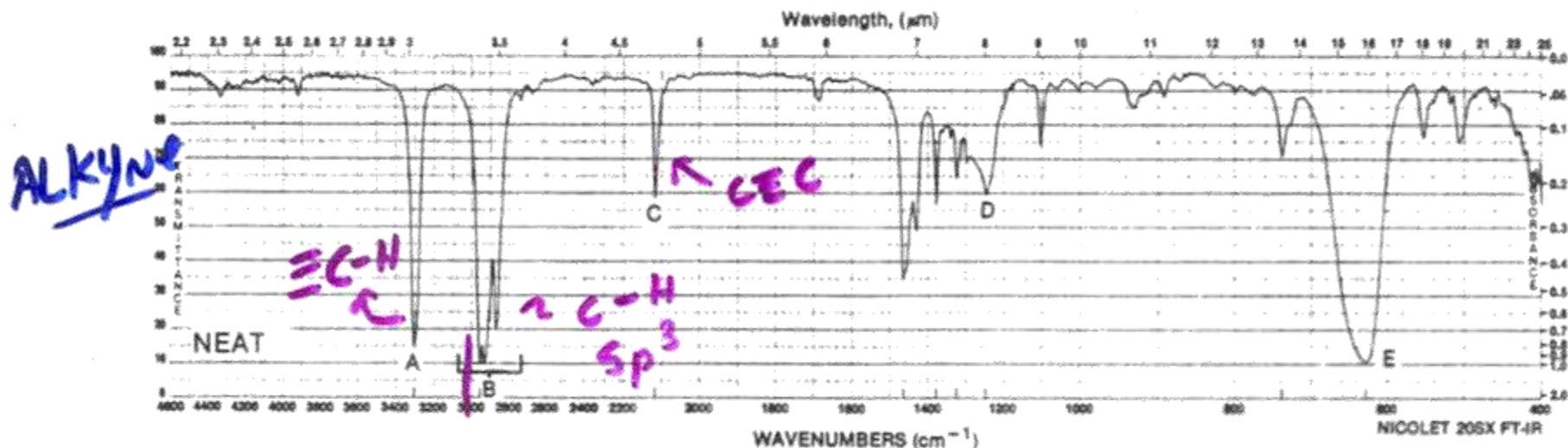
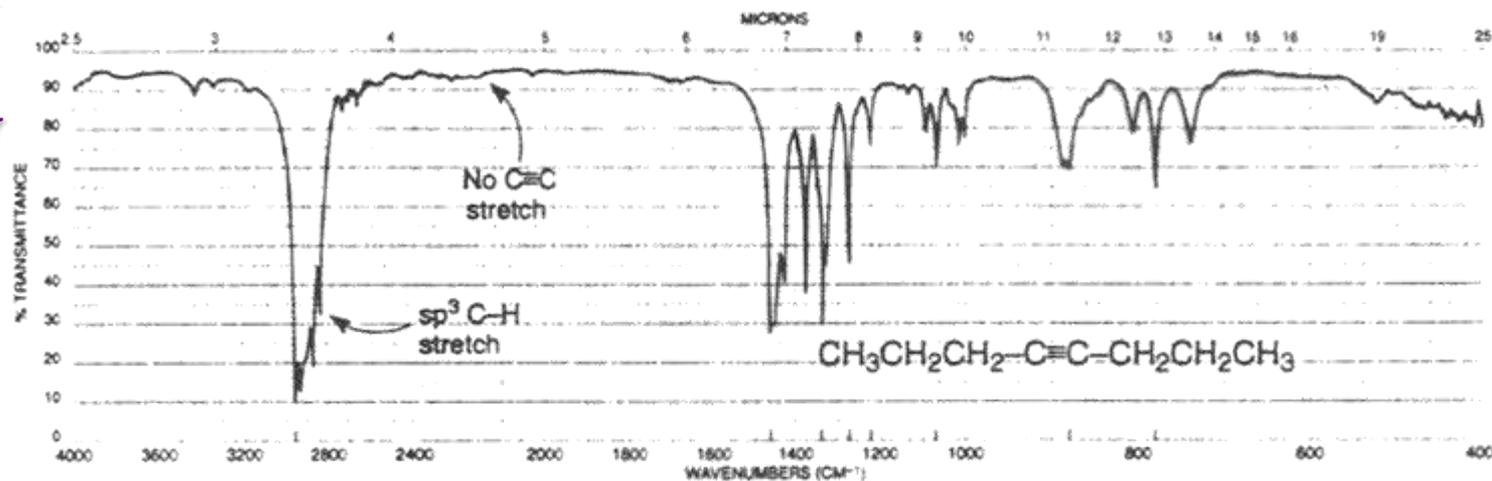
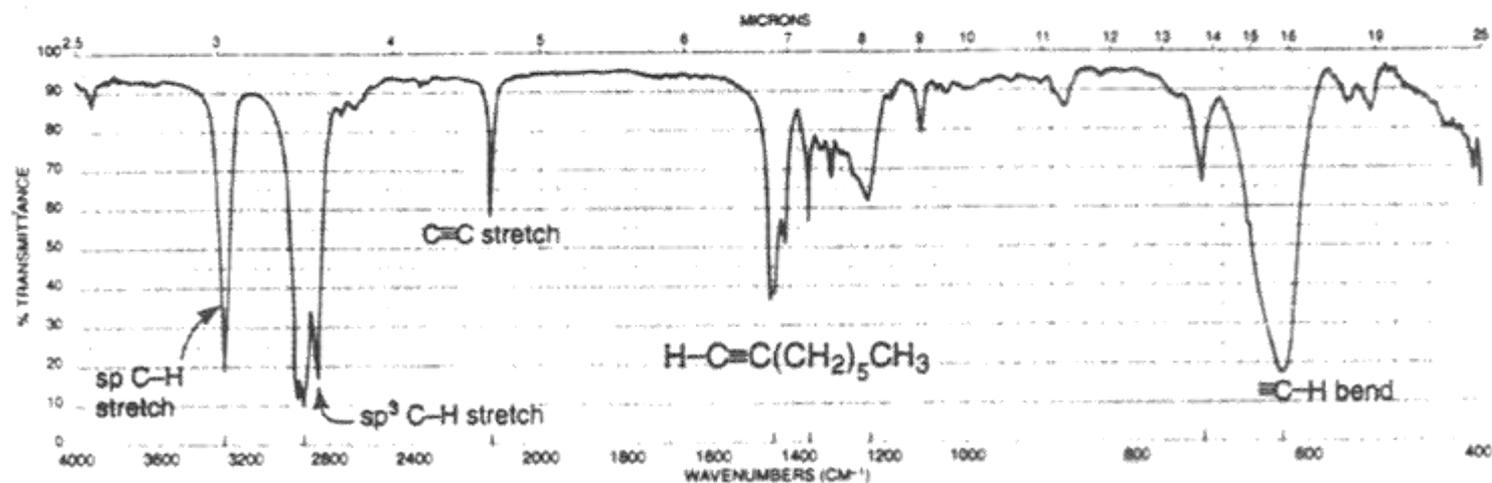


FIGURE 3.12. 1-Hexyne. A. The  $\equiv\text{C}-\text{H}$  stretch,  $3310\text{ cm}^{-1}$ . B. Alkyl  $\text{C}-\text{H}$  stretch (see Fig. 3.8),  $2857-2941\text{ cm}^{-1}$ . C. The  $\text{C}\equiv\text{C}$  stretch,  $2119\text{ cm}^{-1}$ . D. The  $\equiv\text{C}-\text{H}$  bend overtone,  $1250\text{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

# 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 ( $v_i = 0$ ) to First Excited State ( $v_i = 1$ )**

**Transition ( $v_i = 0$ ) to ( $v_j = 2$ ) => Overtone**

# IR : Aromatic

**=C-H** > 3000 cm<sup>-1</sup>

**C=C** 1600 and 1475 cm<sup>-1</sup>

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

**overtone** 2000-1667: useful to assign ring substitution

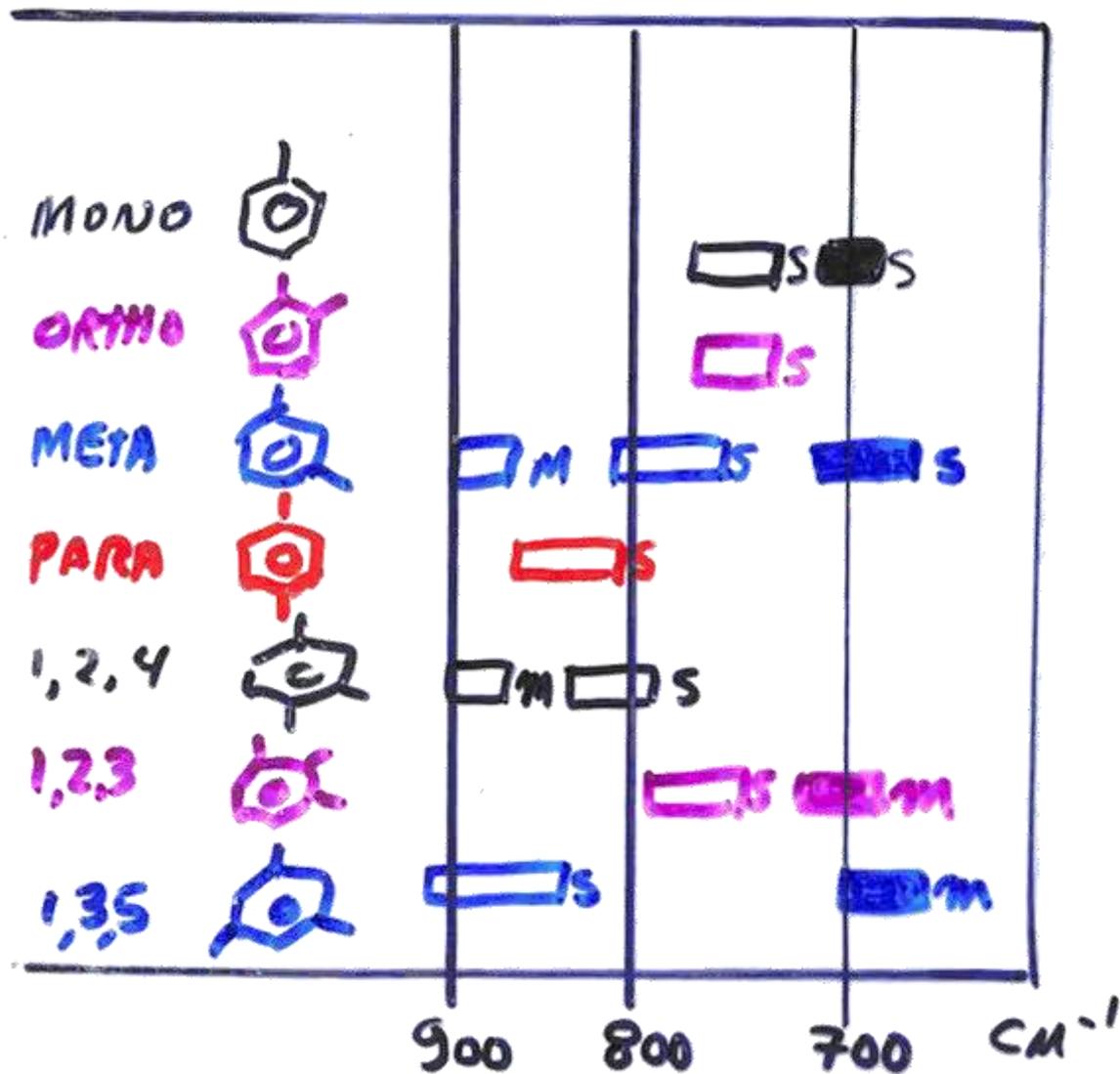
e.g. Naphthalene:

out of plane bending

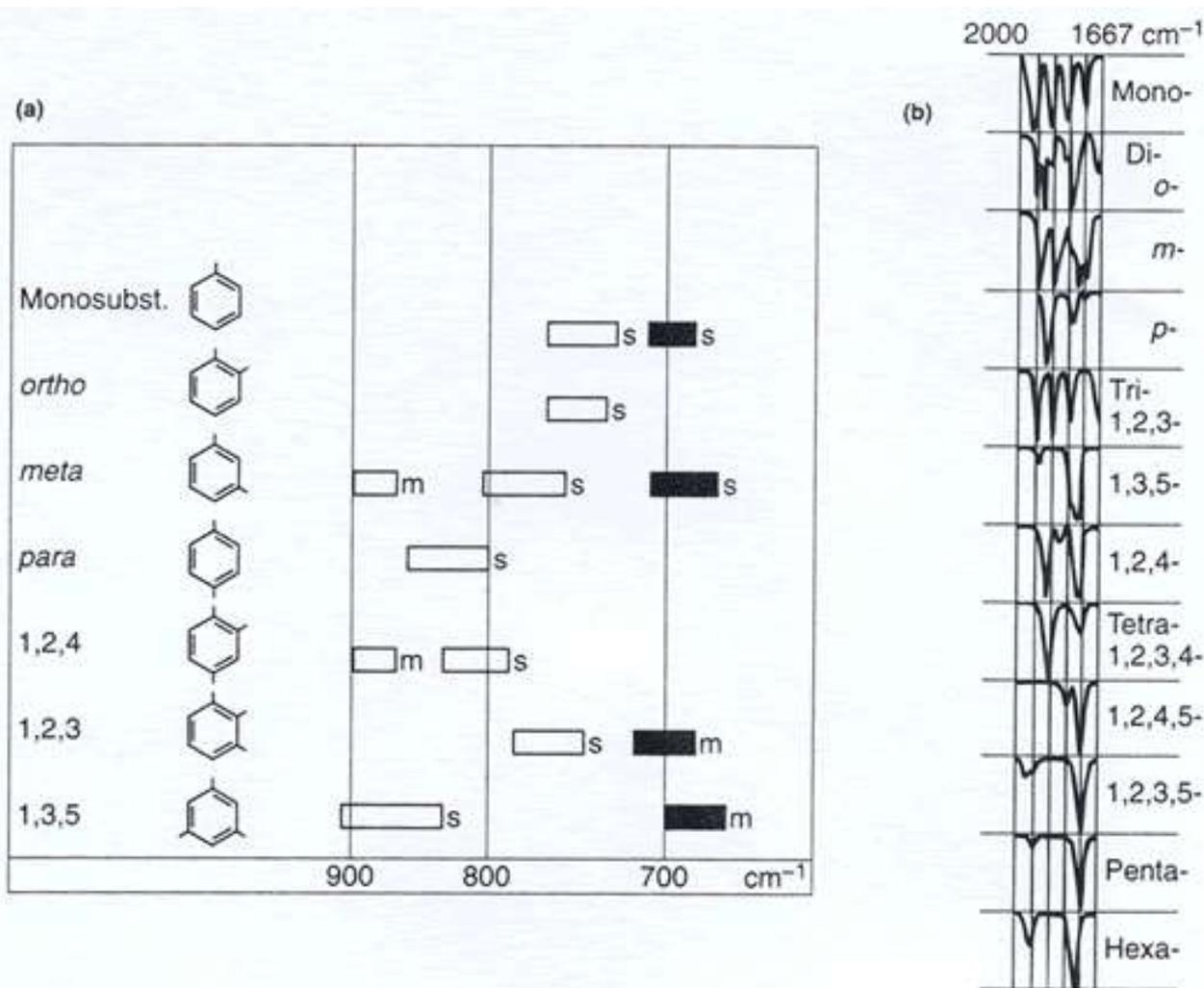
Substitution pattern	$\bar{\nu}$
Isolated H	862-835
2 adjacent H	835-805
4 adjacent H	760-735

# Aromatic substitution: Out of plane bending

out of plane

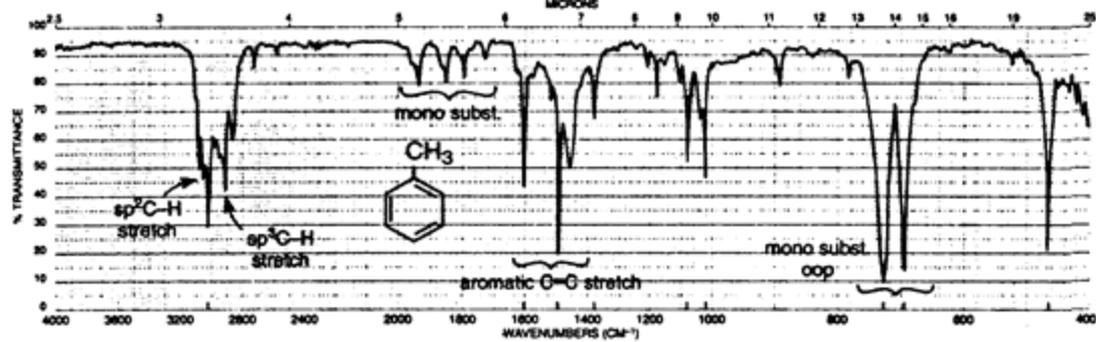


# Aromatic substitution: Out of plane bending

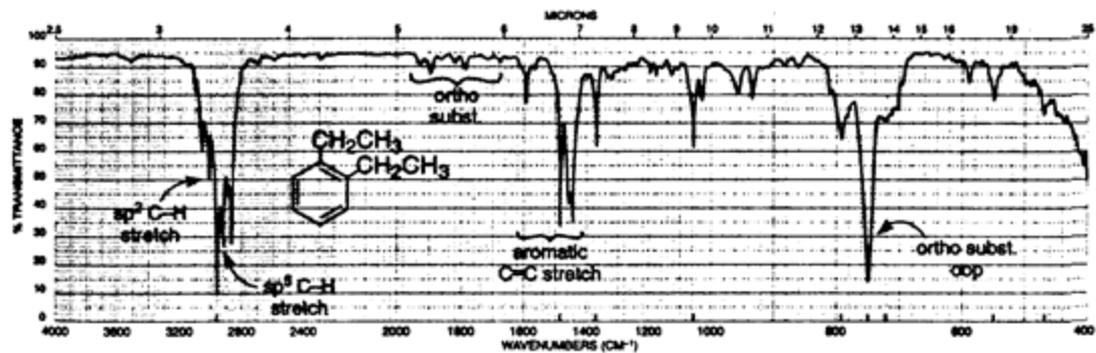


► **FIGURE 2.28** (a) The C—H out-of-plane bending vibrations for substituted benzenoid compounds. (b) The 2000-to-1667-cm<sup>-1</sup> region for substituted benzenoid compounds (from Dyer, John R., *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, Englewood Cliffs, N.J.,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

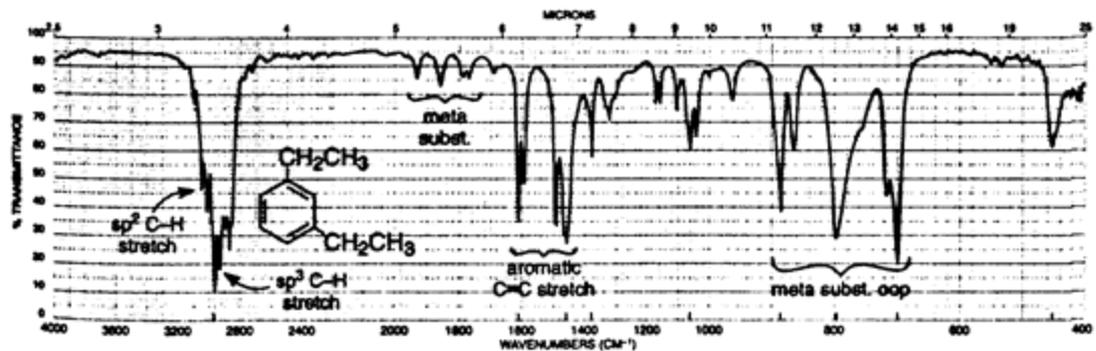




► FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

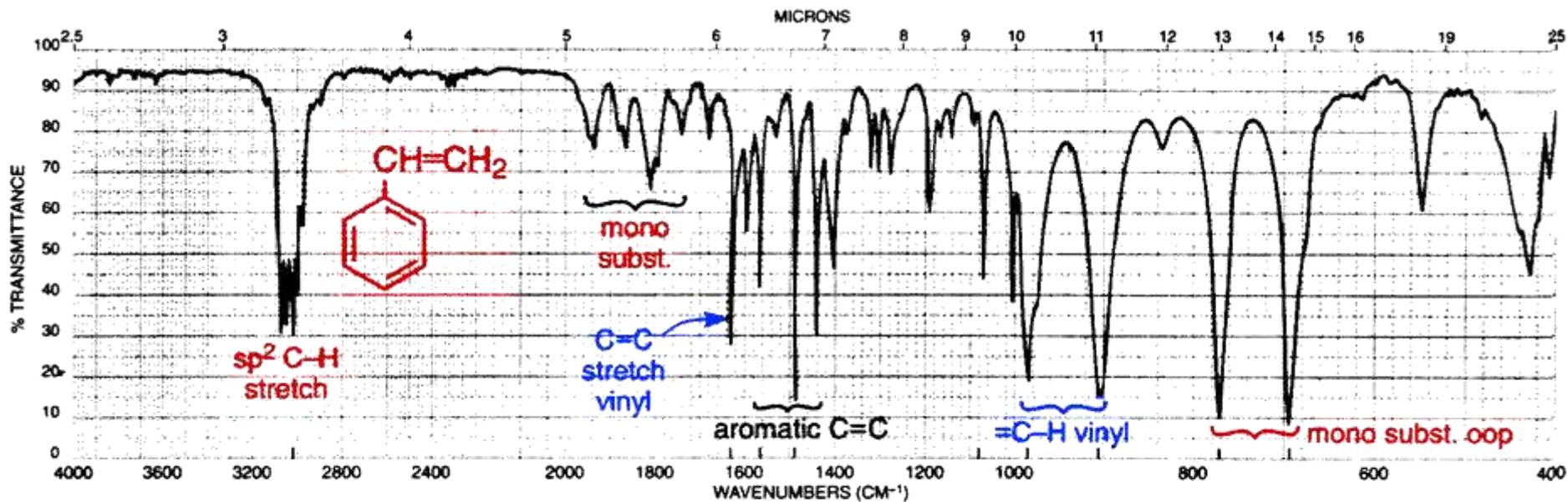


► FIGURE 2.24 The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).



► 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).



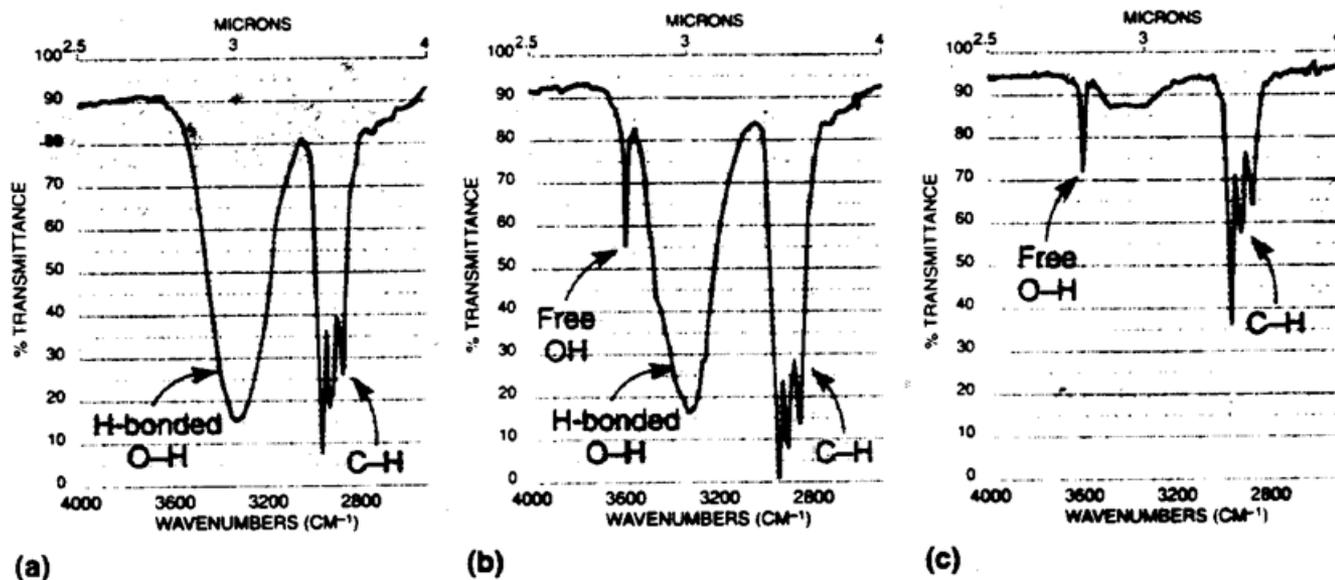
# IR: Alcohols and Phenols

**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  $\text{cm}^{-1}$  (coupled to C-C => C-C-O)**

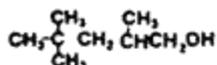
**C-O Vibration is sensitive to substitution:**

<b>Phenol</b>	<b>1220</b>	↓
<b>3` Alcohols</b>	<b>1150</b>	
<b>2` Alcohols</b>	<b>1100</b>	
<b>1` Alcohols</b>	<b>1050</b>	

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

# Alcohol

18667-8 CAS [16325-63-6]  
2,4,4-Trimethyl-1-pentanol, 98%



FW 130.23  
bp 168-169°C  
d 0.818

Fp 140°F  
n<sub>D</sub> 1.4275

IR III, 69G  
NMR II, 1,108C

3335.0	1365.1	1040.3
2955.0	1249.2	989.4
1467.3	1096.8	959.0

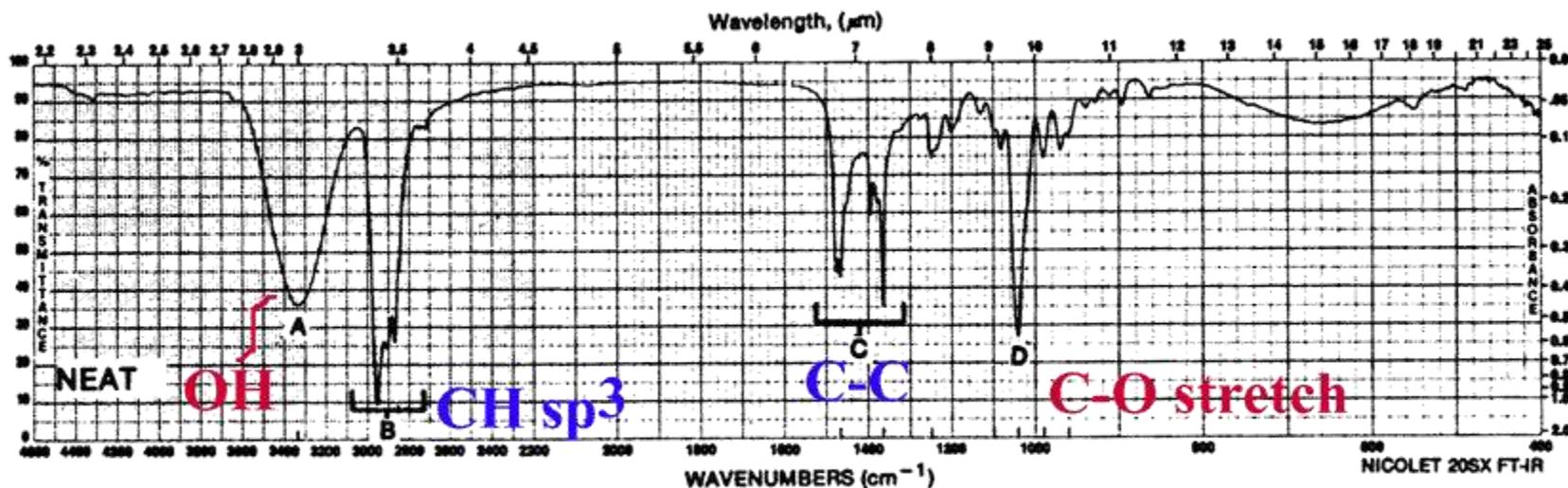
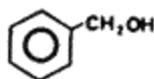


FIGURE 3.15. 2,4,4-Trimethyl-1-pentanol. A. The O—H stretch, intermolecular hydrogen bonding 3335  $\text{cm}^{-1}$ . B. The C—H stretch (see Fig. 3.8, 3000–2800  $\text{cm}^{-1}$ ). C. The C—H bend (see Fig. 3.8). Note the pair of bands for the *gem*-dimethyl group at 1395 and 1365  $\text{cm}^{-1}$ . D. The C—O stretch 1040  $\text{cm}^{-1}$ .

**C-O : 1040  $\text{cm}^{-1}$  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<sub>D</sub> 1.5403

IR III, 874C  
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

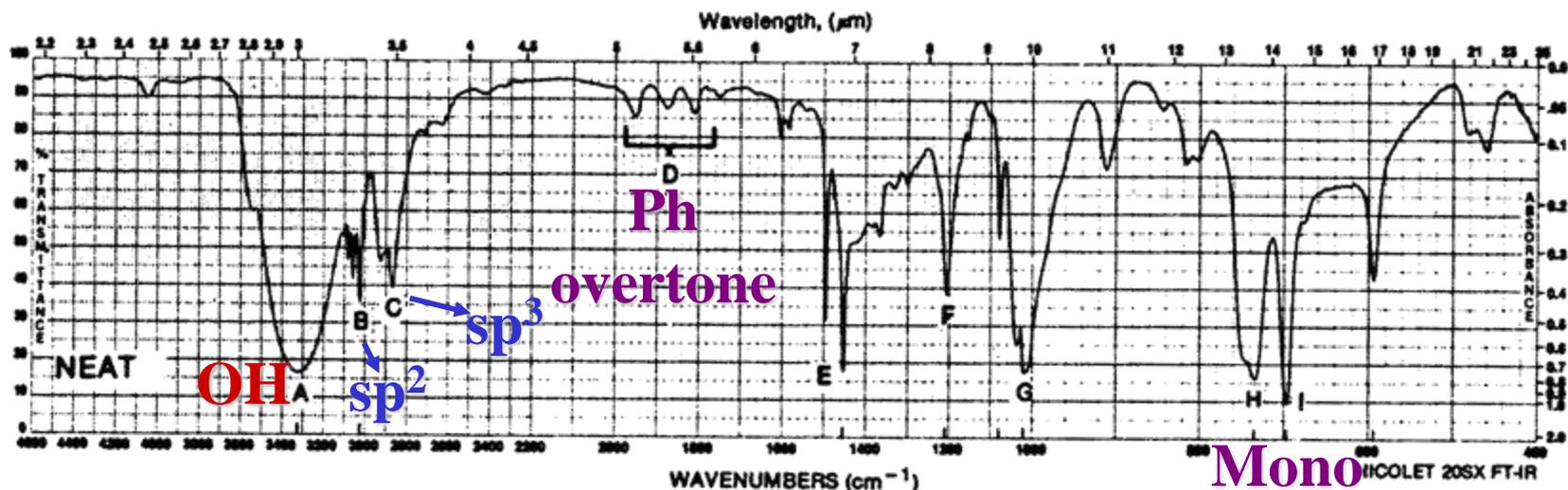


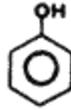
FIGURE 3.14. Benzyl alcohol. A. O—H stretch: intermolecular hydrogen bonded, 3331  $\text{cm}^{-1}$ . B. The C—H stretch: aromatic 3100–3000  $\text{cm}^{-1}$ . C. The C—H stretch: methylene, 2980–2840  $\text{cm}^{-1}$ . D. Overtone or combination bands, 2000–1667  $\text{cm}^{-1}$ . E. The  $\text{C}=\text{C}$  ring stretch. 1497, 1454  $\text{cm}^{-1}$ , overlapped by  $\text{CH}_2$  scissoring, about 1471  $\text{cm}^{-1}$ . F. The

**Mono**  
**Subst. Ph**  
**735 & 697  $\text{cm}^{-1}$**

**C-O : 1080, 1022  $\text{cm}^{-1}$  : primary OH**

# Phenol

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

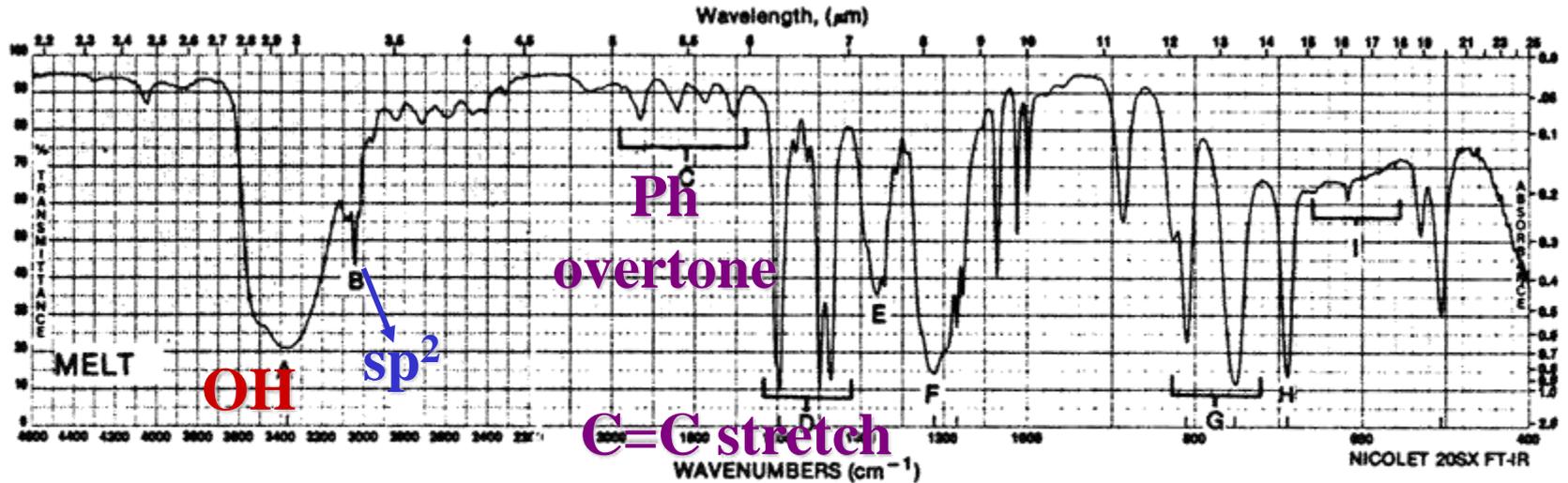


FW 94.11  
mp 39.5-41.5°C  
bp 181°C

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

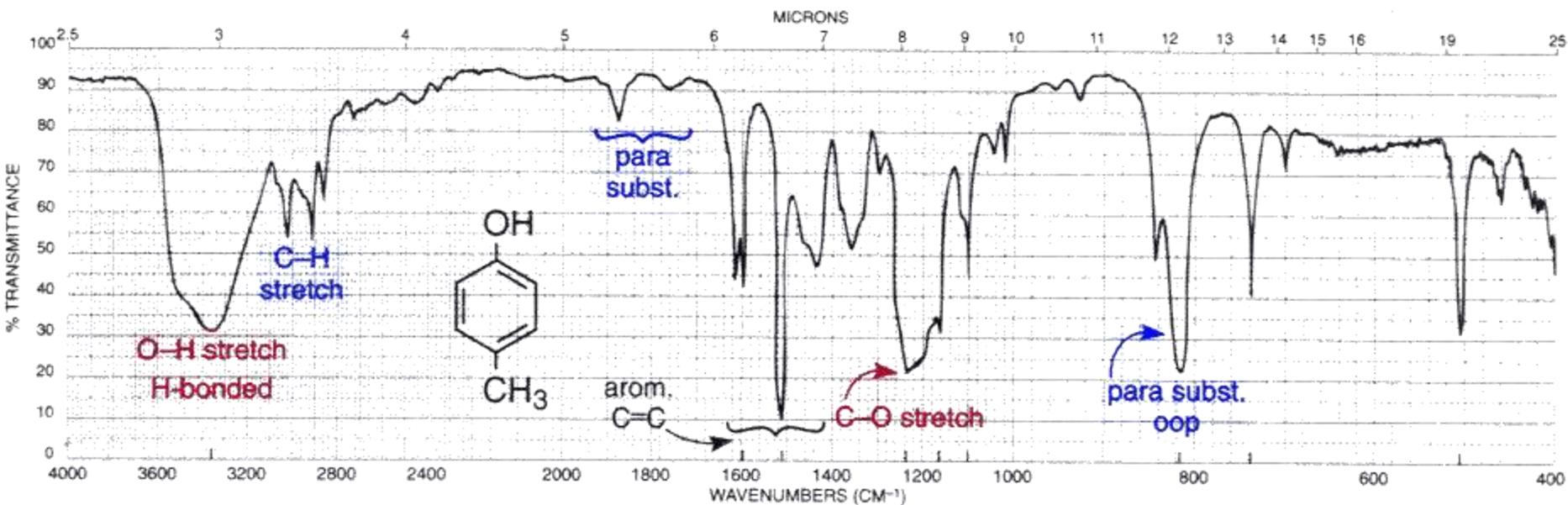


**FIGURE 3.16.** Phenol. A. Broad intermolecular hydrogen bonded, O—H stretch, 3373  $\text{cm}^{-1}$ . B. Aromatic C—H stretch, 3045  $\text{cm}^{-1}$ . C. Overtone or combination bands, 2000–1667  $\text{cm}^{-1}$ . D. The C=C ring stretch, 1595, 1499, 1470  $\text{cm}^{-1}$ . E. In-plane O—H bend,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

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

**Ph-O : 1224  $\text{cm}^{-1}$**

# Phenol



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

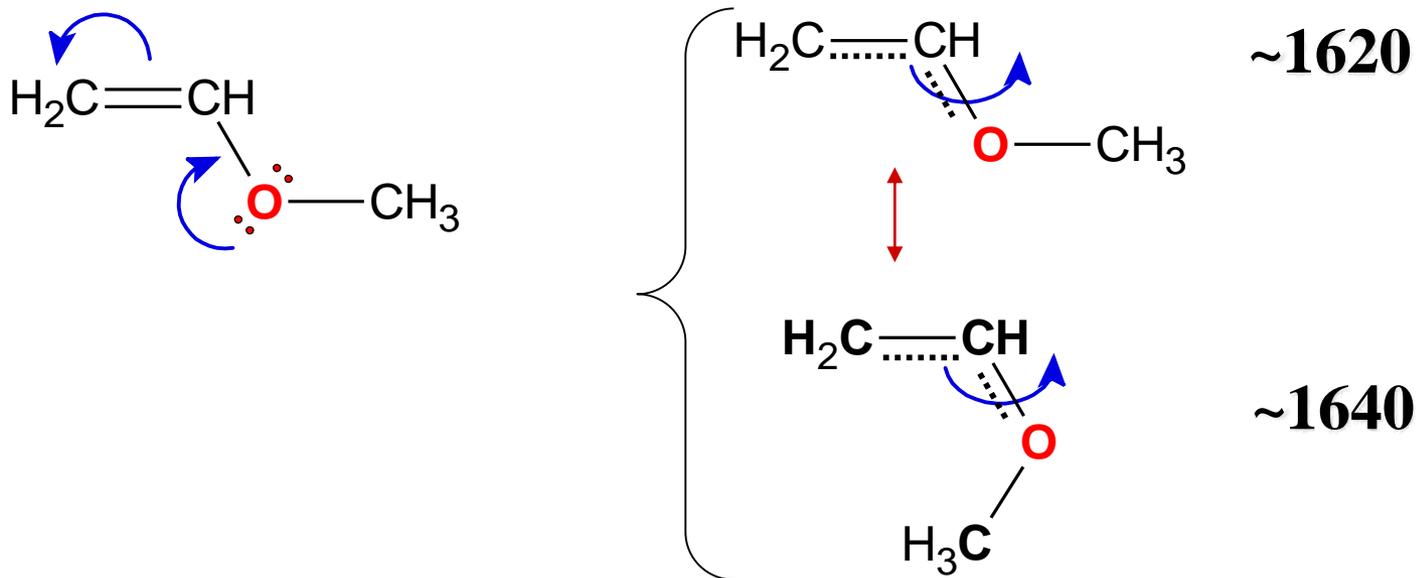
# IR: Ether

**C-O-C**  $\Rightarrow$  **1300-1000  $\text{cm}^{-1}$**

**Ph-O-C**  $\Rightarrow$  **1250 and 1040  $\text{cm}^{-1}$**

**Aliphatic**  $\Rightarrow$  **1120  $\text{cm}^{-1}$**

**C=C in vinyl Ether  $\Rightarrow$  1660-1610  $\text{cm}^{-1}$**   
**appear as Doublet  $\Rightarrow$  rotational isomers**



# Ether

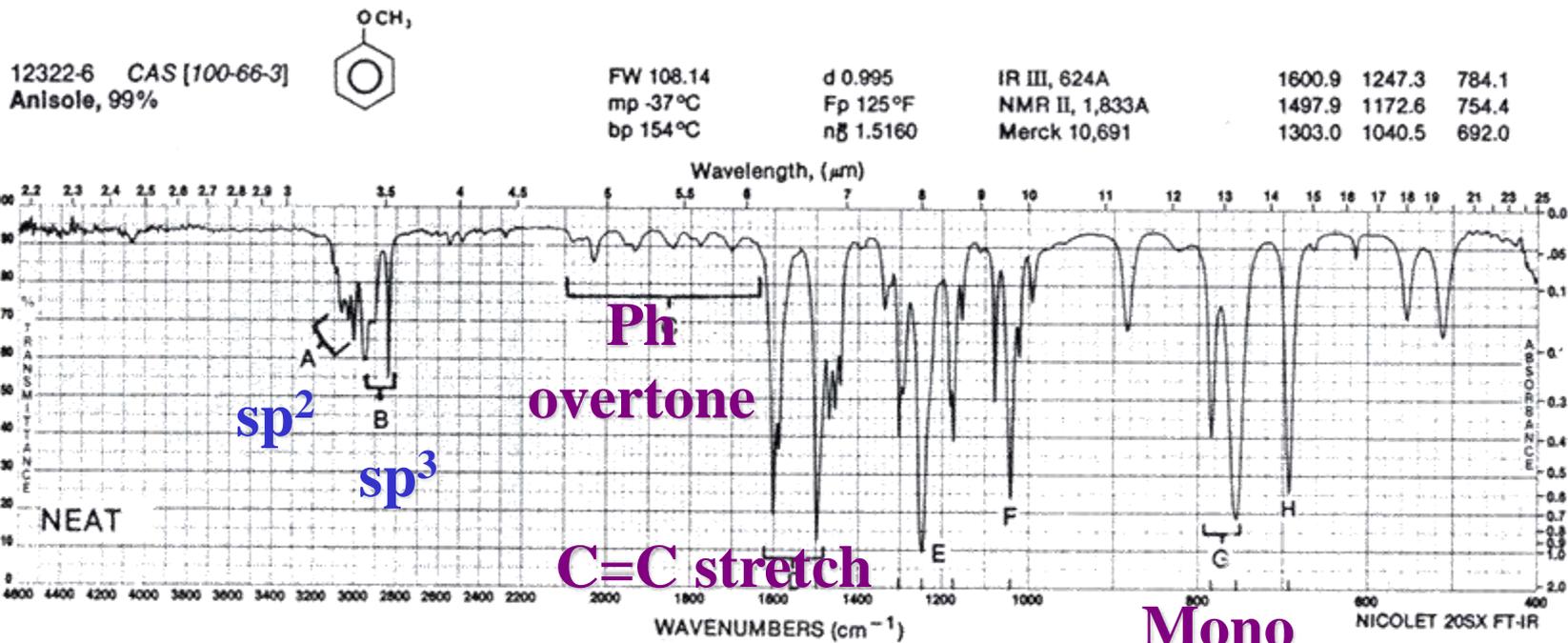


FIGURE 3.19. Anisole. A. Aromatic C—H stretch, 3060, 3030, 3000  $\text{cm}^{-1}$ . B. Methyl C—H stretch, 2950, 2835  $\text{cm}^{-1}$ . C. Overtone-combination region, 2000–1650  $\text{cm}^{-1}$ . D. The C=C ring stretch, 1600, 1498  $\text{cm}^{-1}$ . E. Asymmetric C—O—C stretch, 1247  $\text{cm}^{-1}$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

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

**Ph-O-C : 1247  $\text{cm}^{-1}$  Asymmetric stretch**

**Ph-O-C : 1040  $\text{cm}^{-1}$  Symmetric stretch**

# IR: Carbonyl

From 1850 – 1650  $\text{cm}^{-1}$

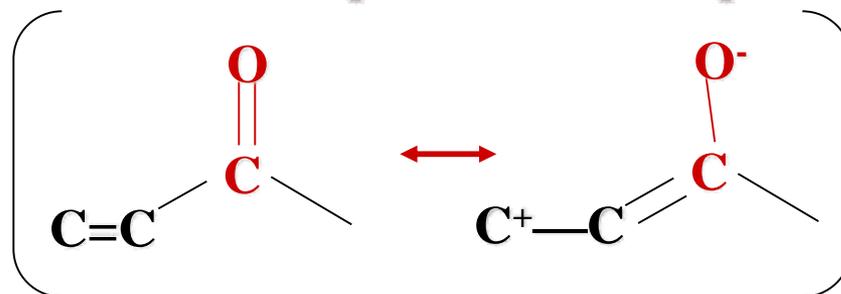
<b>1810</b>	<b>1800</b>	<b>1760</b>	<b>1735</b>	<b>1725</b>	<b>1715</b>	<b>1710</b>	<b>1690</b>
Anhydr Band	Acid Chloride	Anhydr Band 2	Ester	Aldehyde	Ketone	Acid	Amide



**Ketone 1715  $\text{cm}^{-1}$  is used as reference point for comparisons**

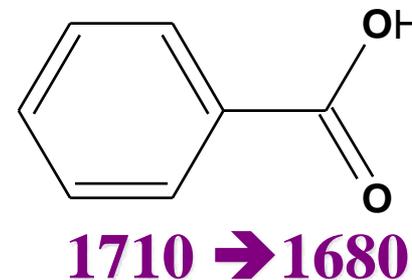
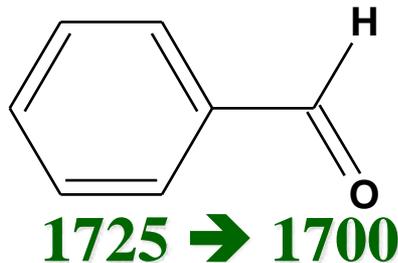
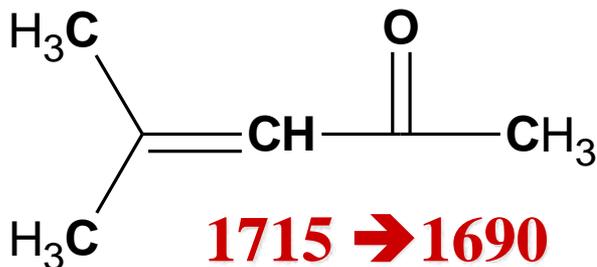
**Factor influencing C=O**

1) conjugation



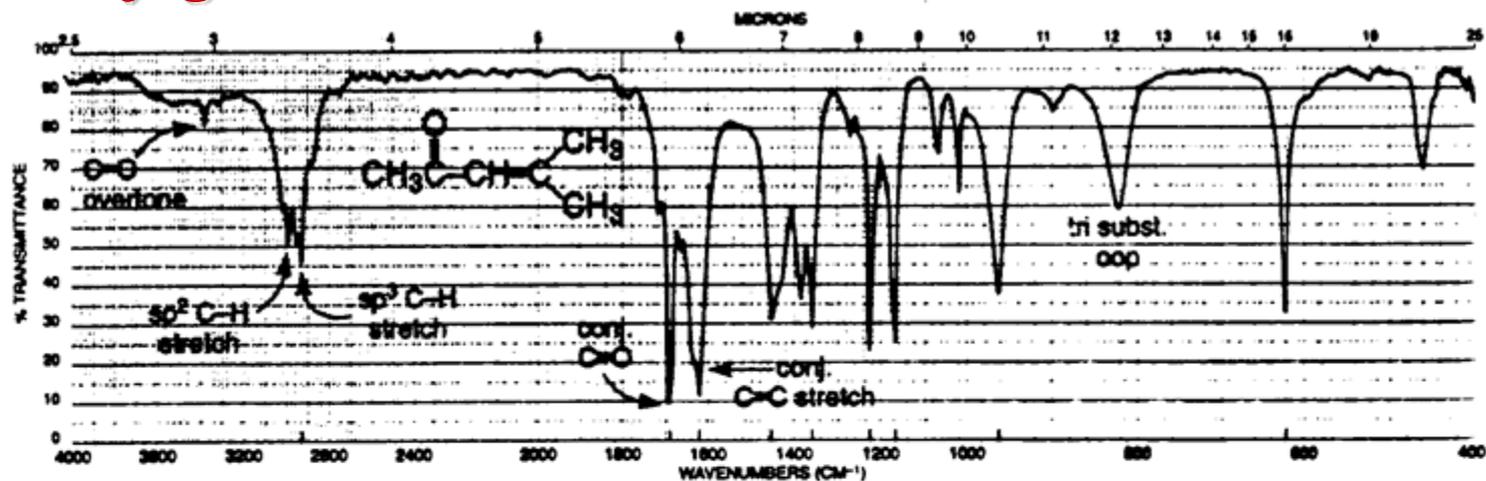
Conjugation increase single bond character of C=O

→ Lower force constant → lower frequency number

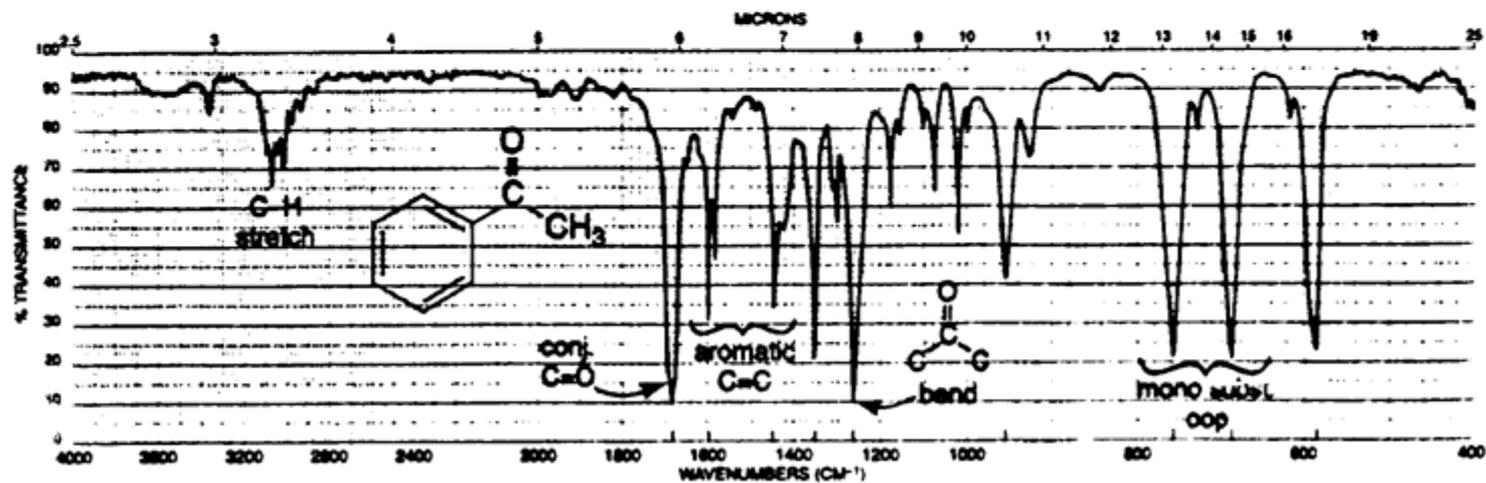


# Ketone and Conjugation

Conjugation: Lower  $\bar{\nu}$



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

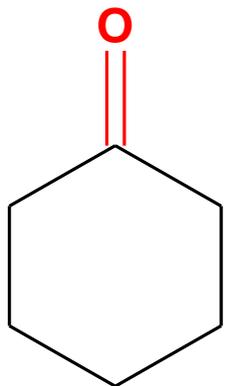
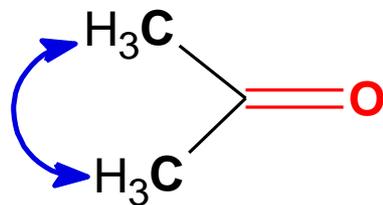


► FIGURE 2.40 The infrared spectrum of acetophenone (neat liquid, KBr plates).

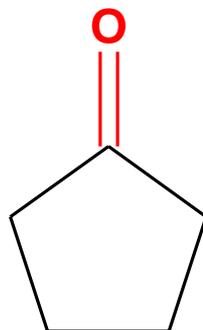
# Ketone and Ring Strain

## Factors influencing C=O

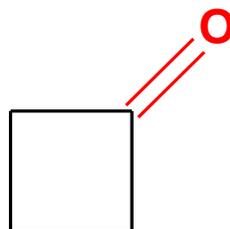
### 2) Ring size



1715 cm<sup>-1</sup>



1751 cm<sup>-1</sup>



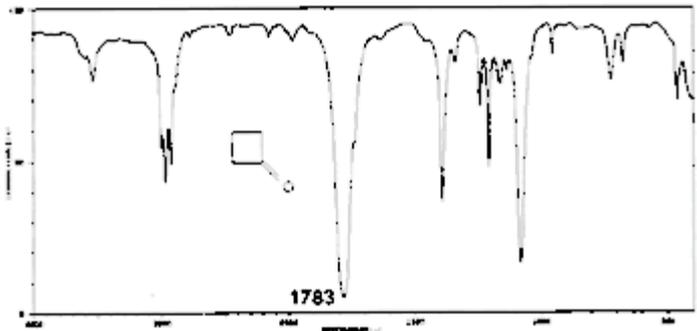
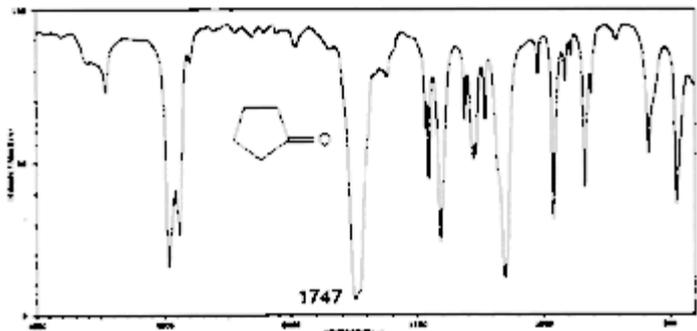
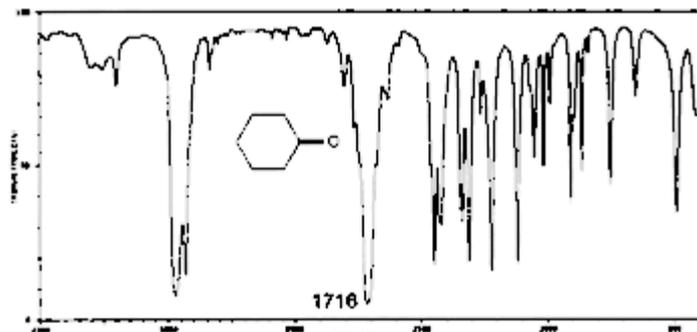
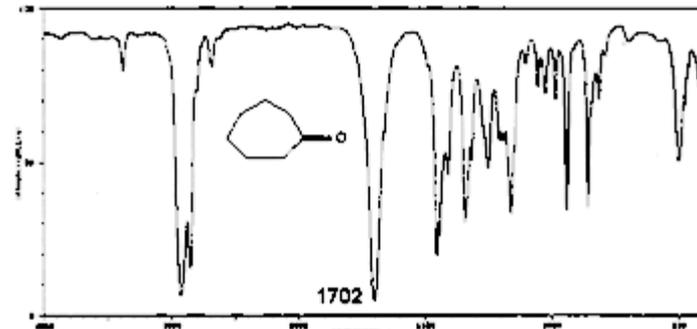
1775 cm<sup>-1</sup>

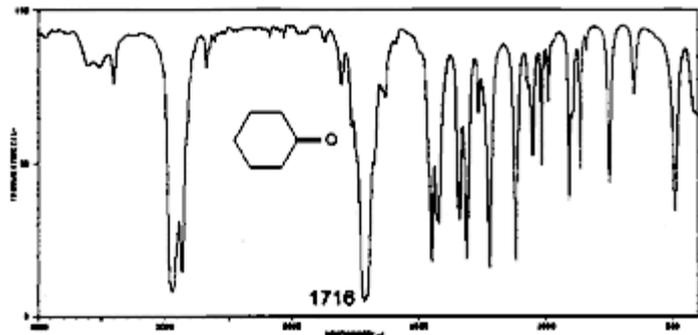
Angle ~ 120°

< 120°

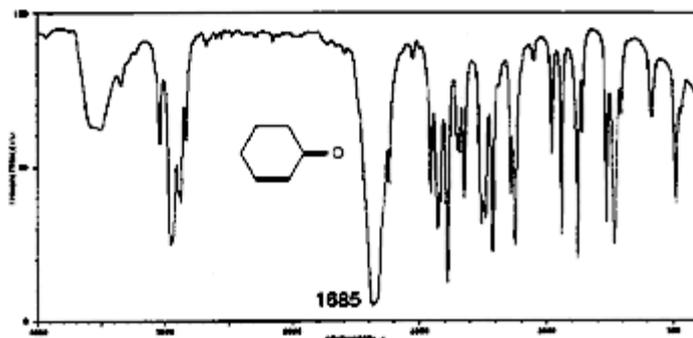
<< 120°

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



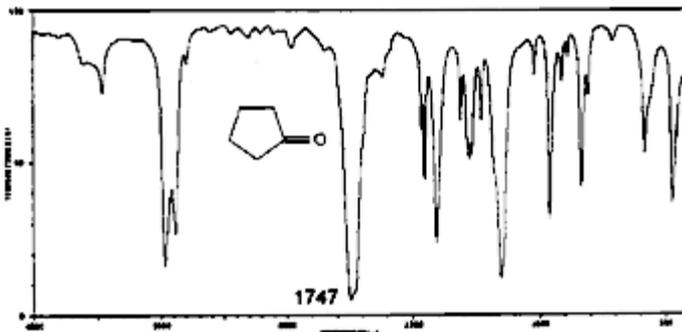


ketone

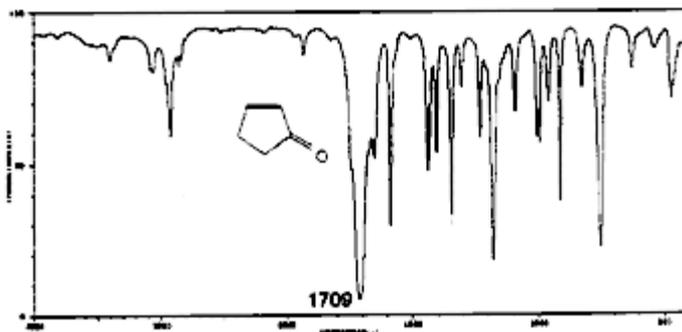


conj. ketone

ketone: Ring strain

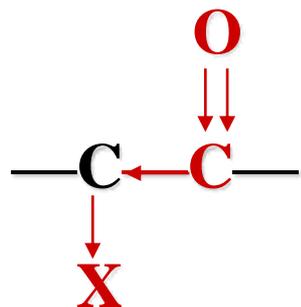


Ring strain + conj.

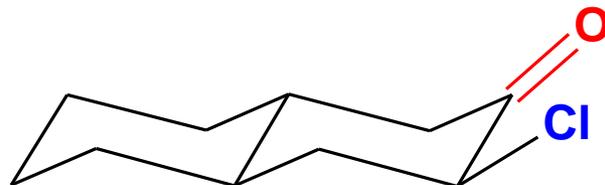


# Factors influencing carbonyl: C=O

## 3) $\alpha$ substitution effect (Chlorine or other halogens)



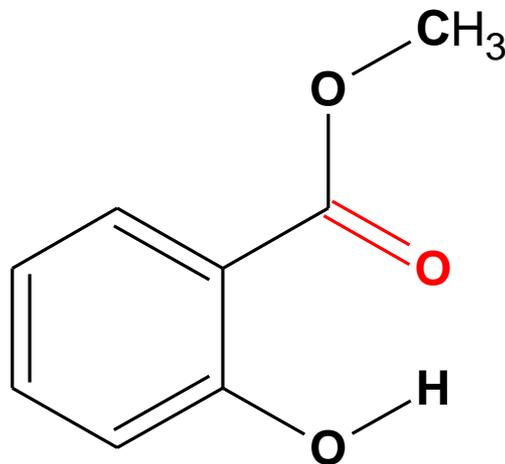
Result in stronger bond  $\rightarrow$  higher frequency  $\bar{\nu}$



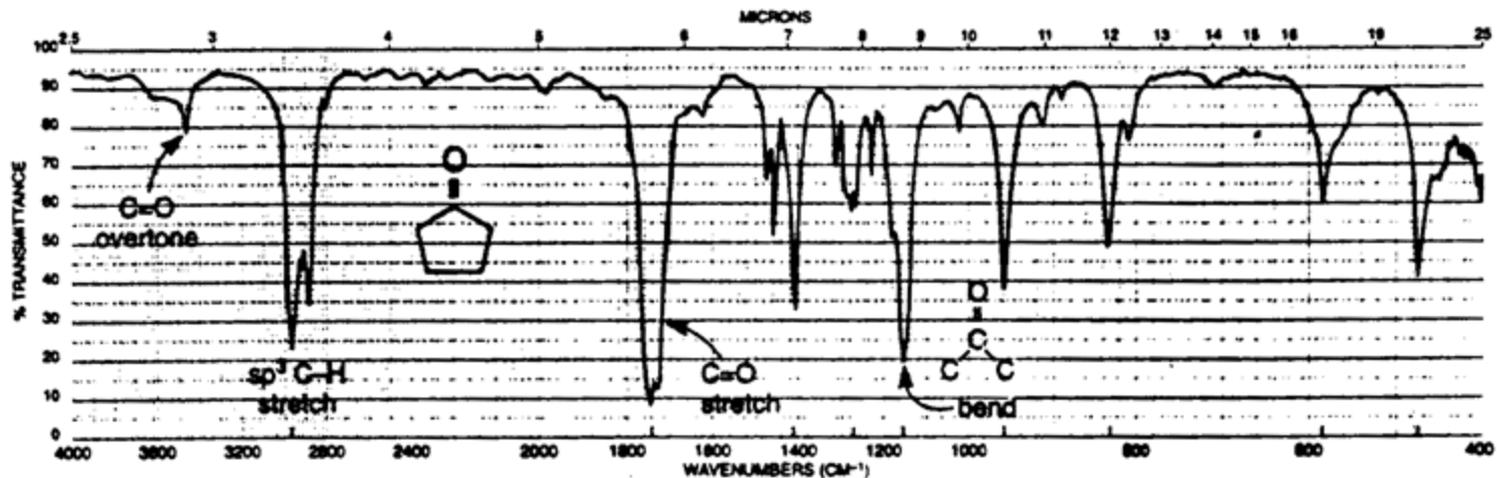
1750  $\text{cm}^{-1}$

## 4) Hydrogen bonding

Decrease C=O strenght  $\rightarrow$  lower frequency

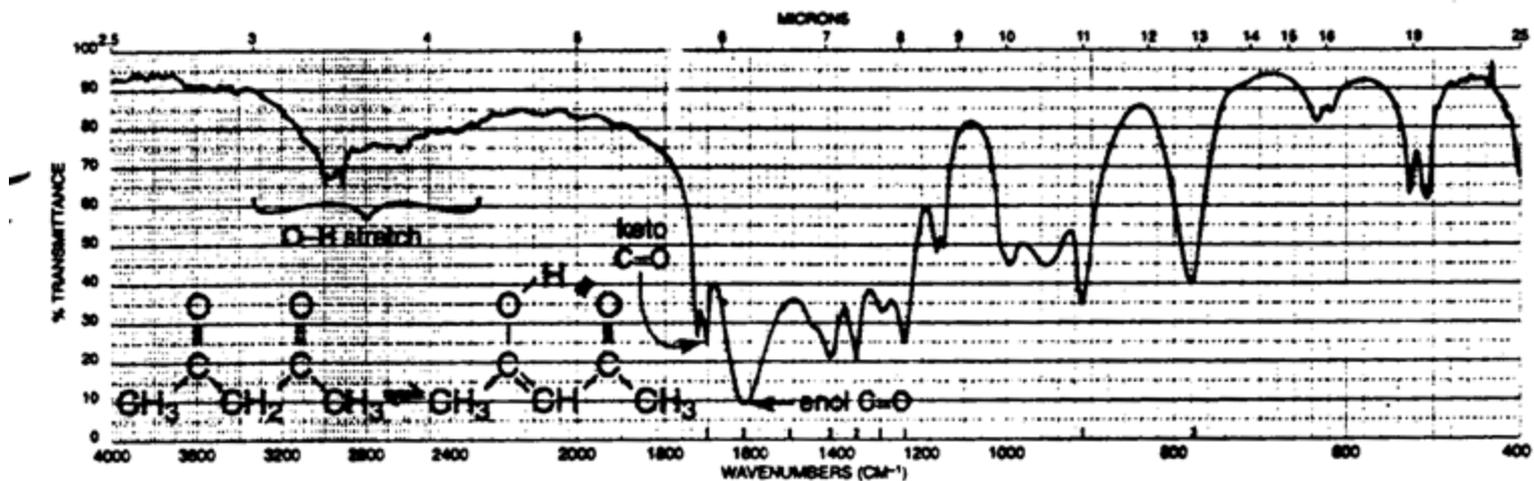


1680  $\text{cm}^{-1}$



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

**Enol**

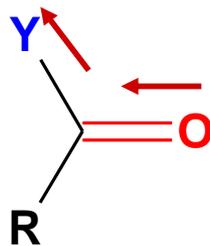


► FIGURE 2.42 The infrared spectrum of 2,4-pentanedione (neat liquid, KBr plates).

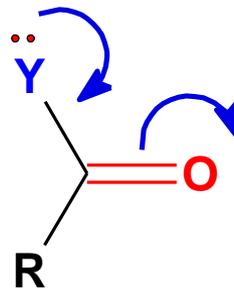
# Factors influencing carbonyl: C=O

## 5) Heteroatom

**Inductive effect**  
**Stronger bond**  
**higher frequency**



e.g. ester



e.g. amides

**Resonance effect**  
**Weaker bond**  
**Lower frequency**

	Y	C=O
inductive	Cl	1815-1785
	Br	1812
	OH (monomer)	1760
	OR (Ester)	1705-1735
resonance	NH <sub>2</sub>	1695-1650
	SR	1720-1690

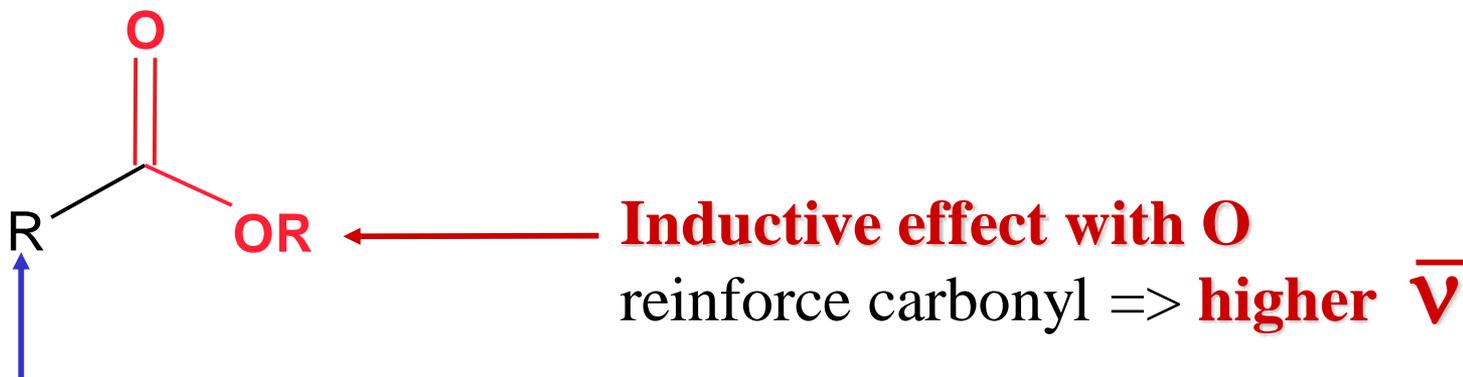
# Ester Carbonyl

Esters

**C=O**  $\bar{\nu} \sim 1750 - 1735 \text{ cm}^{-1}$

*Conjugation => lower freq.*

**O-C : 1300 - 1000 2 or more bands**

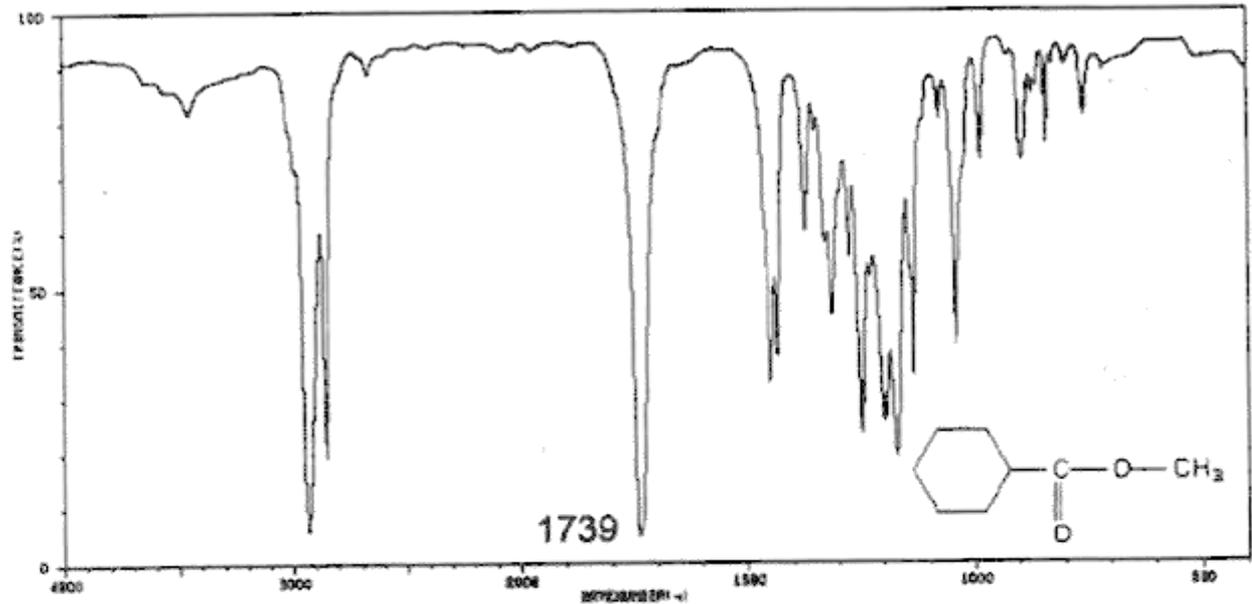


**Conjugation with CO**

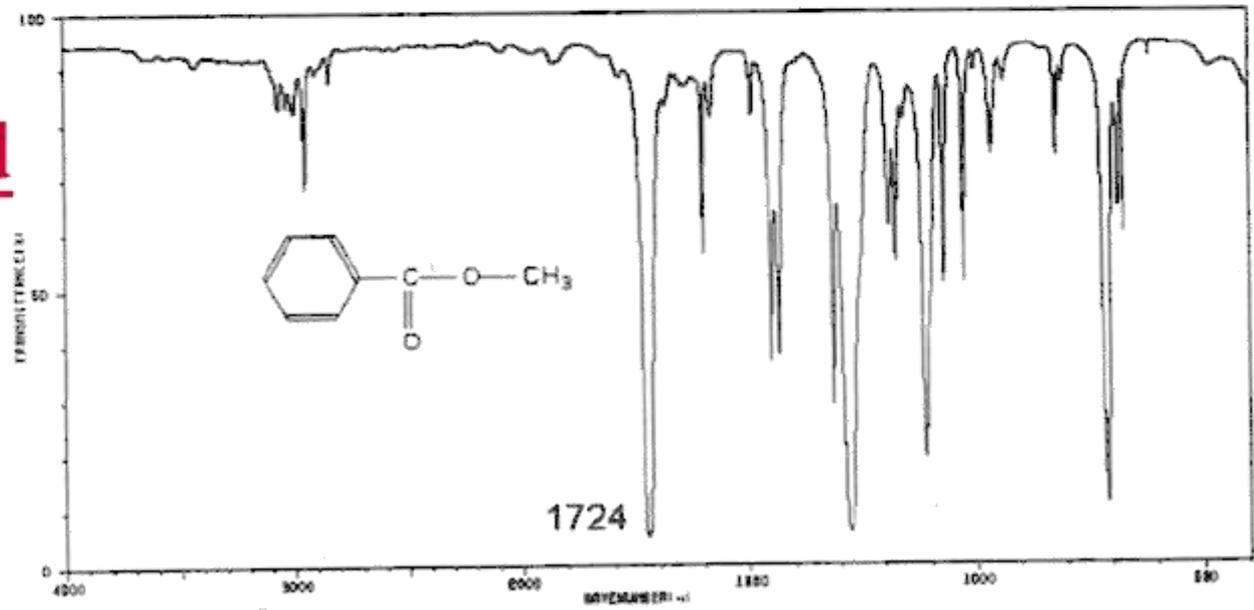
weaken carbonyl => **Lower**  $\bar{\nu}$

# Ester carbonyl: C=O

ESTER

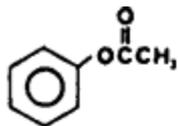


Conjugated  
ESTER



# Ester carbonyl: C=O

10872-3 CAS [122-79-2]  
Phenyl acetate, 97%

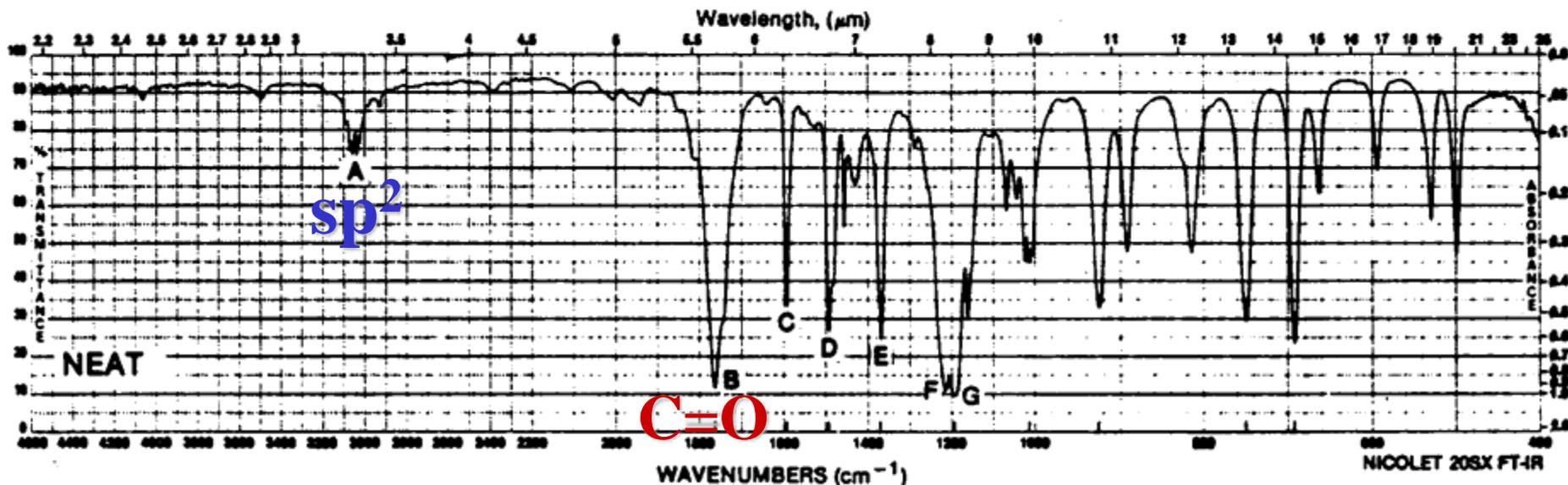


FW 136.15  
bp 196°C  
d 1.073

Fp 170°F  
n<sub>D</sub> 1.5030

IR III, 1038C  
NMR II, 2,301C  
Merck 10,7147

1764.8	1370.6	925.2
1593.8	1193.3	749.0
1493.1	1013.1	691.9



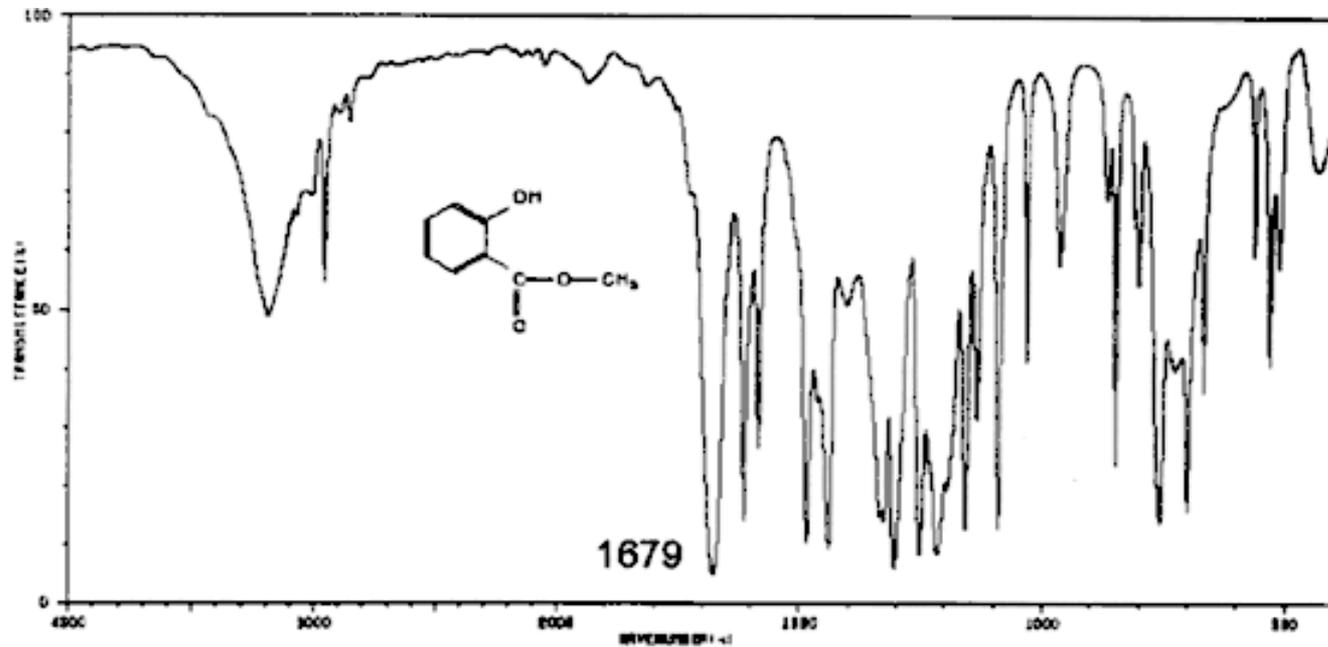
**FIGURE 3.25.** Phenyl acetate. A. Aromatic C—H stretch, 3070, 3040 cm<sup>-1</sup>. B. The C=O stretch, 1765 cm<sup>-1</sup>: this is higher frequency than that from a normal ester C=O stretch (~1740 cm<sup>-1</sup>; see Table 3.3) because of phenyl conjugation with alcohol oxygen; conjugation of an 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<sup>-1</sup>). C. Ring C≡C stretch, 1594 cm<sup>-1</sup>. D. δ<sub>as</sub>CH<sub>3</sub>, 1493 cm<sup>-1</sup>. E. δ<sub>s</sub>CH<sub>3</sub>, 1371 cm<sup>-1</sup>. F. Acetate C(=O)—O stretch, 1215 cm<sup>-1</sup>. G. The O—C≡C asymmetrical stretch, 1193 cm<sup>-1</sup>.

**C=O : 1765 cm<sup>-1</sup>**

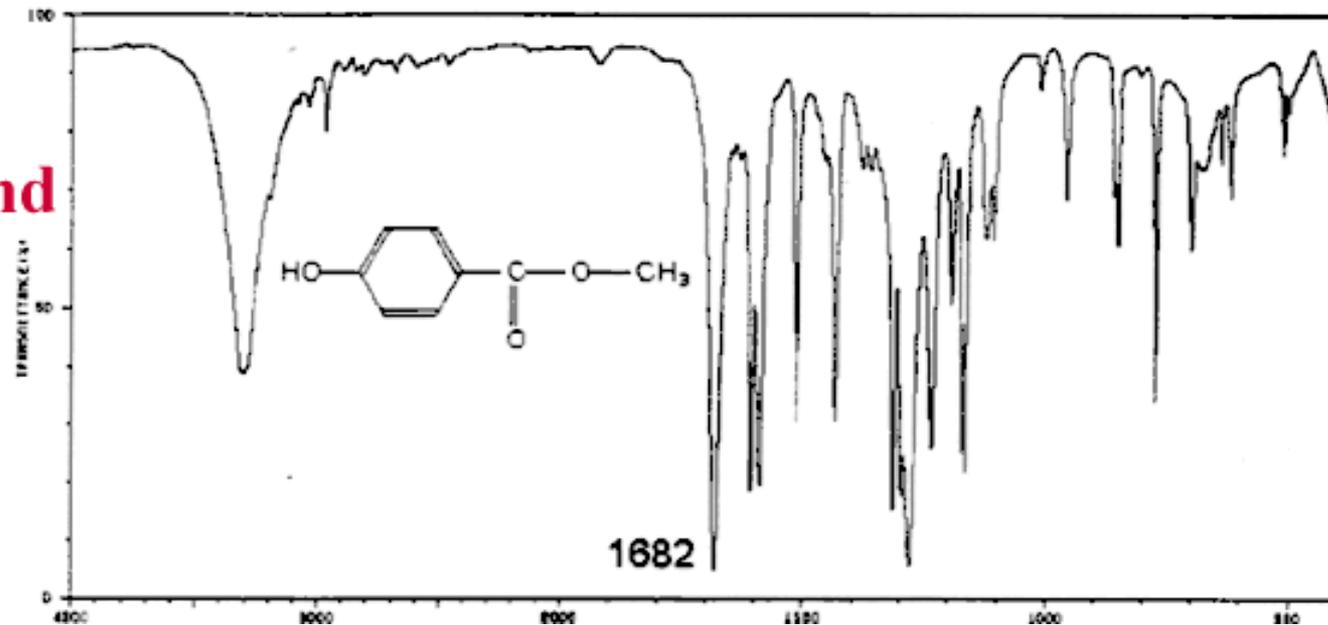
**C-O 1215 cm<sup>-1</sup>  
1193 cm<sup>-1</sup>**

# Ester carbonyl: C=O

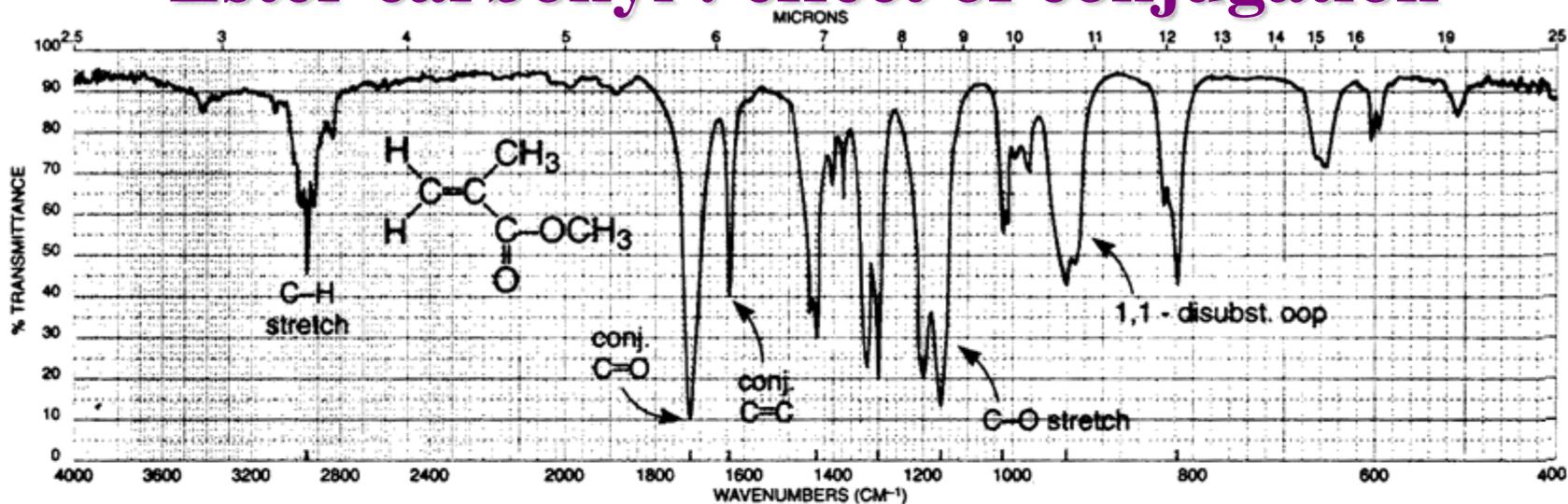
Conjugated  
Ester  
With H-Bond



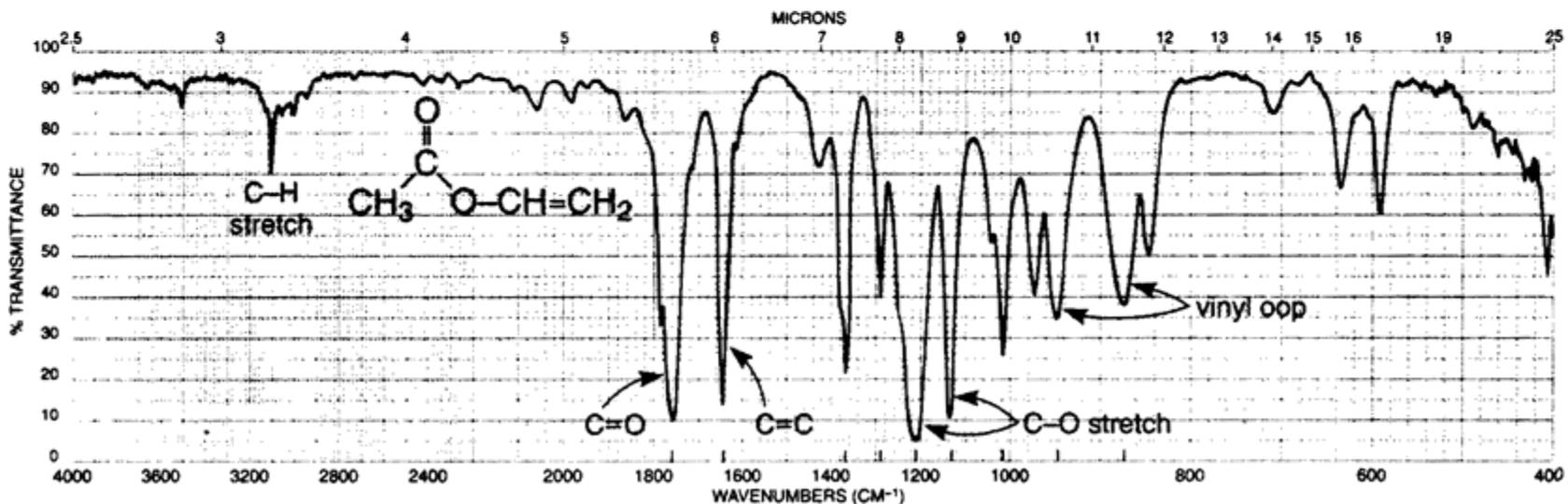
Conjugated  
Ester  
Without H-Bond



# Ester carbonyl : effect of conjugation



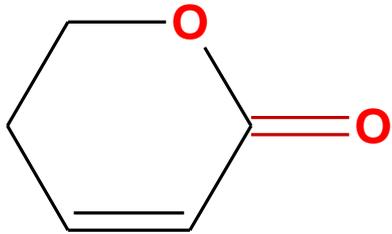
► **FIGURE 2.48** The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).



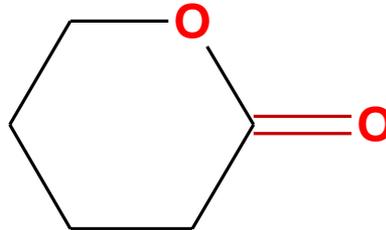
► **FIGURE 2.49** The infrared spectrum of vinyl acetate (neat liquid, KBr plates).

# Lactone carbonyl: C=O

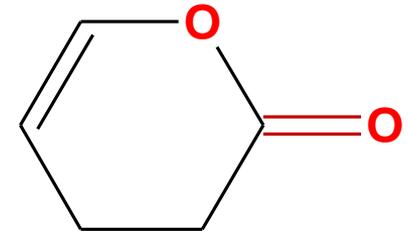
Lactones → Cyclic Ester



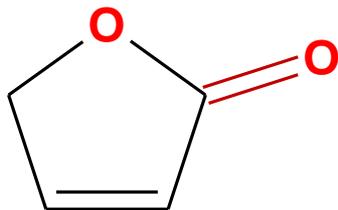
1720



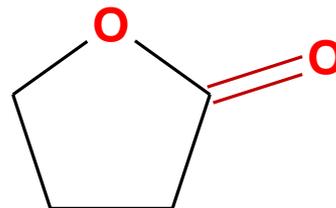
1735



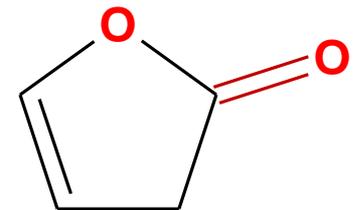
1760



1750



1770

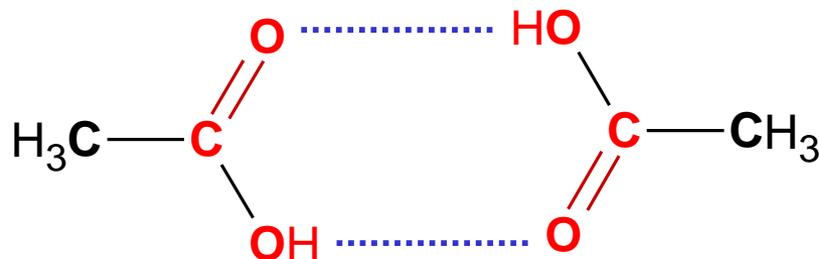


1800

# Carbonyl compounds : Acids

## Carboxylic acid

Exist as dimer :



Strong Hydrogen bond

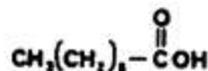
**OH : Very broad → 3400 – 2400 cm<sup>-1</sup>**

**C=O : broad → 1730 – 1700 cm<sup>-1</sup>**

**C—O : 1320 – 1210 cm<sup>-1</sup> Medium intensity**

# Carbonyl compounds : Acids

14687-0 CAS [111-14-8]  
Heptanoic acid, 96%

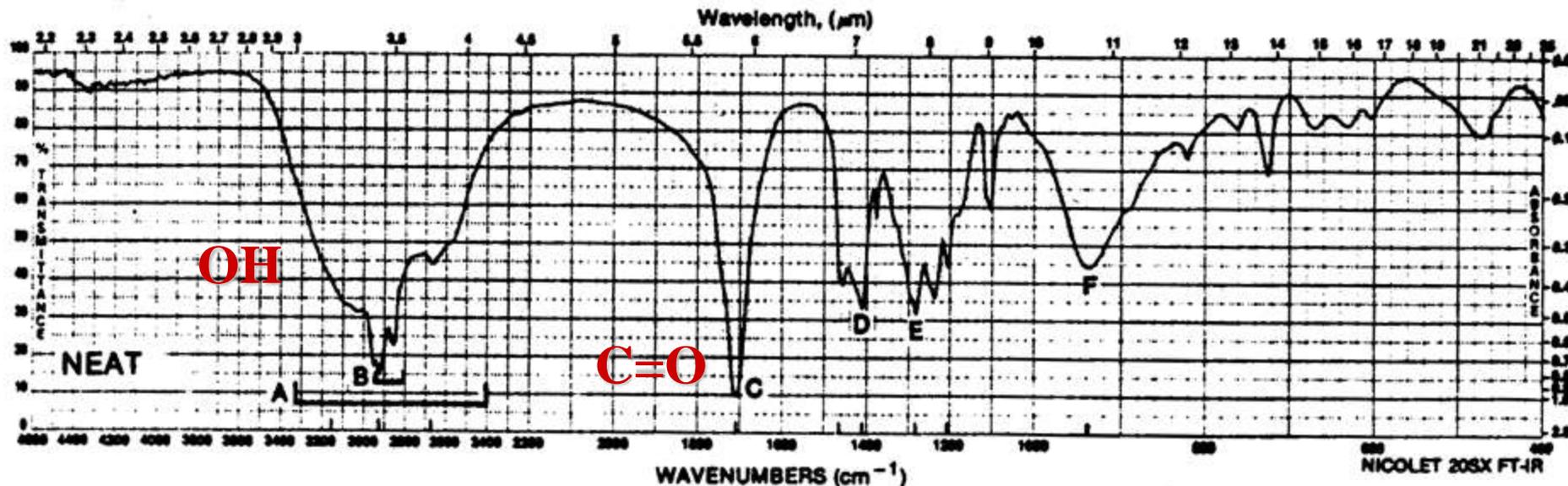


FW 130.19  
mp -10.5°C  
bp 223-223.5°C

d 0.918  
Fp >235°F  
n<sub>D</sub> 1.4221

IR III, 284G  
NMR II, 1,420C  
Merck 10,4552

3156.0	1710.7	1284.7
2931.8	1467.5	1207.6
2676.6	1413.3	938.5



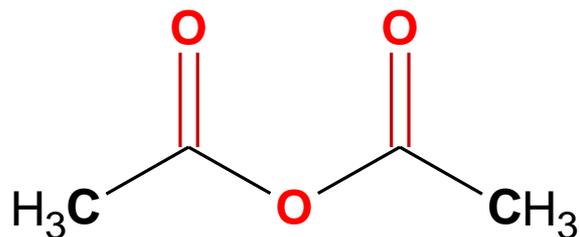
**FIGURE 3.23.** Heptanoic acid. A. Broad O—H stretch, 3300–2500 cm<sup>-1</sup>. B. The C—H stretch (see Fig. 3.8), 2950, 2932, 2855 cm<sup>-1</sup>. Superimposed upon O—H stretch. C. Normal, dimeric carboxylic C=O stretch, 1711 cm<sup>-1</sup>. D. The C—O—H in-plane bend,\* 1413 cm<sup>-1</sup>. E.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

**C=O : 1711 cm<sup>-1</sup>**

**OH : Very Broad 3300 to 2500 cm<sup>-1</sup>**

**C-O : 1285, 1207 cm<sup>-1</sup>**

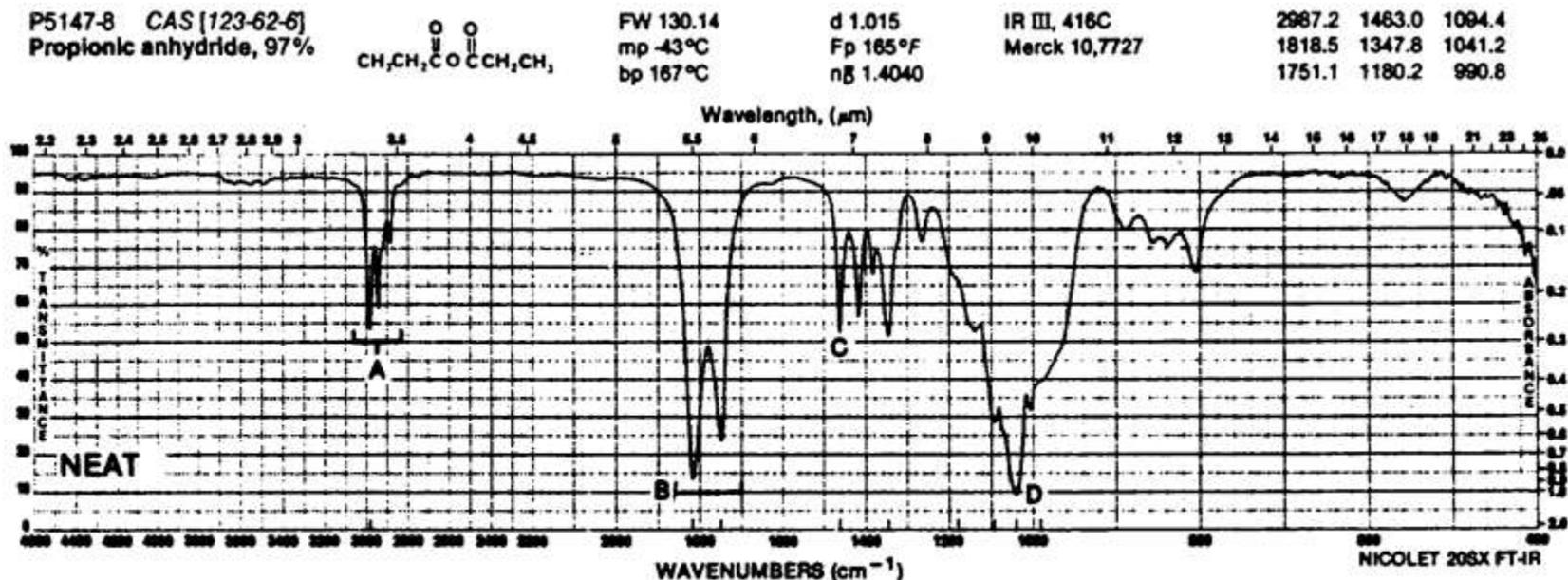
# Anhydrides



**C=O** always has 2 bands:

**1830-1800 and 1775-1740  $\text{cm}^{-1}$**

**C—O** multiple bands 1300 – 900  $\text{cm}^{-1}$



**FIGURE 3.27.** Propionic anhydride A. The C—H stretch, 2987, 2940, 2880  $\text{cm}^{-1}$ . B. Asymmetric and symmetric C=O coupled stretching, respectively: 1818, 1751  $\text{cm}^{-1}$ . See Table 3.3. C.  $\delta_3\text{CH}_2$  (scissoring), 1463  $\text{cm}^{-1}$ . D. C—CO—O—CO—C stretch, 1041  $\text{cm}^{-1}$ .

# Carbonyl compounds : Aldehydes

Aldehydes C=O  $\bar{\nu} \sim 1725 \text{ cm}^{-1}$

Conjugation => lower freq.

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

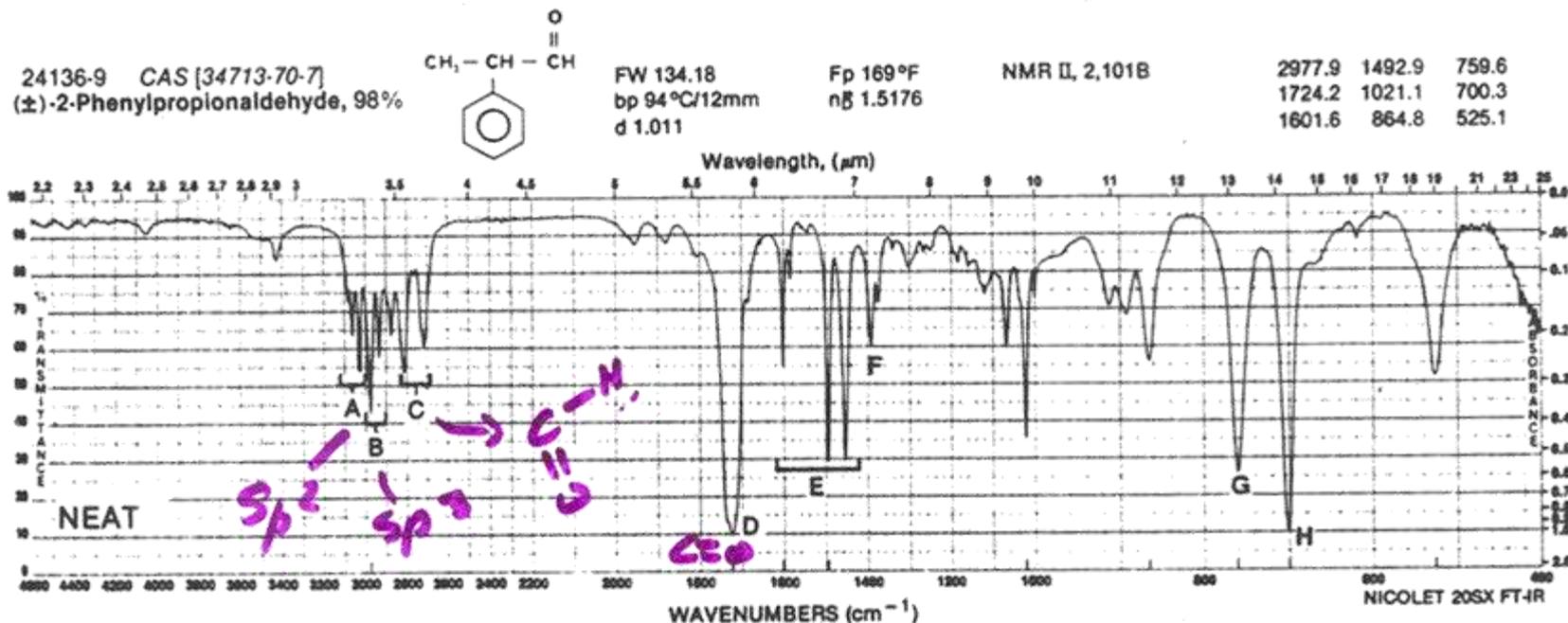
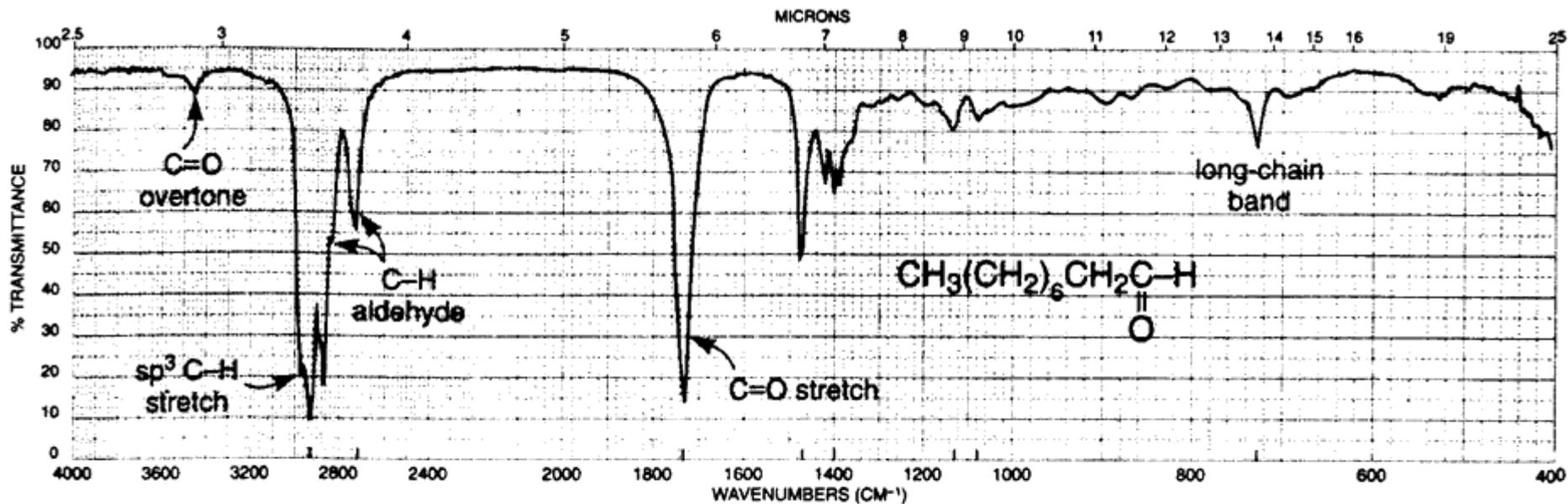


FIGURE 3.22. (±)-2-Phenylpropionaldehyde. A.\* Aromatic, 3070, 3040  $\text{cm}^{-1}$  (see Fig. 3.13). B.\* Aliphatic, 2978, 2940, 2875  $\text{cm}^{-1}$  (see Figs. 3.8 and 3.13). C.\* Aldehydic, C—H stretch, 2825, 2720  $\text{cm}^{-1}$ . Doublet from Fermi resonance with overtone of band at F. D. Normal aldehydic C=O stretch, 1724  $\text{cm}^{-1}$ . Conjugated C=O stretch would be about 1700  $\text{cm}^{-1}$ , for example, as for  $\text{C}_6\text{H}_5\text{CHO}$ . E. Ring C=C stretch, 1602, 1493, 1455  $\text{cm}^{-1}$ . F. Aldehydic C—H bend, 1390  $\text{cm}^{-1}$ . G. Out-of-plane C—H bend, 760  $\text{cm}^{-1}$ . H. Out-of-plane C=C bend, 700  $\text{cm}^{-1}$ .

\*Bands A—C are C—H stretch absorptions  
 Source: Courtesy of Aldrich Chemical Company.

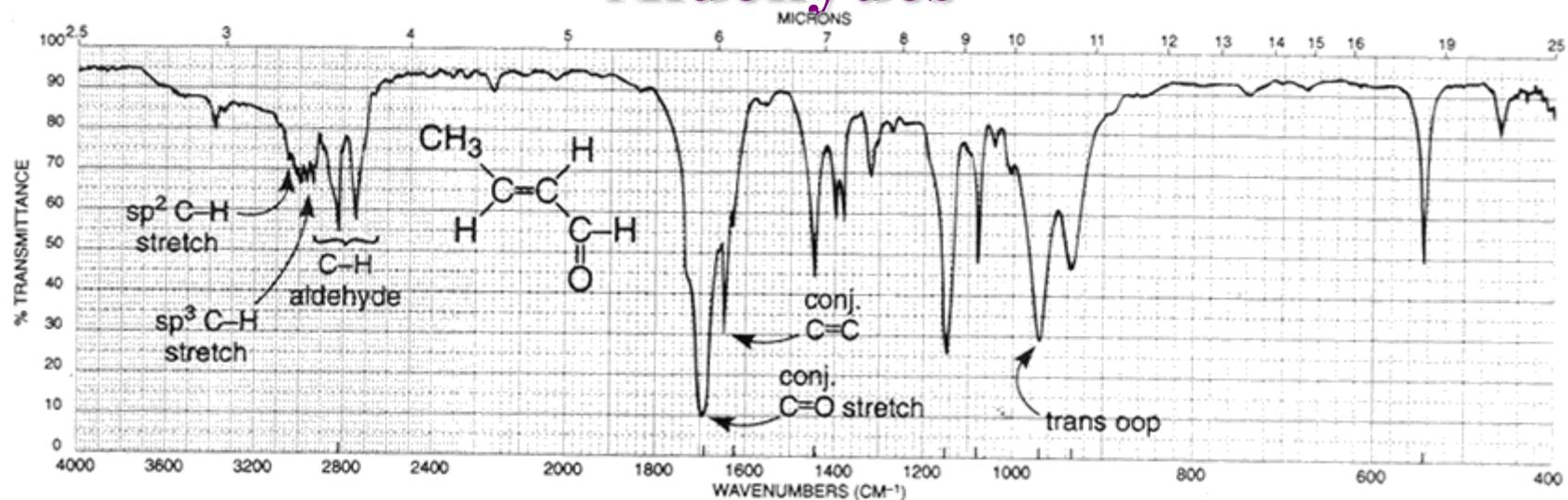
**C=O : 1724  $\text{cm}^{-1}$**

# Carbonyl compounds : Aldehydes

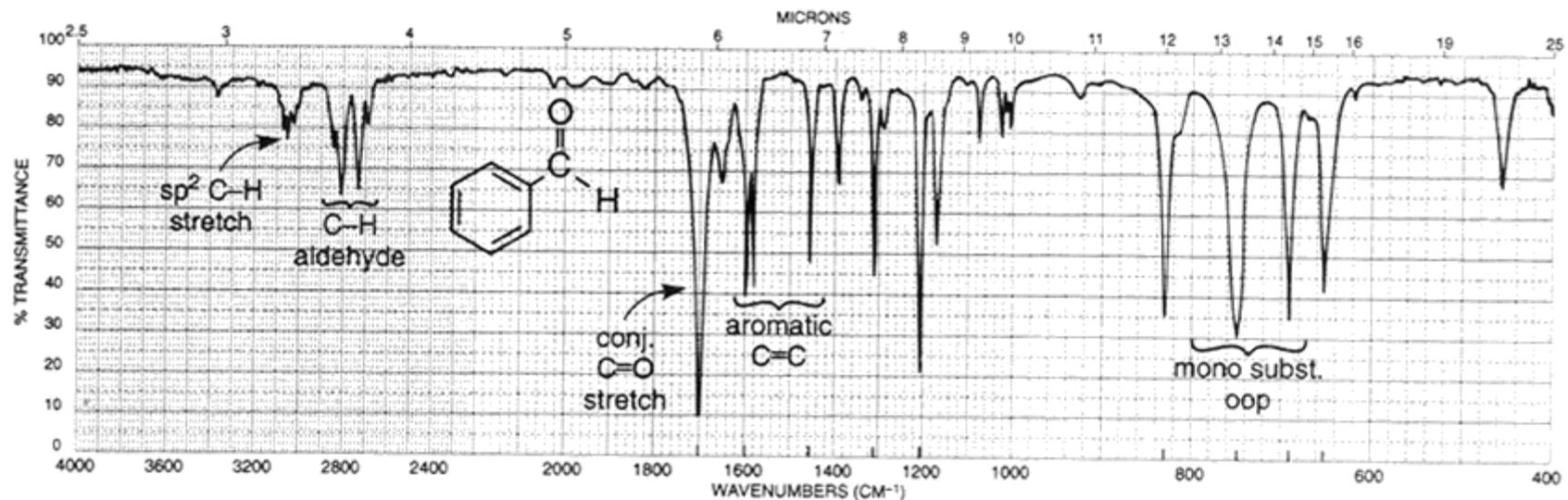


► **FIGURE 2.36** The infrared spectrum of nonanal (neat liquid, KBr plates).

# 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

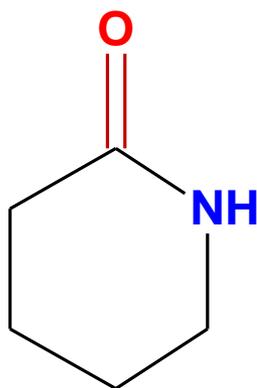
**C=O** ~1680-1630  $\text{cm}^{-1}$  (band I)

**NH<sub>2</sub>** ~ 3350 and 3180  $\text{cm}^{-1}$  (stretch)

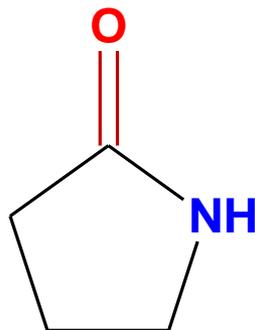
**NH** ~ 3300  $\text{cm}^{-1}$  (stretch)

**NH** ~ 1640-1550  $\text{cm}^{-1}$  (bending)

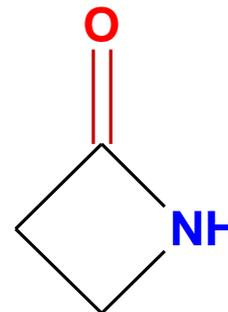
## Lactams



~1660



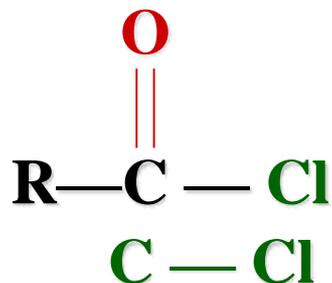
~1705



~1745

$\bar{\nu}$  Increase with strain

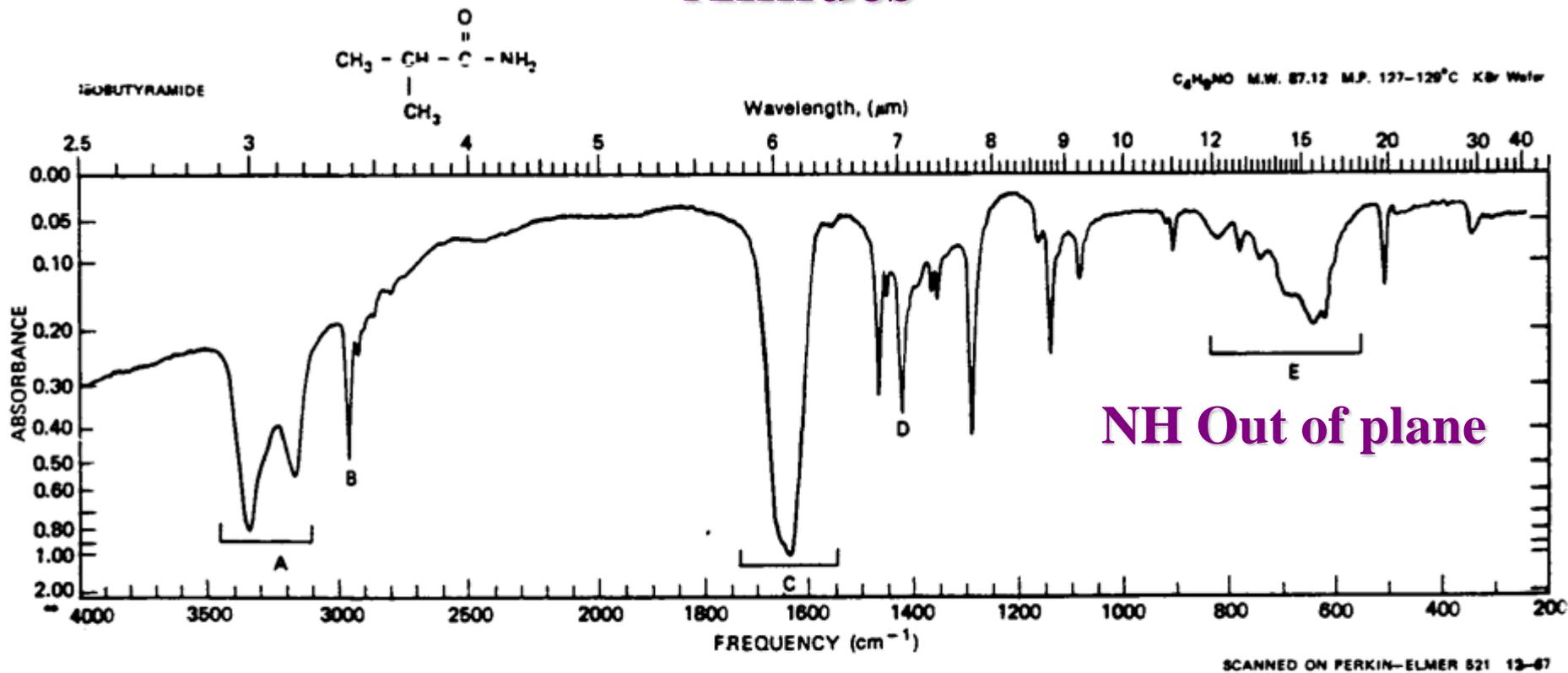
## Acid Chlorides



1810-1775  $\text{cm}^{-1}$

730 - 550  $\text{cm}^{-1}$

# Amides



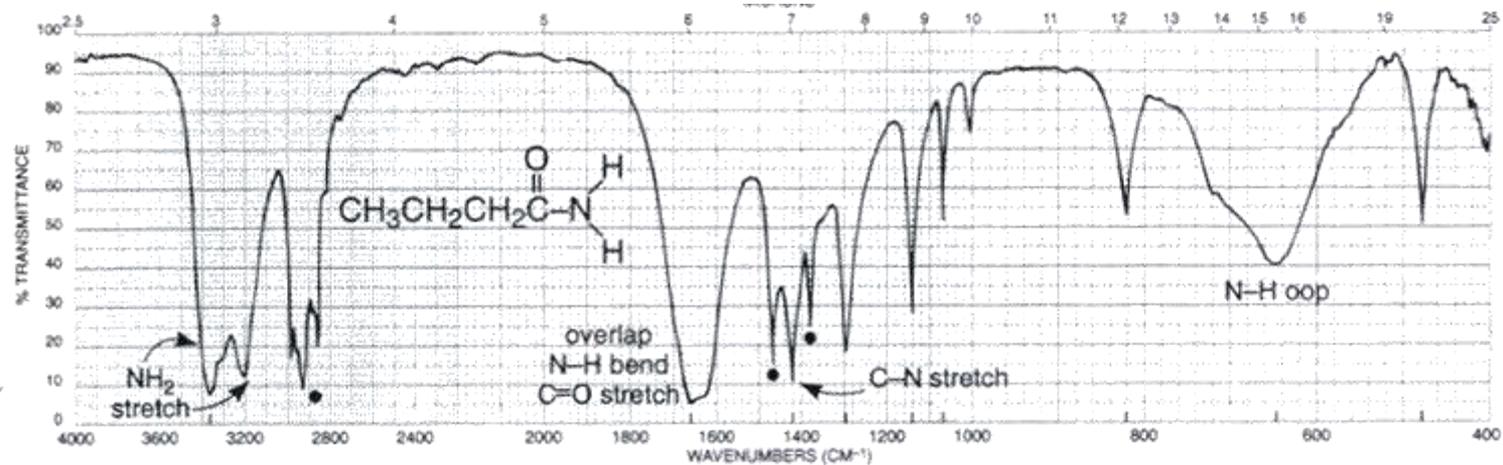
**FIGURE 3.28.** 2-methylpropanamide. \* A. The N—H stretch, coupled, primary amide, hydrogen bonded; asymmetric,  $3352\text{ cm}^{-1}$ ; symmetric,  $3170\text{ cm}^{-1}$ . B. Aliphatic C—H stretch,  $2960\text{ cm}^{-1}$ . C. Overlap C=O stretch, amide I band,  $1640\text{ cm}^{-1}$ ; see Table 3.3.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

\*The CA name for isobutyramide is 2-methylpropanamide.

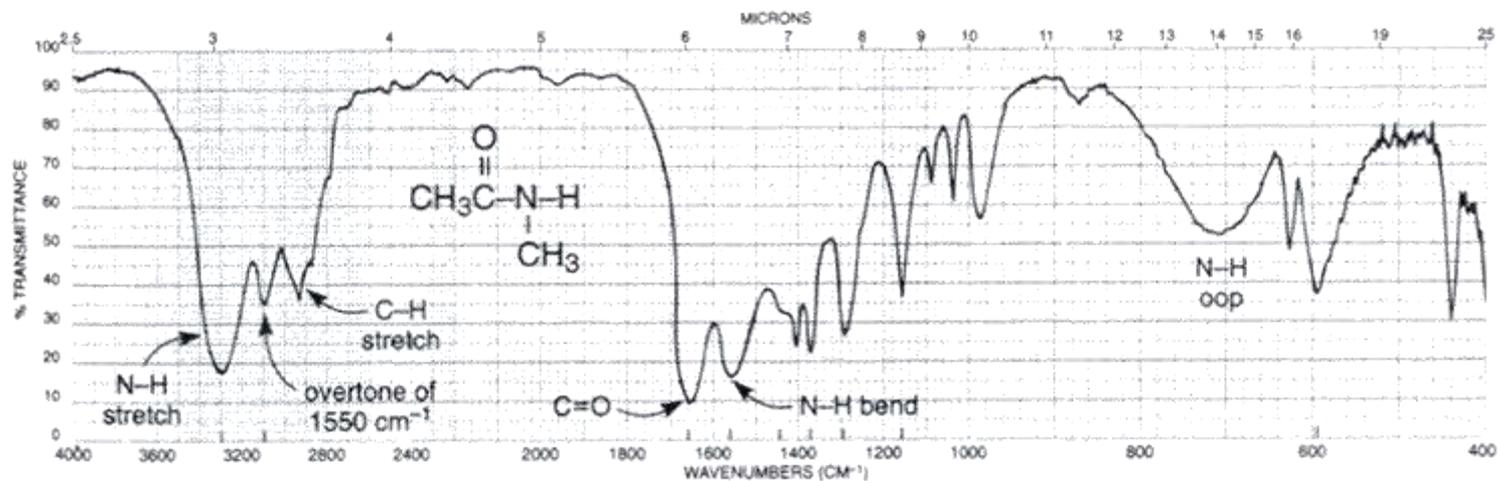
$\text{NH}_2$  : Symmetrical stretch  $\Rightarrow 3170\text{ cm}^{-1}$   
 asymmetrical stretch  $\Rightarrow 3352\text{ cm}^{-1}$

$\text{C}=\text{O}$  :  $1640\text{ cm}^{-1}$

# Amides

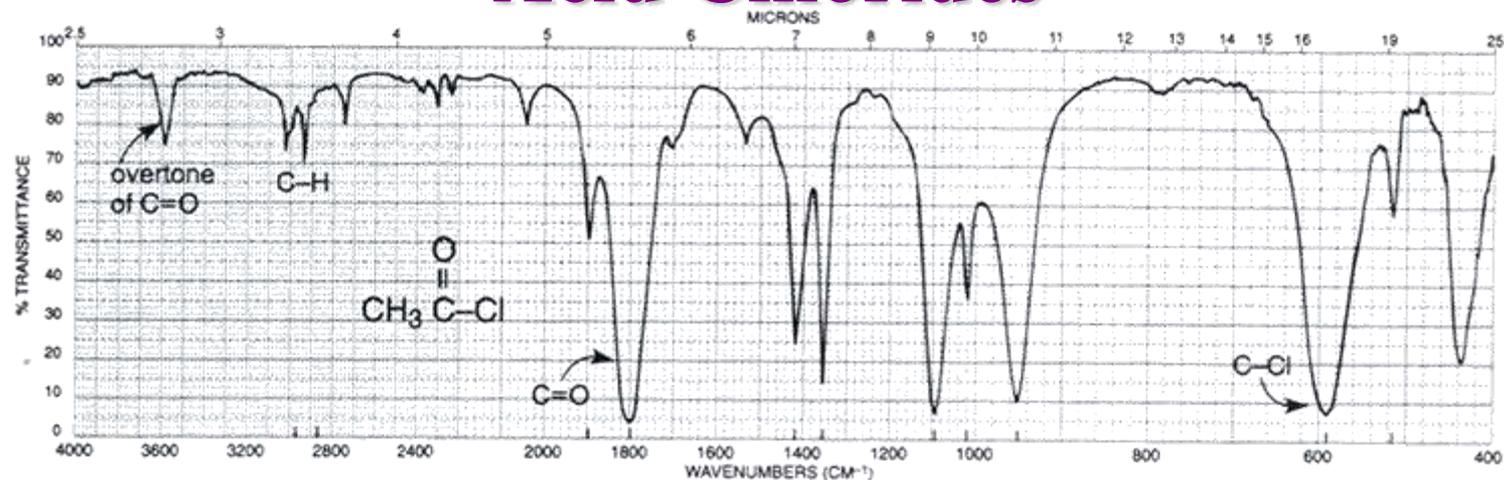


► **FIGURE 2.53** The infrared spectrum of propionamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

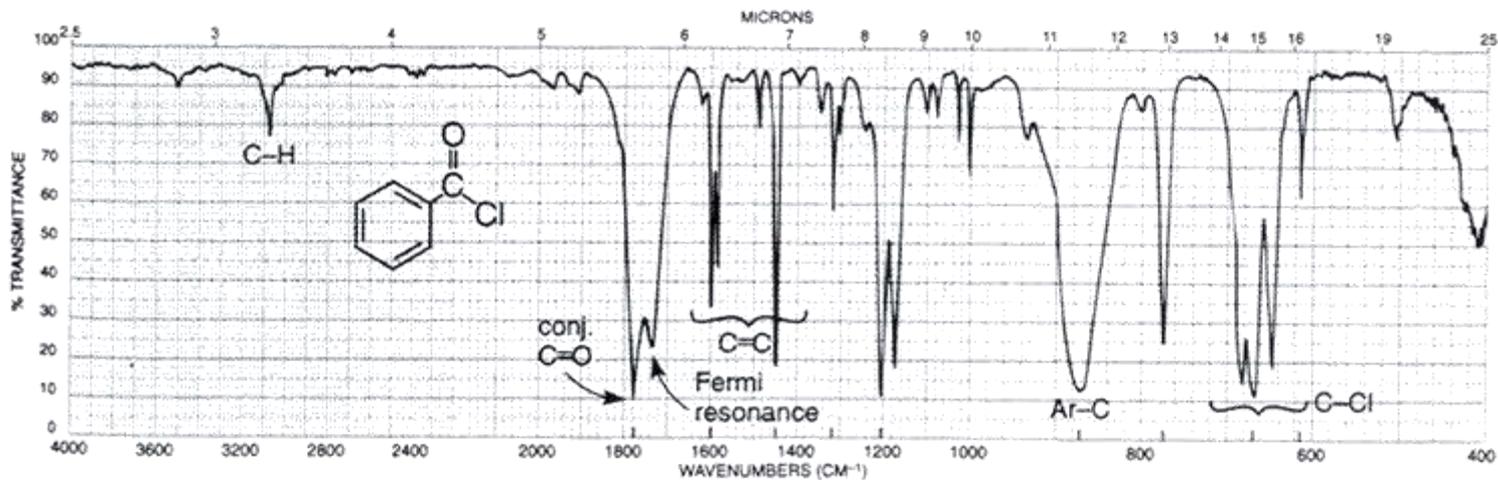


► **FIGURE 2.54** The infrared spectrum of *N*-methylacetamide (neat liquid, KBr plates).

# Acid Chlorides



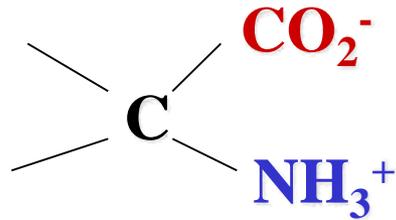
► **FIGURE 2.55** The infrared spectrum of acetyl chloride (neat liquid, KBr plates).



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

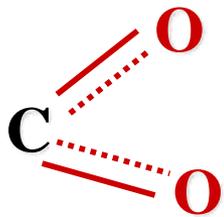
# Amino acid

Exist as zwitterions



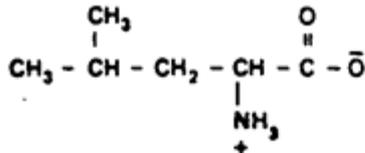
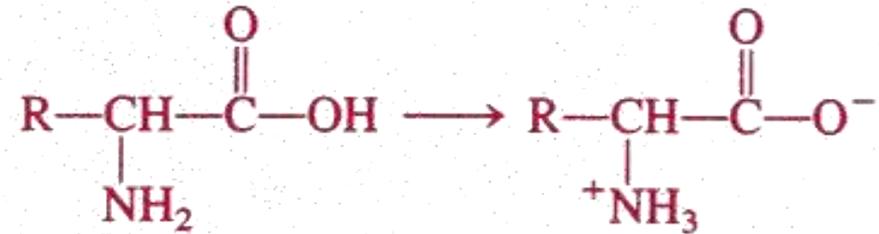
NH<sub>3</sub><sup>+</sup> : very broad 3330-2380

(OH + NH<sub>3</sub><sup>+</sup>)



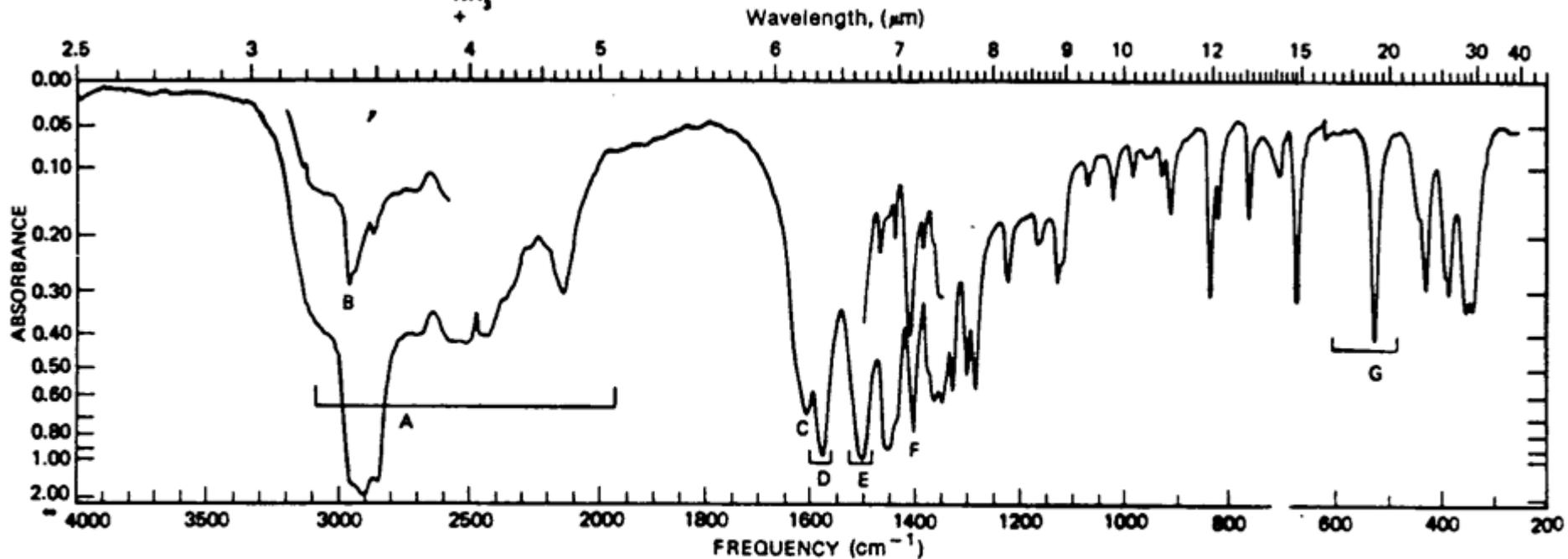
1600 – 1590 strong

# Amino acid



(±) - LEUCINE

$\text{C}_6\text{H}_{13}\text{NO}_2$  M.W. 131.18 M.P. 332°C (dec.) (lit.) Spirt Mull



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Philadelphia, PA. 19104 U.S.A.

SCANN 3 ON PERKIN-ELMER 521 12-67

**FIGURE 3.30.** (±)-Leucine. A. Broad ( $-\text{NH}_3^+$ ) N—H stretch, 3100–2000  $\text{cm}^{-1}$ , extended by combination band at 2140  $\text{cm}^{-1}$ , and other combination-overtone bands. B. Aliphatic C—H stretch (superimposed on N—H stretch), 2967  $\text{cm}^{-1}$ . C. Asymmetric ( $-\text{NH}_3^+$ ) N—H bend, 1610  $\text{cm}^{-1}$ . D. Asymmetric carboxylate ( $\text{C}=\text{O}$ )<sub>2</sub> stretch, 1580  $\text{cm}^{-1}$ . E. Symmetric ( $-\text{NH}_3^+$ ) N—H bend, 1505  $\text{cm}^{-1}$ . F. Symmetric carboxylate ( $\text{C}=\text{O}$ )<sub>2</sub> stretch, 1405  $\text{cm}^{-1}$ . G. Torsional ( $-\text{NH}_3^+$ ) N—H oscillation, 525  $\text{cm}^{-1}$ .

# Amine

NH  $3500 - 3300 \text{ cm}^{-1}$  { NH : 2 bands  
NH : 1 band

NH bending :  $1650 - 1500 \text{ cm}^{-1}$

C-N :  $1350 - 1000 \text{ cm}^{-1}$

NH out-of-plane :  $\sim 800 \text{ cm}^{-1}$

---

## Amine salt

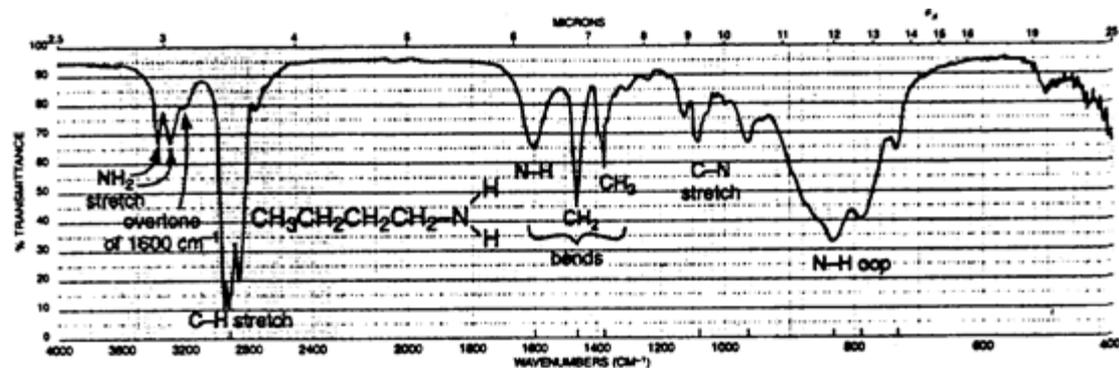
NH<sup>+</sup>  $3500 - 3030 \text{ cm}^{-1}$  broad / strong

Ammonium → primary → secondary → right  $\bar{\nu}$

Left  $\bar{\nu}$

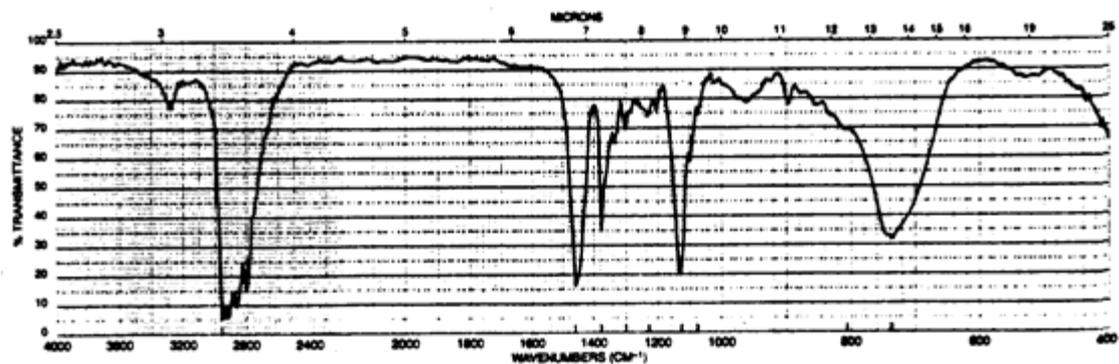
# Amine

## Primary Amine



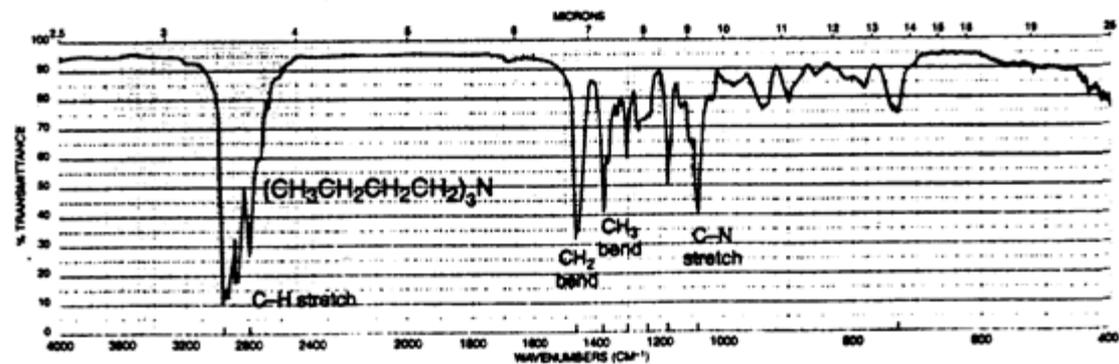
► FIGURE 2.58 The infrared spectrum of butylamine (neat liquid, KBr plates).

## Secondary Amine



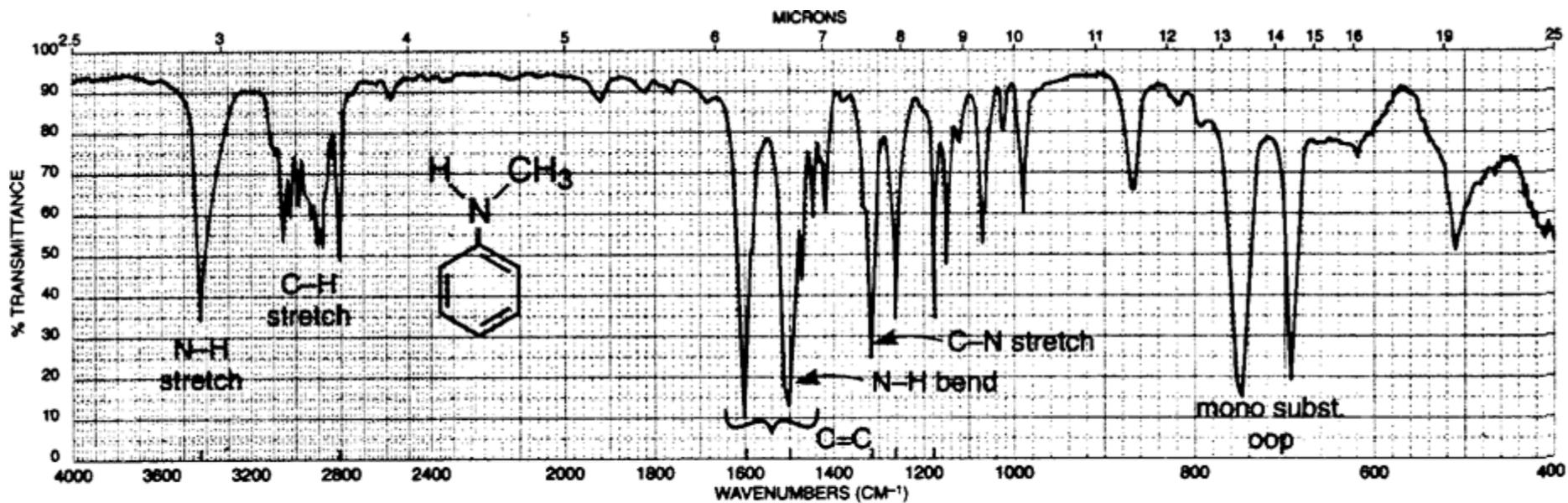
► FIGURE 2.59 The infrared spectrum of dibutylamine (neat liquid, KBr plates).

## 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≡N :**      **Sharp 2250 cm<sup>-1</sup>**

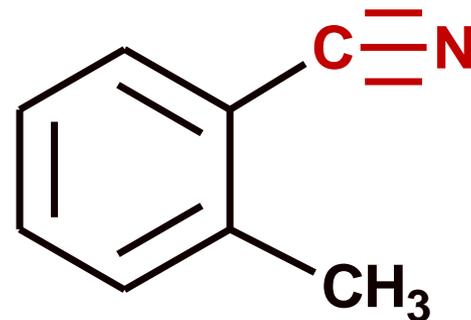
*Conjugation moves to lower frequency*

**Isocyanates**      **R-N=C=O**      **Broad ~ 2270 cm<sup>-1</sup>**

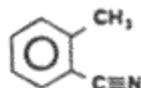
**Isothiocyanates**      **R-N=C=S**      **2 Broad peaks ~ 2125 cm<sup>-1</sup>**

**Imines / Oximes**      **R<sub>2</sub>C=N-R**      **1690 - 1640 cm<sup>-1</sup>**

# Nitrile



11977-6 CAS [529-19-1]  
o-Tolunitrile, 98%



FW 117.15  
mp 13°C  
bp 205°C

d 0.989  
Fp 184°F  
n<sub>D</sub> 1.5279

IR III, 1128D  
Merck 10,9367

2225.6	1384.5	712.0
1601.6	1291.2	562.6
1486.9	760.9	458.9

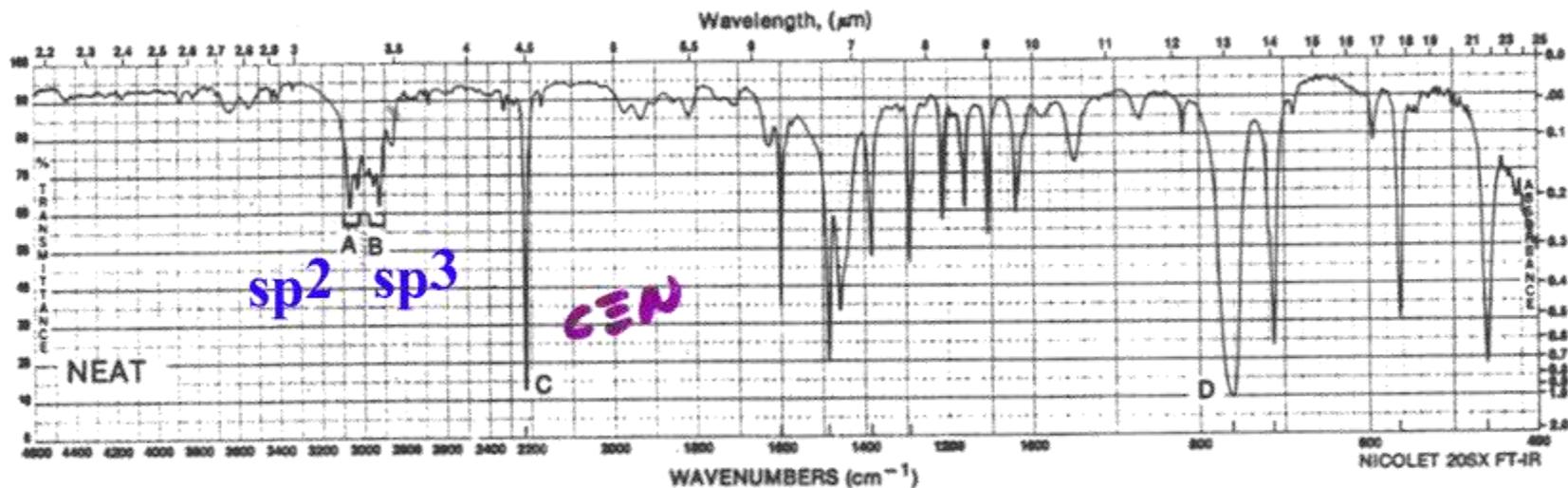
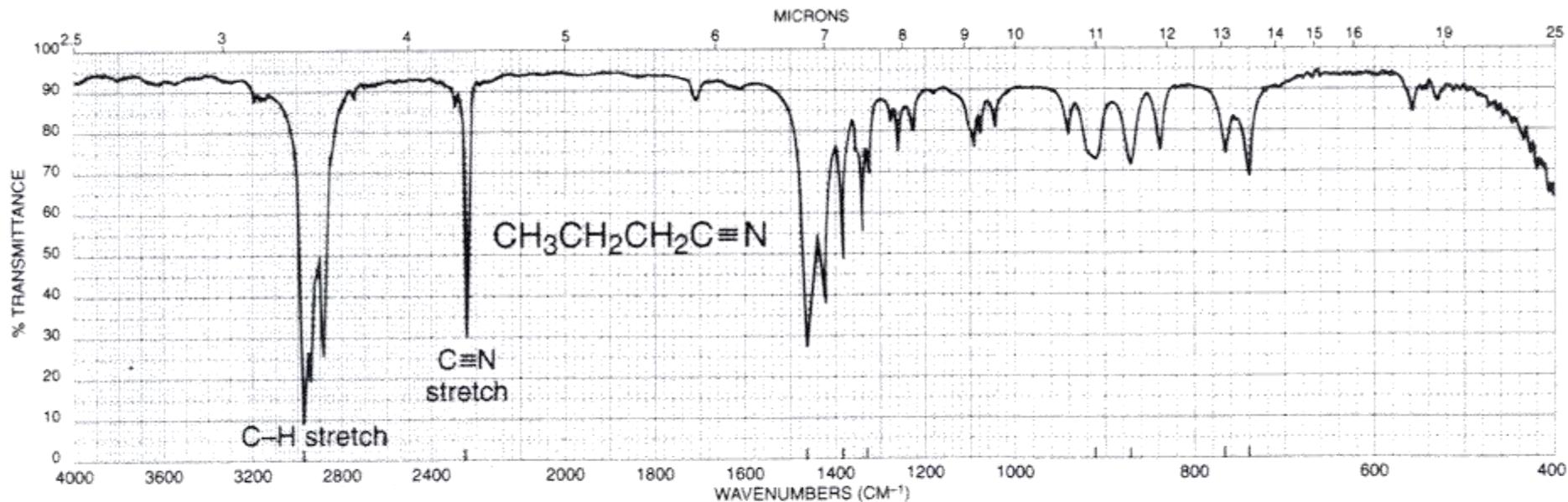


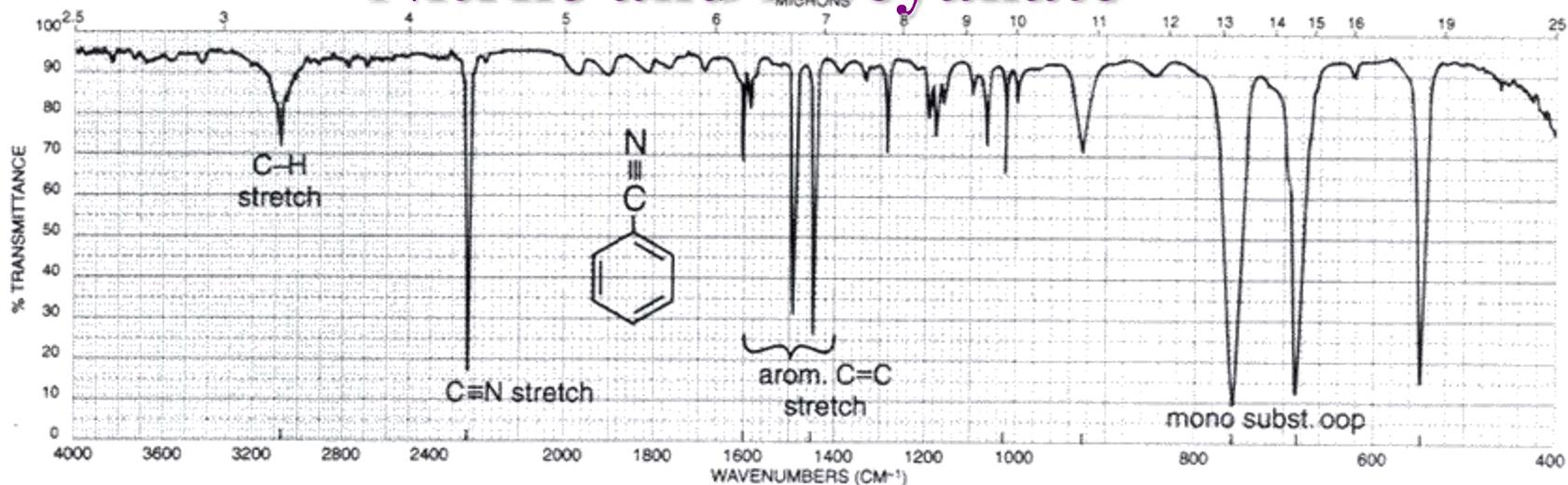
FIGURE 3.31. *o*-Tolunitrile. A. Aromatic C—H stretch, 3070, 3030  $\text{cm}^{-1}$ . B. Aliphatic C—H stretch, 2960, 2930  $\text{cm}^{-1}$ . C. The C $\equiv$ N stretch, 2226  $\text{cm}^{-1}$  (intensified by aryl conjugation; aliphatic nitriles absorb at a higher frequency). D. Out-of-plane C—H bend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

# Nitrile

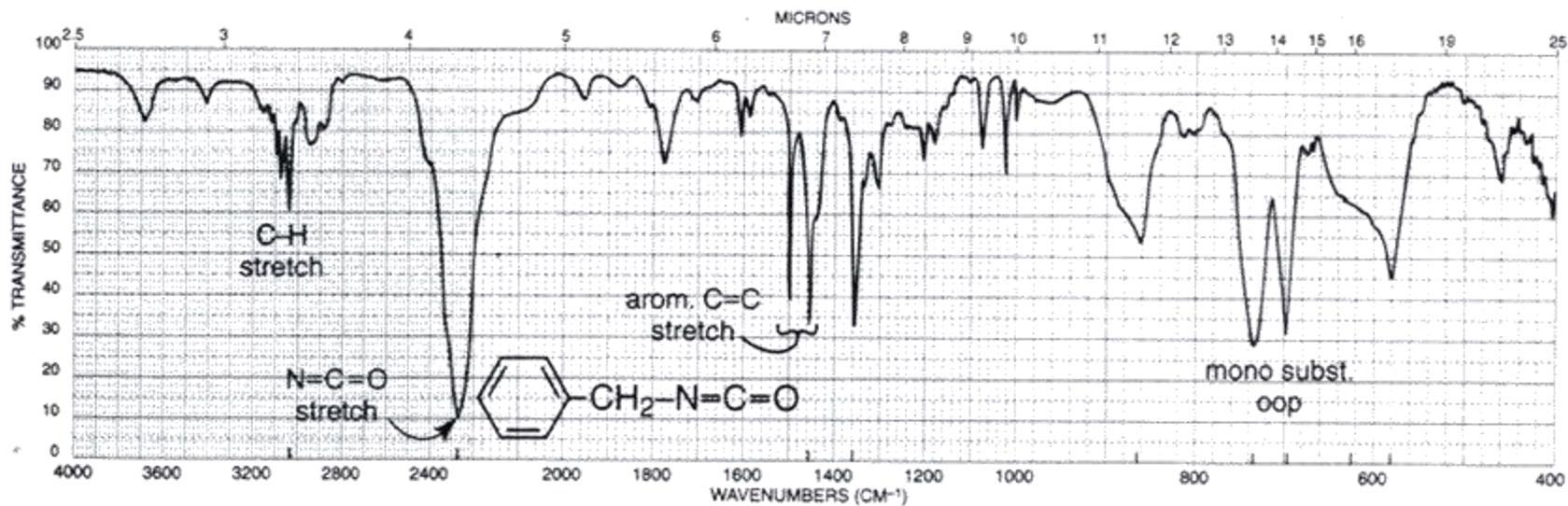


► **FIGURE 2.62** The infrared spectrum of butyronitrile (neat liquid, KBr plates).

# Nitrile and Isocyanate

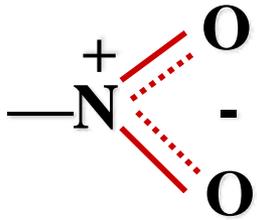


► **FIGURE 2.63** The infrared spectrum of benzonitrile (neat liquid, KBr plates).



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

# Nitro



**Aliphatic : Asymmetric : 1600-1530  $\text{cm}^{-1}$**

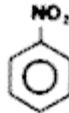
**Symmetric : 1390-1300  $\text{cm}^{-1}$**

**Aromatic : Asymmetric : 1550-1490  $\text{cm}^{-1}$**

**Symmetric : 1355-1315  $\text{cm}^{-1}$**

# Nitro

25237-9 CAS [98-95-3]  
Nitrobenzene, 99 + %



FW 123.11  
mp 5-6°C  
bp 210-211°C

d 1.196  
Fp 190°F  
n<sub>D</sub> 1.5513

Merck 10,6434

1806.2	1107.9	793.3
1523.1	1021.4	702.7
1347.2	852.0	678.3

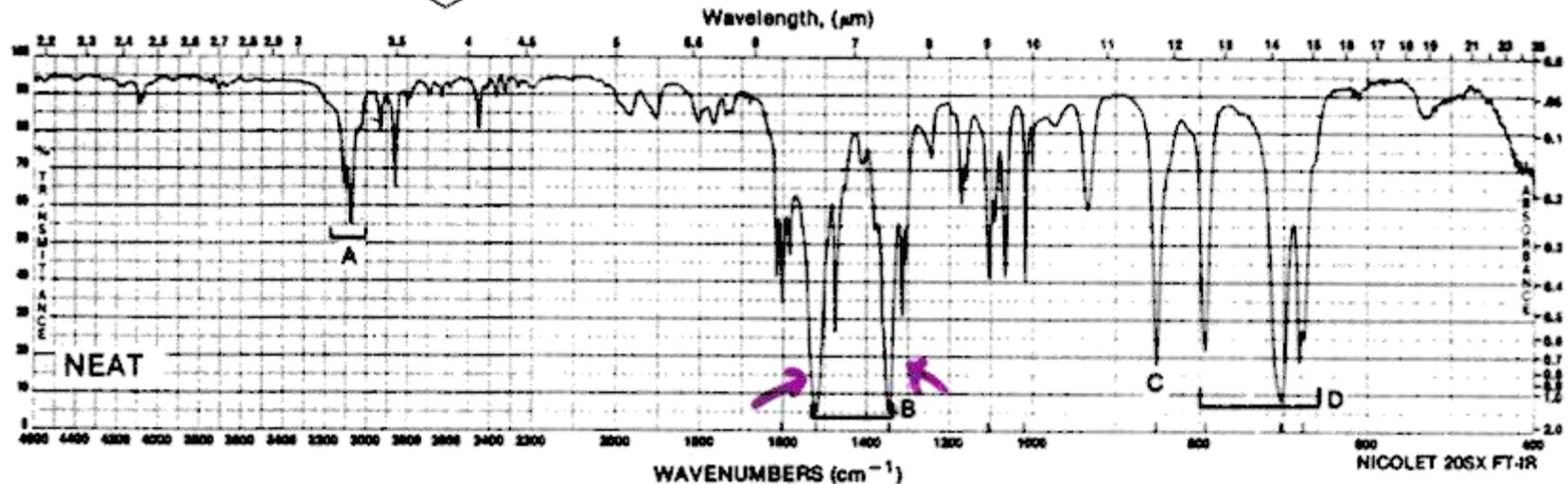
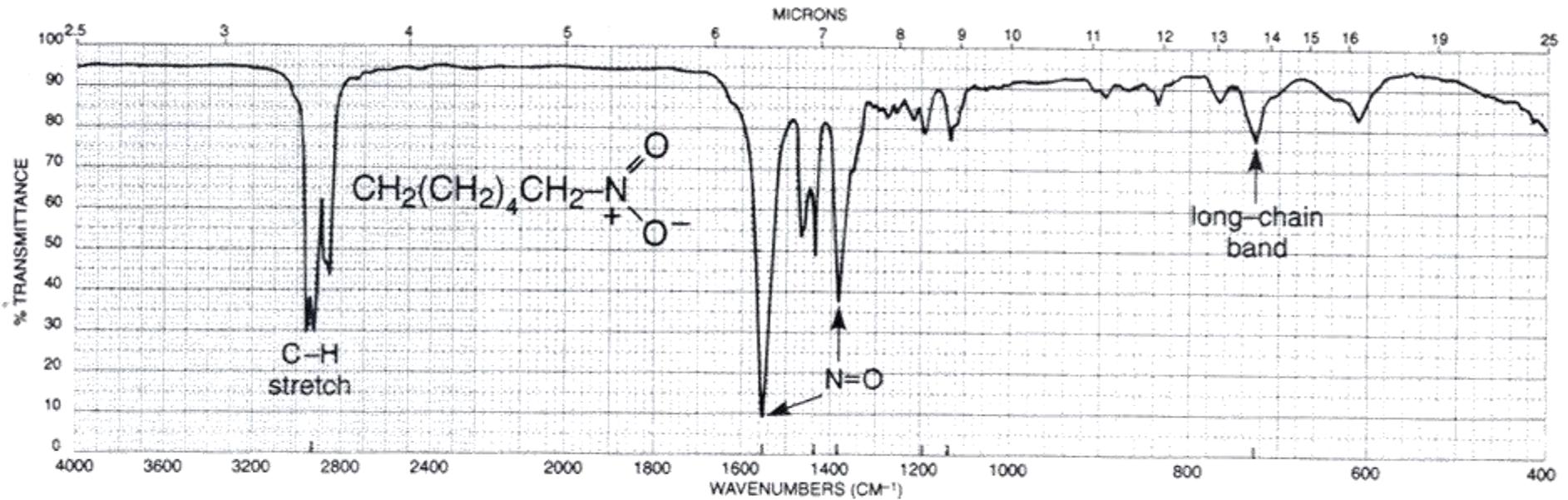


FIGURE 3.32. Nitrobenzene. A. Aromatic C—H stretch, 3100, 3080 cm<sup>-1</sup>. B. Asymmetric (ArNO<sub>2</sub>) (N=O)<sub>2</sub> stretch, 1523 cm<sup>-1</sup>. Symmetric (ArNO<sub>2</sub>) (N≡O)<sub>2</sub> stretch 1347 cm<sup>-1</sup>. C. C—N stretch for ArNO<sub>2</sub>, 852 cm<sup>-1</sup>. D. Low-frequency bands are of little use in determining the nature of ring substitution since these absorption patterns result from interaction of NO<sub>2</sub> 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<sub>2</sub> : { 1523 ASYM.  
          { 1347 SYM

# Nitro



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

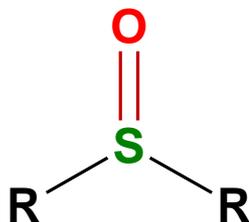
# Sulfur

**Mercaptans**      **S – H : weak 2600-2550 cm<sup>-1</sup>**

*Since only few absorption in that range it confirm its presence*

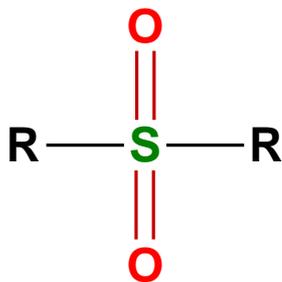
**Sulfides, Disulfides : no useful information**

**Sulfoxides:**



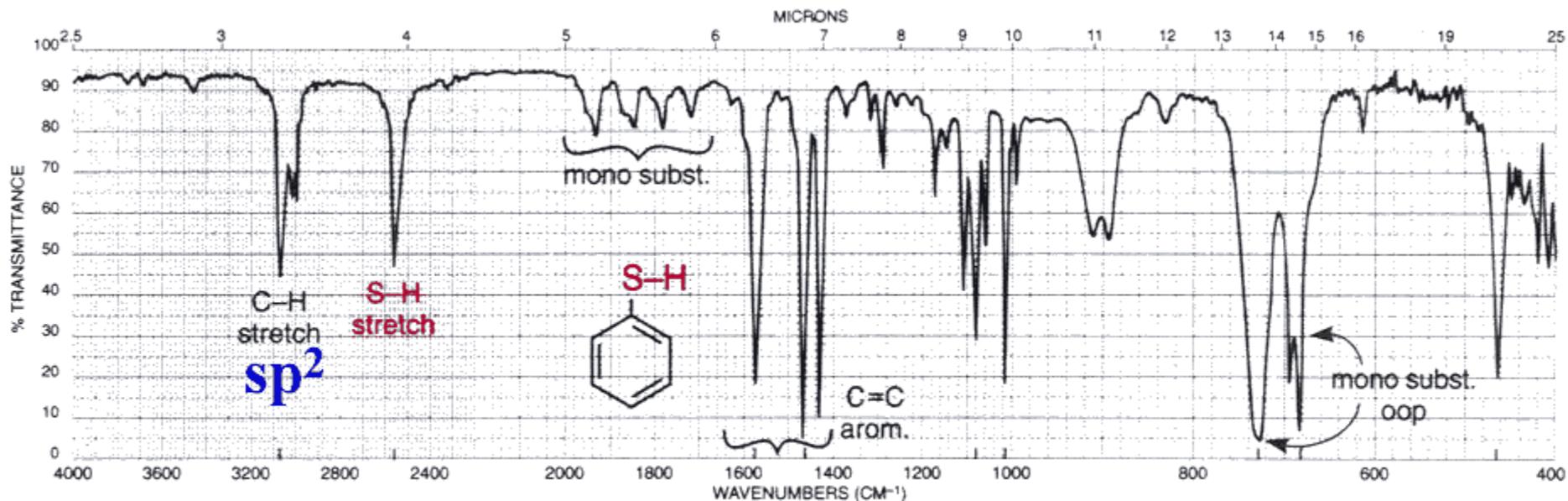
**Strong ~ 1050 cm<sup>-1</sup>**

**Sulfones:**



**2 bands :**      { **Asymmetrical ~ 1300 cm<sup>-1</sup>**  
**Symmetrical ~ 1150 cm<sup>-1</sup>**

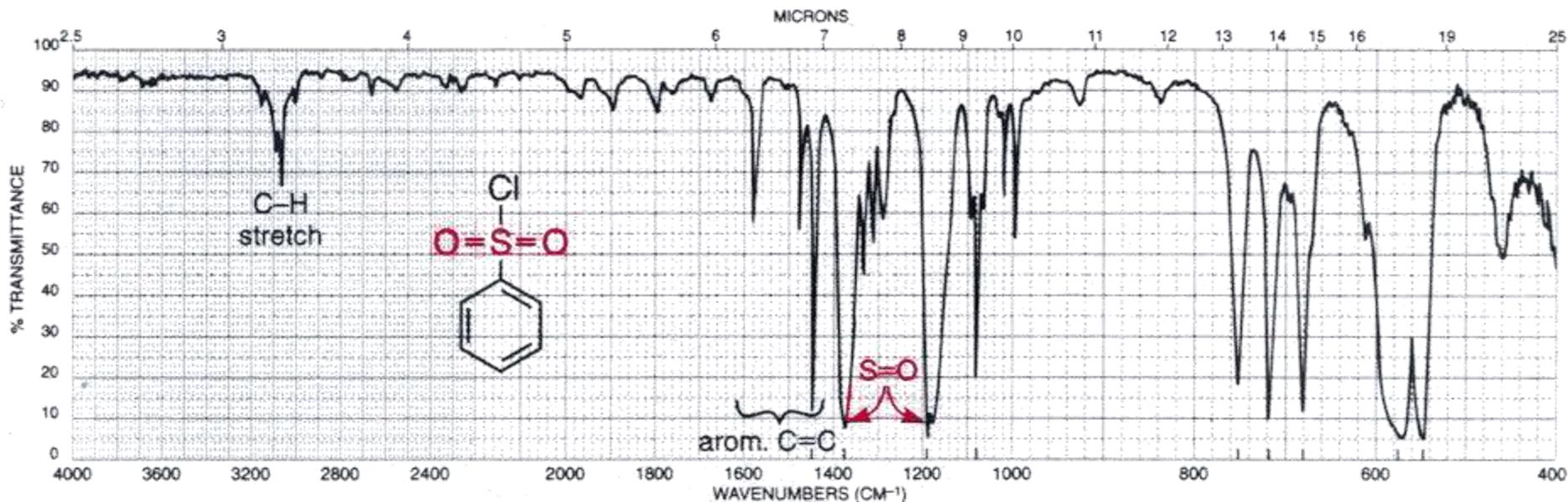
# Sulfur: Mercaptan R-S-H



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

# Sulfur: Sulfonyl Chloride

**S=O : Asymmetrical stretch: 1375 cm<sup>-1</sup>**  
**Symmetrical Stretch : 1185 cm<sup>-1</sup>**



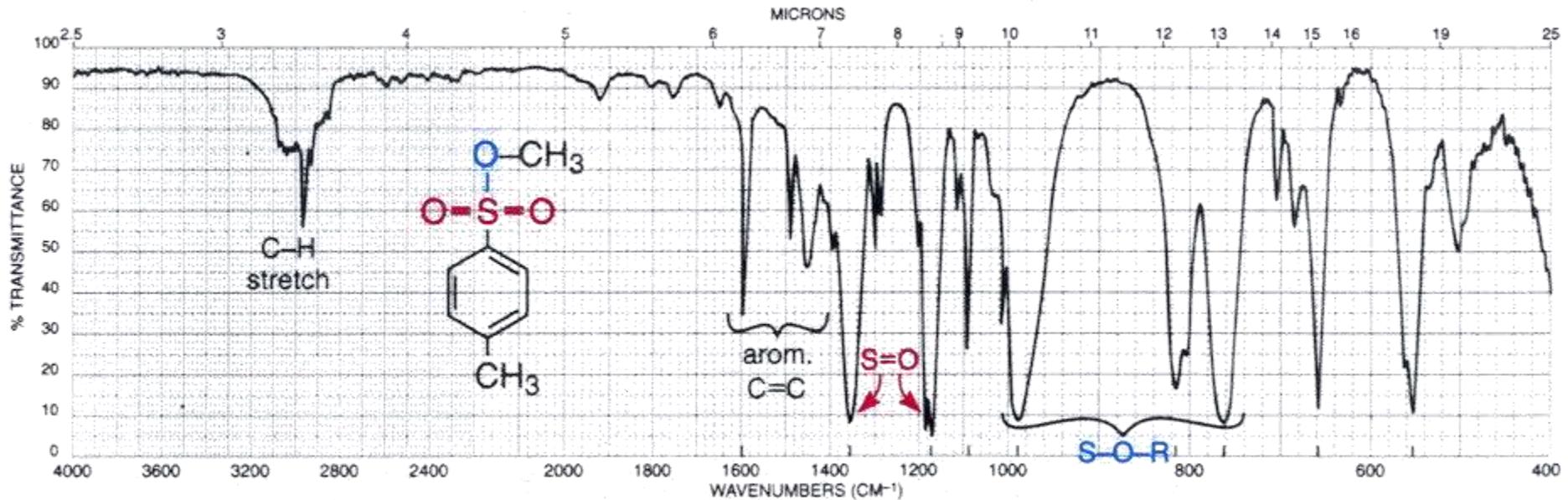
► **FIGURE 2.69** The infrared spectrum of benzenesulfonyl chloride (neat liquid, KBr plates).

# Sulfur: Sulfonate

**S=O : Asymmetrical stretch: 1350 cm<sup>-1</sup>**

**Symmetrical Stretch : 1175 cm<sup>-1</sup>**

**S-O : several bands between 1000 – 750 cm<sup>-1</sup>**



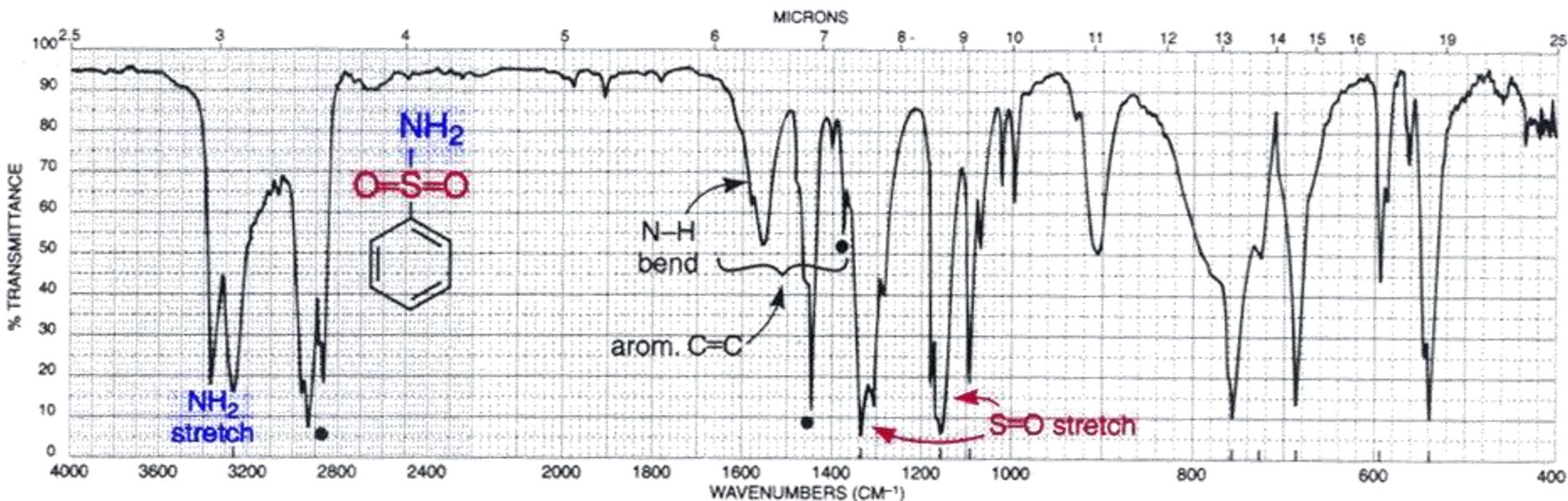
► **FIGURE 2.70** The infrared spectrum of methyl *p*-toluenesulfonate (neat liquid, KBr plates).

# Sulfur: Sulfonamide

**S=O : Asymmetrical stretch: 1325 cm<sup>-1</sup>**  
**Symmetrical Stretch : 1140 cm<sup>-1</sup>**

**NH<sub>2</sub> stretch: 3350 and 3250 cm<sup>-1</sup>**

**NH Bend: 1550 cm<sup>-1</sup>**



► **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

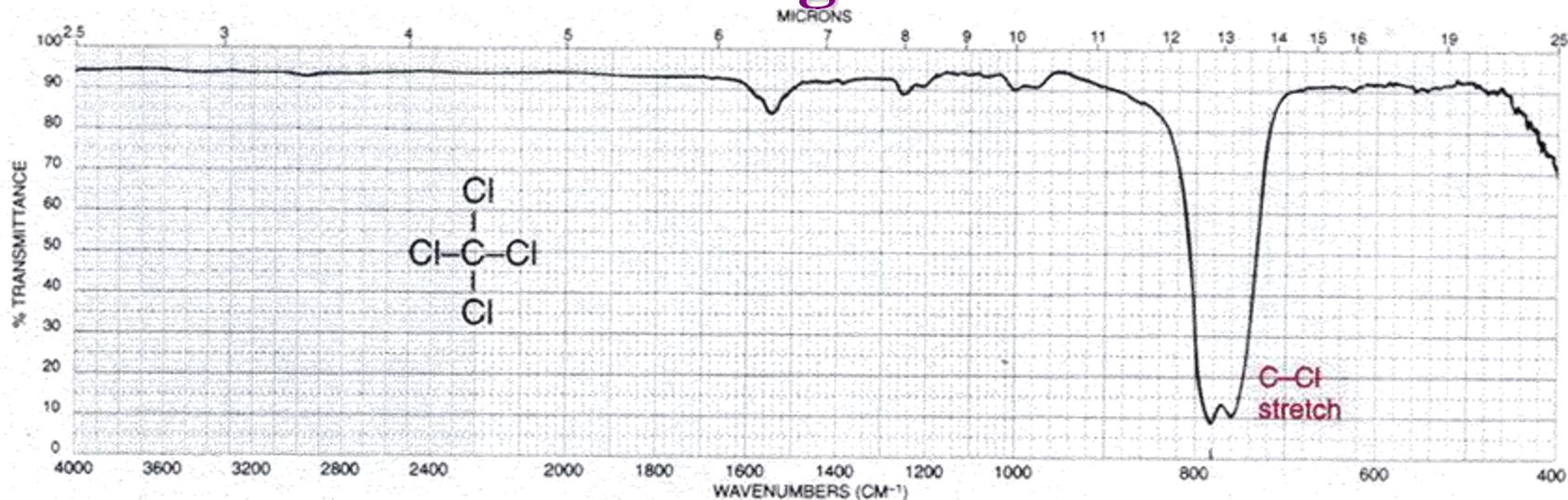
**C—F : 1400 – 1000 cm<sup>-1</sup>**

**C—Cl : strong 785 – 540 cm<sup>-1</sup>**

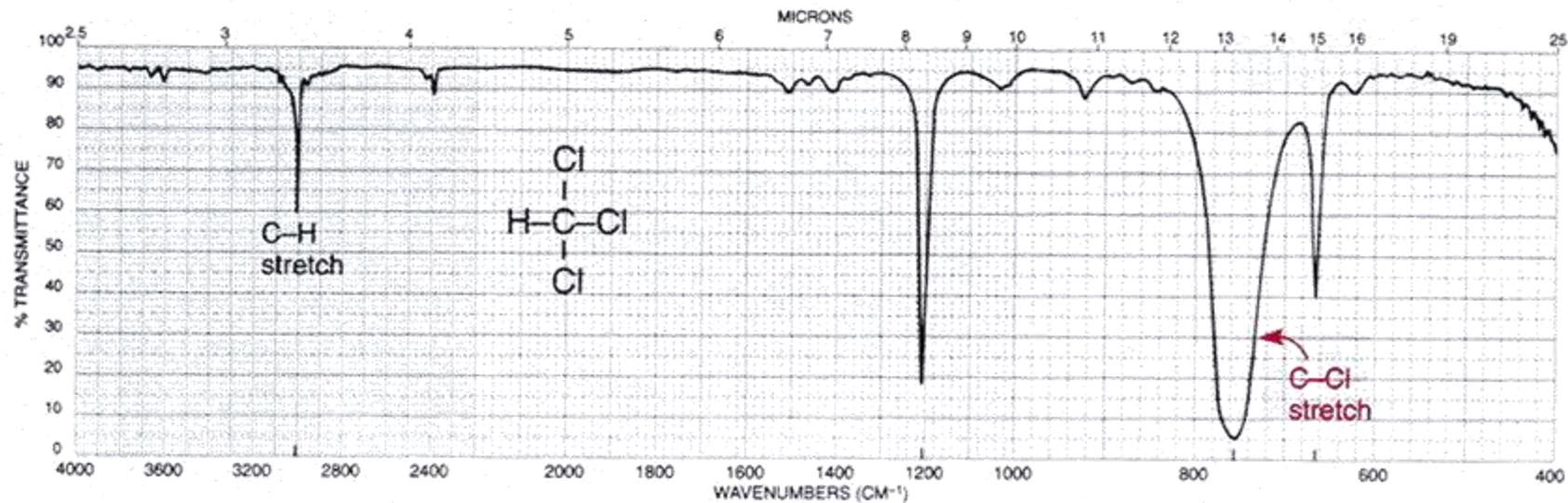
**C—Br : 650 – 510 cm<sup>-1</sup> (out of range with NaCl plates)**

**C—I : 600 – 485 cm<sup>-1</sup> (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).

# Phosphorus

**Phosphines:  $R-PH_2$   $R_2PH$**

**$P-H$  : Sharp  $2320 - 2270 \text{ cm}^{-1}$**

**$PH_2$  bending :  $1090 - 1075$  and  $840 - 810 \text{ cm}^{-1}$**

**$PH$  bending :  $990 - 886 \text{ cm}^{-1}$**

**Phosphine Oxide :  $R_3 P=O$**

**$P=O$  very strong :  $1210 - 1140 \text{ cm}^{-1}$**

**Phosphate Esters :  $(OR)_3 P=O$**

**$P=O$  very strong :  $1300 - 1240 \text{ cm}^{-1}$**

**$P-O$  very strong :  $1088 - 920 \text{ cm}^{-1}$**

**$P-O$  :  $845 - 725 \text{ cm}^{-1}$**

# Silicon

**Si-H :** { **2200 cm<sup>-1</sup> (Stretch)**  
**950 – 800 cm<sup>-1</sup> (bend)**

**Si-O-H :** { **OH: 3700 – 3200 cm<sup>-1</sup> (Stretch)**  
**Si-O : 830 – 1110 cm<sup>-1</sup>**