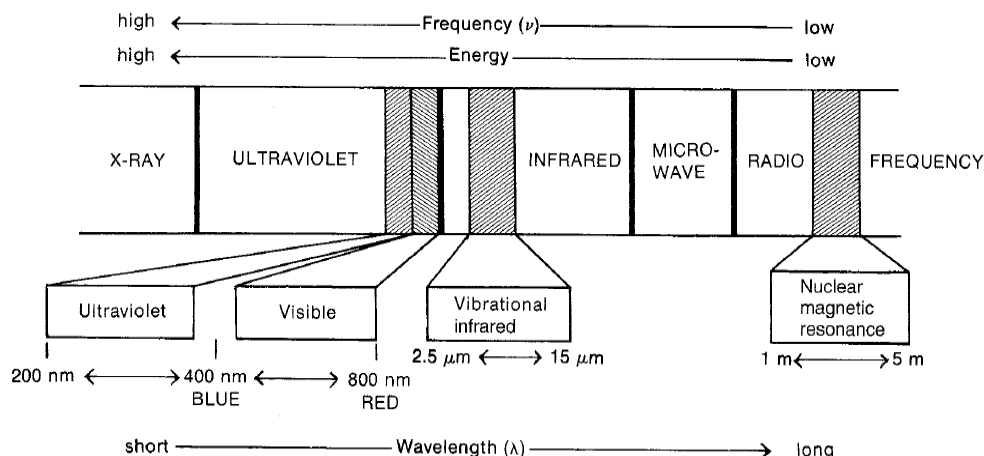


Spectroscopie infrarouge

Les transitions énergétiques se font ici entre les niveaux d'énergie de rotation des molécules ou entre leurs niveaux d'énergie de vibration.

Les transitions entre niveaux de rotation apparaissent dans l'I.R. lointain (de 20 à 250 μm ou de 500 à 40 cm^{-1}). Les transitions entre niveaux vibrationnels apparaissent de 1 à 20 μm (ou de 10 000 à 500). Nous ferons porter notre étude sur les transitions vibrationnelles. On constate qu'elles nécessitent plus d'énergie que les transitions rotationnelles. Aussi la lumière excitatrice provoquera-t-elle, pour chaque transition vibrationnelle, une multitude de transitions rotationnelles, qui vont donner au pic de transition vibrationnelle l'allure d'une bande d'absorption.



Modes de vibration

- Élongation

Appelé aussi vibration de valence ou "stretching", ce mode concerne la vibration de la molécule le long des liaisons. La fréquence de l'onde électromagnétique qui induit la vibration d'élongation est donnée par la relation :

$$\nu \text{ (Hz)} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

où k est la constante de force de la liaison (considérée ici comme un ressort), proportionnelle à l'énergie de liaison, et μ la masse réduite des deux atomes reliés par cette liaison.

Ainsi, les liaisons multiples, plus énergétiques que les simples, auront une constante de force plus élevée, donc une fréquence de vibration (remplacée dans la pratique par le nombre d'onde) plus élevée que celles des liaisons simples entre atomes identiques :

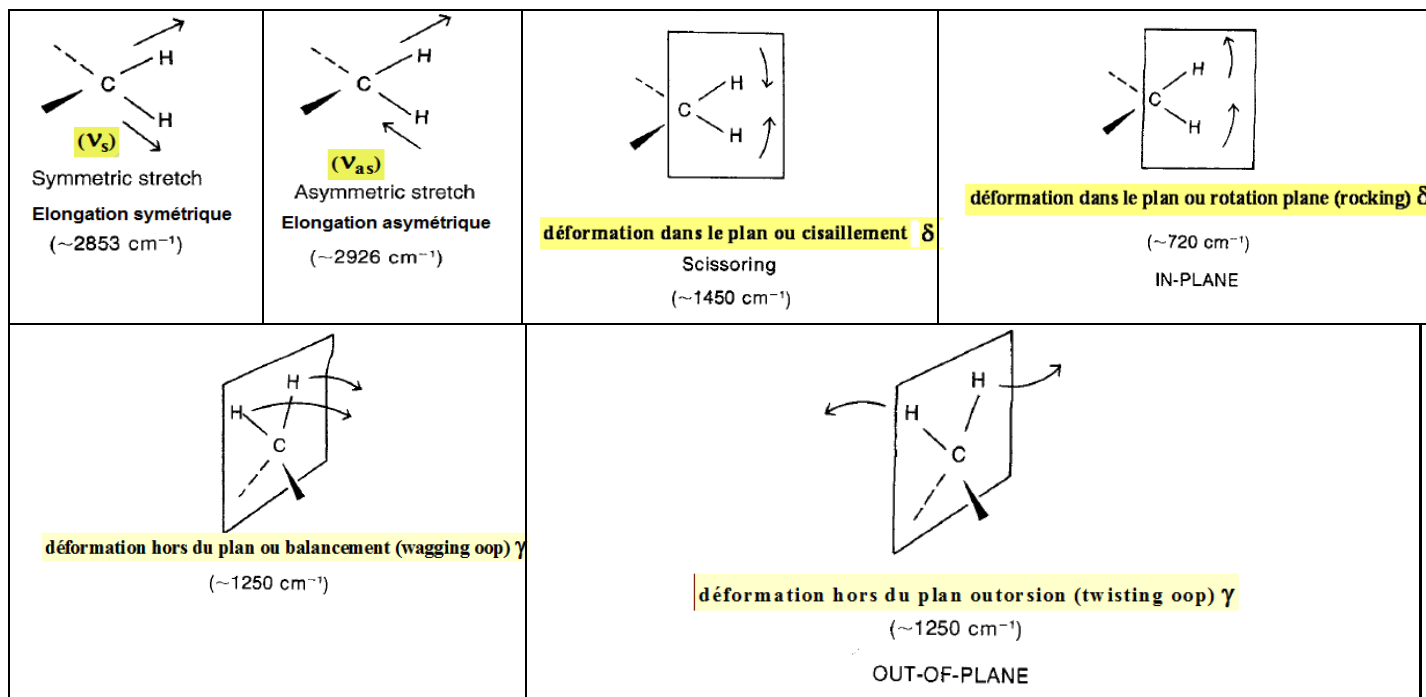
- C-C absorbe vers 1100 cm^{-1}
- C=C vers 1600 cm^{-1}
- C \equiv C vers 2100 cm^{-1}

Par contre, les liaisons X-H, où X est un atome quelconque (C, N, O, ...), auront une fréquence d'élongation plus élevée que celle d'une liaison C-X, car la masse réduite m y est plus petite

- pour C-H, $\mu = 0,92 \text{ u.m.a}$
- pour C-C, $\mu = 6 \text{ u.m.a}$

Déformations dans et hors du plan

Considérons une structure . En plus de la vibration de valence, l'angle des liaisons peut varier : il y a flexion ou déformation. Ces déformations peuvent avoir lieu dans le plan des deux liaisons concernées (on les note d) ou hors du plan (on les note g ou r). Il y a aussi possibilité de déformations symétriques et asymétriques. voici quelques exemples :



Facteurs influençant les fréquences d'absorption

- Masses des atomes liés :

le nombre d'onde augmente avec l'augmentation des masses des atomes liés.

C-H	C-C	C-O	C-Cl	C-Br	C-I
3000 cm ⁻¹	1200 cm ⁻¹	1100 cm ⁻¹	750 cm ⁻¹	600 cm ⁻¹	500 cm ⁻¹

- La force des liaisons chimiques :

Le nombre d'onde augmente avec la force de la liaison chimique.

C,C triple bond	C=C	C-C
2150 cm ⁻¹	1650 cm ⁻¹	1200 cm ⁻¹

Type d'hybridation de la liaison chimique :

La force de liaison augmente dans le sens sp > sp² > sp³.

C-H (sp)	C-H (sp ²)	C-H (sp ³)
3300 cm ⁻¹	3100 cm ⁻¹	2900 cm ⁻¹

La résonance :

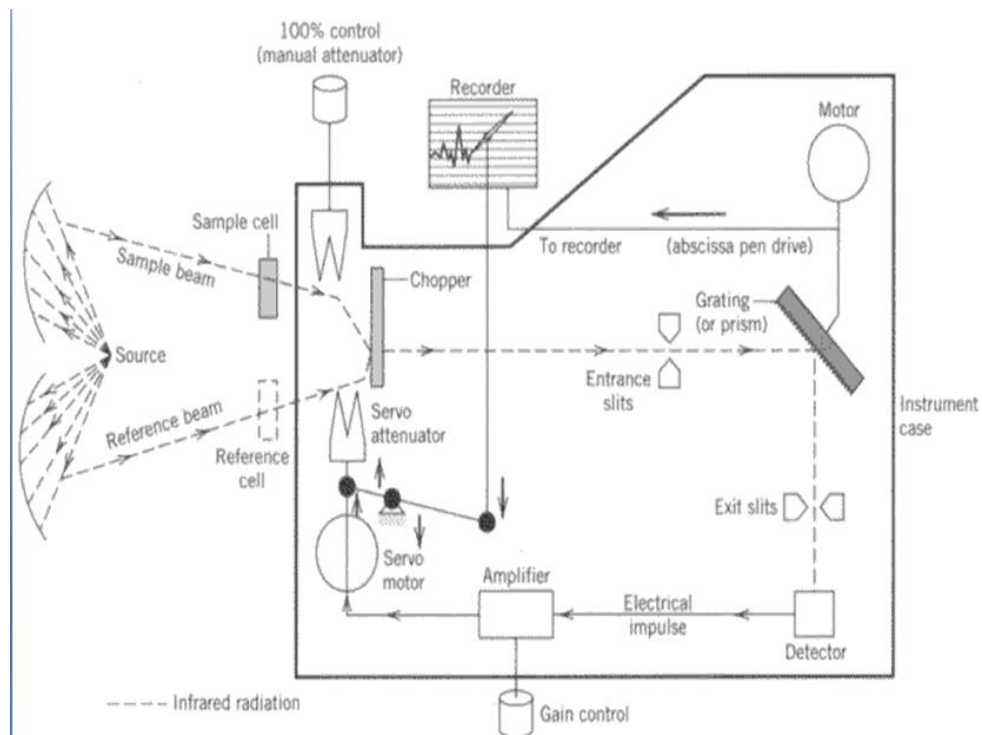
La conjugaison abaisse le nombre d'onde.

isolated ketones	α,β-unsaturated ketone	α,β,γ,δ-unsaturated ketone
1715 cm ⁻¹	1690 cm ⁻¹	1675 cm ⁻¹

Instrumentation

Un spectrophotomètre infra-rouge est composé de :

- Une source de lumière
- Un compartiment à échantillon
- Un prisme pour décomposer la lumière de la source (système dispersif)
- Un détecteur
- Un enregistreur.



Application de l'I.R. à la détermination des diverses fonctions d'un composé organique

Non seulement la nature des deux atomes vibrants intervient dans la valeur de la constante de force, mais aussi l'environnement électronique. Aussi chaque groupement fonctionnel aura-t-il des fréquences caractéristiques d'élongation et de déformation. Nous allons passer en revue les diverses fonctions grâce à l'étude de quelques spectres.

Type of Vibration			Frequency (cm ⁻¹)	Intensity
C-H	Alkanes	(stretch)	3000-2850	s
	-CH ₃	(bend)	1450 and 1375	m
	-CH ₂ -	(bend)	1465	m
	Alkenes	(stretch)	3100-3000	m
		(out-of-plane bend)	1000-650	s
	Aromatics	(stretch)	3150-3050	s
		(out-of-plane bend)	900-690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900-2800	w
			2800-2700	w
C-C	Alkane	Not interpretatively useful		
C=C	Alkene	1680-1600	m-w	
	Aromatic	1600 and 1475	m-w	
C≡C	Alkyne	2250-2100	m-w	
C=O	Aldehyde	1740-1720	s	
	Ketone	1725-1705	s	
	Carboxylic acid	1725-1700	s	
	Ester	1750-1730	s	
	Amide	1680-1630	s	
	Anhydride	1810 and 1760	s	
	Acid chloride	1800	s	
	C-O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300-1000	s

O-H	Alcohols, phenols		
	Free	3650-3600	m
	H-bonded	3400-3200	m
N-H	Carboxylic acids	3400-2400	m
	Primary and secondary amines and amides		
	(stretch)	3500-3100	m
	(bend)	1640-1550	m-s
C-N	Amines	1350-1000	m-s
C=N	Imines and oximes	1690-1640	w-s
C≡N	Nitriles	2260-2240	m
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270-1940	m-s
N=O	Nitro (R-NO ₂)	1550 and 1350	s
S-H	Mercaptans	2550	w
S=O	Sulfoxides	1050	s
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375-1300 and 1350-1140	s
C-X	Fluoride	1400-1000	s
	Chloride	785-540	s
	Bromide, iodide	<667	s

ALKANES

C-H Stretch occurs around 3000 cm^{-1} .

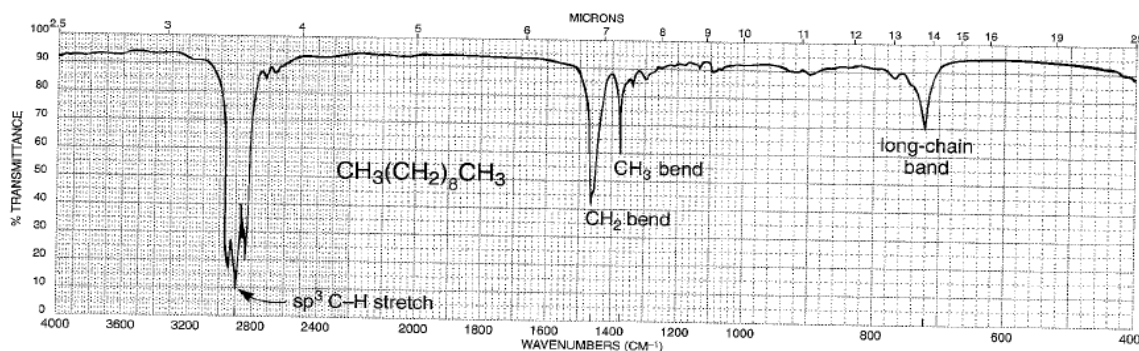
In alkanes (except strained ring compounds), sp^3 C-H absorption always occurs at frequencies less than 3000 cm^{-1} ($3000\text{--}2840\text{ cm}^{-1}$).

CH₂ Methylene groups have a characteristic bending absorption of approximately 1465 cm^{-1} .

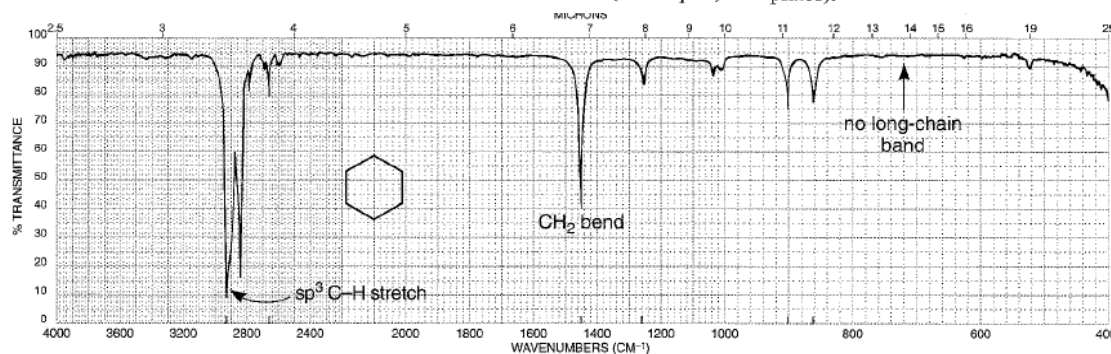
CH₃ Methyl groups have a characteristic bending absorption of approximately 1375 cm^{-1} .

CH₂ The bending (rocking) motion associated with four or more CH₂ groups in an open chain occurs at about 720 cm^{-1} (called a long-chain band).

C-C Stretch not interpretatively useful; many weak peaks.



The infrared spectrum of decane (neat liquid, KBr plates).



The infrared spectrum of cyclohexane (neat liquid, KBr plates).

ALKENES

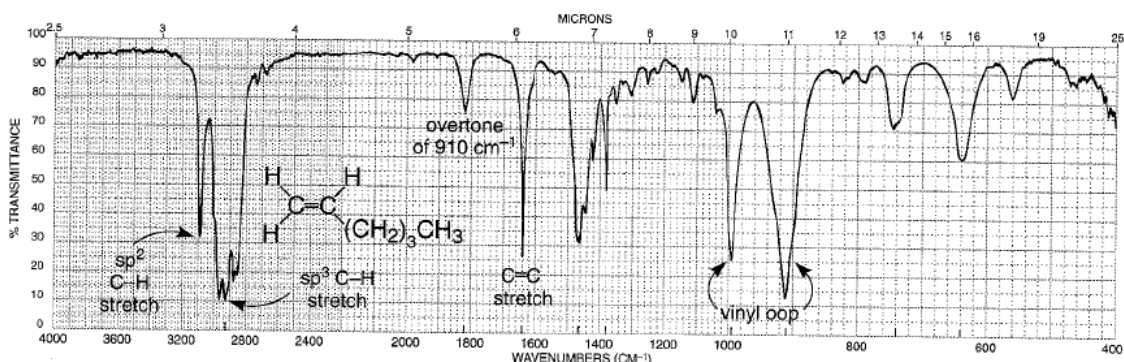
$=C-H$ Stretch for sp^2 C-H occurs at values greater than 3000 cm^{-1} .
($3095-3010\text{ cm}^{-1}$)

$=C-H$ Out-of-plane (oop) bending occurs in the range $1000-650\text{ cm}^{-1}$.

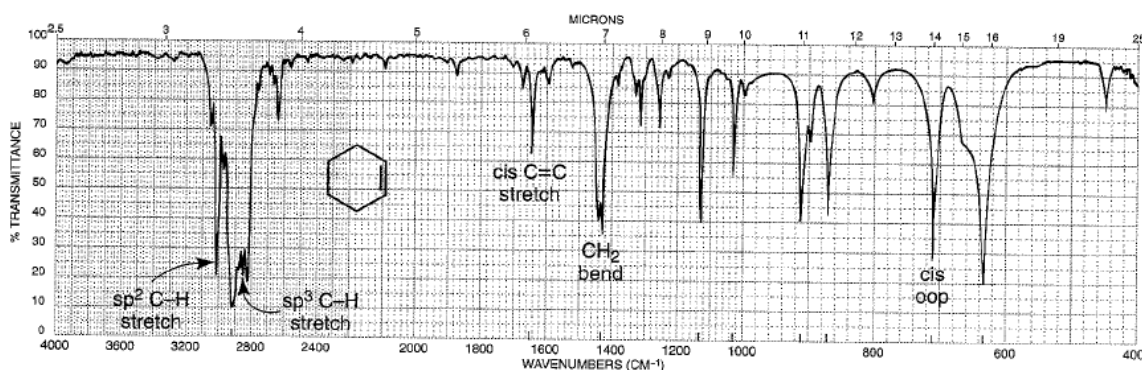
$C=C$ Stretch occurs at $1660-1600\text{ cm}^{-1}$; often conjugation moves $C=C$ stretch to lower frequencies and increases the intensity.

Symmetrically substituted bonds (e.g., 2,3-dimethyl-2-butene) do not absorb in the infrared (no dipole change).

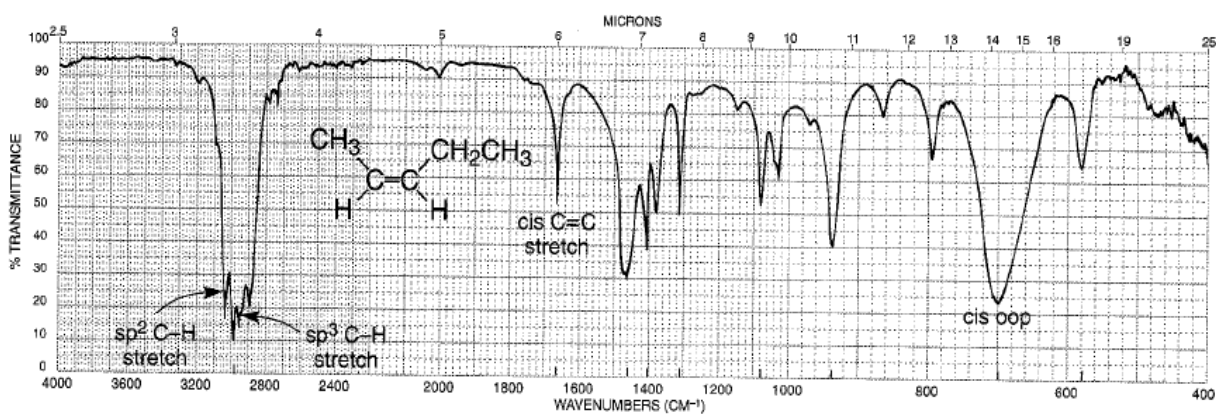
Symmetrically disubstituted (*trans*) double bonds are often vanishingly weak in absorption; *cis* are stronger.



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



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



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

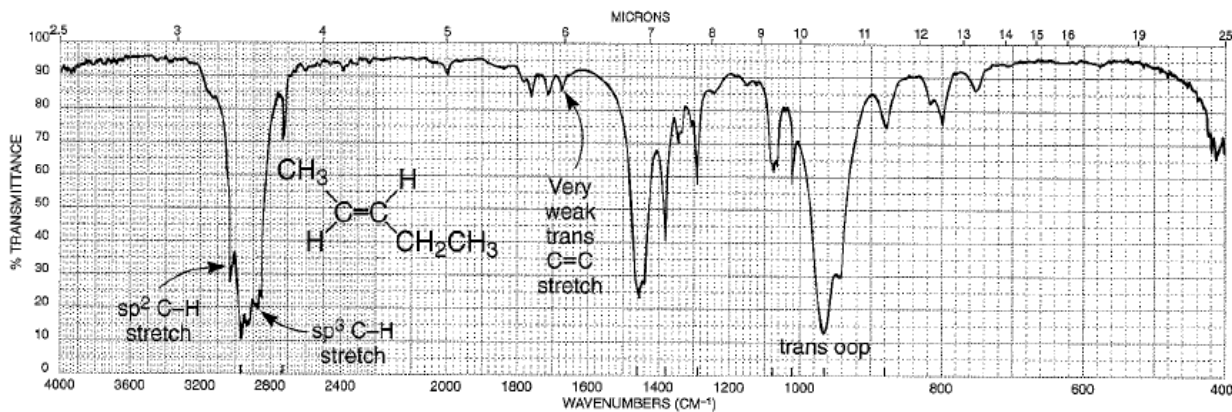
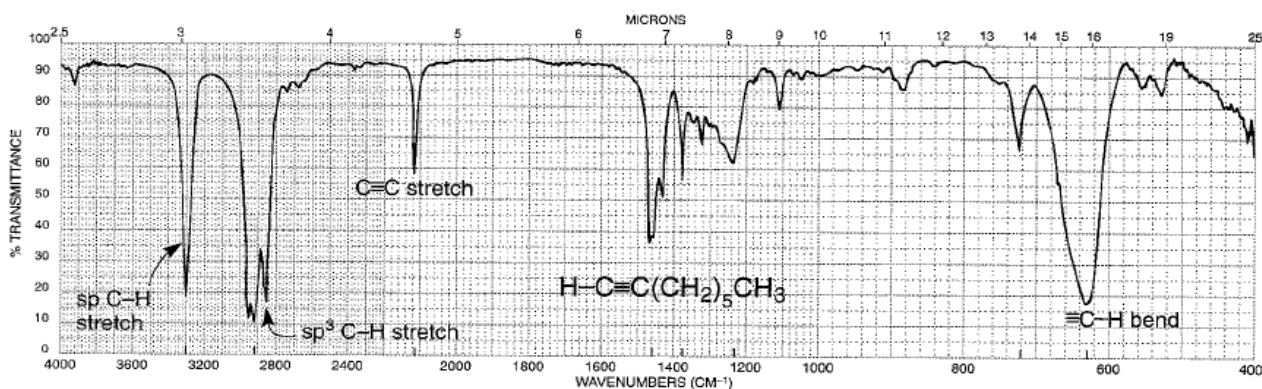


FIGURE 2.13 The infrared spectrum of *trans*-2-pentene (neat liquid, KBr plates).

ALKYNES

$\equiv\text{C}-\text{H}$ Stretch for *sp* C—H usually occurs near 3300 cm^{-1} .

$\text{C}\equiv\text{C}$ Stretch occurs near 2150 cm^{-1} ; conjugation moves stretch to lower frequency. Disubstituted or symmetrically substituted triple bonds give either no absorption or weak absorption.



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

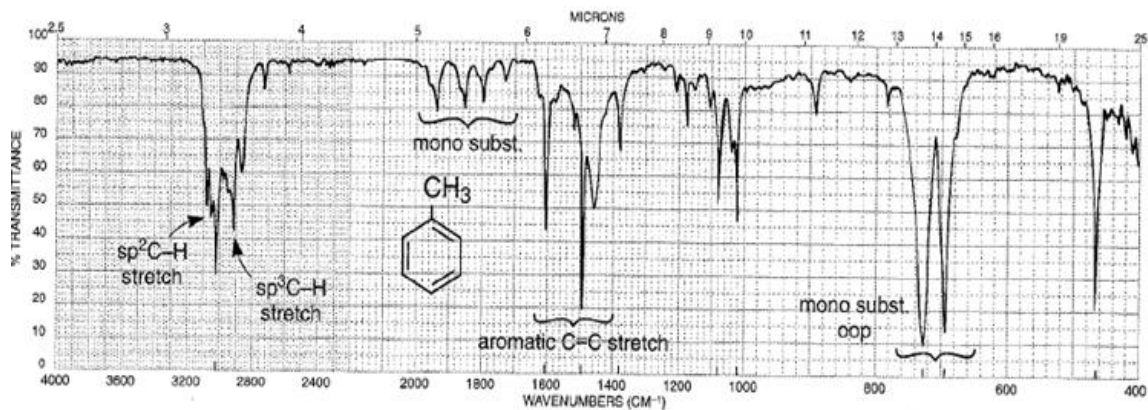
AROMATIC RINGS

$\equiv\text{C}-\text{H}$ Stretch for *sp*² C—H occurs at values greater than 3000 cm^{-1} ($3050\text{--}3010\text{ cm}^{-1}$).

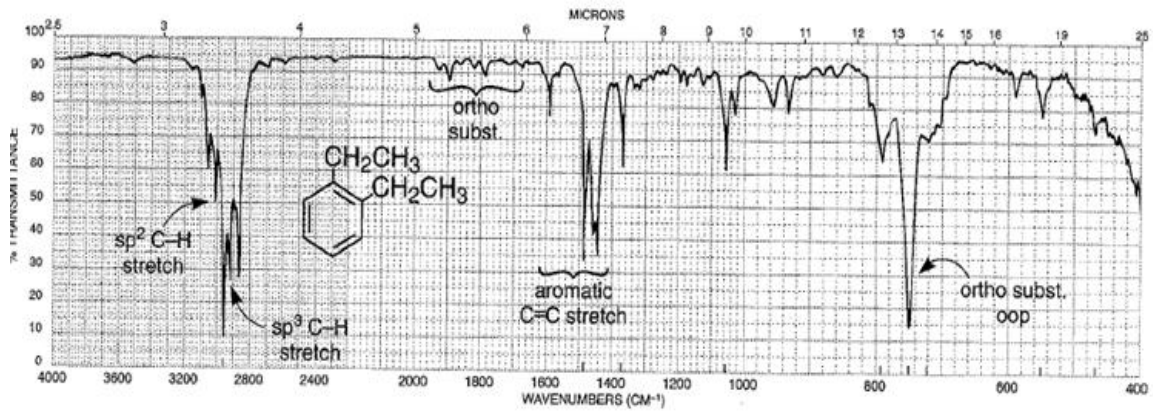
$\equiv\text{C}-\text{H}$ Out-of-plane (oop) bending occurs at $900\text{--}690\text{ cm}^{-1}$. These bands can be used with great utility to assign the ring substitution pattern (see discussion).

$\text{C}=\text{C}$ Ring stretch absorptions often occur in pairs at 1600 cm^{-1} and 1475 cm^{-1} .

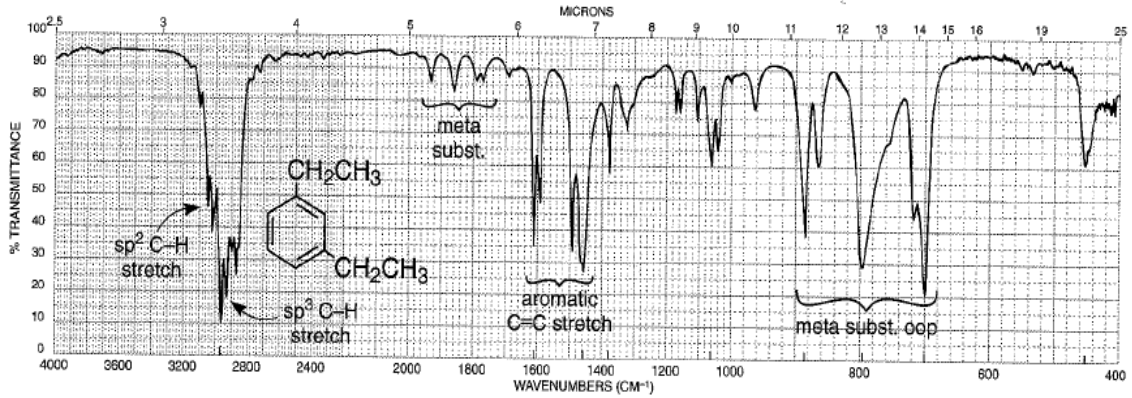
Overtone/combination bands appear between 2000 and 1667 cm^{-1} . These *weak* absorptions can be used to assign the ring substitution pattern (see discussion).



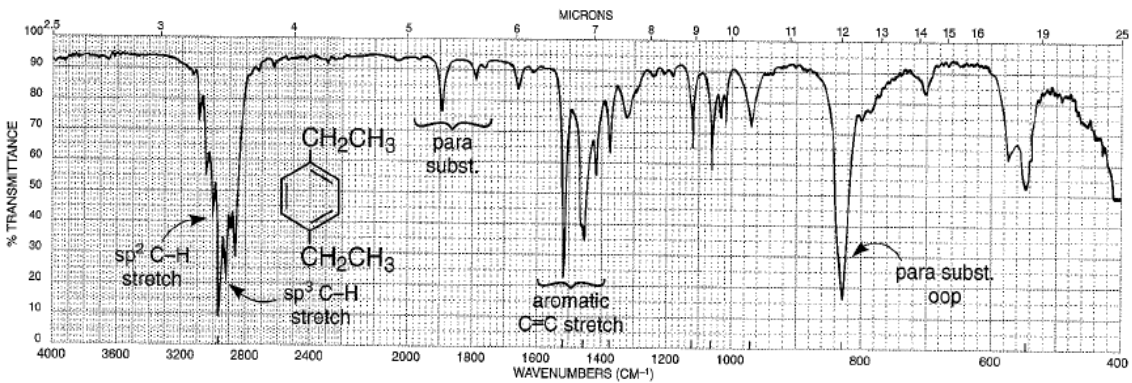
The infrared spectrum of toluene (neat liquid, KBr plates).



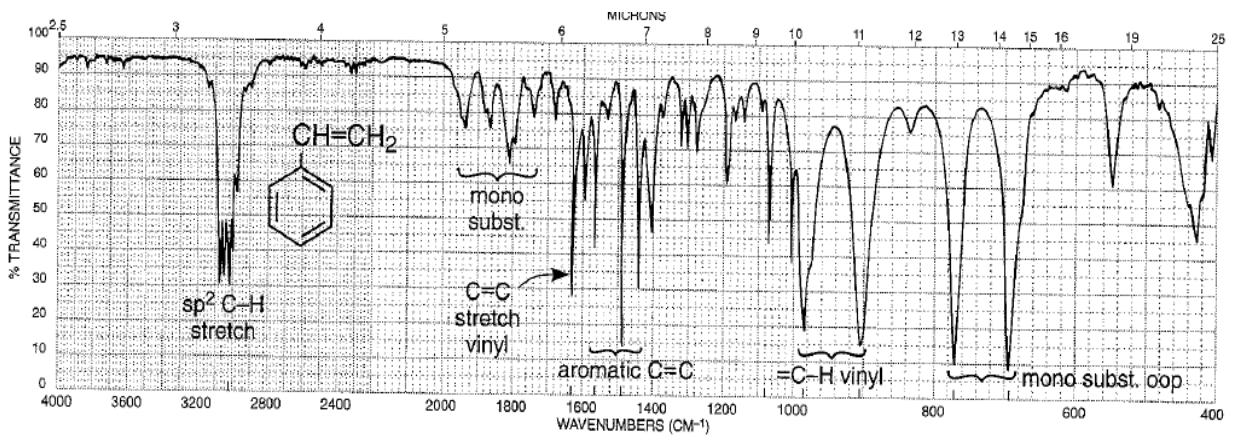
The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).



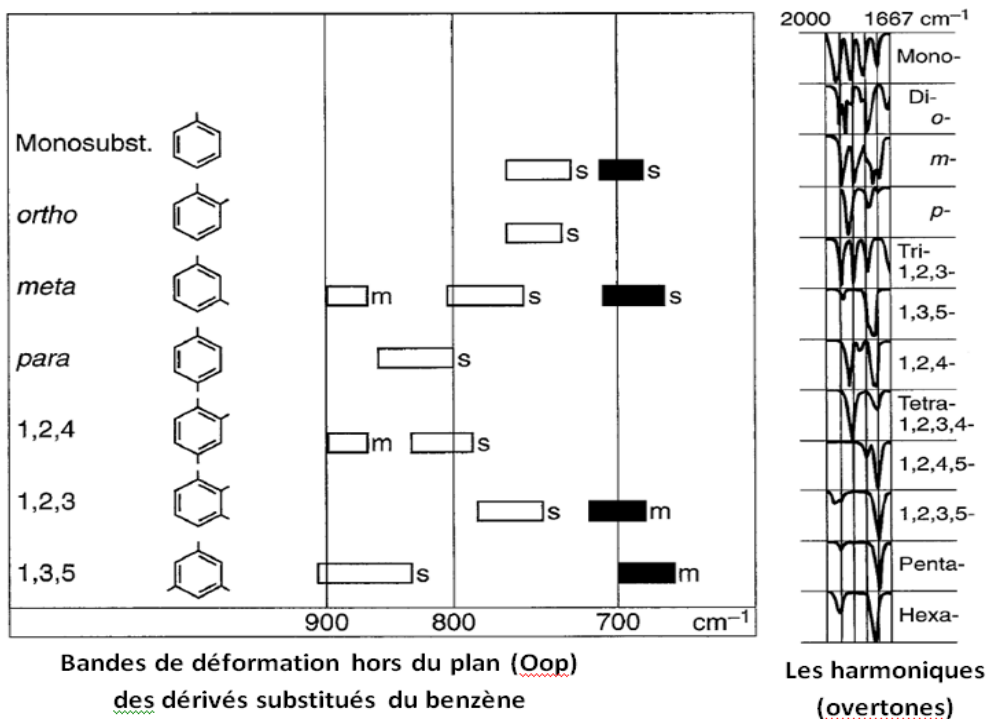
The infrared spectrum of *meta*-diethylbenzene (neat liquid, KBr plates).



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



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



ALCOHOLS AND PHENOLS

O—H

The free O—H stretch is a *sharp* peak at $3650\text{--}3600\text{ cm}^{-1}$. This band appears in combination with the hydrogen-bonded O—H peak when the alcohol is dissolved in a solvent

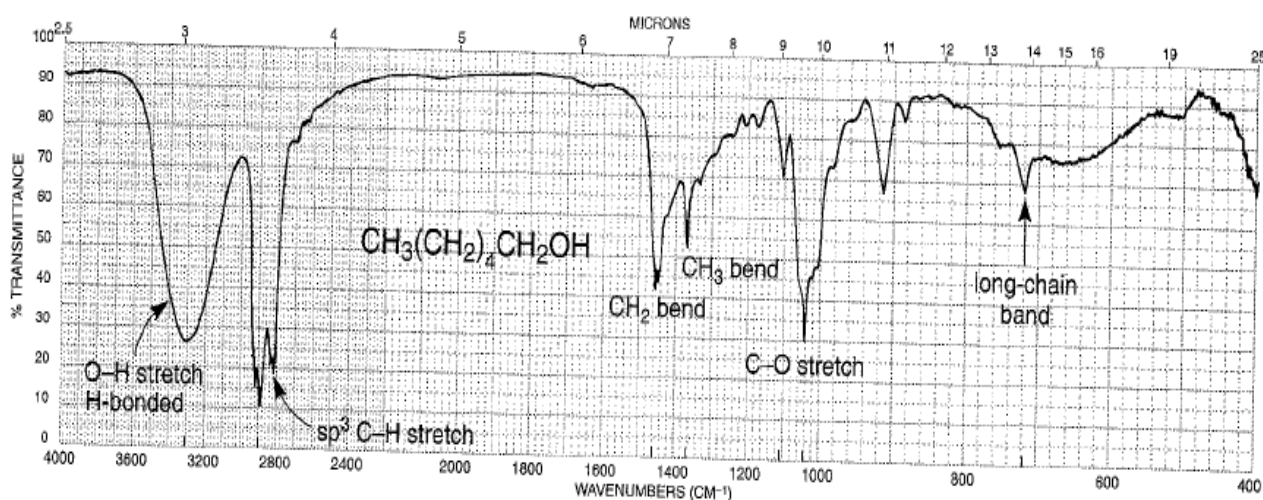
The hydrogen-bonded O—H band is a *broad* peak at $3400\text{--}3300\text{ cm}^{-1}$. This band is usually the only one present in an alcohol that has not been dissolved in a solvent (neat liquid). When the alcohol is dissolved in a solvent, the free O—H and hydrogen-bonded O—H bands are present together, with the relatively weak free O—H on the left

C—O—H

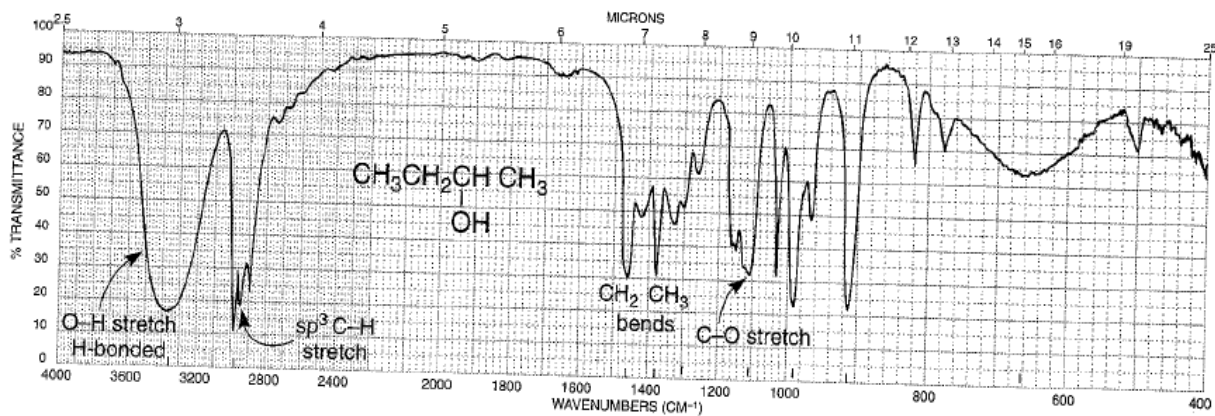
Bending appears as a broad and weak peak at $1440\text{--}1220\text{ cm}^{-1}$ often obscured by the CH_3 bendings.

C—O

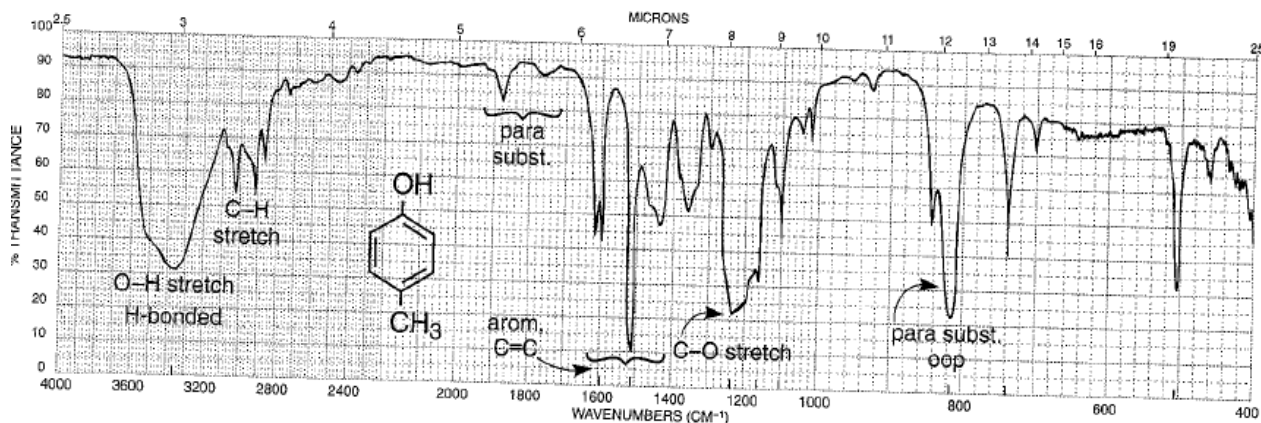
Stretching vibration usually occurs in the range $1260\text{--}1000\text{ cm}^{-1}$. This band can be used to assign a primary, secondary, or tertiary structure to an alcohol



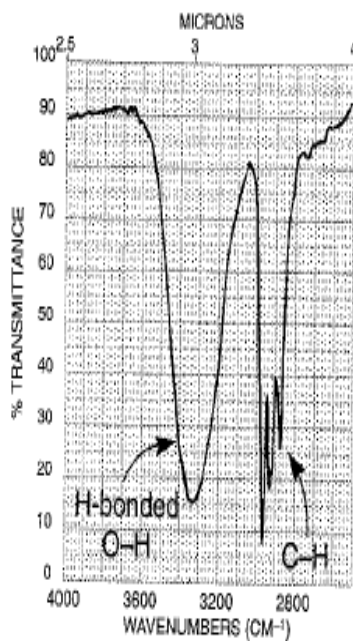
The infrared spectrum of 1-hexanol (neat liquid, KBr plates).



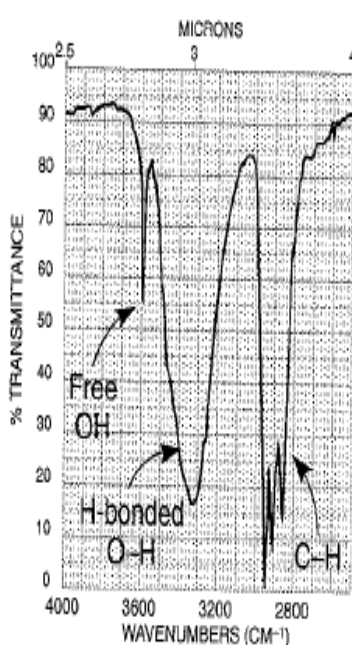
The infrared spectrum of 2-butanol (neat liquid, KBr plates).



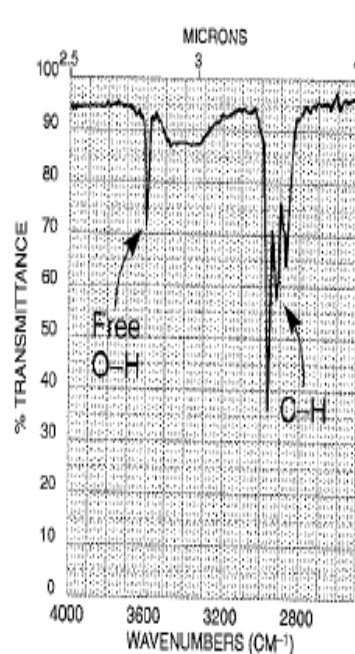
The infrared spectrum of *para*-cresol (neat liquid, KBr plates).



(a)



(b)



(c)

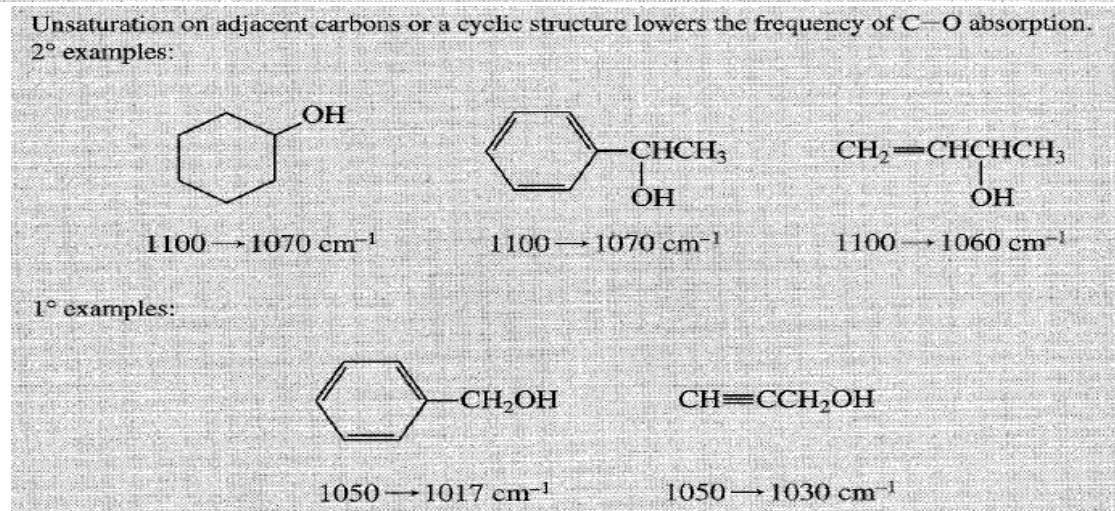
The O-H stretch region. (a) Hydrogen-bonded O-H only (neat liquid). (b) Free and hydrogen-bonded O-H (dilute solution). (c) Free and hydrogen-bonded O-H (very dilute solution).

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

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

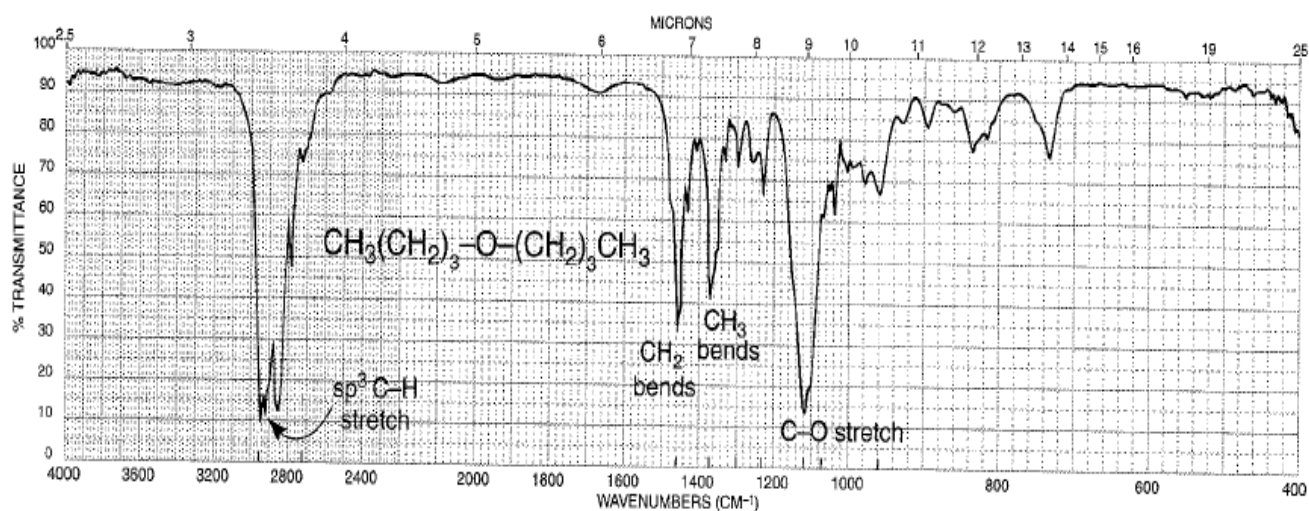
Decrease \downarrow Increase \downarrow

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

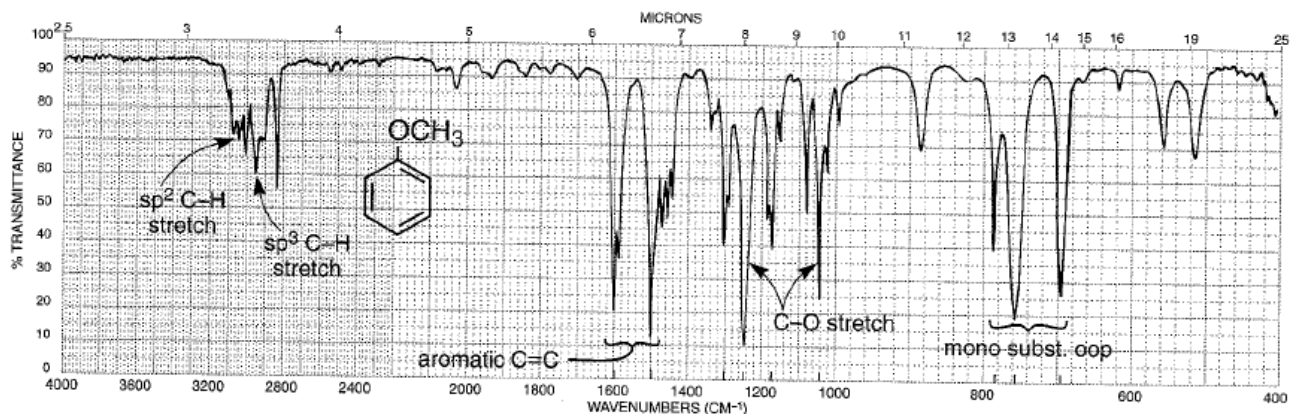


ETHERS

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



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



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

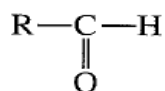
CARBONYL COMPOUNDS

← cm^{-1} →							
1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

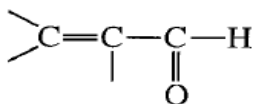
Normal base values for the C=O stretching vibrations for carbonyl groups.

ALDEHYDES

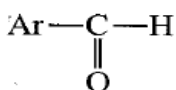
C=O



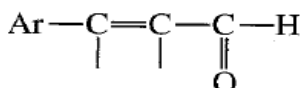
C=O stretch appears in range $1740\text{--}1725\text{ cm}^{-1}$ for normal aliphatic aldehydes.



Conjugation of C=O with $\alpha,\beta\text{ C}=\text{C}$; $1700\text{--}1680\text{ cm}^{-1}$ for C=O and 1640 cm^{-1} for C=C.



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



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

C-H

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

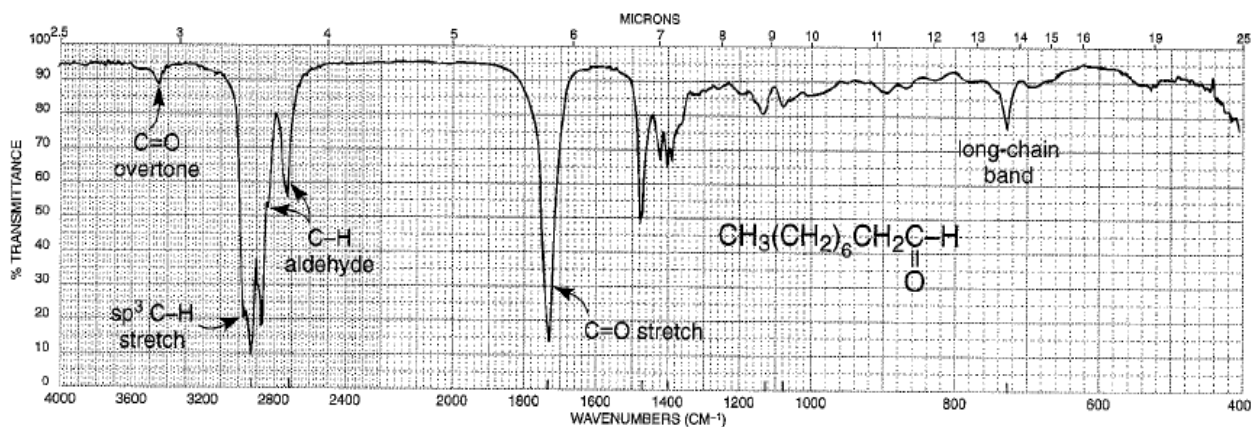


FIGURE 2.36 The infrared spectrum of nonanal (neat liquid, KBr plates).

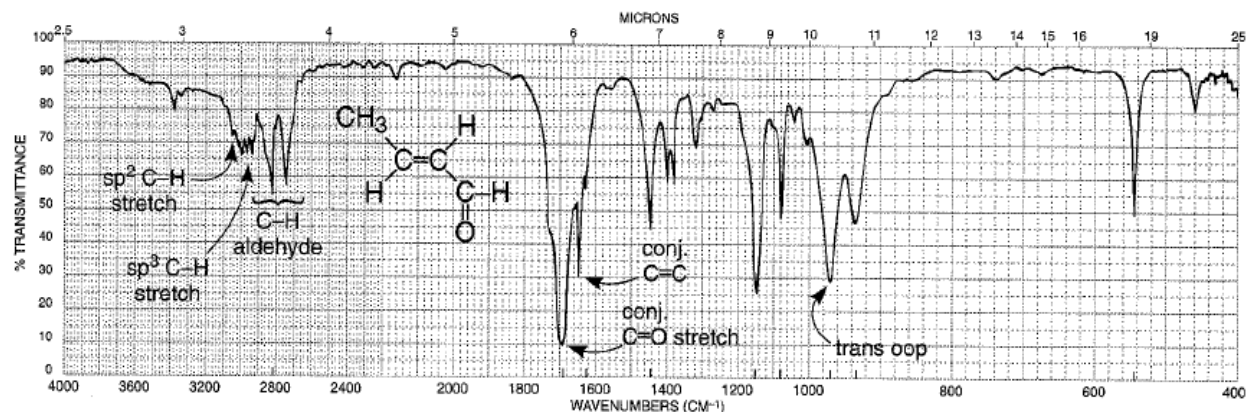
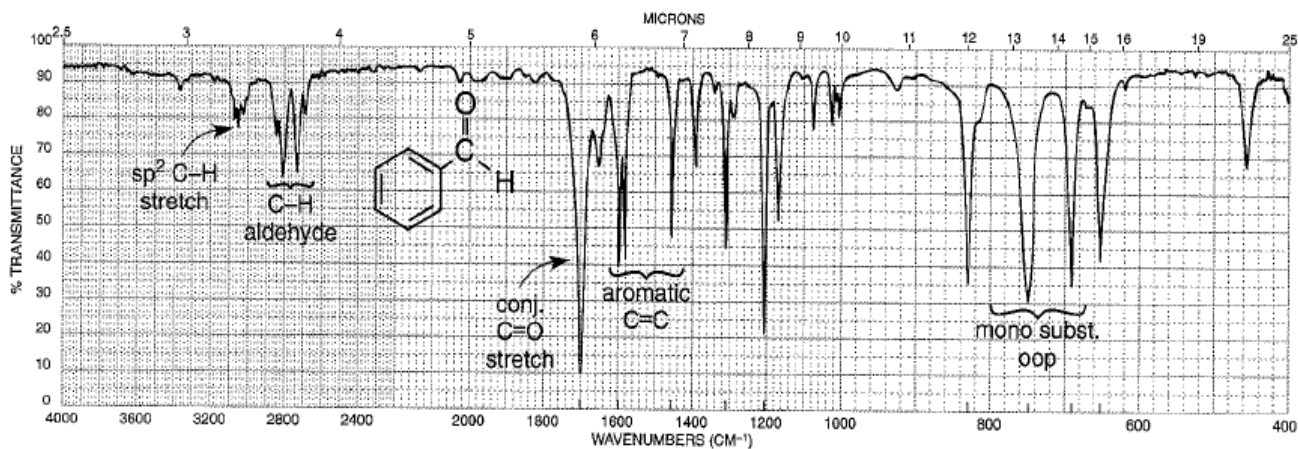
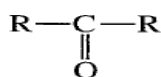


FIGURE 2.37 The infrared spectrum of crotonaldehyde (neat liquid, KBr plates).

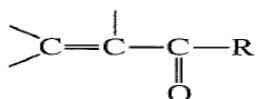


The infrared spectrum of benzaldehyde (neat liquid, KBr plates).

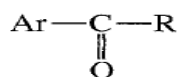
KETONES



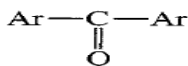
C=O stretch appears in range $1720\text{--}1708\text{ cm}^{-1}$ for normal aliphatic ketones.



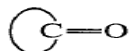
Conjugation of C=O with α,β C=C; $1700\text{--}1675\text{ cm}^{-1}$ for C=O and $1644\text{--}1617\text{ cm}^{-1}$ for C=C.



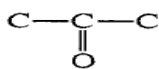
Conjugation of C=O with phenyl; $1700\text{--}1680\text{ cm}^{-1}$ for C=O and $1600\text{--}1450\text{ cm}^{-1}$ for ring.



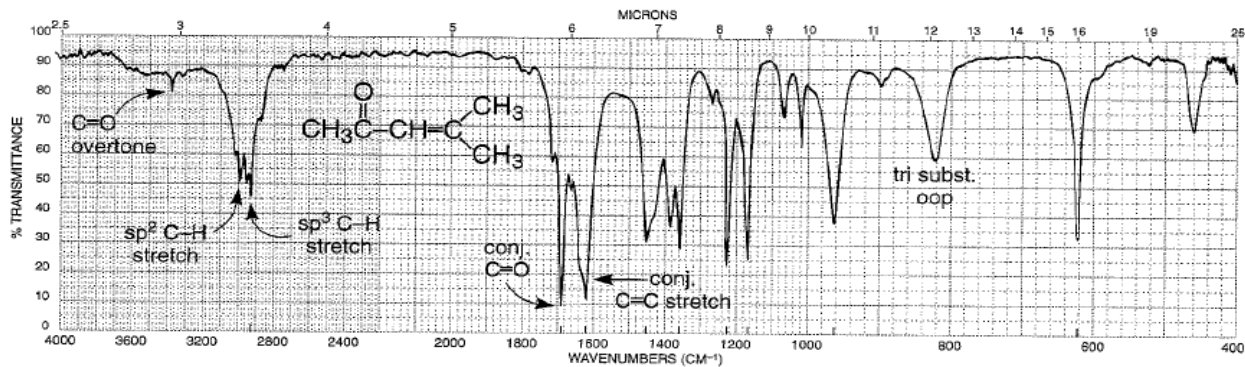
Conjugation with two aromatic rings; $1670-1600\text{ cm}^{-1}$ for $\text{C}=\text{O}$.



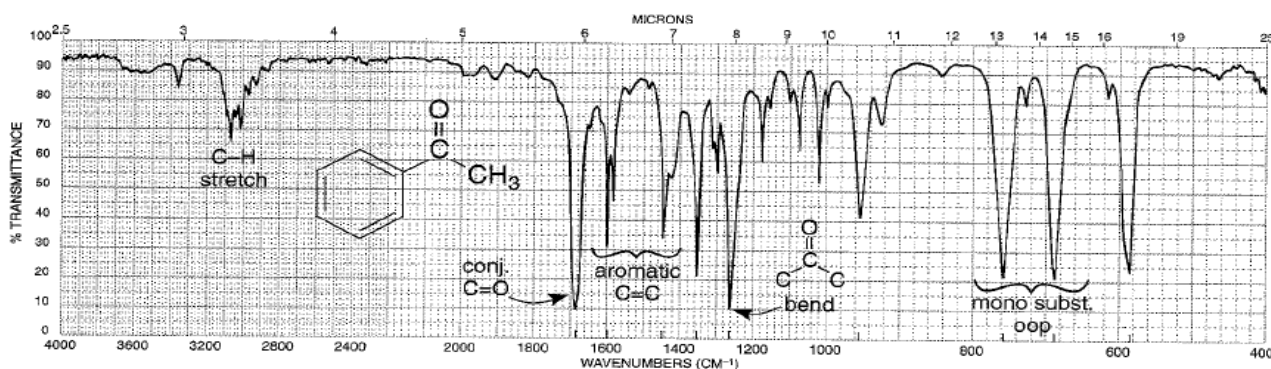
Cyclic ketones; $\text{C}=\text{O}$ frequency increases with decreasing ring size.



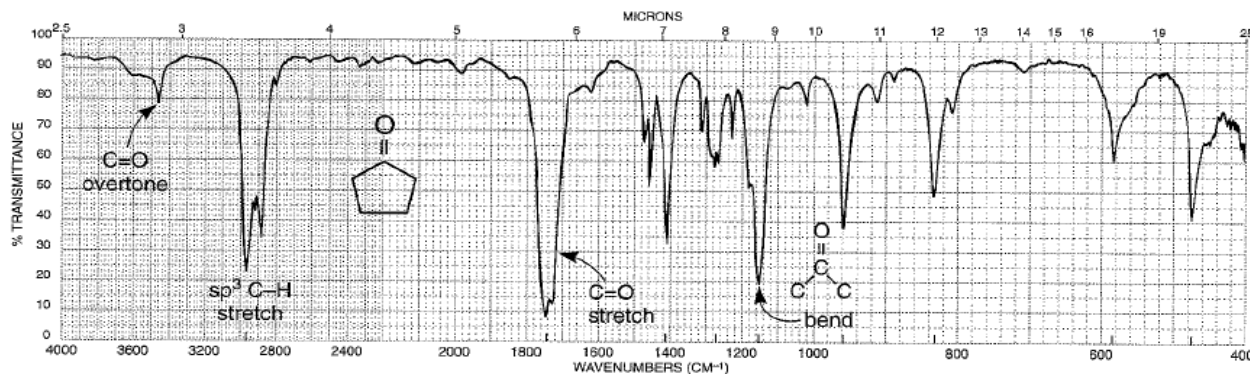
Bending appears as a medium-intensity peak in the range $1300-1100\text{ cm}^{-1}$.



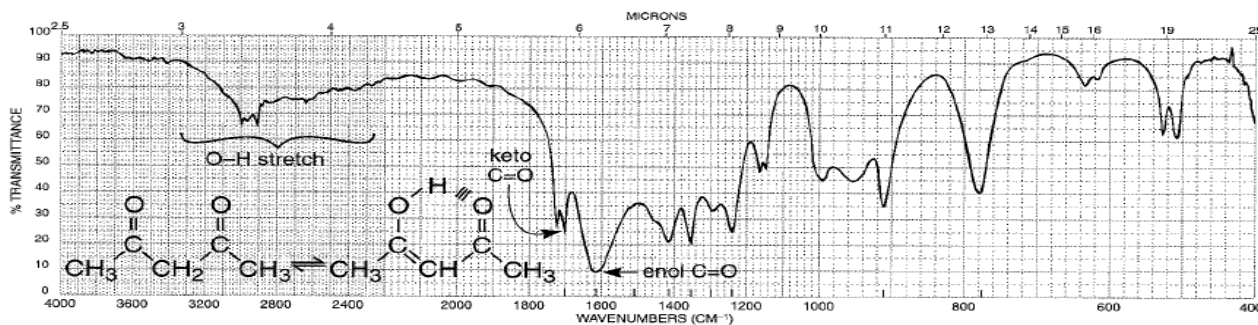
The infrared spectrum of mesityl oxide (neat liquid, KBr plates).



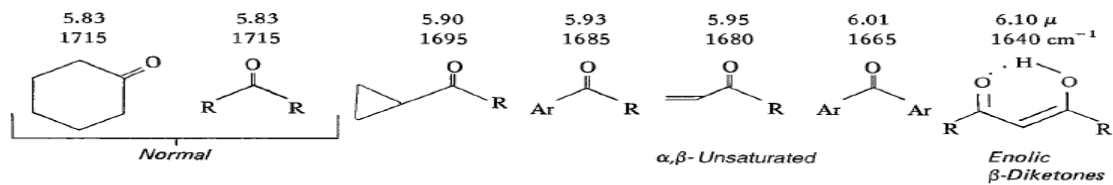
The infrared spectrum of acetophenone (neat liquid, KBr plates).



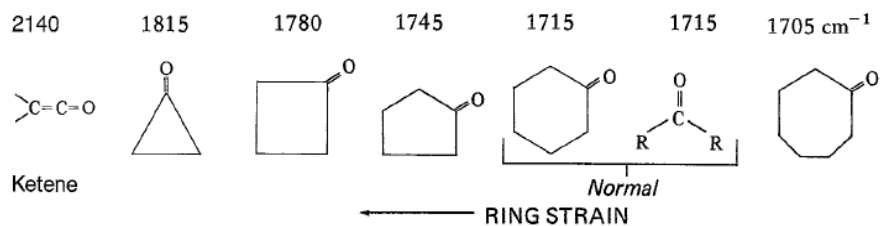
The infrared spectrum of cyclopentanone (neat liquid, KBr plates).



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



The C=O stretching vibrations in conjugated ketones.



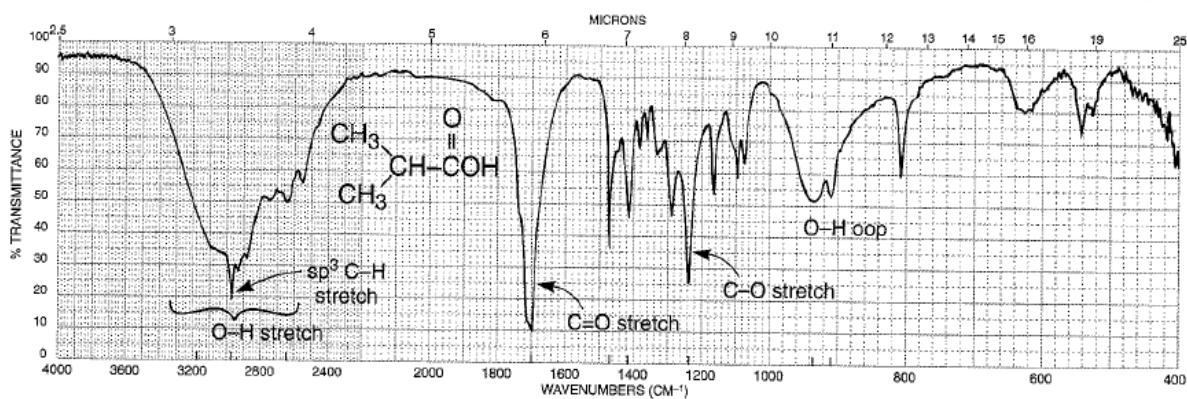
The C=O stretching vibrations for cyclic ketones and ketene.

SPECTRAL ANALYSIS BOX

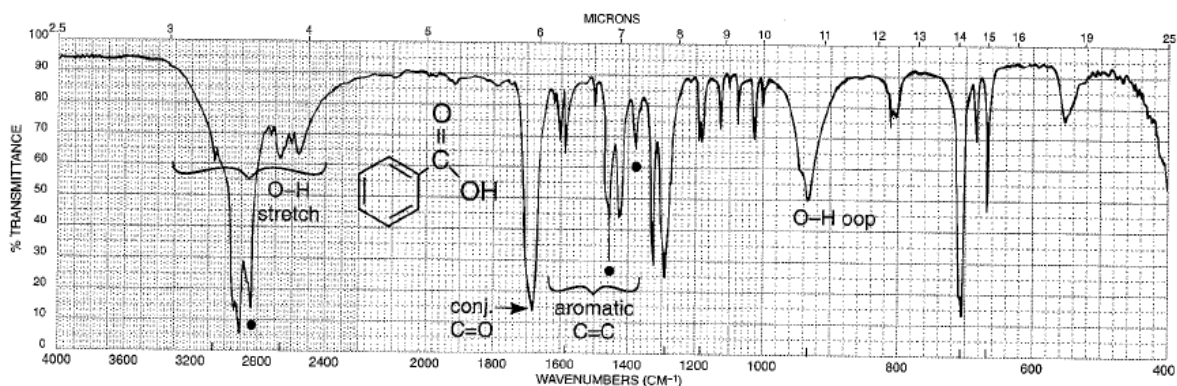
CARBOXYLIC ACIDS

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

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



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

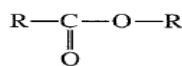


The infrared spectrum of benzoic acid (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

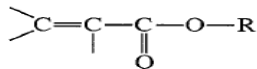
SPECTRAL ANALYSIS BOX

ESTERS

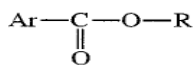
C=O



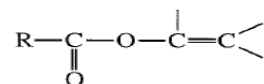
C=O stretch appears in range 1750–1735 cm^{-1} for normal aliphatic esters.



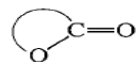
Conjugation of C=O with α,β C=C; 1740–1715 cm^{-1} for C=O and 1640–1625 cm^{-1} for C=C (two bands for some C=C, *cis* and *trans*, p. 52.)



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



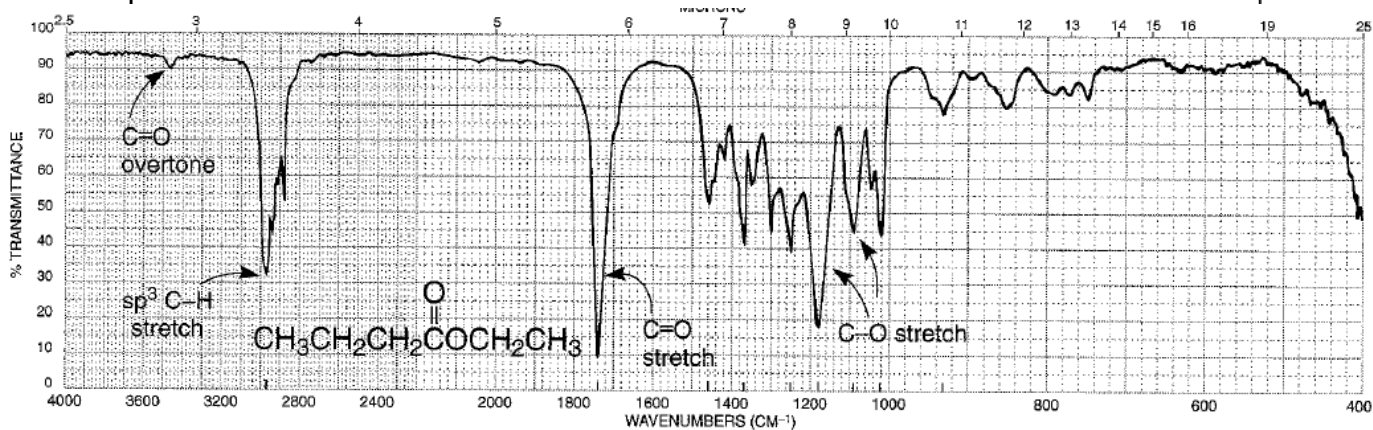
Conjugation of a single-bonded oxygen atom with C=C or phenyl; 1765–1762 cm^{-1} for C=O.



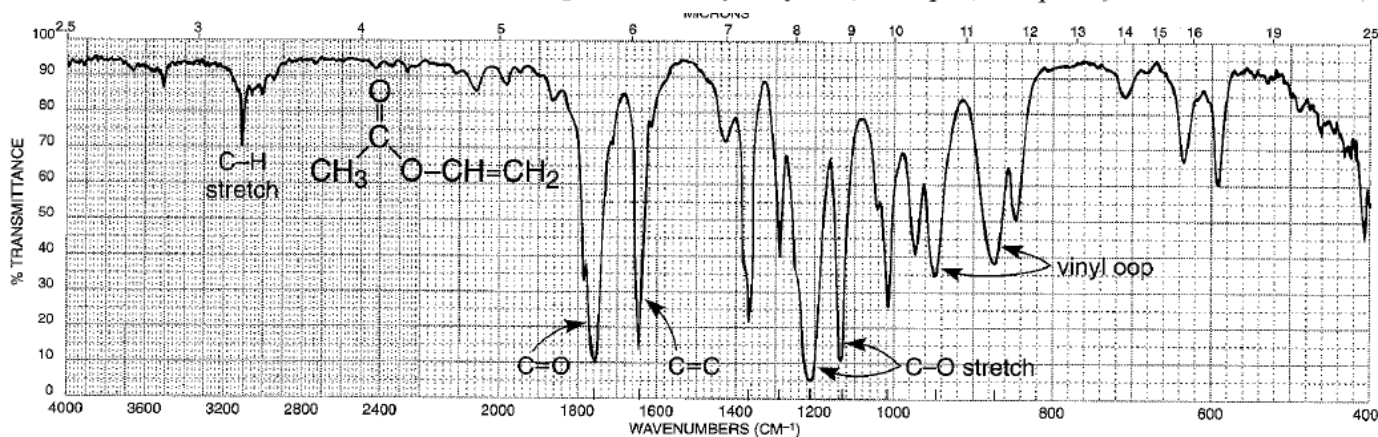
Cyclic esters (lactones); C=O frequency increases with decreasing ring size.

C-O

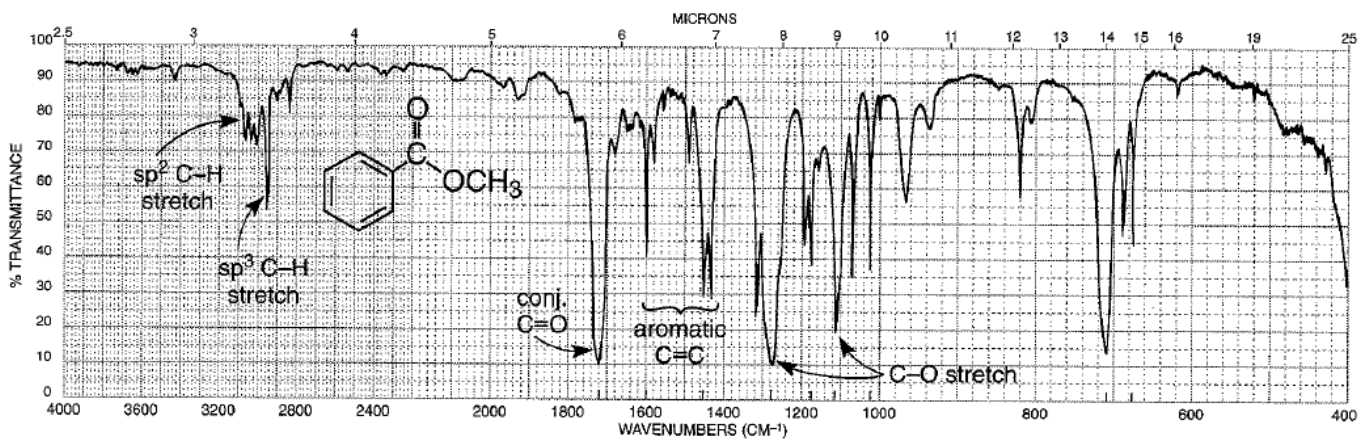
Stretch in two or more bands, one stronger and broader than the other, occurs in the range 1300–1000 cm^{-1} .



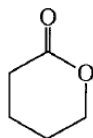
The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).



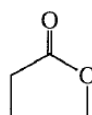
The infrared spectrum of vinyl acetate (neat liquid, KBr plates).



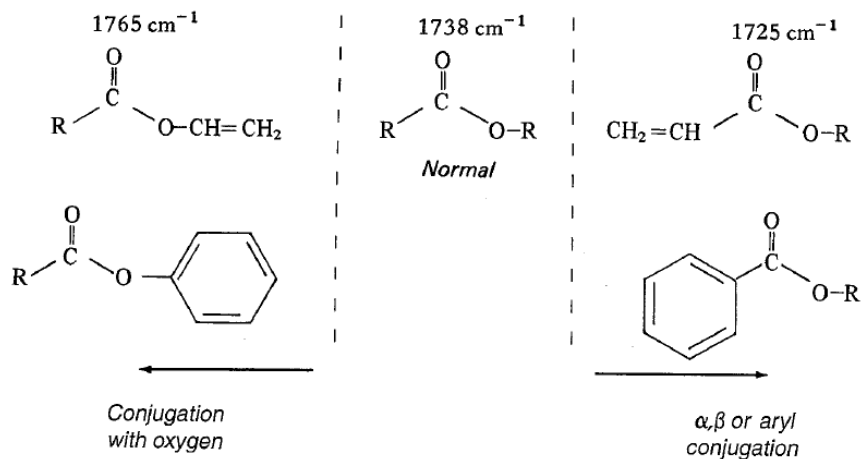
The infrared spectrum of methyl benzoate (neat liquid, KBr plates).



δ -Valerolactone
1735 cm^{-1}



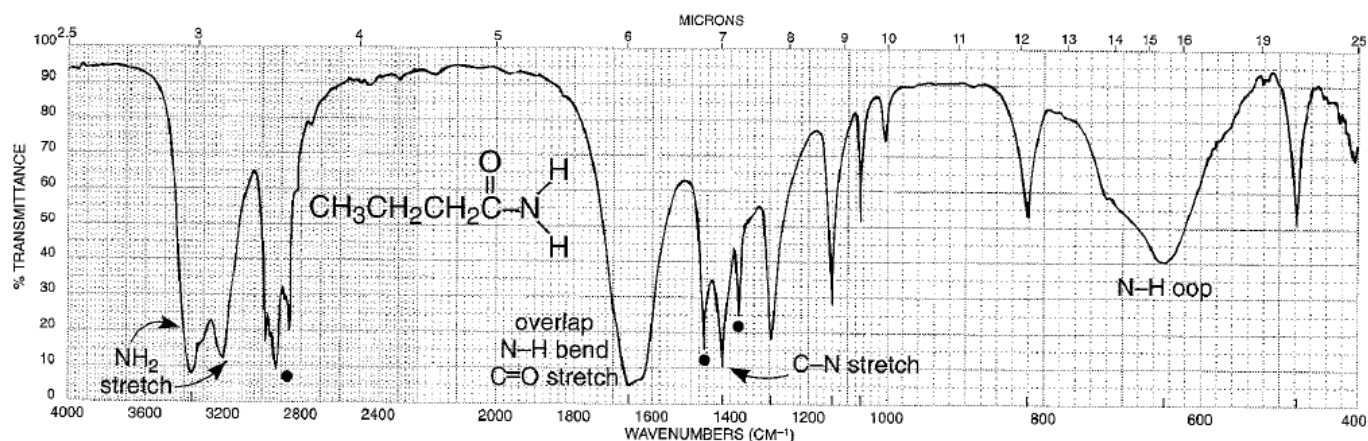
γ -Butyrolactone
1770 cm^{-1}



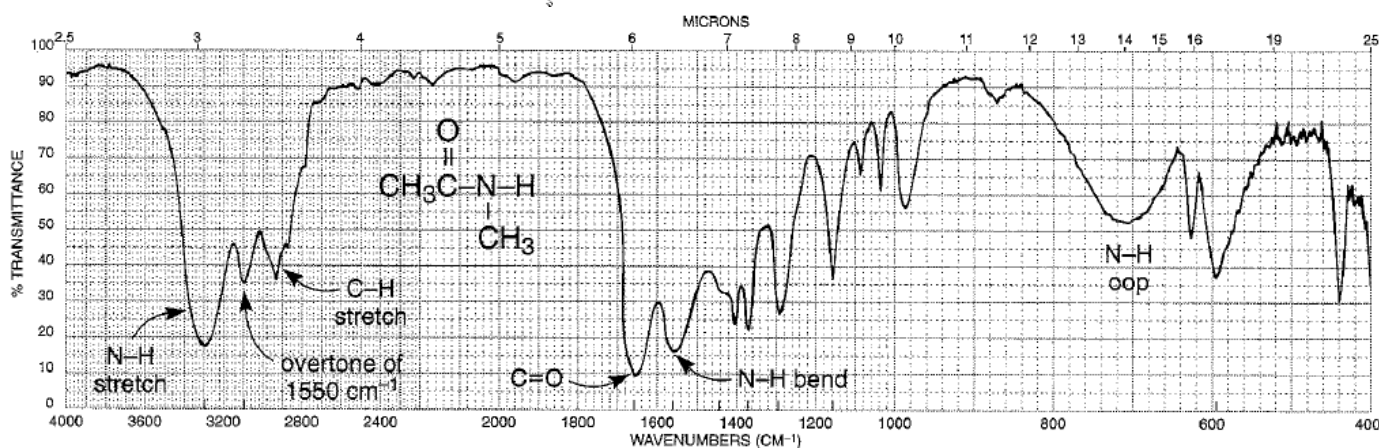
Ring-Size Effects (cm^{-1})	α,β Conjugation (cm^{-1})	Conjugation with Oxygen (cm^{-1})
1735	1725	1760
1770	1750	1800
1820		

AMIDES

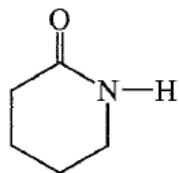
- C=O Stretch occurs at approximately $1680\text{--}1630\text{ cm}^{-1}$.
- N-H Stretch in primary amides ($-\text{NH}_2$) gives two bands near 3350 and 3180 cm^{-1} . Secondary amides have one band ($-\text{NH}$) at about 3300 cm^{-1} .
- N-H Bending occurs around $1640\text{--}1550\text{ cm}^{-1}$ for primary and secondary amides.



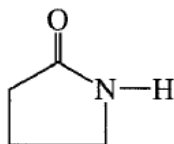
The infrared spectrum of propionamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands



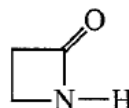
The infrared spectrum of *N*-methylacetamide (neat liquid, KBr plates).



$\sim 1660\text{ cm}^{-1}$



$\sim 1705\text{ cm}^{-1}$

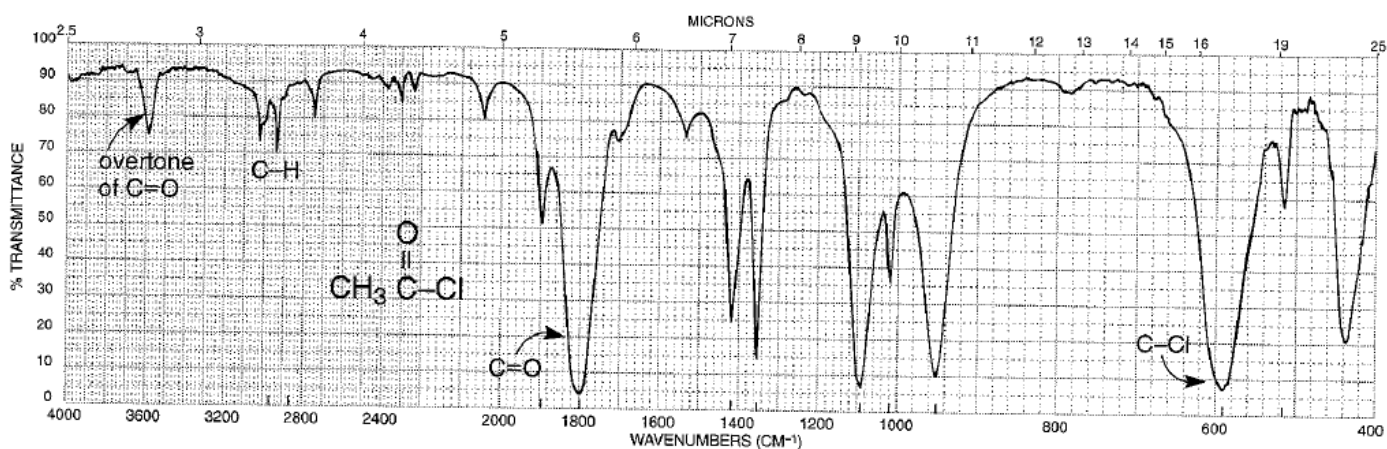


$\sim 1745\text{ cm}^{-1}$

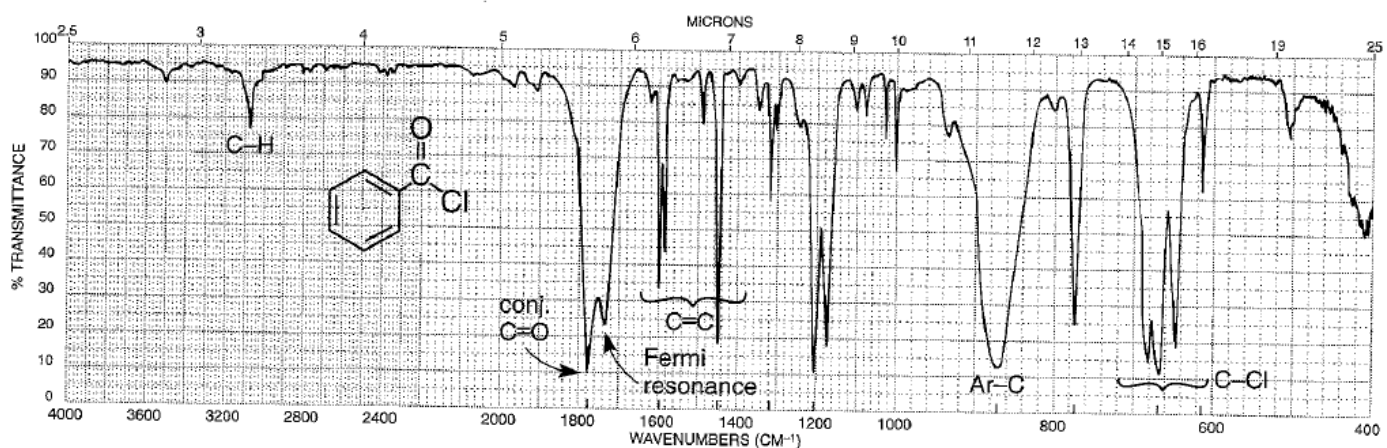
ACID CHLORIDES

C=O Stretch occurs in the range $1810\text{--}1775\text{ cm}^{-1}$ in unconjugated chlorides. Conjugation lowers the frequency to $1780\text{--}1760\text{ cm}^{-1}$.

C-Cl Stretch occurs in the range $730\text{--}550\text{ cm}^{-1}$.



The infrared spectrum of acetyl chloride (neat liquid, KBr plates).

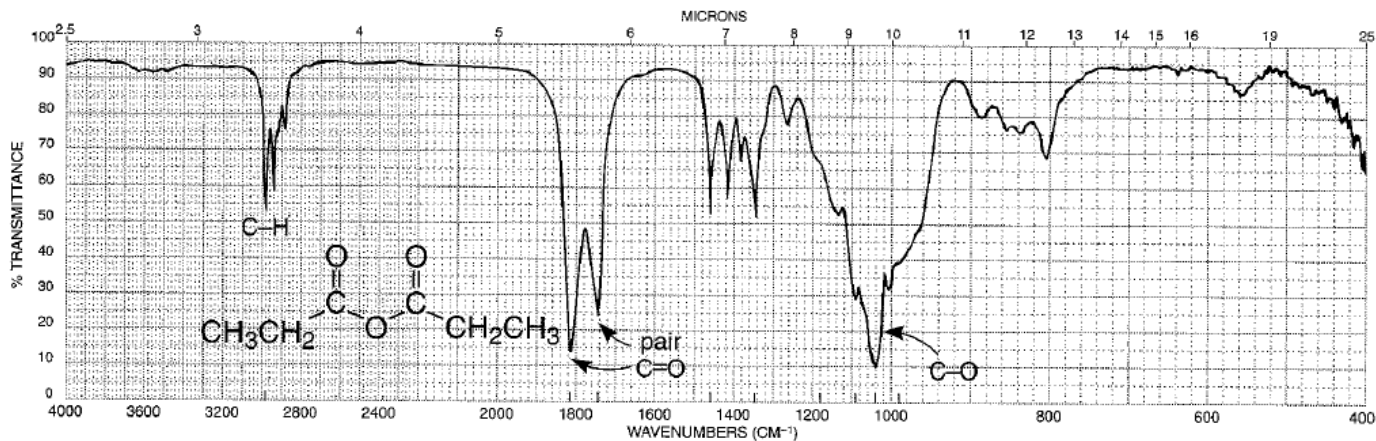


The infrared spectrum of benzoyl chloride (neat liquid, KBr plates).

ANHYDRIDES

C=O Stretch always has two bands, $1830\text{--}1800\text{ cm}^{-1}$ and $1775\text{--}1740\text{ cm}^{-1}$, with variable relative intensity. Conjugation moves the absorption to a lower frequency. Ring strain (cyclic anhydrides) moves the absorptions to a higher frequency.

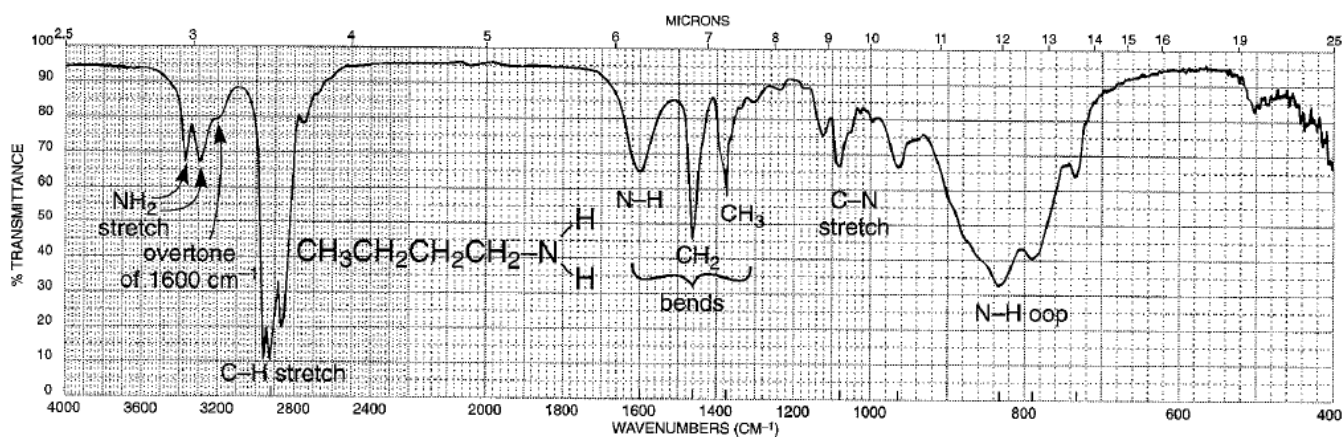
C-O Stretch (multiple bands) occurs in the range $1300\text{--}900\text{ cm}^{-1}$.



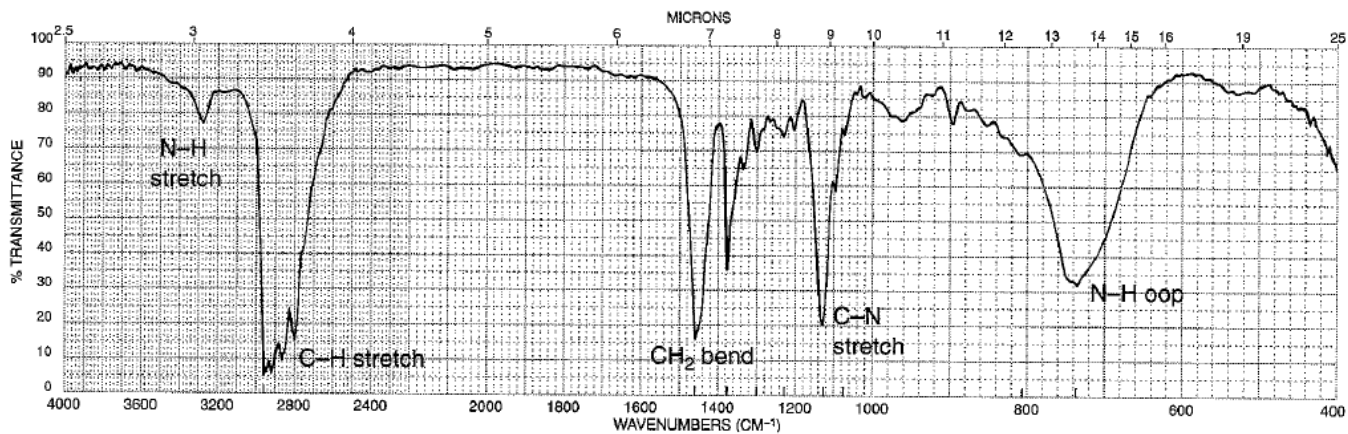
The infrared spectrum of propionic anhydride (neat liquid, KBr plates).

AMINES

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



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



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

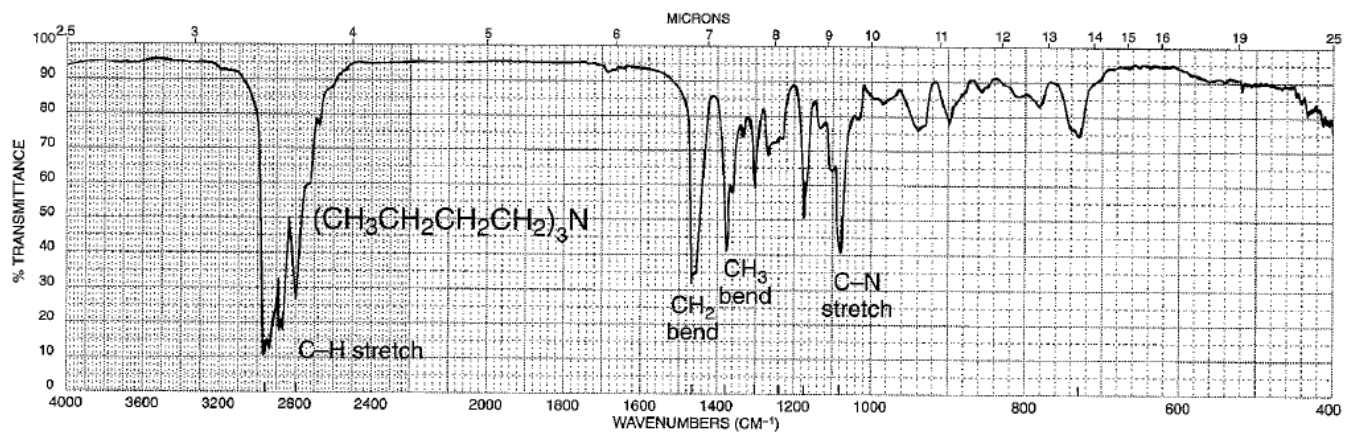
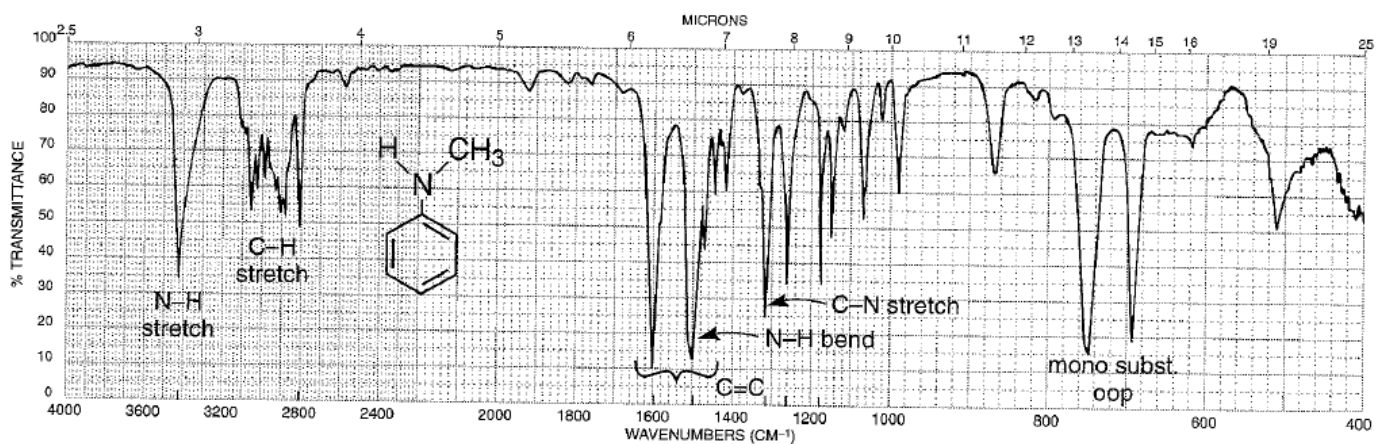


FIGURE 2.60 The infrared spectrum of tributylamine (neat liquid, KBr plates).



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

NITRILES $R-C\equiv N$

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

ISOCYANATES $R-N=C=O$

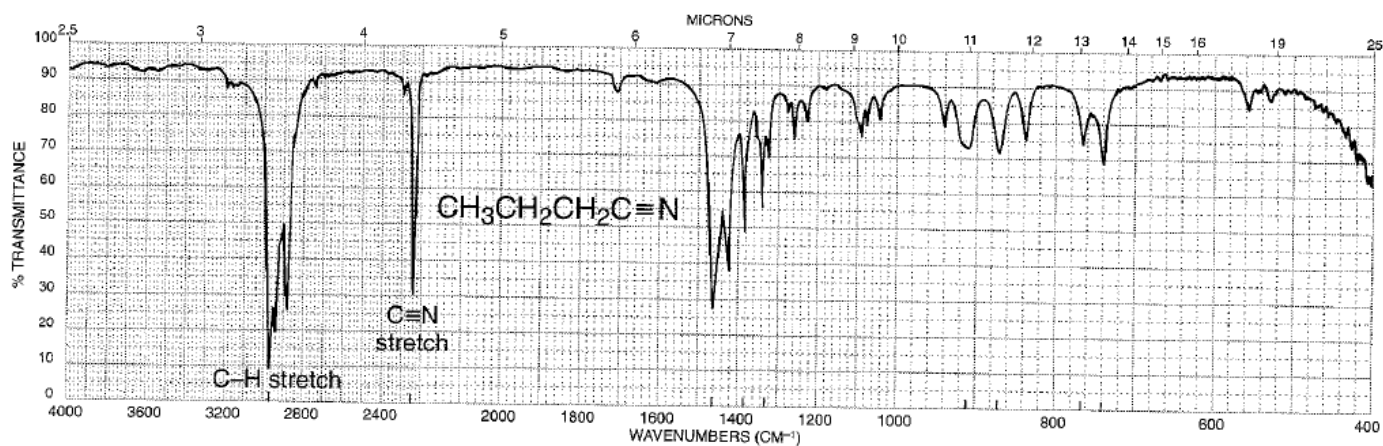
$-N=C=O$ Stretch in an isocyanate gives a broad, intense absorption near 2270 cm^{-1} .

ISOTHIOCYANATES $R-N=C=S$

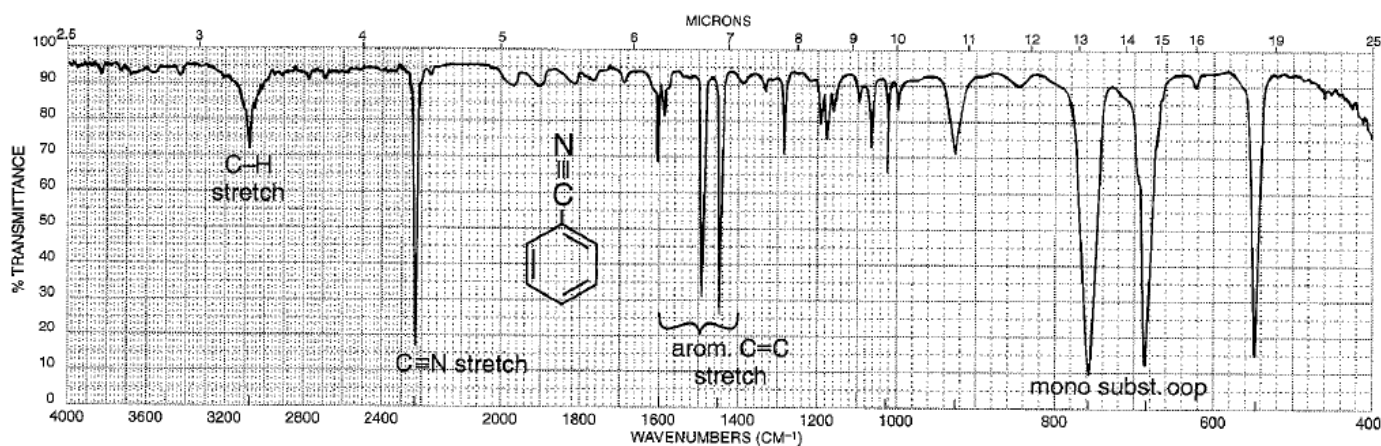
$-N=C=S$ Stretch in an isothiocyanate gives one or two broad, intense absorptions centering near 2125 cm^{-1} .

IMINES $R_2C=N-R$

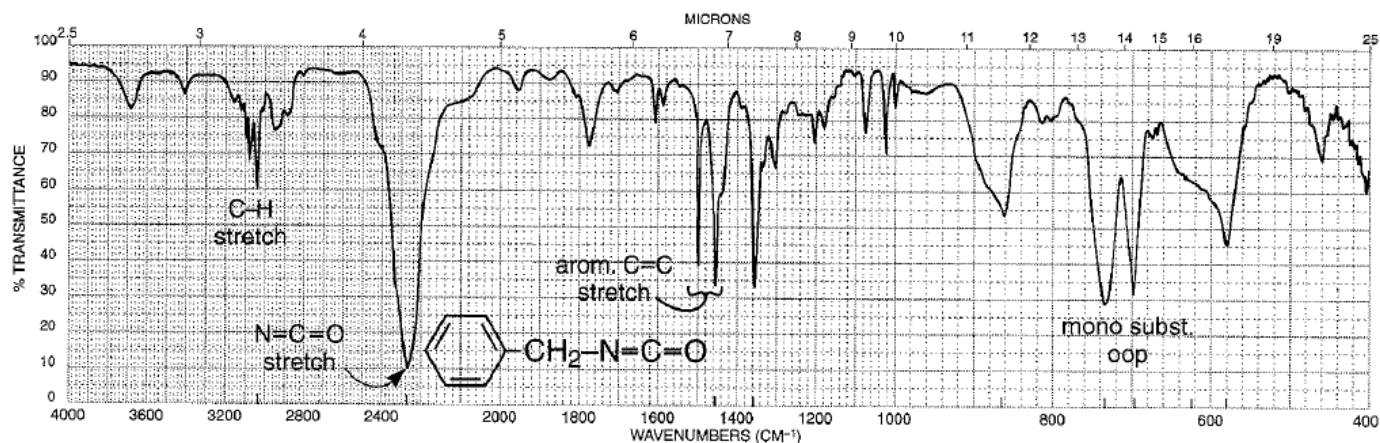
$-C=N-$ Stretch in an imine, oxime, and so on gives a variable-intensity absorption in the range $1690-1640\text{ cm}^{-1}$.



The infrared spectrum of butyronitrile (neat liquid, KBr plates).

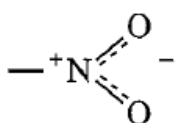


The infrared spectrum of benzonitrile (neat liquid, KBr plates).



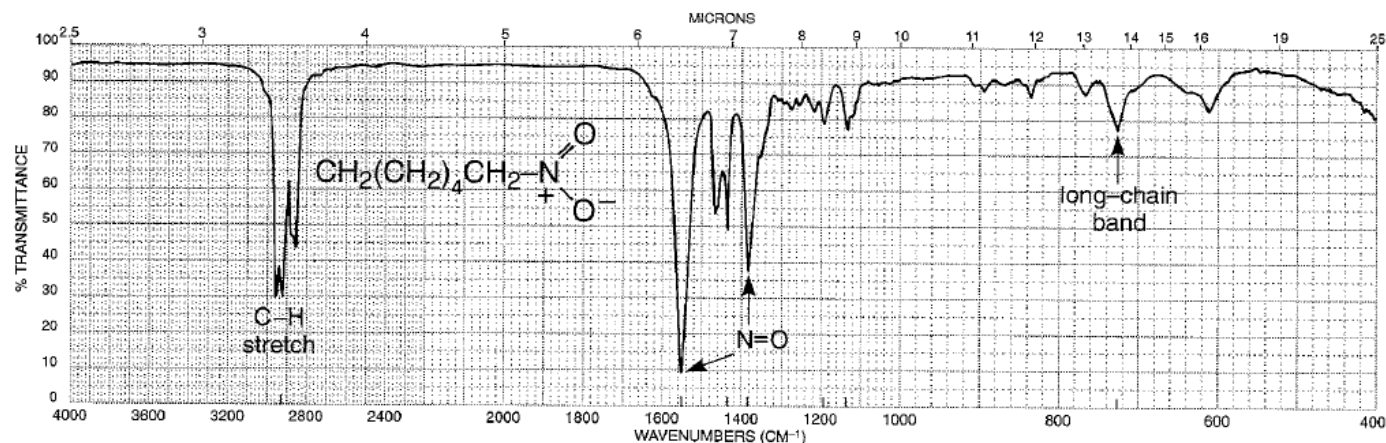
The infrared spectrum of benzyl isocyanate (neat liquid, KBr plates).

NITRO COMPOUNDS

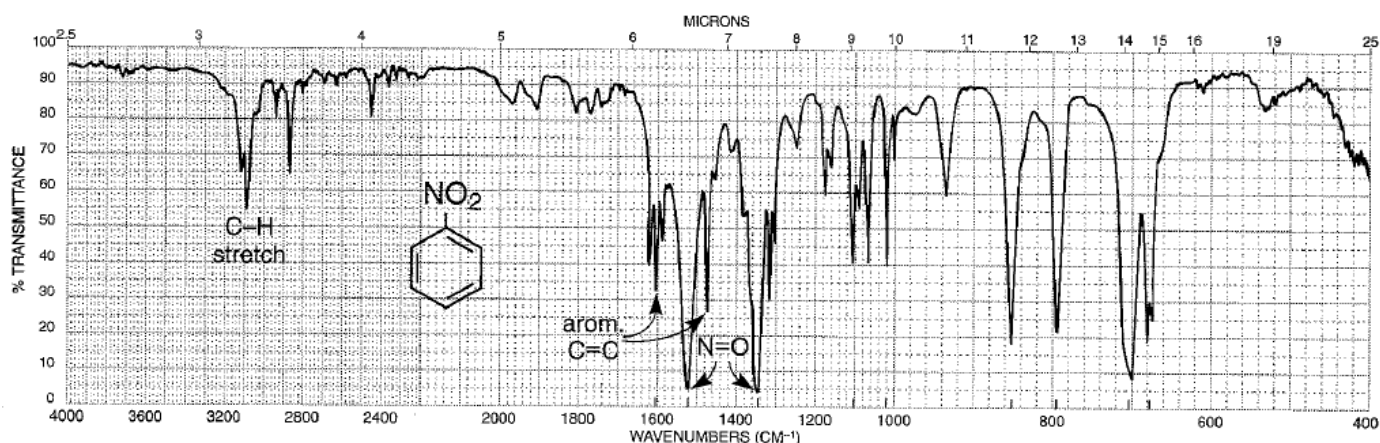


Aliphatic nitro compounds: asymmetric stretch (strong), $1600\text{--}1530\text{ cm}^{-1}$; symmetric stretch (medium), $1390\text{--}1300\text{ cm}^{-1}$.

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

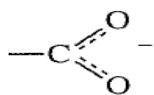


The infrared spectrum of 1-nitrohexane (neat liquid, KBr plates).



The infrared spectrum of nitrobenzene (neat liquid, KBr plates).

CARBOXYLATE SALTS $R-C(=O)O^- Na^+$



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

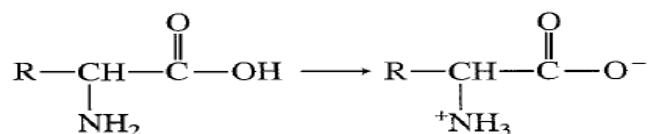
Frequency of $C=O$ absorption is lowered from the value found for the parent carboxylic acid because of resonance (more single-bond character).

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

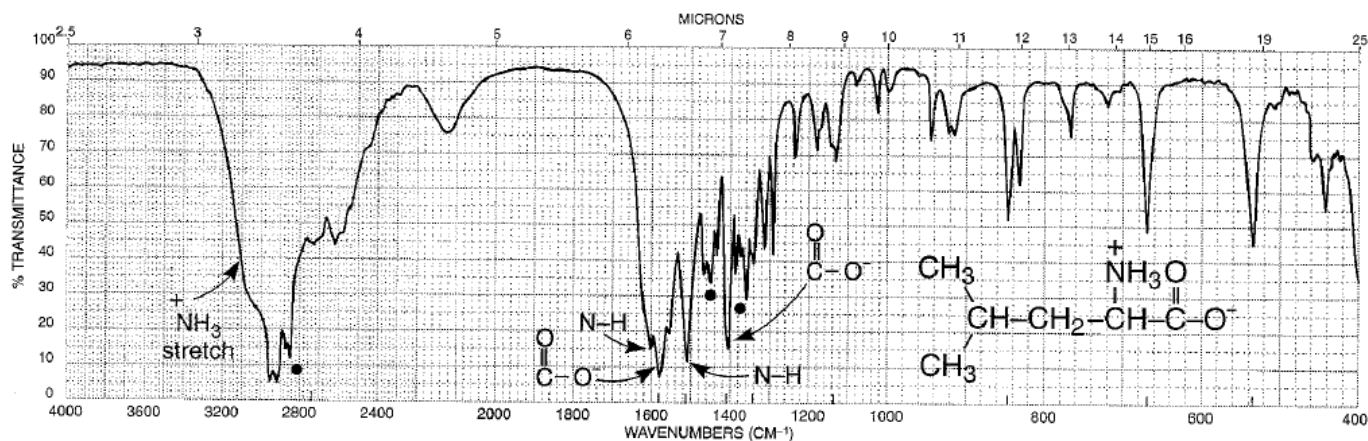
N—H Stretch (broad) occurs at $3300\text{--}2600\text{ cm}^{-1}$. The ammonium ion absorbs to the left in this range, while the tertiary amine salt absorbs to the right. Primary and secondary amine salts absorb in the middle of the range, $3100\text{--}2700\text{ cm}^{-1}$. A broad band often appears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

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

AMINO ACIDS



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



The infrared spectrum of leucine (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands

MERCAPTANS R-S-H

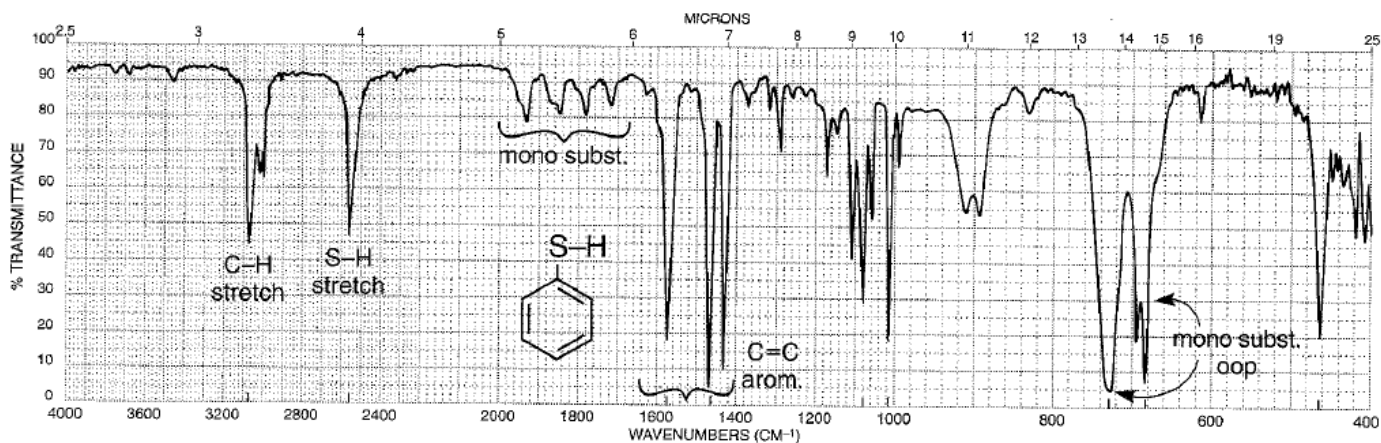
S-H Stretch, one weak band, occurs near 2550 cm^{-1} and virtually confirms the presence of this group, since few other absorptions appear here.

SULFIDES R-S-R

Little useful information is obtained from the infrared spectrum.

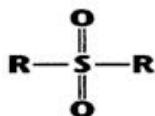
SULFOXIDES R-S(=O)-R

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



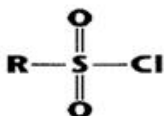
The infrared spectrum of benzenethiol (neat liquid, KBr plates).

SULFONES R-S(=O)₂-R



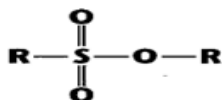
S=O Asymmetric stretch (strong) occurs at 1300 cm^{-1} , symmetric stretch (strong) at 1150 cm^{-1} .

SULFONYL CHLORIDES R-S(=O)₂-Cl



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

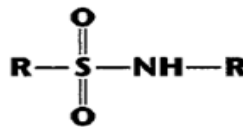
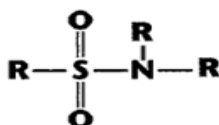
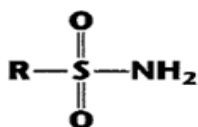
SULFONATES



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

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

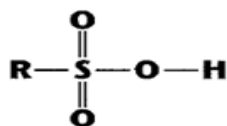
SULFONAMIDES (Solid State)



S=O Asymmetric stretch (strong) occurs at 1325 cm^{-1} , symmetric stretch (strong) at 1140 cm^{-1} .

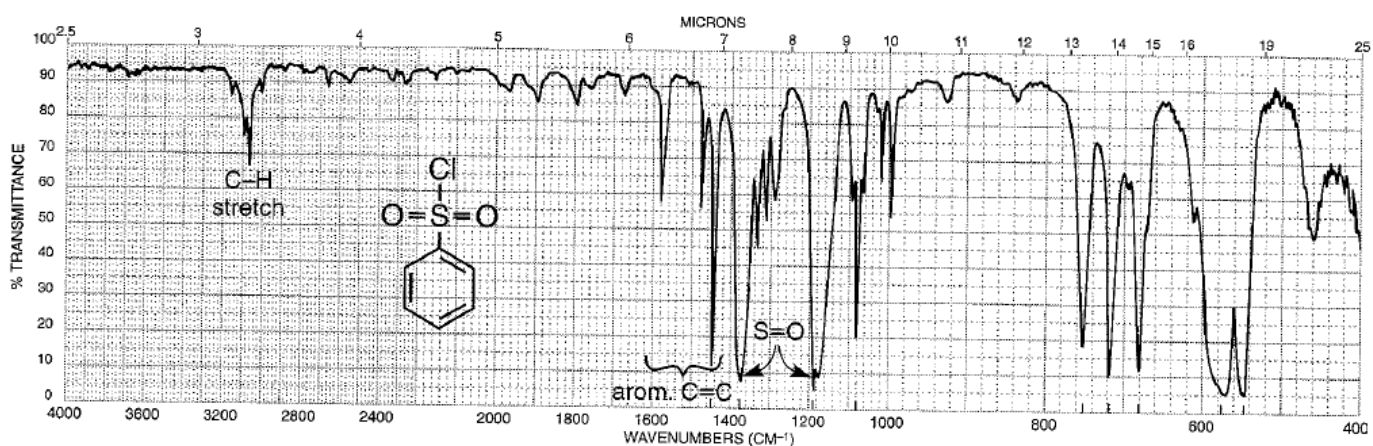
N-H Primary stretch occurs at 3350 and 3250 cm^{-1} ; secondary stretch occurs at 3250 cm^{-1} ; bend occurs at 1550 cm^{-1} .

SULFONIC ACIDS (Anhydrous)

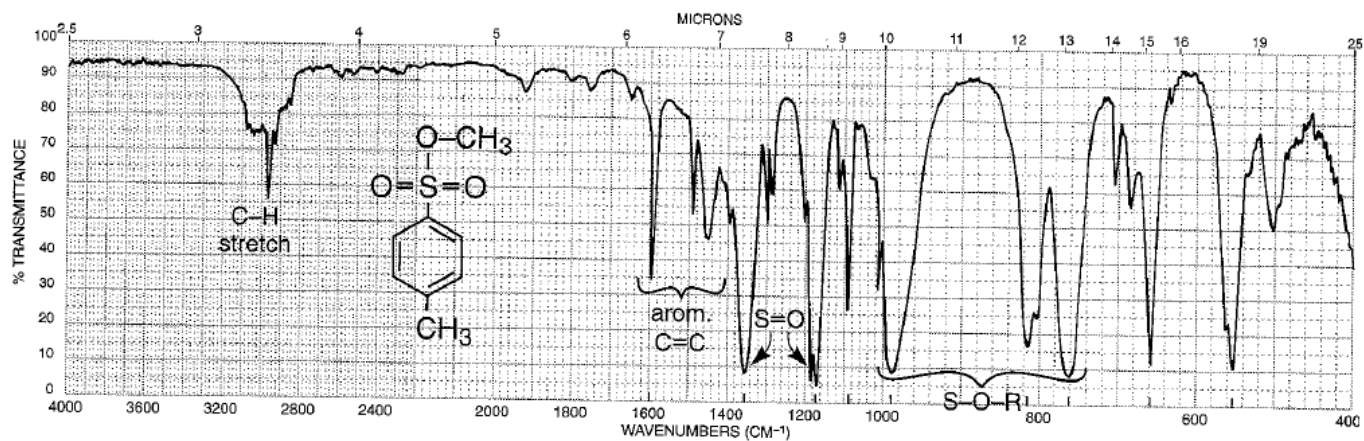


S=O Asymmetric stretch (strong) occurs at 1350 cm^{-1} , symmetric stretch (strong) at 1150 cm^{-1} .

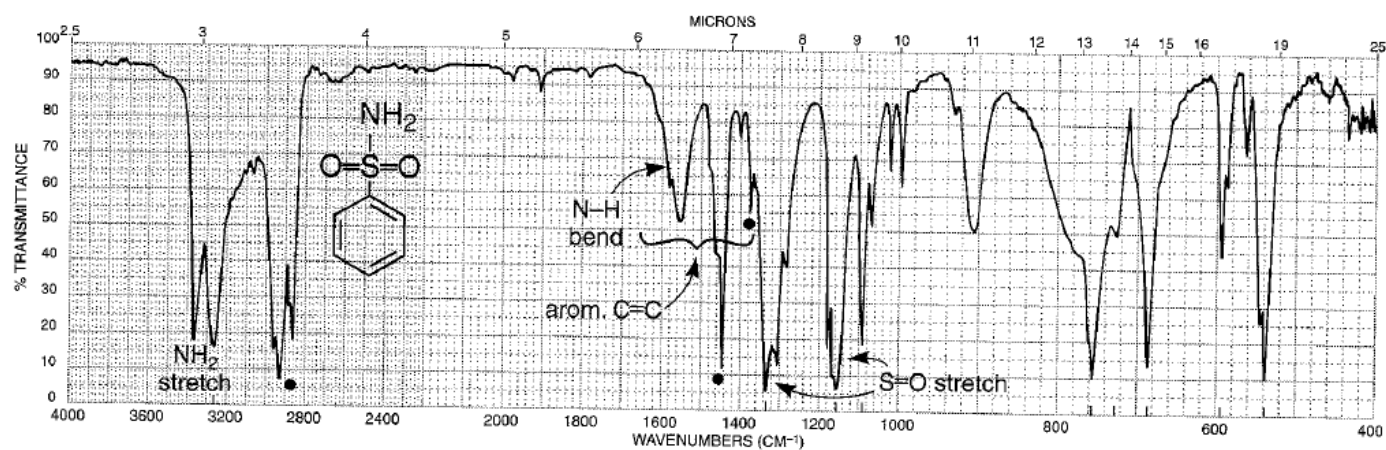
S-O Stretch (strong) occurs at 650 cm^{-1} .



The infrared spectrum of benzenesulfonyl chloride (neat liquid, KBr plates).



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



The infrared spectrum of benzenesulfonamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands

FLUORIDES R-F

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

CHLORIDES R-Cl

C-Cl Stretch (strong) in aliphatic chlorides occurs in the range $785\text{--}540\text{ cm}^{-1}$. Primary chlorides absorb at the upper end of this range, while tertiary chlorides absorb near the lower end. Two or more bands may be observed, due to the different conformations which are possible.

Multiple substitution on a single-carbon atom results in an intense absorption at the upper-frequency end of this range: CH_2Cl_2 (739 cm^{-1}), HCCl_3 (759 cm^{-1}), and CCl_4 (785 cm^{-1}). Aryl chlorides absorb between 1100 and 1035 cm^{-1} .

$\text{CH}_2\text{-Cl}$ Bend (wagging) at $1300\text{--}1230\text{ cm}^{-1}$.

BROMIDES R-Br

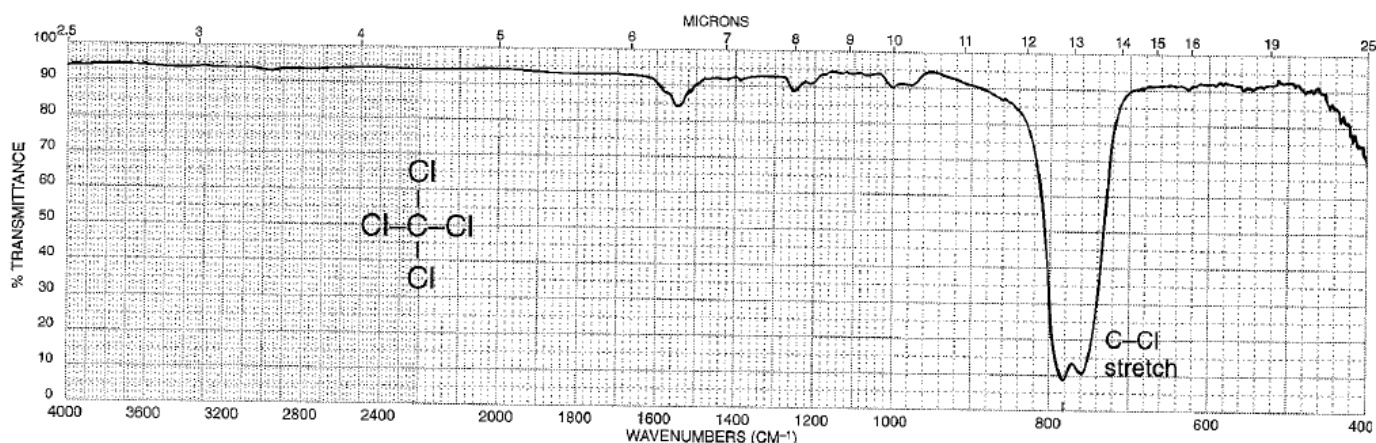
C-Br Stretch (strong) in aliphatic bromides occurs at $650\text{--}510\text{ cm}^{-1}$, out of the range of routine spectroscopy using NaCl plates or cells. The trends indicated for aliphatic chlorides hold for bromides. Aryl bromides absorb between 1075 and 1030 cm^{-1} .

$\text{CH}_2\text{-Br}$ Bend (wagging) at $1250\text{--}1190\text{ cm}^{-1}$.

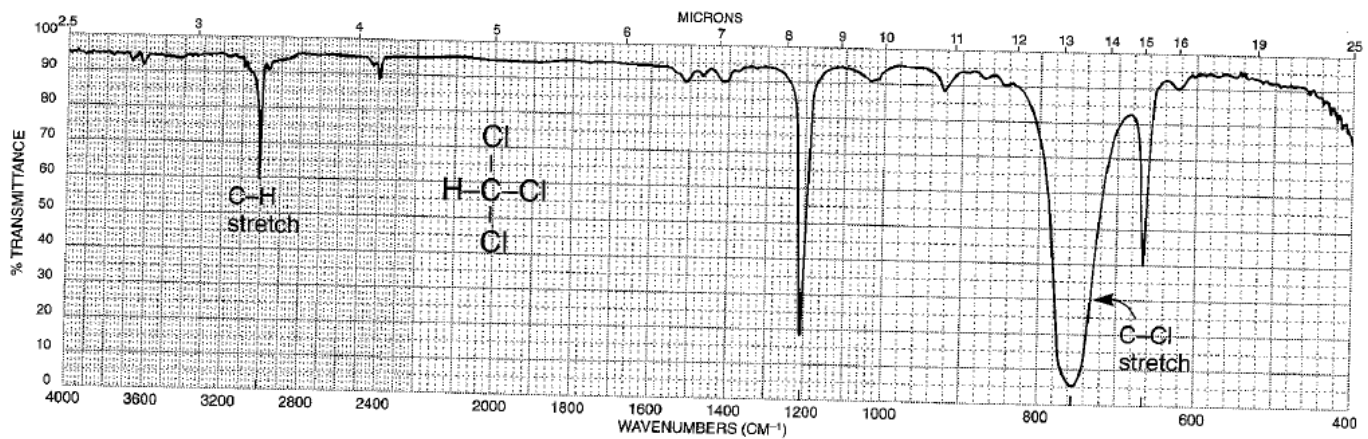
IODIDES R-I

C-I Stretch (strong) in aliphatic iodides occurs at $600\text{--}485\text{ cm}^{-1}$, out of the range of routine spectroscopy using NaCl plates or cells. The trends indicated for aliphatic chlorides hold for iodides.

$\text{CH}_2\text{-I}$ Bend (wagging) at $1200\text{--}1150\text{ cm}^{-1}$.



The infrared spectrum of carbon tetrachloride (neat liquid, KBr plates).



The infrared spectrum of chloroform (neat liquid, KBr plates).

Techniques d'examen des échantillons

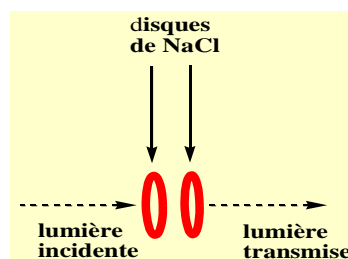
Toutes sortes d'échantillons peuvent actuellement faire l'objet d'études dans le moyen infra-rouge. De nombreux dispositifs ont été imaginés pour répondre à un grand nombre d'application qualitative et quantitative.

Procédés par transmission

- Pour les gaz, on utilise des cellules dont le trajet optique est au minimum de quelques centimètres mais qui peut atteindre plusieurs mètres, pour les faibles absorbances, par un jeu de réflexions multiples sur des miroirs internes à la cellule. Le volume interne devient assez important.

La technique CPG/IR fait appel à des cellules à gaz filiformes d'un volume de quelques dizaines de μl ($L = 10 \text{ cm}$ et $\varnothing < 1 \text{ mm}$), dont les parois latérales sont dorées pour être réfléchissantes.

- L'examen des liquides est généralement réalisé avec des cellules à parois démontables. Pour les observations qualitatives, on écrase modérément une gouttelette de l'échantillon entre deux disques de NaCl ou de KBr, sans intercalaires. Par contre, pour l'analyse quantitative, on utilise soit des cuves en quartz (trajet optique = 1 à 5 cm), soit des cuves à épaisseur fixe ou variable dont on contrôle périodiquement le trajet optique, généralement inférieur à 1 mm.



Pour les solides, on a le choix entre plusieurs techniques :

- On disperse quelques milligrammes d'échantillon dans une huile de paraffine (encore appelée NUJOL) qui
-
-
- ne présente que trois bandes principales d'absorption en dehors des quelles le spectre de l'échantillon est exploitable. On peut compléter ce premier spectre par un second réalisé dans l'hexachlorobutadiène, transparent dans les domaines où le NUJOL est opaque.

On broie le solide en présence de KBr (0,1 à 0,2 % d'échantillon) sec dans un petit mortier généralement en agate. Ce mélange est ensuite comprimé sous une pression de 5 à 8 tonnes/cm², avec une presse hydraulique ou manuelle. La pastille

frittée qui en résulte, d'aspect translucide, correspond à une dispersion de l'échantillon dans une matrice solide (KBr).

- Enfin si le solide peut être mis en solution, on est amené au cas général de l'examen d'un liquide. Il n'existe malheureusement pas de solvant transparent sur toute l'étendue du moyen infrarouge. Ce procédé permet de faire des mesures quantitatives pour toute longueur d'onde à laquelle le solvant n'absorbe pas.

ANALYSE QUANTITATIVE

La précision des mesures d'absorbance et les possibilités de retraitement des spectres ont favorisé l'analyse quantitative par infrarouge. La méthode est devenue très utilisée à la fois parce qu'il est facile dans le moyen IR de repérer dans un spectre de mélange des bandes spécifiques au composé à doser et parce qu'on dispose de méthodes de traitement statistiques efficaces pour le proche IR.

Analyse quantitative dans le moyen infrarouge

Pour les échantillons solides dispersés au sein d'un disque de KBr dont l'épaisseur n'est pas mesurable avec précision, on ajoute un composé à usage de référence interne (carbonate de calcium, naphthalène, nitrure de sodium), en égale quantité à tous les standards ainsi qu'à l'échantillon.

Pour les liquides, les mesures d'absorbance se font dans des cuves à parcours optique ℓ faible, pour minimiser l'absorbance propre au solvant, dont aucun n'est vraiment transparent dans ce domaine. L'incertitude sur la valeur de ℓ est liée à la fragilité des matériaux utilisés pour faire les fenêtres des cellules et à leur construction. Cela impose d'étalonner périodiquement leur trajet optique.

Analyse Qualitative

Avec la disponibilité de l'acquisition de données informatisées et de stockage, il est possible de construire des bibliothèques de base de données de spectres de référence standard. Lorsqu'un spectre d'un composé inconnu est obtenu, son identité peut souvent être déterminée par la recherche grâce à une bibliothèque de spectres de référence. Ce processus est connu sous le nom spectrale recherche. Des comparaisons sont faites par un algorithme qui calcule la différence cumulée entre l'absorbance de l'échantillon et des spectres de référence. Par exemple, un algorithme simple utilise l'équation suivante :

$$D = \sum_{i=1}^n |(A_s)_i - (A_r)_i|$$

où **D** est l'écart cumulatif, **As** est l'absorbance de l'échantillon à la longueur d'onde **i** nombre d'onde, **Ar** est l'absorbance du composé de référence à la même longueur d'onde ou nombre d'onde, et **n** est le nombre de points pour lesquels les spectres ont été numérisés. La différence cumulée est calculée pour chaque spectre de référence. Le composé de référence avec la plus petite valeur de **D** fournit le plus proche du composé inconnu. La précision de la recherche spectrale est limitée par le nombre et le type de composés inclus dans la bibliothèque et par l'effet de la matrice de l'échantillon sur le spectre.

Un autre avantage de l'acquisition de données informatisée est la possibilité de soustraire un spectre d'un autre. Couplé à une recherche spectrale, il est possible, en cherchant à plusieurs reprises et en soustrayant les spectres de référence, de déterminer l'identité de plusieurs composants dans un échantillon sans la nécessité d'une séparation. Un exemple est montré dans la figure 10.33 dans laquelle la composition d'un

mélange constitué de mannitol et le chlorhydrate de cocaïne a été identifié grâce à ce procédé. La figure 10.33a montre le spectre du mélange. Une recherche dans la bibliothèque spectrale sélectionne le mannitol (figure 10.33b) en tant que susceptible de faire partie du mélange. En soustrayant du spectre de mannitol de celui du mélange de spectre laisse le résultat de la figure 10.33c qui correspond le mieux au spectre de chlorhydrate de cocaïne (Figure 10.33d) dans la bibliothèque spectrale. En soustrayant le spectre de ce dernier, il ne reste qu'un signal résiduel de petite taille (figure 10.33e).

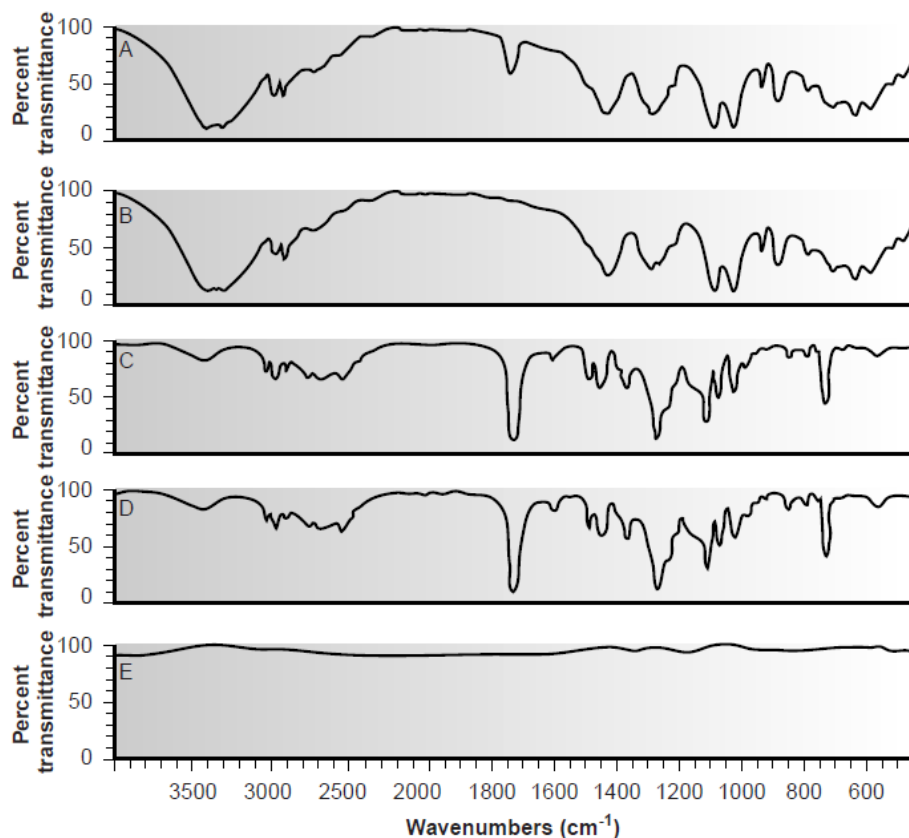


Figure 10.33

Spectral searching and stripping in the analysis of a mixture of mannitol and cocaine hydrochloride. (a) IR spectrum for the mixture; (b) Library IR spectrum of mannitol; (c) Result of subtracting mannitol's IR spectrum from that of the mixture; (d) Library IR spectrum for cocaine hydrochloride; (e) Result of subtracting the spectrum of cocaine hydrochloride from the mixture's IR spectrum.