IR Spectroscopy of Hydrocarbons

Hydrocarbons contain only **carbon-carbon** bonds and **carbon-hydrogen** bonds.

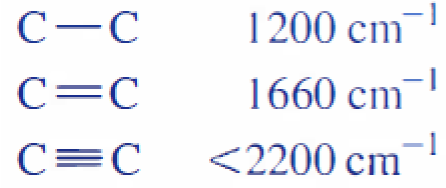
Carbon-Carbon Bond Stretching

C - C single bond absorptions (and most other absorptions in the fingerprint region) are not very reliable.

An infrared spectrum does not provide enough information to identify a structure conclusively (unless an authentic spectrum is available to compare "**fingerprints**").

But, the absorptions of the carbon-carbon and carbon-hydrogen bonds can indicate the presence of **double** and **triple** bonds.

Carbon-carbon bond stretching frequencies:

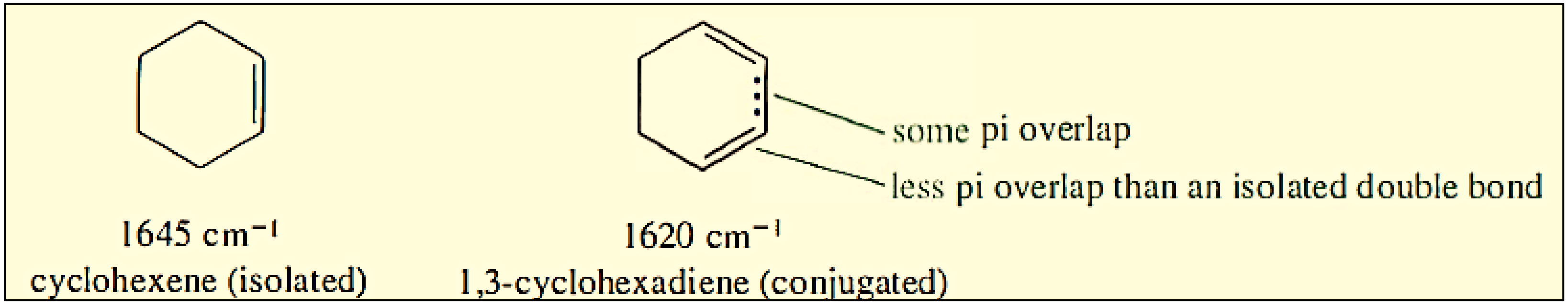


$C-C$	$1200\ cm^{-1}$
$C=C$	$1660\ cm^{-1}$
$C\equiv C$	$<2200\ cm^{-1}$

Effect of Conjugation:

Most unsymmetrically substituted double bonds produce observable stretching absorptions in the region of 1600 to 1680 cm^{-1}.

Isolated double bonds absorb around 1640 to 1 680 cm^{-1}, and **conjugated** double bonds absorb around 1620 to 1 640 cm^{-1}.

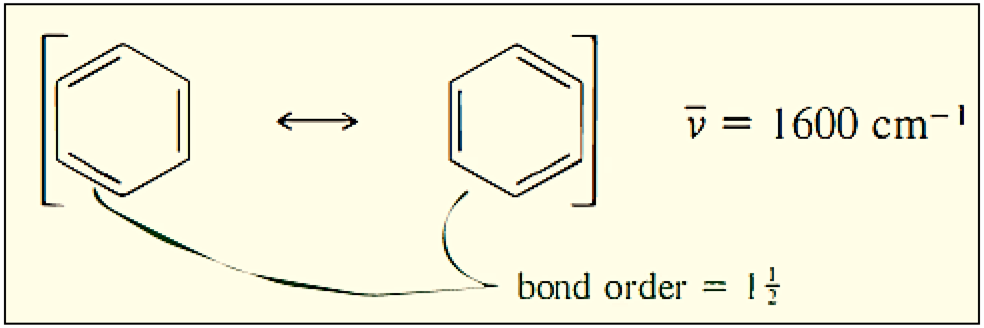


1645 cm^{-1}
cyclohexene (isolated)

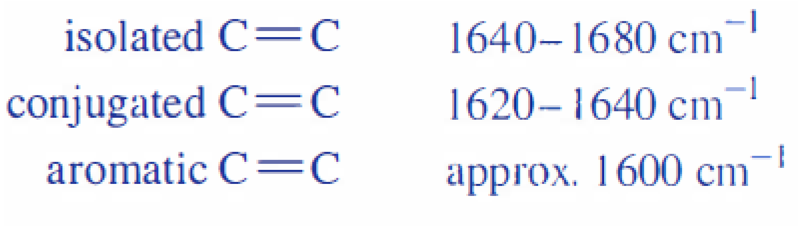
1620 cm^{-1}
1,3-cyclohexadiene (conjugated)

The **aromatic** C=C bonds are more like 1.5 bonds than true C=C.

Their reduced π bonding results in **less stiff** bonds with **lower** stretching frequencies, around 1600 cm^{-1}.



Characteristic C=C stretching frequencies:



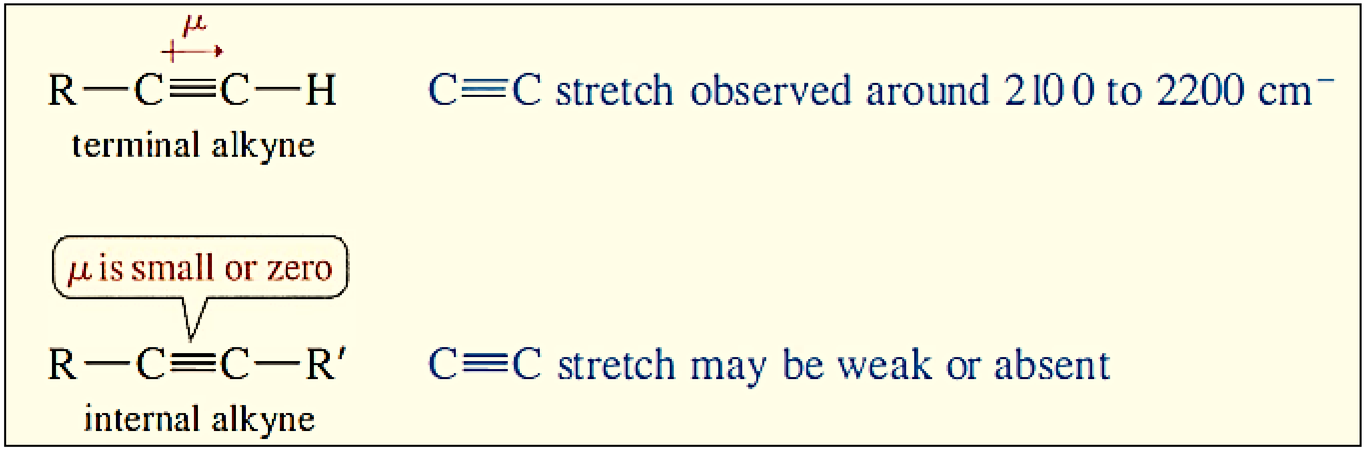
isolated C=C	1640–1680 cm^{-1}
conjugated C=C	1620–1640 cm^{-1}
aromatic C=C	approx. 1600 cm^{-1}

Because C≡C bonds are **stronger** and **stiffer** than C=C, they absorb IR light at **higher** frequencies.

Most alkyne C≡C bonds have stretching frequencies between 2100 and 2200 cm^{-1}.

Terminal alkynes usually give sharp C≡C stretching signals of moderate intensity.

The C≡C stretching absorption of an internal alkyne may be weak or absent, however, due to the symmetry of the disubstituted triple bond with a very small or zero dipole moment.



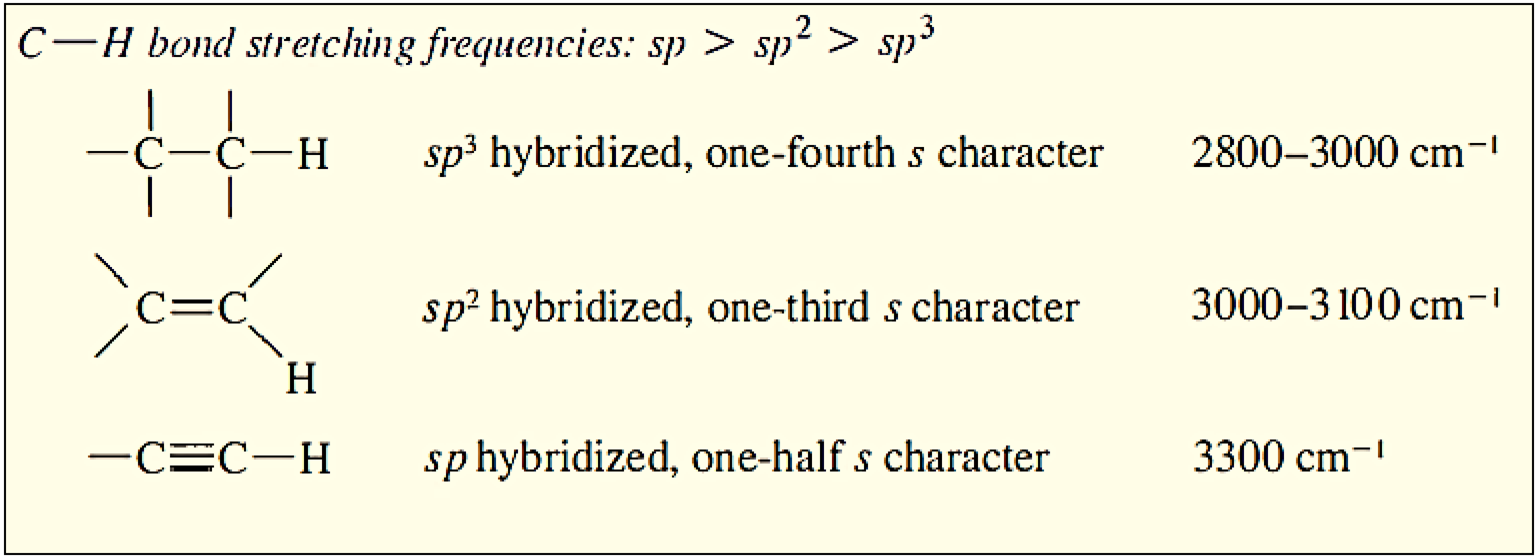
C≡C stretch observed around 2100 to 2200 cm^{-}

C≡C stretch may be weak or absent

Carbon-Hydrogen Bond Stretching

The *s* orbital is closer to the nucleus than the *p* orbitals, and **stronger**, **stiffer** bonds result from orbitals with more *s* character.

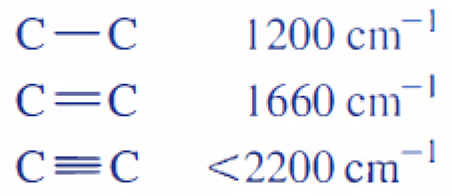
C-H bond with higher *s* character absorbs IR light at higher frequency.



C—H bond stretching frequencies: $sp > sp^2 > sp^3$

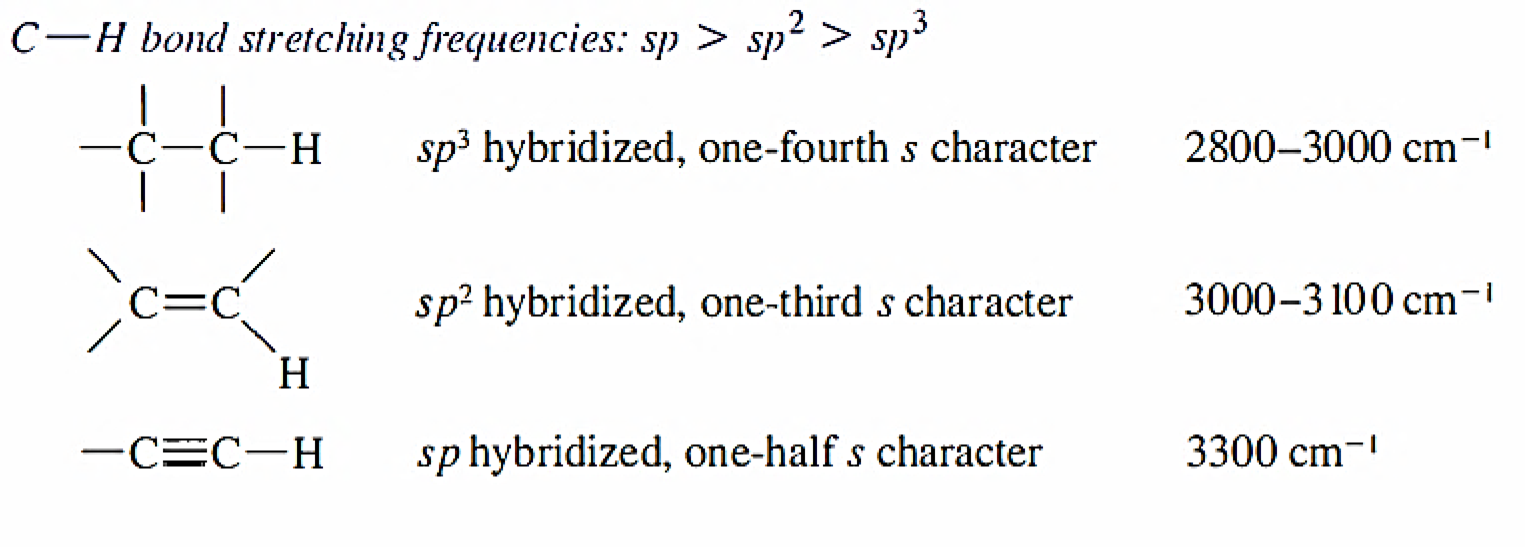
$-C-C-H$	sp^3 hybridized, one-fourth *s* character	2800–3000 cm^{-1}
$C=C$ H	sp^2 hybridized, one-third *s* character	3000–3100 cm^{-1}
$-C\equiv C-H$	*sp* hybridized, one-half *s* character	3300 cm^{-1}

Hydrocarbons stretching frequencies:



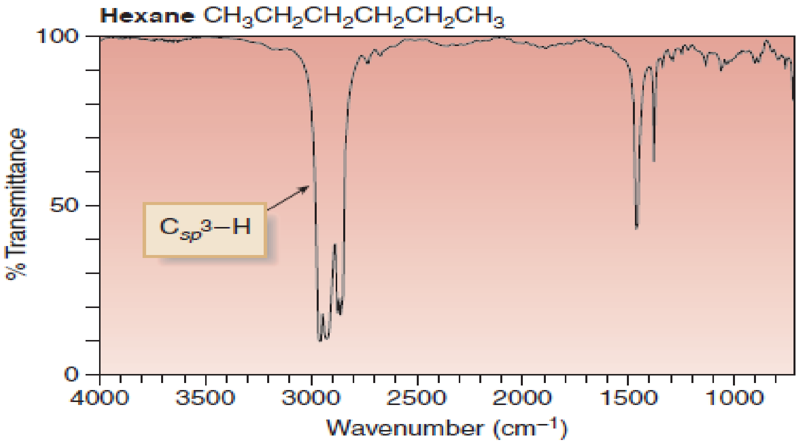
C—C	1200 cm^{-1}
C═C	1660 cm^{-1}
C≡C	<2200 cm^{-1}

isolated C═C	1640–1680 cm^{-1}
conjugated C═C	1620–1640 cm^{-1}
aromatic C═C	approx. 1600 cm^{-1}

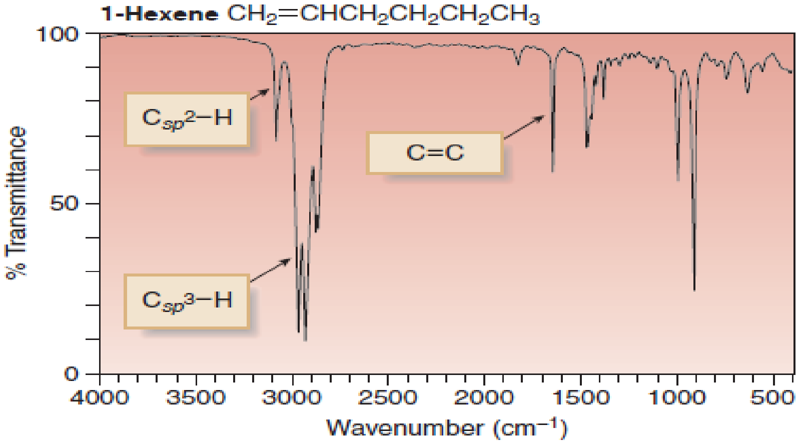


C—H bond stretching frequencies: sp > sp^2 > sp^3

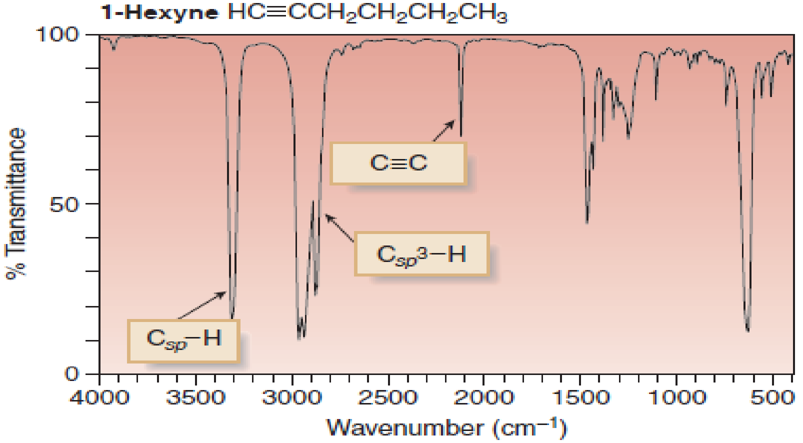
$-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-H$	*sp^3* hybridized, one-fourth *s* character	2800–3000 cm^{-1}
$>C=C<_{H}$	*sp^2* hybridized, one-third *s* character	3000–3100 cm^{-1}
—C≡C—H	*sp* hybridized, one-half *s* character	3300 cm^{-1}


Hexane $CH_3CH_2CH_2CH_2CH_2CH_3$

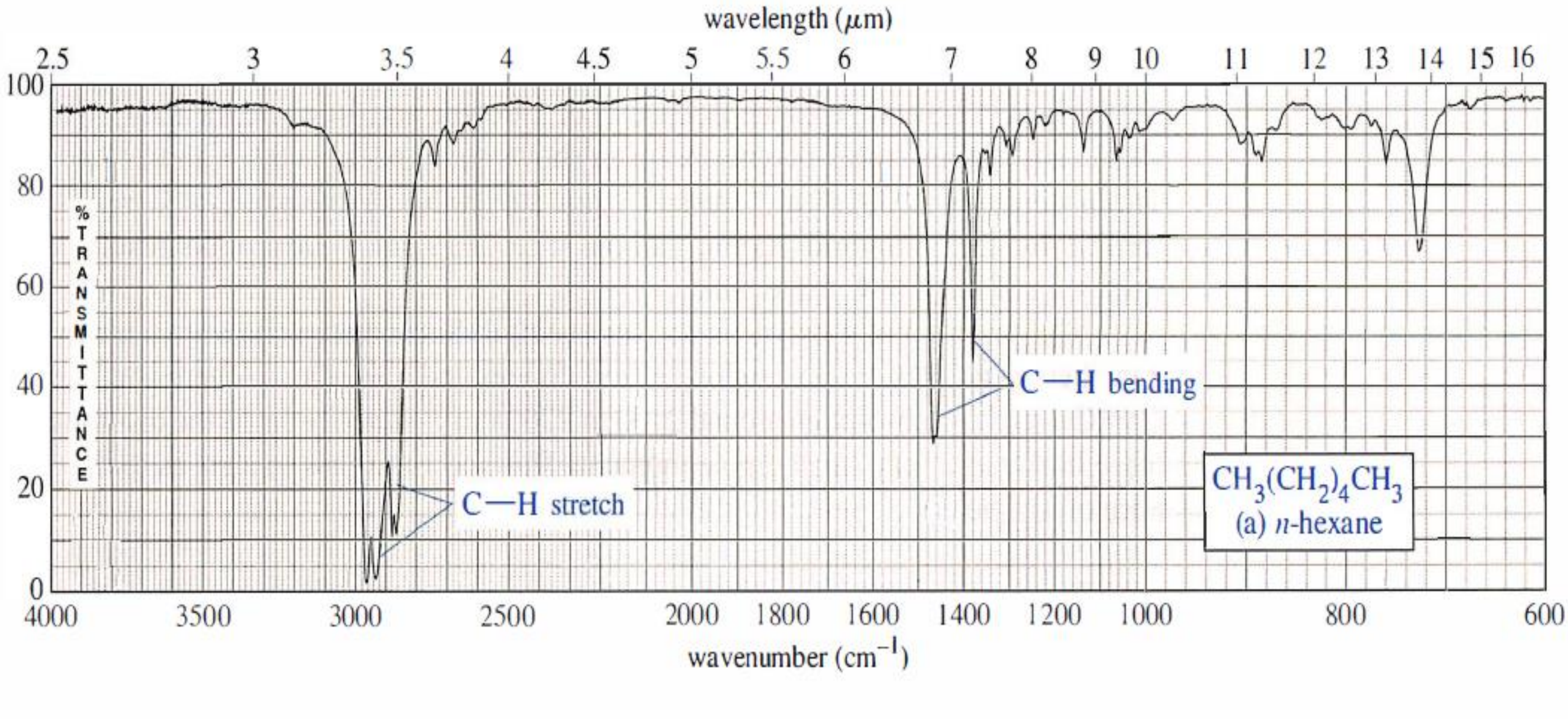
- The **alkane** $CH_3CH_2CH_2CH_2CH_2CH_3$ has only C−C single bonds and sp^3 hybridized C atoms. Therefore, it has only one major absorption above 1500 cm^{-1}, its $C_{sp^3}-H$ absorption at 3000–2850 cm^{-1}.

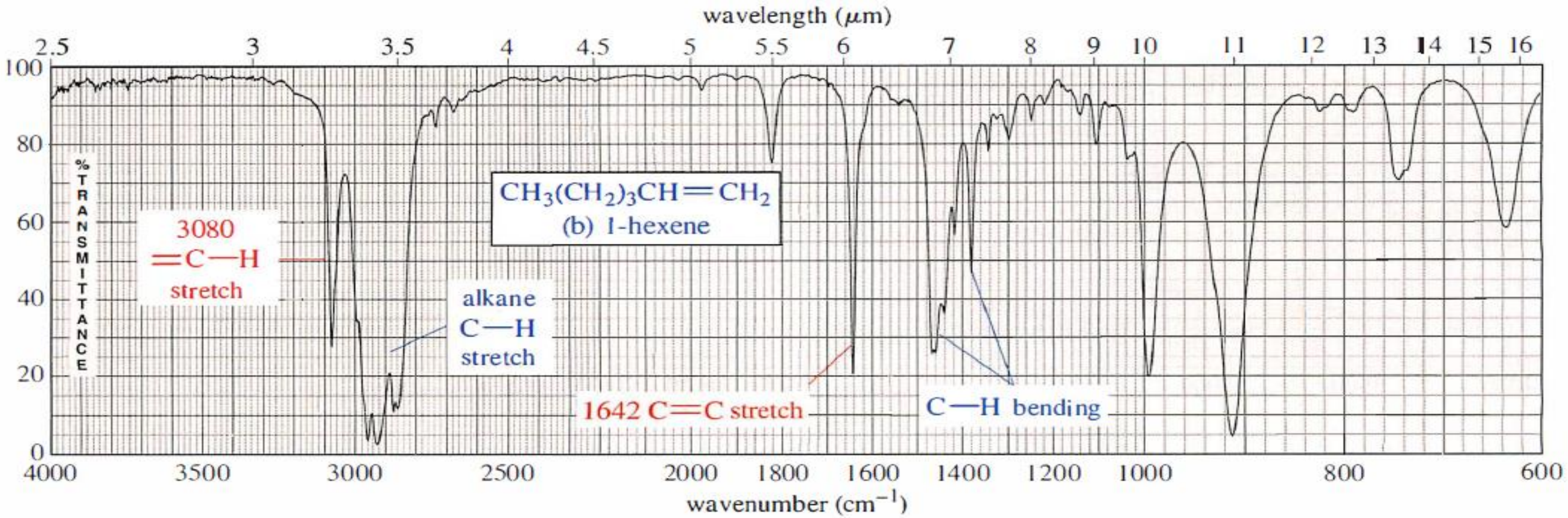

1-Hexene $CH_2=CHCH_2CH_2CH_2CH_3$

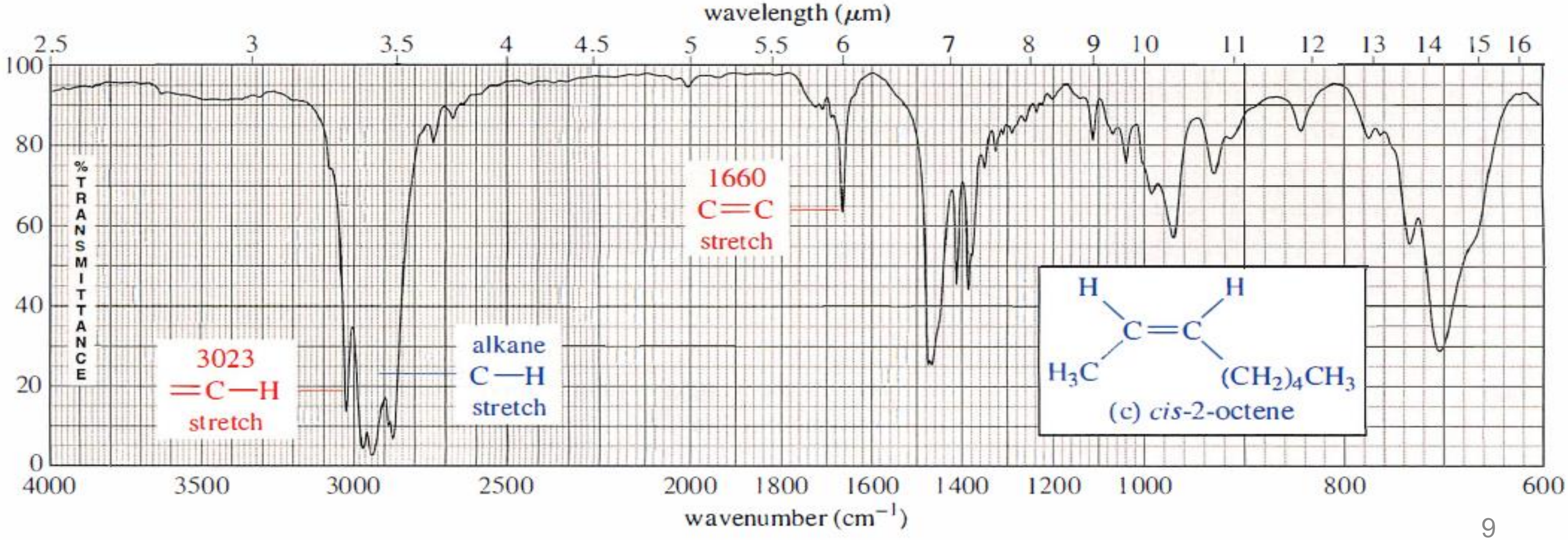
- The **alkene** $CH_2=CHCH_2CH_2CH_2CH_3$ has a C=C and $C_{sp^2}-H$, in addition to its sp^3 hybridized C atoms. Therefore, there are three major absorptions above 1500 cm^{-1}:
  - $C_{sp^2}-H$ at 3150–3000 cm^{-1}
  - $C_{sp^3}-H$ at 3000–2850 cm^{-1}
  - C=C at 1650 cm^{-1}

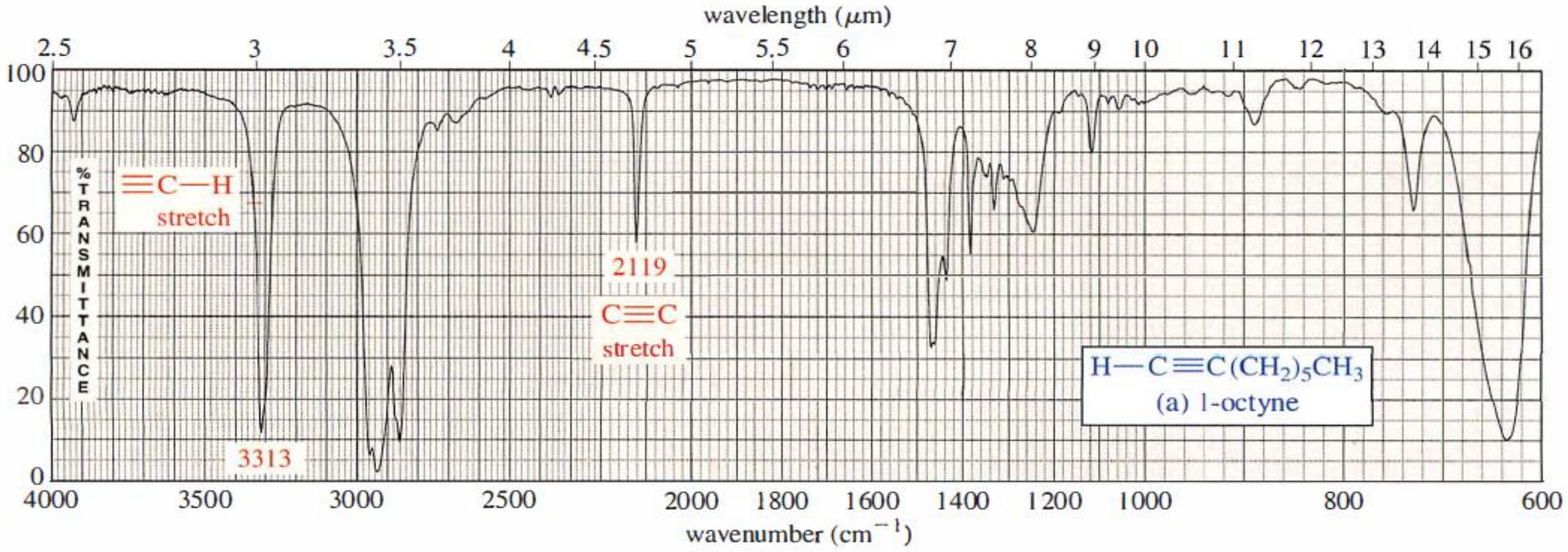

1-Hexyne $HC\equiv CCH_2CH_2CH_2CH_3$

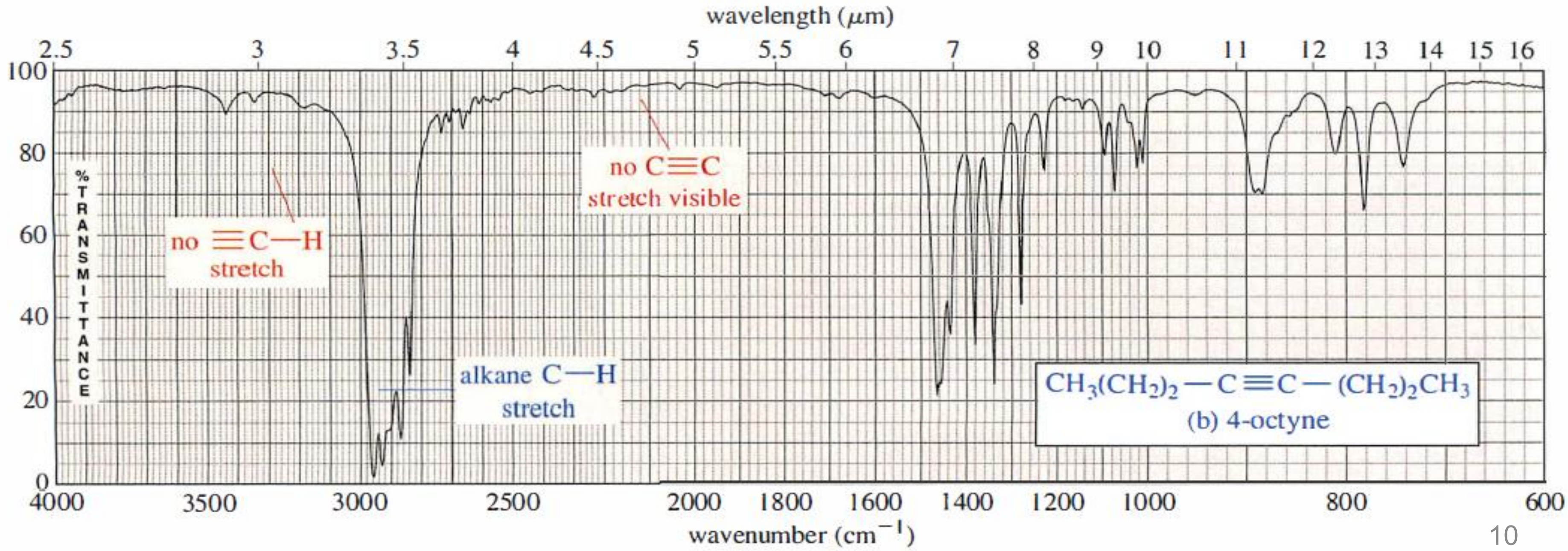
- The **alkyne** $HC\equiv CCH_2CH_2CH_2CH_3$ has a C≡C and $C_{sp}-H$, in addition to its sp^3 hybridized C atoms. Therefore, there are three major absorptions:
  - $C_{sp}-H$ at 3300 cm^{-1}
  - $C_{sp^3}-H$ at 3000–2850 cm^{-1}
  - C≡C at ~2250 cm^{-1}


wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
C—H stretch
C—H bending
$CH_3(CH_2)_4CH_3$
(a) *n*-hexane
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

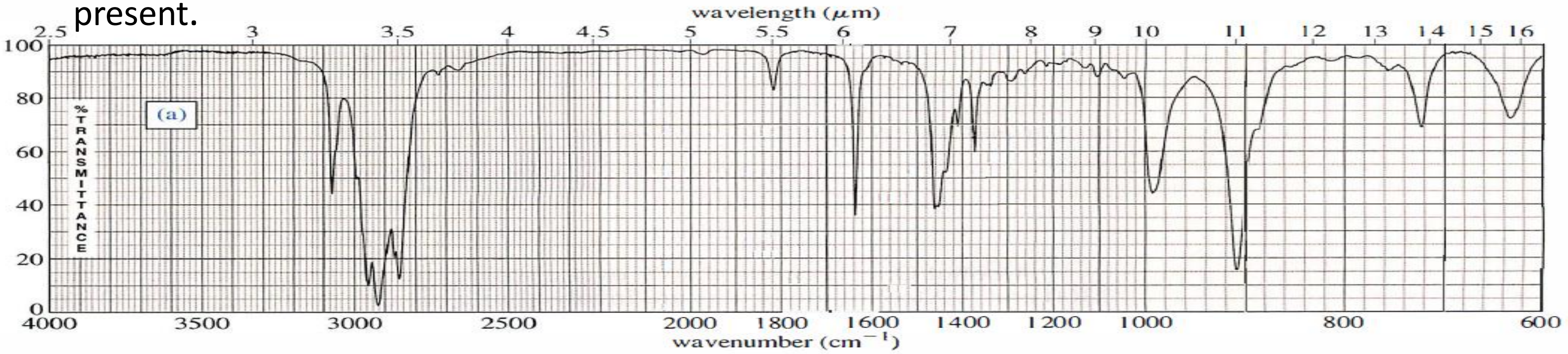

wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
3080
$=C-H$
stretch
alkane
$C-H$
stretch
$CH_3(CH_2)_3CH{=}CH_2$
(b) 1-hexene
1642 $C{=}C$ stretch
$C-H$ bending
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

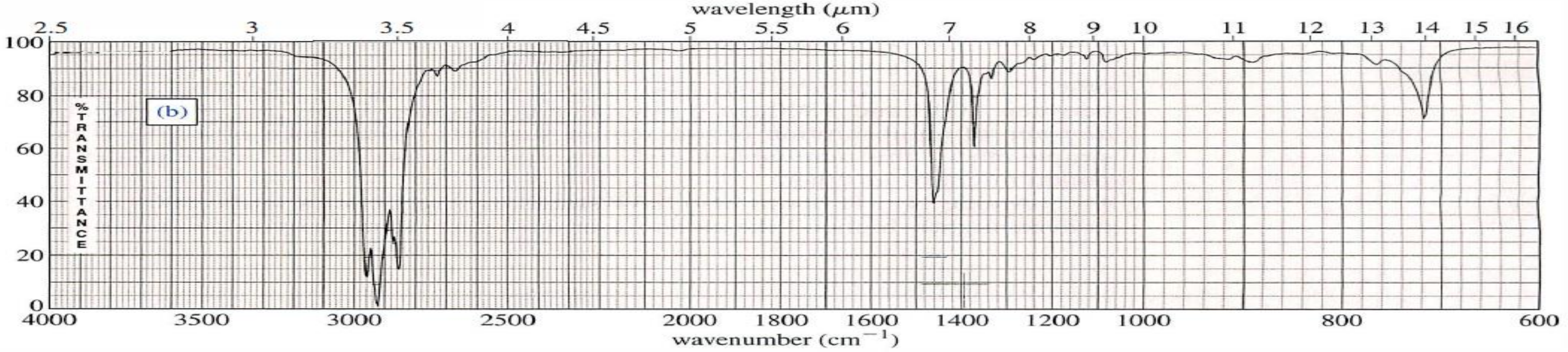

wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
3023
$=C-H$
stretch
alkane
$C-H$
stretch
1660
$C{=}C$
stretch
H
H
C=C
H_3C
$(CH_2)_4CH_3$
(c) *cis*-2-octene
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

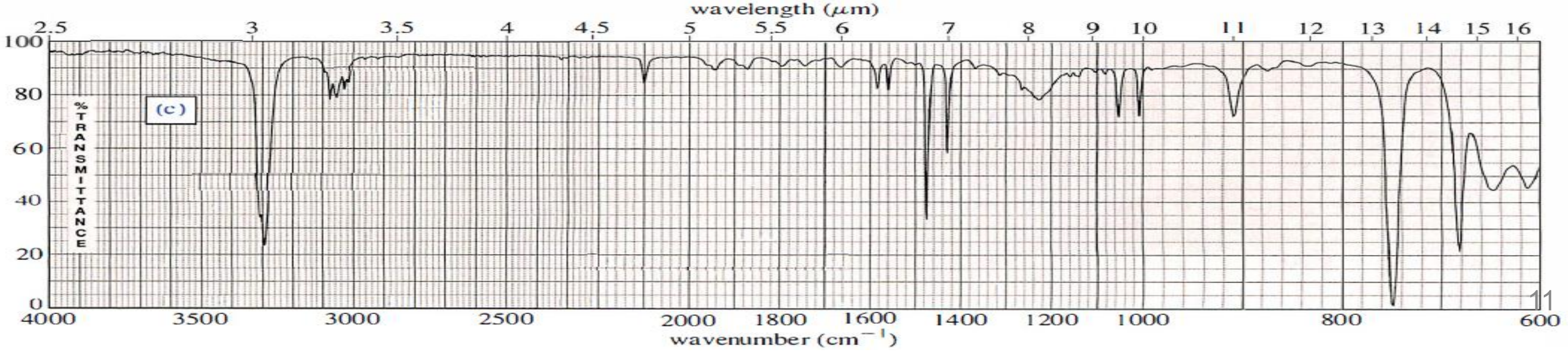

wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
≡C—H
stretch
3313
2119
C≡C
stretch
$H—C≡C(CH_2)_5CH_3$
(a) 1-octyne
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})


wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
no ≡C—H
stretch
no C≡C
stretch visible
alkane C—H
stretch
$CH_3(CH_2)_2—C≡C—(CH_2)_2CH_3$
(b) 4-octyne
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

Problem: For each hydrocarbon spectrum, determine whether the compound is an alkane, an alkene, an alkyne, or an aromatic hydrocarbon. More than one unsaturated group may be present.



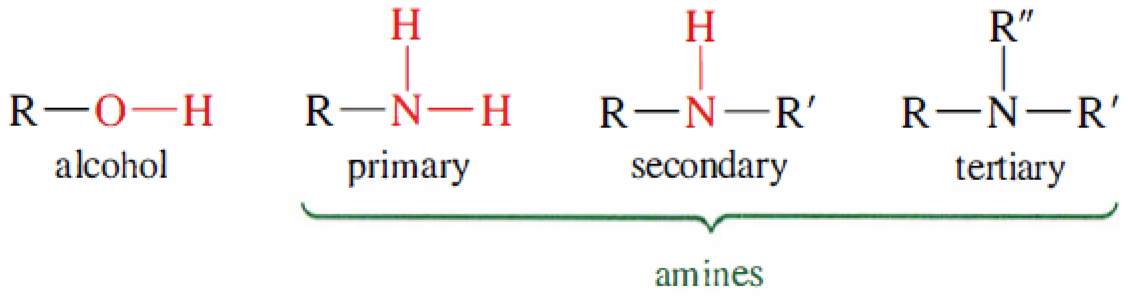




Characteristic Absorptions of Alcohols and Amines:

The 0-H bonds of alcohols and the N-H bonds of amines are strong and stiff.

The vibration frequencies of 0-H and N-H bonds therefore occur at higher frequencies than those of most C-H bonds (except for alkynyl ≡C-H bonds).

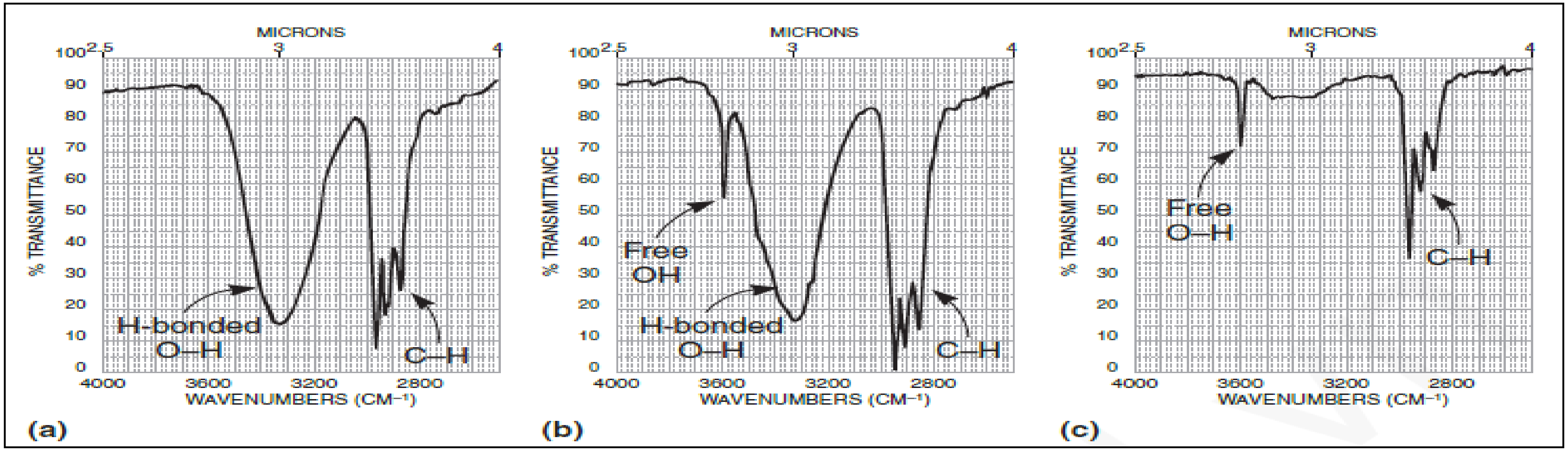


O—H and N—H stretching frequencies

alcohol O—H	3300 cm^{-1}, broad
acid O—H	3000 cm^{-1}, broad
amine N—H	3300 cm^{-1}, broad with spikes

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

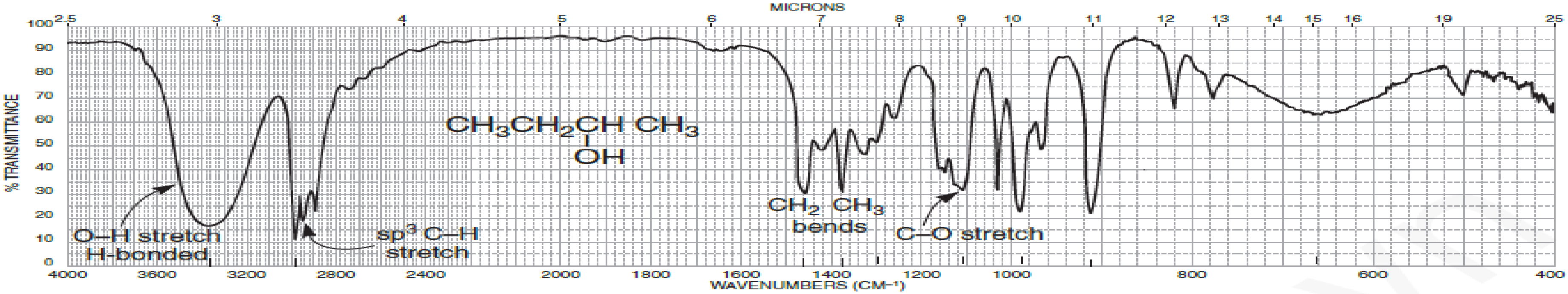
The hydrogen-bonded O-H band is a *broad* peak at 3400–3300 cm^{-1}. This band is usually the only one present in an alcohol that has not been dissolved in a solvent (neat liquid). When the alcohol is dissolved in a solvent, the free O-H and hydrogen-bonded O-H bands are present together, with the relatively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

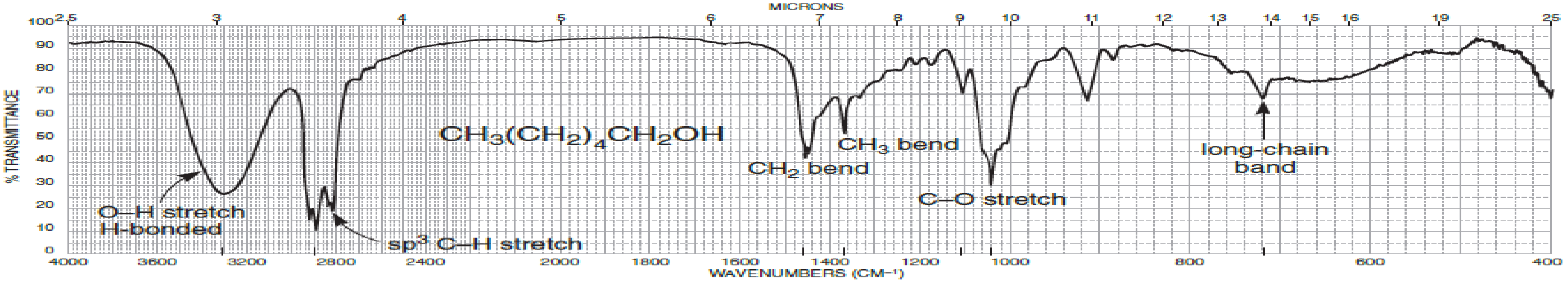


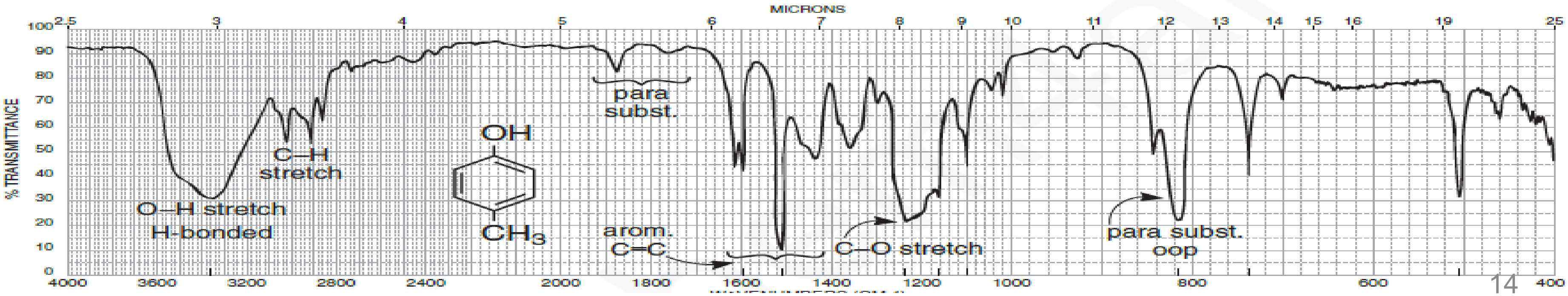
(a) Hydrogen-bonded O-H only (neat liquid).
(b) Free and hydrogen-bonded O-H (dilute solution).
(c) Free and hydrogen-bonded O-H (very dilute solution).

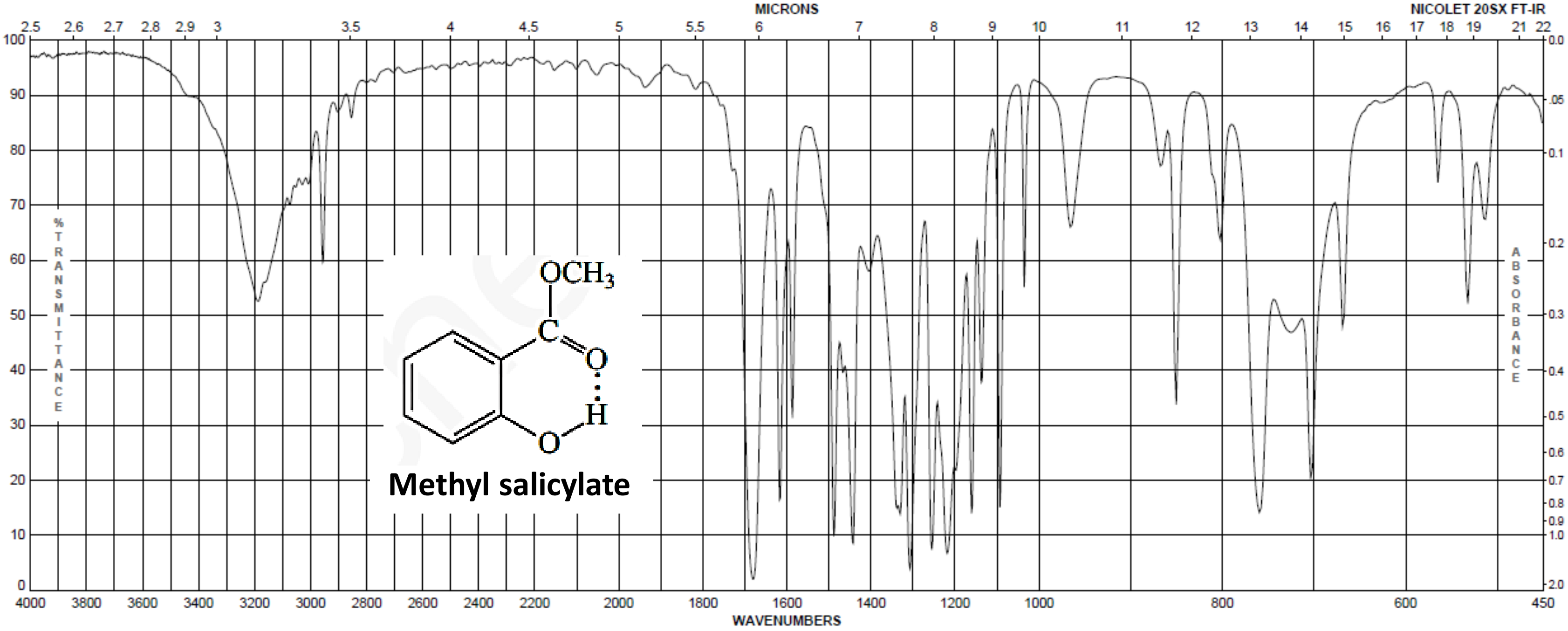
C-O-H Bending appears as a broad and weak peak at 1440–1220 cm^{-1}, **often obscured by the CH_3 bendings**.

C-O Stretching vibration usually occurs in the range 1260–1000 cm^{-1}. This band can be used to assign a primary, secondary, or tertiary structure of an alcohols, or to determine whether a phenolic compound is present.



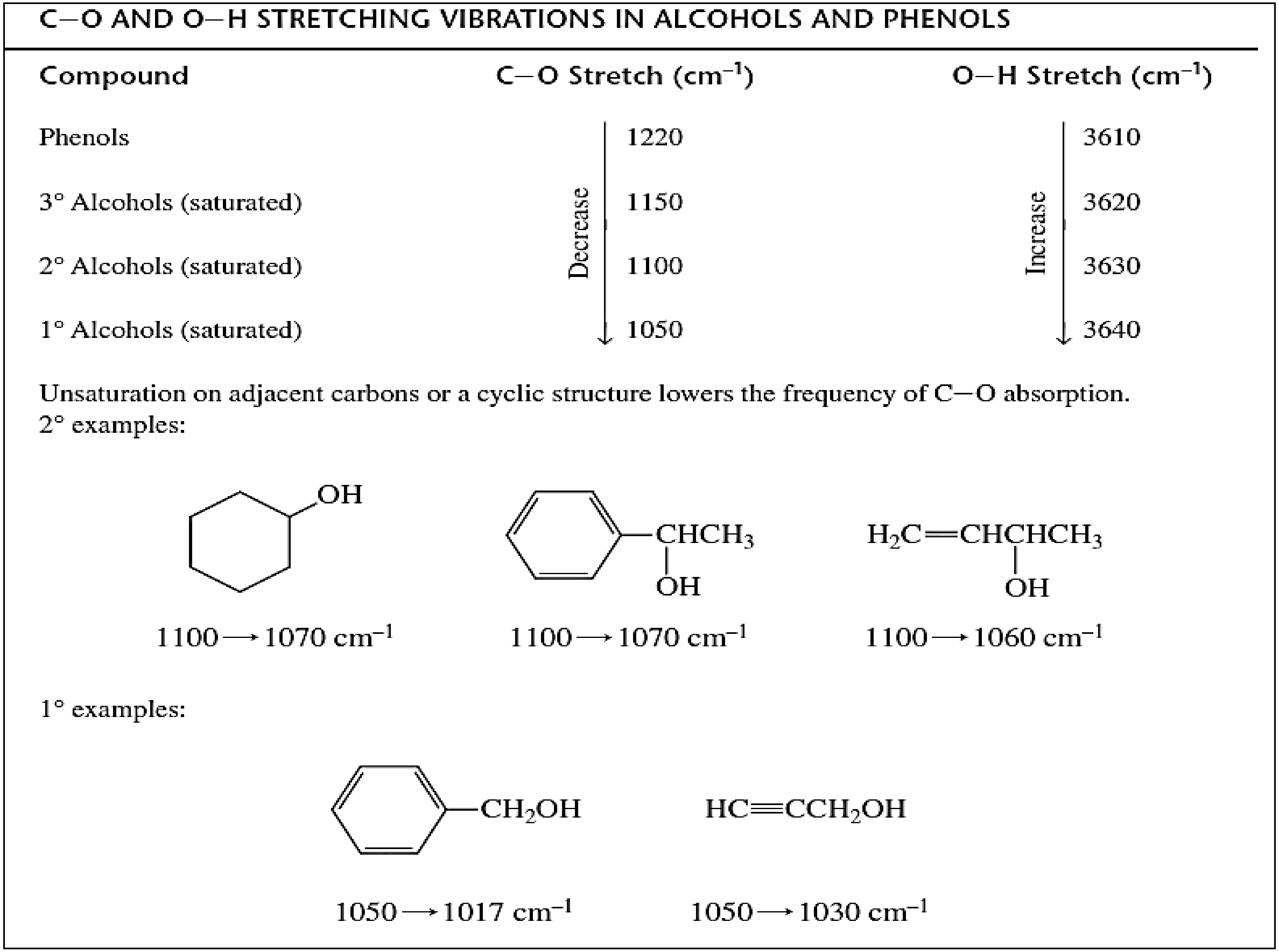






Intramolecular hydrogen bonding, present in *ortho*-carbonyl-substituted phenols, usually shifts the broad O-H band to a lower frequency. For example, the O-H band is centered at about 3200 cm^{-1} in the neat spectrum of methyl salicylate, while O-H bands from normal phenols are centered at about 3500 cm^{-1}.

The intramolecular hydrogen-bonded band does not change its position significantly even at high dilution because the internal bonding is not altered by a change in concentration.



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

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

2° examples:

$1100 \rightarrow 1070\ cm^{-1}$

$C_6H_5CH(OH)CH_3$

$1100 \rightarrow 1070\ cm^{-1}$

$H_2C{=}CHCH(OH)CH_3$

$1100 \rightarrow 1060\ cm^{-1}$

1° examples:

$C_6H_5CH_2OH$

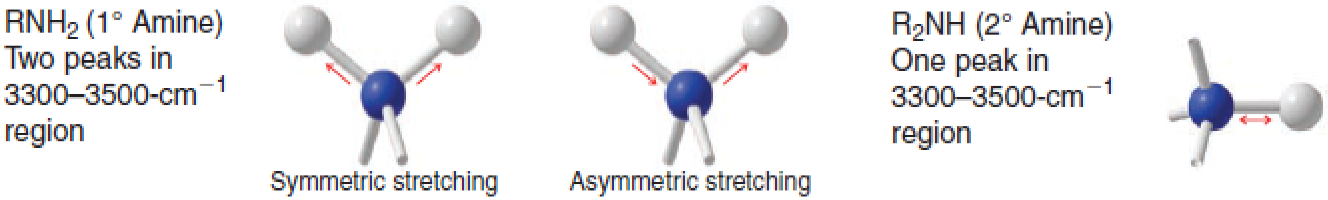
$1050 \rightarrow 1017\ cm^{-1}$

$HC{\equiv}CCH_2OH$

$1050 \rightarrow 1030\ cm^{-1}$

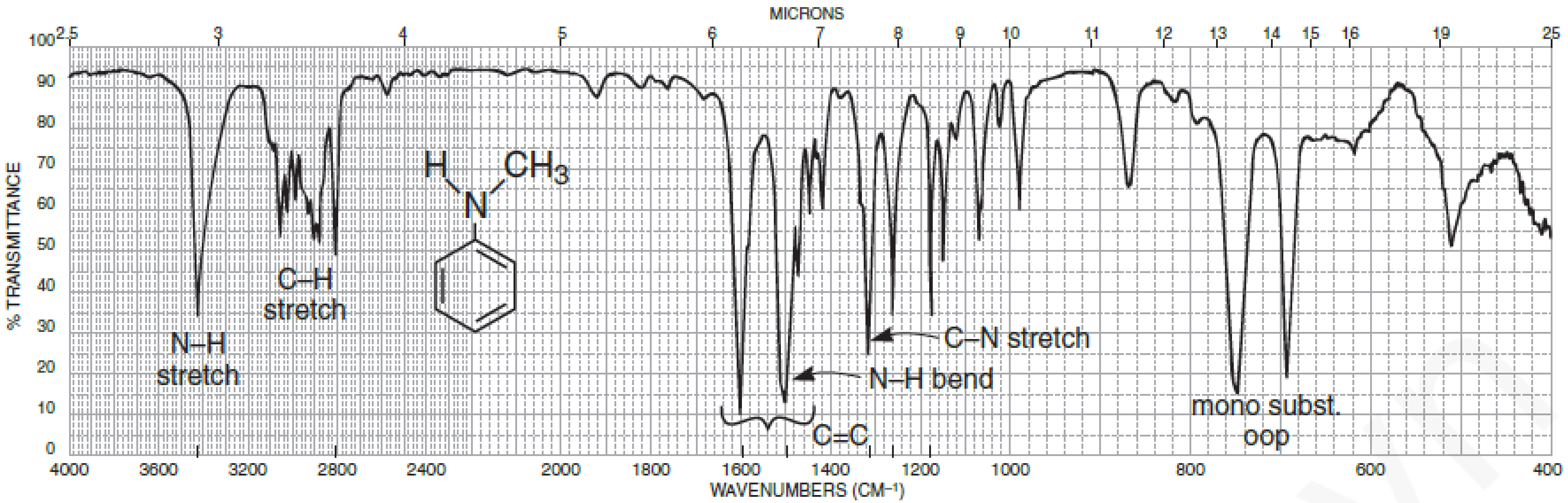
These numbers should be considered *base* values. These C-O absorptions are shifted to lower frequencies when unsaturation is present on adjacent carbon atoms or when the O-H is attached to a ring. Shifts of 30 to 40 cm^{-1} from the base values are common.

- Primary (1°) and secondary (2°) amines give absorptions of moderate strength in the 3300–3500 cm^{-1} region.
- Primary amines exhibit two peaks in this region due to symmetric and asymmetric **stretching** of the two N-H bonds.

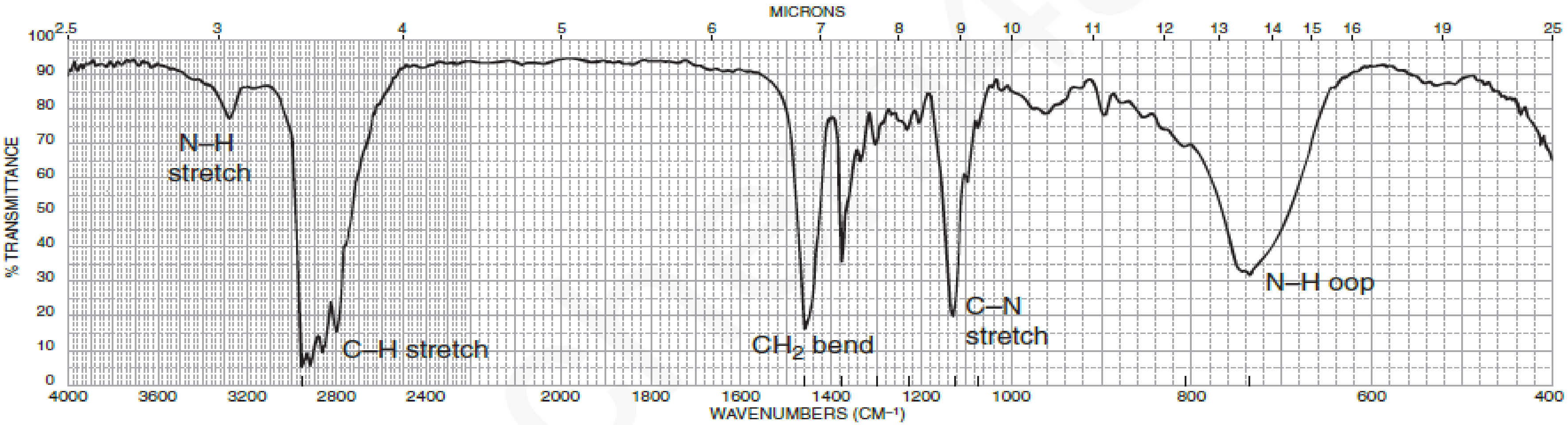


- Secondary amines exhibit a single peak (weak one for aliphatic compounds and a stronger one for aromatic secondary amines).
- Hydrogen bonding causes N-H **stretching** peaks of 1° and 2° amines to **broaden**.
- Tertiary amines show no N-H absorption because they have no such bond.

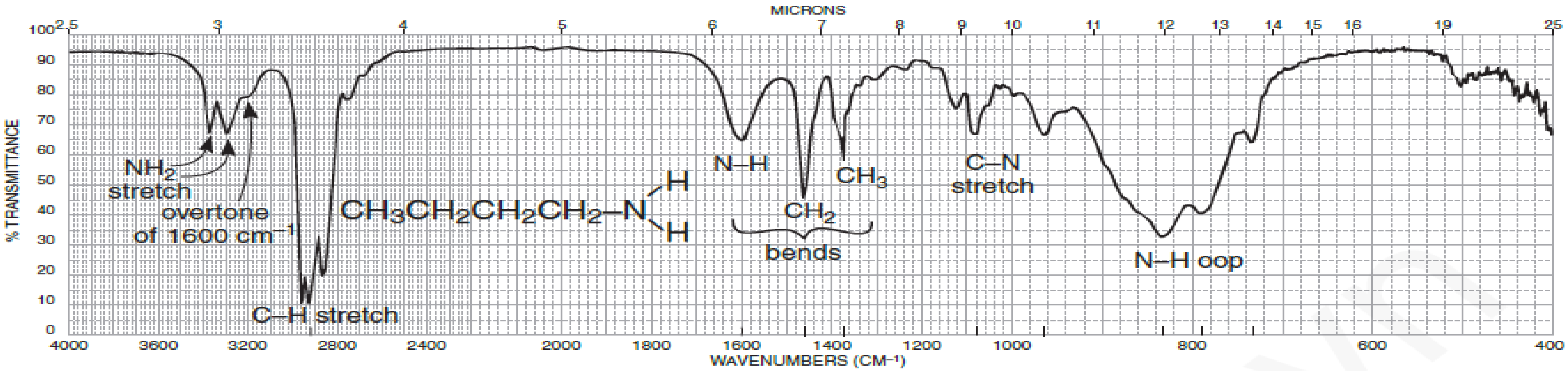
- N-H **Bend** (scissoring) in primary amines results in a broad band in the range 1640–1560 cm−1.
- In aromatic secondary amines, the band shifts to a lower frequency and appears near 1500 cm^{-1}. However, in aliphatic secondary amines the N-H bending vibration is very weak and usually is not observed.
- N-H Out-of-plane **bending** absorption can sometimes be observed near 800 cm^{-1}.
- C-N **Stretch** occurs in the range 1350–1000 cm^{-1}. **Aliphatic** amines absorb from 1250 to 1000 cm^{-1}, whereas **aromatic** amines absorb from 1350 to 1250 cm^{-1}. (*Why?!*)



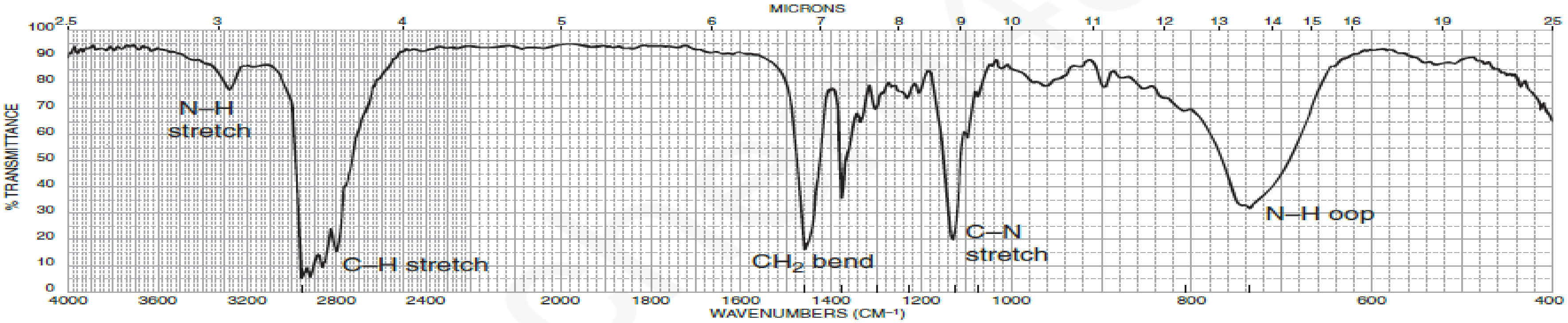
The infrared spectrum of *N*-methylaniline (neat liquid, KBr plates).



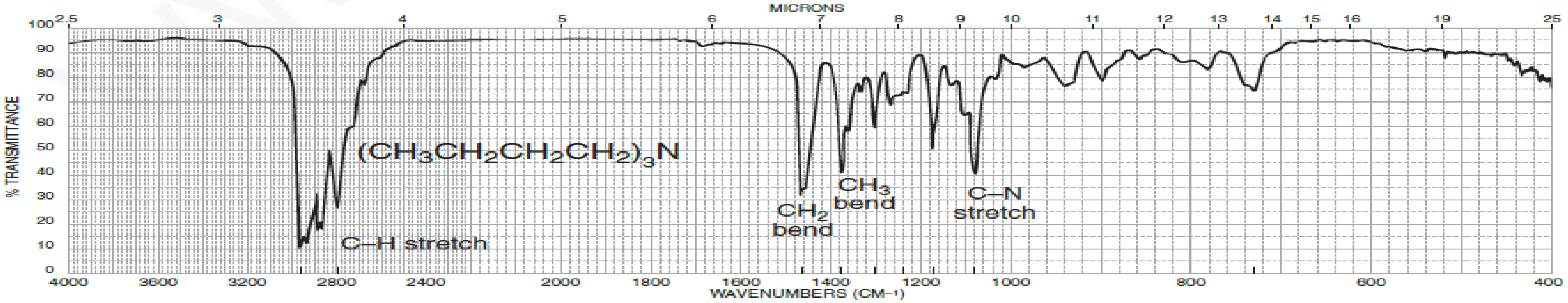
The infrared spectrum of dibutylamine (neat liquid, KBr plates).



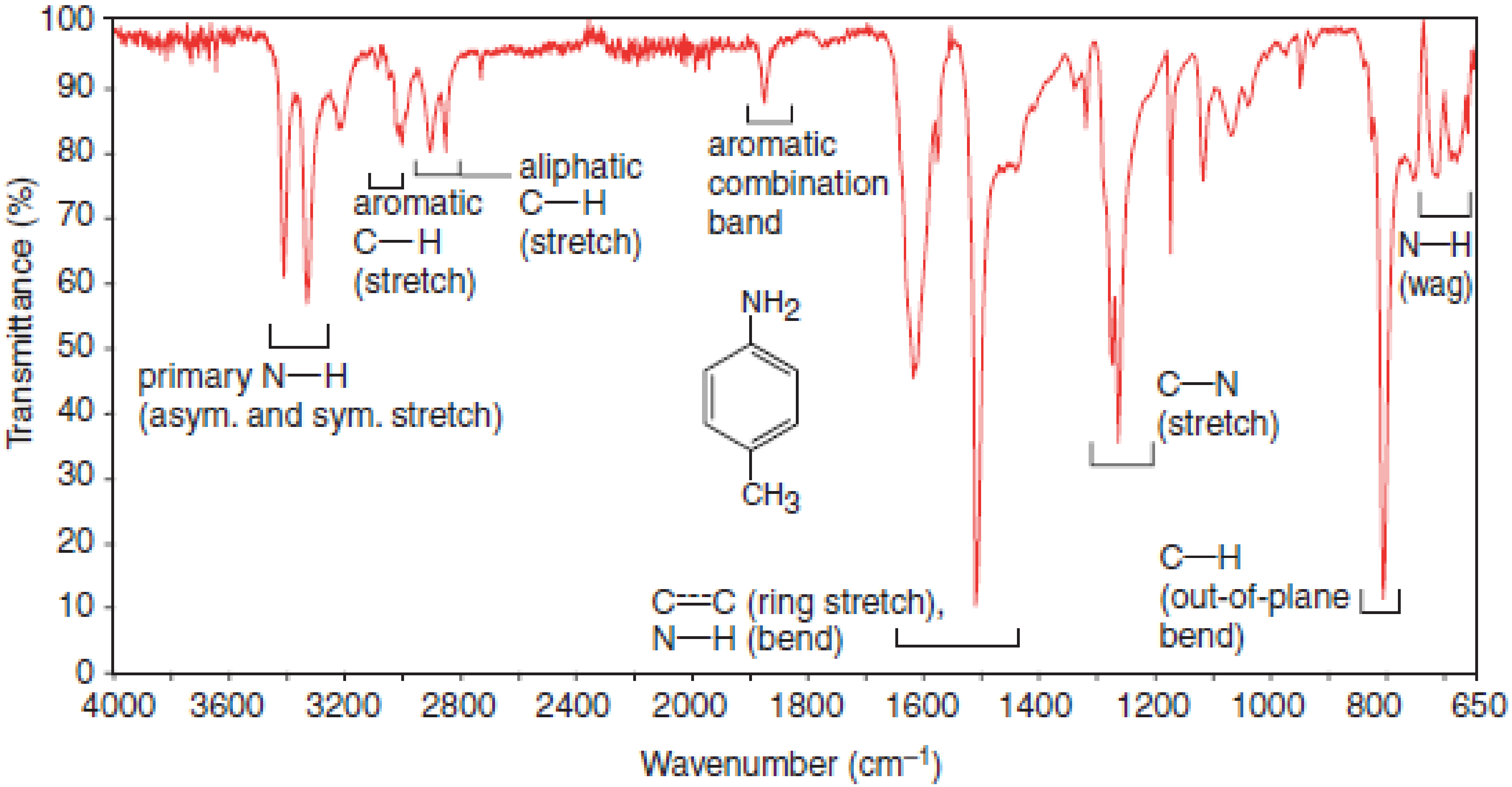
The infrared spectrum of butylamine (neat liquid, KBr plates).



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



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


100
90
80
70
60
50
40
30
20
10
0
Transmittance (%)
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650
Wavenumber (cm^{-1})
primary N—H
(asym. and sym. stretch)
aromatic
C—H
(stretch)
aliphatic
C—H
(stretch)
aromatic
combination
band
NH_2
CH_3
C==C (ring stretch),
N—H (bend)
C—N
(stretch)
C—H
(out-of-plane
bend)
N—H
(wag)

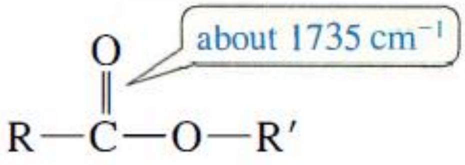
Characteristic Absorptions of Carbonyl Compounds:

Because it has a large dipole moment, the C=O double bond produces intense infrared stretching absorptions.

Carbonyl groups absorb at frequencies around 1700 cm^{-1}, but the exact frequency depends on the specific functional group and the rest of the molecule.

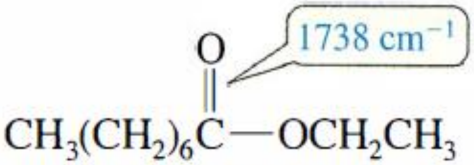
Some carbonyl groups absorb at frequencies higher than 1710 cm^{-1}. For example, simple carboxylic esters absorb around 1735 cm^{-1}.

These higher-frequency absorptions are also seen in strained cyclic ketones (in a five-membered ring or smaller). In a small ring, the angle strain on the carbonyl group forces more electron density into the C=O double bond, resulting in a stronger, stiffer bond.



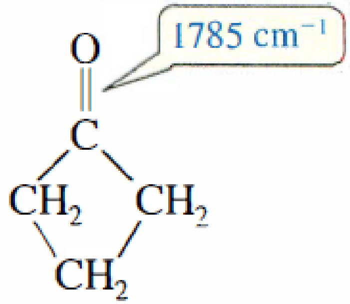
$R-\overset{O}{\overset{\|}{C}}-O-R'$

a carboxylic ester



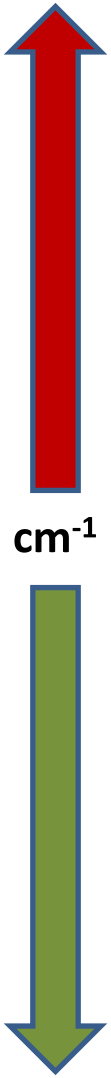
$CH_3(CH_2)_6\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

ethyl octanoate



cyclobutanone

The normal base values for the C=O stretching vibrations for the different carbonyl groups are:

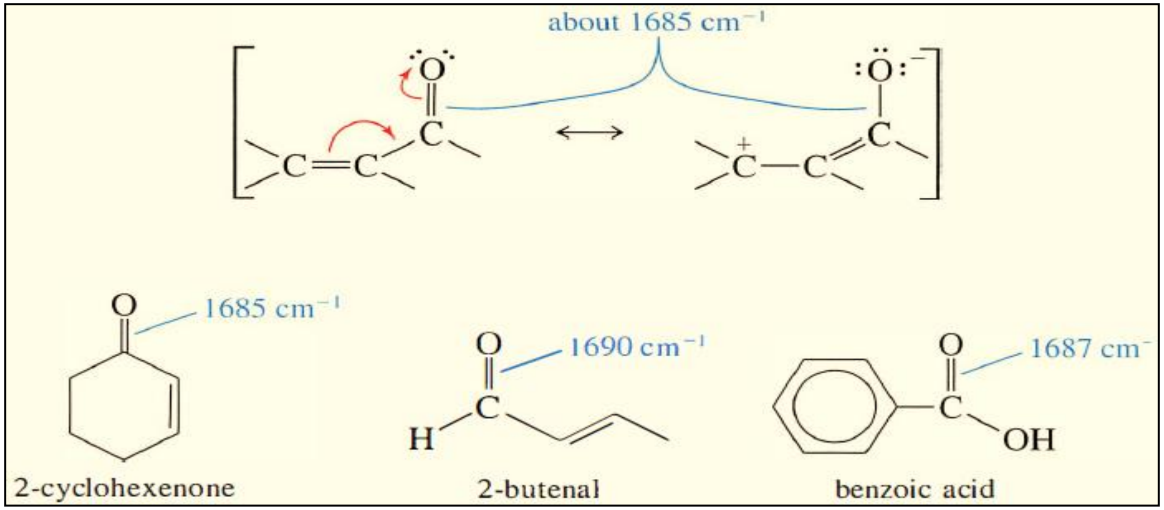


1810	**Anhydride 1**
1800	**Acid chloride**
1760	**Anhydride2**
1735	**Ester**
1725	**Aldehyde**
1715	**Ketone**
1710	**Carboxylic acid**
1690	**Amide**

Factors that influence the C=O stretching vibrations:

1- Resonance lowering of Carbonyl Frequencies:

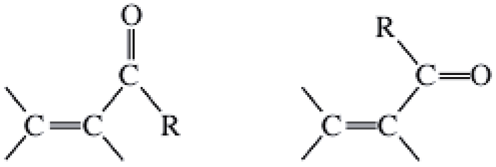
Delocalization of the *pi* electrons reduces the electron density of the carbonyl double bond, weakening it and lowering the stretching frequency from about 1710 cm^{-1} to about 1685 cm^{-1} for conjugated ketones, aldehydes, and acids.



The C=C absorption of a conjugated carbonyl compound may not be apparent in the IR spectrum because it is so much weaker than the C=O absorption.

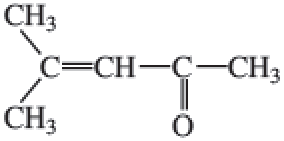
The presence of the C=C double bond is often inferred from its effect on the C=0 frequency and the presence of unsaturated =C-H absorptions above 3000 cm^{-1}.

Often, two closely spaced C=O absorption peaks are observed for these conjugated systems, resulting from two possible conformations, the *s-cis* and *s-trans.*

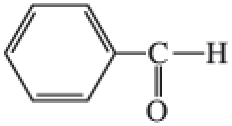


s-cis *s-trans*

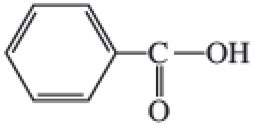
The *s-cis* conformation absorbs at a frequency higher than the *s-trans* conformation. In some cases, the C=O absorption is broadened rather than split into the doublet.



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



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

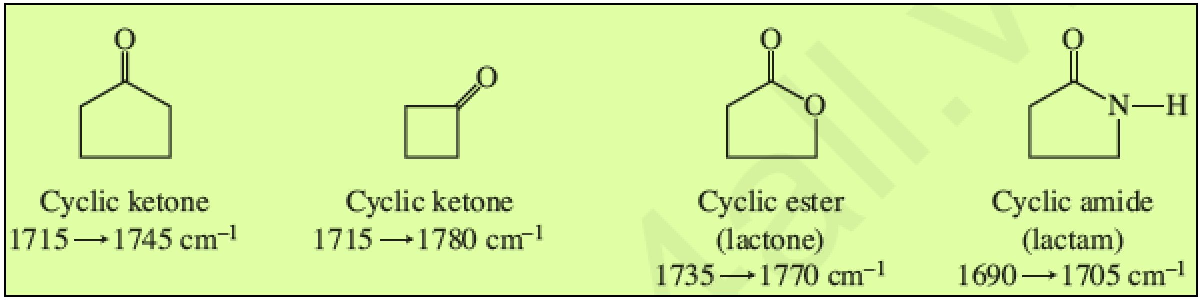


Aryl-substituted acid
1710 → 1680 cm^{-1}

2- Ring-Size Effects:

Six-membered rings with carbonyl groups are unstrained. Decreasing the ring size *increases the frequency* of the C=O absorption.

For ketones and esters, there is often a 30 cm^{-1} increase in frequency for each carbon removed from the unstrained six-membered ring values.



Cyclic ketone
1715 → 1745 cm^{-1}

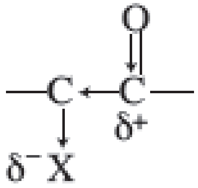
Cyclic ketone
1715 → 1780 cm^{-1}

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

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

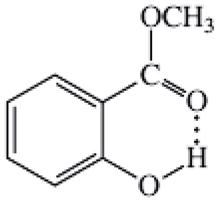
3- α-Substitution Effects:

When the carbon next to the carbonyl is substituted with a chlorine (or other halogen) atom, the carbonyl band shifts to a *higher frequency.*



4- Hydrogen-Bonding Effects:

Hydrogen bonding to a carbonyl group lengthens the C=O bond and lowers the absorption frequency.

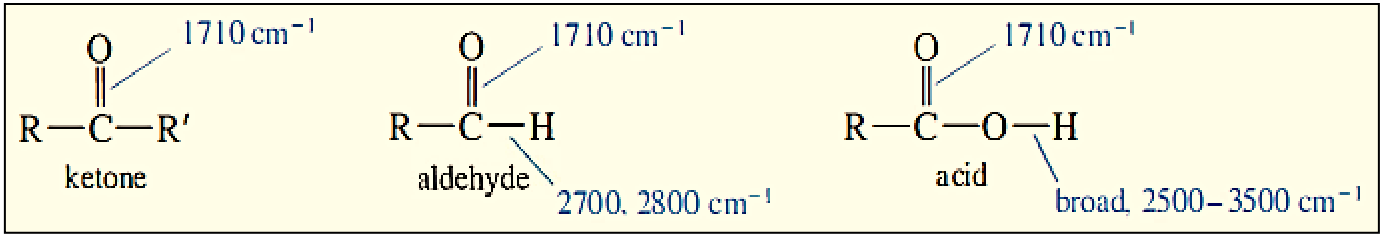


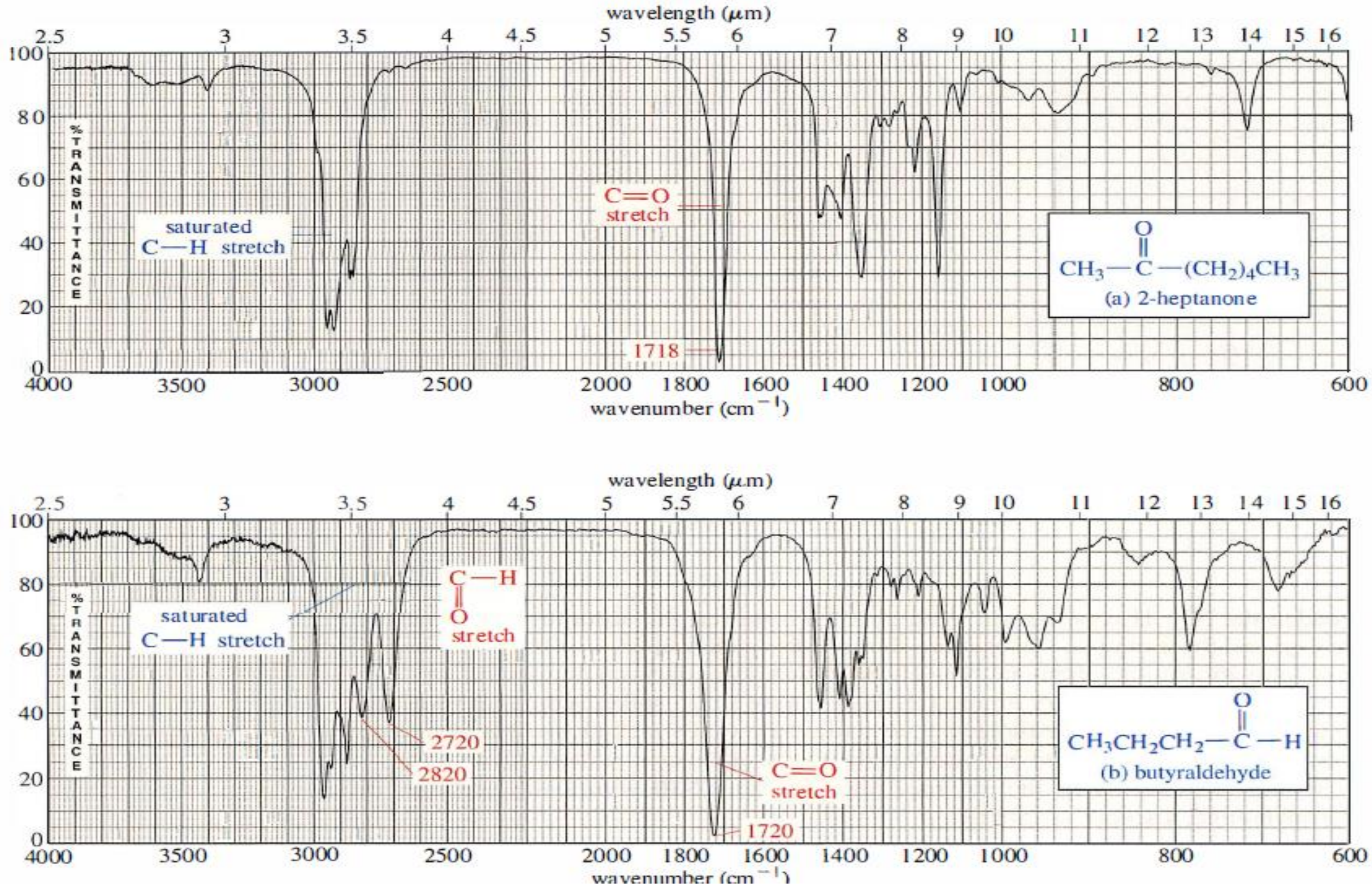
Methyl salicylate
1680 cm⁻¹

Simple Ketones, Aldehydes, and Acids:

The C=O stretching vibrations of simple ketones, aldehydes, and carboxylic acids occur at frequencies around 1710 cm^{-1}.

These frequencies are higher than those for C=C double bonds because the C=0 double bond is stronger and stiffer.



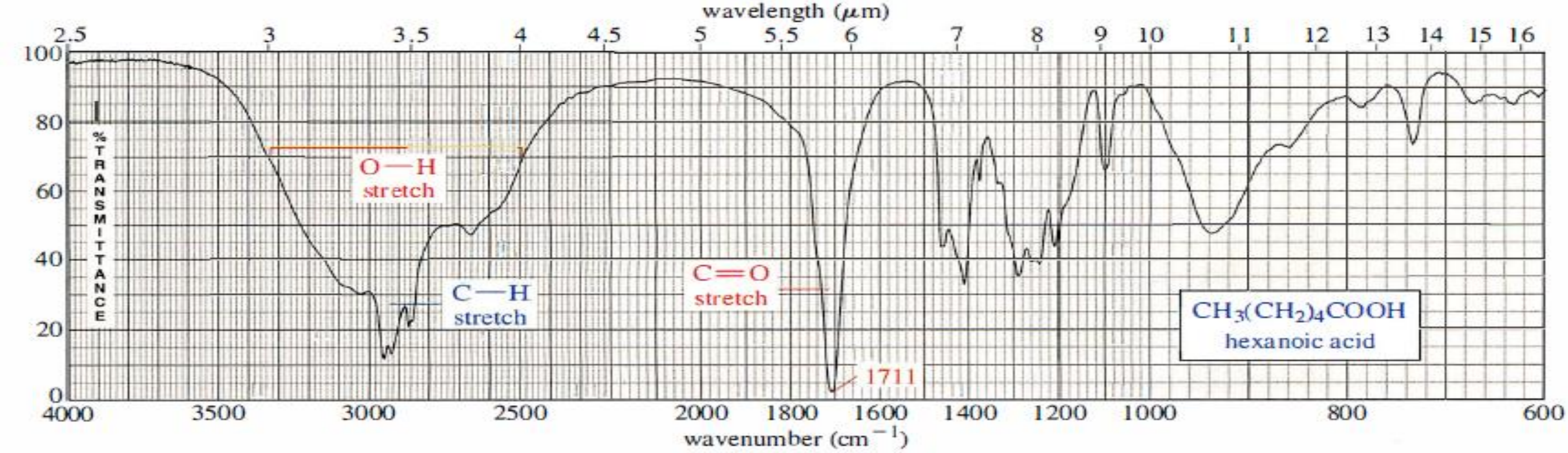


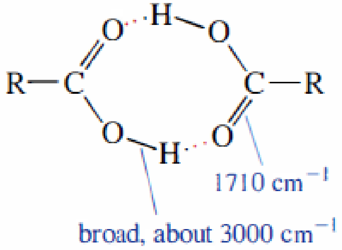
Infrared spectra of (a) 2-heptanone and (b) butyraldehyde. Both the ketone and the aldehyde show intense carbonyl absorptions near 1710 cm^{-1}. In the aldehyde spectrum, there are two peaks (2720 and 2820 cm^{-1}) characteristic of the **aldehyde C-H stretch**.

A carboxylic acid produces a characteristic broad 0-H absorption in addition to the intense carbonyl stretching absorption.

Because of the unusually strong hydrogen bonding in carboxylic acids, the broad 0-H stretching frequency is shifted to about 3000 cm^{-1}, centered on top of the usual C-H absorption. This broad 0-H absorption gives a characteristic overinflated shape to the peaks in the C-H stretching region.

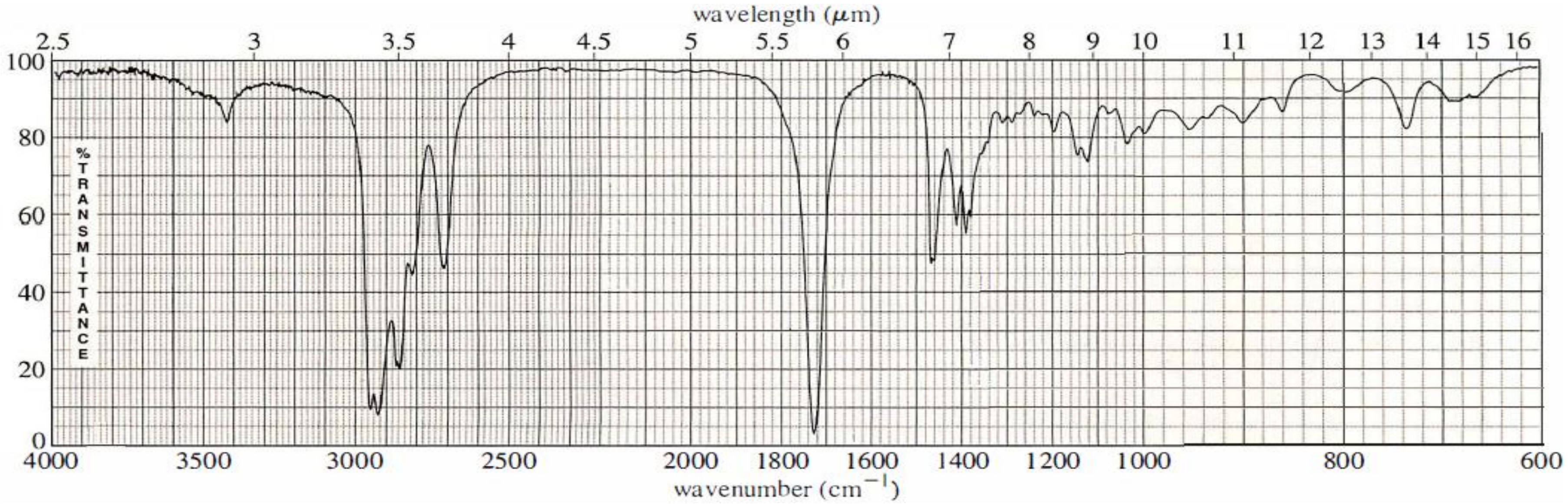
Participation of the acid carbonyl group in hydrogen bonding frequently results in broadening of the strong carbonyl absorption as well.





Problem:

Determine the functional group(s) in the compound whose IR spectrum appears here.



A weak peak around 3400 cm^{-1}, a strong peak about 1720 cm^{-1}, and an unusual C-H stretching region.

The C-H region has two additional peaks around 2720 and 2820 cm^{-1}.

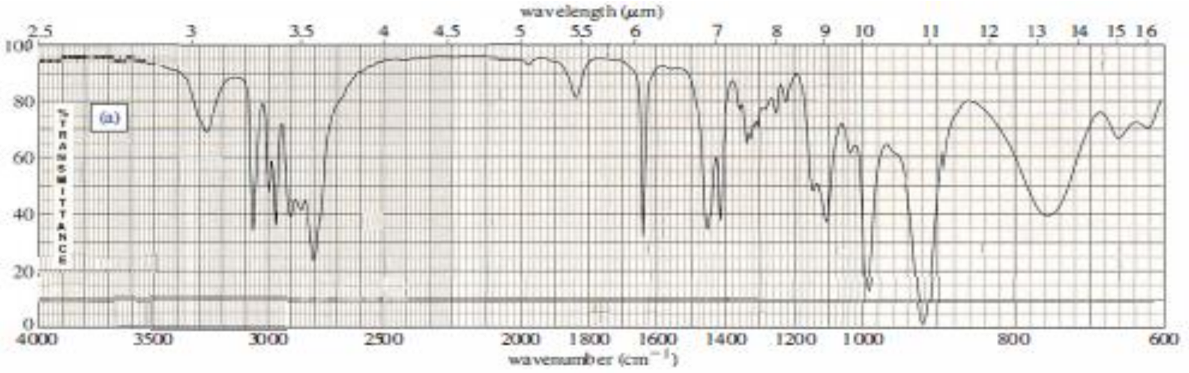
The strong peak at 1725 cm^{-1} must be a C=0, and the peaks at 2720 and 2820 cm^{-1} suggest an aldehyde.

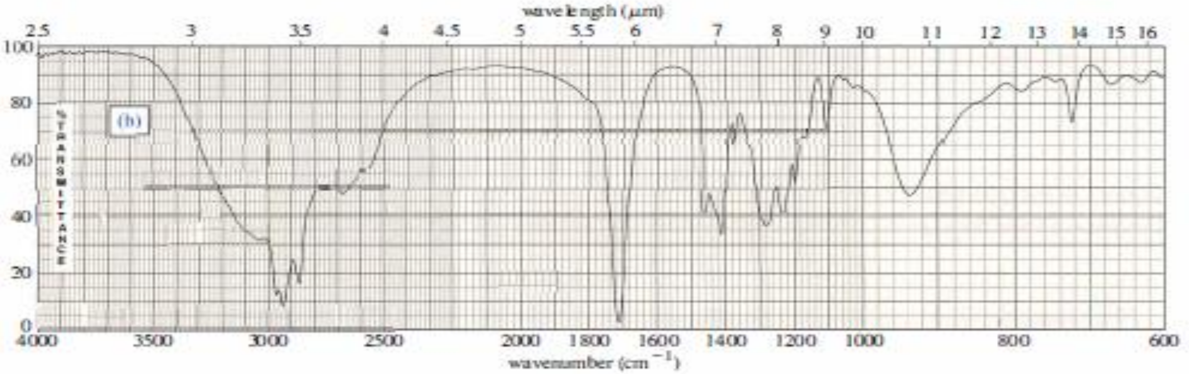
The weak peak around 3400 cm^{-1} might be mistaken for an alcohol 0-H.

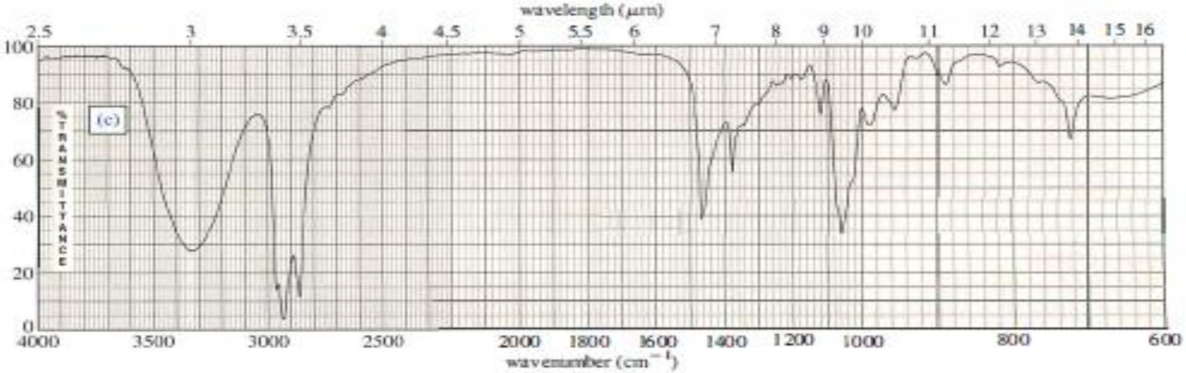
Problem:

Spectra are given for three compounds. Each compound has one or more of the following functional groups: alcohol, amine, ketone, aldehyde, and carboxylic acid.

Determine the functional group(s) in each compound.



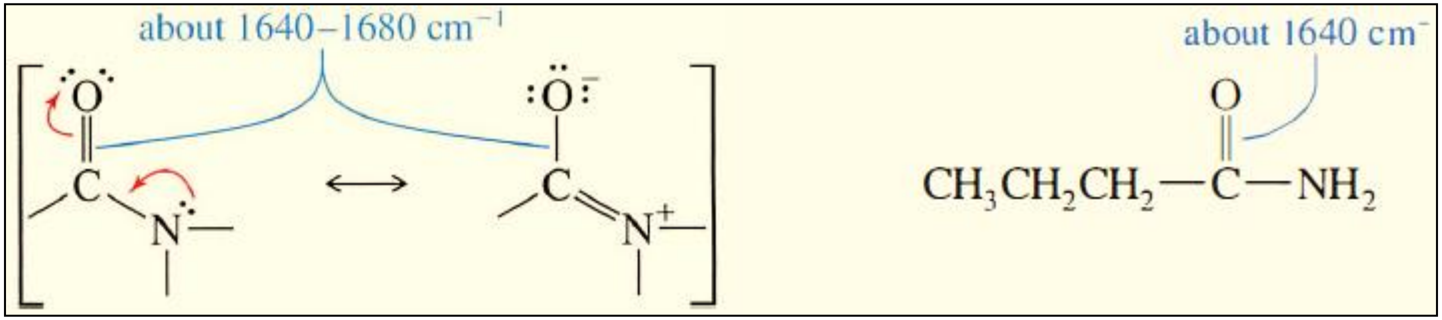




Amides:

The carbonyl groups of amides absorb at particularly low IR frequencies: about 1640 to 1680 cm^{-1}.

The dipolar resonance structure places part of the *pi* bond between carbon and nitrogen, leaving less than a full C=0 double bond.



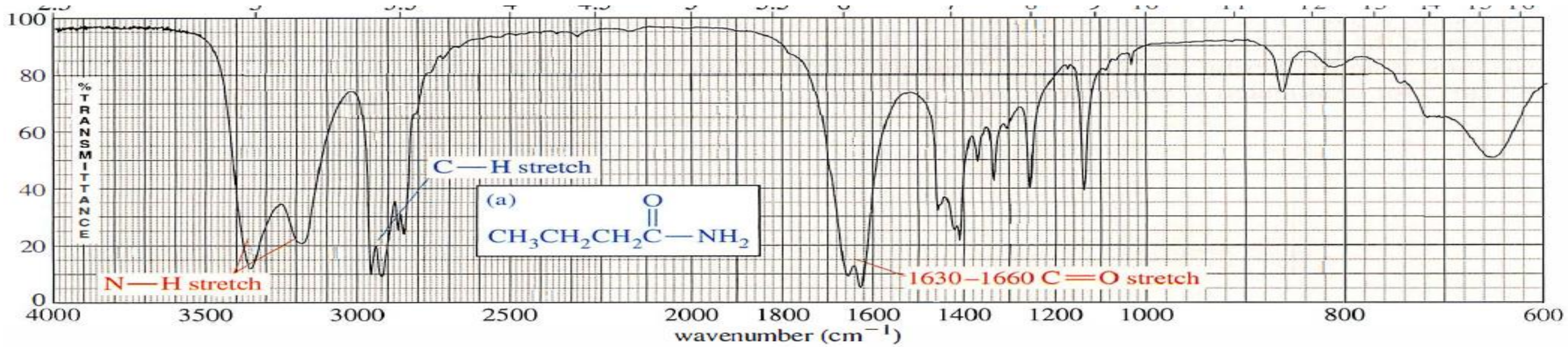
Like primary amines, most primary amides show two spikes in the N–H stretching region (about 3300 cm^{-1})

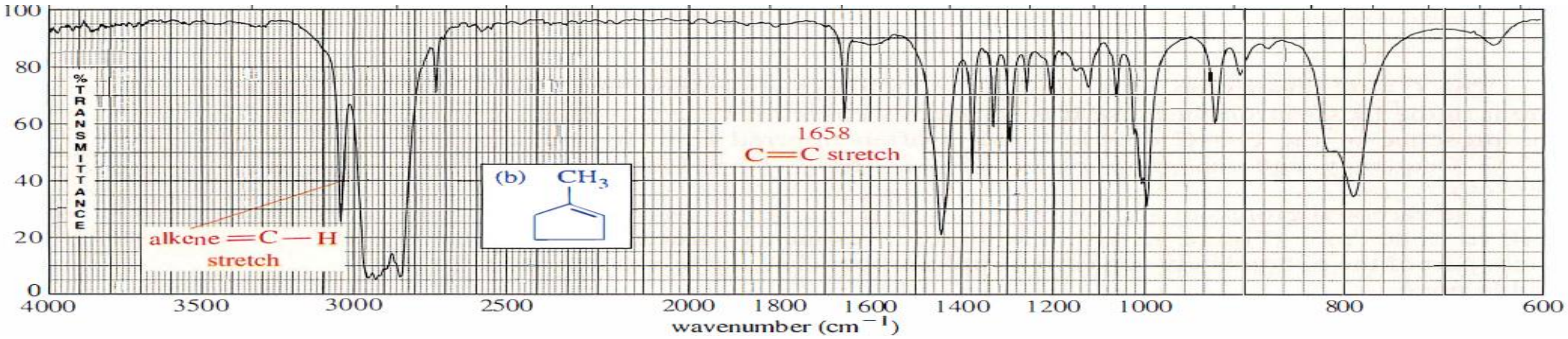
Secondary amides (like secondary amines) generally show one N–H spike.

The very low frequency of the amide carbonyl might be mistaken for an alkene C=C stretch.

So, how can we distinguish between C=O and C=C absorptions, even when they appear in the same region of the spectrum?!

In the spectra of butyramide (C=O about 1640 cm^{-1}) and 1-methylcyclopentene (C=C at 1658 cm^{-1}) we can see three differences:





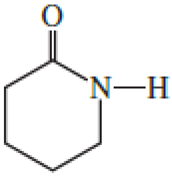
1. The amide carbonyl absorption is much stronger than the absorption of the alkene double bond.
2. There are prominent N-H stretching absorptions in the amide spectrum.
3. There is an unsaturated C-H stretching (just to the left of 3000 cm^{-1}) in the alkene spectrum.

- Conjugation does not reduce the C=O frequency in amides. The introduction of α,β, unsaturation causes an *increase in frequency* from the base value given.

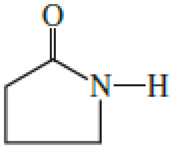
- Apparently, the introduction of *sp*2-hybridized carbon atoms removes electron density from the carbonyl group and strengthens the bond instead of interacting by resonance as in other carbonyl examples.

- Since the parent amide group is already highly stabilized, the introduction of the C=C unsaturation does not overcome this resonance.

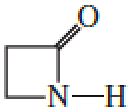
- Cyclic amides (lactams) give the expected increase in C=O frequency for decreasing ring size.



~1660 cm^{-1}

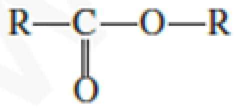
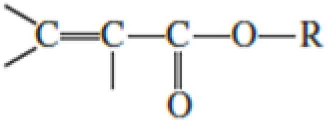
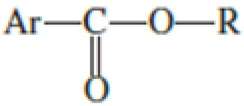
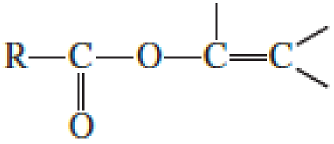
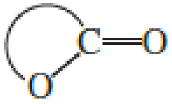


~1705 cm^{-1}

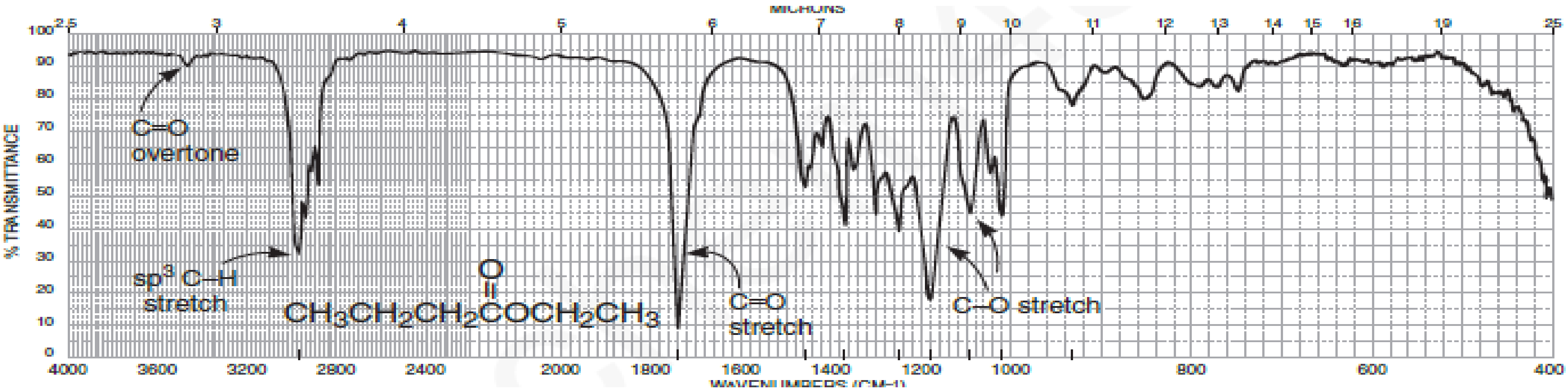


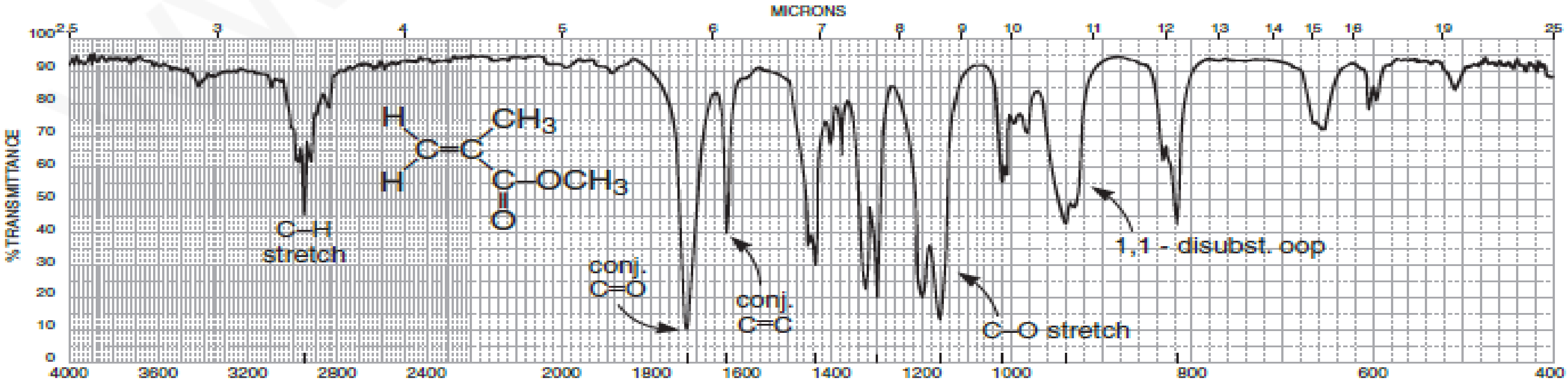
~1745 cm^{-1}

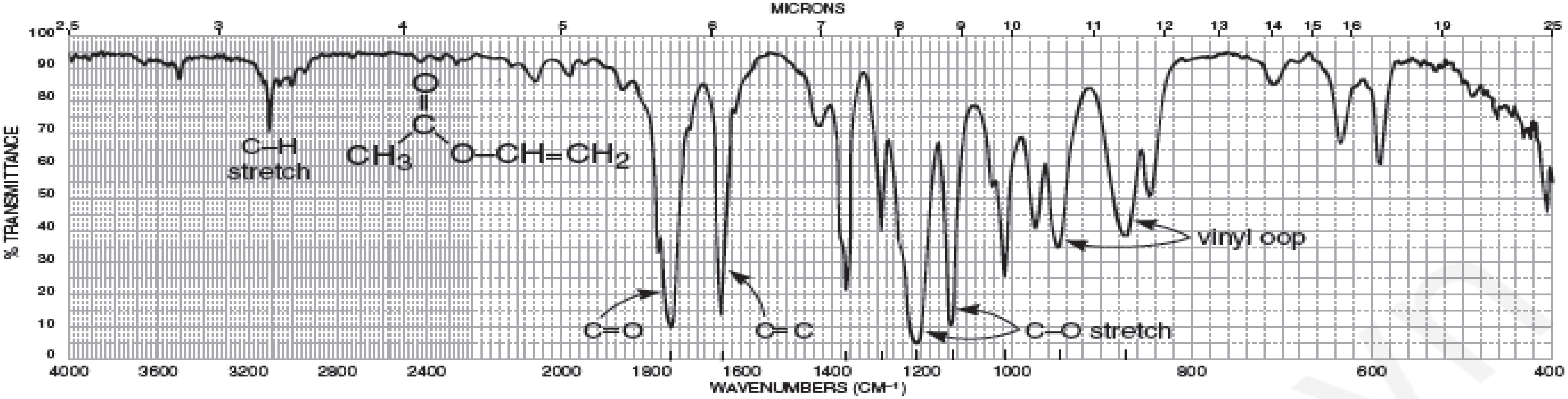
Esters:

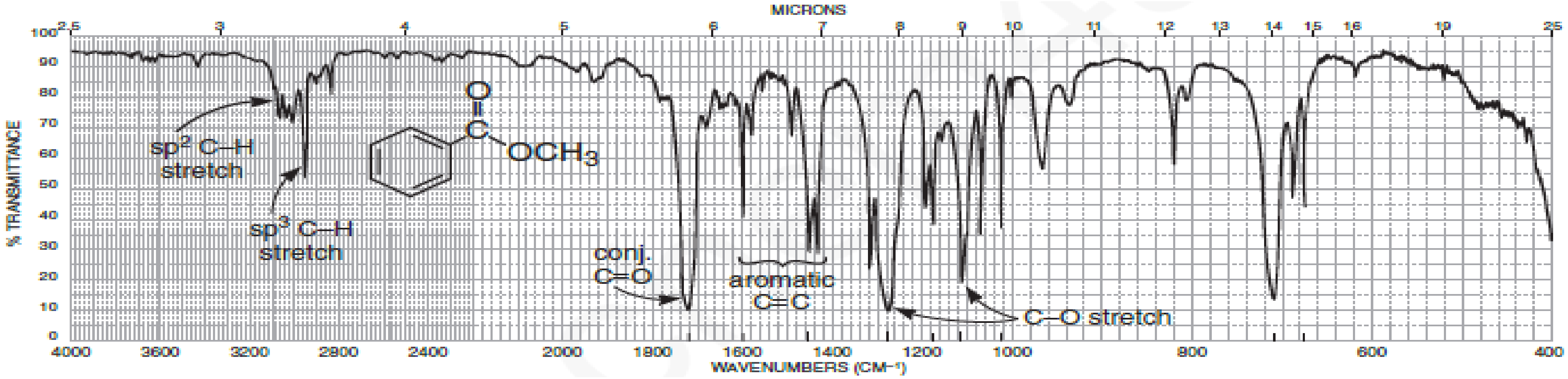
 $\mathrm{R{-}\underset{\underset{O}{\Vert}}{C}{-}O{-}R}$	C=O stretch appears in the range 1750–1735 cm^{-1} for normal aliphatic esters.
	Conjugation of C=O with α,β C=C; 1740–1715 cm^{-1} for C=O and 1640–1625 cm^{-1} for C=C (two bands for some C=C, *cis* and *trans*).
 $\mathrm{Ar{-}\underset{\underset{O}{\Vert}}{C}{-}O{-}R}$	Conjugation of C=O with phenyl; 1740–1715 cm^{-1} for C=O and 1600–1450 cm^{-1} for ring.
	Conjugation of a single-bonded oxygen atom with C=C or phenyl; 1765–1762 cm^{-1} for C=O.
	Cyclic esters (lactones); C=O frequency increases with decreasing ring size.
C—O	Stretch in two or more bands, one stronger and broader than the other, occurs in the range 1300–1000 cm^{-1}.

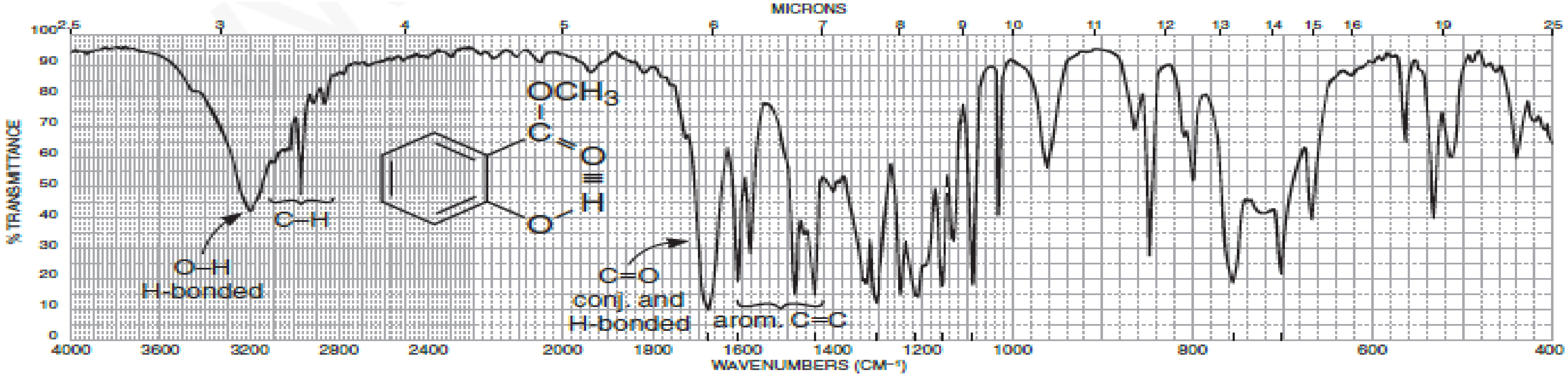
Examples:


MICRONS
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
19
25
% TRANSMITTANCE
100
90
80
70
60
50
40
30
20
10
0
C=O
overtone
sp^3 C–H
stretch
O
CH$_3$CH$_2$CH$_2$COCH$_2$CH$_3$
C=O
stretch
C–O stretch
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS (CM-1)

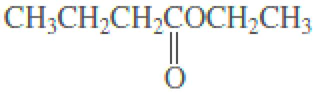

MICRONS
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
19
25
% TRANSMITTANCE
100
90
80
70
60
50
40
30
20
10
0
H
H
CH$_3$
C=C
C–OCH$_3$
O
C–H
stretch
conj.
C=O
conj.
C=C
C–O stretch
1,1 - disubst. oop
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400


MICRONS
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
19
25
% TRANSMITTANCE
100
90
80
70
60
50
40
30
20
10
0
C–H
stretch
O
C
CH$_3$
O–CH=CH$_2$
C=O
C=C
C–O stretch
vinyl oop
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS (CM^{-1})


MICRONS
WAVENUMBERS (CM⁻¹)
% TRANSMITTANCE
sp² C–H stretch
sp³ C–H stretch
O
C
OCH3
conj. C=O
aromatic C=C
C–O stretch

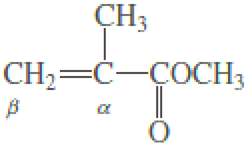

MICRONS
WAVENUMBERS (CM⁻¹)
% TRANSMITTANCE
OCH3
C
O
H
O
O–H H-bonded
C–H
C=O conj. and H-bonded
arom. C=C

Conjugation with a Carbonyl Group (α,β Unsaturation or Aryl Substitution):
The C=O stretching vibrations are shifted by about 15 to 25 cm^{-1} to lower frequencies with α,β unsaturation or aryl substitution.



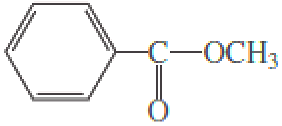
$CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}OCH_2CH_3$

Ethyl butyrate
1738 cm^{-1}



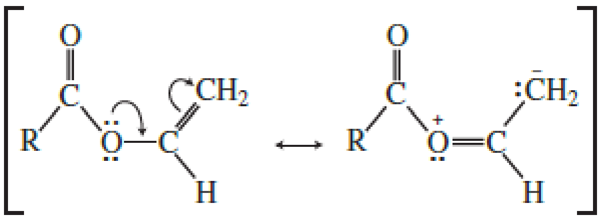
$\underset{\beta}{CH_2}{=}\underset{\alpha}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}OCH_3$

Methyl methacrylate
1725 cm^{-1}

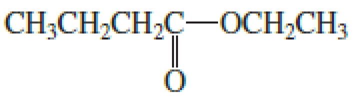


Methyl benzoate
1724 cm^{-1}

Conjugation with the Ester Single-Bonded Oxygen:
Conjugation involving the single-bonded oxygen shifts the C=O vibrations to higher frequencies.

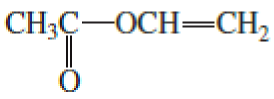


Examples:



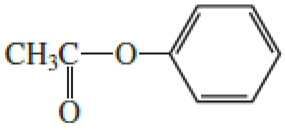
$CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}{-}OCH_2CH_3$

Ethyl butyrate
1738 cm^{-1}

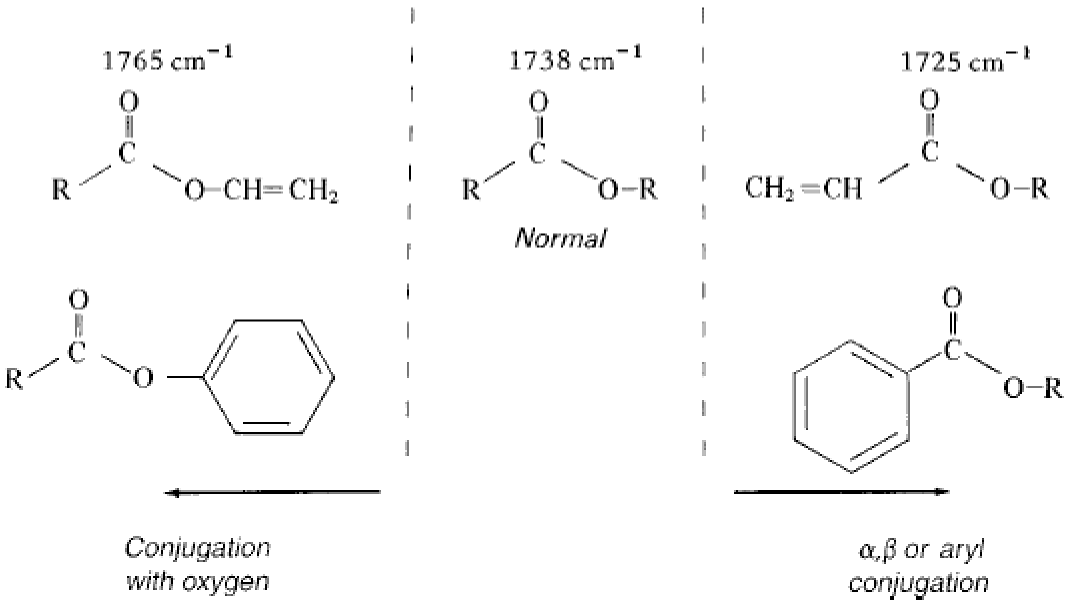


$CH_3\underset{\underset{O}{\|}}{C}{-}OCH{=}CH_2$

Vinyl acetate
1762 cm^{-1}

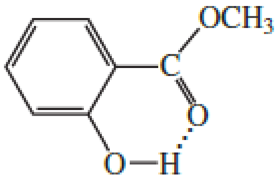


Phenyl acetate
1765 cm^{-1}



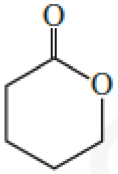
The effect of α,β unsaturation or aryl substitution and conjugation with oxygen on the C=O vibrations in noncyclic (acyclic) esters.

Hydrogen-Bonding Effects:
When intramolecular (internal) hydrogen bonding is present, the C=O is shifted to a lower frequency.

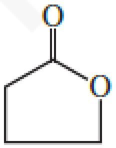


Methyl salicylate
1680 cm^{-1}

Cyclic Esters (Lactones):
The C=O vibrations are shifted to higher frequencies with decreasing ring size.

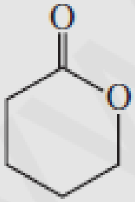
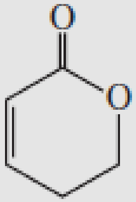
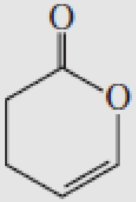
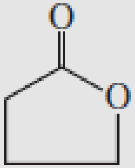
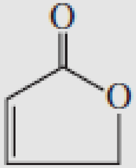
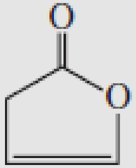
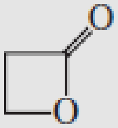


δ-Valerolactone
1735 cm^{-1}



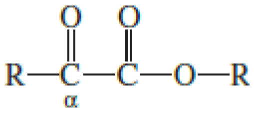
γ-Butyrolactone
1770 cm^{-1}

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

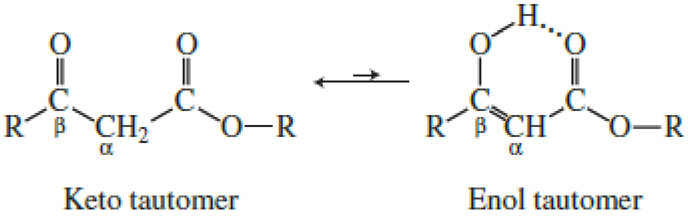
Ring-Size Effects (cm^{-1})		α,β Conjugation (cm^{-1})		Conjugation with Oxygen (cm^{-1})	
	1735		1725		1760
	1770		1750		1800
	1820				

α-Halo Effects:
Halogenation on the carbon leads to an increase in the C=O frequency.

α-Keto Esters:
In principle, one should see two carbonyl groups for a compound with "ketone" and "ester" functional groups. Usually, one sees a shoulder on the main absorption band near 1735 cm^{-1} or a single broadened absorption band.



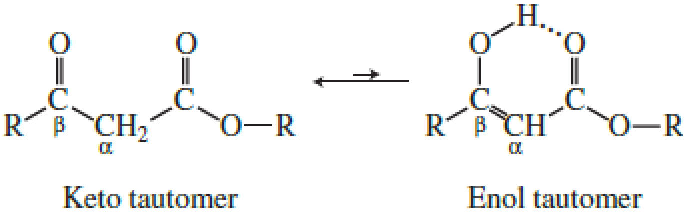
β-Keto Esters:
Although this class of compounds exhibits tautomerization less evidence exists for the enol form because β-keto esters do not enolize to as great an extent.



β-Keto esters exhibit a strong-intensity doublet for the two carbonyl groups at about 1720 and 1740 cm^{-1} in the “keto” tautomer, presumably for the ketone and ester C=O groups.

Evidence for the weak-intensity C=O band in the “enol” tautomer (often a doublet) appears at about 1650 cm^{-1}.

Because of the low concentration of the enol tautomer, one generally cannot observe the broad O-H stretch that was observed in β-diketones



C-O Stretching Vibrations in Esters:

Two (or more) bands appear for the C-O stretching vibrations in esters in the range from 1300 to 1000 cm^{-1}.

The C-O stretch next to the carbonyl group (the “acid” side) of the ester appears between 1300 and 1150 cm^{-1} for most common esters.

The C-O stretch for the “alcohol” part of the ester may appear as a weaker band in the range from 1150 to 1000 cm^{-1}.

In analyzing the 1300- to 1000-cm^{-1} region to confirm an ester functional group, do not worry about fine details. It is usually sufficient to find at least one very strong and broad absorption to help identify the compound as an ester.

Acid Chlorides:

C=O Stretching Vibrations

Acid chlorides show a very strong band for the C=O group that appears in the range of 1810–1775 cm^{-1} for aliphatic acid chlorides.

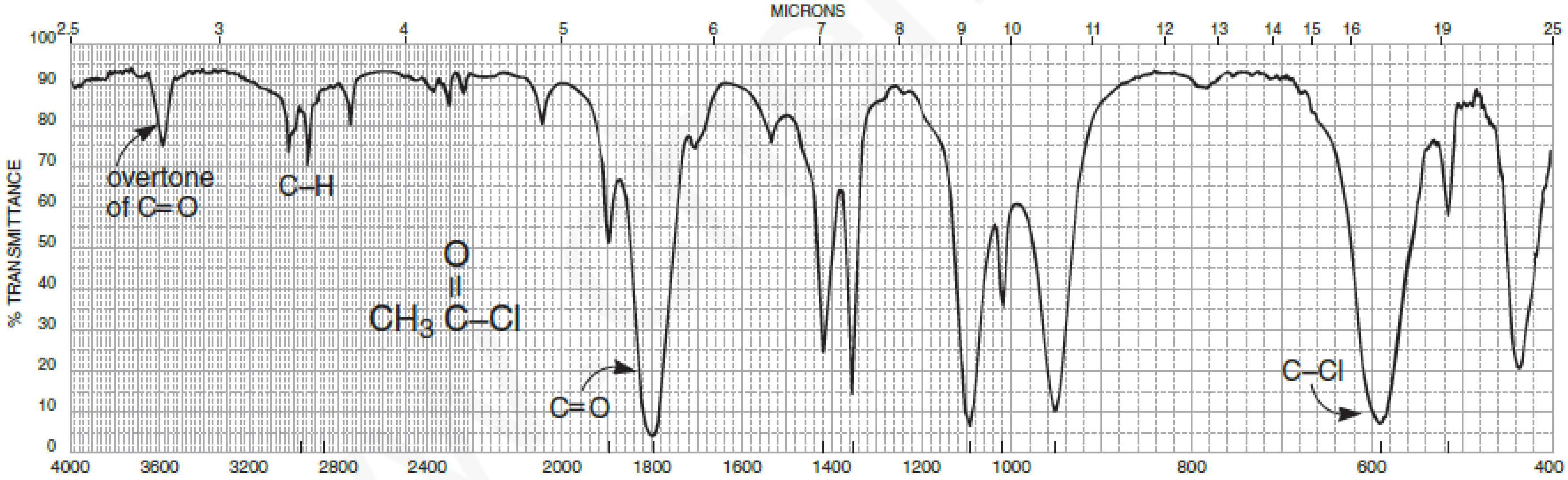
Conjugation lowers the frequency.

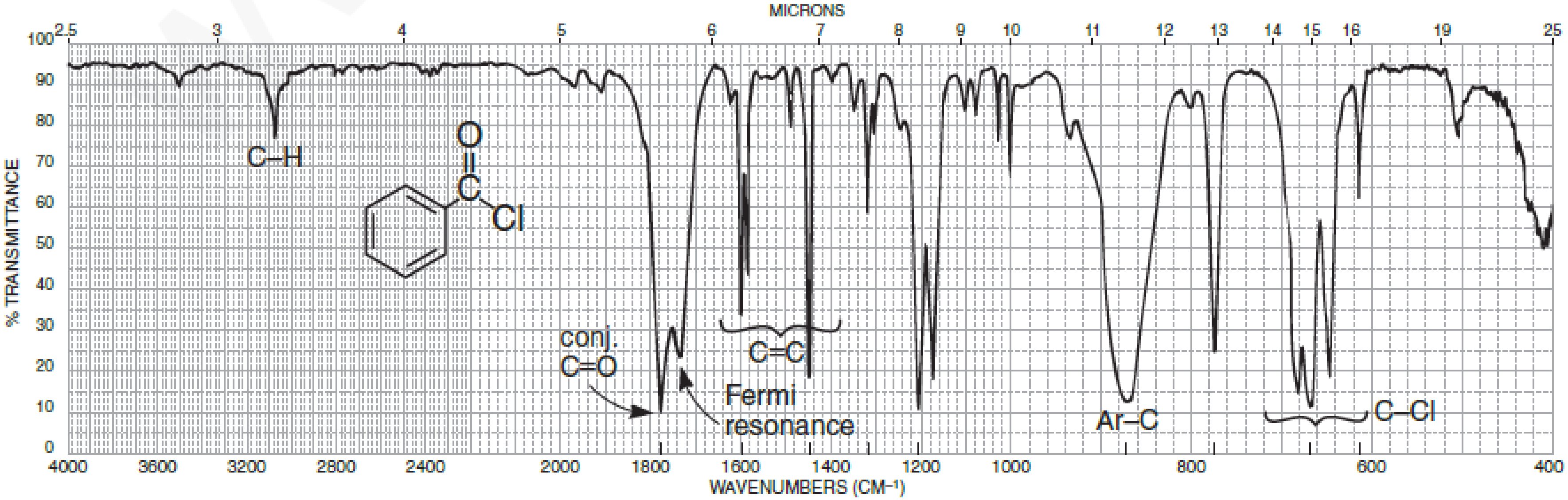
The strong carbonyl absorption appears at a characteristically high frequency of about 1800 cm^{-1} for saturated acid chlorides.

Conjugated acid chlorides absorb at a lower frequency (1780 to 1760 cm^{-1}).

C-Cl Stretching Vibrations

These bands, which appear in the range from 730 to 550 cm^{-1}, are best observed if KBr plates or cells are used.





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

Anhydrides:

Anhydrides show two strong bands for the C=O groups.

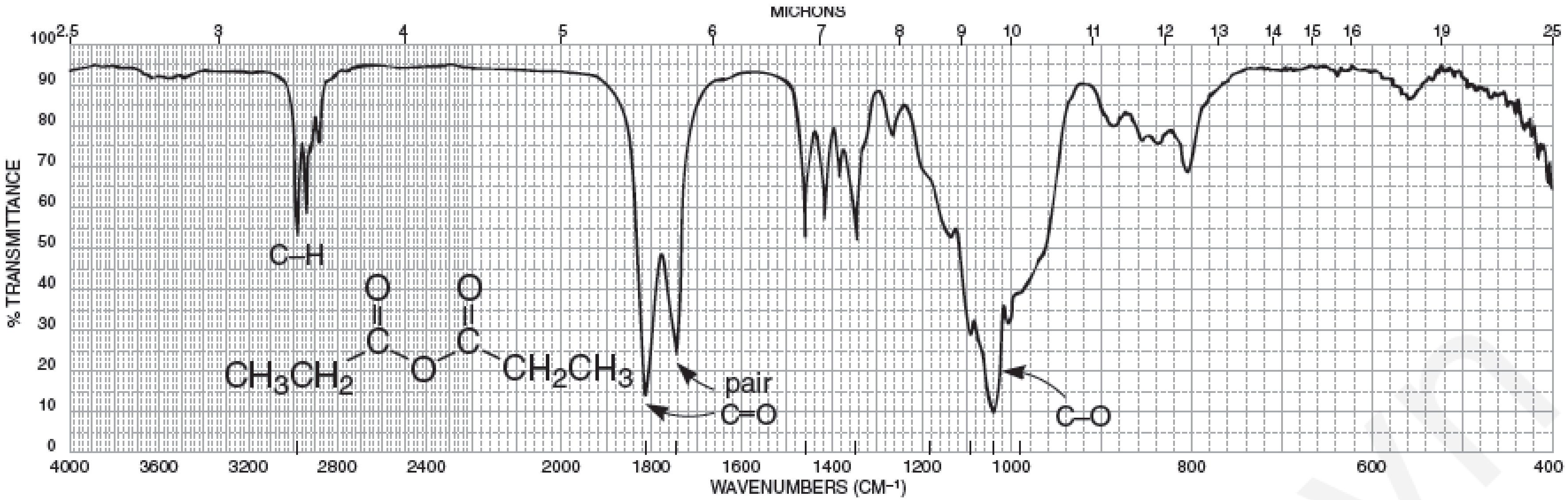
Simple alkyl-substituted anhydrides generally give bands near 1820 and 1750 cm^{-1}.

Conjugation shifts each of the bands to lower frequencies (about 30 cm^{-1} each).

Simple five-membered ring anhydrides have bands at near 1860 and 1780 cm^{-1}

Anhydrides and acid chlorides are the most common functional groups that have a C=O peak appearing at such a high frequency.

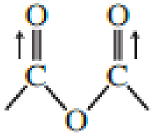
C=O	Stretch always has two bands, 1830–1800 cm^{-1} and 1775–1740 cm^{-1}, with variable relative intensity. Conjugation moves the absorption to a lower frequency. Ring strain (cyclic anhydrides) moves the absorptions to a higher frequency.
C–O	Stretch (multiple bands) occurs in the range 1300–900 cm^{-1}.



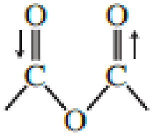
The infrared spectrum of propionic anhydride (neat liquid, KBr plates).

The characteristic pattern for noncyclic and saturated anhydrides is the appearance of *two strong bands,* not necessarily of equal intensities, in the regions from 1830 to 1800 cm^{-1} and from 1775 to 1740 cm^{-1}.

The two bands result from asymmetric and symmetric stretch.



~1760 cm^{-1}



~1800 cm^{-1}

Conjugation shifts the absorption to a lower frequency, while cyclization (ring strain) shifts the absorption to a higher frequency.

The *strong* and *broad* C-O stretching vibrations occur in the region from 1300 to 900 cm^{-1}.

ETHERS

Simple aliphatic ethers can be distinguished from alkanes by the presence of the C-O band.

The most prominent band is that due to C-O stretch, 1300–1000 cm^{-1}.

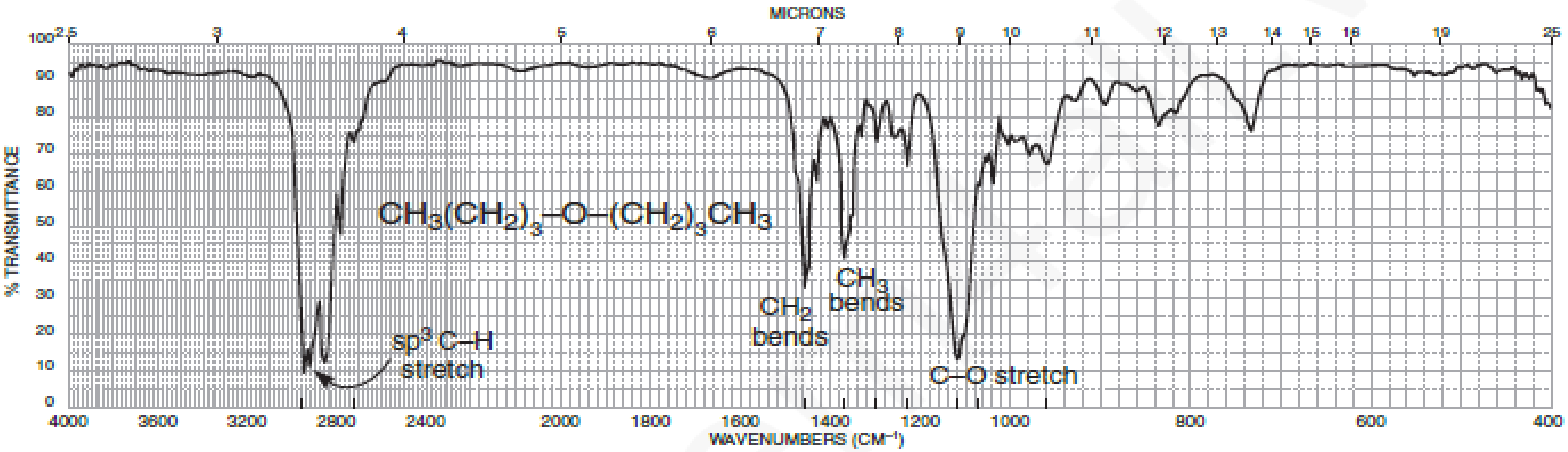
Absence of C=O and O-H is required to ensure that C-O stretch is not due to an ester or an alcohol.

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}.

Dialkyl Ethers:

R—O—R

The asymmetric C-O-C stretching vibration leads to a single strong absorption that appears at about 1120 cm^{-1}, as seen in the spectrum of dibutyl ether.



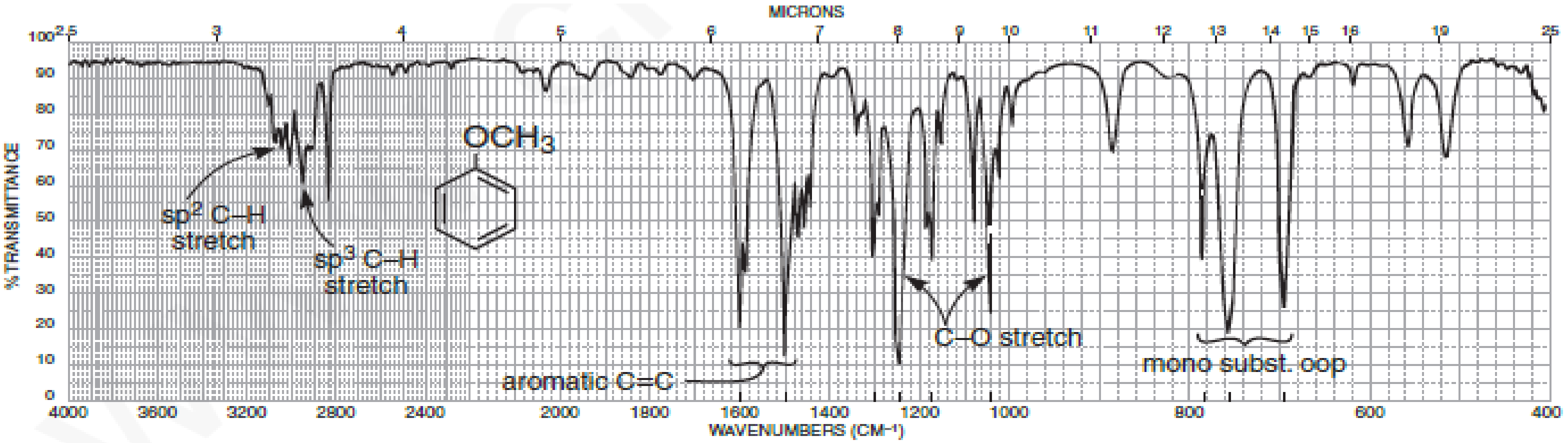
The infrared spectrum of dibutyl ether (neat liquid, KBr plates).

The symmetric stretching band at about 850 cm−1 is usually very weak. The asymmetric C-O-C absorption also occurs at about 1120 cm^{-1} for a six-membered ring containing oxygen.

Aryl and Vinyl Ethers:

$Ar{-}O{-}R \qquad CH_2{=}CH{-}O{-}R$

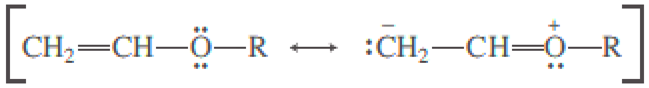
Aryl alkyl ethers give rise to *two* strong bands: an asymmetric C-O-C stretch near 1250 cm−1 and a symmetric stretch near 1040 cm^{-1}, as seen in the spectrum of anisole.



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

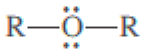
Vinyl alkyl ethers also give two bands: one strong band assigned to an asymmetric stretching vibration at about 1220 cm−1 and one very weak band due to a symmetric stretch at about 850 cm^{-1}.

The shift in the asymmetric stretching frequencies in aryl and vinyl ethers to values higher than were found in dialkyl ethers can be explained through resonance.



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

Resonance
1220 cm^{-1}

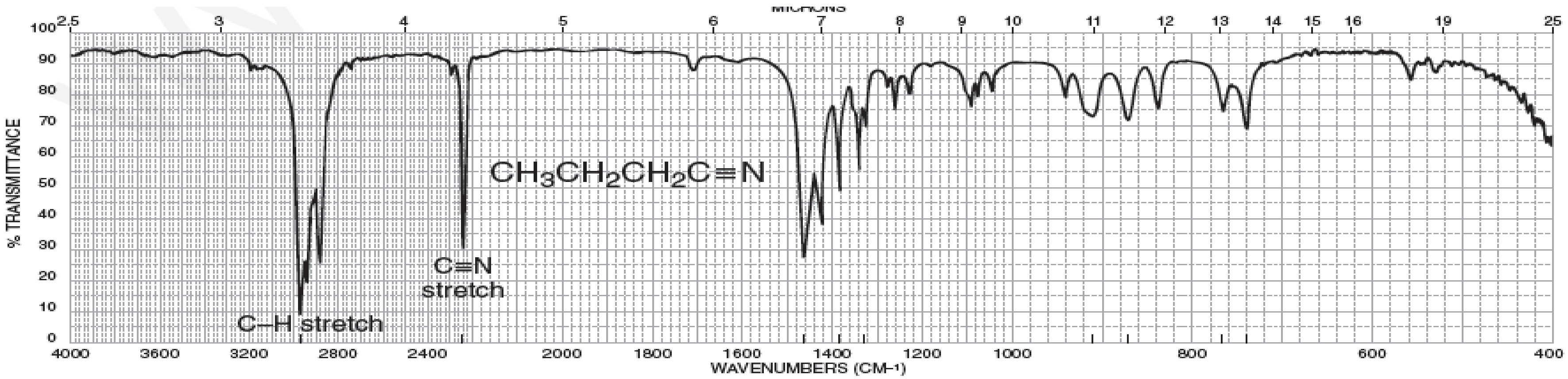


$$\mathrm{R{-}\underset{\cdot\cdot}{\ddot{O}}{-}R}$$

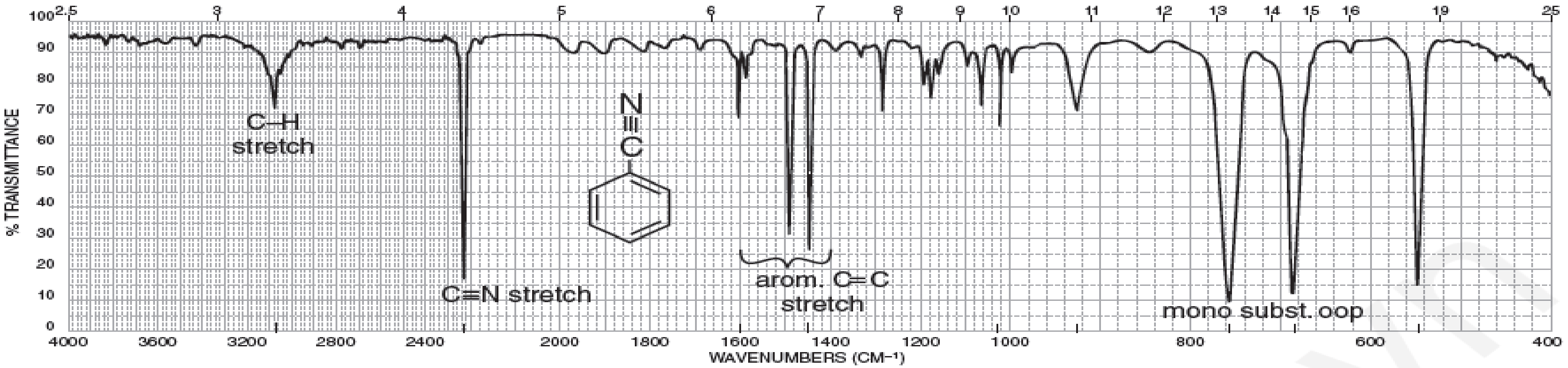
No resonance
1120 cm^{-1}

Nitriles:

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.



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



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

The C≡N group in a nitrile gives a medium-intensity, sharp band in the triple-bond region of the spectrum (2270 to 2210 cm^{-1}).

The C≡C bond, which absorbs near this region (2150 cm^{-1}), usually gives a weaker and broader band unless it is at the end of the chain.

Aliphatic nitriles absorb at about 2250 cm^{-1}, whereas their aromatic counterparts absorb at lower frequencies, near 2230 cm^{-1}.

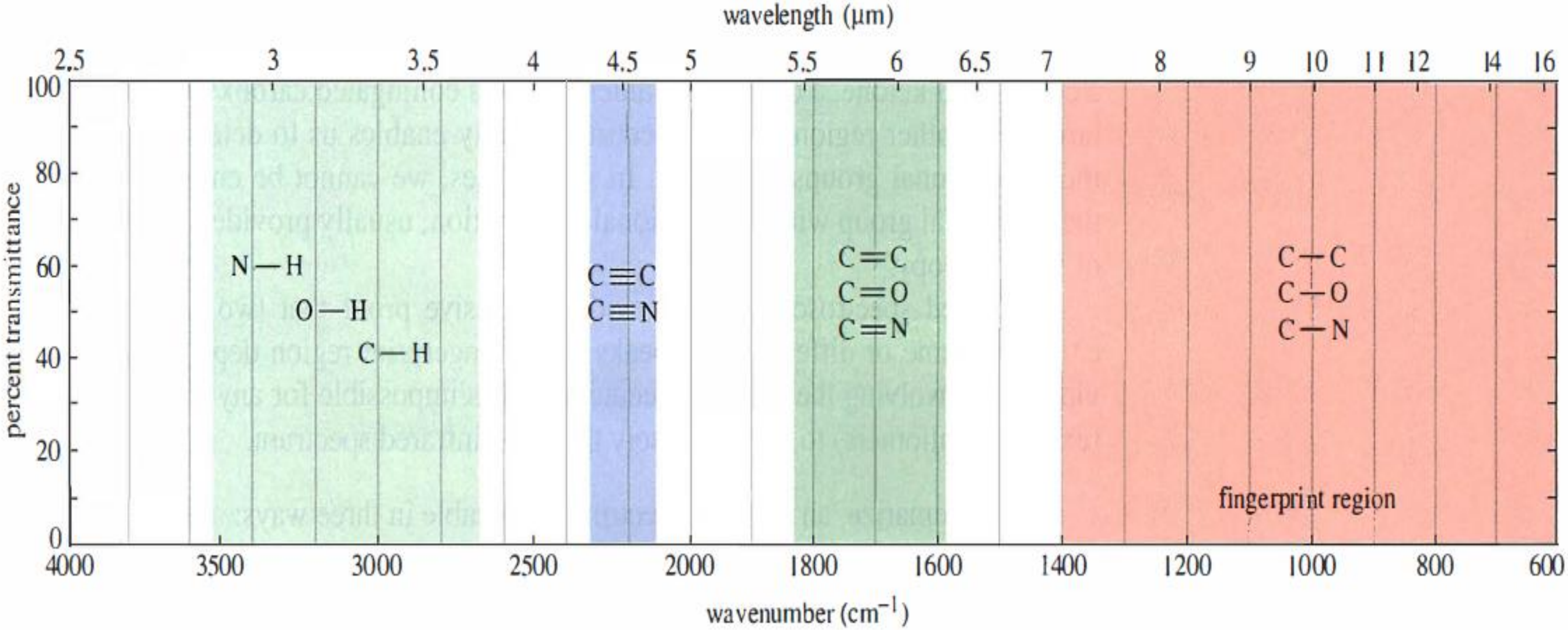
C=N:

The C=N bond absorbs in about the same range as a C=C bond.

Although the C=N band varies in intensity from compound to compound, it usually is more intense than that obtained from the C=C bond.

An oxime (R-CH=N-O-H) gives a C=N absorption in the range from 1690 to 1640 cm^{-1} and a broad O-H absorption between 3650 and 2600 cm^{-1}.

An imine (R-CH=N-R) gives a C=N absorption in the range from 1690 to 1650 cm^{-1}.


wavelength (µm)
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3
3.5
4
4.5
5
5.5
6
6.5
7
8
9
10
11
12
14
16
percent transmittance
100
80
60
40
20
0
N—H
O—H
C—H
C≡C
C≡N
C=C
C=O
C=N
C—C
C—O
C—N
fingerprint region
4000
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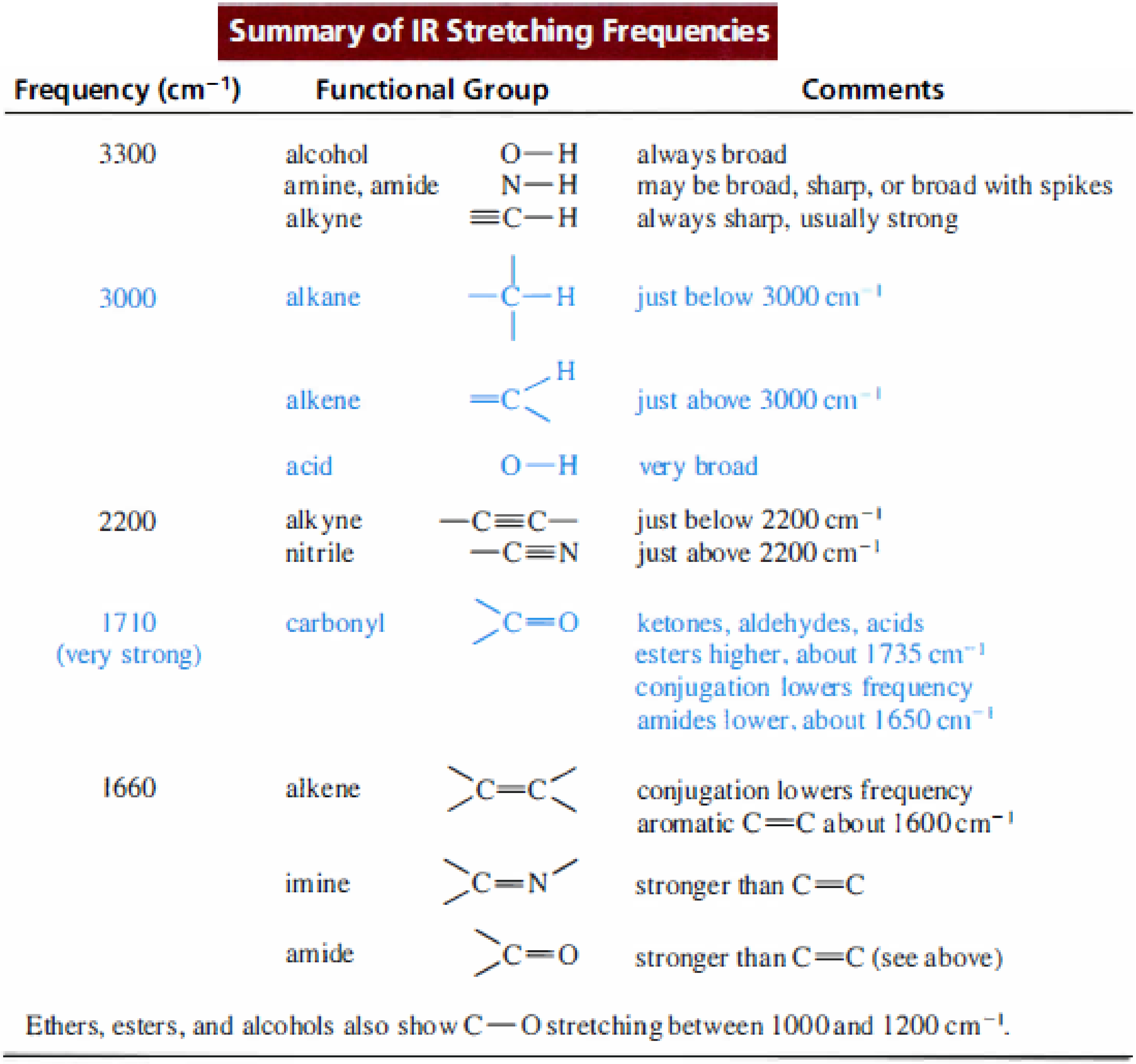
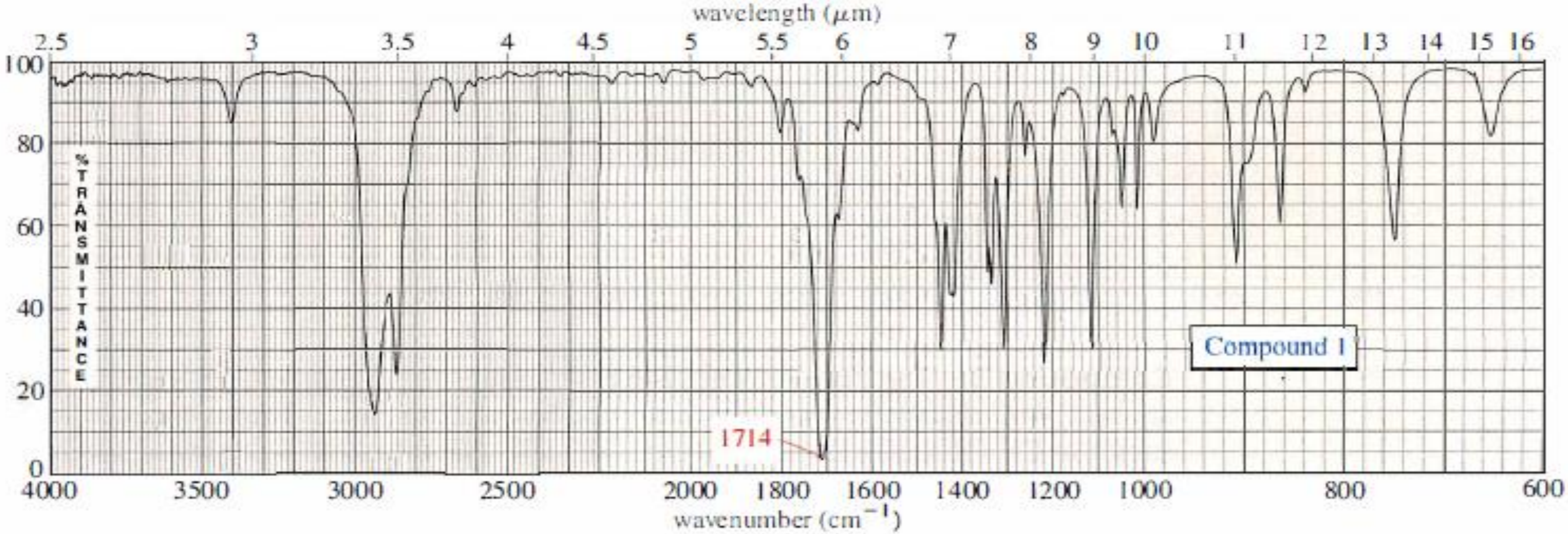
1000
800
600
wavenumber (cm⁻¹)

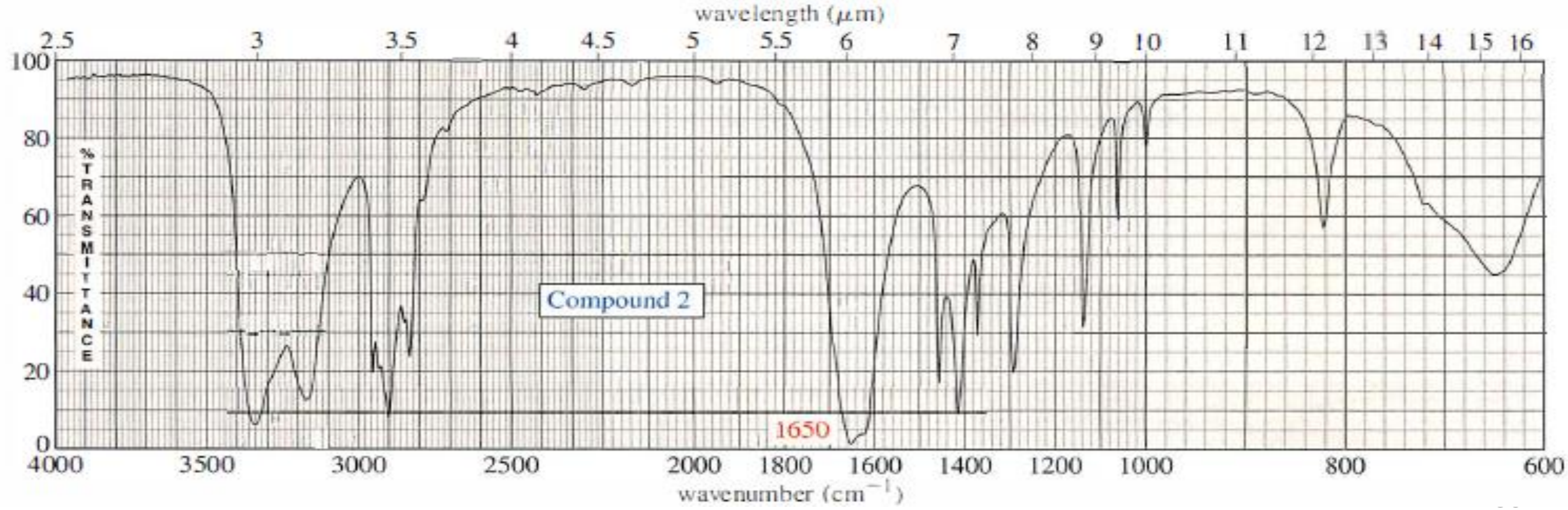


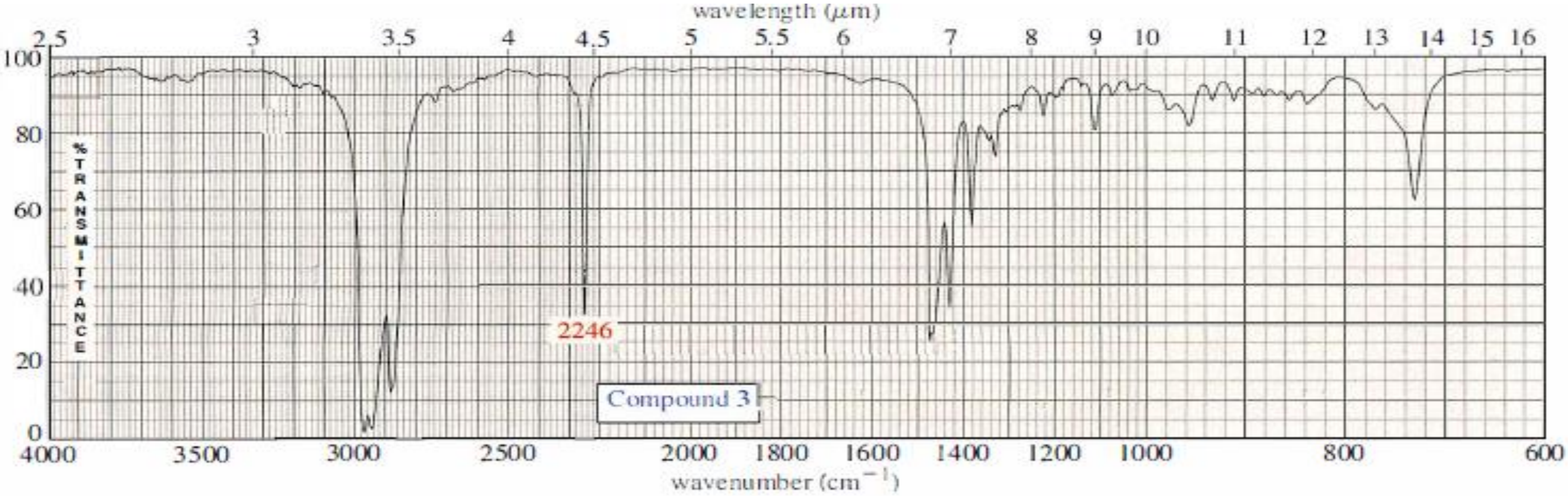
Summary of IR Stretching Frequencies

Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	$\equiv$C—H	always sharp, usually strong
3000	alkane	—C—H	just below 3000 cm^{-1}
	alkene	=C—H	just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C$\equiv$C—	just below 2200 cm^{-1}
	nitrile	—C$\equiv$N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl	>C=O	ketones, aldehydes, acids esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene	>C=C<	conjugation lowers frequency aromatic C=C about 1600 cm^{-1}
	imine	>C=N—	stronger than C=C
	amide	>C=O	stronger than C=C (see above)

Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.


Compound 1


Compound 2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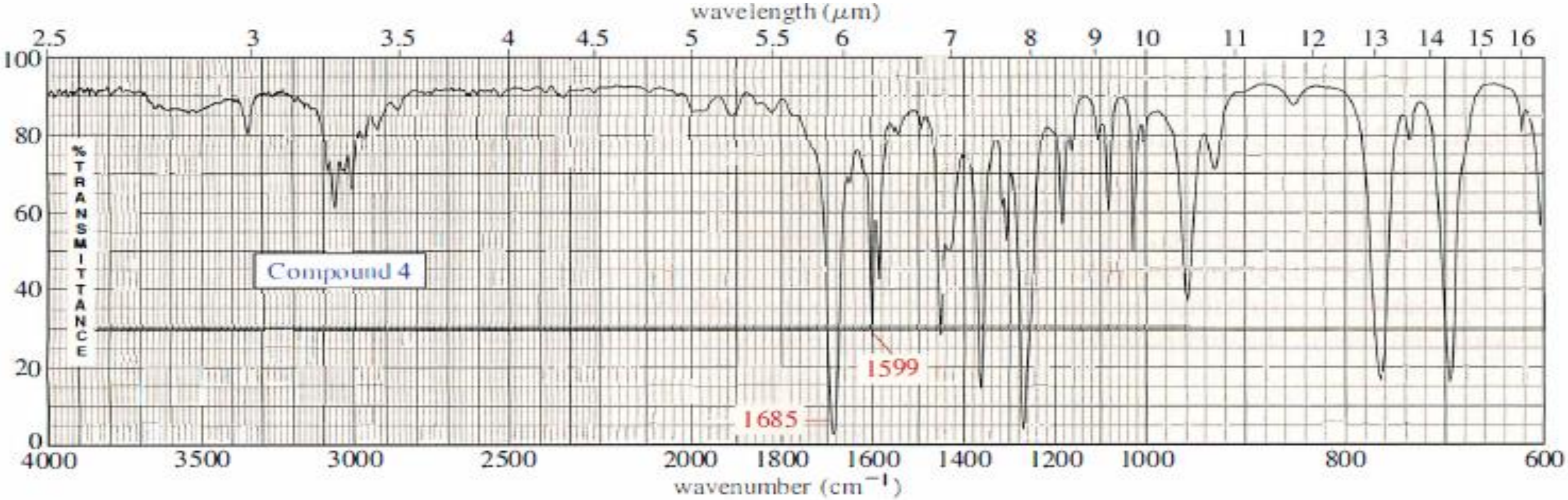
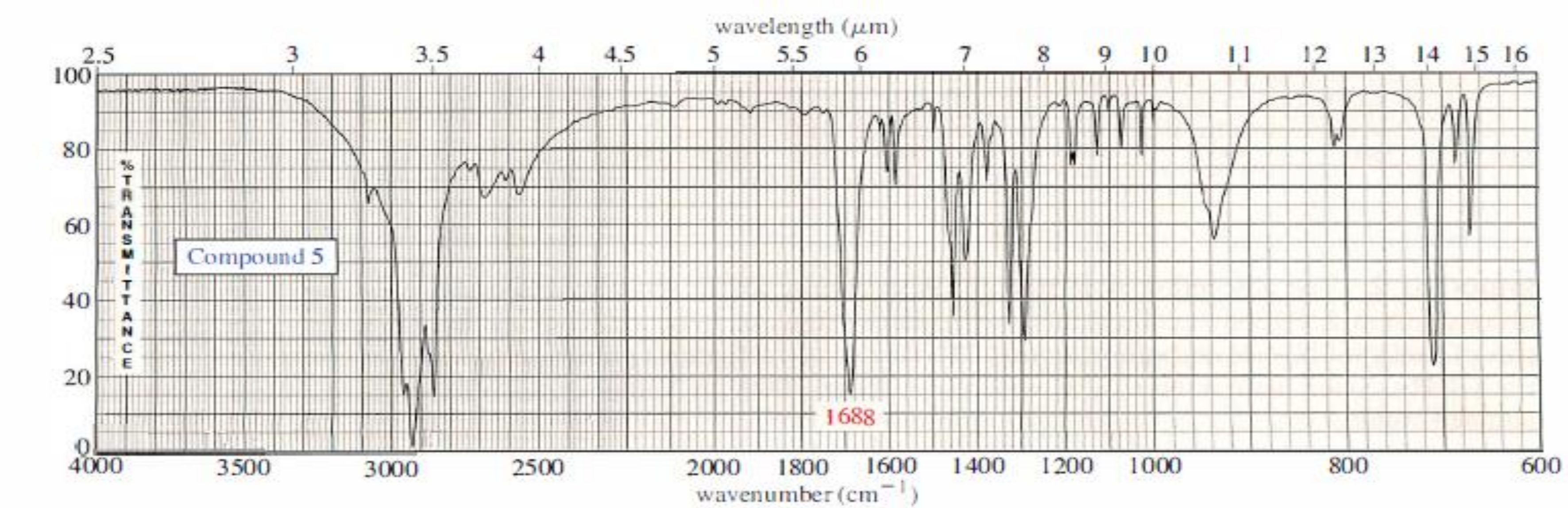

Compound 4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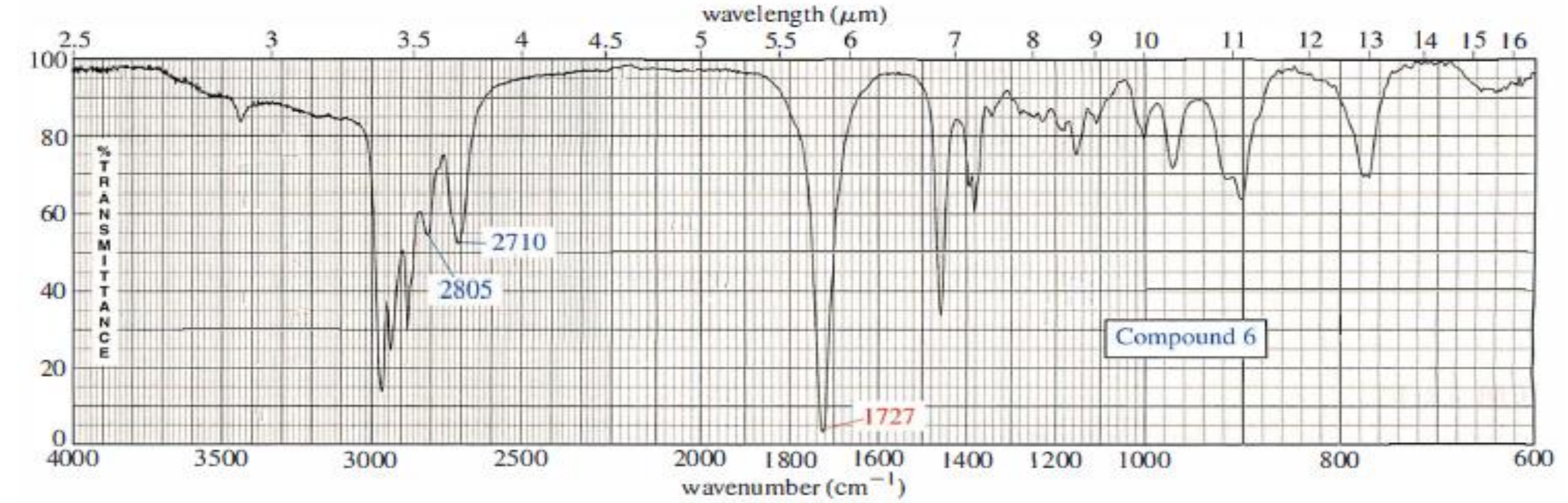
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
Compound 5
1688
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})


wavelength (μm)
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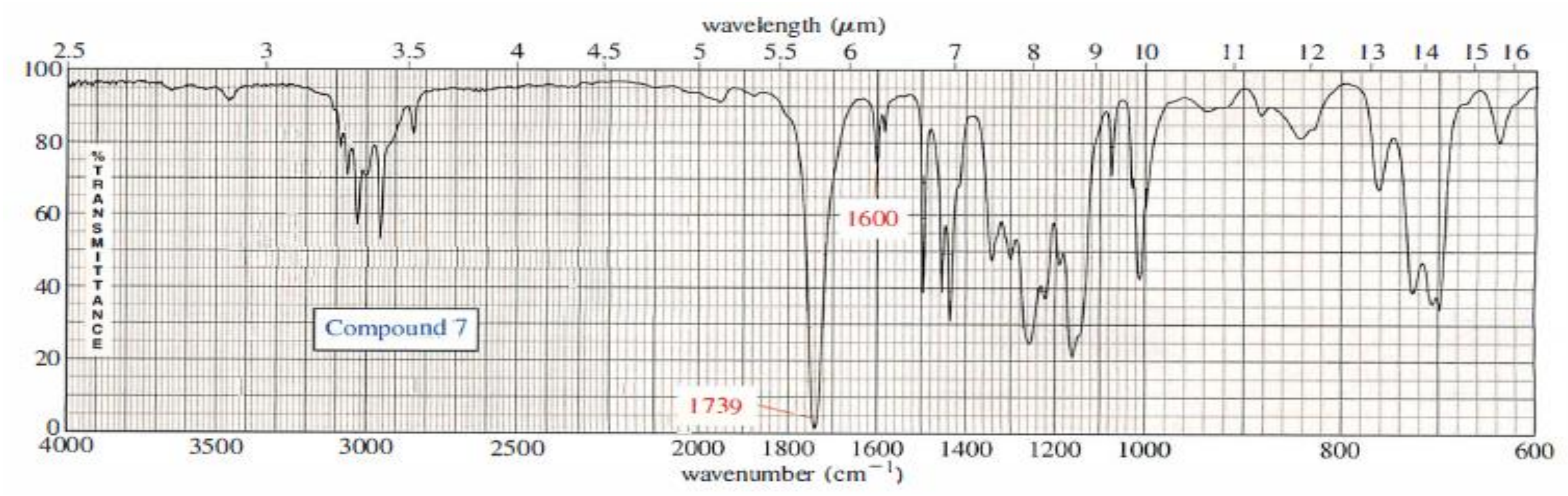
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
2710
2805
1727
Compound 6
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})


wavelength (μm)
2.5
3
3.5
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4.5
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5.5
6
7
8
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10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
Compound 7
1600
1739
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm⁻¹)