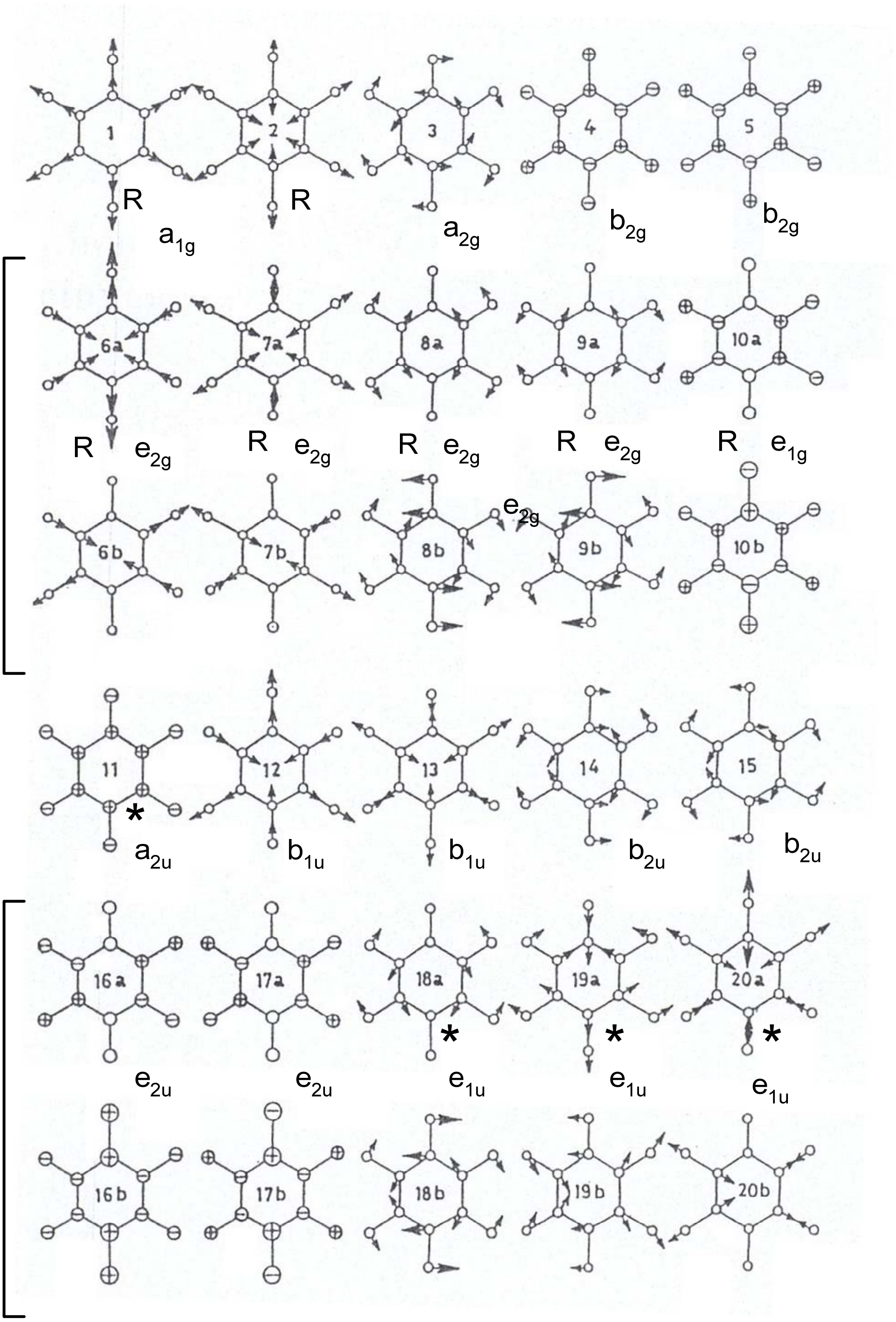
5.3.2 Benzene and its derivatives



Normal modes of benzene (30 vibrations)

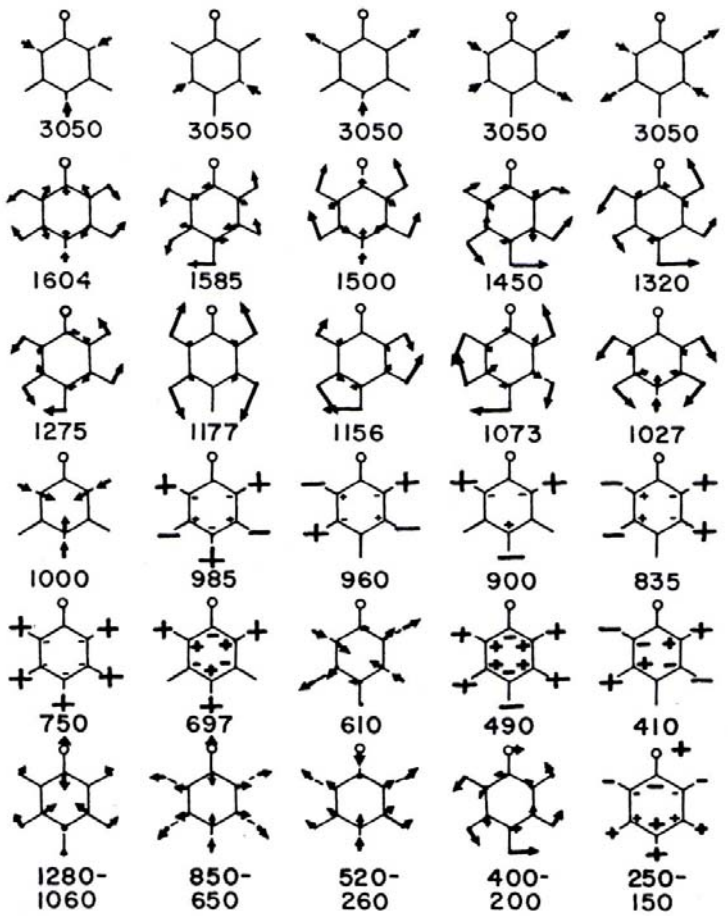
Normal vibrations of benzene and substituted benzenes

Benzene		X—substituted benzenes				
	D_{6h}	C_{2v} C_s	a_1 a'	a_2 a''	b_1 a''	b_2 a'
νCH	2, 7, 13, 20	νCH, νCX	2, 7a, 13, 20a			7b, 20b
νPh	1, 8, 14, 19		1, 8a, 19a			8b, 14, 19b
δCH	3, 9, 15, 18	δCH, δCX	9a, 18a			3, 9b, 15, 18b
δPh	6, 12		6a, 12			6b
γCH	5, 10, 11, 17	γCH, γCX		10a, 17a	5, 10b, 11, 17b	
γPh	4, 16			16a	4, 16b	

Absorption regions (cm^{-1}) of the normal vibrations of monosubstituted benzenes

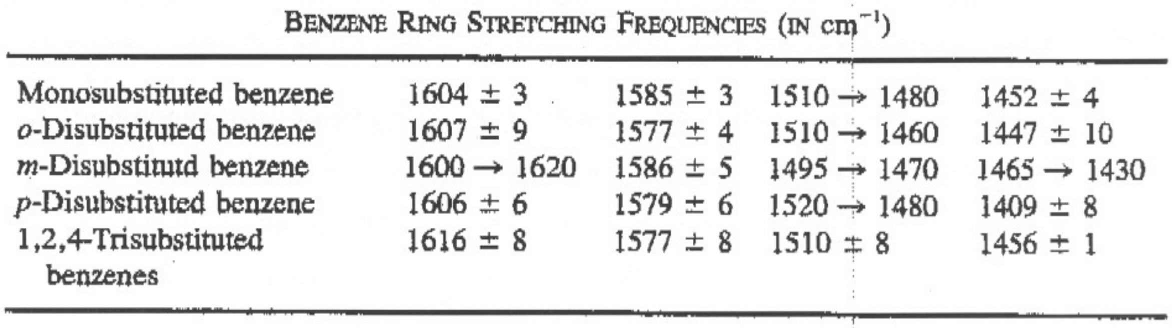
Vibration		Wilson	Mono light	Mono heavy
νCH	CH stretching vibration	20a	3085 ± 20	3085 ± 20
νCH	CH stretching vibration	20b	3070 ± 20	3075 ± 15
νCH	CH stretching vibration	2	3060 ± 20	3055 ± 15
νCH	CH stretching vibration	13	3040 ± 20	3040 ± 20
νCH	CH stretching vibration	7b	3020 ± 20	3020 ± 20
νPh	Phenyl ring stretching vibration	8a	1605 ± 15	1590 ± 20
νPh	Phenyl ring stretching vibration	8b	1585 ± 15	1575 ± 15
νPh	Phenyl ring stretching vibration	19a	1485 ± 25	1475 ± 15
νPh	Phenyl ring stretching vibration	19b	1450 ± 20	1435 ± 15
νPh	Phenyl ring stretching vibration	14	1335 ± 35	1310 ± 25
δCH	CH in-plane deformation	3	1295 ± 25	1275 ± 25
νCX	Phenyl—X stretching vibration	7a (X)	1195 ± 90	1090 ± 30
δCH	CH in-plane deformation	9a	1175 ± 20	1180 ± 15
δCH	CH in-plane deformation	9b	1150 ± 20	1165 ± 10
δCH	CH in-plane deformation	15	1070 ± 20	1065 ± 15
δCH	CH in-plane deformation	18a	1020 ± 20	1025 ± 10
νPh	Phenyl ring stretching vibration	1	1000 ± 10	1000 ± 05
γCH	CH out-of-plane deformation	5	980 ± 20	980 ± 15
γCH	CH out-of-plane deformation	17a	960 ± 25	965 ± 10
γCH	CH out-of-plane deformation	17b	900 ± 35	915 ± 20
γCH	CH out-of-plane deformation	10a	840 ± 25	835 ± 20
γCH	CH out-of-plane deformation	11	775 ± 45	745 ± 25
δPh	Phenyl ring in-plane deformation	12 (X)	750 ± 80	700 ± 50
γPh	Phenyl ring out-of-plane deform.	4	695 ± 15	685 ± 15
δPh	Phenyl ring in-plane deformation	6b	625 ± 15	605 ± 15
γPh	Phenyl ring out-of-plane deform.	16b (X)	510 ± 90	475 ± 55
δPh	Phenyl ring in-plane deformation	6a (X)	420 ± 115	355 ± 90
γPh	Phenyl ring out-of-plane deform.	16a	405 ± 25	405 ± 15
δCX	Phenyl—X in-plane deformation	18b (X)	300 ± 110	250 ± 60
γCX	Phenyl—X out-of-plane deform.	10b (X)	205 ± 70	170 ± 30

Mono light = benzenes substituted with a light atom (atomic mass < 25).
Mono heavy = benzenes substituted with a heavy atom (atomic mass > 25).
(X) = substituent-sensitive vibration.



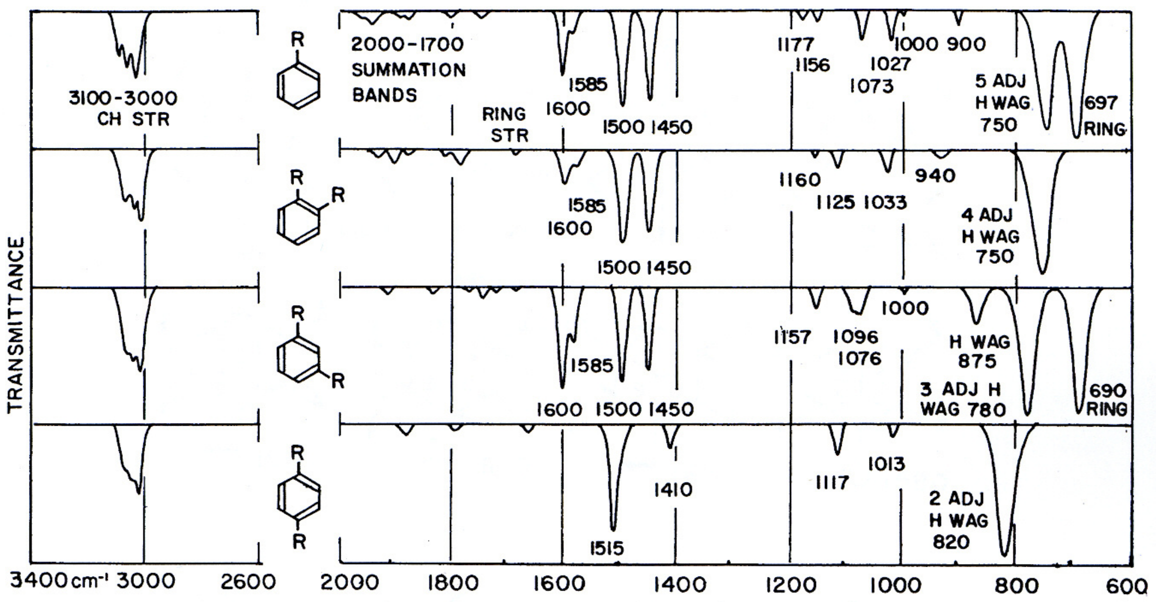
The approximate normal modes of vibration of the monosubstituted benzene ring. These have frequencies in cm^{-1} usually within 30 cm^{-1} or better of the values given, except for the substituents sensitive modes which are collected in the bottom row.

Characteristic bands in 1610-1400 cm^{-1} region ν(CC) ring stretching: 1610-1400 cm^{-1} (4 vibrations)



BENZENE RING STRETCHING FREQUENCIES (IN cm^{-1})

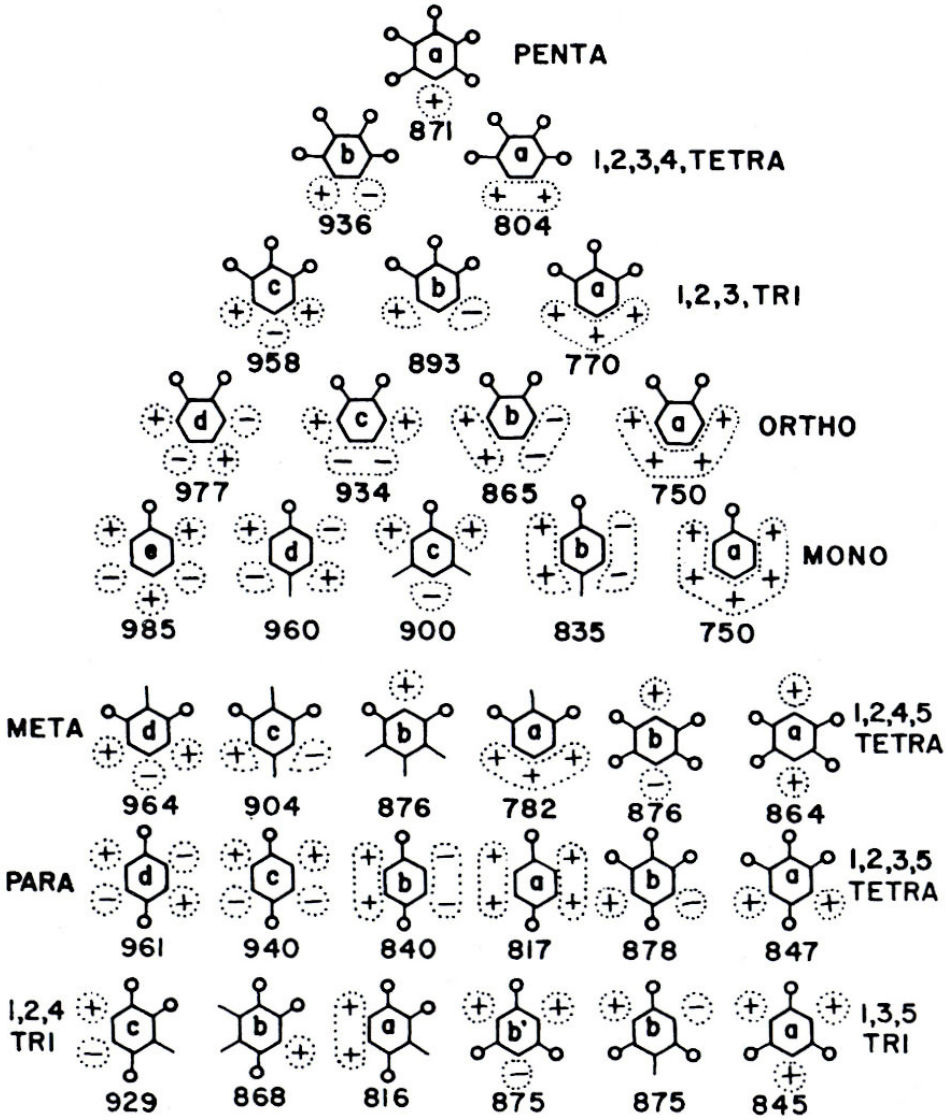
Monosubstituted benzene	1604 ± 3	1585 ± 3	1510 → 1480	1452 ± 4
o-Disubstituted benzene	1607 ± 9	1577 ± 4	1510 → 1460	1447 ± 10
m-Disubstitutd benzene	1600 → 1620	1586 ± 5	1495 → 1470	1465 → 1430
p-Disubstituted benzene	1606 ± 6	1579 ± 6	1520 → 1480	1409 ± 8
1,2,4-Trisubstituted benzenes	1616 ± 8	1577 ± 8	1510 ± 8	1456 ± 1



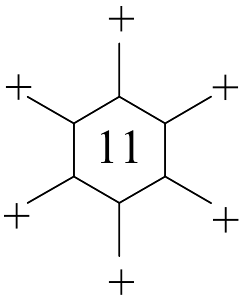
The general appearance of monosubstituted benzenes and ortho, meta, and para disubstituted benzenes in the infrared spectra. Some intensity variations and some frequency shifts may be expected with different substituents.

Characteristic bands in 900-700 cm^{-1} region

a. γ(CH) out-of-plane deformations
   Mono: 11, (750 vs); 10a ,(835); 17b, (900); 17a, (960) 5, (985)



The out-of-plane CH wag modes of substituted benzenes. Plus and minus stand for out-of-plane hydrogen displacement. Standing wave patterns are indicated by enclosing adjacent hydrogens which are wagging in-phase within an antinodal region (dotted region).
Frequencies in cm^{-1} are usually within 30 cm^{-1} those given.



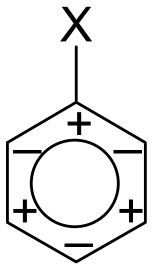
γ(CH)

Five adjacent CH out-of-plane deformation bands in cm^{-1}

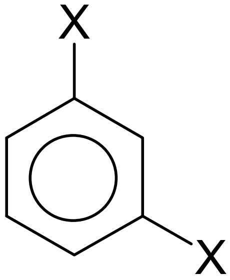
Substituent	**γ(CH)**	**Substituent**	**γ(CH)**
$-CF_3$	770	-COO	805
$-CH_2Cl$	765	$-NO_2$	793
$-CR_3$	763	$-CH{=}CH_2$	775
$-CHR_2$	759	-CO-Cl	772
-CN, C≡C	758	-CO-R	761
-F	753	$-NH_2$	752
$-CH_2R$	743	-OH	751
-Cl	741	$-SO_2X$	750
-Br	737	-CO-H	748
-I	729	$-NH_3^+$	742
$-CH_3$	728	$-SH_2$	737

γ(CCC) vibrations (4)

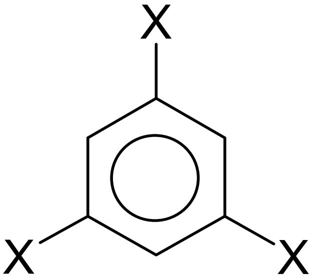
Strong bands for



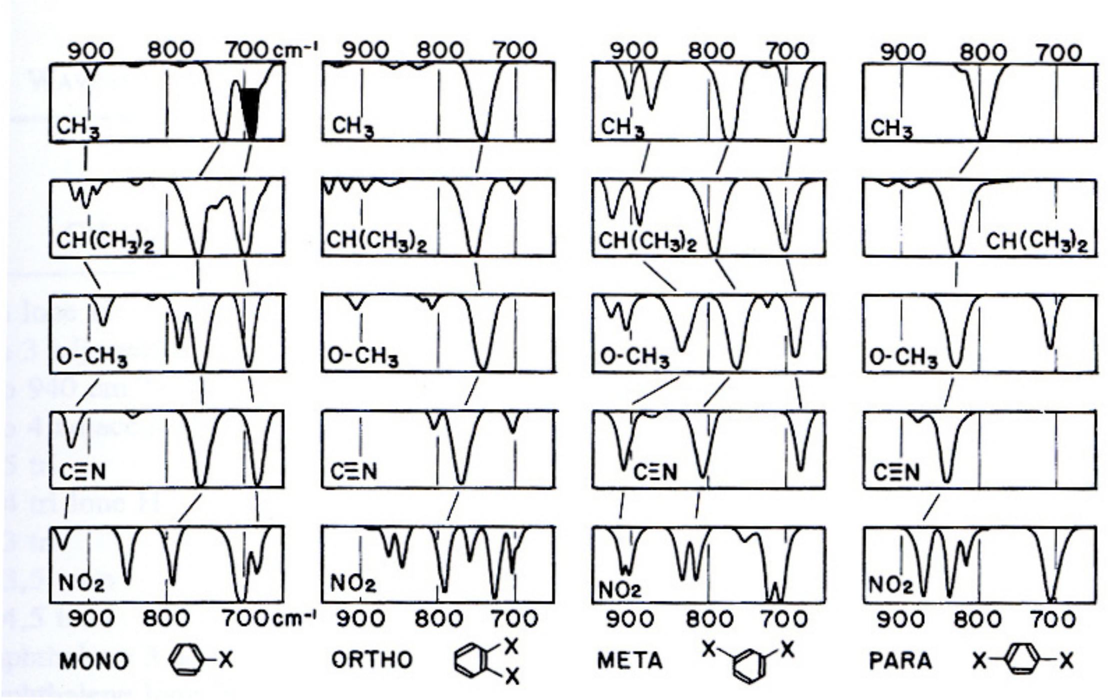
694 cm^{-1}



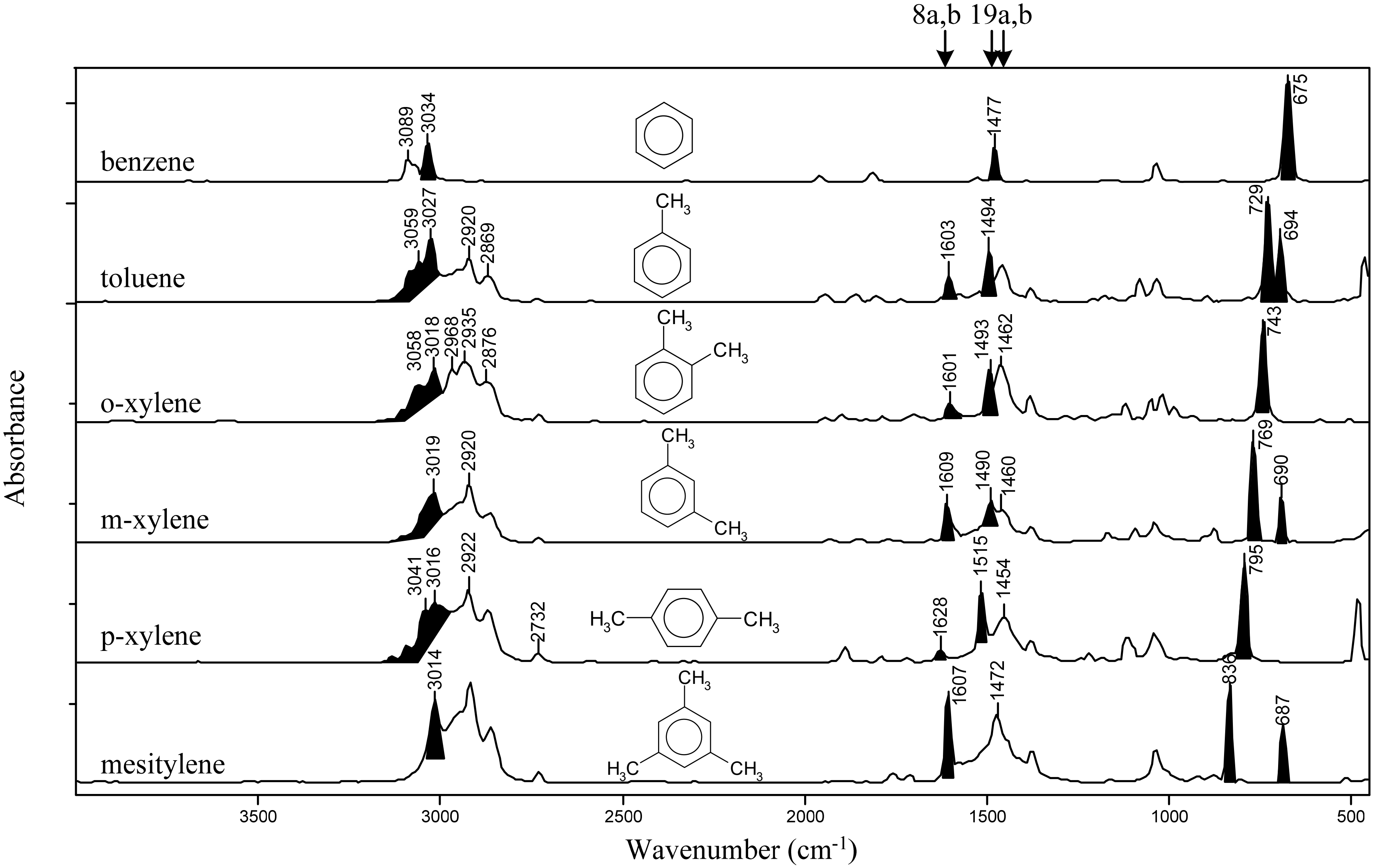
691 cm^{-1}



687 cm^{-1}

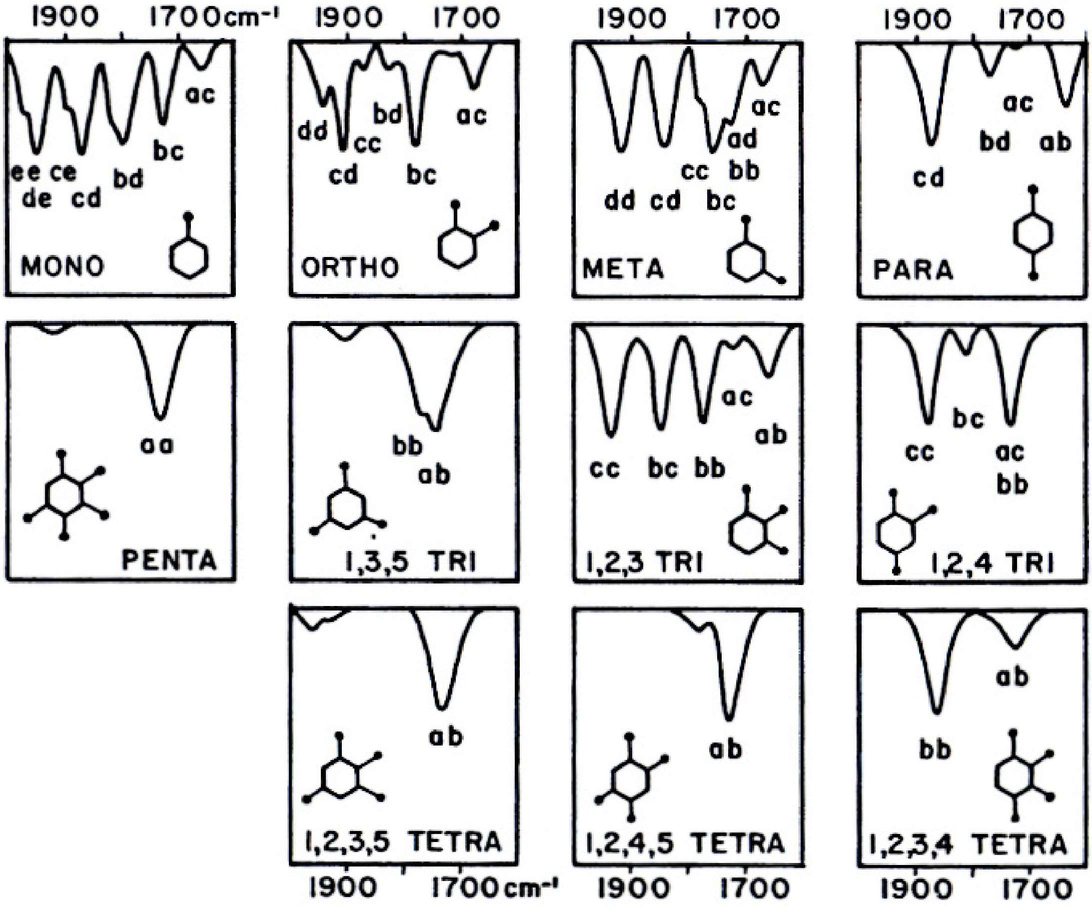


The bands obtained in the 900-700 cm^{-1} region in the infrared spectra of some benzene ring derivatives. The X substitutes are indicated on each spectrum. In the disubstituted compounds both X substituents are the same.


8a,b
19a,b
benzene
3089
3034
1477
675
toluene
CH_3
3059
3027
2920
2869
1603
1494
729
694
o-xylene
CH_3
CH_3
3058
3018
2968
2935
2876
1601
1493
1462
743
m-xylene
CH_3
CH_3
3019
2920
1609
1490
1460
769
690
p-xylene
H_3C
CH_3
3041
3016
2922
2732
1628
1515
1454
795
mesitylene
CH_3
H_3C
CH_3
3014
1607
1472
836
687
Absorbance
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

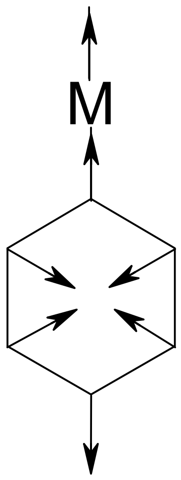
Summation of bands in 1650-2000 cm^{-1} region

The out-of-plane aromatic CH bending vibrations, γ(CH), in the 1000-700 cm^{-1} region give rise relatively prominent summation bands.
These band pattern can be used to help determining the ring substitution.
Note: in C=O substituted benzenes, however, these bands are disturbed

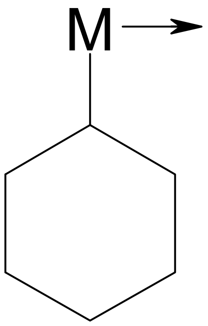


Characteristic patterns of summation bands for various substituted benzene rings. The double letters (ee and others) are the binary combinations of modes seen in Fig. on page 275.

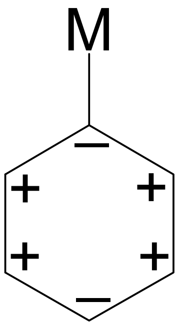
Metal (element) –sensitive modes of metal phenyls



6a



18b

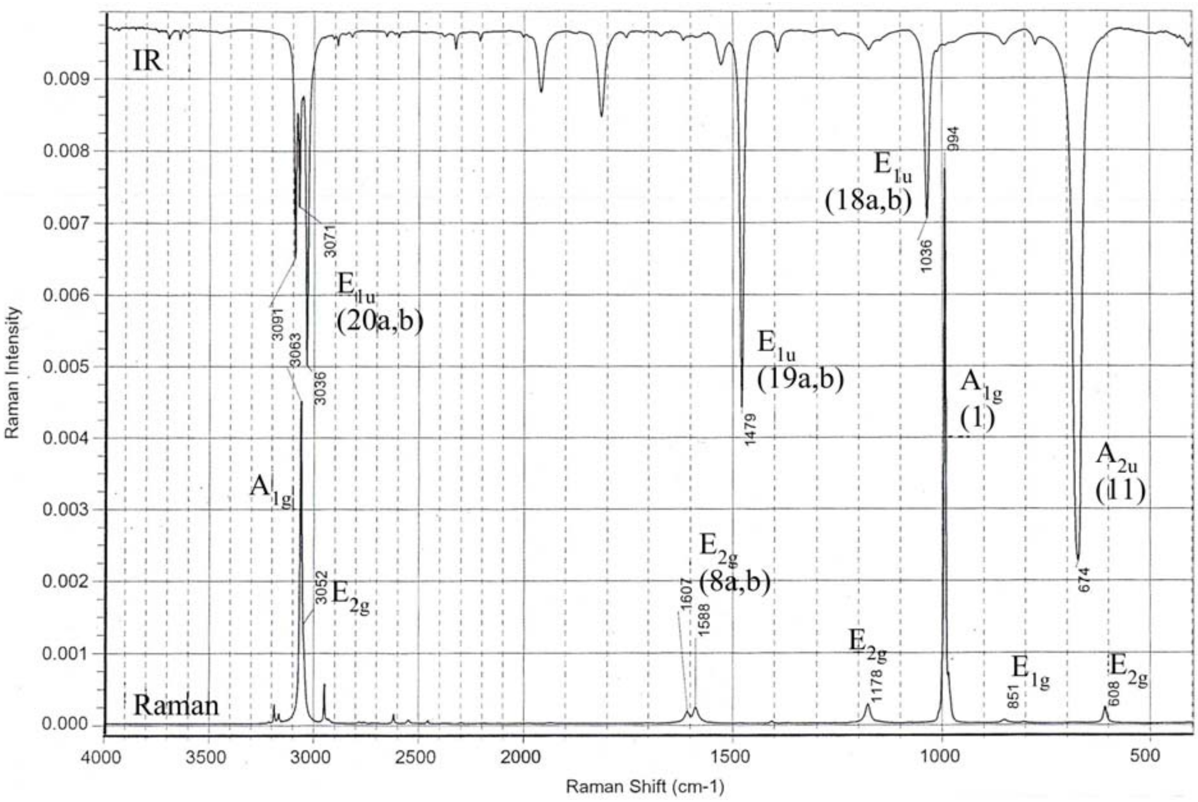


16b

Compound	Frequencies (cm^{-1})		
	6a	**18b**	**16b**
Al(C_6H_6)$_3$	420	207	323
Ga(C_6H_6)$_3$	315	180	245
In(C_6H_6)$_3$	270	180	195
Si(C_6H_5)$_4$	435	185	261
Ge(C_6H_5)$_4$	323	168	232
Sn(C_6H_5)$_4$	268	152	225
Pb(C_6H_5)$_4$	223	147	181

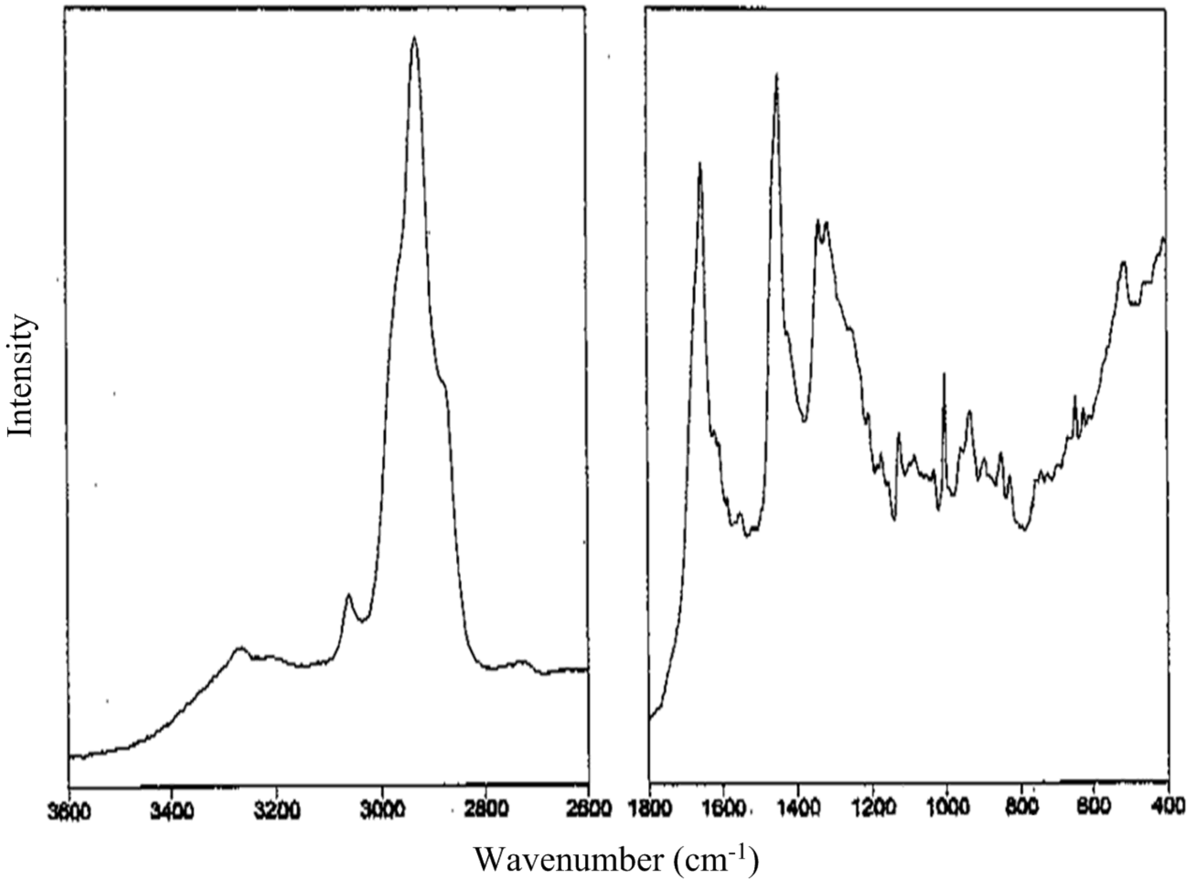
Strong band in Raman spectrum

The ν_1 breathing mode is very strong in the Raman spectra near 1000 cm^{-1}. Important marker for phenylalanine in biological samples.



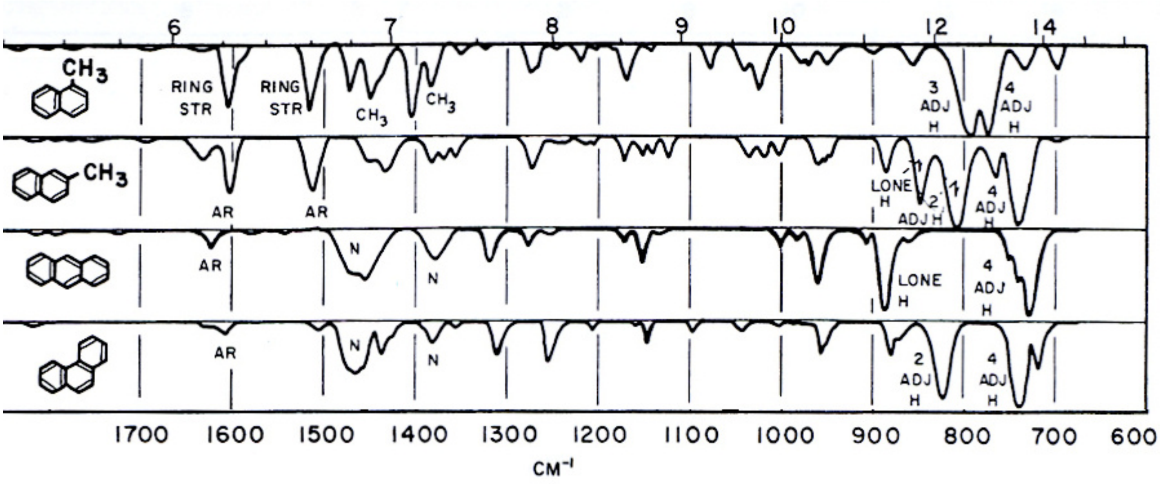
IR and Raman spectrum of liquid benzene

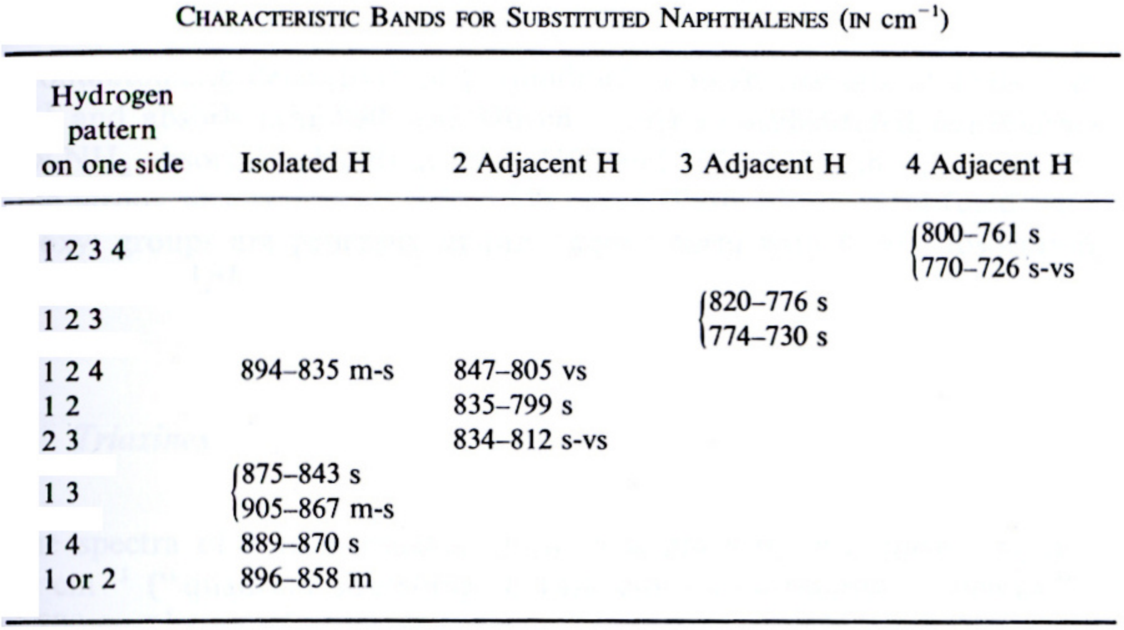
FT-Raman spectrum of human nail.



Condensed ring aromatics

The classification of substituents is given in terms of adjacent hydrogens. The characteristic γ(CH) bands are in the 900-700 cm^{-1} region.





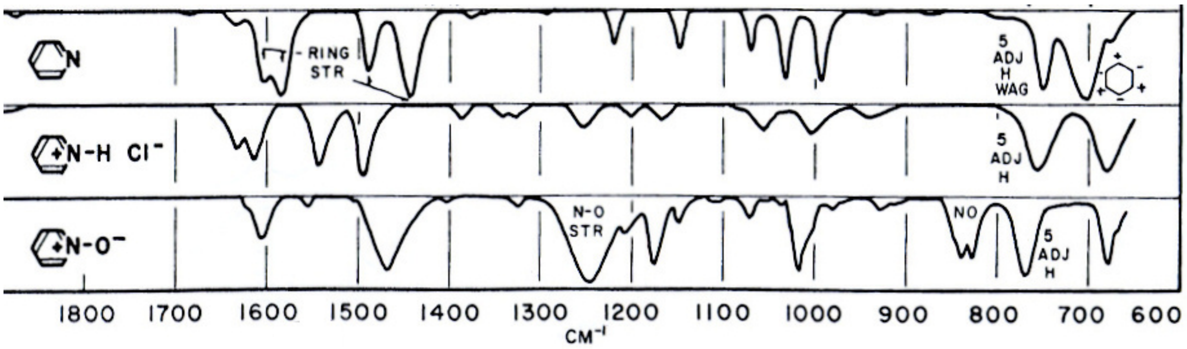
CHARACTERISTIC BANDS FOR SUBSTITUTED NAPHTHALENES (IN cm^{-1})

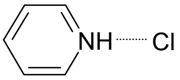
Hydrogen pattern on one side	Isolated H	2 Adjacent H	3 Adjacent H	4 Adjacent H
1 2 3 4				800–761 s 770–726 s-vs
1 2 3			820–776 s 774–730 s	
1 2 4	894–835 m-s	847–805 vs		
1 2		835–799 s		
2 3		834–812 s-vs		
1 3	875–843 s 905–867 m-s			
1 4	889–870 s			
1 or 2	896–858 m			

In the 3 and 4 adjacent hydrogen regions two bands are seen.

Pyridines

IR spectrum is very similar to monosubstituted benzenes (light substituent)



For  broad band at 2600 cm^{-1} (νNH···Cl)

Pyridine Ring Stretching Frequencies[1] (in cm^{-1})

2-Substituted pyridine	1615 → 1585	1572 ± 4	1471 ± 6	1433 ± 5
3-Substituted pyridine	1595 ± 5	1577 ± 5	1485 → 1465	1421 ± 4
4-Substituted pyridine	1603 ± 5	1561 ± 8	1520 → 1480	1415 ± 4
Polysubstituted pyridine	1610 – 1597	1588 – 1564	1555 – 1490	
2-Substituted pyridine *N*-oxides	1640 → 1600	1567 ± 10	1540 → 1480	1435 ± 10
3-Substituted pyridine *N*-oxides	1605 ± 4	1563 ± 3	1480 ± 6	1434 ± 5
4-Substituted pyridine *N*-oxides	1645 → 1610	—	1483 ± 6	1443 ± 7

Out-of-Plane Vibrations[1] (in cm^{-1})

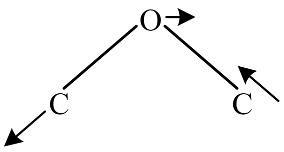
2-Substituted pyridine	780–740 4 adjacent H wag	
3-Substituted pyridine	820–770 3 adjacent H wag	730–690 ring bend
4-Substituted pyridine	850–790 2 adjacent H	
2-Substituted pyridine *N*-oxides	790–750 4 adjacent H	
3-Substituted pyridine *N*-oxides	820–760 3 adjacent H wag	680–660 ring bend
4-Substituted pyridine *N*-oxides	855–820 2 adjacent H	

5.3.3. Oxygen containing compounds

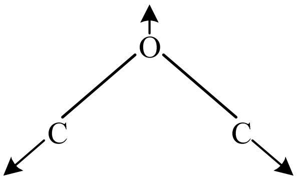
Ethers

When an oxygen atom is substituted for a carbon atom is a n-aliphatic chain skeletal stretching mode of C-O-C is observed (cs. 1150-800 cm^{-1}).

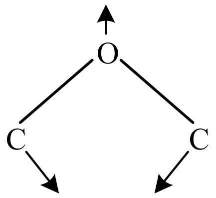
Characteristic vibrations C-O-C group:



ν_a(~1120 cm^{-1})
very strong

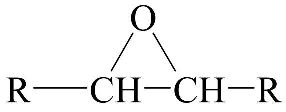


ν_s(~850 cm^{-1})
weak



δ (~390 cm^{-1})
weak, medium

C-O-C asym stretch in ethers:

R-O-R	Ar-O-R	CH_2=CH-O-R	
Dialkyl	Aryl	Vinyl	Epoxides
1140-1085 cm^{-1}, vs	1310-1210, vs 1050-1010, vs	1225-1200 cm^{-1}, s	1280-1230 cm^{-1}, m, s 950-815 cm^{-1}, vs

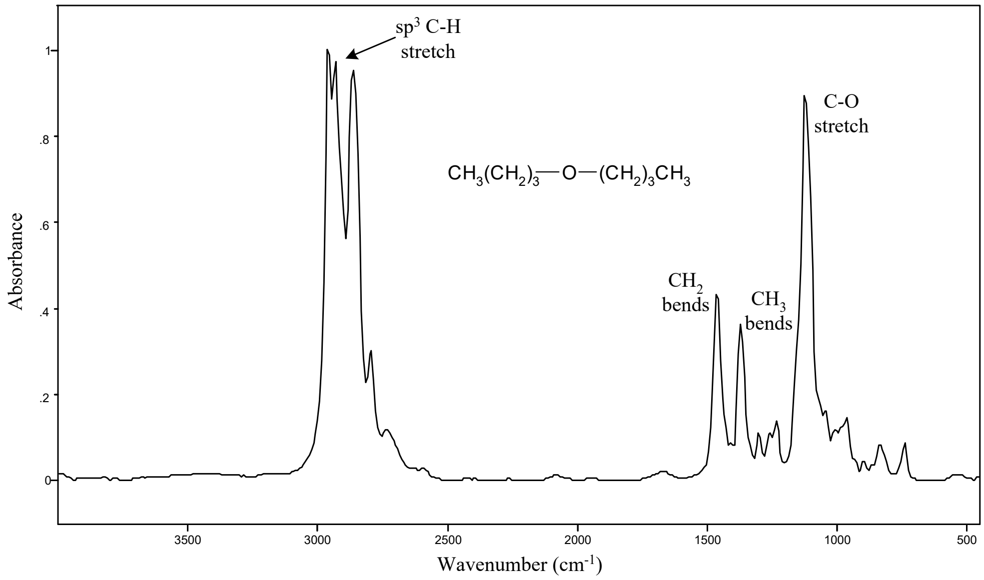
Aliphatic ethers:

The $–CH_2$-O-CH_2- group gives risen to a strong band at 1140-1085 cm^{-1}. Other characteristic features (cm^{-1}).

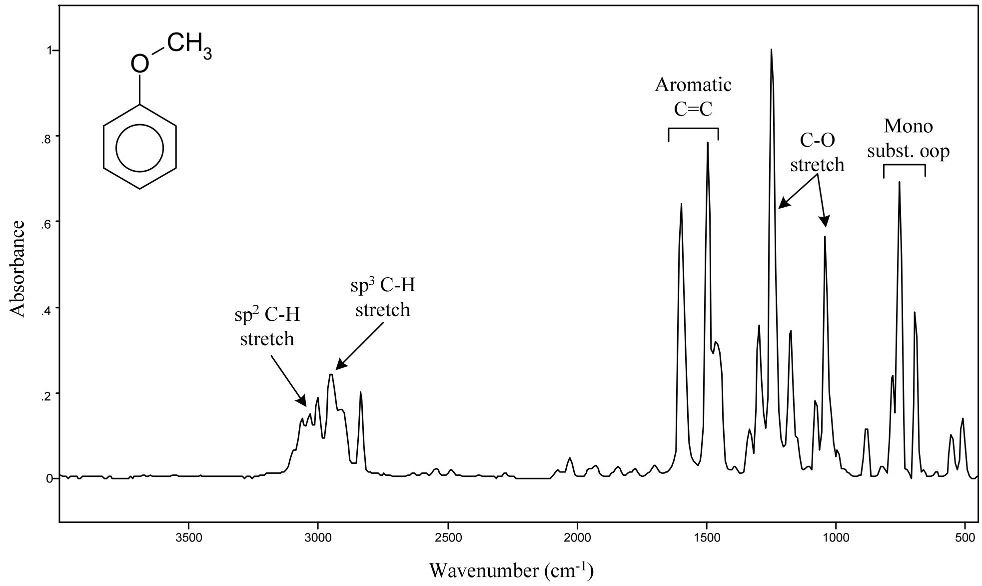
cm^{-1}	Assignment
2940 s	ν_a (CH_2)
2875 w	ν_s(CH_2)
1475 s	δ(CH_2)
1350 w	ω(CH_2)
1285 w	τ(CH_2)
1120 vs	ν_a(COC)

850 w	ν_s(COC)
805 w	ρ(CH2)
395 w	δ(COC)

For R-O-CH_3 groups the frequency shift in $\delta_s(CH_3)$ which shifts from 1375 cm^{-1} to about 1450 cm^{-1}, due to electro negativity of the oxygen.



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



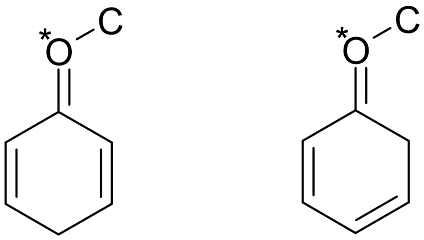
The infrared spectrum of anisole (neat liquid, KBr plates)

Aromatic ethers

The methoxy group in Ph-O-CH_3 usually gives rise to a sharp isolated band near 2850 cm^{-1}.

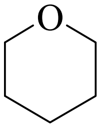
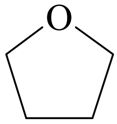
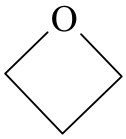
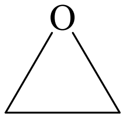
Anisole has two “ether” bands at 1250 and at 1049 cm^{-1}. Diphenyl ether (Ph-O-Ph) does not have 1049 cm^{-1} band, only the 1250 cm^{-1} band.

The aromatic carbon-oxygen bond has a higher force constant than the aliphatic carbon-oxygen bond due to resonance, which is one of the reasons for the higher vibrational frequency.



The ring C-O vibration interacts with the other ring frequencies (X-sensitive modes).

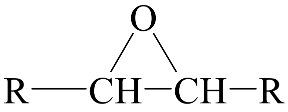
Cyclic ether linkages

	 Pentamethylene oxide	 Tetramethylene oxide	 Trimethylene oxide	 Ethylene oxide
ν^*_a cm^{-1}	1048	1071	983	892
ν^*_s cm^{-1}	813	913	1028	1270

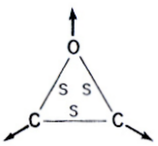
$\nu^*_a = \nu_a$(C-O-C), $\nu^*_s = \nu_s$(C-O-C),

The CH and CH_2 groups in the rings absorb either at 3050-3029 or 3004-2990 cm^{-1} or in a few cases in both regions.

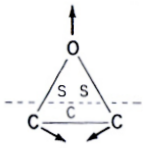
C_2H_2O



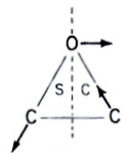
$$R\!-\!\!\!\!\!\underset{\;}{\overset{\;\;\;O}{CH\!-\!CH}}\!-\!R$$



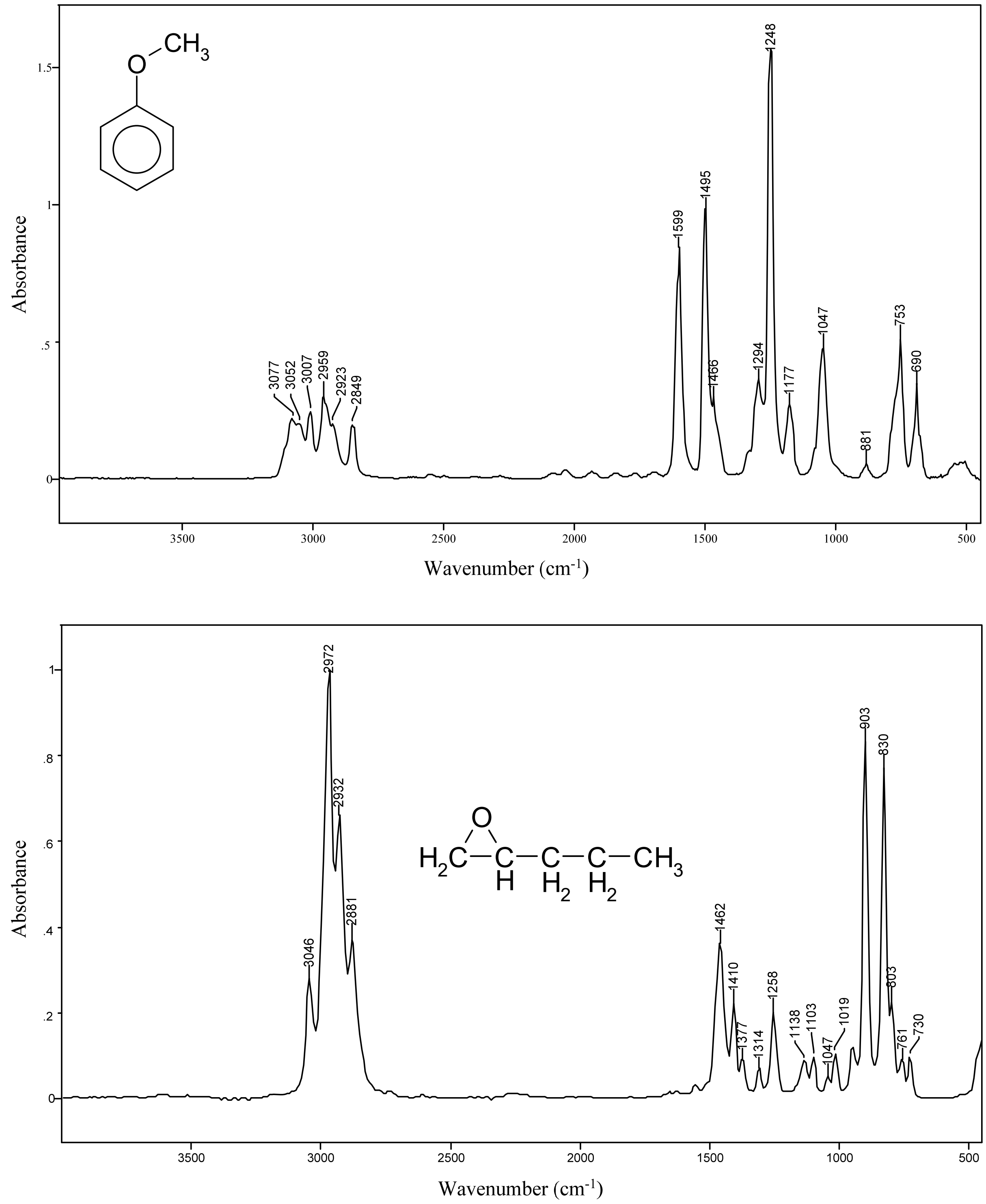
1270 cm^{-1}
1280-1230 cm^{-1},
m



877 cm^{-1}
880-750 cm^{-1},
vs



892 cm^{-1}
950-815 cm^{-1},
vs



FTIR spectra of liquid (film) samples

Vinyl ethers

The asymmetric C-O-C stretch of alkyl vinyl ethers gives rise to a strong band at 1225-1200 cm^{-1}, very near 1203 cm^{-1} in most cases. The vinyl carbon-oxygen bond is stiffened by resonance.

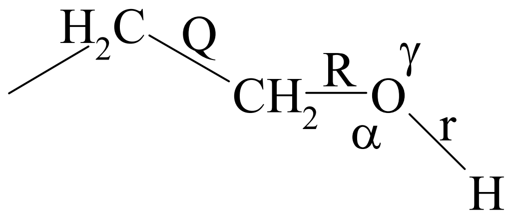
$$CH_2{=}CH\text{-}O\text{-}C \qquad \overset{-}{C}H_2\text{-}CH\text{-}\overset{+}{O}\text{-}C$$

Spectral regions for alkyl vinyl ethers (cm^{-1})

vinyl CH stretch	3125-3098, 3078-3060, 3050-3000
C=C *gauche*	1660-1635
C=C *cis*	1620-1610
=CH rock	1323-1320
C-O-C asym stretch	1225-1200
trans =CH wag	970-960
$=CH_2$ wag	820-810
C-O-C sym stretch	870-820

Alcohols and Phenols

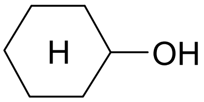
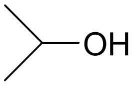
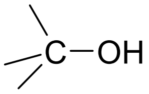
Internal coordinates

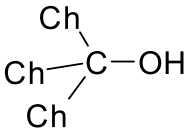


Linear combination of internal coordinates	Approximate frequencies (cm^{-1})
ν (OH) = r	3300(120) vs, (H-bonded)
δ (COH) = A	1400(35) w
ν_a(CCO) = R – Q	1065(25) s
γ(OH)	450(200) w

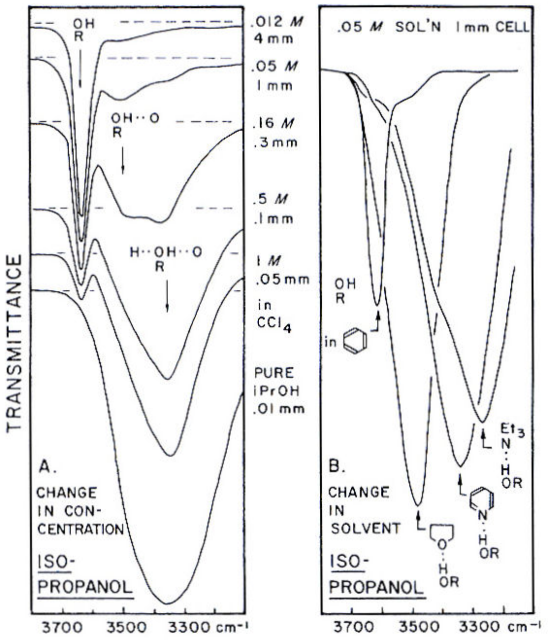
-CH_2-CH_2-OH group has the following strong characteristic bands:

OH str	3300 (120) vs, b (H-bonded)
CH_2 asym str.	2950 (30) vs
CH_2 sym str	2885 (45) s
CH_2 scis	1450 (23) s
COH deform	1400 (35) w
C-C-O asym str	1065 (25) s

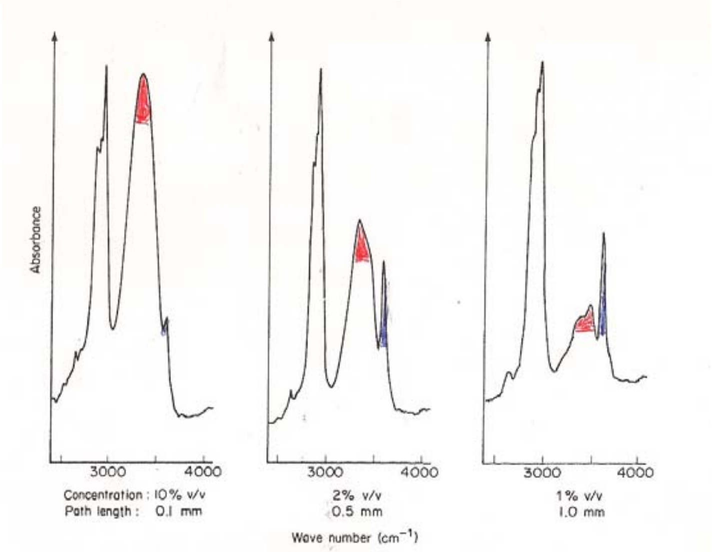
Primary (cm^{-1})	Secondary (cm^{-1})		Tertiary (cm^{-1})
			
3300 (120)	3330 (50)	3370 (30)	3470 (110)



Cyclohexyl
3610 cm^{-1} (free)

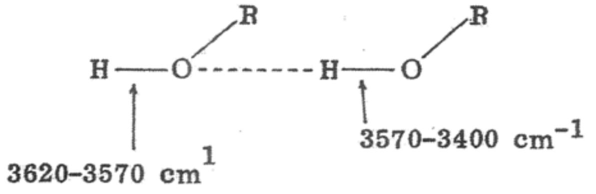


Effect of hydrogen bonding on the OH stretching vibration of isopropanol. (A) Shows the effect of changing the isopropanol concentration in CC$_4$ (M = molar) and compensating for dilution by increasing the cell thickness (given in mm). The number of isopropanol molecules in the spectrometer beam remains constant. The background level is adjusted to prevent overlap. (B) Shows the effect of changing the solvent (benzene, tetrahydrofuran, pyridine, and triethylamime) while 1eaving the isopropanol concentration: (0.05 M) and the cell thickness (1 mm) unchanged.

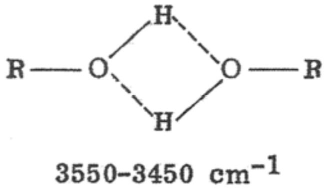


Infrared spectrum of isopropanol solutions in CCl_4In liquid and solid state: dimmers, polymers

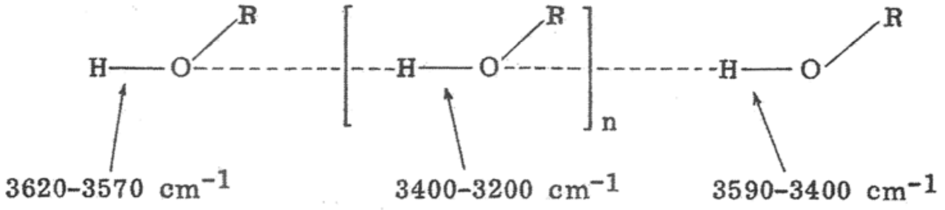
Due to H-bond: – frequency downshift
– intensity enhancement (with H-bond the polarity of OH bond increases)
– band broadening



dimer

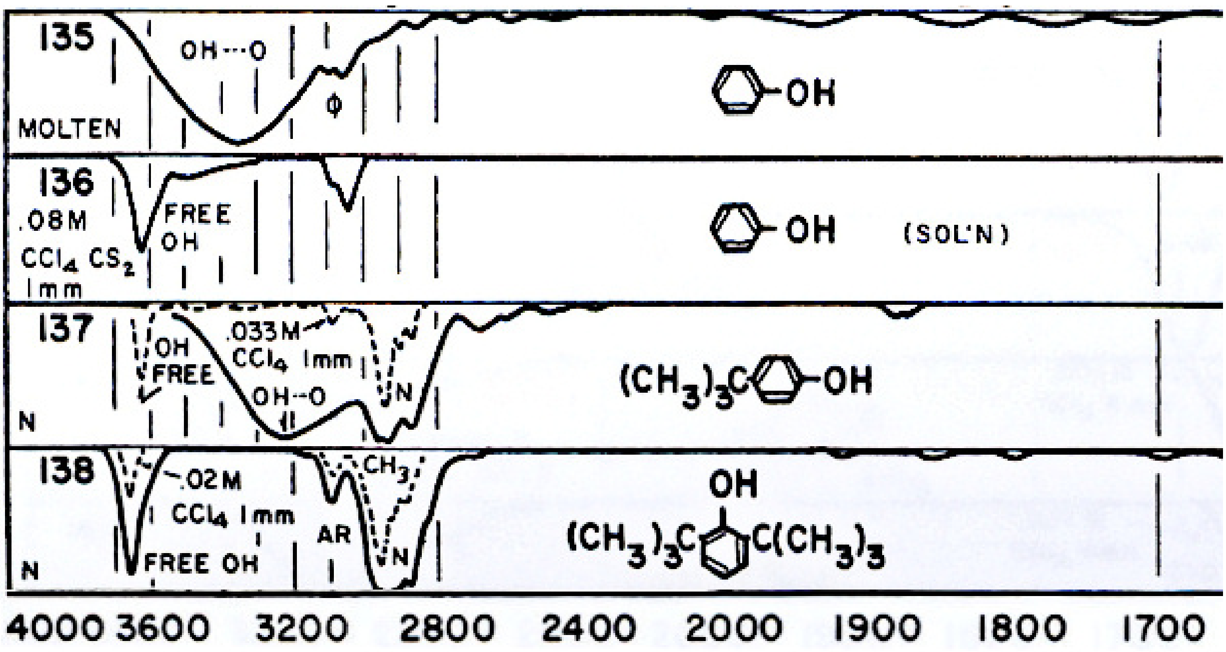


cyclic dimer



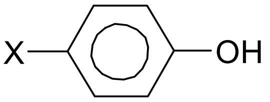
polymer

OH stretching in phenols

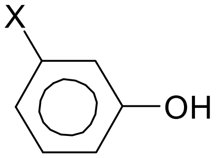


Naphtols

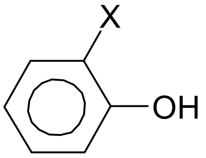
3310 (99) cm^{-1}



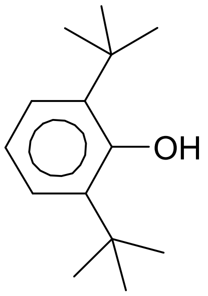
3310 (90) cm^{-1}



3260 (40) cm^{-1}

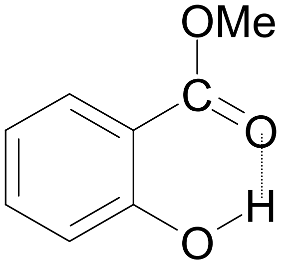


3475 (90) cm^{-1}

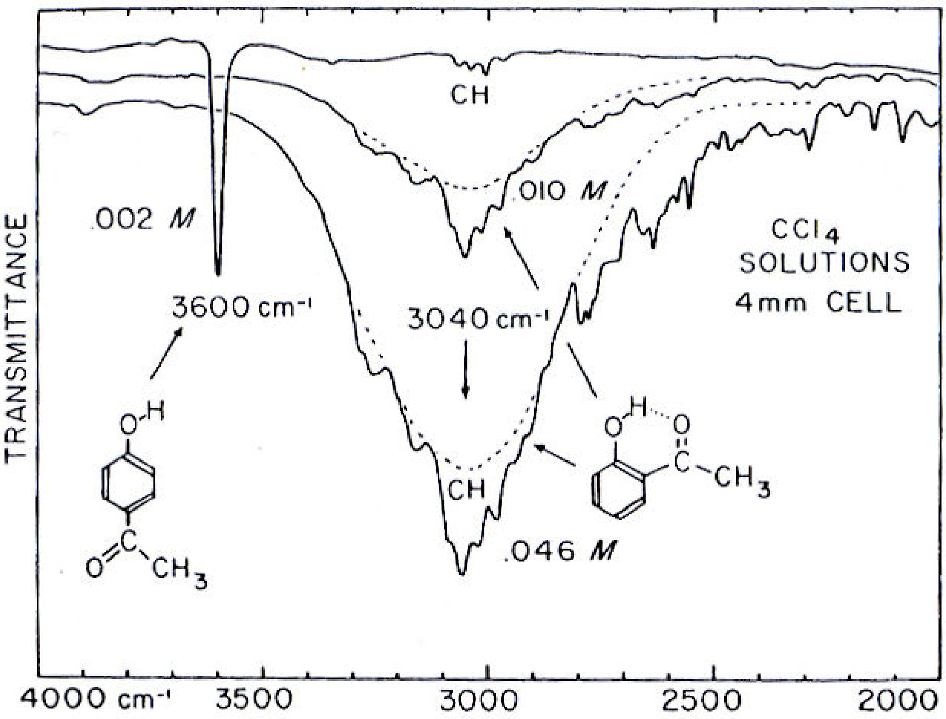


(t-Butyl)
3690 cm^{-1} (free)

Intramolecular hydrogen bonding



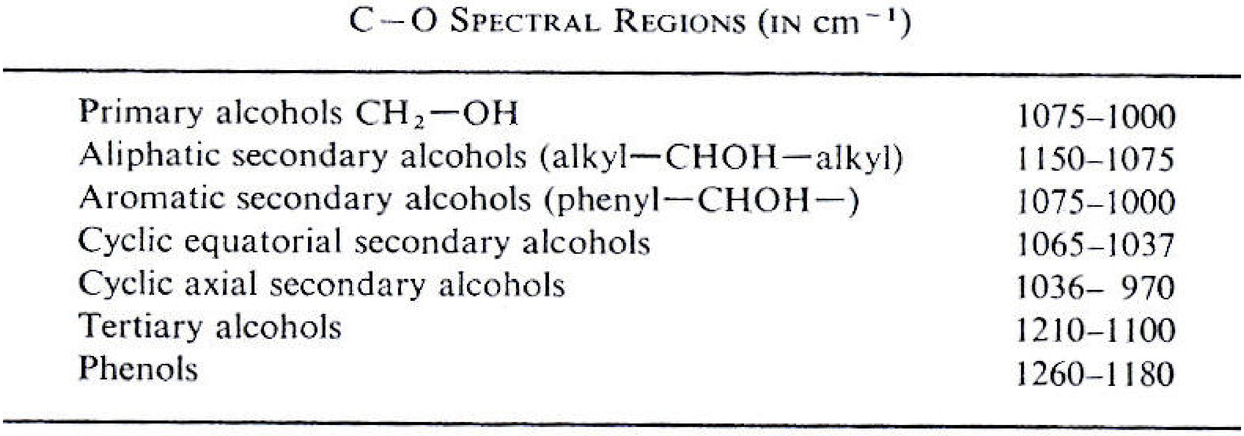
Methyl salicylate



Hydroxyacetophenones are shown in CCl_4 solution in a 4-mm cell. In the *para* isomer the free OH stretch in dilute solution gives rise to a sharp band at 3600 cm^{-1} which is much shifted from the intermolecular bonded OH···O stretch broad band in the solid state at 3130 cm^{-1} (not shown). In the *ortho* isomer the internally bonded OH···O group gives rise to a broad band centring at 3040 cm^{-1} with superimposed CH stretch bands and combination bands intensified by Fermi resonance. The OH···O group remains internally bonded even in dilute solution (shown here in two concentrations) in marked contrast to that for the *para* isomer.

C-O stretch

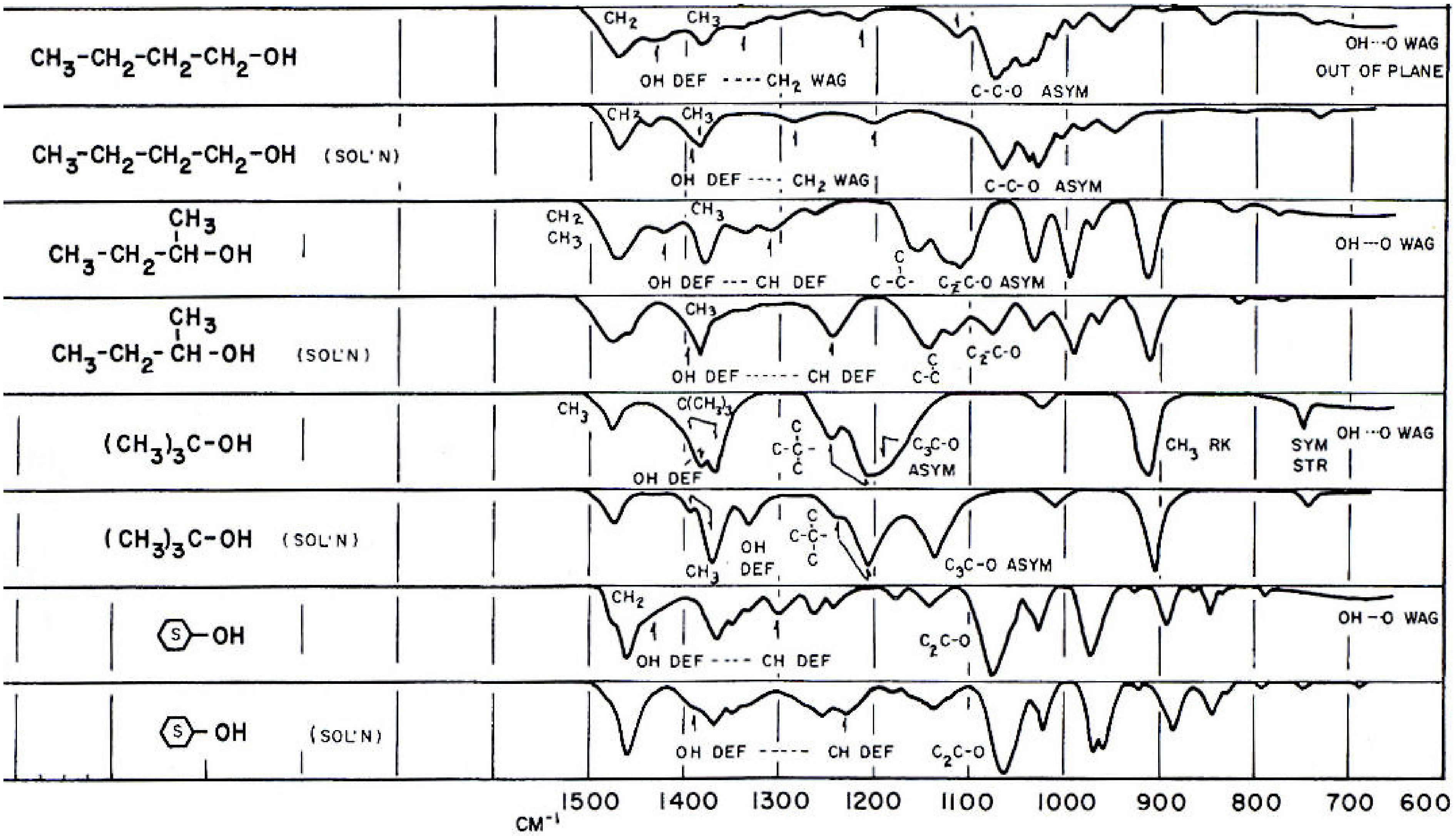
The vibrations involving the stretching of the C-O bond give rise to strong infrared bands

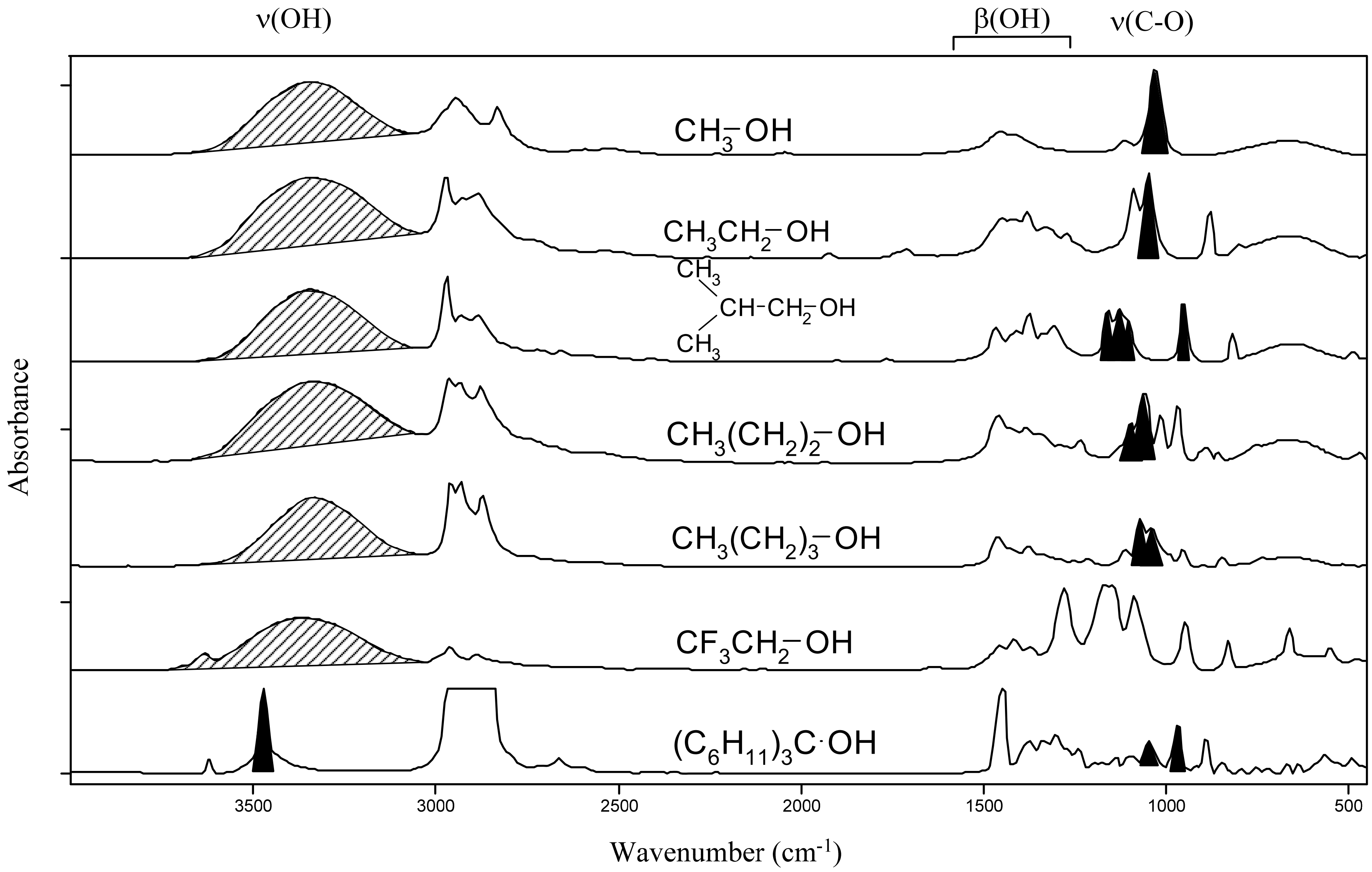


C–O SPECTRAL REGIONS (IN cm^{-1})

Primary alcohols CH_2-OH	1075–1000
Aliphatic secondary alcohols (alkyl—CHOH—alkyl)	1150–1075
Aromatic secondary alcohols (phenyl—CHOH—)	1075–1000
Cyclic equatorial secondary alcohols	1065–1037
Cyclic axial secondary alcohols	1036– 970
Tertiary alcohols	1210–1100
Phenols	1260–1180

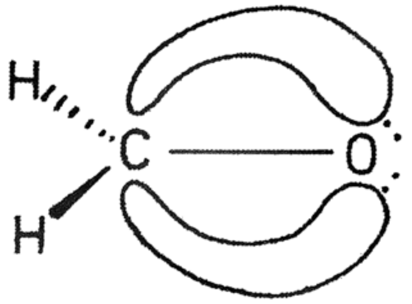
In primary alcohols, this band involves asymmetric C-C-O stretching.

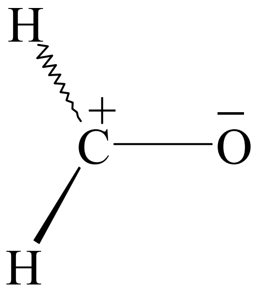

CH3-CH2-CH2-CH2-OH
CH2
CH3
OH DEF ---- CH2 WAG
C-C-O ASYM
OH ···O WAG
OUT OF PLANE
CH3-CH2-CH2-CH2-OH (SOL'N)
CH2
CH3
OH DEF ---- CH2 WAG
C-C-O ASYM
CH3-CH2-CH(CH3)-OH
CH2
CH3
OH DEF --- CH DEF
C-C(C)-
C2C-O ASYM
OH ---O WAG
CH3-CH2-CH(CH3)-OH (SOL'N)
CH3
OH DEF ------ CH DEF
C-C(C)
C2C-O
(CH3)3C-OH
CH3
C(CH3)3
OH DEF
C-C(C)(C)-
C3C-O
ASYM
CH3 RK
SYM
STR
OH ···O WAG
(CH3)3C-OH (SOL'N)
CH3
OH
DEF
C-C(C)(C)-
C3C-O ASYM
S-OH
CH2
OH DEF ---- CH DEF
C2C-O
OH —O WAG
S-OH (SOL'N)
OH DEF ----- CH DEF
C2C-O
1500
1400
1300
1200
1100
1000
900
800
700
600
CM-1


ν(OH)
β(OH)
ν(C-O)
CH3–OH
CH3CH2–OH
CH3
CH–CH2–OH
CH3
CH3(CH2)2–OH
CH3(CH2)3–OH
CF3CH2–OH
(C6H11)3C·OH
Absorbance
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

CARBONYL COMPOUNDS

The **π** -electrons of carbonyl groups due to different electro negativity of carbon and oxygen strongly polarized.



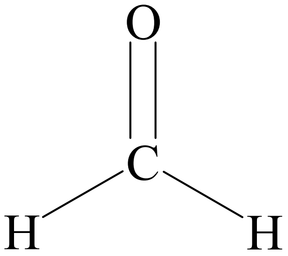


The bonded atoms or groups exhibit strong influence on bond polarity:

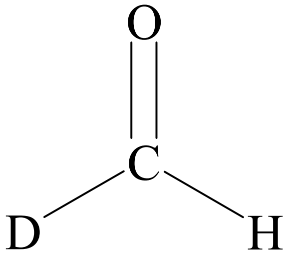
- increasing polarity ($–NH_2$) → decreasing frequency
- decreasing polarity (–Cl) → increasing frequency

The C=O stretching band very strong in the IR spectra generally observed in the 1900 – 1550 cm^{-1} region. Factors influencing band position:

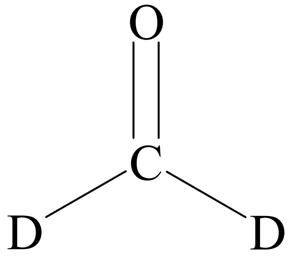
a.) Mass effect



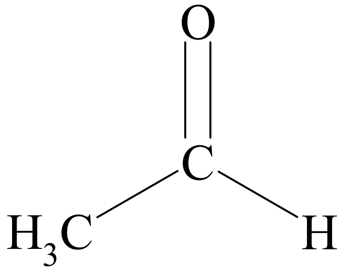
1746 cm^{-1}



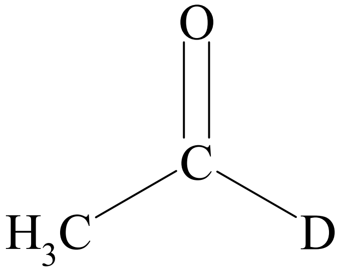
1723 cm^{-1}



1700 cm^{-1} (gas)

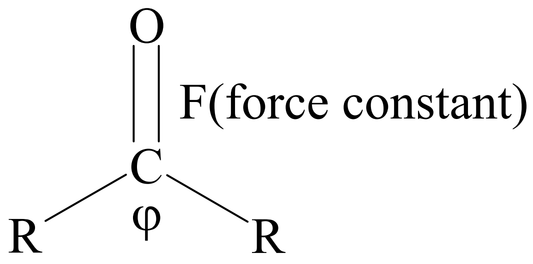


1714 cm^{-1}



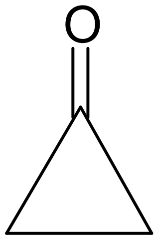
1702 cm^{-1}
(Raman, liquid)

b.) Bond angle effect

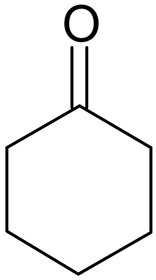


Saturated ketones:
ν (CO) = 1278 + 68F – 2.2φ
F – C=O force constant (Ncm^{-1}), (F = 10.2 Ncm^{-1} for unconjugated ketones)
φ - CCC angle in degrees

Cyclic ketones:



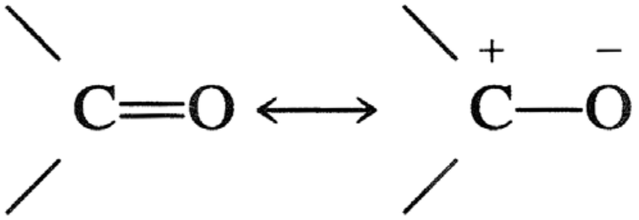
1815 cm^{-1}



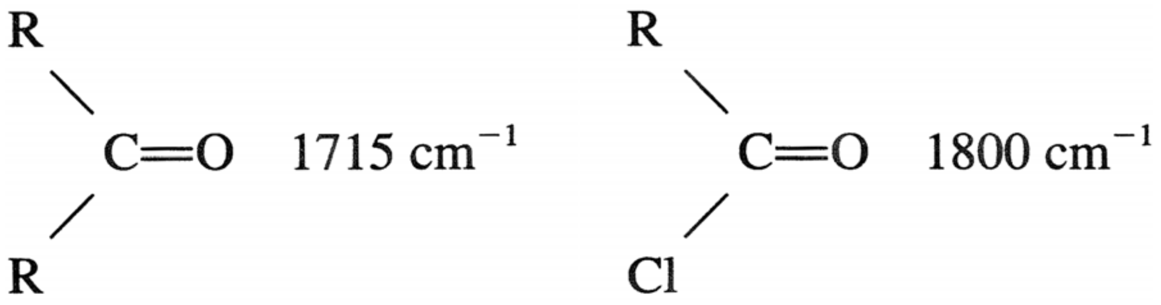
1715 cm^{-1} (normal)

c.) Inductive effect

The tendency of the carbonyl oxygen to attract electrons

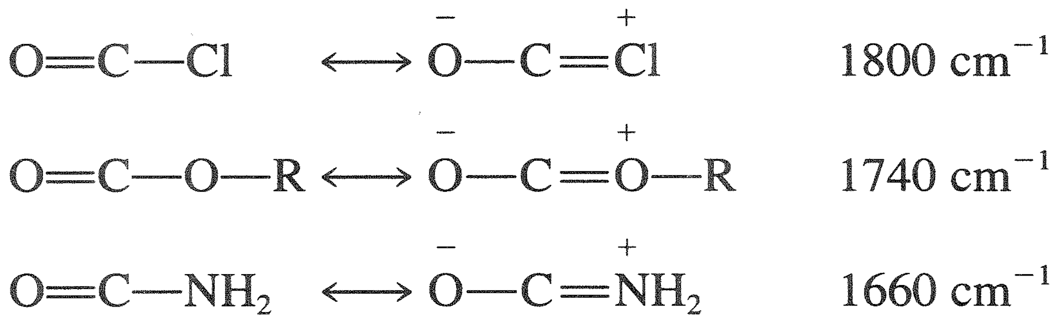


results in a weakening of the C=O force constant and a lowering of the C=O frequency. Electron attracting groups attached to the carbon atom compete with the oxygen for electrons, resulting in less contribution from the polar form and a higher frequency. As an example of this, ketones absorb near 1715 cm^{-1} whereas acid chlorides absorb near 1800 cm^{-1}.



d.) Mesomeric effect

In the mesmeric effect, the **heteroatom** attached to the C=O group donates a non-bonding electron, and the C=O oxygen attracts an electron which weakens the C=O force constant and lowers the frequency.

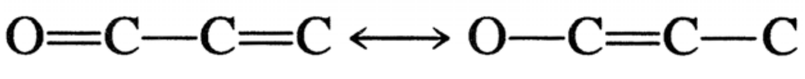


$$O{=}C{-}Cl \longleftrightarrow \overset{-}{O}{-}C{=}\overset{+}{Cl} \qquad 1800\ cm^{-1}$$

$$O{=}C{-}O{-}R \longleftrightarrow \overset{-}{O}{-}C{=}\overset{+}{O}{-}R \qquad 1740\ cm^{-1}$$

$$O{=}C{-}NH_2 \longleftrightarrow \overset{-}{O}{-}C{=}\overset{+}{N}H_2 \qquad 1660\ cm^{-1}$$

Conjugation of carbonyls with double bonds or aromatic rings usually results in a band shift to lower wavenumbers of about 20-30 cm^{-1}, due again to a redistribution of electrons which weakens the C=O bond.



$$O{=}C{-}C{=}C \longleftrightarrow \overset{-}{O}{-}C{=}C{-}\overset{+}{C}$$

Steric effects may remove the co planarity of the conjugated system and thus reduce the effect of conjugation.

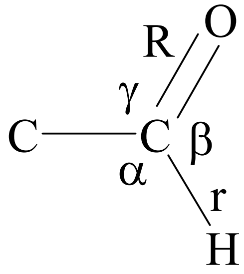
Hydrogen bonding affects carbonyl frequencies, but the largest effects occur when hydrogen bonding is combined with mesomeric effects. When a carbonyl is hydrogen bonded and resonance can occur which puts a partial negative charge on the oxygen atom accepting the hydrogen bond and a partial positive charge on the OH group, the partial bonding of the hydrogen to two atoms enhances resonance and electron delocalization,

$$\mathrm{C{=}O\cdots H{-}O{-}} \longleftrightarrow \mathrm{C{-}}\overset{-}{\mathrm{O}}\mathrm{\cdots H{-}}\overset{+}{\mathrm{O}}{=} \longleftrightarrow \mathrm{C{-}}\overset{-}{\mathrm{O}}\cdots\overset{+}{\mathrm{H}}\quad \mathrm{O}{=}$$

and lowers the C=O frequency. This effect can be seen in o-hydroxy acetophenones, the enol form of acetylacetone types, carboxylic acid dimers, etc.

ALDEHYDES

Internal coordinates



Linear combination of internal coordinates	Approximate frequencies for saturated aldehydes (cm^{-1})
ν (CH) = r	~ 2840
ν (C=O) = R	~ 1755
β(CH) = α – β (def)	~ 1375
γ(CH) = ρ(CCOH) (wag)	~ 865
δ(CCO) = γ	~ 565

Aldehydes are the first representatives of carbonyl containing molecules.

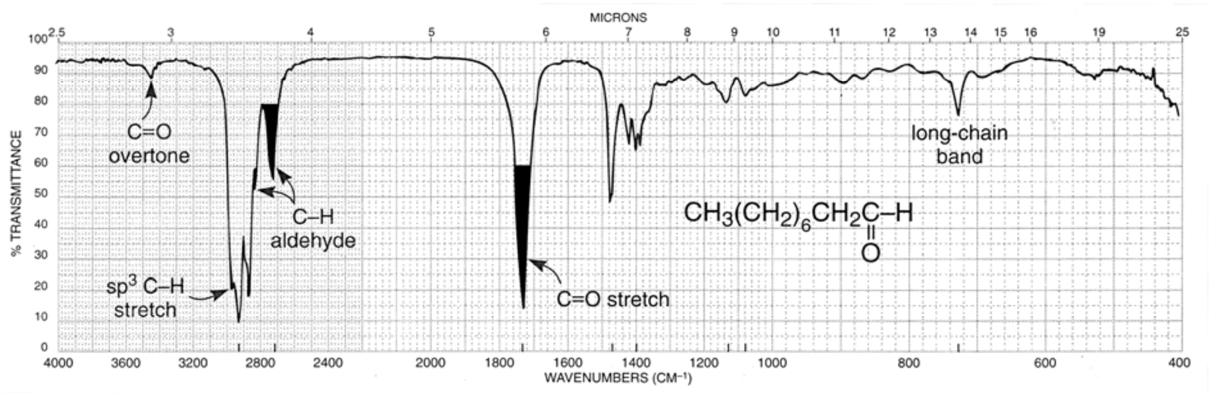
1.) C=O groups can be obtained in a great number of organic molecules.
2.) All C=O stretching modes exhibit very strong bands in the IR spectrum.
3.) The spectral range 1750±200 cm^{-1} is ideal for observation, there are no very strong absorption of other functional groups in this spectral range.

Characteristic vibrations of formyl group (cm^{-1})

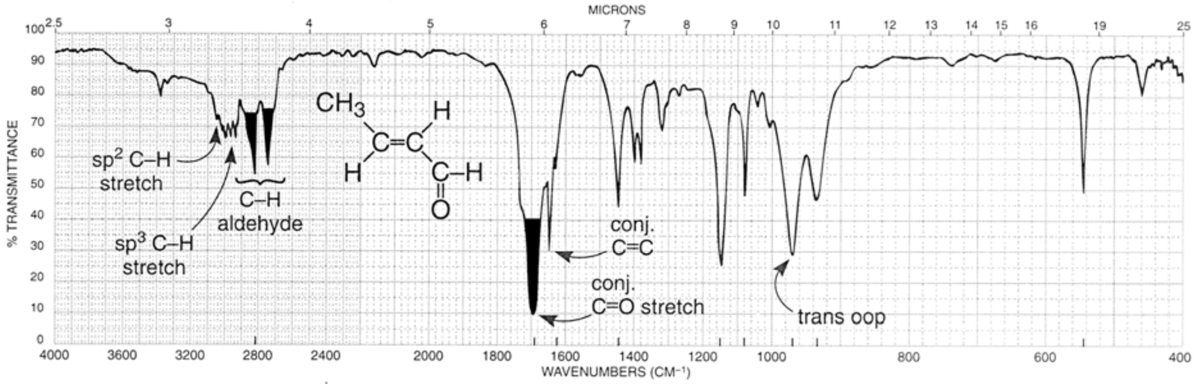
	Saturated	Unsaturated	Aromatic
CH str (s)	2840 (30)	2830 (30)	2850 (45)
2xCH def (s)	2720 (20)	2720 (20)	2755 (35)
C=O str (vs)	1755 (35)	1685 (35)	1690 (30)
CH def (w)	1375 (25)	1380 (25)	1380 (25)
CH wag (vw)	865 (125)	860 (150)	865 (145)
C–C=O def (vw)	565 (100)	640 (100)	645 (55)

C=O stretch at approximately 1755 cm^{-1} is common. Conjugation moves the absorption to lower frequency, close to 1700 cm-1.

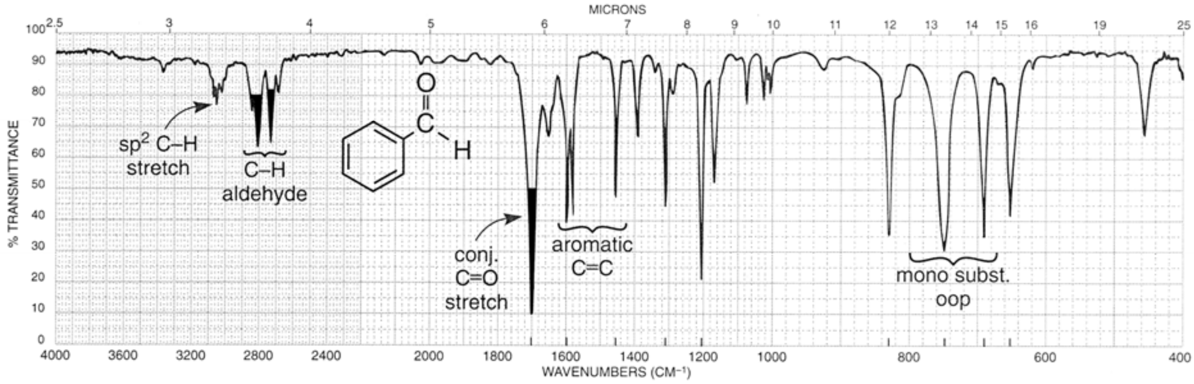
CH stretch, aldehyde hydrogen (–CHO) consist of medium / strong bands at about 2840 and 2750 cm^{-1}. Note that the CH stretch in alkyl chains does not usually extend to frequencies as low as 2750 cm^{-1}.



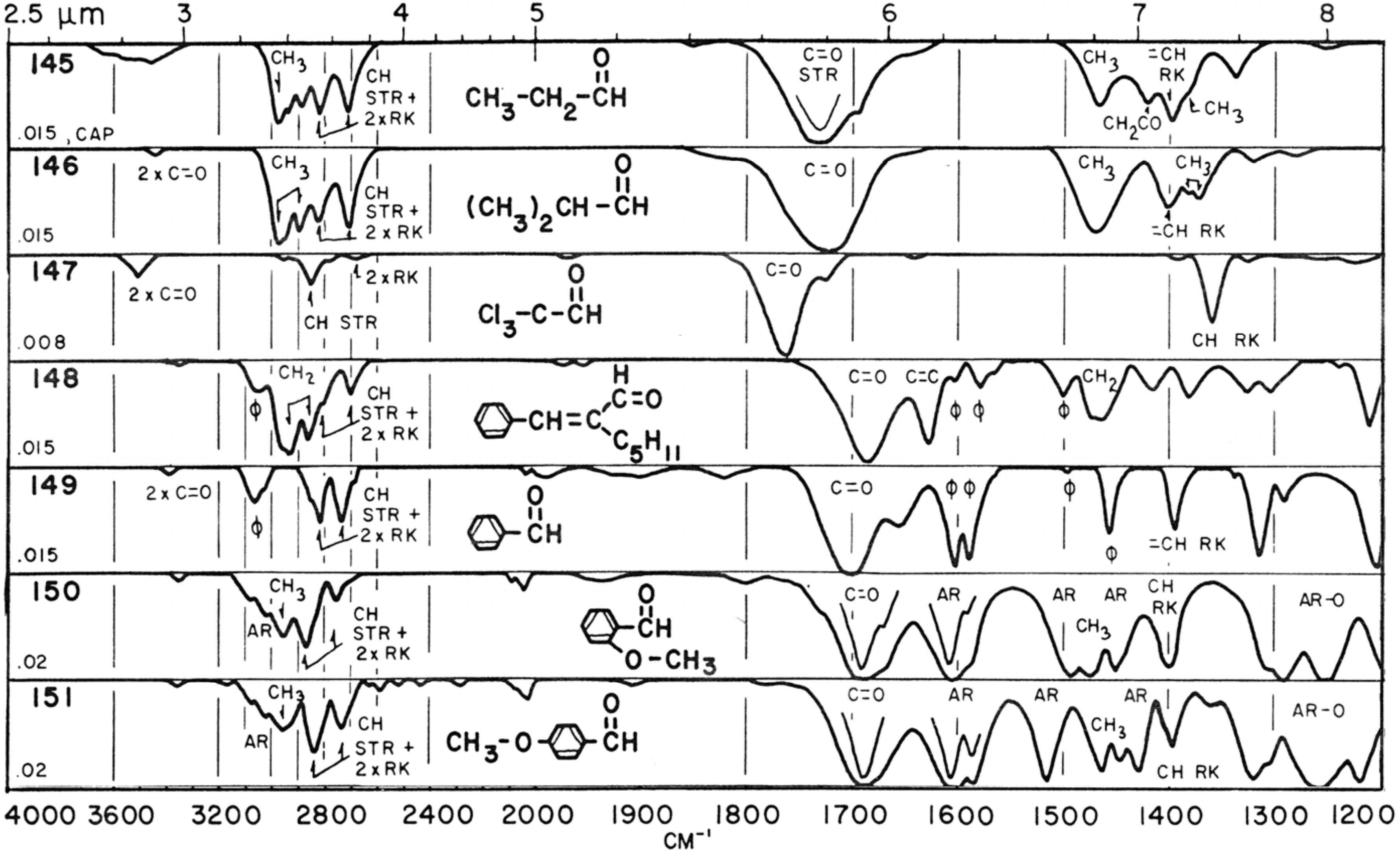
The infrared spectrum of nonanal (neat liquid, KBr plates)



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



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


2.5 µm
3
4
5
6
7
8
145
.015 , CAP
CH3
CH STR + 2 x RK
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}H$
C=O STR
CH3
=CH RK
CH2CO
CH3
146
.015
2 x C=O
CH3
CH STR + 2 x RK
$(CH_3)_2CH-\overset{O}{\overset{\|}{C}}H$
C=O
CH3
CH3
=CH RK
147
.008
2 x C=O
2 x RK
CH STR
$Cl_3-C-\overset{O}{\overset{\|}{C}}H$
C=O
CH RK
148
.015
CH2
ϕ
CH STR + 2 x RK
C=O
C=C
ϕ ϕ
ϕ
CH2
149
.015
2 x C=O
ϕ
CH STR + 2 x RK
C=O
ϕϕ
ϕ
ϕ
=CH RK
150
.02
CH3
AR
CH STR + 2 x RK
O-CH3
C=O
AR
AR
AR
CH RK
CH3
AR-O
151
.02
CH3
AR
CH STR + 2 x RK
CH_3-O-
C=O
AR
AR
AR
CH3
CH RK
AR-O
4000
3600
3200
2800
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
CM⁻¹

Aldehyde CH Vibration

In most aldehydes with alkyl groups or aromatic ring next to the carbonyl, the aldehyde CH give rise to two bands at 2900–2800 and 2775–2695 cm^{-1} and to a band at 1410–1380 cm^{-1}. The 1390 cm^{-1} band is assigned to the in plane hydrogen rocking vibrations.

Aliphatic aldehydes have bands at 2840(30) and 2720(20) cm^{-1}. Some *ortho*-substituted benzaldehydes with substituents such as halogen, nitro or metoxy absorb at 2880(20) and 2760(10) cm^{-1}, these regions differing somewhat from all other benzaldehydes due to possibly to a steric effect.

The two bands in the CH stretch region where only one fundamental is expected is most satisfactorily explained as an interaction of the CH stretch fundamental with the overtone of the CH bending vibration near 1390 cm^{-1}. This must involve Fermi resonance of the overtone with the fundamental, which means that both bands near 2830 and 2740 cm^{-1} involve aldehyde CH stretch and both bands involve the overtone of the 1390 cm^{-1} CH deformation.

Aldehyde Carbonyl Vibration

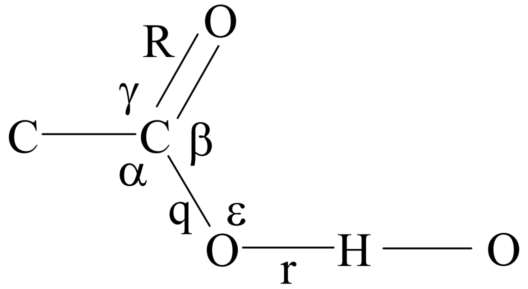
The most intense band in the aldehyde spectrum is usually due to the carbonyl stretching vibration. Most aliphatic aldehydes absorb strongly at 1755(30) cm^{-1}. Most aromatic aldehydes absorb at 1690(30) cm^{-1}. Salicyl-aldehyde absorbs at 1666 cm^{-1} due to conjugated internal hydrogen bonding as in the *ortho*-hydroxyphenones. As with other carbonyl compounds conjugation lowers the frequency. The chloro acetaldehydes in CCl4 absorbes as follows:

Cl_3CCHO	Cl_2HCCHO	ClH_2CCHO
1768 cm^{-1}	1748 cm^{-1}	1730 cm^{-1}

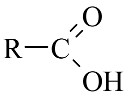
No doubling is observed as in the ketones.

CARBOXYLIC ACIDS, ANHYDRIDES, ESTERS

Internal coordinates



ρ(oop of C(C=O)C)
τ(C–C–O–H) torsion

Linear combination of internal coordinates	Absorption region (cm^{-1})  (R=aliphatic)
ν(OH…O) = r	3050(50)
ν(C=O) = R	1735(50)
δ(OH…O) = ε	1395(55)
ν(C–O) = q	1245(75)
γ(OH…O) = τ	905(75)
δ(OCO) = $2\beta - \alpha - \gamma$	705(75)
γ(C=O) = ρ(oop)	580(100)
δ(COO) = $2\alpha - \beta - \gamma$	465(80)

General characterisation of – C(=O)OH group.

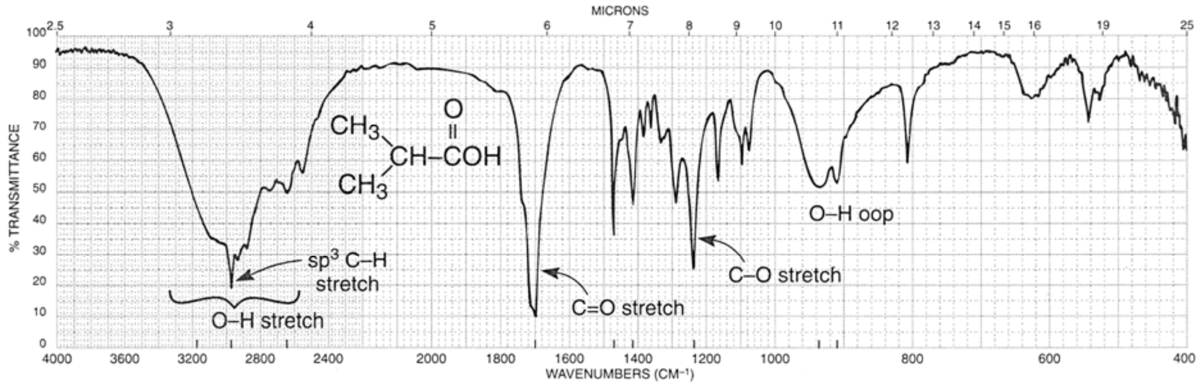
O–H	Stretch, usually very broad (strong H–bonded), occurs at 3050(50) cm^{-1} and often overlaps the C–H absorptions.
C=O	Stretch, usually occurs at 1735(50) cm^{-1}. Conjugation moves the absorption to a lower frequency.
C–O	Stretch occurs at 1245(75) cm^{-1}, medium intensity.
OH···O	Out of plain deformation at 905(65) cm^{-1}.

The –C(=O)OH group has the following IR vibration (cm^{-1})
(in dimeric form)

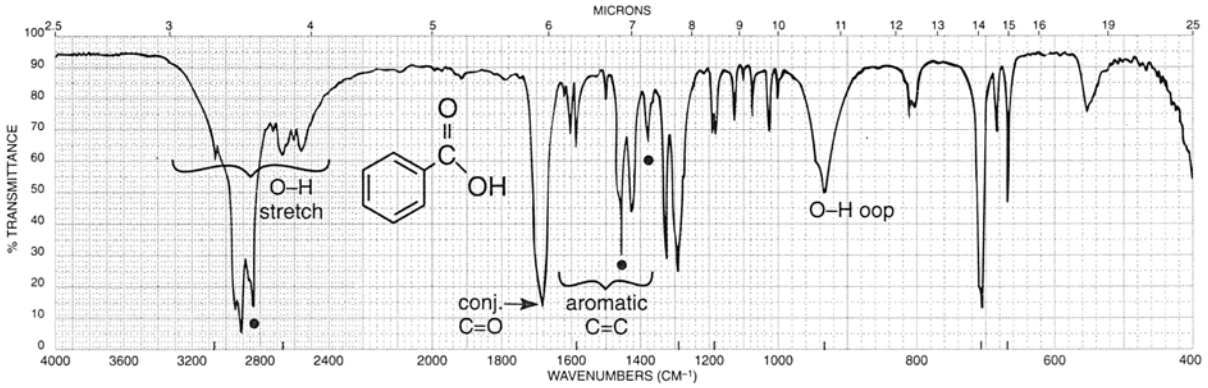
	Aliphatic	Aromatic
ν(OH···O)	[a]**3050**(50) s, vb	**2950**(50) m, b
ν(C=O)	**1735**(50) vs	**1680**(20) vs
δ(OH···O) (i.p.)	1395(55) w	1415(25) w*
ν(C–O)	**1245**(75) m, s	**1300**(30) s, m
γ(OH···O) (o.o.p.)	**905**(65) m, b	**900**(50) m
δ(C=O)	705(75) vw	770(50) vw*
γ(C=O)	580(100) w, m	660(55) w*
ρ(COO)	465(80) w	530(35) w

*Bands can be overlap with aromatic ring vibrations
[a]Well defined characteristic bands are in bold.

Next figure shows typical IR spectrum of aliphatic (isobutiric) and aromatic (benzoic) acids.



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



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

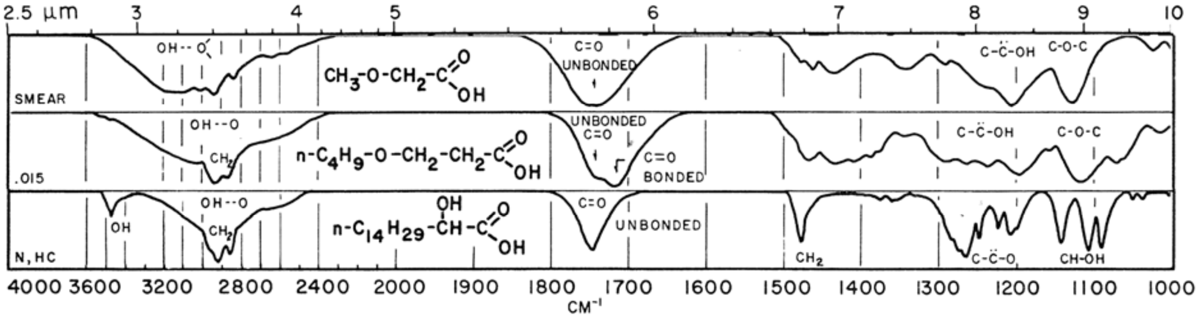
Monomer acids

Measurement: a) in vapour state (at ~150°C)
b) in diluted nonpolar solvent (CCl_4) solution

The “free”OH stretching vibration absorbs sharply and weakly at~3520(30) cm^{-1}.

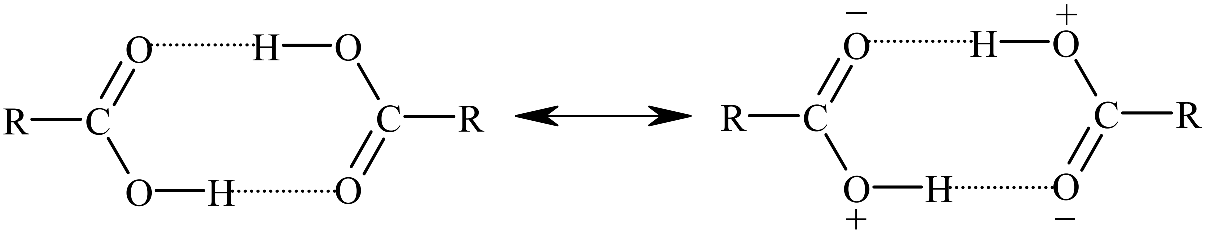
Spectral Regions of Monomer Carbonyls (in cm^{-1})

OH stretch	3520(30) w, sharp
C=O stretch	1770(30) vs
C–OH deformation (i.p.)	1230(50) m
C–O stretch	1130(60) s
C–OH deformation (o.o.p)	820(30) m, b



Dimeric acids

Carboxylic acids with no other polar groups in the molecule usually exist predominantly as the hydrogen bonded dimmer, even in CCl_4 solution although some acids exist at least partially in the hydrogen-bonded polymeric form.

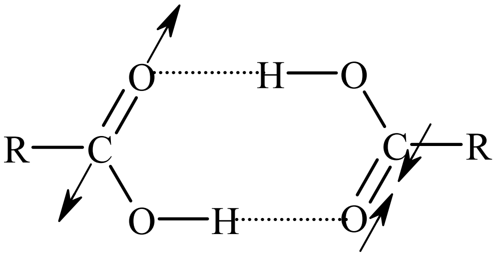


When dimer is considered:

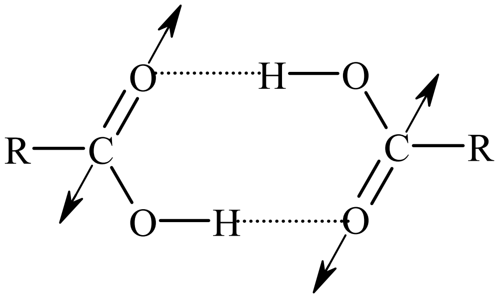
a) two carbonyl stretchings will be

b) a center of symmetry (i) formed

c) ν_a(C=O) will be only IR and ν_s(C=O) will be only Raman active.



ν_a(C=O)
~1700 cm^{-1}



ν_s(C=O)
~1660 cm^{-1}

about 40 cm^{-1} splitting

Cl_3C-COOH dimer

IR band: 1742 cm^{-1}

Raman band: 1687 cm^{-1}

Characteristic combination bands:

between 2700 and 2500 cm^{-1} due to
overtones 1420 → 2840 cm^{-1} →2x $\delta(OH\cdots O)$
overtones 1300 → 2600 cm^{-1} →2x $\nu(C–O)$
combination 1420+1300 → 2720 cm^{-1} →$\delta(OH\cdots O) + \nu(C–O)$

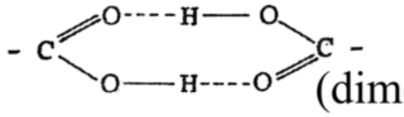
$\delta(OH\cdots O)$ $\nu(C–O)$

Strongly interacting vibrations

The C=O stretch depends on the state of the sample and solvent polarity

Gas

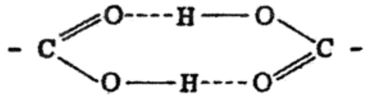
-COOH (monomer)



(dimer)

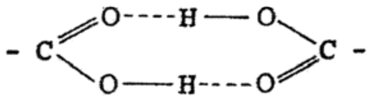
ν = 1780 cm^{-1} ν_a = 1730 cm^{-1}

Liquid



ν_a = 1710 cm^{-1}

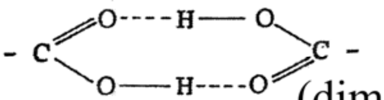
Solid



ν_a = 1750 cm^{-1}

In apolar solvent

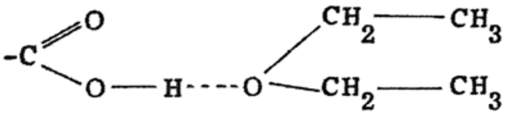
-COOH (monomer)



(dimer)

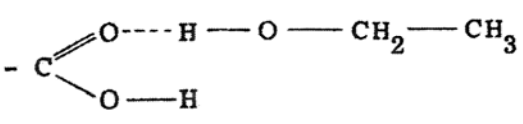
ν = 1760 cm^{-1} ν_a = 1710 cm^{-1}

In ether solution

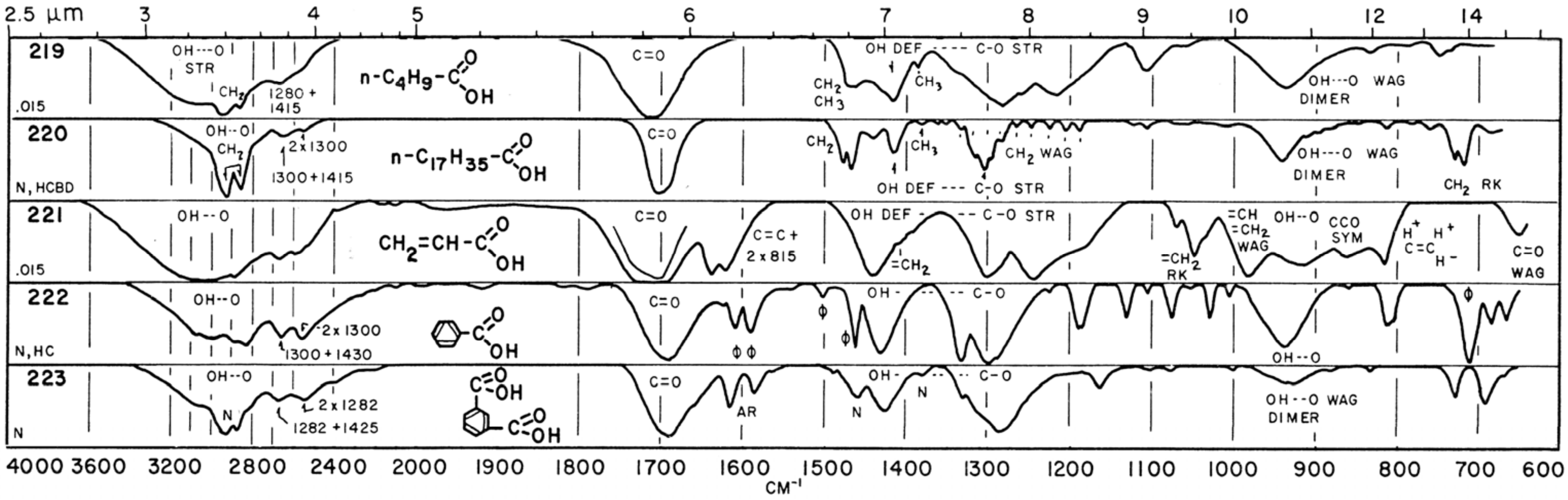


ν = 1735 cm^{-1}

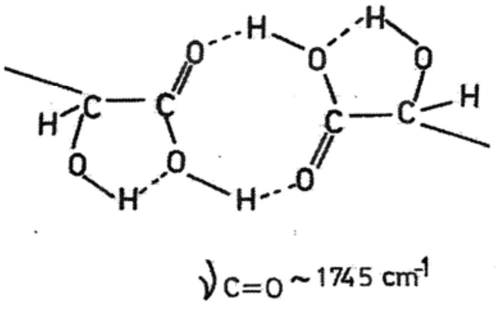
In alcohol solution



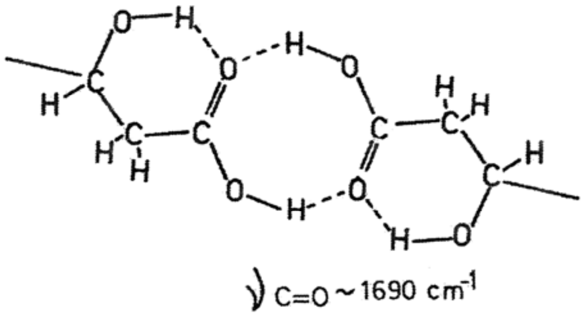
ν = 1720 cm^{-1}


2.5 µm
3
4
5
6
7
8
9
10
12
14
219
.015
OH---O STR
CH2
1280 + 1415
$n-C_4H_9-C(=O)OH$
C=O
OH DEF ---- C-O STR
CH2 CH3
CH3
OH---O WAG DIMER
220
N, HCBD
OH--O
CH2
2x1300
1300+1415
$n-C_{17}H_{35}-C(=O)OH$
C=O
CH2
CH3
CH2 WAG
OH DEF --- C-O STR
OH---O WAG DIMER
CH2 RK
221
.015
OH--O
$CH_2=CH-C(=O)OH$
C=O
C=C + 2x815
OH DEF ---- C-O STR
=CH2
=CH2 RK
=CH =CH2 WAG
OH--O
CCO SYM
H+ H+ C=C H-
C=O WAG
222
N, HC
OH--O
2x1300
1300+1430
OH
C=O
ϕ ϕ
ϕ
ϕ
OH- ---- C-O
OH--O
ϕ
223
N
OH--O
N
2x1282
1282+1425
C=O OH
C=O OH
C=O
AR
OH- N -- C-O
N
OH--O WAG DIMER
4000 3600 3200 2800 2400 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600
CM⁻¹

Dimer associates in a – and b – hydroxyl carboxylic acides:



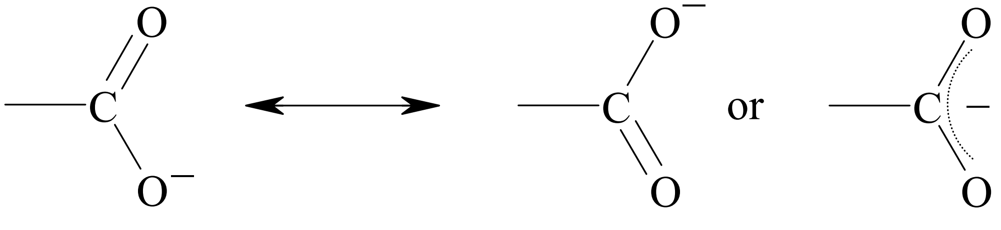
α–hydroxy
hydrogen bond to
carbonyl OH
(ν(CO) moves upwards)

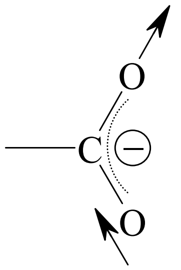


β–hydroxyl
two H – bonds to
carboxylic oxygen
(ν(CO) is strongly shifted
to lower cm^{-1})

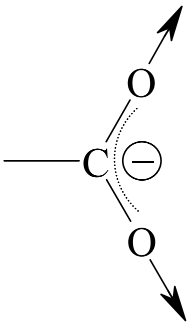
Carboxyl salts and complexes

When a salt is made from a carboxylic acid, the C=O and C–O are replaced by two equivalent carbon-oxygen bonds which are intermediate in force constant between the C=O and C–O.



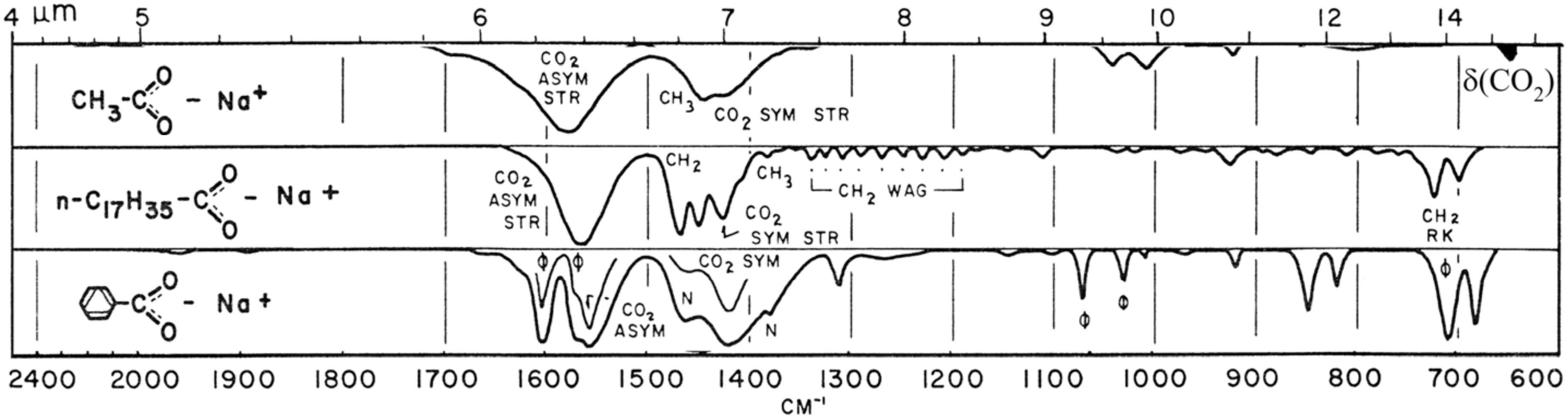


$\nu_a\,(CO_2)$
strong IR
1600 (50) cm^{-1}

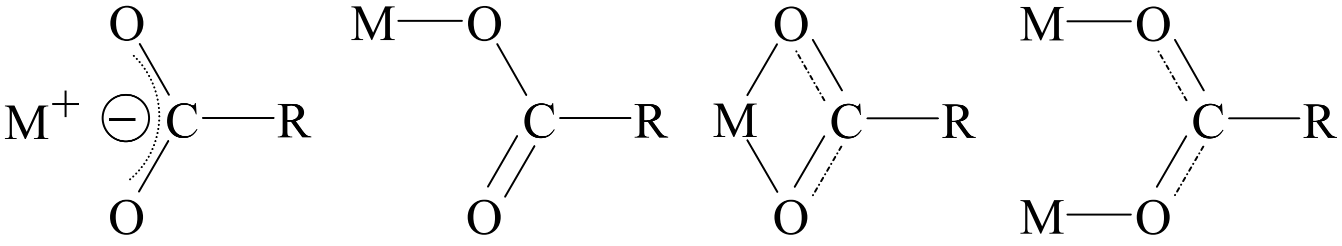


$\nu_s\,(CO_2)$
medium, week IR/
strong Raman
1400 (50) cm^{-1}

HCOONa	CH_3COONa	Assignment
2841 w	-	$\nu(CH)$
1567 vs	1578 vs	$\nu_a\,(CO_2)$
1366 s,m	1411 s,m	$\nu_s\,(CO_2)$
722 w	646 w	$\delta(CO_2)$
-	615 w	$\omega\,(CO_2)$
-	460 w	$\rho\,(CO_2)$


4 µm
5
6
7
8
9
10
12
14
CH3-C(=O)O - Na+
CO2 ASYM STR
CH3
CO2 SYM STR
δ(CO2)
n-C17H35-C(=O)O - Na +
CO2 ASYM STR
CH2
CH3
CO2 SYM STR
CH2 WAG
CH2 RK
C6H5-C(=O)O - Na +
Φ
Φ
Γ
CO2 ASYM
N
CO2 SYM
N
Φ
Φ
Φ
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CM⁻¹

The carboxylate ion may coordinate to a metal in one of the following modes:



Ionic	unidentate	bidentate	bridging
$\Delta\nu$ (CO_2)	$\Delta\nu$ (CO_2)	$\Delta\nu$ (CO_2)	$\Delta\nu$ (CO_2)
180 (20) cm^{-1}	340 (100) cm^{-1}	120 (80) cm^{-1}	160 (30) cm^{-1}

(1) Unidentate complexes (structure I) exhibit Δ values $[\nu_a\,(CO_2^-) - \nu_s(CO_2^-)]$ that are much greater than the ionic complexes.

(2) Chelating (bidentate) complexes (structure II) exhibit Δ values that are significantly less than the ionic values.

(3) The Δ values for bridging complexes (structure III) are greater than those of chelating (bidentate) complexes, and close to the ionic values.

Carboxyl Stretching Frequencies and Structures of Carboxylate Complexes (cm^{-1})

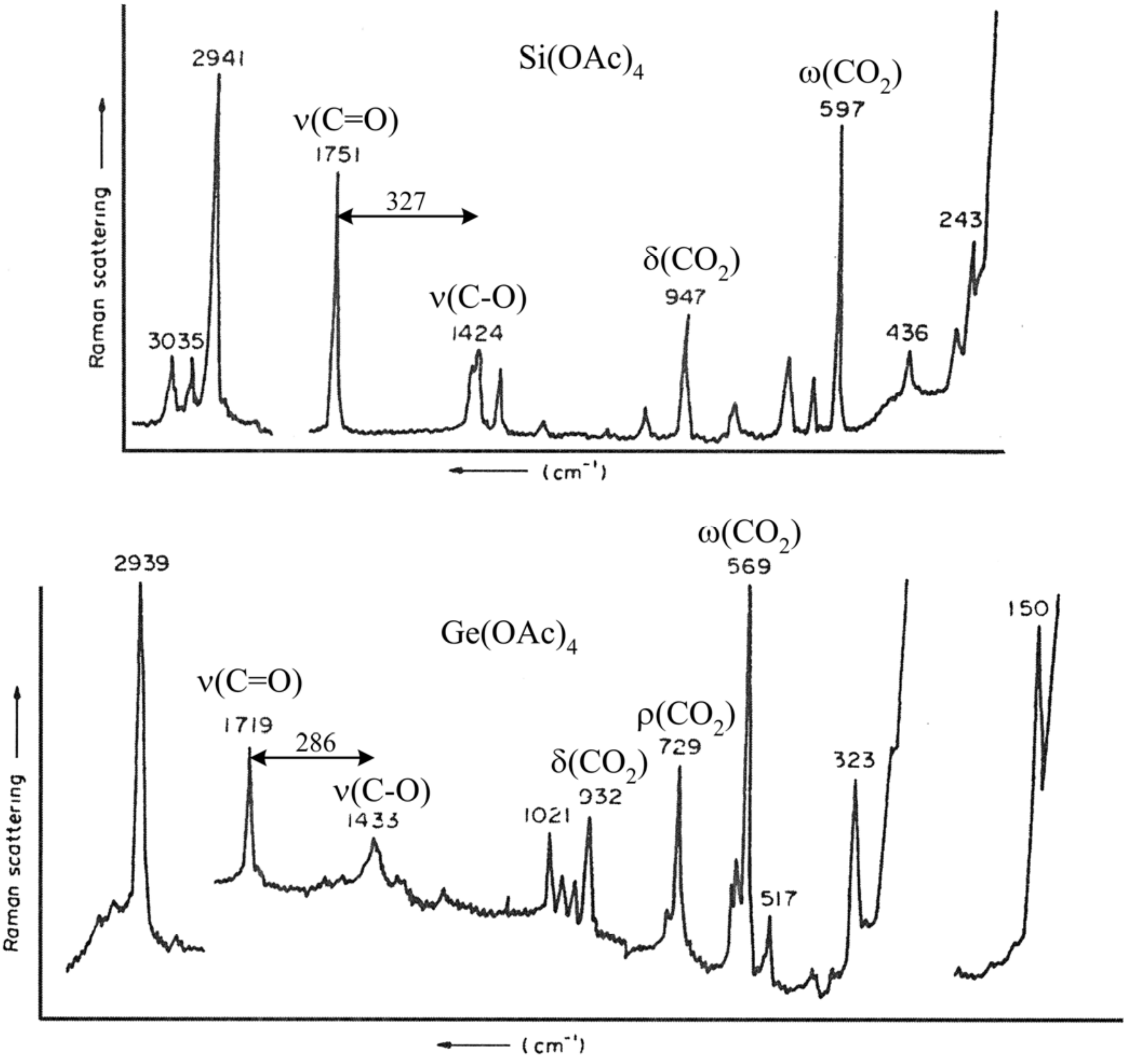
Compound	$\nu_a(COO)^a$	$\nu_s(COO)^a$	Δ	Structure
$HCOO^-$	1567	1366	201	Ionic
CH_3COO^- (OAc^-)	1578	1414	164	Ionic
$Rh(OAc)(CO)(PPh_3)_2$	1604	1376	228	Unidentate
$Ru(OAc)(CO)_2(PPh_3)$	1613	1315	298	Unidentate
$Si(OAc)_4$	1745^b	1290^b	455	Unidentate
$Ge(OAc)_4$	1710^b	1280^b	430	Unidentate
$RuCl(OAc)(CO)(PPh_3)_2$	1507	1465	42	Bidentate
$RuH(OAc)(PPh_3)_2$	1526	1449	77	Bidentate
$Ph_2Sn(CH_3-COO)_2$	1610	1335	265	Asym. bidentate
$Ph_2Sn(CH_2Cl-COO)_2$	1620	1240	380	Asym. bidentate
$Ph_2Te(CCl_3-COO)_2$	1705	1270	435	Asym. bidentate
$Rh_2(OAc)_2(CO)_3(PPh_3)$	1580	1440	140	Bridging
$[Ru(CO)_2(C_2H_5COO)]_n$	1548	1410	138	Bridging
$[Cr_3O(OAc)_6(H_2O_3)]^+$	1621	1432	189	Bridging
$[Mn_2O_2(OAc)]^{2+}$	1548	1387	171	Bridging
$[Pd(OAc)_2(PPh_3)]_2$	1629	1314	315	Unidentate
	1580	1411	169	Bridging
$CrO_2(OAc)_2$	1710	1240	470	Unidentate
	1610	1420	190	Bidentate
$Cp_2Zr[Cr(CO)_3(RCOO)]_2{}^c$	1641	1329	312	Unidentate
	1542	1377	165	Bidentate

---

[a] These correspond to the $\nu(C{=}O)$ (free) and $\nu(C{-}O)$ (coordinated) of the unidenlate carboxylates, respectively.

[b] IR frequency.

[c] $R = C_6H_5$.

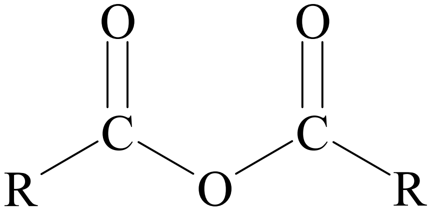
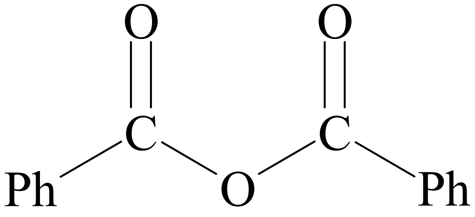
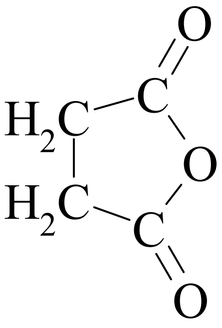
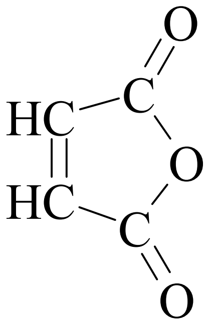


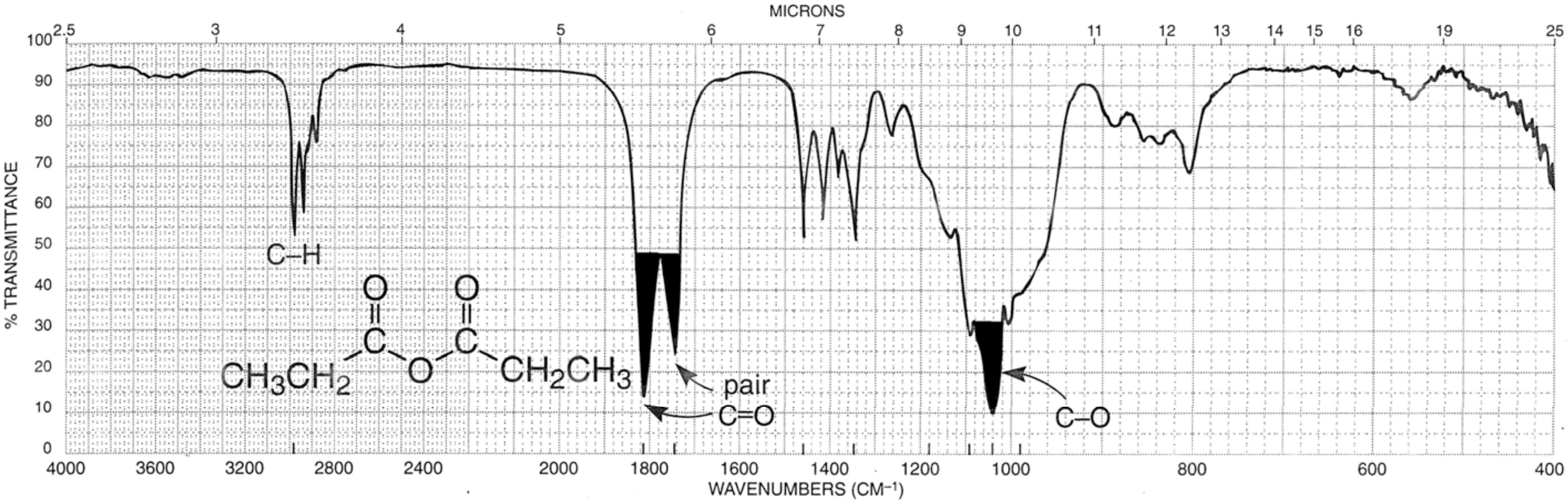
Raman spectra of Si(OAc)$_4$ and Ge(OAc)$_4$ in the solid state

(514.5 nm excitation) - (unidentate coordination)

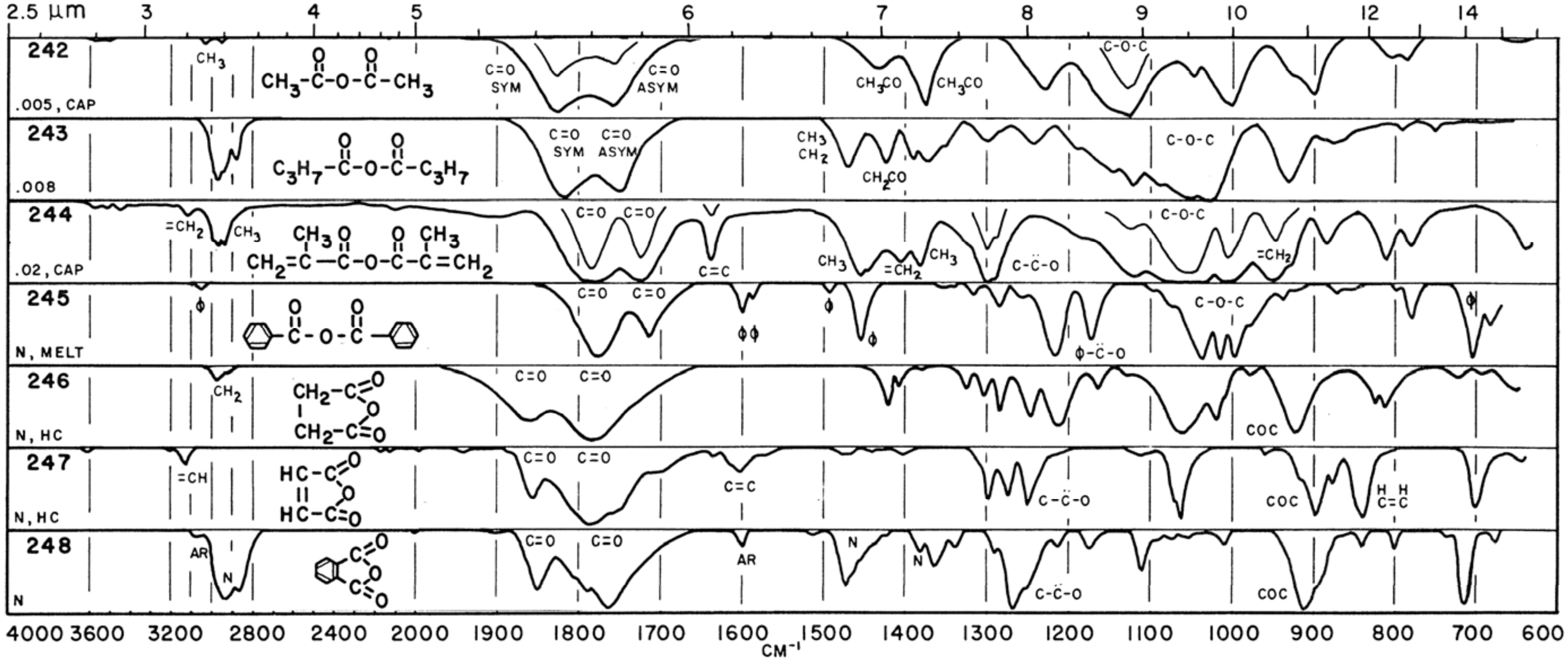
ANHYDRIDES

Structure:

	 unconjugated	 Conjugated	 cyclic	 cyclic conjugated
ν_a (C=O)	~1820 vs	~ 1770 vs	1860 (15) s	~1850 s
ν_s (C=O)	~1750 s	~1720 s	1790 (10) vs	~1770 vs
ν_a (C–O– C)	1080 (40) s,b	~1030 (20)s,b	~920 s	~900 s

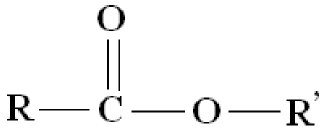


The infrared spectrum of propionic anhydride (neat liquid, KBr plates).


2.5 µm
3
4
5
6
7
8
9
10
12
14
242
.005, CAP
CH3
$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$
C=O SYM
C=O ASYM
CH3CO
CH3CO
C-O-C
243
.008
$C_3H_7-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_3H_7$
C=O SYM
C=O ASYM
CH3 CH2
CH2CO
C-O-C
244
.02, CAP
=CH2
CH3
$CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$
C=O
C=O
C=C
CH3
=CH2
CH3
C-C̈-O
C-O-C
=CH2
245
N, MELT
ϕ
C=O
C=O
ϕϕ
ϕ
ϕ
ϕ-C̈-O
C-O-C
ϕ
246
N, HC
CH2
C=O
C=O
COC
247
N, HC
=CH
C=O
C=O
C=C
C-C̈-O
COC
H H C=C
248
N
AR
N
C=O
C=O
AR
N
N
C-C̈-O
COC
4000
3600
3200
2800
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CM⁻¹

ESTERS

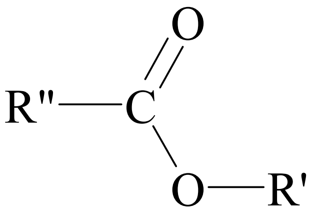
C=O Stretch occurs in the range 1750-1735 cm^{-1} in normal esters. Conjugation in R part moves the absorption to a lower frequency; conjugation with the O in the R′ part moves the absorption to a higher frequency. Ring strain in cyclic esters (lactones) moves the absorption to a higher frequency.



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

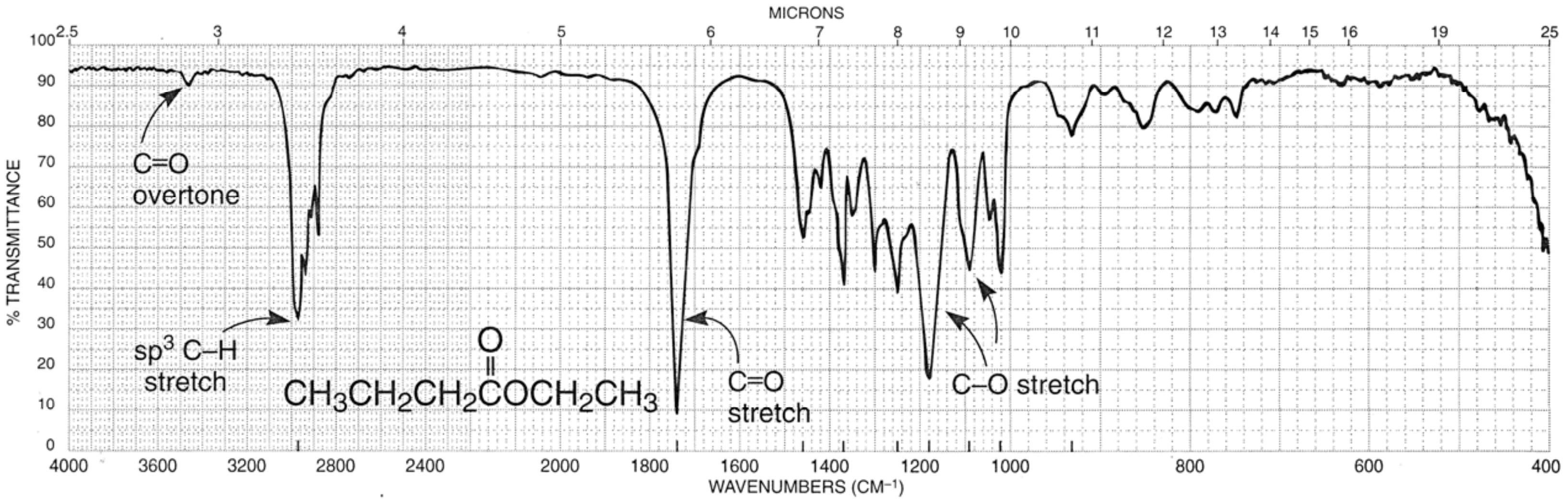
C–O Strech in two or more bands, one stronger and broader than the other, occurs in the range 1300-1000 cm^{-1}.

Characteristic vibrations of ester groups

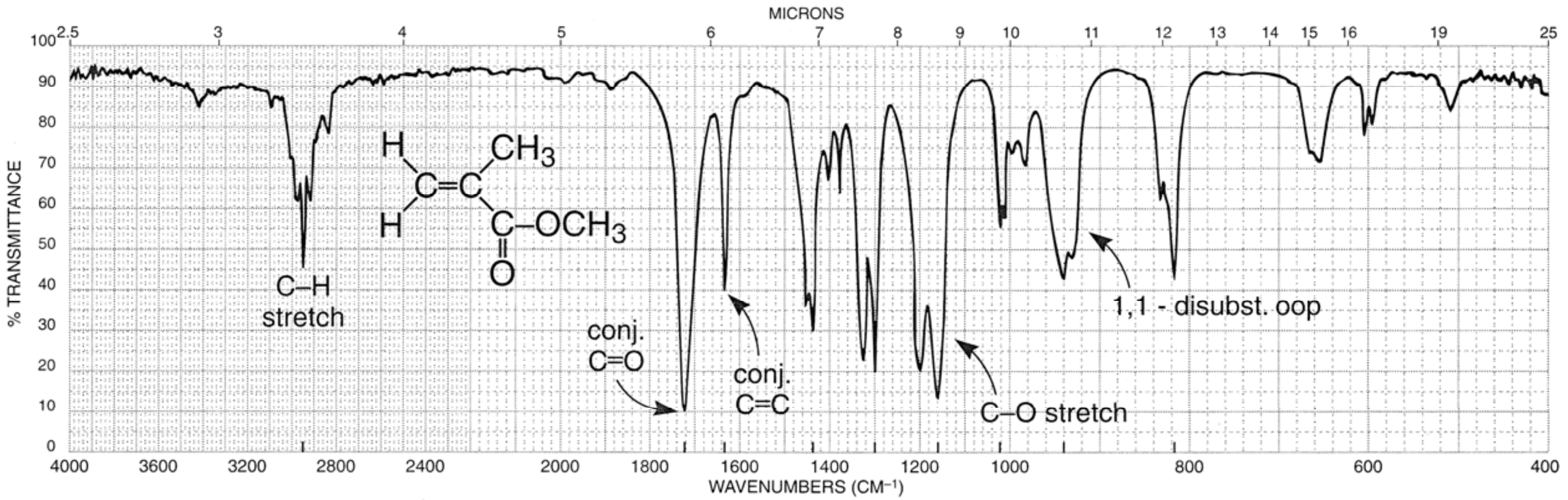
	Assignment
1750 (50) vs*	ν(C=O)
1255 (60) s, vs	ν(C–O) carboxyl
1000 (100) m	ν(C–O) (R′)**
700 (110) w	δ(C=O), i.p.
630 (130) vw	γ(C=O) o.o.p
430 (80) vw	ρC(=O)–O
320 (70) w	δ (COC)

*Characteristic strong bands are bold

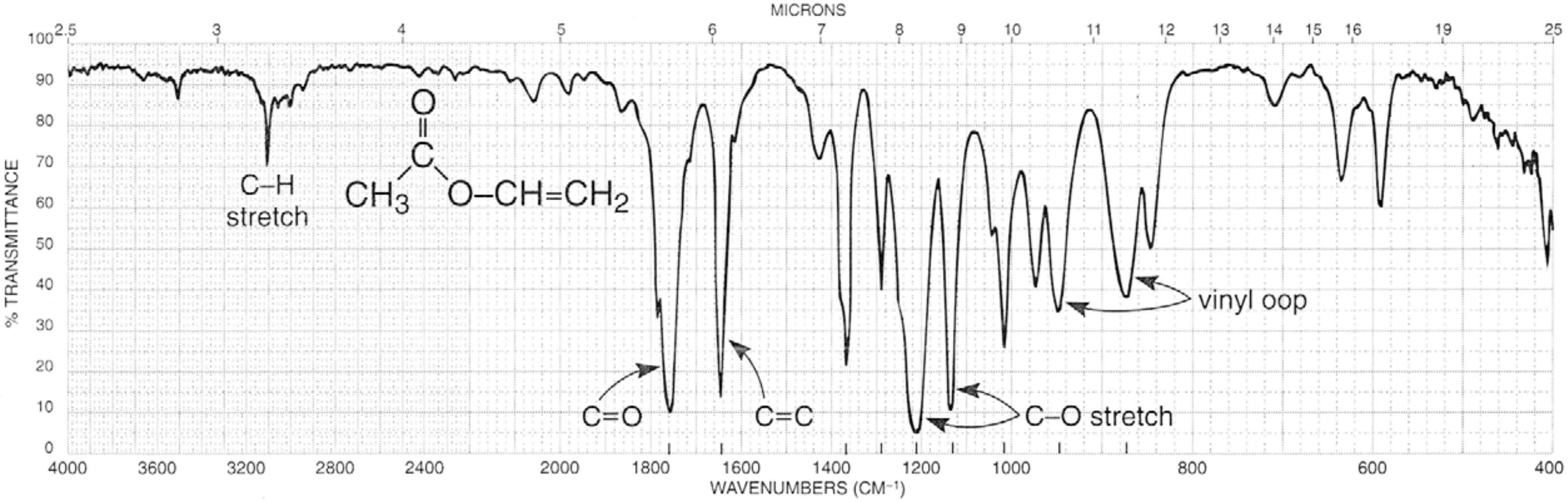
** when R′ is not a long chain or Ph group



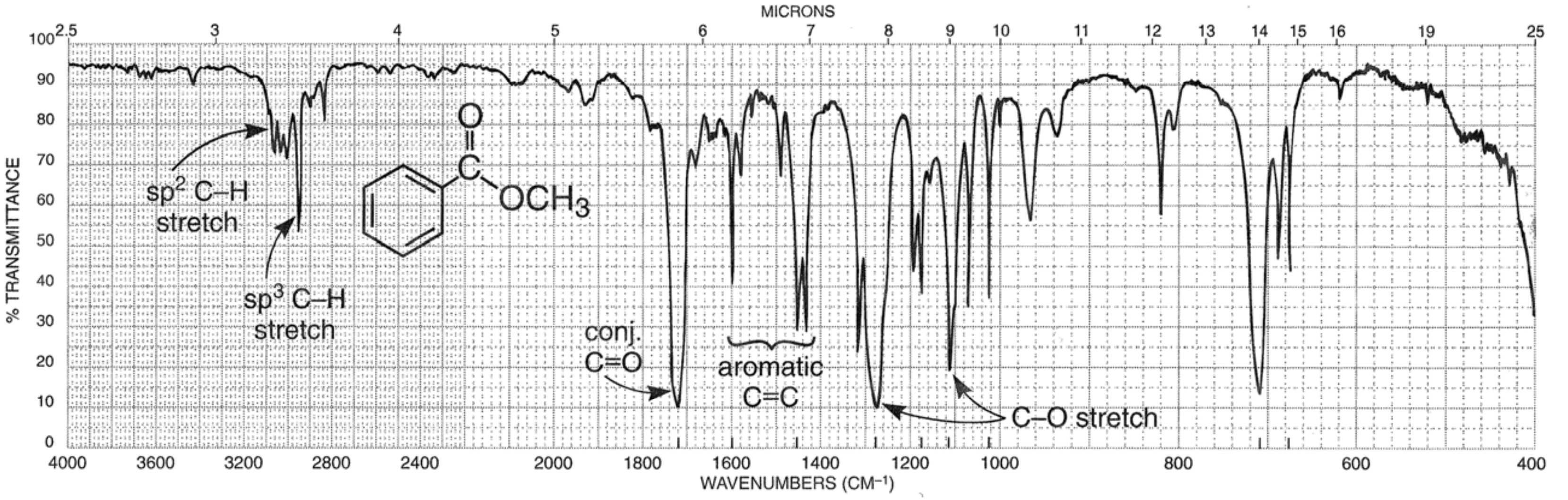
The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).



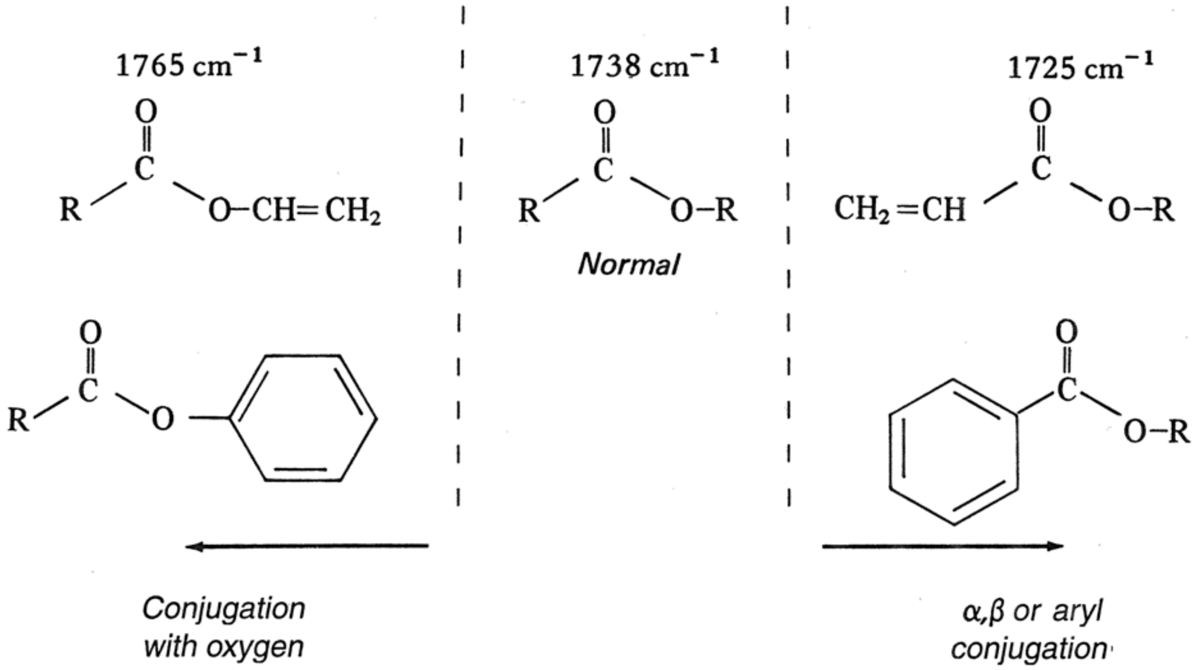
The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).



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



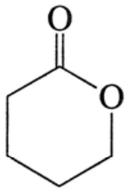
The infrared spectrum of methyl benzoate (neat liquid, KBr plates).



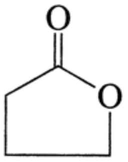
The effect of α,β unsaturation or aryl substitution and conjugation with oxygen on the C=O vibrations in noncyclic (acyclic) esters.

Cyclic esters (Lactones)

The C=O vibrations are shifted to higher frequencies with decreasing ring size, as predicted earlier. The unstrained, six-membered cyclic ester δ-valerolactone absorbs at about the same value as a noncyclic ester (1735 cm^{-1}). Because of increased angle strain, γ-butyrolactone absorbs at about 35 cm^{-1} higher than δ-valerolactone.



δ-Valerolactone
1735 cm^{-1}

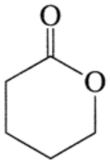
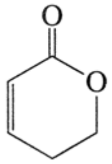
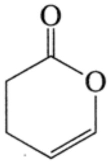
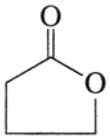
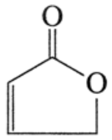
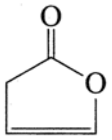
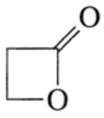


γ-Butyrolactone
1770 cm^{-1}

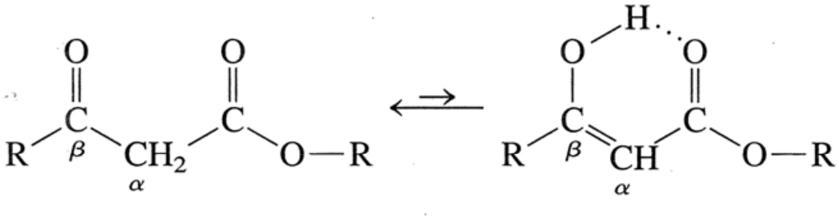
The table presents some typical lactones together with their C=O streching absorption values. Inspection of these values reveals the influence of ring size, conjugation with a carbonyl group, and conjugation with the single-bond oxygen.

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

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		1720		1760
	1770		1750		1800
	1820				

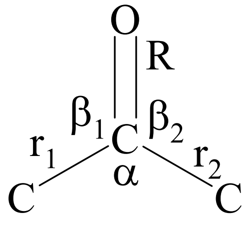
***β*-Keto Esters.** Although this class of compounds exhibits tautomerization like that observed in *β*-diketones (p. 60), less evidence exists for the enol form because *β*-keto esters do not enolize to as great an extent. *β*-Keto esters exhibit a *strong-intensity* doublet for the two carbonyl groups 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.



Keto tautomer   Enol tautomer

KETONES

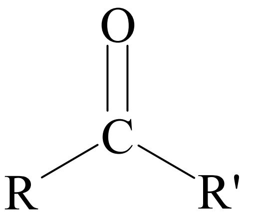
Internal coordinates



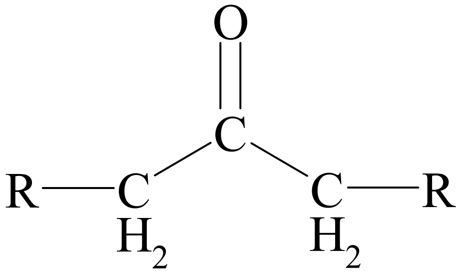
2N – 3 = 5
N – 3 = 1

ρ(oop of C(C=O)C)

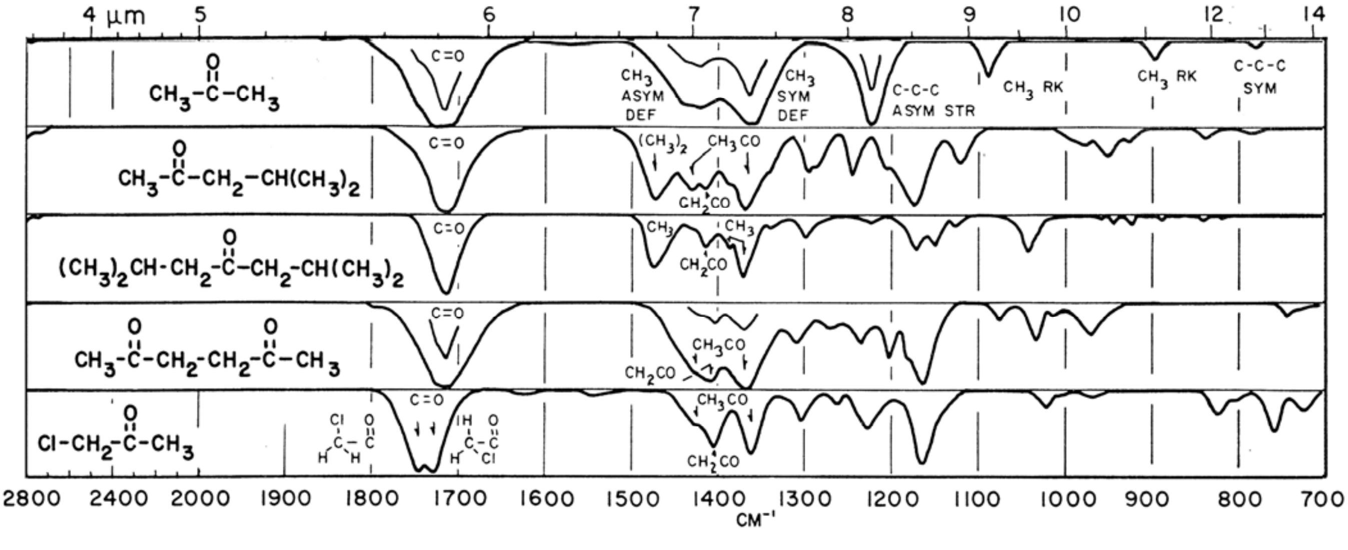
Linear combination of internal coordinates		Absorption region (cm^{-1}) R–CO–CH_3 (R=aliphatic)
ν(C=O) =	R	1735(45)
νa(CCC) =	$r_1 - r_2$	1015(60)
νs(CCC) =	$r_1 + r_2$	895(80)
δ(C=O) =	$\beta_1 - \beta_2$	555(70)
γ(C=O) =	ρ(oop)	460(50)
δ(CCC) =	$2\alpha - \beta_1 - \beta_2$	375(50)

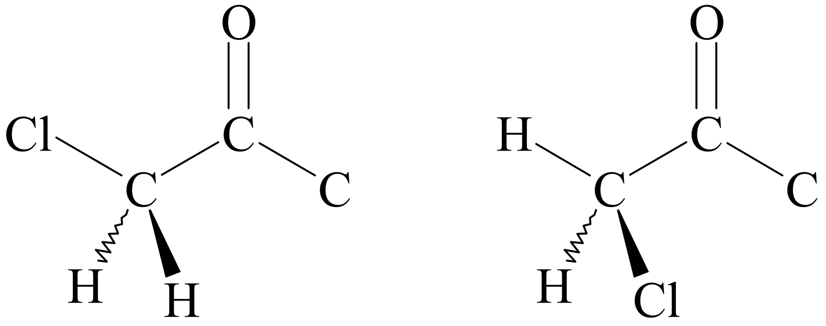


Characteristic vibrations

Acetone (IR / Raman)		
1730 vs / **1711** s, p	~ 1720 vs	ν(C=O)
1215 vs / 1220 m, dp	~ 1015s	νa(CCC)
780 w / **790** vs, p	~ 895w	νs(CCC)
530 s / 530 m, dp	~ 520 vw	δ(C=O) i.p.
480 w / 490 w, dp	~ 460 m	γ(C=O) o.o.p.

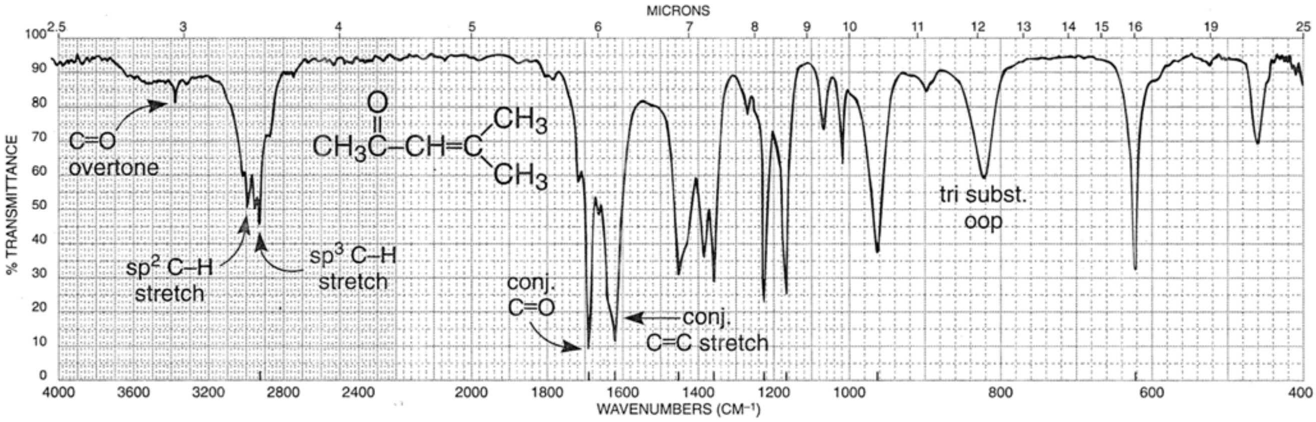
C=O	Stretch at approximately 1715 cm^{-1} is normal. Conjugation moves the absorption to a lower frequency. Ring strain moves the absorption to a higher frequency in a cyclic ketone.
C–C–C	Asymmetric C–C–C stretching appears as a medium or strong intensity band in the range 1300–1100 cm^{-1}. Symmetric C–C–C stretching exhibit very strong Raman line at 790 cm^{-1}.



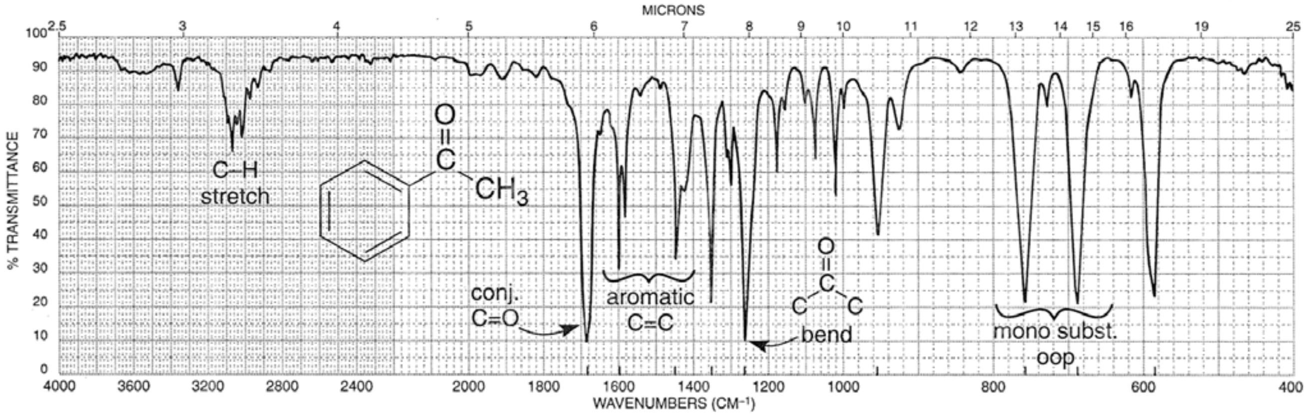


1745 cm^{-1} 1725 cm^{-1}

Rotational isomers in α-chloro ketones.

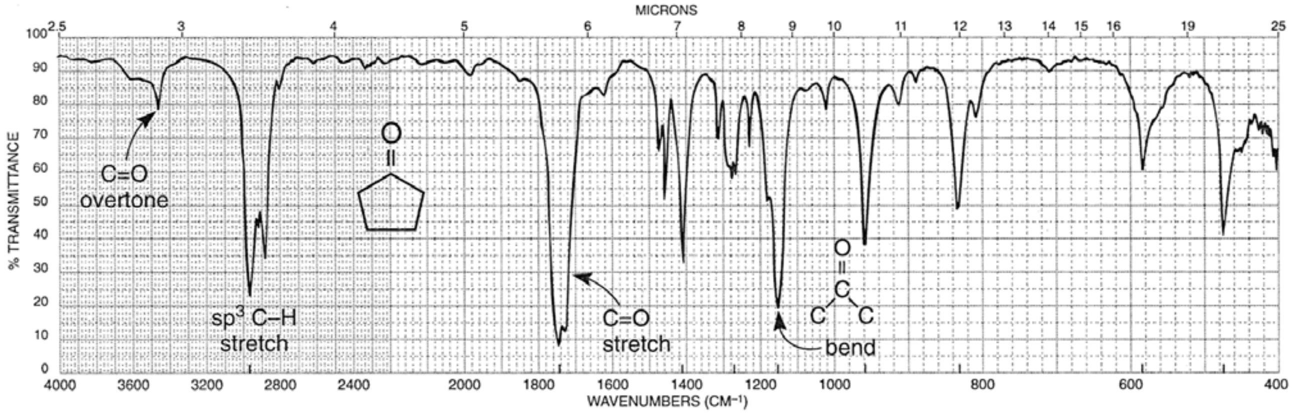


The infrared spectrum of mesityl oxide (neat liquid, KBr plates).

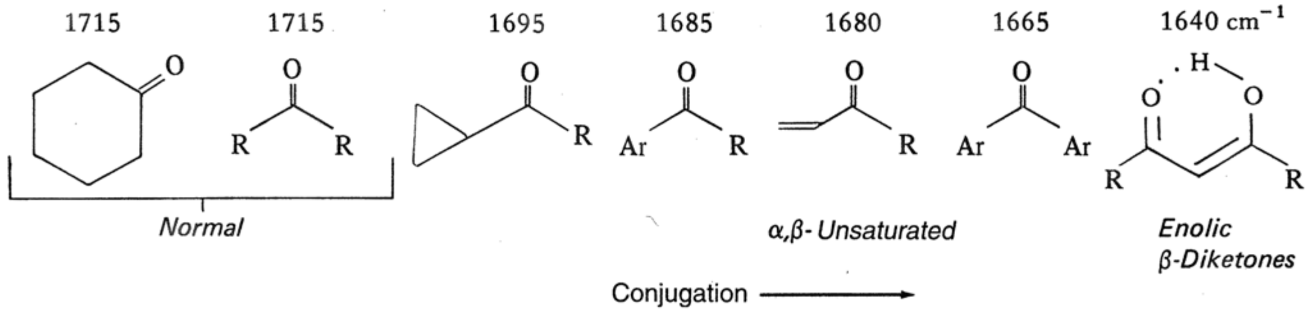


The infrared spectrum of acetophenone (neat liquid, KBr plates).

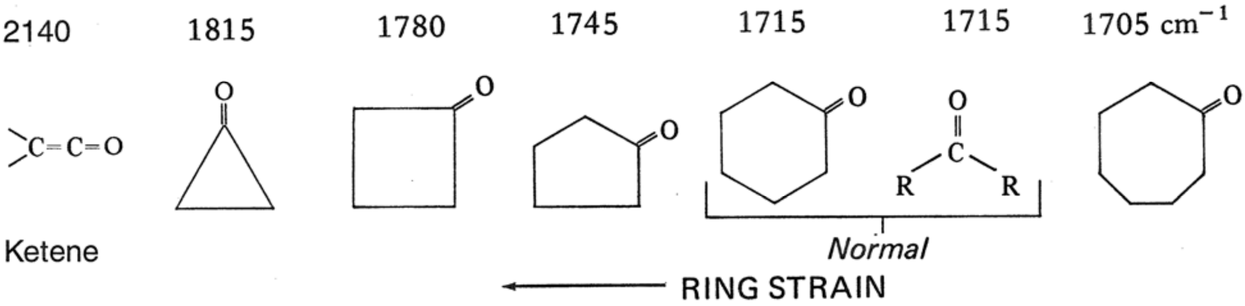
Cyclyc Ketones



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

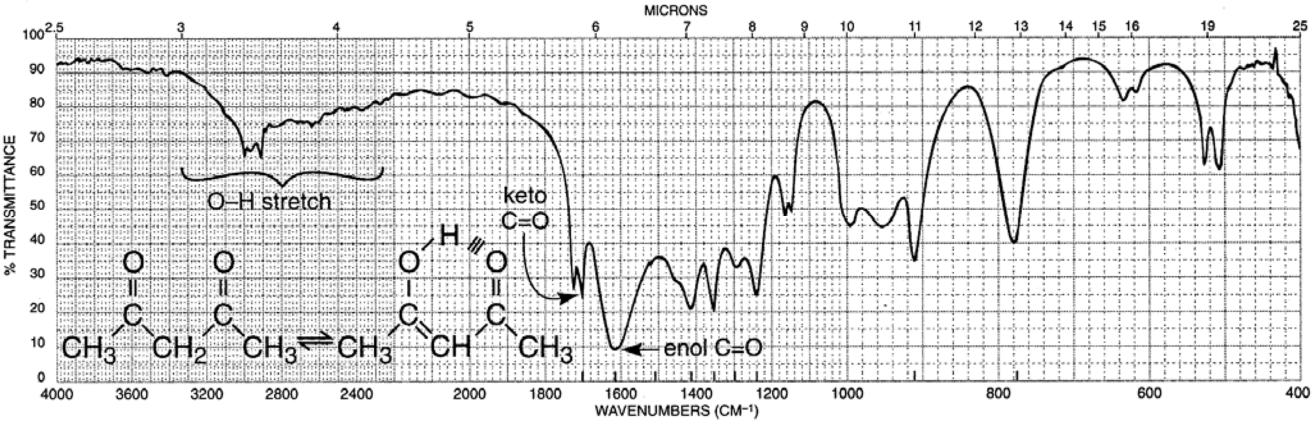


The C═O stretching vibrations in conjugated ketones.

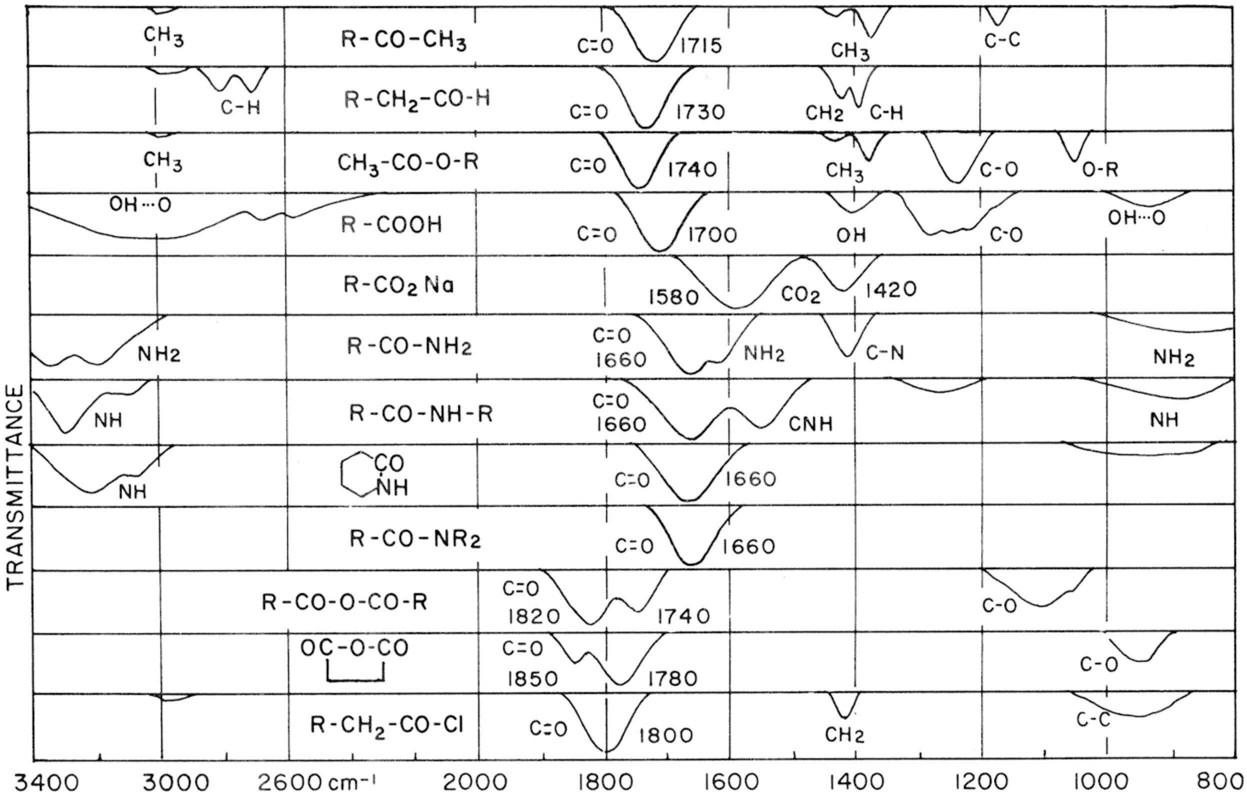


The C═O stretching vibrations for cyclic ketones and ketene.

Keto-enol tutomeria



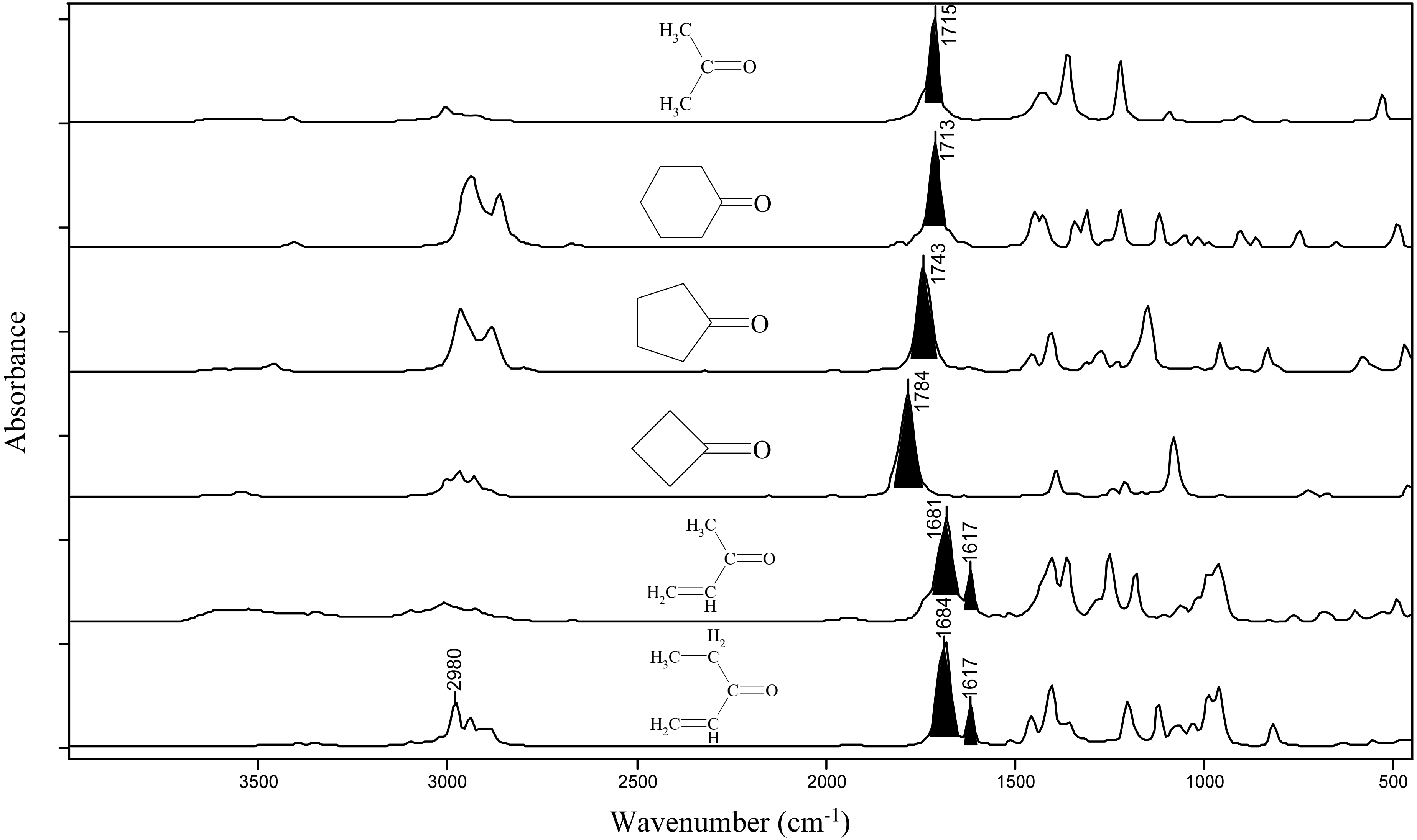
The infrared spectrum of 2,4-pentanedione (neat liquid, KBr plates).

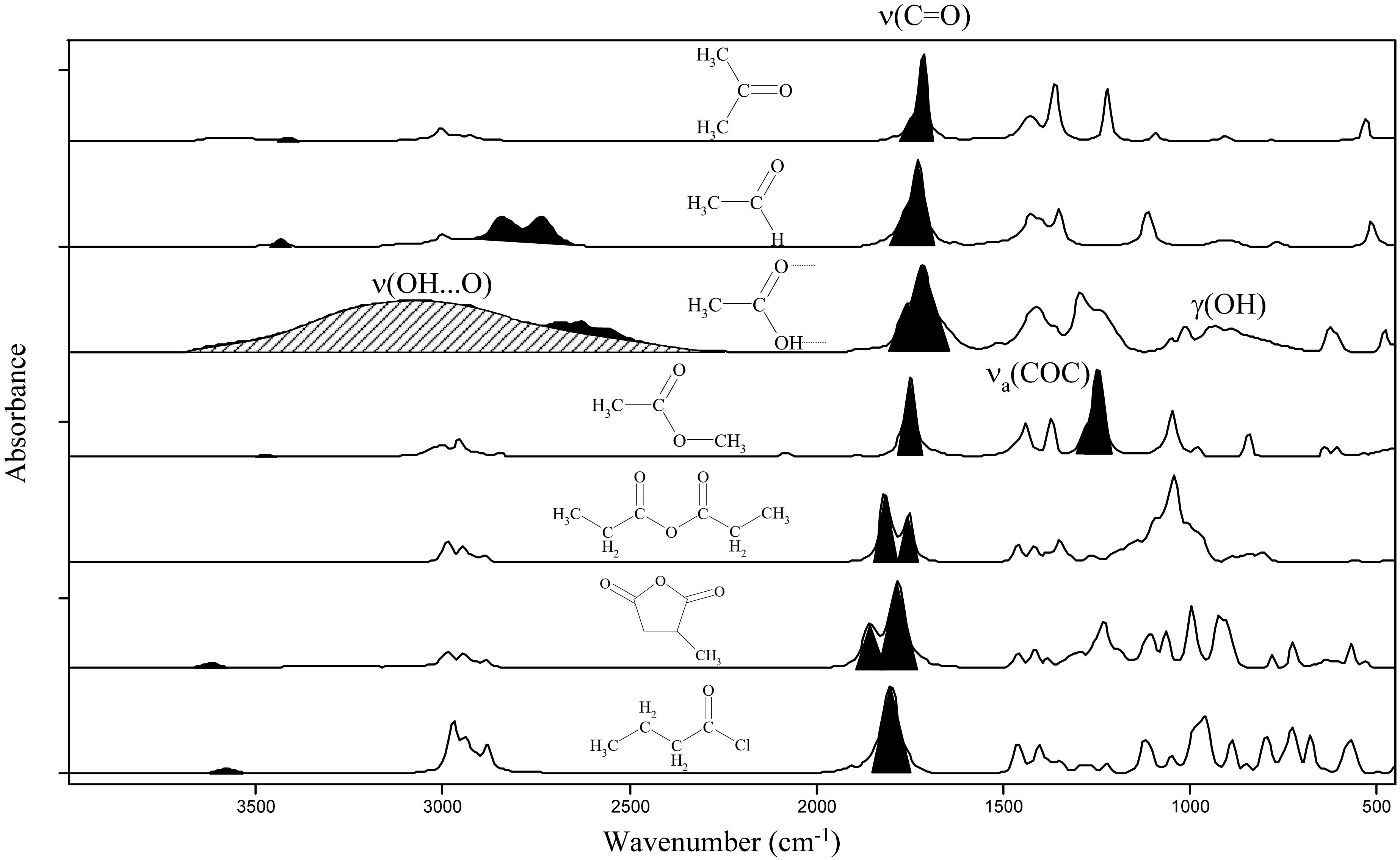


Some general features for a selection of carbonyl compounds, which show some bands from the attached groups, are illustrated.

C=O Spectral Regions (in cm^{-1})

Dialkyl ketones	1725–1705
Singly conjugated ketones	1700–1670
Doubly conjugated ketones	1680–1640
α-Chloro ketone (Cl near O) (cyclic equatorial)	ca. 1745
α-Chloro ketone (Cl not near O) (cyclic axial)	ca. 1725
Ketone in five membered ring (unconjugated)	1750–1740
o-Hydroxy aryl ketones	1670–1630
1, 3-Diketones, enol form	1640–1580
Aliphatic aldehydes	1740–1720
Aromatic aldehydes	1710–1685
Formate esters	1725–1720
Other saturated esters	1750–1735
Conjugated esters (electron attracting groups on the oxygen raise the C=O frequency)	1735–1715

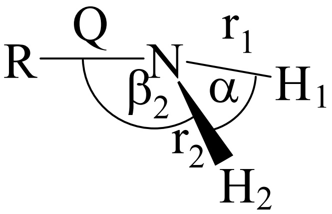

Absorbance
Wavenumber (cm^{-1})
3500
3000
2500
2000
1500
1000
500
H$_3$C
C
O
H$_3$C
1715
1713
1743
1784
H$_3$C
C
O
H$_2$C
C
H
1681
1617
H$_2$
H$_3$C
C
C
O
H$_2$C
C
H
2980
1684
1617


ν(C=O)
ν(OH...O)
γ(OH)
ν$_a$(COC)
H$_3$C
C=O
H$_3$C
O
H$_3$C—C
H
O
H$_3$C—C
OH
O
H$_3$C—C
O—CH$_3$
O O
H$_3$C C C O C C CH$_3$
H$_2$ H$_2$
O O O
CH$_3$
H$_2$
O
H$_3$C C C C Cl
H$_2$
Absorbance
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

5.3.4 NITROGEN CONTAINING COMPOUNDS

AMINES (C_s point group)

a) Primary amines



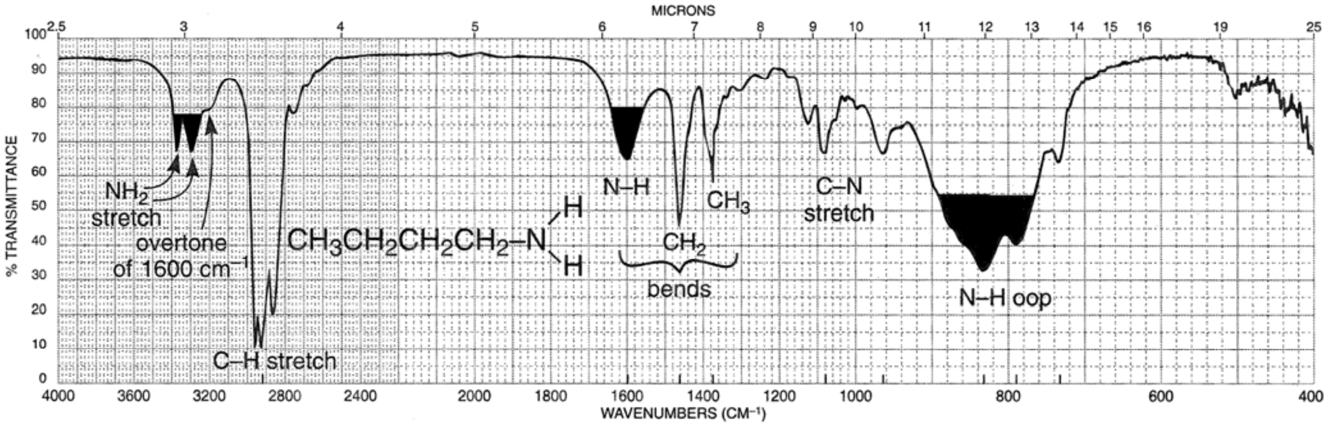
$\nu_a(NH_2)$:	$r_1 - r_2$		A''
$\nu_s(NH_2)$:	$r_1 + r_2$	(p)	A'
$\delta(NH_2)$:	$2\alpha - \beta_1 - \beta_2$	(p)	A'
$\rho/\tau(NH_2)$:	$\beta_1 - \beta_2$		A''
$\omega(NH_2)$:	$\beta_1 + \beta_2$	(p)	A'
$\nu(NC)$:	Q	(p)	A'

R–NH_2 absorption regions (cm^{-1}):

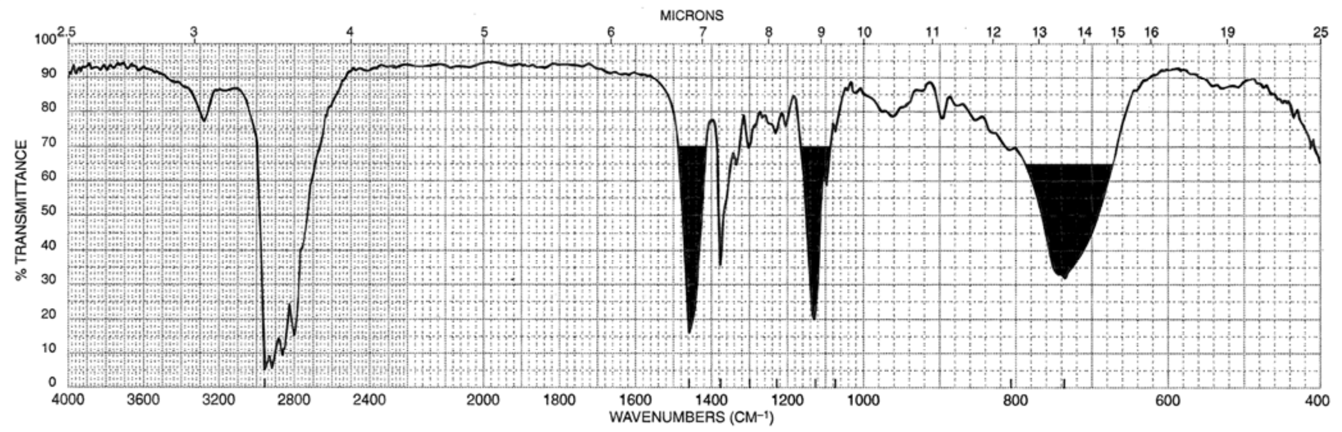
	R = alkyl (cm^{-1})	R = aromatic (cm^{-1})	N–bonded (cm^{-1})
$\nu_a(NH_2)$	3365(25) m, s	3410(70)	3350(40)
$\nu_s(NH_2)$	3290(30) m, s	3320(70)	3250(70)
$\delta(NH_2)$	1615(20) m	1620(20)	1620(20)
$\rho/\tau(NH_2)$	1195(90) w	1070(50)	1195(90)
$\omega(NH_2)$	840(55) s, b	620(100)	830(50)
$\nu(NC)$	1180(200) w	– *	?

* Coupled with aromatic ring vibrations.

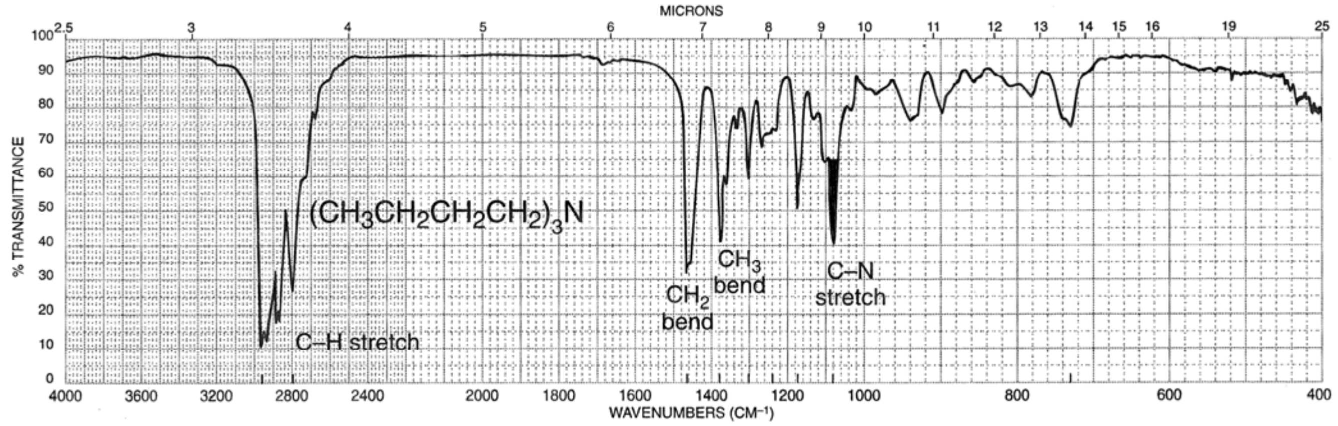
Relations: (a) $\nu_s(NH_2) = 345.5 + 0.876\ \nu_a(NH_2)$
(b) $\nu_s(NH_2) = 0.98\ \nu_a(NH_2)$



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

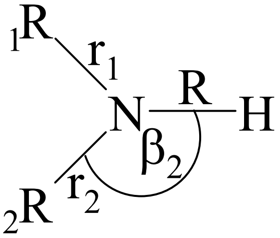


The infrared spectrum of dibutylamine (neat liquid, KBr plates).

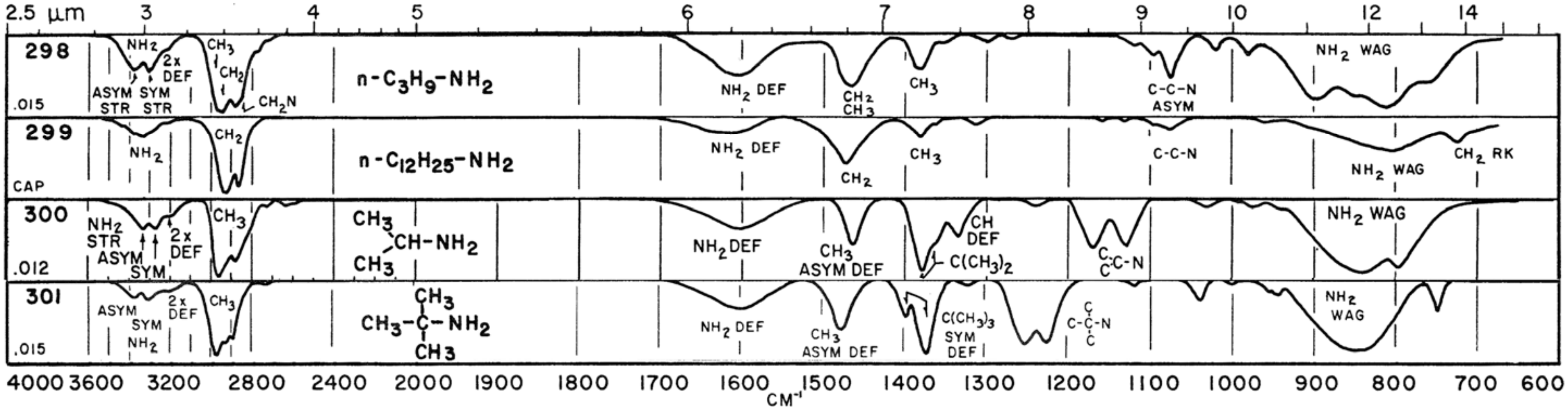


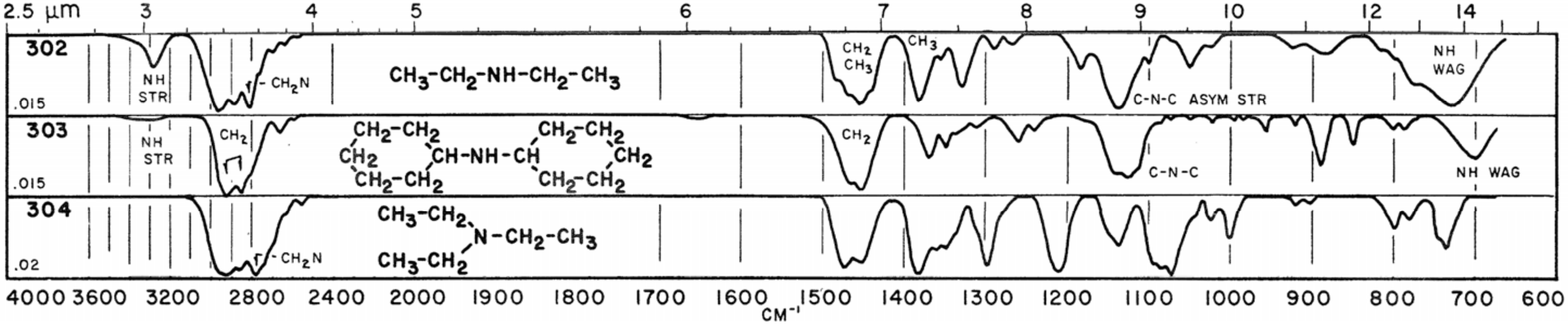
The infrared spectrum of tributylamine (neat liquid, KBr plates).

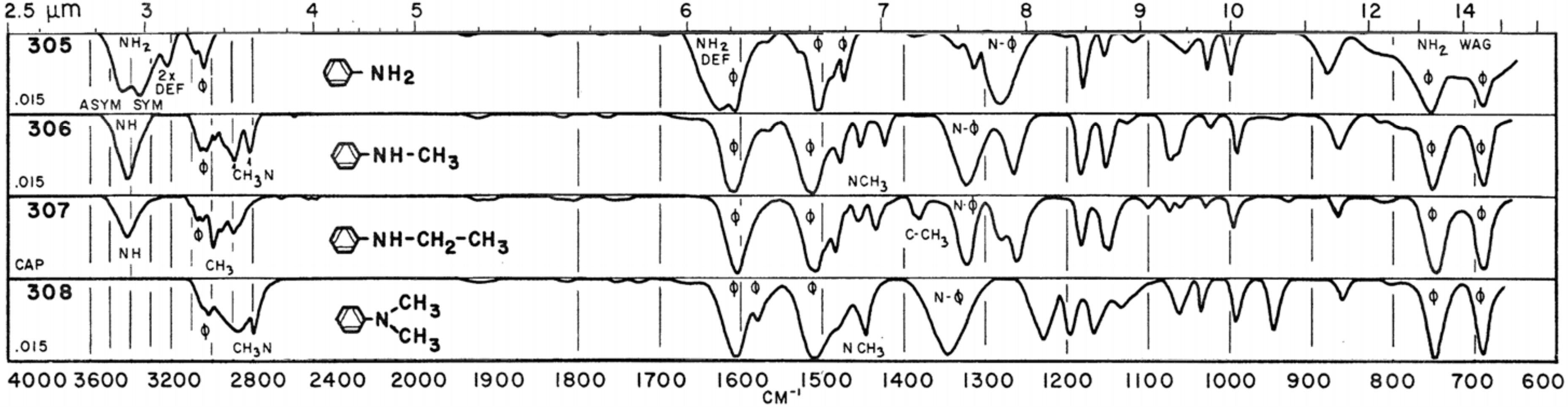
a) Secondary amines



	$R = CH_3$ (cm^{-1})	R = Ph (cm^{-1})
$\nu(NH)$	3265(50) m	3400(40)
$\delta(NH)$	1530(50)	1530(50)
$\nu_a(NC_2)$	1150(30)	1140(15)
$\nu_s(NC_2)$	995(80) w	985(70)


2.5 µm
3
4
5
6
7
8
9
10
12
14
298
.015
NH2
ASYM STR
SYM STR
2x DEF
CH3
CH2
CH2N
n-C3H9-NH2
NH2 DEF
CH2 CH3
CH3
C-C-N ASYM
NH2 WAG
299
CAP
NH2
CH2
n-C12H25-NH2
NH2 DEF
CH2
CH3
C-C-N
NH2 WAG
CH2 RK
300
.012
NH2 STR ASYM
SYM
2x DEF
CH3
CH3 CH-NH2 CH3
NH2 DEF
CH3 ASYM DEF
C(CH3)2
CH DEF
C C-C-N
NH2 WAG
301
.015
ASYM
SYM NH2
2x DEF
CH3
CH3-C(CH3)(CH3)-NH2
NH2 DEF
CH3 ASYM DEF
C(CH3)3 SYM DEF
C-C(C)(C)-N
NH2 WAG
4000
3600
3200
2800
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CM-1


2.5 µm
3
4
5
6
7
8
9
10
12
14
302
.015
NH STR
- CH₂N
CH₃-CH₂-NH-CH₂-CH₃
CH₂ CH₃
CH₃
C-N-C ASYM STR
NH WAG
303
.015
NH STR
CH₂
CH₂-CH₂ CH₂ CH-NH-CH CH₂ CH₂-CH₂
CH₂
C-N-C
NH WAG
304
.02
- CH₂N
CH₃-CH₂ N-CH₂-CH₃ CH₃-CH₂
4000 3600 3200 2800 2400 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600
CM⁻¹

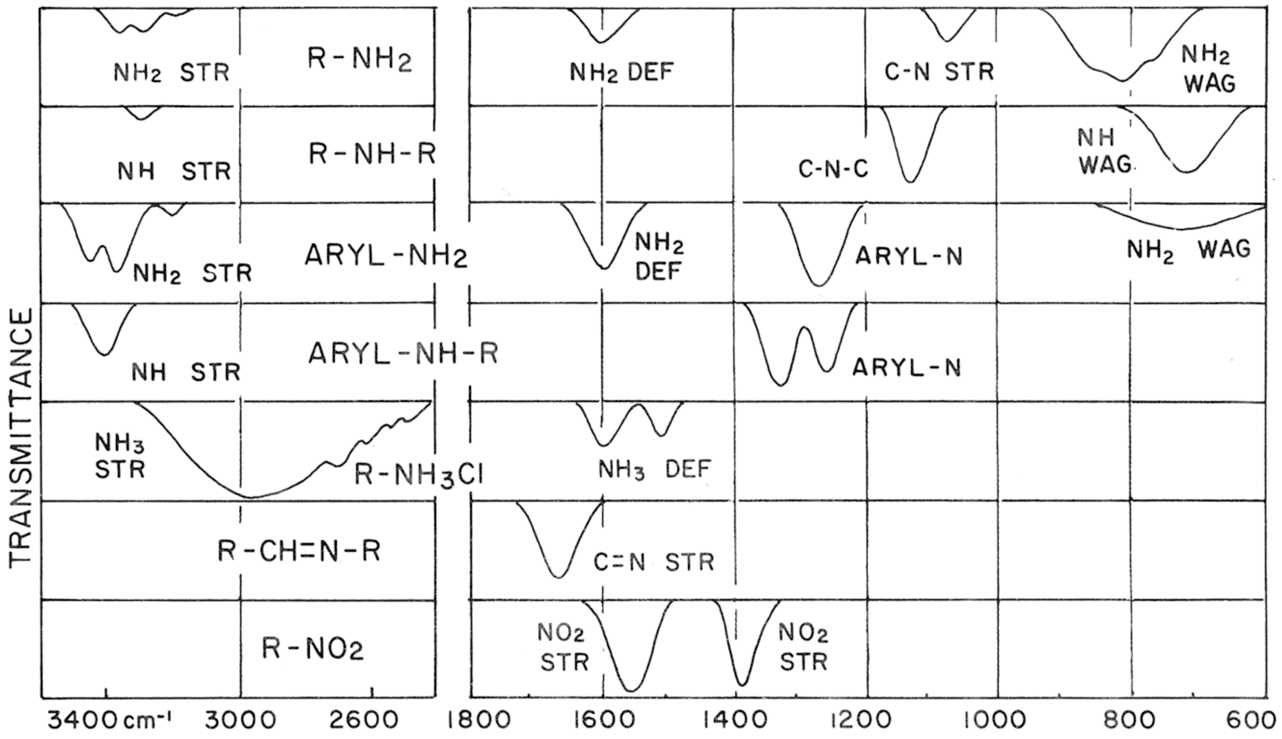

2.5 µm
3
4
5
6
7
8
9
10
12
14
305
.015
NH₂
2x DEF
ASYM SYM
ϕ
NH₂
NH₂ DEF
ϕ
ϕ ϕ
N-ϕ
NH₂ WAG
ϕ ϕ
306
.015
NH
ϕ
CH₃N
NH-CH₃
ϕ
ϕ
NCH₃
N-ϕ
ϕ ϕ
307
CAP
NH
ϕ
CH₃
NH-CH₂-CH₃
ϕ
ϕ
C-CH₃
N-ϕ
ϕ ϕ
308
.015
ϕ
CH₃N
N CH₃ CH₃
ϕ ϕ
ϕ
N CH₃
N-ϕ
ϕ ϕ
4000 3600 3200 2800 2400 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600
CM⁻¹

AMINES, C=N, AND N=O COMPOUNDS

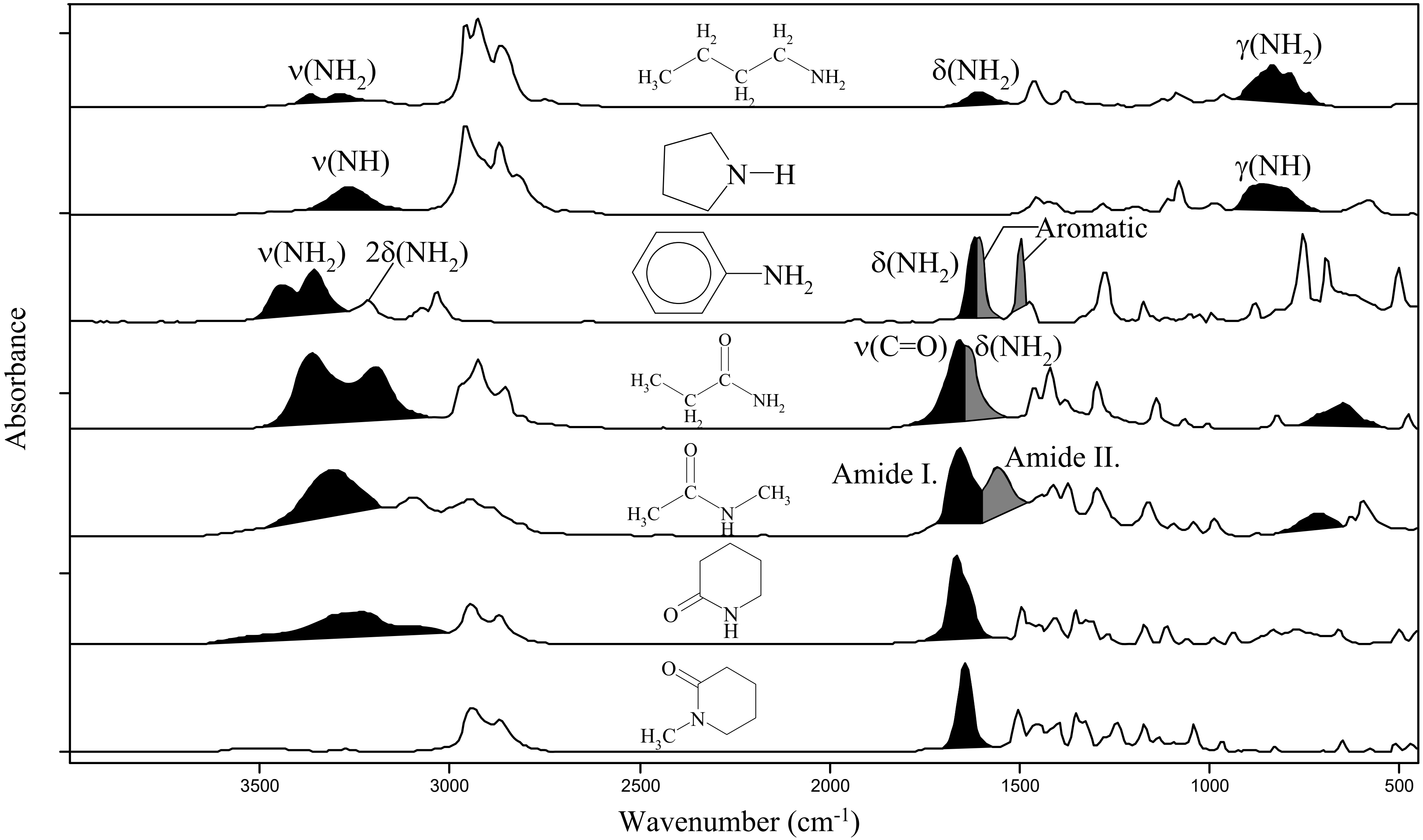
NH_2 Stretch in Amines

In Fig. **below** general spectral features are shown for amines and other selected nitrogen compounds to be discussed in this chapter.

The NH_2 group gives rise to absorption at 3550–3330 cm^{-1} (asymmetric stretch) and at 3450–3250 cm^{-1} (symmetric stretch). A relationship has been developed relating the two bands,[1] namely, $\bar{\nu}_{\mathrm{sym}} = 345.5 + 0.876\ \bar{\nu}_{\mathrm{asym}}$, this relationship holding for NH_2 groups in which the two NH bonds are equivalent. Using equations related to those for the triatomic case this relationship has been reduced to $\bar{\nu}_{\mathrm{sym}} = 0.98\ \bar{\nu}_{\mathrm{asym}}$.



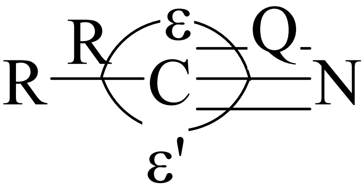
General spectra expected for amines, anilines, imines, and nitro compounds.


ν(NH2)
δ(NH2)
γ(NH2)
H2
C
H3C
C
H2
H2
C
NH2
ν(NH)
γ(NH)
N—H
ν(NH2)
2δ(NH2)
NH2
δ(NH2)
Aromatic
ν(C=O)
δ(NH2)
O
H3C
C
C
H2
NH2
Amide I.
Amide II.
O
C
H3C
N
H
CH3
O
N
H
O
N
H3C
Absorbance
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

CYANIDES, ISONITRILES

Absorption region of the normal vibrations of R–C≡N groups:

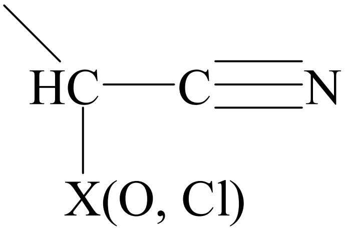
Internal coordinates



Vibrations	Coordinate involved	Region (cm^{-1}) R = aliphatic	Region (cm^{-1}) R = Ph
ν(C≡N)	Q	2250(20)	2230(10)
ν(C–CN)	R	955(65)	–
γ(C–C≡N)	ε	365(25)	
δ(C–C≡N)	ε'	225(65)	

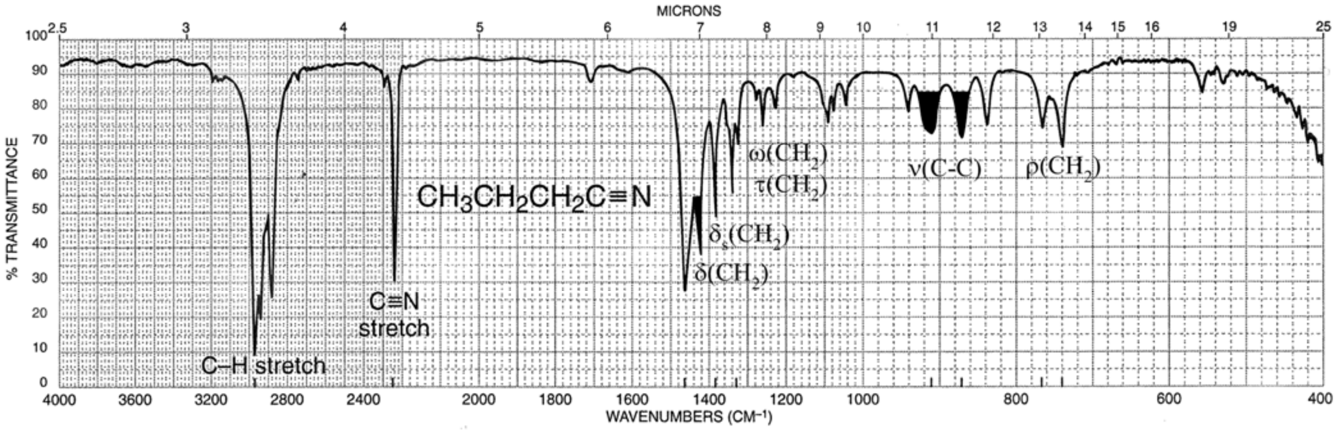
Aliphatic nitriles

– The C≡N stretching band is weakened in intensity when:



– The CH_2 group has scissoring mode at 1425 cm^{-1}.

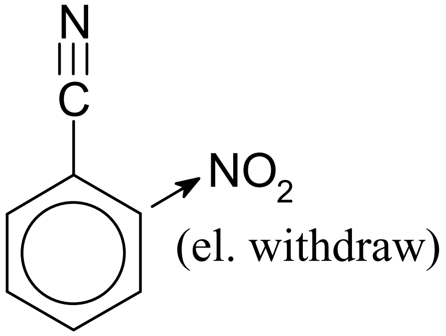
– Conjugations lower the C≡N frequency due to resonance

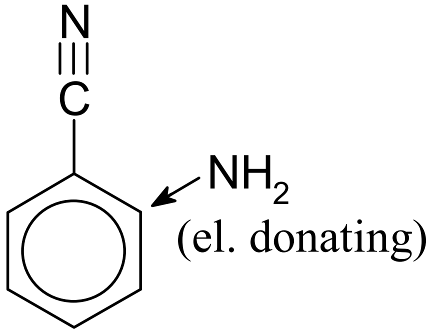


The infrared spectrum of butyronitrile (neat liquid, KBr plates).

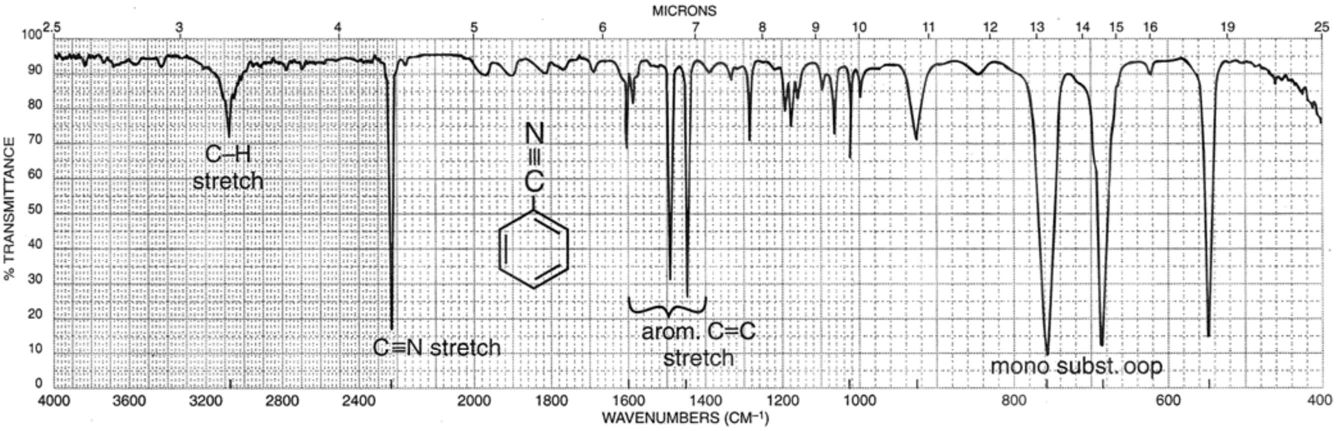
Benzonitriles

– The intensity of C≡N stretching band is quite variable and depends on the nature of substituent





– decrease intensity	– increase intensity
– increase the frequency	– decrease the frequency



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

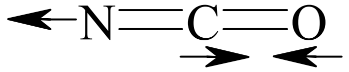
ISOCYANIDES

$\mathrm{R{-}\overset{+}{N}{\equiv}\overset{-}{C}}$ ~2140 $\mathrm{cm^{-1}}$

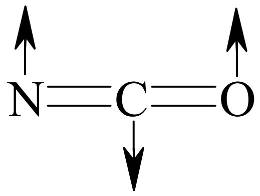
$\mathrm{Ph{-}\overset{+}{N}{\equiv}\overset{-}{C}}$ ~2115 $\mathrm{cm^{-1}}$

ISOCYANATES

The most characteristic group vibrations are:

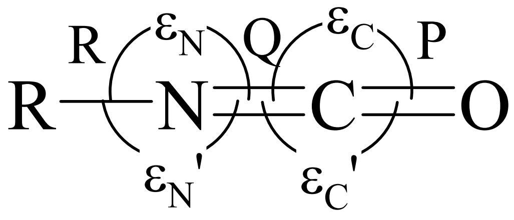


vs, broad
2270(20) $\mathrm{cm^{-1}}$



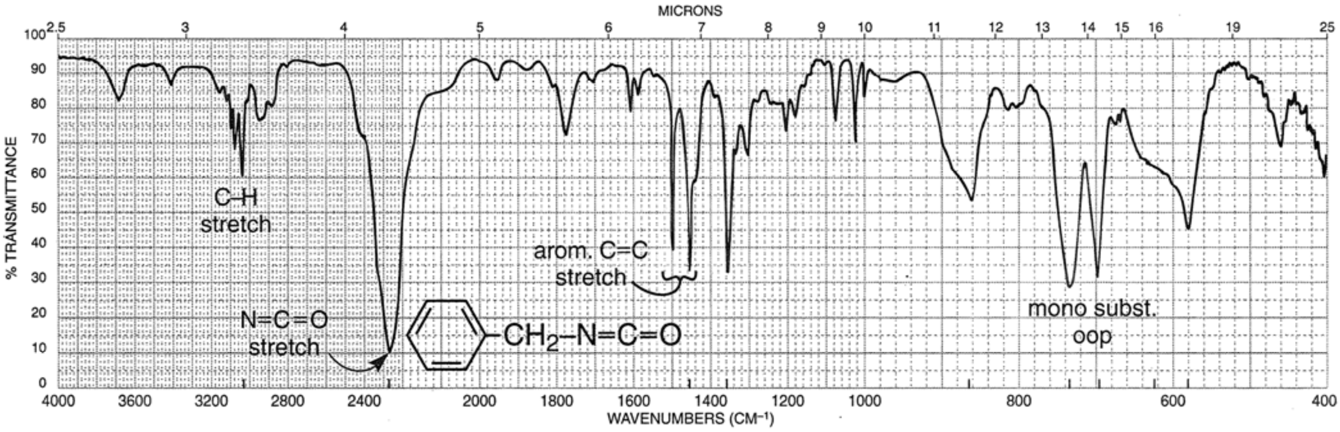
m, broad
600(30) $\mathrm{cm^{-1}}$

Internal coordinates



Characteristic vibrations (R = aliphatic):

Vibrations	Coordinates	Region ($\mathrm{cm^{-1}}$)
ν_a(N=C=O)	Q – P	2270(20) vs, broad
ν_s(N=C=O)	Q + P	1420(20) m
ν(C–N)	R	725(75) w
γ(N=C=O)	ε_C	600(30) m, broad
δ(N=C=O)	ε_C’	575(25) w
δ(C–N=C)	ε_N	155(25) vw



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

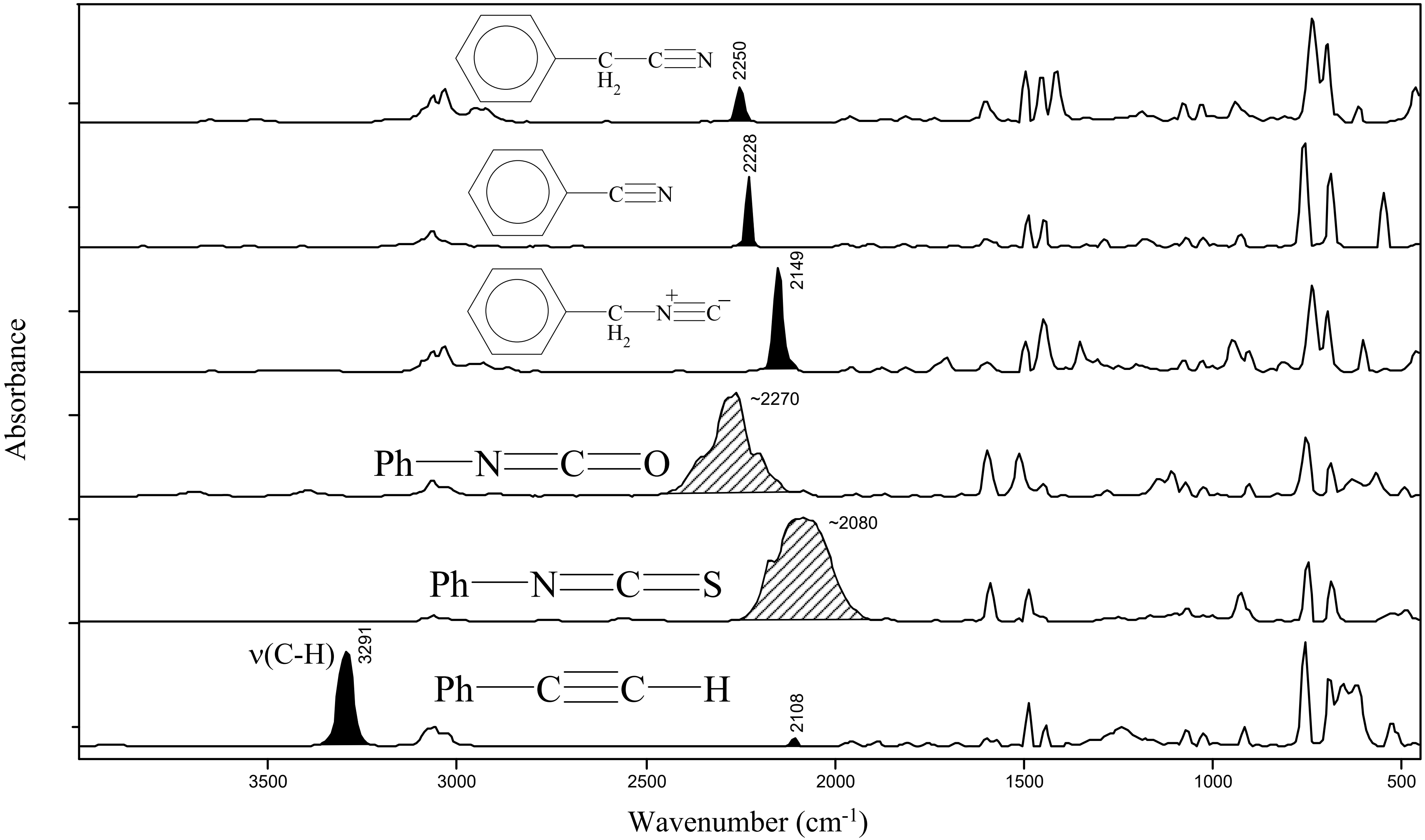
Comparison (2300–1900 cm^{-1})

$X\equiv Y-Z$	$X=Y=Z$
triple bond	***cumulated double bond***
– weaker IR, sharp	– stronger IR, broader band (ν_a)
– strong Raman	– weaker Raman

– Multiple bonds in this region due to
FERMI RESONANCE!

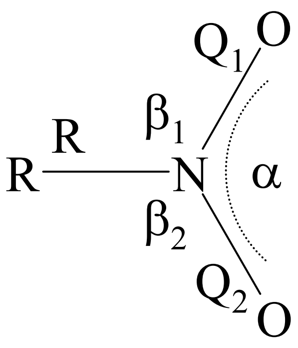
THE 2300–1900 cm^{-1} REGION

$-C\equiv C-H$	2140–2100 cm^{-1}	Weak–variable
$-C\equiv C-$	2260–2190	Very weak-variable
$C=C=CH_2$	2000–1900	Strong
$CH_2-C\equiv N$	2260–2240	Medium weak
$C=C-C\equiv N$	2235–2215	Medium
aryl-$C\equiv N$	2240–2220	Variable
$-C\equiv N\rightarrow O$	2304–2288	Strong
$-N=C=O$	2275–2263	Very strong
$-S-C\equiv N$	2170–2135	Medium strong
$-N=C=S$	2150–2050	Very strong
$>N-C\equiv N$	2225–2175	Strong
$-N=C=N-$	2150–2100	Very strong
$>C=C=N-$	2050–2000	Very strong
$-CH=\overset{+}{N}=\overset{-}{N}$	2132–2012	Very strong
$-N=\overset{+}{N}=\overset{-}{N}$	2170–2080	Very strong
aryl-$\overset{+}{N}\equiv N$	2309–2136	Medium
$-\overset{+}{N}\equiv\overset{-}{C}$	2165–2110	Strong
$>C=C=O$	2200–2100	Very strong
$[C\equiv N]^-$	2200–2070	Medium
$[Fe(C\equiv N)_6]^{4-}$	2010	Medium
$[Fe(C\equiv N)_6]^{3-}$	2100	Medium
$[N=C=O]^-$	2220–2130	Strong
$[N=C=S]^-$	2090–2020	Strong
metal(CO)	2170–1900	Strong


Absorbance
Wavenumber (cm-1)
3500
3000
2500
2000
1500
1000
500
2250
2228
2149
~2270
~2080
3291
2108
ν(C-H)
Ph—N═C═O
Ph—N═C═S
Ph—C≡C—H

ORGANIC NITRO COMPOUNDS

Internal coordinates:

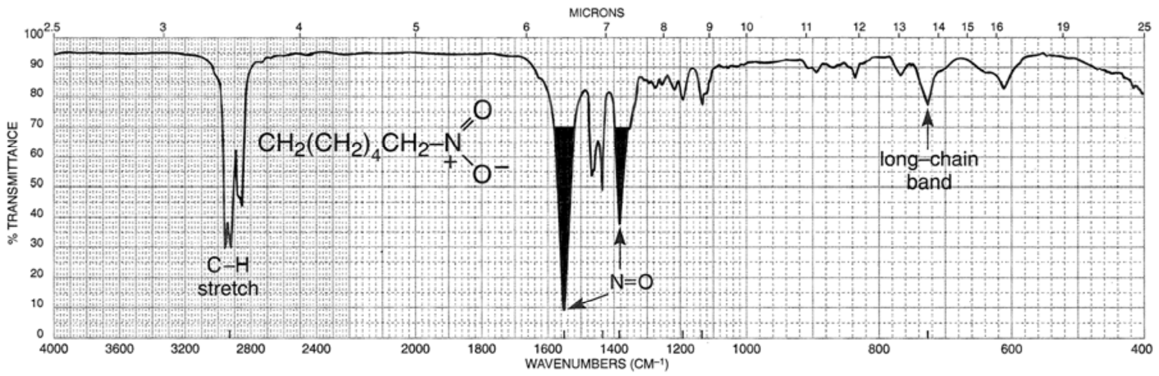


+ $\rho(NO_2)$ - wagging

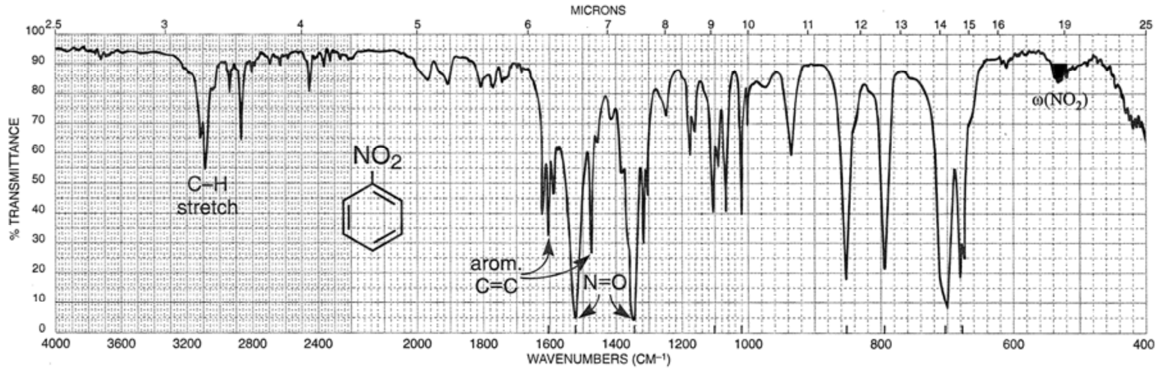
+ $\chi(NO_2)$ - torsion

Vibrations	Coordinate	Aliphatic (cm^{-1})	α-unsaturated, aromatic (cm^{-1})
$\nu_a(NO_2)$	$Q_1 - Q_2$	1570(20) vs	1535(30) s
$\nu_s(NO_2)$	$Q_1 + Q_2$	1380(20) s	1345(30) s
$\delta(NO_2)$	$2\alpha - \beta_1 - \beta_2$	700(70) w	850(60)*
$\omega(NO_2)$	P	480(50) vw	545(45) w
$\chi(NO_2)$	X	~ 60 vvw	~70 vvw

* Overlapping with aromatic vibrations.



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



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

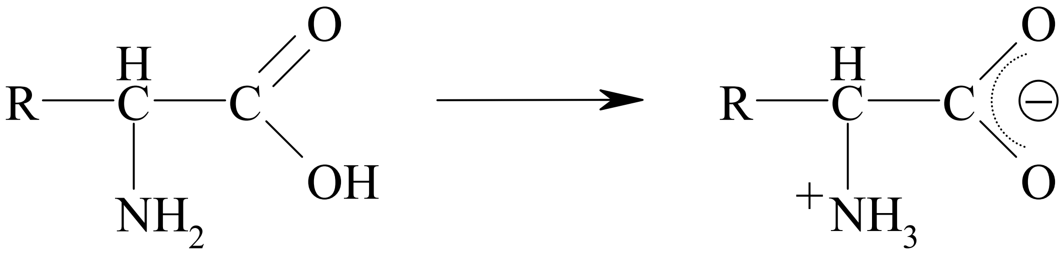
NO_2 STRETCHING FREQUENCIES

	Asymmetric stretch (cm^{-1})	Symmetric stretch (cm^{-1})
$C-CH_2-NO_2$	1556–1545	1388–1368
$C-CH(CH_3)-NO_2$	1549–1545	1364–1357
$C(CH_3)_2-NO_2$	1553–1530	1359–1342
$CHX-NO_2(X=Cl, Br)$	1580–1556	1368–1340
CX_2-NO_2	1597–1569	1339–1323
CCl_3-NO_2	1610	1307
$C(NO_2)_2$	1590–1570	1340–1325
$N-NO_2$	1630–1530	1315–1260
$O-NO_2$	1660–1625	1285–1270
Nitro alkene	1550–1500	1360–1290
Aromatic nitro	1530–1500	1370–1330
p-Aminonitro aromatic	(Hydrogen bonded)	1330–1270
o-Aminonitro aromatic	(Hydrogen bonded)	1260–1210

5.3.5. AMINO ACIDS, UREAS, CARBAMATES

Amino acids

Amino acids usually exist as zwitterions:



Characteristic groups: $-NH_3^+$ and $-COO^-$.

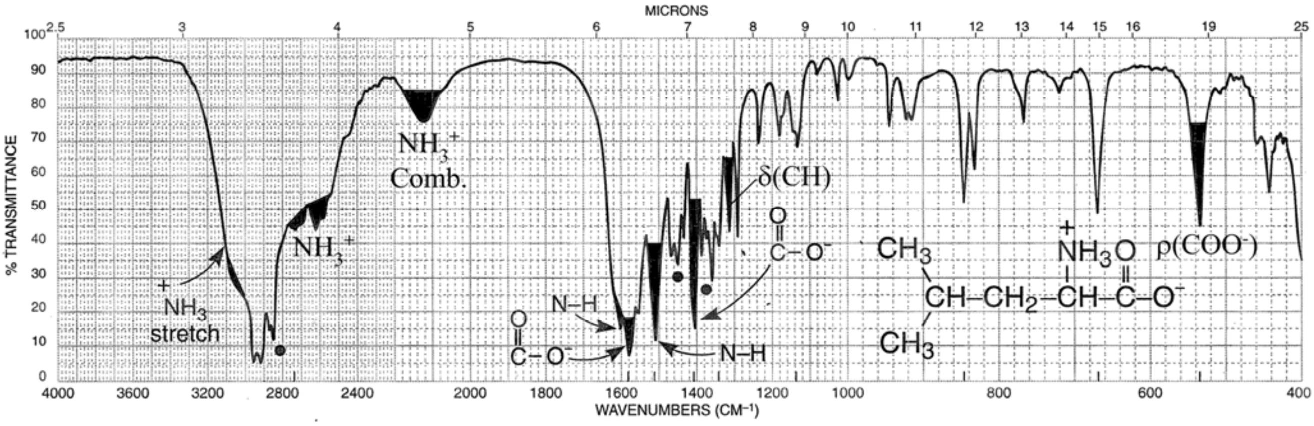
Absorption regions of the normal vibrations of $-CH_2-NH_3^+$ group:

Vibrations	Spectral range (cm^{-1})	α-amino acids (cm^{-1})
$\nu_a(NH_3^+)$	3135(105) s	3100 – 2600 broad strong multiple peaks
$\nu_a'(NH_3^+)$	3045(70) s	
		2200 – 2000 region medium combination bands
$\delta_a(NH_3^+)$	1605(45) vs	1625(30) s
$\delta_a'(NH_3^+)$	1575(55) vs	
$\delta_s(NH_3^+)$	1525(50) w, m	1510(20) s
$\rho(NH_3^+)$	1070(100) m	
$\rho'(NH_3^+)$	1030(100) m	
δ (CCN)	480(55) w	
torsion	175(65) vw	

Characteristic –COO⁻ bands

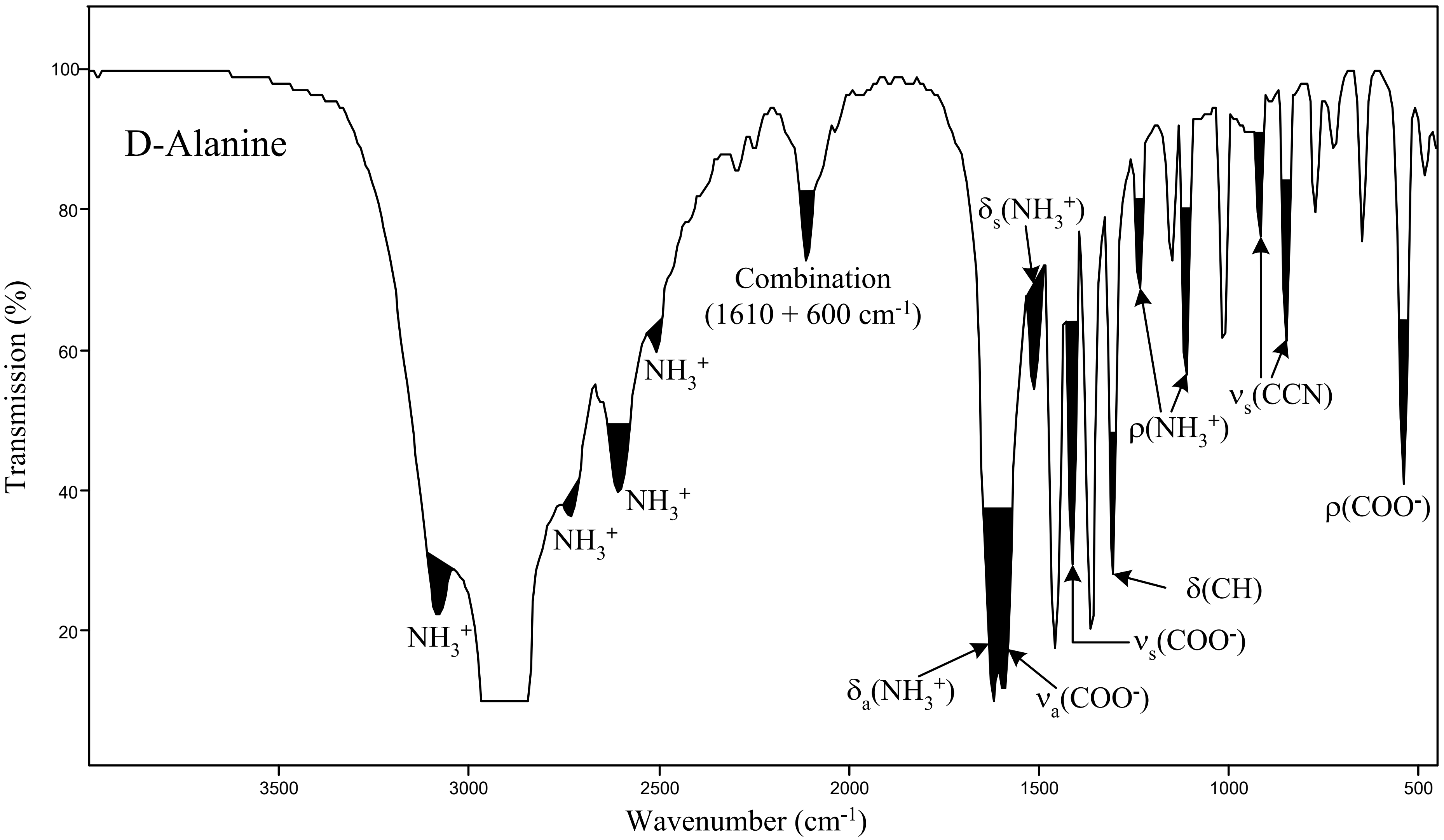
Vibrations	Spectral range (cm^{-1})	α-amino acids (cm^{-1})
$\nu_a(COO^-)$	1585(25) vs	1580(30) vs
$\nu_s(COO^-)$	1410(30) m, s	1410(40) m, s
$\rho(COO^-)$	530(60) m, s	530(100) s, m

* The scissoring and wagging modes of COO^- (735(90) and 625(55) cm^{-1}, respectively) are generally weak bands.

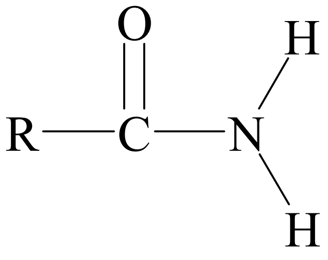


The infrared spectrum of leucine (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands.

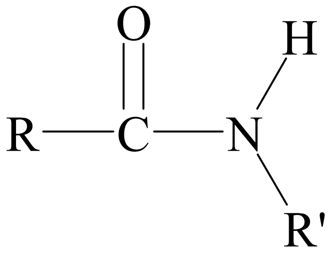
Characteristic δ(CH) band at ~1300 cm^{-1} observed as sharp, medium intensity feature.


D-Alanine
Transmission (%)
100
80
60
40
20
Wavenumber (cm^{-1})
3500
3000
2500
2000
1500
1000
500
NH_3^+
NH_3^+
NH_3^+
NH_3^+
Combination
(1610 + 600 cm^{-1})
$\delta_s(NH_3^+)$
$\delta_a(NH_3^+)$
$\nu_a(COO^-)$
$\nu_s(COO^-)$
δ(CH)
$\rho(NH_3^+)$
$\nu_s(CCN)$
$\rho(COO^-)$

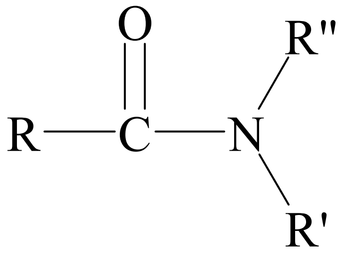
AMIDES



Primary amide



Secondary amide



Tertiary amide

Primary amides

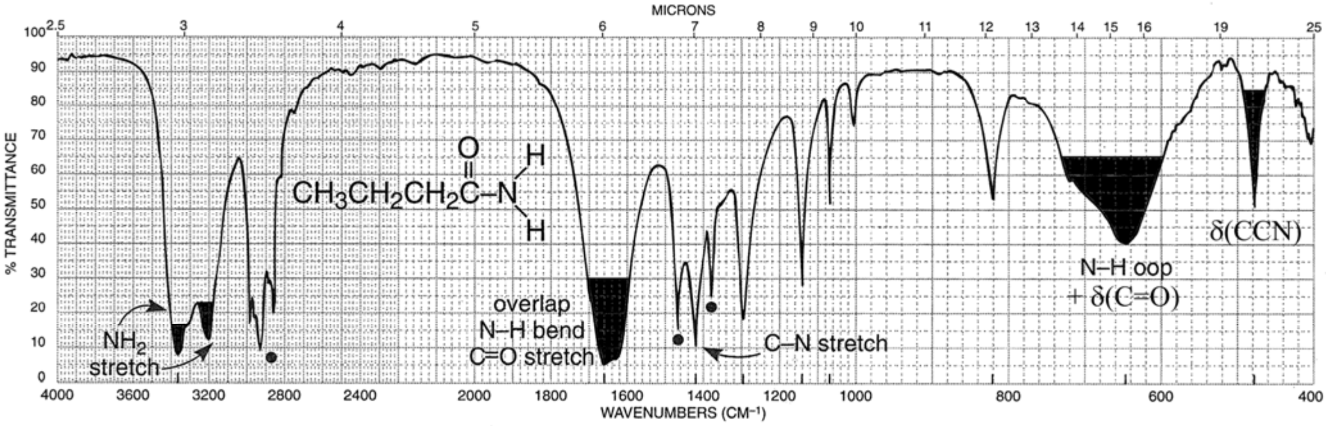
Adsorption regions of –C(=O)NH_2 group:

Vibrations	α-saturated (cm^{-1})	α-unsaturated (aromatic) (cm^{-1})
$\nu_a(NH_2)$ (A)[a]	3370(40) vs	3370(30) vs
$\nu_s(NH_2)$ (B)	3205(45) vs	3180(30) vs
$\nu(C{=}O)$ (I)	1680(35) vs	1660(15) vvs
$\delta(NH_2)$ (II)	1615(25) vs	1610(10) s
$\nu(CN)$ (III)	1380(80) m, s	1385(40) vs
$\rho(NH_2)$	1130(40)*	1115(25) w
$\tau(NH_2)$ (VII)	765(45) w	780(40) w, m
$\omega(NH_2)$ (V)	670(50) vs, b	660(50) w, m
$\delta(C{=}O)$ (IV)	600(50) w	605(35) w
$\gamma(C{=}O)$ (VI)	550(50) w, m	550(40) w
$\delta(CCN)$	430(50) m	475(55) m

* Overlaping with alkyl chain vibrations

[a] Amide vibrations:

Amide A	$\nu_a(NH_2)$
Amide B	$\nu_s(NH_2)$
Amide I	$\nu(C{=}O)$
Amide II	$\delta(NH_2)$
Amide III	$\nu(CN)$
Amide IV	$\delta(C{=}O)$
Amide V	$\omega(NH_2)$
Amide VI	$\gamma(C{=}O)$
Amide VII	$\tau(NH_2)$



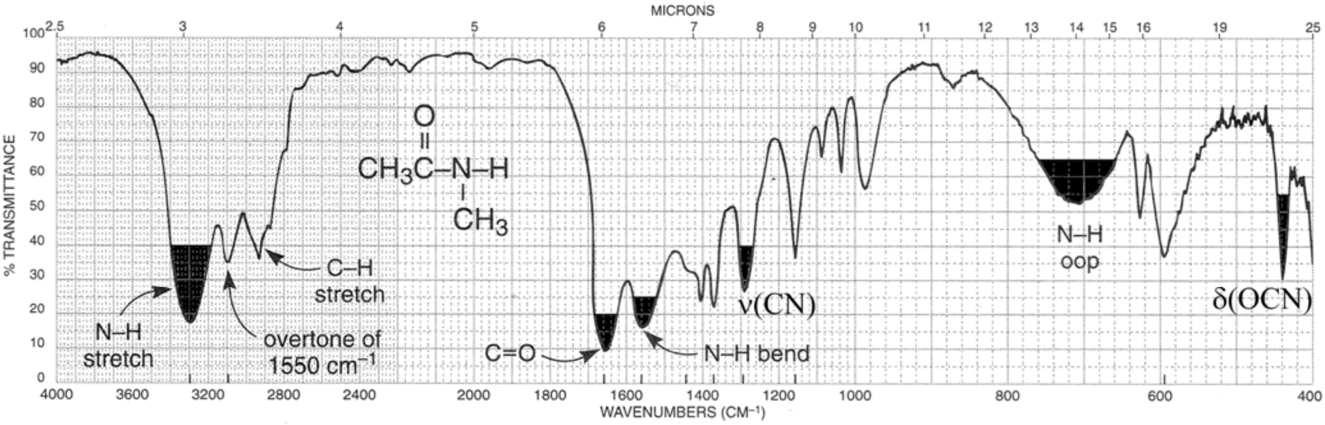
The infrared spectrum of propionamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands.

Secondary amides

Adsorption regions of –C(=O)NH–CH_3 group:

Vibrations	Region (cm^{-1})
ν(NH) (A)	3315(45) vvs
Overtone Amide (B)	~3100 (2x1550) m,s
ν(C=O) (I)	1680(60) vvs
δ(NH) / ν(CN) (II)	1550(50) vs
ν(CN) / δ(NH) (III)	1270(55) m, s
ν(N–C’)	1015(95)
γ(NH) (V)	735(60) s, vb
δ(C=O) (IV)	695(75)*
γ(O=C–N) (VI)	450(100) m
δ(CNC’)	315(60)

*overlapping with γ(NH)



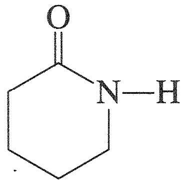
The infrared spectrum of N-methylacetamide (neat liquid, KBr plates).

Tertiary amides

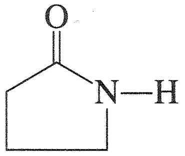
They cannot form hydrogen bonds, have C=O frequencies that are not influenced by associations.

ν(C=O) 1655(30) cm^{-1} as very strong band

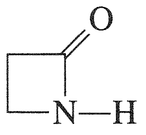
Cyclic amides (lactams) give the expected increase in C=O frequency for decreasing ring size.



~1660 cm^{-1}



~1705 cm^{-1}



~1745 cm^{-1}

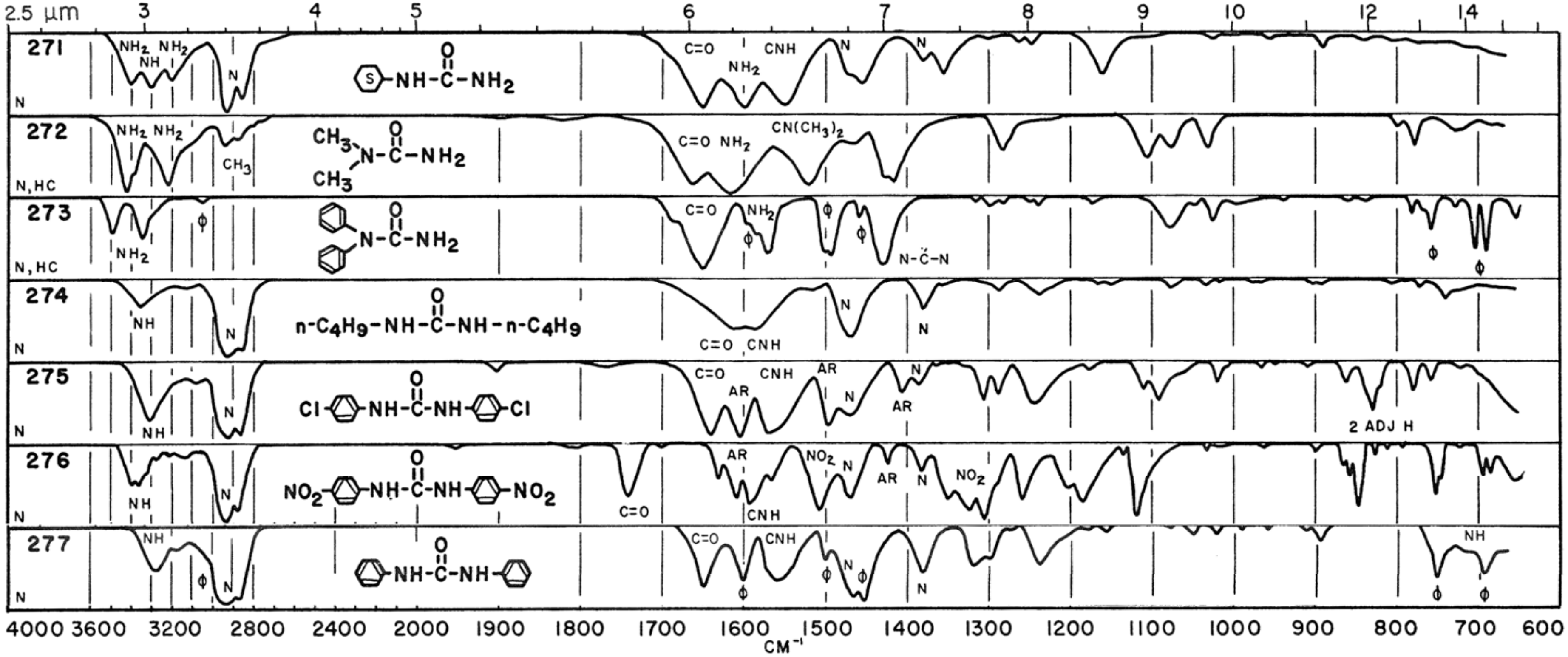
UREAS

Spectra of ureas show many similarities to spectra of previously described amides.

$$\left.\begin{array}{l}-C{=}O\\ -NH_2\end{array}\right\}$$ bands are similar to those of amides (small shifts)

Approximate Wavenumbers (cm^{-1}) for Substituted Ureas

Group	$\nu_a(NH_2)$	$\nu(NH)$	$\nu_s(NH_2)$	$\nu(C{=}O)$	$\delta(NH_2)$	$\delta(CNH)$
$R_2N–CO–NR_2$	–	–	–	1640	–	–
RNH–CO–NHR	–	3340	–	1625	–	1585, 1535 w
$R_2N–CO–NH_2$	3410	–	3200	1660	1610	–
$RNH–CO–NH_2$	3430	3350	3220	1650	1600	1560


2.5 μm
3
4
5
6
7
8
9
10
12
14
271
N
NH₂ NH NH₂
N
C=O NH₂ CNH
N
N
S–NH–C(=O)–NH₂
272
N, HC
NH₂ NH₂
CH₃
C=O NH₂
CN(CH₃)₂
(CH₃)₂N–C(=O)–NH₂
273
N, HC
NH₂
φ
C=O NH₂
φ
φ
φ
N–C–N
φ
φ
(C₆H₅)₂N–C(=O)–NH₂
274
N
NH
N
C=O CNH
N
N
n-C₄H₉–NH–C(=O)–NH–n-C₄H₉
275
N
NH
N
C=O AR CNH
AR N
N AR
2 ADJ H
Cl–C₆H₄–NH–C(=O)–NH–C₆H₄–Cl
276
N
NH
N
C=O
AR CNH
NO₂ N
AR N
NO₂
NO₂–C₆H₄–NH–C(=O)–NH–C₆H₄–NO₂
277
N
NH
φ N
C=O CNH
φ
φ
N φ
N
NH
φ φ
C₆H₅–NH–C(=O)–NH–C₆H₅
4000
3600
3200
2800
2400
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CM⁻¹