Spectroscopic Identification of Organic Molecules

Infrared Spectroscopy

Exclusively for the summer course at
East China University of Science and Technology

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Infrared Spectroscopy

1. Introduction

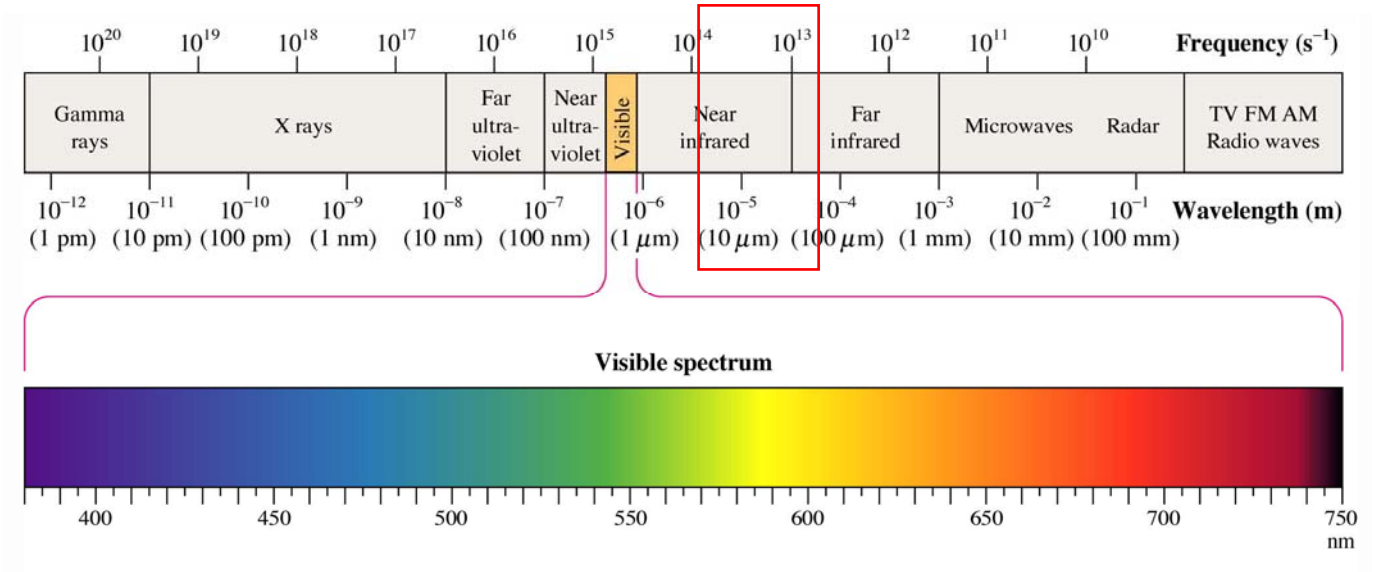
The range between 4000 cm^{-1} ~ 400 cm^{-1} is of practical use.

Near IR (14,290~4000 cm^{-1}); Far IR (700~200 cm^{-1})

Normally complex spectrum related with vibro-rotational motion of molecule is obtained.

Identification of certain functional groups

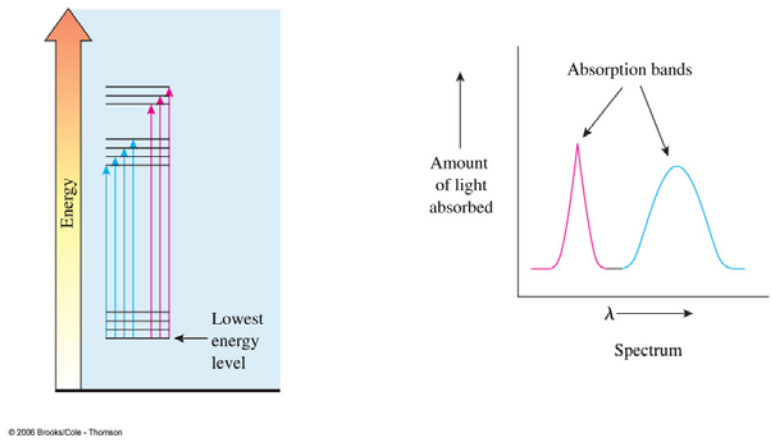
Peak-by-peak correlation – identification with authentic sample



2. Theory

▶Infrared radiation in the range 10,000~100 cm^{-1} is absorbed and converted by organic molecule into energy of **molecular vibration**.

The vibrational spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes.



▶**Band Intensities** can be expressed either as transmittance (*T*) or Absorbance (*A*).

Transmittance (*T*): the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample: I/I_0 x 100 (%)

Absorbance (*A*): $A = \log_{10} (1/T)$

▶**The frequency of absorption** depends on ① the relative masses of the atoms, ② the force constants of the bonds, and the geometry of the atoms.

Band positions in IR are presented as wavenumber (1/cm or cm^{-1})

Wavenumber (cm^{-1}) = 1/λ (cm) vs. Frequency (Hz or s^{-1}) = c/λ, where or c = 3 x 10^{10} cm/s.

Hooke's law (harmonic oscillator model of two masses)

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f}{(MxMy)/(Mx + My)}}$$

where $\bar{\nu}$ = the vibrational frequency (cm^{-1})
c = velocity of light (cm/s)
f = force constant of bond (dyne/cm)
Mx and My = mass (g) of atom x and atom y, respectively.

Force constant

TABLE 2.1 IR Absorption Regions Using Hooke's Law

Bond Type	Force Constant f in dyne/cm	Absorption Region (cm^{-1})	
		Calculated	Observed
C—O	5.0×10^5	1113	1300–800
C—C	4.5×10^5	1128	1300–800
C—N	4.9×10^5	1135	1250–1000
C=C	9.7×10^5	1657	1900–1500
C=O	12.1×10^5	1731	1850–1600
C≡C	15.6×10^5	2101	2150–2100
C—D	5.0×10^5	2225	2250–2080
C—H	5.0×10^5	3032	3000–2850
O—H	7.0×10^5	3553	3800–2700

Deuteration Study.

$M_C M_H/(M_C + M_H) \approx M_C M_H/(M_C) = M_H$ ($M_C >> M_H$)

Frequency(C–H)/ frequency(C–D) = $(2/1)^{1/2}$

▶ **Solvents for IR**

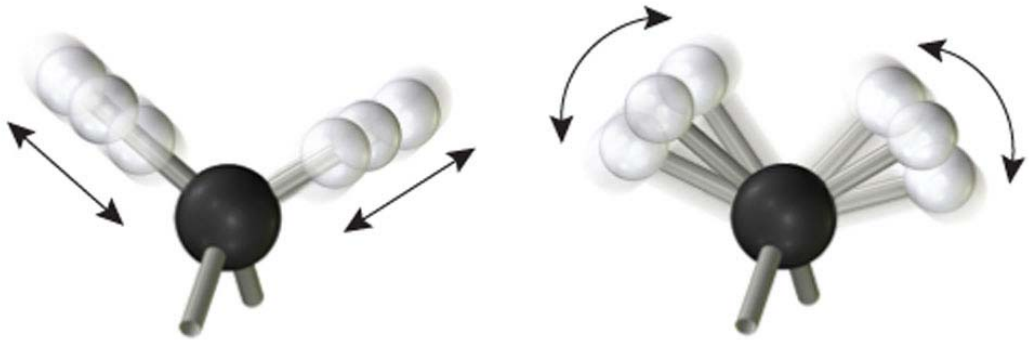
Table 1.2 lists some of the more common solvents used in IR spectroscopy. Clearly, spectra must be run in several solvents to obtain a spectrum of the entire mid-IR region.

Table 1.2 Opaque Regions in Common IR Solvents

Solvent	Opaque Regions (cm^{-1})	
CCl_4	700–850	
CS_2	1400–1600	2100–2200
$CHCl_3$	600–820	1175–1250
C_2Cl_4	750–950	
Benzene	600–750	3000–3100
CH_2Cl_2	600–820	1200–1300
Acetone	1100–1850	2800–3000
Cyclohexane	2600–3000	
Ethyl ether	1050–1200	2700–3000
Hexane, heptane	1400–1500	2800–3000
DMSO	900–1100	
Toluene	600–750	2800–3200

※CS_2 may react with primary and secondary amines

▶**Types of molecular vibration** – stretching (change of inter-atomic distance) and bending (change of bond angle).



Vibrations that result in a rhythmical **change in the dipole moment** of the molecule are observed in IR.

Degrees of freedom

Each atom has **three degrees of freedom** corresponding to the Cartesian coordinates (x, y, z) necessary to describe its position relative to other atoms in the molecule.

A molecule of n atoms has **3n** degrees of freedom.

Molecular motions: translational, vibrational, and rotational motions

For nonlinear molecules, 3 degrees of freedom describe translation and 3 degrees of freedom describe rotation; the remaining **3n–6** degrees of freedom are vibrational degrees of freedom (fundamental vibrations).

Linear molecules: 3n–5 vibrational degrees of freedom (2 degrees of freedom are required to describe rotation).

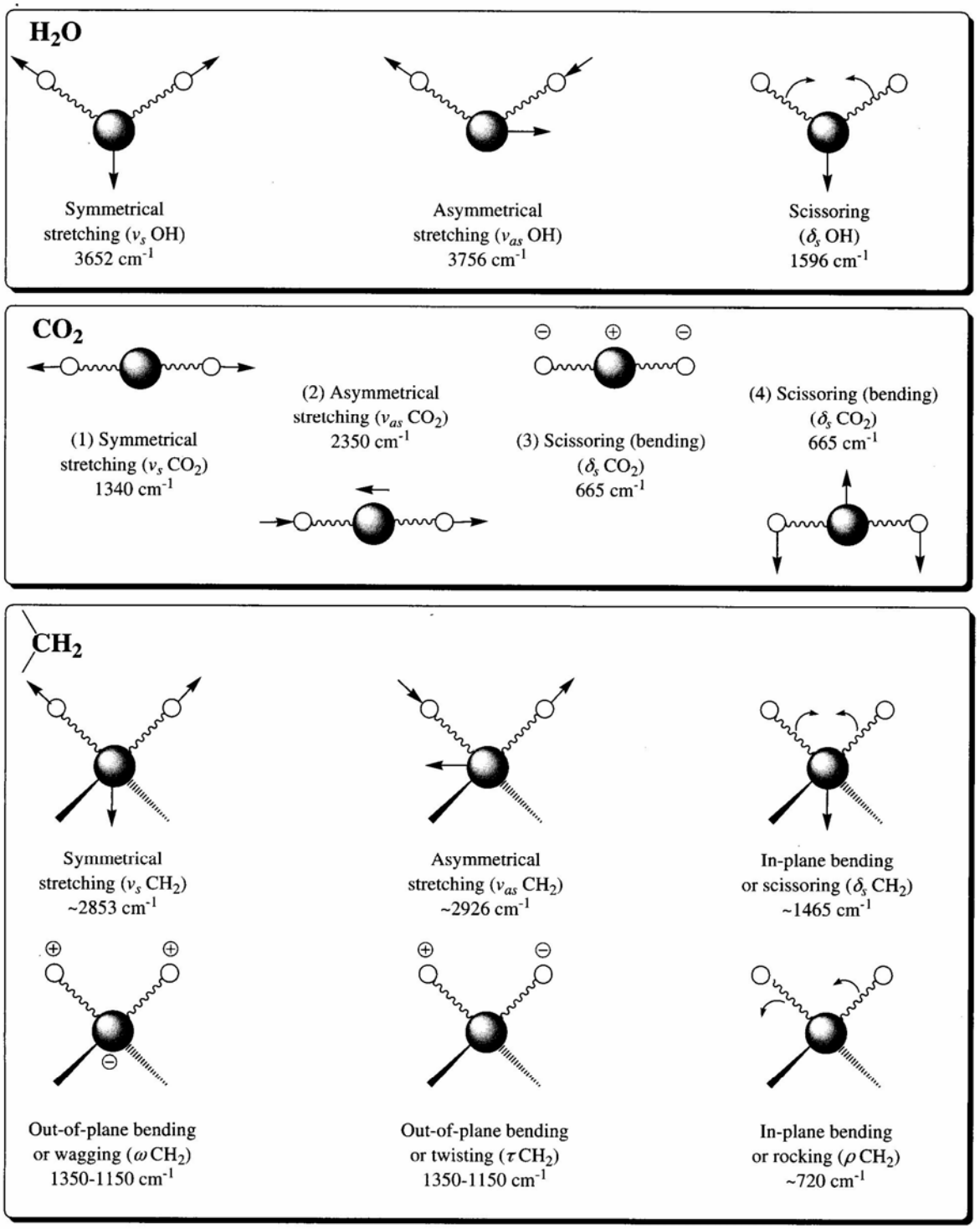


FIGURE 2.1. (Top) Vibrational modes for H_2O. (Middle) Vibrational modes for linear CO_2. (Bottom) Vibrational modes for a CH_2 group (+ and − indicate movement perpendicular to the plane of the page).

▶Interpretation of Spectra

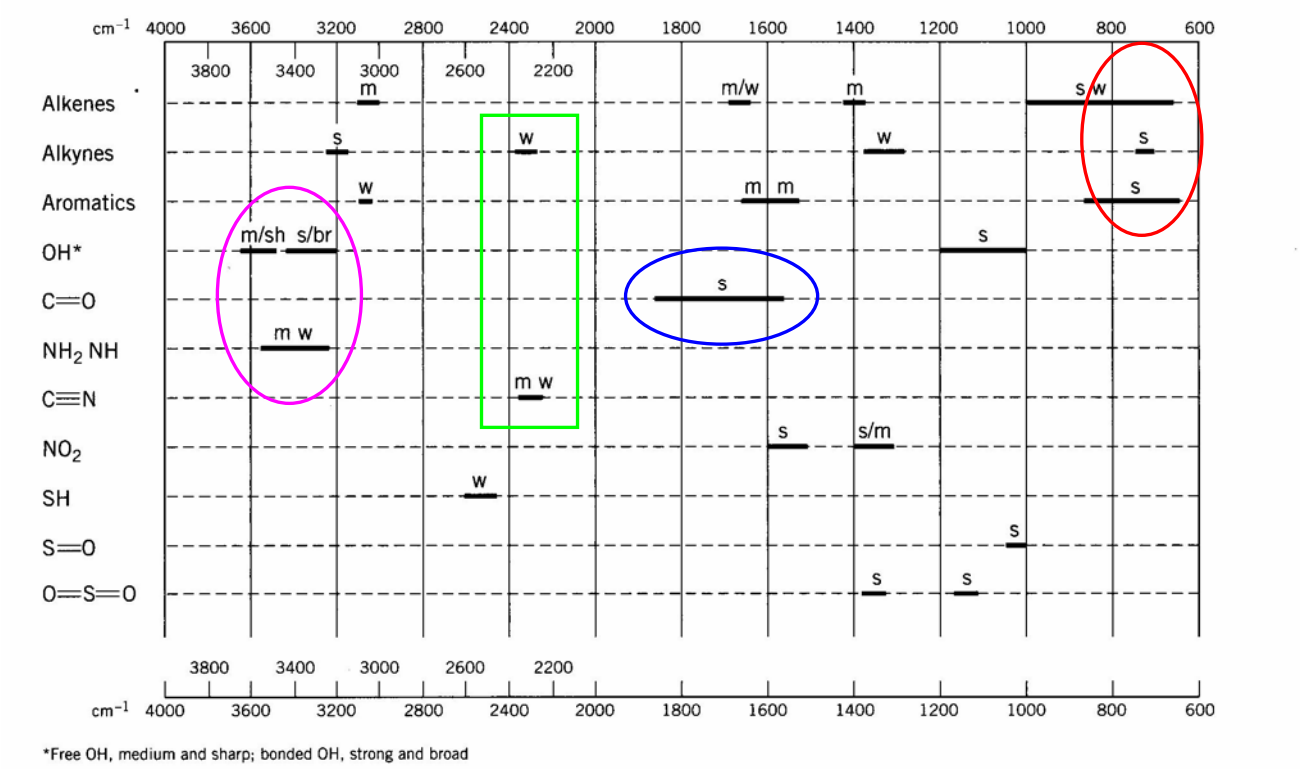


FIGURE 2.7. Simplified chart of several common functional groups with very characteristic absorptions. s = strong, m = medium, w = weak, sh = sharp, br = broad.

1. The high-frequency portion (4000–1300 cm^{-1}) – functional group region

The characteristic stretching frequencies of OH, NH, and C=O etc.

Strong skeletal bands for aromatics and hetero-aromatics in 1600–1300 cm^{-1}

2. The low-frequency portion (900–650 cm^{-1})

The lack of strong absorption bands indicates non-aromatic structure. Aromatics display strong out-of-plane C–H bending and ring bending absorption.

Broad, moderately intense absorption suggests the presence of carboxylic acid dimers, amines, or amides (out-of-plane bending)

3. The intermediate portion (1300–900 cm^{-1}) – finger-print region

Interacting vibrational modes are observed. Specific structure can be assigned.

The C–C–O absorption band in 1260–1000 cm^{-1} makes it possible to assign a specific structure to the alcohol compounds (OH).

4. **Characteristic Group Absorptions of Organic Molecules**

Qualitative analysis of peak frequencies

ν (X–H) > ν (C≡X) > ν (C–X) > δ (X–H) > ν (C–X) > δ (C–X)

(X = C, N, O)

▶Alkanes

Four vibrations: **ν (C–H)**, **δ (C–H)**, ν (C–C), δ (C–C)

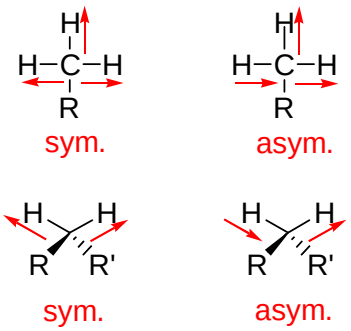
ν (C–C) is week, and appears in the broad region of 1200–800 cm^{-1}.

δ (C–C) occurs at very low frequencies (below 500 cm^{-1})

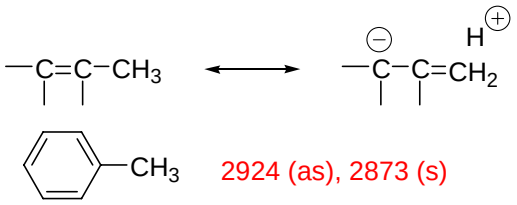
① C–H Stretching Vibrations ν (C–H): 3000–2840 cm^{-1}.

Methyl group: 2962 (as) and 2872 (s)

Methylene group: 2926 (as) and 2853 (s)

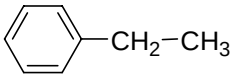


※Hyper-conjugation effect – lower ν (C–H): 2930–2920 cm^{-1} (as).



2924 (as), 2873 (s)

cf.



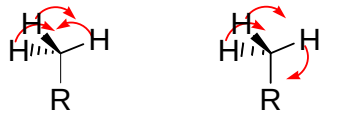
2968 (as), 2874 (s)

② C–H bending Vibrations

Methyl group: 1450 (as) 1375 (s)

Methylene group: scissoring (1465), rocking (720);

wagging, and twisting (1350–1150)



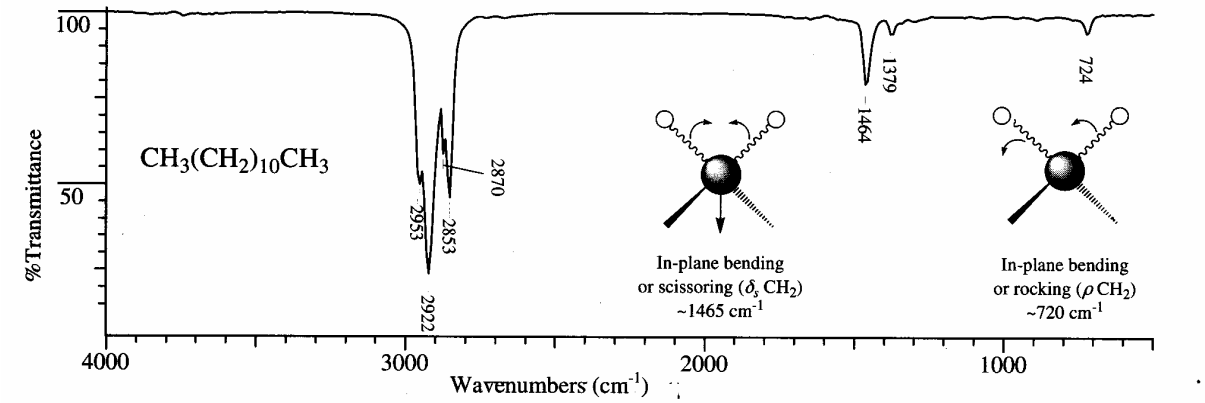


FIGURE 2.8. Dodecane. C—H stretch: 2953 cm^{-1} $\nu_{as}CH_3$, 2870 cm^{-1} ν_sCH_3, 2922 cm^{-1} $\nu_{as}CH_2$, 2853 cm^{-1} ν_sCH_2. C—H bend: 1464 cm^{-1} δ_sCH_2, 1450 cm^{-1} $\delta_{as}CH_3$, 1379 cm^{-1} δ_s CH_3. CH_2 rock: 724 cm^{-1} ρ CH_2.

※Geminal dimethyl splitting – strong doublet (resonance) at 1385–1380 and 1370–1365 cm^{-1}.

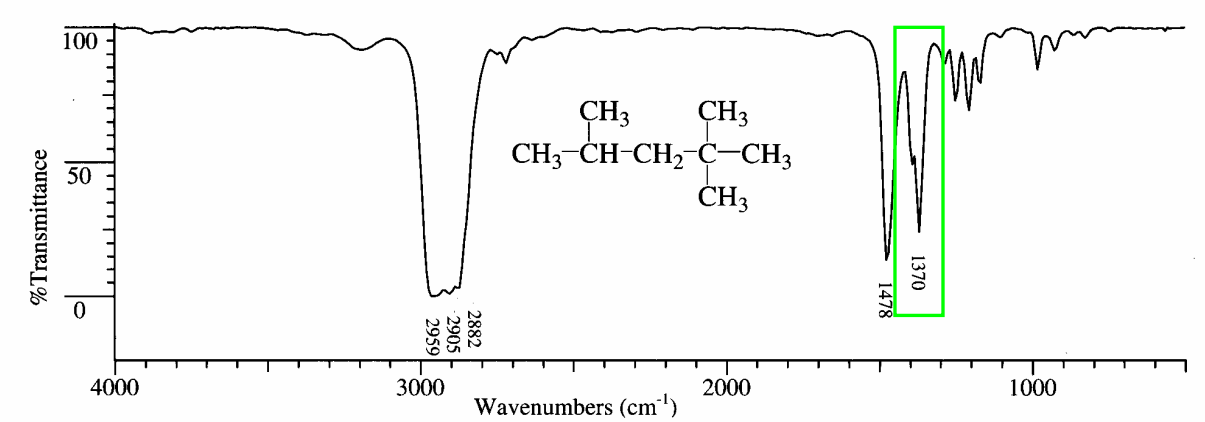
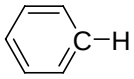


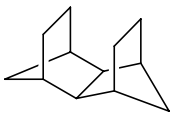
FIGURE 2.9. 2,2,4-Trimethylpentane.* C—H stretch (see Figure 2.8). C—H bend (see Figure 2.8). There are overlapping doublets for the *t*-butyl and the isopropyl groups at 1400–1340 cm^{-1}. Compare the absence of a methylene rocking band(s) 1000–800 cm^{-1} to Figure 2.8.

More S-character in the C–H bonding gives higher value in ν (C–H).

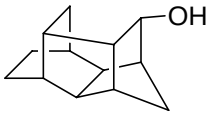
Functional group	Hybridization (% s-character)	ν (C–H)
≡C–H	sp (50)	3310–3200
=C(H)–	sp^2 (33)	3090–3020
	sp^2 aromatic (33)	3030
–C(H)–, –CH_3	sp^3 (25)	2962 (as) 2872 (s)
–CH_2–	sp^3 (25)	2926 (as) 2853 (s)
–C(H)–	sp^3 (25)	2890

Selected examples

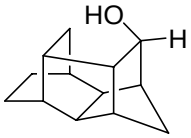
(1) Steric compression



ν (C-H) 3031



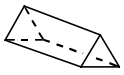
3048



3083

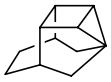
(2) Cyclopropanes: angle strain (high s-character in C–H bond)

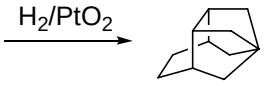
s (32%)
3050 (as)



prismane

s (35%)
3066 (as)





3100 cm^{-1} disappeared

(3) Halides

ν (C–H)		F	Cl	Br	I
CH_3X	asym	2982	3042	3056	3060
	sym	2964	2966	2972	2970
CH_2X_2	asym	3012	3048	3065	3049
	sym	2949	2985	2988	2967
CHX_3		3031	3040	3040	–

3077
2985

2967
2841

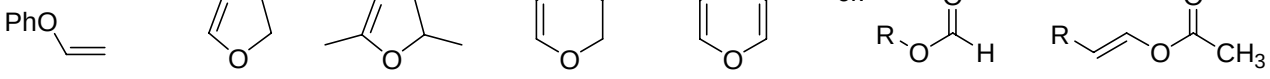
▶Alkenes

1. ν (C–H) olefinic: > 3000 cm^{-1}
2. ν (C–H) saturated
3. **ν (C=C): 1667–1640 cm^{-1} (m~w)**
4. δ (C–H) in-plane bending
5. **δ (C–H) out-of-plane bending: 1000–650 cm^{-1}**

ν (C=C): 1650 cm^{-1}

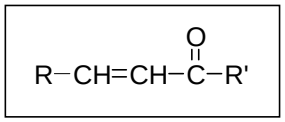
※Moderate (m) to weak (w) absorption for unconjugated alkenes. Tetra-substituted C=C can not be detected unless N, O is not attached.

① Enol ethers: 1690–1640 (strong)



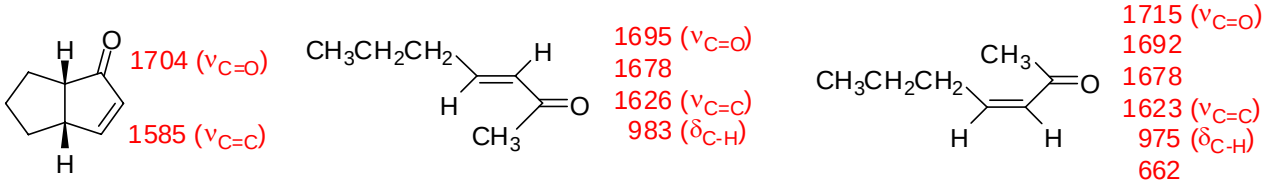
Δν = 53 cm^{-1} Δν = 53 cm^{-1}

② Conjugated double bonds

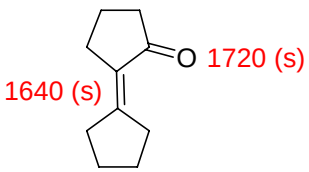


ν (C=C) – lower wave-number, stronger ε
δ (C–H) trans 985–975 cm^{-1}
δ (C–H) cis 975–968, 690–660 cm^{-1}

Examples



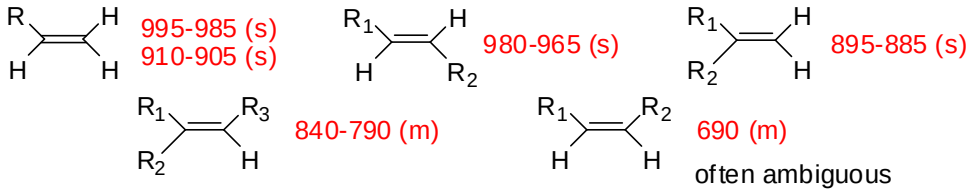
※ Strong ν (C=C) in s-cis-conjugation



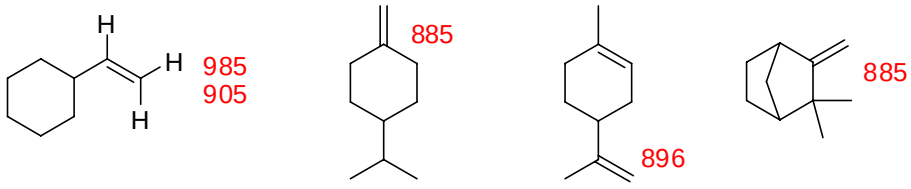
If | ν (C=O) – ν (C=C) | > 75 cm^{-1}, ν (C=O) and ν (C=C) are comparable in intensities.

If | ν (C=O) – ν (C=C) | < 75 cm^{-1}, ν (C=O) is stronger than ν (C=C) as in s-trans-configuration.

δ (C–H) out-of-plane bending



Examples



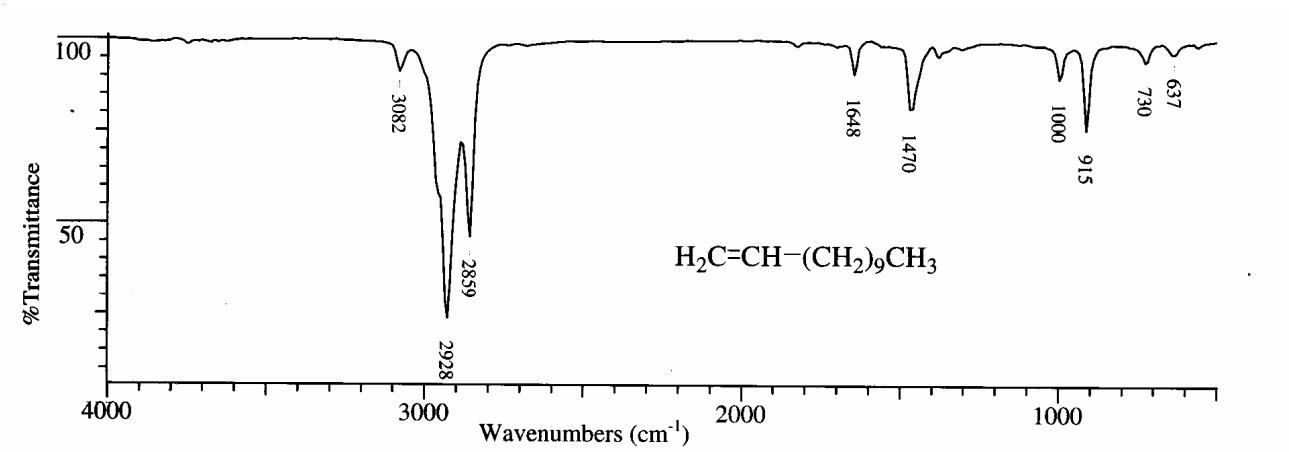


FIGURE 2.10. 1-Dodecene. C—H stretch (see Figure 2.8). Note alkene C—H stretch at 3082 cm^{-1}. C=C stretch, 1648 cm^{-1}, see Appendix Table C-1. Out-of-plane C—H bend: 1000 cm^{-1}, (alkene) 915 cm^{-1}. Methylene rock: 730 cm^{-1}.

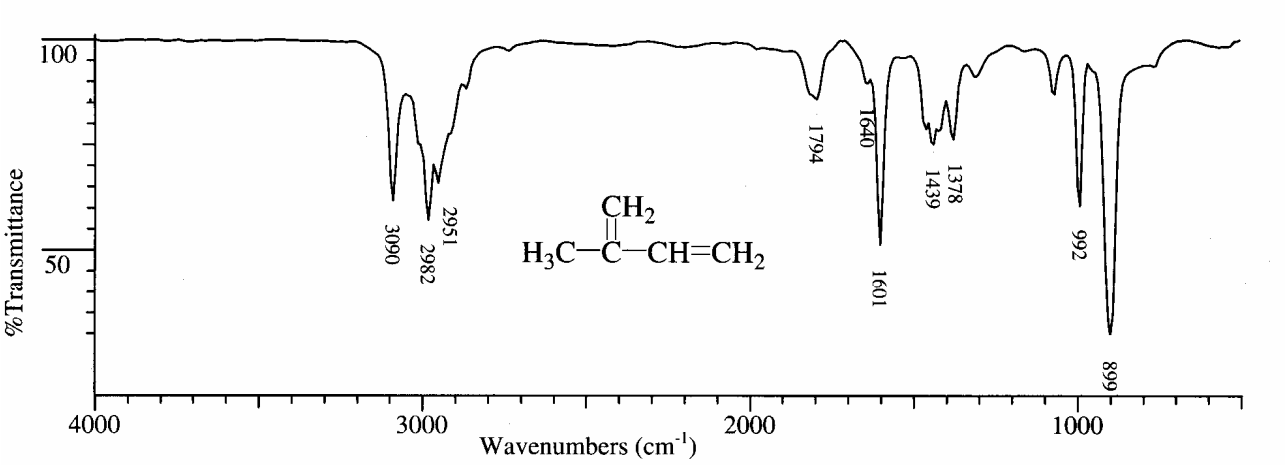


FIGURE 2.11. Isoprene. C—H stretch: =C—H 3090 cm^{-1}. Coupled C=C—C=C stretch: symmetric 1640 cm^{-1} (weak), asymmetric 1601 cm^{-1} (strong). C—H bend (saturated, alkene in-plane). C—H out-of-plane bend: 992 cm^{-1}, 899 cm^{-1} (see vinyl, Appendix Table C-1.)

▶ Aromatics

1. ν (C–H): 3100–3000 cm^{-1}
2. **Overtone and combination bands: 2000–1667 cm^{-1}**
3. ν (C=C): 1600–1450 cm^{-1} (1600, 1580, 1500, 1450 cm^{-1})
4. δ (C–H) in-plane bending: 1225–950 cm^{-1}
5. **δ (C–H) out-of-plane bending: < 900** cm^{-1}**.**

Substitution patterns can be distinguished by overtone/combination bands and out-of-plane bending.

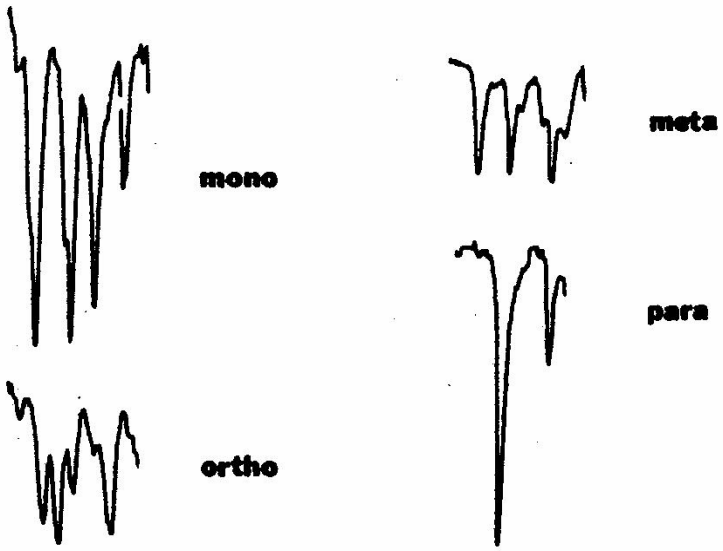
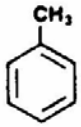


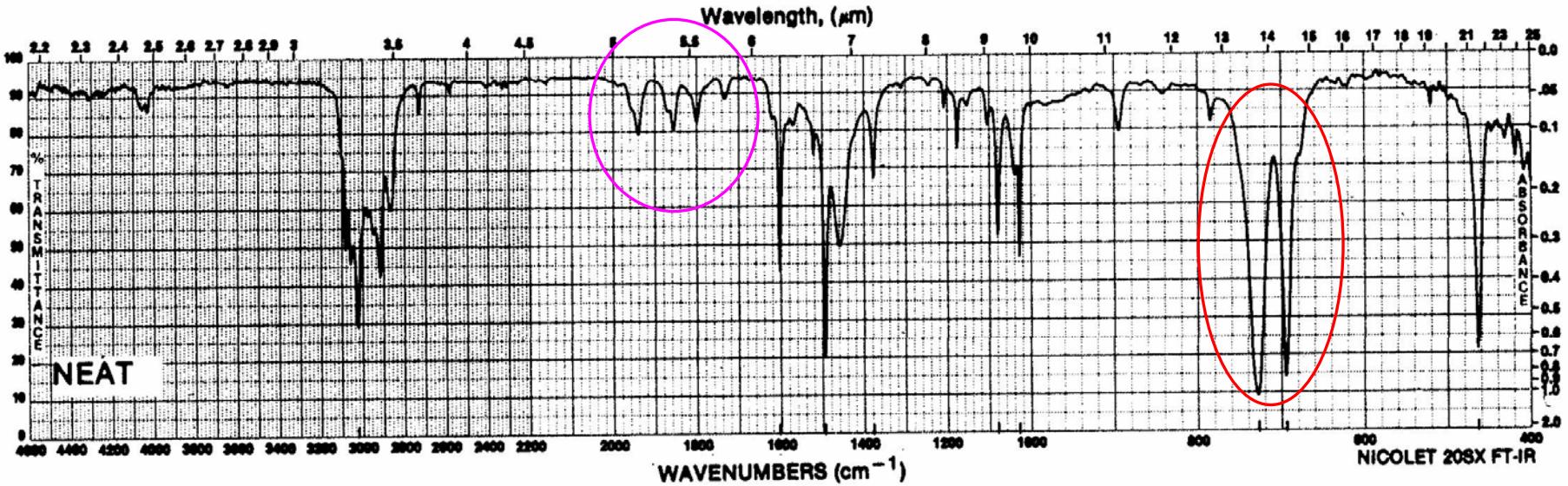
Figure 2.5 Characteristic patterns observed in the region 1650–2000 cm^{-1} for mono-, *ortho*-, *meta*-, and *para*-substituted benzenes.

Monosubstituted	770–730 cm^{-1} and 710–690 cm^{-1}
Ortho-substituted	770–735 cm^{-1}
Meta-substituted	810–750 cm^{-1} and 710–690 cm^{-1}
Para-substituted	860–800 cm^{-1}

15500-4 *CAS [108-88-3]*
Toluene, 99 + %

FW 92.14	d 0.867	IR III, 561B	3026.4	1378.6	728.4
mp -93 °C	Fp 40 °F	NMR II, 1,733B	1604.3	1081.2	694.4
bp 111 °C	nβ 1.4968	Merck 10,9357	1495.4	1029.9	464.1





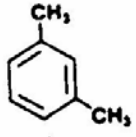
18556-6 *CAS [108-38-3]*
***m*-Xylene, 99%**

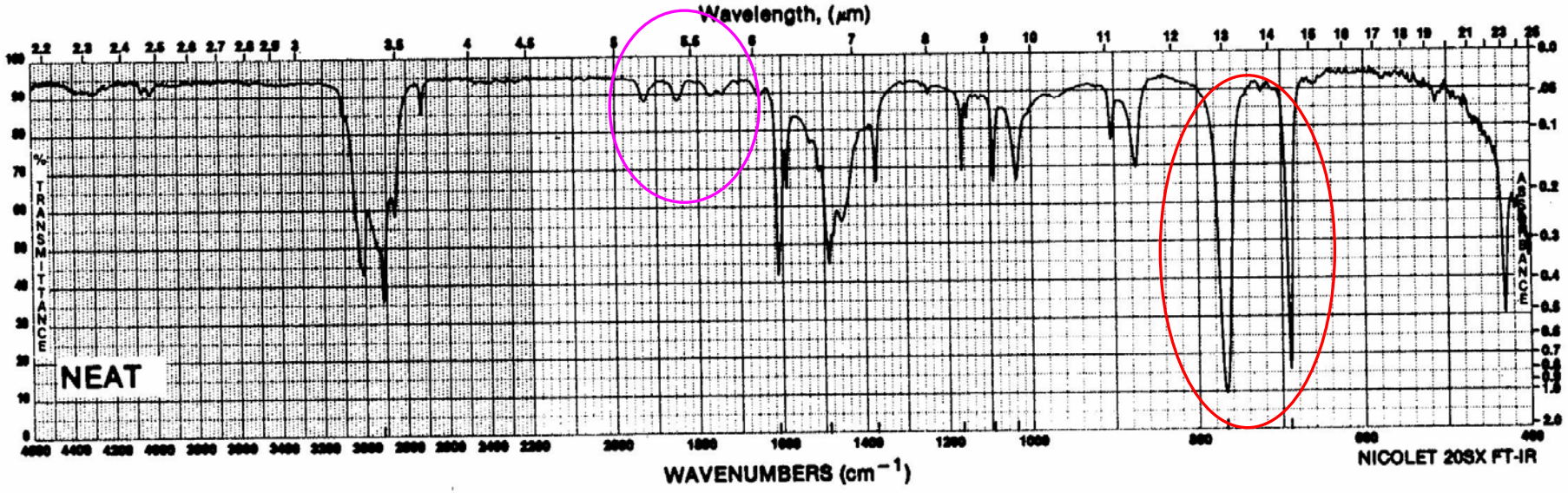
FW 106.17
bp 138-139°C
d 0.868

Fp 77°F
nD 1.4970

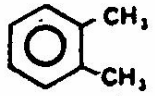
IR III, 565A
Merck 10,9890

2921.2 1376.3 1039.7
1613.9 1170.0 768.3
1491.9 1094.5 691.1

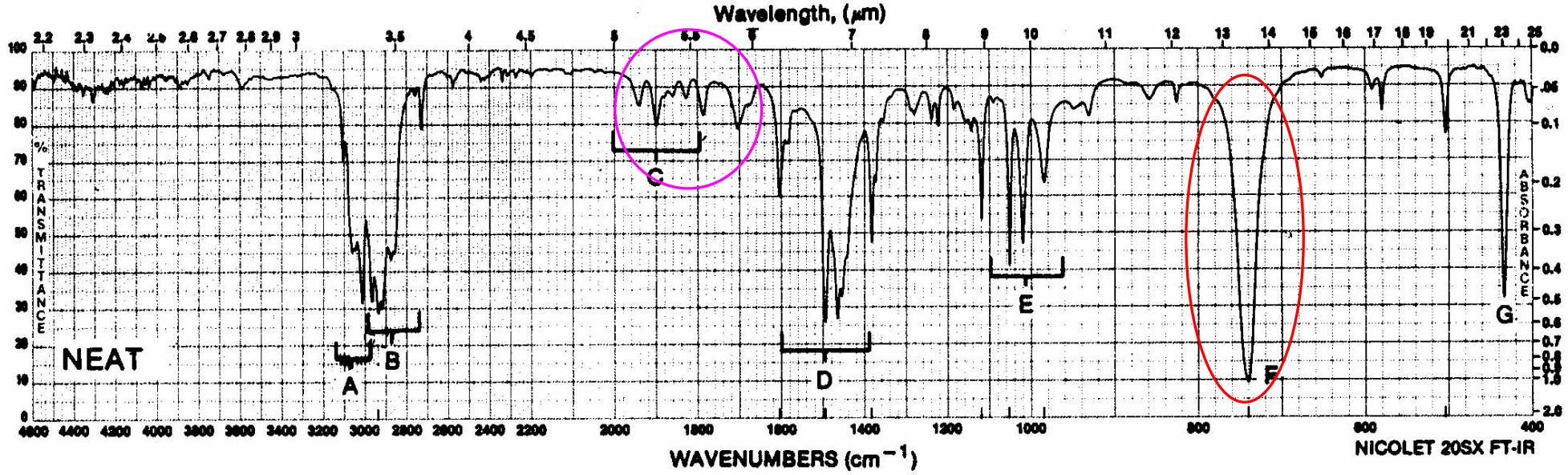




X104-0 *CAS [95-47-6]*
o-Xylene, 97%



FW 106.17	d 0.897	IR III, 564D	2939.6	1383.8	985.1
mp -23°C	Fp 90°F	NMR II, 1,740B	1605.7	1119.6	741.3
bp 143-145°C	nβ 1.5048	Merck 10,9890	1495.2	1052.5	505.3



▶▶X≡Y & X=Y=Z Groups ν: 2500–1900 cm^{-1}

X, Y, Z = C, N, O

▶ Acetylenes ν (C≡C): sharp, absent in symmetrical molecule

① R–C≡C–H

ν (C≡C): 2140–2100 cm^{-1} (w), no band for the symmetrically substituted alkynes
ν (≡C–H): 3310–3200 cm^{-1} (s)
δ (≡C–H): 700–600 cm^{-1} (s)

Examples

CH_3–C≡C–H: 2150 (m) CH_3CH_2–C≡C–H: 2120 (m)

$(CH_3)_2CH$–C≡C–H: 2135 (m) $HO(CH_2)_5$–C≡C–H: 2140 (m)

② R–C≡C–R'

ν (C≡C): 2260–2190 cm^{-1} (w)

Examples

CH_3–C≡C–C_4H_9: 2210 (w) C_2H_5–C≡C–C_3H_7: 2190 (vw)

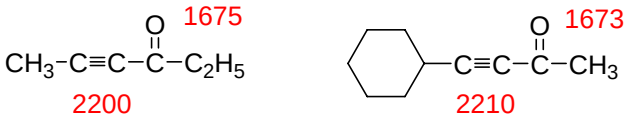
C_2H_5–C≡C–$(CH_2)_3OH$: 2260 (vw)

CH_3–$(CH_2)_3$–C≡C–CH_2–C≡C–H: 2240, 2300, 2135, 3300 (ν_{C-H})

③ **Conjugation** with a double bond or a phenyl group – shift to a **lower frequency**

H–C≡C–C≡C–H: 2033 $CH_3(CH_2)_3CH$=CH–C≡CH: 2114, 1618 ($\nu_{C=C}$)

④ **Conjugation** with a C=O group – ν (C≡C): not much change, but intensity increases



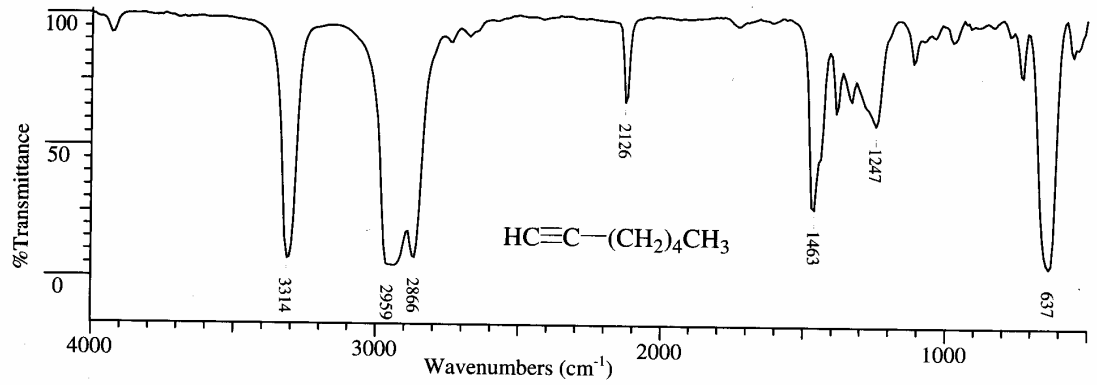
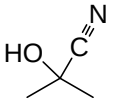


FIGURE 2.12. 1-Heptyne. ≡C—H stretch, 3314 cm^{-1}. Alkyl C—H stretch 1450–1360 cm^{-1} (see Figure 2.8), 2960–2860 cm^{-1}. C≡C stretch, 2126 cm^{-1}. C—H bend: 1463 cm^{-1} $\delta_s CH_2$, 1450 cm^{-1} $\delta_{as} CH_3$. ≡C—H bend overtone, 1247 cm^{-1}. ≡C—H bend fundamental, 637 cm^{-1}.

▶ Nitriles (R–C≡N) **$\nu_{C\equiv N}$: 2300–2200 cm^{-1},**

Intensity: sharp and variable



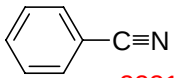
The intensity is diminished if an oxygen-containing group is present near C≡N bond

1/3~1/4 of the normal intensity

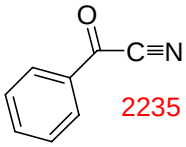
① Aliphatic C≡N: 2250 ± 10 cm^{-1}

$N\equiv CCH_2CH_2CH_2C\equiv N$: 2254

② Aromatic C≡N: 2235 ± 5 cm^{-1}



2231



2235

③ **Conjugation** with a C=C double bond: 2225 ± 8 cm^{-1}

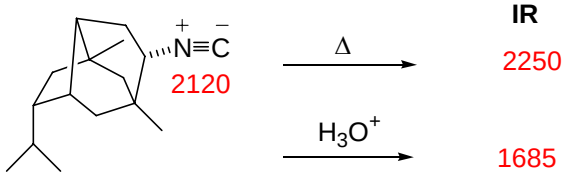
$N\equiv C–CH=CH–CH_2CH_2–C\equiv N$

2225 2258

▶ Isonitriles ($R–N^+\equiv C^-$) **$\nu_{N\equiv C}$: Aliphatic 2183–2120 cm^{-1}, Aromatic 2145 cm^{-1}**

Very strong intensity

ν ($C–N_{\equiv C}$) 1594 cm^{-1} (this peak is absent in nitrile)



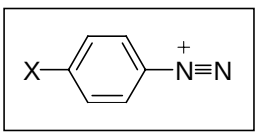
9-Isocyanopupukeanane

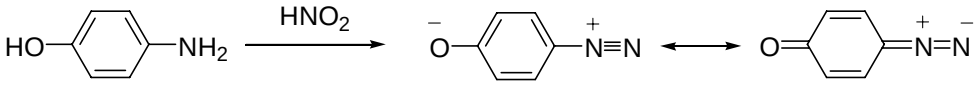
▶ Diazonium Salts ($R–N^+\equiv N$) **$\nu_{N^+\equiv N}$: 2280–2240 cm^{-1},**

Substitution effect

Donating group: X = $N(CH_3)_2$ 2125 cm^{-1}

Withdrawing group: X = NO_2 2294 cm^{-1}





2173–2014 cm^{-1} $\nu(C=N^+=N^-)$

X=Y=Z

asymmetric ν: ca. 2000 cm^{-1}

symmetric ν: ca. 1100 cm^{-1} (weak and not practical)

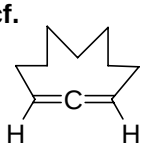
▶ Azide ($R-N=N^+=N^-$) asymmetric ν: 2169–2080 cm^{-1} (sometimes split)
symmetric ν: 1343–1177 cm^{-1}

▶ Allene (C=C=C) $\nu_{C=C}$: 2200–1950 cm^{-1} singlet or doublet (vibrational coupling)

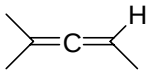
① Terminal allenes: strong $\delta_{C=C=}CH_2$ ca. 850 cm^{-1}

$H_2C=C=CH_2$	ν(C=C=C)	1957 (vs)	δ(CH_2)	842 (m)
$H_3C-CH=C=CH_2$		1961 (vs)		858 (vs)
$(H_3C)_2C=C=CH_2$		1930 (s)		845 (vs)
c-Hx=C=CH_2		1955 (s)		843 (s)

cf.



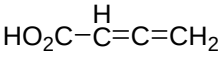
1960



1940 (w)

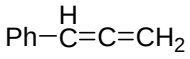
② Terminal allenes conjugated with $-CO_2H$, $-CO_2R$, $-CONH_2$, $-COCl$, $-COR$

$\nu_{C=C}$ Doublet

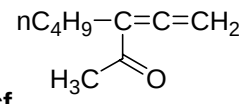


1930, 1900 (s)
850 (s)

cf.

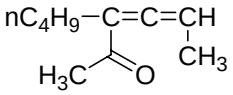


1955 (s)
860 (s)



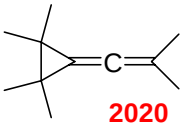
1930, 1910 (s)
855 (s)

cf.

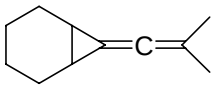


1960 (s)

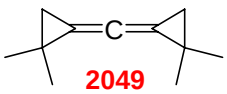
③ Strained allenes: above 2000 cm^{-1}



2020



2030, 2000

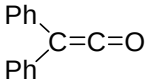


2049

▶ Isocyanates ($R-N=C=O \longleftrightarrow R-N^+\equiv C-O^-$) ν: 2275–2230 cm^{-1} very strong
Most aromatic / aliphatic $-N=C=O$: 2275–2263 cm^{-1}
But, $CH_3-N=C=O$: 2231 cm^{-1}

▶ Ketenes ($RR'C=C=O$)
asymmetric ca. 2150 cm^{-1}: strong
symmetric ca. 1120 cm^{-1}

$H_2C=C=O$ **2160, 1130**



2130

▶Alcohols and Phenols

ν (O–H), δ (O–H), ν (C–O)

(1) **Free** ν (O–H): no hydrogen-bonded

Measurement should be in CCl_4, which is dried over P_2O_5, and concentration should be lower than 0.01 mole/L.

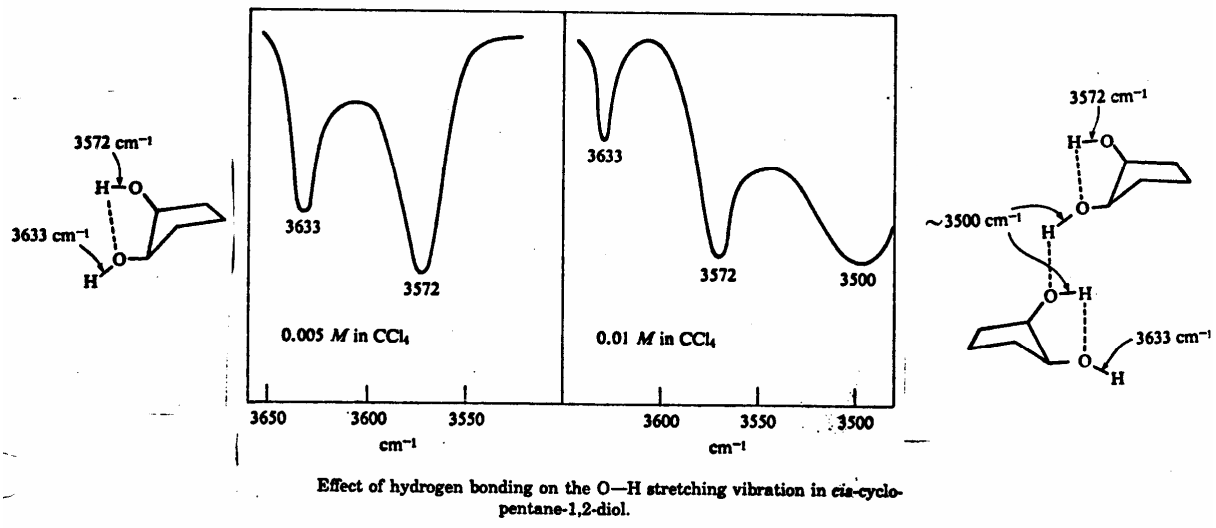
primary OH	3644–3635 cm^{-1} (3640)
secondary OH	3630–3625 cm^{-1} (3628)
tertiary OH	3620–3615 cm^{-1} (3617)
phenolic OH	3615–3595 cm^{-1}

ν (O–H) of R–OH

	R–OH	I	II	III	
1°	CH_3OH CH_3CH_2OH $CH_3CH_2CH_2OH$	3644 3637 3640	 3627 3626		
2°	$(CH_3)_2CHOH$ $CH_3(CH_2)_2CHOH$		3627 3629	3617 3615	
3°	$(CH_3)_3COH$ $CH_3CH_2(CH_3)_2COH$			3617 3617	
		3640	3628	3617	

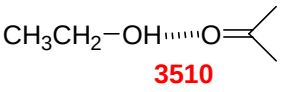
I II III

(2) Inter- & Intramolecular H-bonding



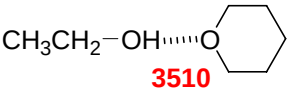
Effect of hydrogen bonding on the O—H stretching vibration in *cis*-cyclopentane-1,2-diol.

(2-1) Intermolecular H-bonding (concentration dependent)



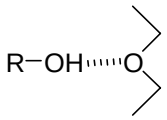
(a) Dimeric association: ~3500 cm^{-1}

EtOH and Acetone (in CCl_4): 3510



EtOH and dioxane (in CCl_4): 3510

R(alkyl)–OH and diethyl ether: 3492–3482

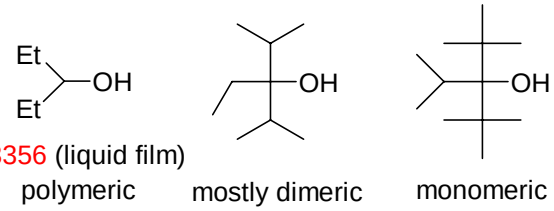


3492-3482

(b) Polymeric association: 3400–3200 cm^{-1}

i) Steric effect

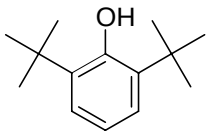
①



3356 (liquid film)

polymeric mostly dimeric monomeric

②

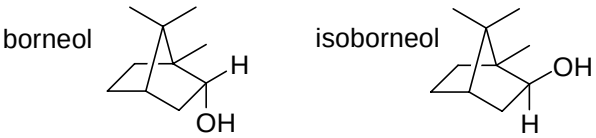


3646 (liquid film)
3647 (CCl_4 solution) } no association (monomeric)

ii) Stereochemical application

$\Delta \nu = \nu_{OH}$(free) − ν_{OH}(H-bonded)

Larger Δ ν indicate stronger H-bonding



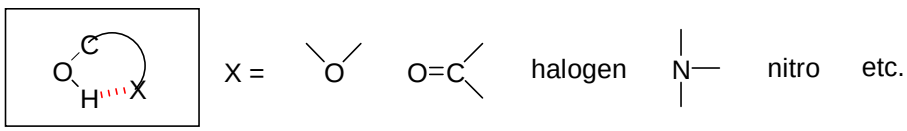
free OH (CS_2)	3623	3619
bonded OH (nujol)	3433	3483
Δ ν =	190	136

(2-2) Intramolecular H-bonding (concentration independent)

ν (OH) 3570–3450 cm^{-1} (relatively weak)

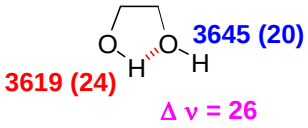
※If the band disappeared upon dilution (< 0.005 M), this must be due to the intermolecular dimeric association.

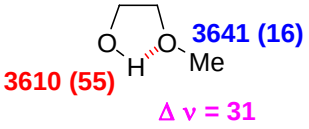
(a) Single-bridge complex: 3600–3500 cm^{-1}

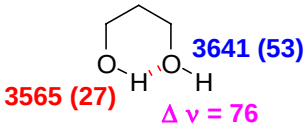


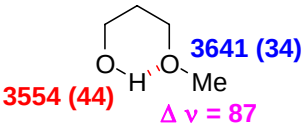
i) $HO(CH_2)_nOH$, $MeO(CH_2)_nOH$

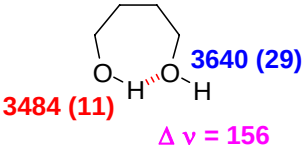
ν_{max} (ε)

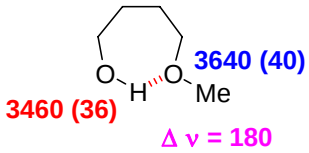


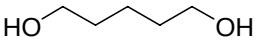






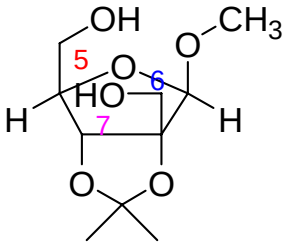






no intramolecular H-bonding

ii) Restricted rotation



ν_{OH} (0.005 M in CCl_4)

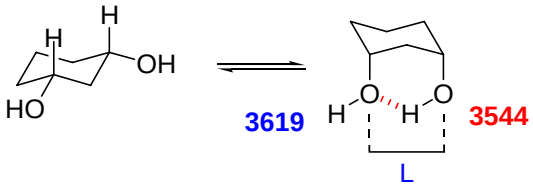
3642 (ε 19)

3604 (ε 52), Δ ν = 38

3574 (ε 26), Δ ν = 68

3485 (ε 55), Δ ν = 157

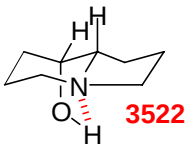
iii) Intramolecular diol (OH−−−O distance)

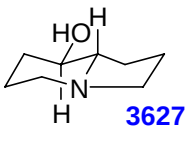


$$\Delta \nu = \frac{250 \times 10^{-8}}{L} - 74$$

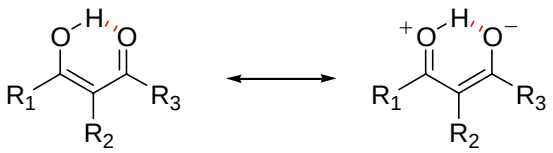
Δ ν = 75 cm^{-1}, L = 1.68 Å (1.64 Å)

iv) −OH −−− NR_3





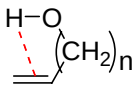
(b) Chelation



ν (OH) ~2700 cm^{-1}, (broad, ε small)

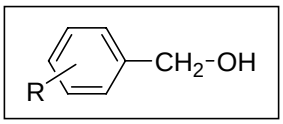
(c) OH − − − π 3600–3500 cm^{-1}, Δ ν = 15–50 cm^{-1}

① CH_2=CH–$(CH_2)_n$–OH

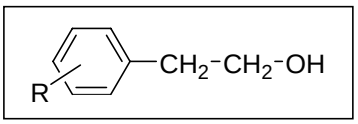


n = 1	3635, 3619	Δ ν = 16 cm^{-1}
n = 2	3635, 3596	Δ ν = 39.1 cm^{-1}
n = 3	3638, 3625	Δ ν = 13 cm^{-1}

② Benzyl alcohol



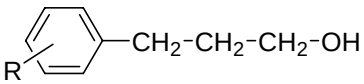
R	ν	A x 10^{-3} (integrated intensity)		
m-NO_2	3616 (3.70)	3635 (4.41)		Δ ν = 18.9
p-NO_2	3616 (3.98)	3636 (5.15)		Δ ν = 19.5
m-Cl	3617 (3.74)	3636 (2.88)		Δ ν = 19.4
p-Cl	3617 (3.56)	3635 (2.58)		Δ ν = 18.2
H	3617 (4.26)	3636 (2.59)		Δ ν = 19.2
m-CH_3O	3617 (4.04)	3636 (2.40)		Δ ν = 19.3
p-CH_3O	3617 (4.33)	3636 (1.75)		Δ ν = 18.9



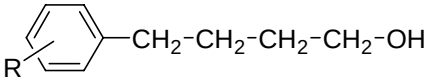
③ Phenetyl alcohols

NH_2	*m*	3598 (3.62)	3625 (0.60)	3636 (1.82)	Δ ν = 37.5
	p	3598 (3.14)	3623 (0.53)	3635 (2.23)	Δ ν = 37.2
CH_3O	*m*	3602 (3.34)	3624 (0.66)	3636 (2.14)	Δ ν = 33.5
	p	3603 (2.96)	3623 (0.69)	3636 (2.19)	Δ ν = 33.3
H		3606 (2.62)	3626 (0.68)	3636 (2.36)	Δ ν = 29.6
Cl	*m*	3611 (2.25)	3625 (0.71)	3635 (2.78)	Δ ν = 24.2
	p	3610 (2.23)	3625 (0.88)	3635 (2.61)	Δ ν = 25.3
NO_2	*m*	3615 (1.20)	3625 (1.52)	3635 (4.29)	Δ ν = 20.0
	p	3614 (1.37)	3626 (1.42)	3635 (3.99)	Δ ν = 21.0

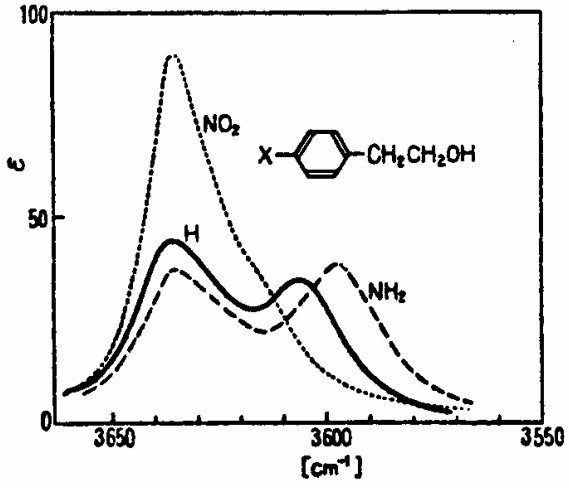
cf.



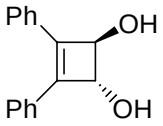
OH --- π bonding only when R is electron releasing groups



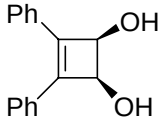
No OH --- π interaction



④ Cyclobutenediol



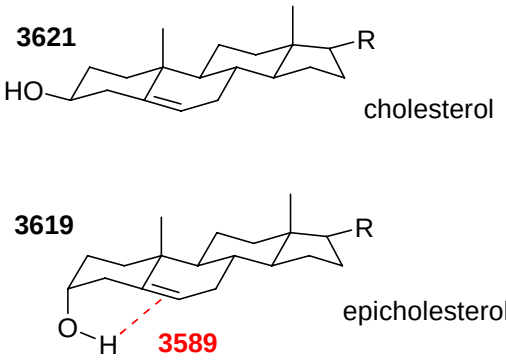
OH --- π
3603 ($CHCl_3$)

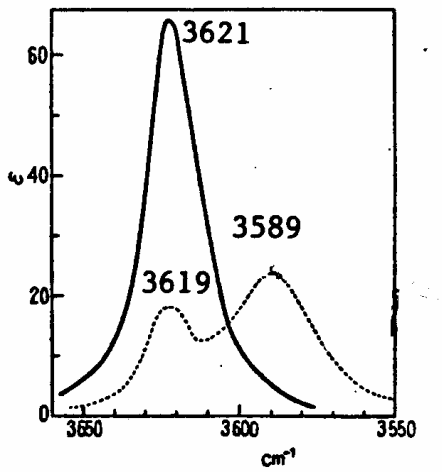


OH --- π
3602 ($CHCl_3$)

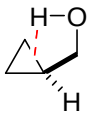
OH --- O
3557 ($CHCl_3$)

⑤ Cholesterol





⑥ Cyclopropyl carbinols

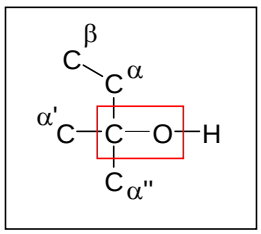


3621
3615

(3) ν (C–O) in alcohols

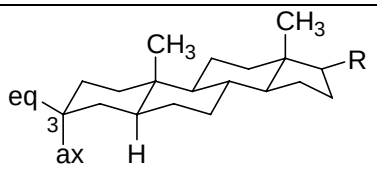
	ν C–O	ν O–H
Primary OH	1050	3644–3635
Secondary OH	1100	3630–3625
Tertiary OH	1150	3620–3615
Phenolic OH	1200	3615–3595

(a) ν (C–O):



α-branching: −15 cm^{-1}
α-unsaturation (including phenyl): −30
Ring formation between α,α': −50
α-unsaturation & α'-branching: −90
α– and α'–unsaturations: −90
α–, α'–, and α''–unsaturations: −140

(b) ν_{C-O} (eq–OH) > ν_{C-O} (ax–OH)
ν_{O-H} (ax–OH) > ν_{O-H} (eq–OH)

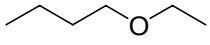
ν_{C-O}	3–OH	3–OMe	3–OAc	
3β (eq)	1040	1100	1030	
3α (ax)	1000	1090	1020	

▶Ethers

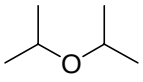
(1) Saturated ethers: ν_{C-O} 1150–1070 cm^{-1} (asymmetric), intense

Examples

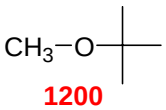
1122



1124

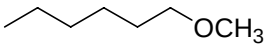


1112

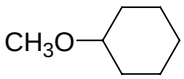


1200

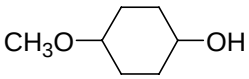
Note also: ν C–H (CH_3–O–) 2830–2815 cm^{-1}



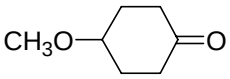
2825



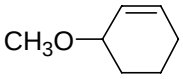
2815



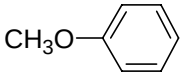
2820 (cis)
2822 (trans)



2824



2818

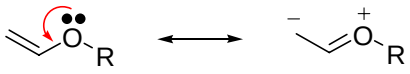


2832

(2) Unsaturated ethers:

ν_{C-O} 1275–1200 cm^{-1} (asymmetric), intense

1075–1020 cm^{-1} (symmetric), weak



※Intensity increases in $\nu_{C=C}$

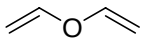
Examples

$CH_3-O-CH=CH_2$ **1235, 1212 (gas)**

*n*Pr–O–$CH=CH_2$ **1203 (CS_2)**

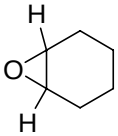
$C_2H_5-O-CH=CH_2$ **1205 (CS_2)**

Ph–CH_2–O–$CH=CH_2$ **1205 (CS_2)**

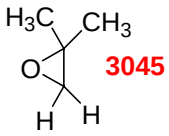


1280~1265 cm^{-1}

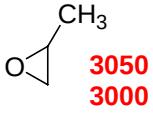
(3) Epoxides: ν_{C-H} 3040–3000 cm^{-1}; ν_{C-H} (CH_2) 3050 cm^{-1}



2099



3045



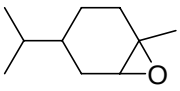
3050
3000

i) 8 μ band: ca. 1250 cm^{-1} (symmetric stretching of the epoxide ring)

ii) 11 μ band: 950–810 cm^{-1} (asymmetric stretching of the epoxide ring)

iii) 12 μ band: 840–750 cm^{-1}

※Both 11 μ and 12 μ bands shift to lower frequency when epoxide is conjugated with alkenes or aromatic rings



1247
842
761

1266
950
827

877
812

(4) Acetals, Ketals: ν_{C-O} 1190−1040 cm^{-1}; 3~5 bands

(a) Ketals

1195−1158; 1143−1124; 1098−1063 (asymmetric ν)

1056−1038 (symmetric ν)

(b) Acetals

An additional band @ 1110

(c) Enol Ketal, Acetal

ν(C-O) **~1230**
1175-1145
1142
1087

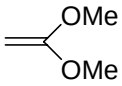
ν(C=C) **1635**

ν(C-O) **1177-1145**
1087-1075

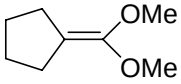
ν(C=C) **1630**

cf. enol ether: ν(C-O) 1240-1150; ν(C=C) 1690-1640

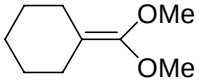
(d) Ketene Ketal



ν(C−O) **1036**
ν(C=C) **1639**



998
1712



995
1702

▶▶Amines, Imines, and Ammonium Salts

▶Amine ν (N–H), δ (N–H) in-plane, out-of-plane

ν (N–H)

(1) Free ν (N–H)

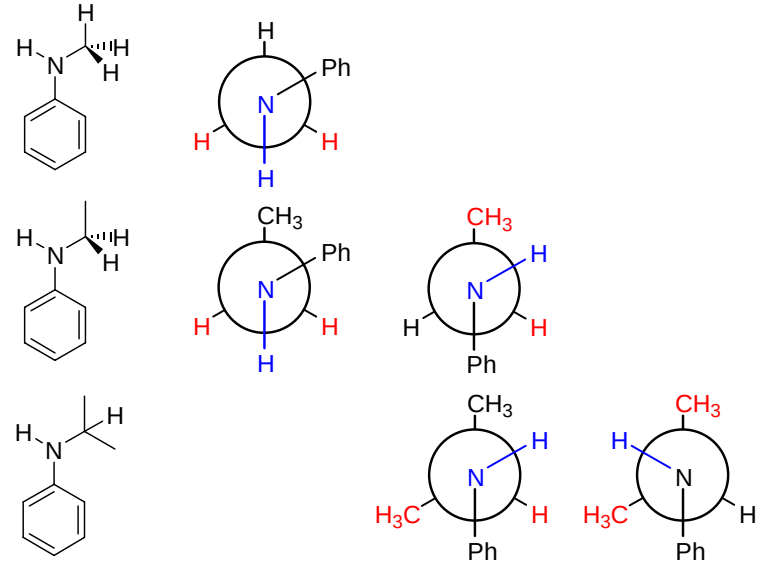
primary ($-NH_2$) 3550–3420 cm^{-1} (asymmetric) weak

3450–3320 cm^{-1} (symmetric) weak

Secondary (–NH–) 3450–3310 cm^{-1} weak

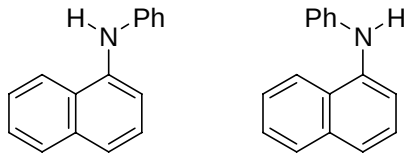
★Conformational Isomers

(a)



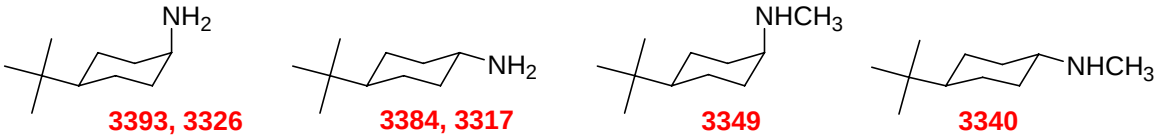
(I) 3444 **(II) 3421** **(III) 3395**

(b)



Two ν (N–H) bands are observed due to the conformational isomers.

★ ν (N–H)ax > ν (N–H)eq



3393, 3326 asym sym **3384, 3317** **3349** **3340**

(2) ν (N–H) for hydrogen-bonded $-NH_2$ and –NH–

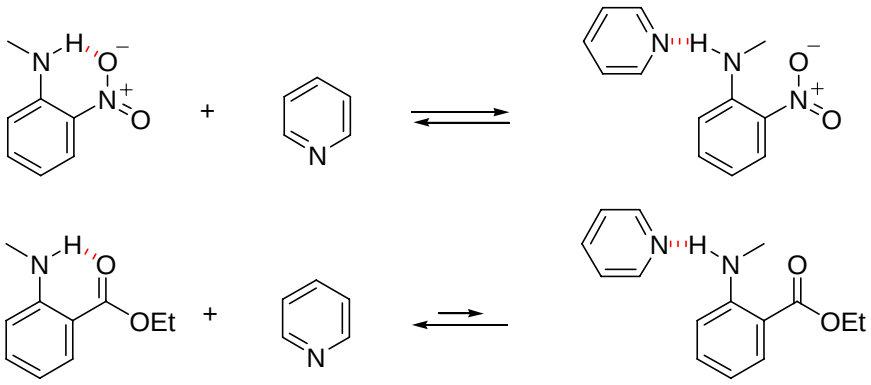
Intermolecular **ν (N–H)** 3320–3000 cm^{-1}

Intramolecular **ν (N–H)** 3500–3200 cm^{-1}

★ Aniline in ether-type solvent: broad peak at 3240–3230 cm^{-1}

Aniline in ketone-type solvent: broad peak at 3320–3240 and 3300–3150 cm^{-1}

★ NO_2 forms strong hydrogen-bonding with –OH, but does not form with NH



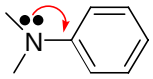
ν (C–N)

Aliphatic C–N: 1220–1020 (not practical)

Aromatic amine: primary 1340–1250

secondary 1350–1280

tertiary 1360–1310



▶ Imine (R–C=N–H)

ν (N–H): 3400–3300

ν (C=N): ca. 1670 (aliphatic), 1640 (aromatic), 1618 (conjugated).

▶ Ammonium Salts

$^{+}NH_4$: 3300–3030 (ν $^{+}NH_4$), 1430–1390

$RN^{+}H_3$: ca. 3000 (m), 1600–1675

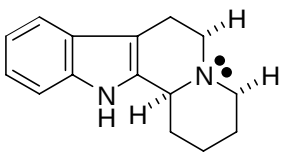
$R_2N^{+}H_2$: 2700–2250, 1600–1575 (scissoring of $^{+}NH_2$)

$R_3N^{+}H$: **2700–2250** (ν ^{+}NH)

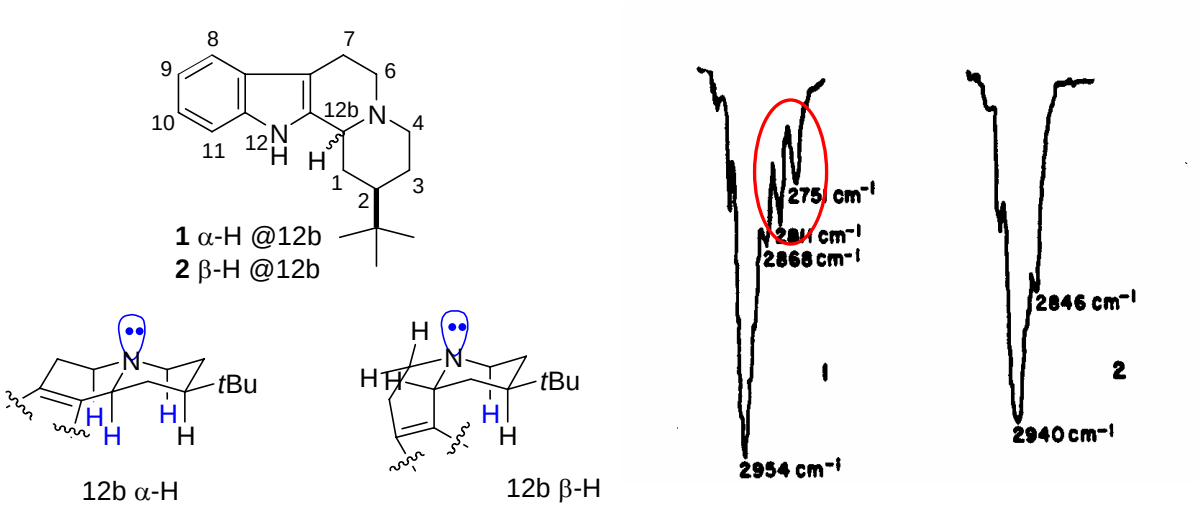
$C=N^{+}HR$: 2500–2300 (ν ^{+}NH), **2200–1800** (m), 1680 (ν $C=N^{+}$)

"**Bohlmann Bands**"

Quinolizidines having a trans ring fusion show characteristic absorption bands in the 2800–2700 cm^{-1} region. These absorptions result from a specific interaction between the Nitrogen lone pair and **at least two axial H's** on carbons adjacent to the Nitrogen atom.



2856, 2807, 2757 cm^{-1}



▶▶Carbonyl Compounds (ν C=O: 1900–1550 cm^{-1})

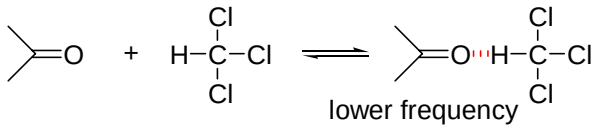
▶Factors that influence the band shifts

(1) External factors

Vapor phase: highest ν C=O

Liquid phase: dilute solution in non-polar solvents (CCl_4, CS_2) – higher ν C=O

cf. $CHCl_3$ has a reasonable acidity

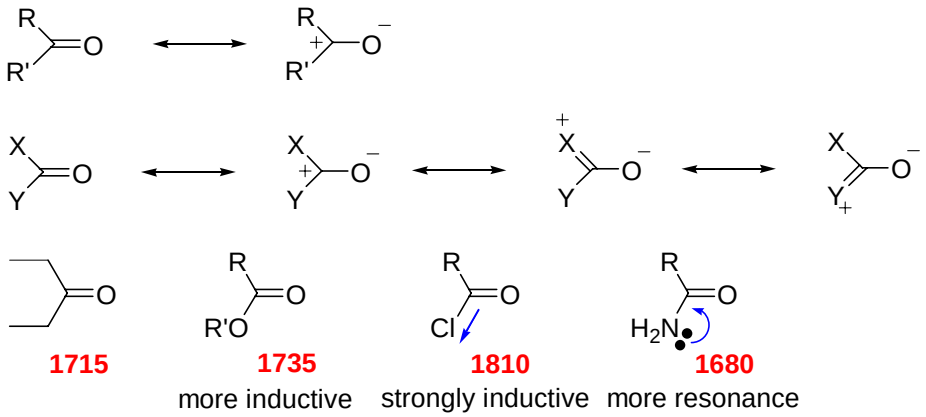


Solid state: polar matrices give lower ν C=O

(2) Internal factors

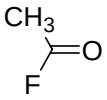
A. Electronic and steric nature of the substituents

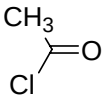
Resonance (p–bonding) vs. Inductive effects (σ–bonding)

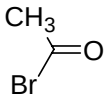


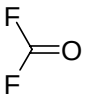
It is more difficult to stretch the $^{+}$C=O bond than the C=O bond.

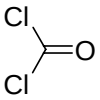
Examples of inductive effect

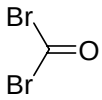

1840 (liq)


1806 (liq)

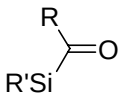

1814 (liq)

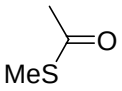

1928 (gas)

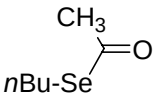

1827 (gas)

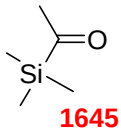

1826 (gas)

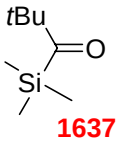
Examples of resonance effect

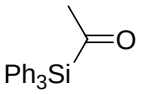

1690

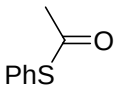

1698 (CCl_4)

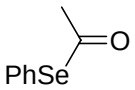

1712 (CCl_4)


1645 (CCl_4)


1637 (CCl_4)

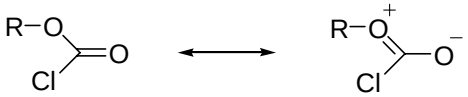

1645 (CCl_4)

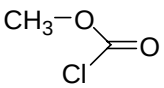

1714 (CCl_4)
1704 ($CHCl_3$)

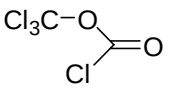

1723 (CCl_4)

Notes:

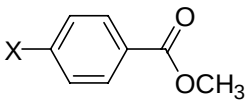
① Esters of chloroformic acid


1800-1760 cm^{-1}


1786 (CCl_4)


1806 (CCl_4)

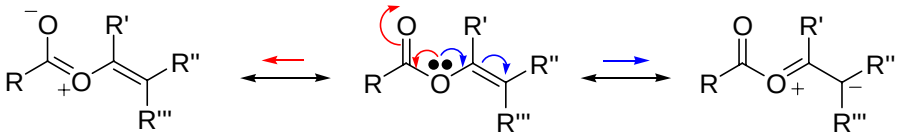
② Methyl benzoates



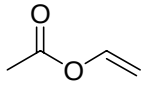
X	ν C=O
NO_2	1736.9
Br	1734.8
I	1733.0
F	1732.4
H	1731.9
Cl	1730.6
CH_3	1728.3
OH	1722.7
CH_3O	1722.1
$(CH_3)_2N$	1715.0
NH_2	1712.2

③ Enol esters

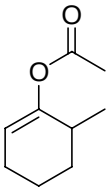
ν C=O: ~1760 cm^{-1} ν C=C: ~1650-1690 cm^{-1} (strong)



e.g.

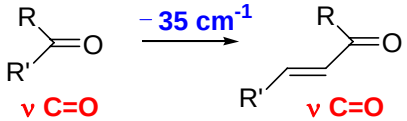


1763 cm^{-1} (CCl_4)



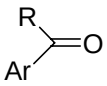
1750 (CCl_4)
1680

B. Conjugation shift



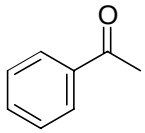
ν C=O ~1715 → ν C=O ~1680 (**1685-1665**)

ν(C=C) intensity increases compared with that of isolated C=C.

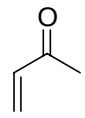


ν C=O: smaller shift (1700-1680)

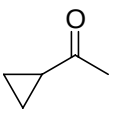
Examples



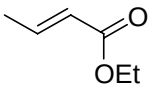
1692 (CCl_4)



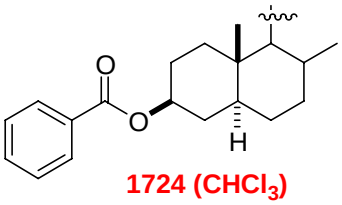
1684 (CCl_4)



1704 (CCl_4)

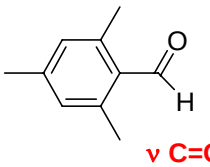


1712 ($CHCl_3$)

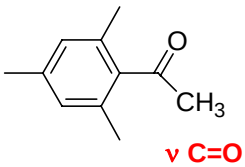


1724 ($CHCl_3$)

C. Steric hindrance: affecting conjugation



ν C=O 1680

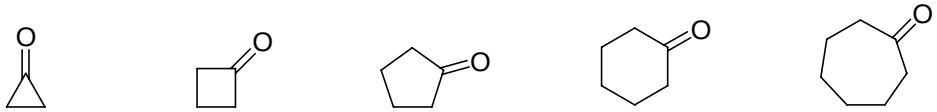


ν C=O 1700

D. Ring strains

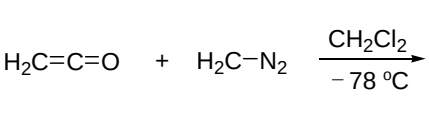
① Ketones **ν(C=O) = 1947 − 2.2θ**

more s-character in C=O

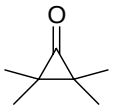


ν(C=O)	1813	1780	1745	1715	1705
θ	60	90	102	117	122

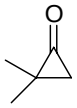
Examples



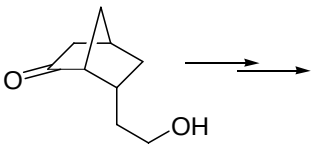
3045 ν(C-H)
1813 ν(C=O)



1843
1823

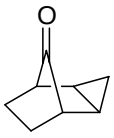


3050
1815
1387, 1380

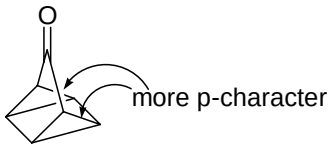


1735 **1750**

more s character in C=O



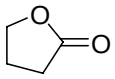
1790 (liquid)



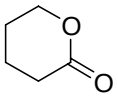
1746 (CCl_4)

② Lactones

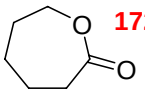
1841 (CCl_4)



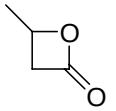
1770 (liq)
1774 ($CHCl_3$)
1783 (CCl_4)



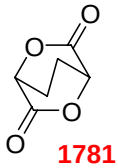
1730 (liq)
1732 ($CHCl_3$)
1748 (CCl_4)



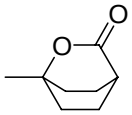
1727 (CCl_4)



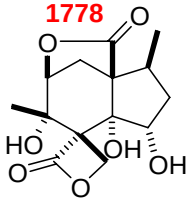
1818 (CCl_4)



1781

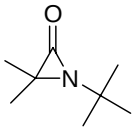


1760



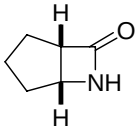
1778
1832

③ Lactams

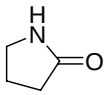


1840 ($CHCl_3$)
1837 (CCl_4)

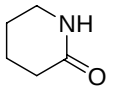
1745



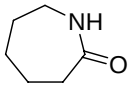
1748 (liq)
1748 (CH_2Cl_2)



1691 (liq)
1690 ($CHCl_3$)
1702 (CCl_4)

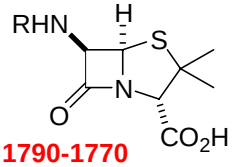


1651 (KBr)
1667 ($CHCl_3$)
1673 (CCl_4)



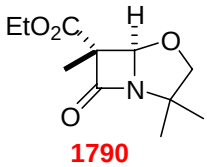
1660 ($CHCl_3$)
1671 (CCl_4)

Penicillin series

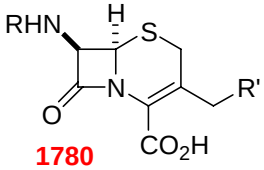


1790-1770

1737

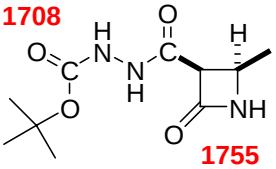


1790



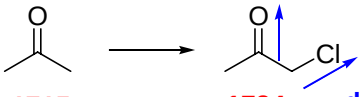
1780

1675
1708



1755

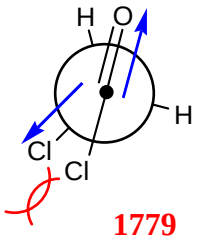
E. Haloketones



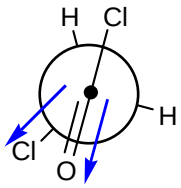
1715 **1724**

dipole-dipole repulsion

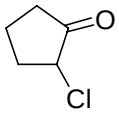
shifts its ν(C=O) to a higher frequency



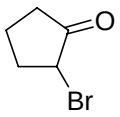
1779



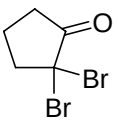
1804



1755



1750



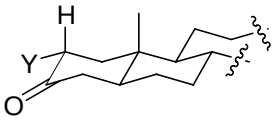
1764

A conformation in which dipole-dipole repulsion is minimized

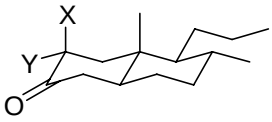
In general, shift caused by an a-halogen is the following order:

I (0~10) < Br (0~20) < Cl (0~25) < F

Geometrical factors: No shift when the angle between C=O and C–X exceeds 90°.



Y = H **1718**
Y = Br **1733**
Y = Cl **1738**



X = Y = H **1718**
X = Y = Br **1735**
X = Y = Cl **1742**

(3) Hydrogen bonding

A. Carboxylic acid

Vapor phase: 1780 cm^{-1} (monomer); 1730 cm^{-1} (dimer) intermolecular H-bonding

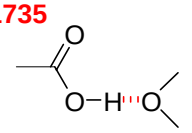
Liquid: 1710 cm^{-1} (dimer)

Solution:

Non-polar solvent: 1760 cm^{-1} (monomer); 1710 cm^{-1} (dimer)

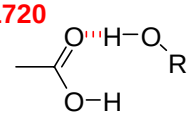
Polar solvent:

1735

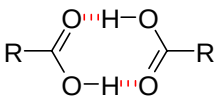


in ether

1720



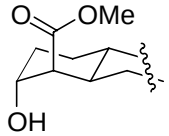
in alcohol



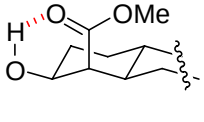
~920 cm^{-1}
(O-H out-of-plane bending)

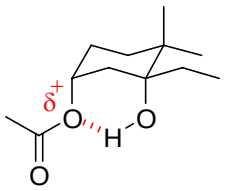
B. Intramolecular H-bonding involving carbonyl groups

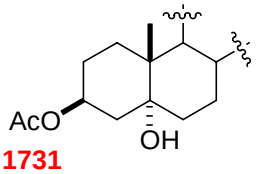
1722



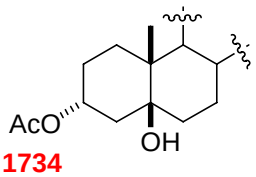
1709



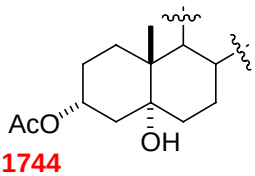




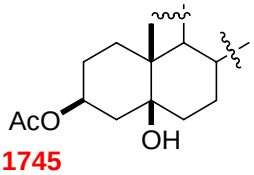
1731



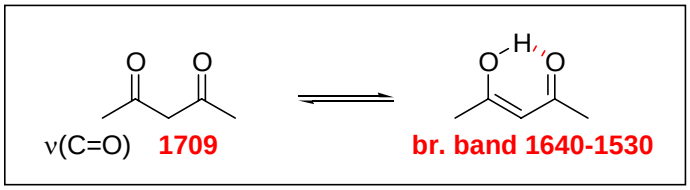
1734

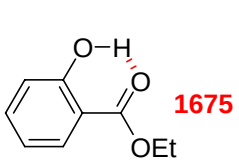


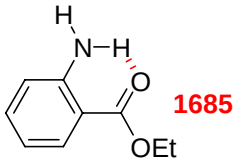
1744

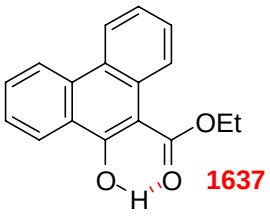


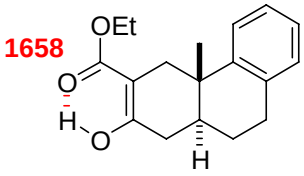
1745

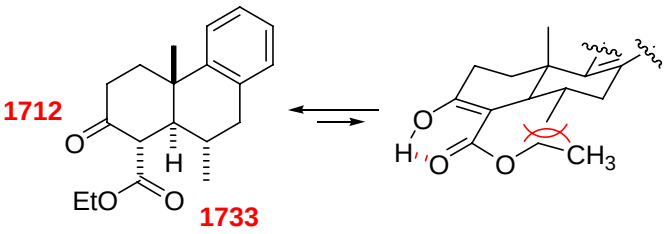


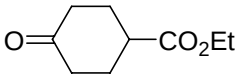
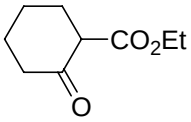
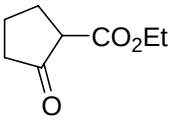
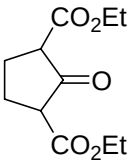








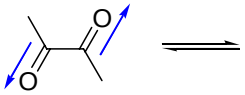


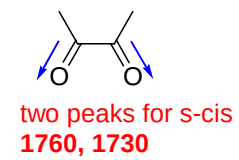
Cyclic Keto-esters	ν(C=O) Ester	ν(C=O) Ketone	Chelated Ester
	1736	1718	–
	1744	1718	1656
	1725	1756	1660
	1736	1763	1671

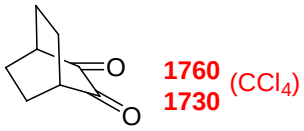
(4) Vibrational couplings

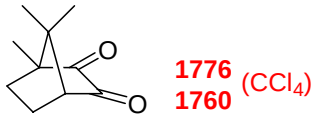
Interaction of two vibrating absorptions, which must be close enough to each other, to give splitting into **two bands**.

A. Diones





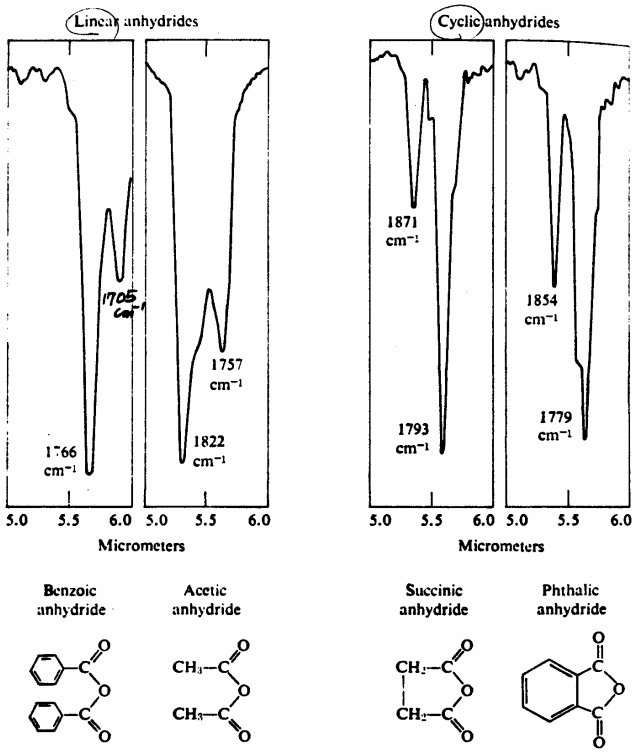


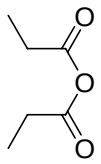


B. Acid anhydrides

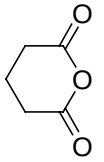
1820, 1760 cm^{-1}: $\Delta\nu \sim 60$ cm^{-1} (35~90 cm^{-1})

Cyclic and linear anhydrides can be distinguished by the intensity comparison of the coupled vibrations.





1817 (s)
1750 (w) CCl_4



1802 (w)
1761 (s) CCl_4

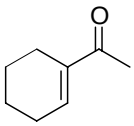
▶ Aldehydes and Ketones

A. Aldehydes: characteristic ν(C–H) bands at 2820 and 2720 cm^{-1}.

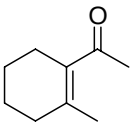
B. s-cis enones: increased intensity of ν(C=C)

C. Conjugation effects:

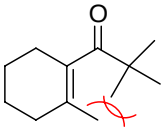
①



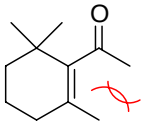
ν(C=O) **1665**
ν(C=C) **1637**



1678
1621

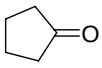


1684

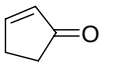


1693
1650

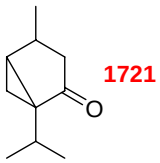
②



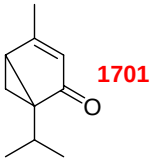
1742



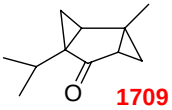
1715



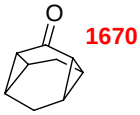
1721



1701

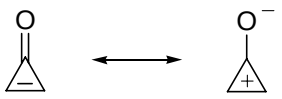


1709



1670

③

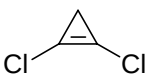


1864
1833 (in CCl_4)

mp -28 °C (recrystallized from dry ether at -78 °C)
no peak at 1600 cm^{-1}

cf.

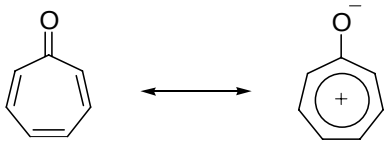
ν(C=C) **1641**



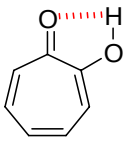
1805

1768

④

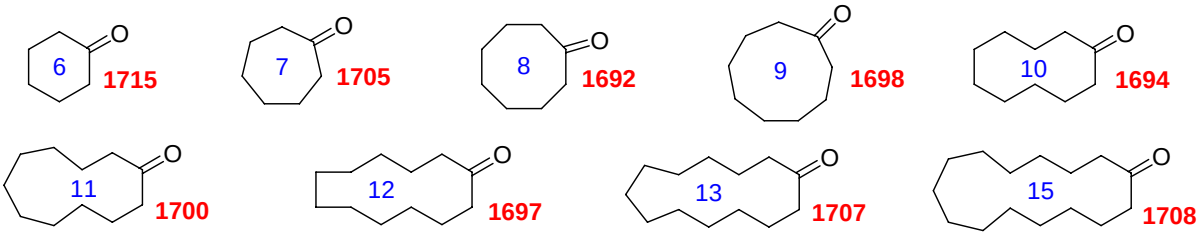


ν(C=O)	ν(C=C)	
1638	1580	(liquid)
1645	1595	(CCl_4)
1651	1613	(gas)



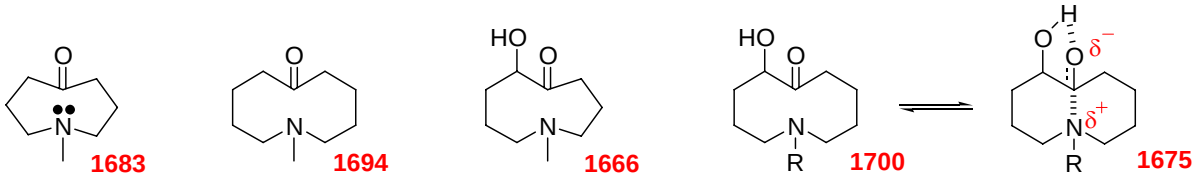
1613
1548 (KBr)

D. Ring-size dependence

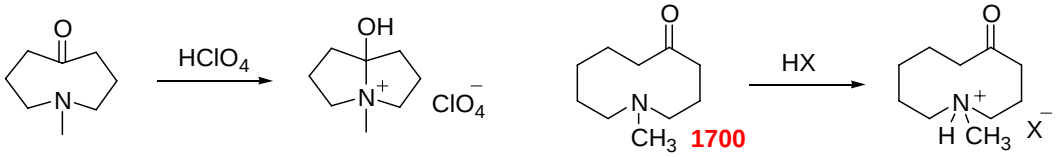


E. Trans-annular effects

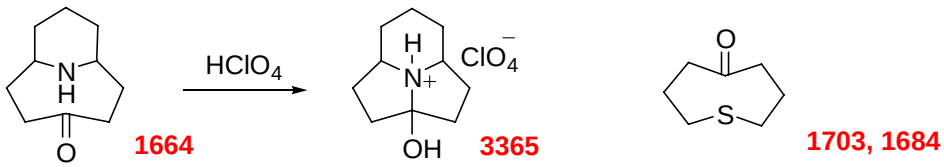
①



two bands can be seen by careful analysis



②



▶ Carboxylic acids

A. ν(C=O): **1760 cm^{-1}** monomer, **1710 cm^{-1}** dimer

B. δ(OH) out-of-plane **~920 cm^{-1}** (broad) dimeric carboxylic acid

C. Conjugation

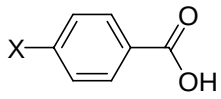
①

R–CH=CH–CO_2H: 1718 cm^{-1} (monomer in dioxane)

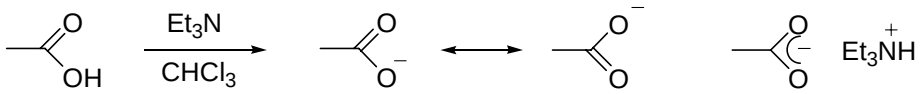
Ar–CH=CH–CO_2H: 1720 cm^{-1} (monomer in dioxane)

Dimeric conjugated –CO_2H: 1710–1680 cm^{-1}

②

	X	ν(C=O) in MeOH (monomer)	ν(C=O) in CCl_4 (dimer)
	NO_2	1720	–
	Cl	1713	1699
	H	1705	1696
	CH_3O	1695	1691

D. Carboxylates



1610-1550 cm^{-1} (asymmetric) & 1400 cm^{-1} (symmetric)

▶Esters and Lactones

(1) Esters: ν(C=O) 1745−1725 cm^{-1}

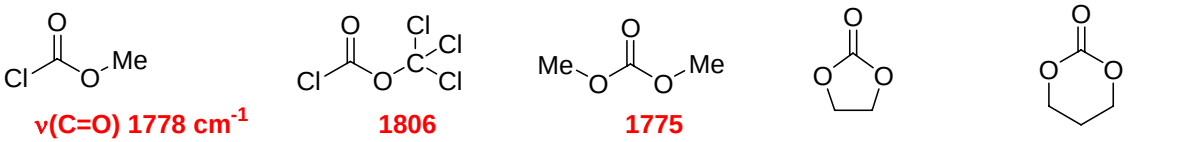
ν(C−O−C) 1300−1050 cm^{-1} two bands (asymmetric and symmetric)

Asymmetric band ν(C−O−C) is usually stronger than ν(C=O), broad and occasionally split into two

ν(C-O) ~1190 cm^{-1} **1180** **1240** **1165**

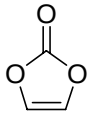
A. Inductive effect gives higher ν(C=O)

1,2- vs. 1,3-diols



ν(C=O) 1778 cm^{-1} **1806** **1775** **1817, 1763 (w)** **1777, 1753 (w)**

B. Vinyl ester, enol ester: higher ν(C=O)



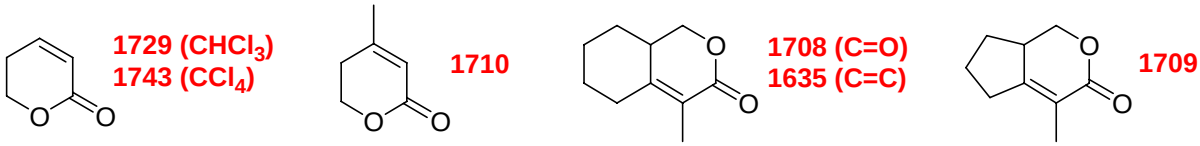
1833
1770

(2) Lactones

A. Ring-size dependence

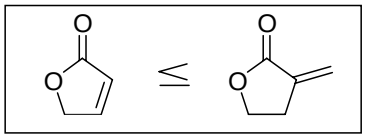
B. Conjugation effect

① ν(C=O): 20~30 cm^{-1} lower than the saturated lactones

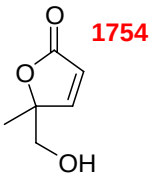


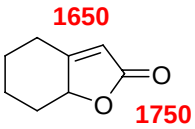
1729 ($CHCl_3$)
1743 (CCl_4)
1710
1708 (C=O)
1635 (C=C)
1709

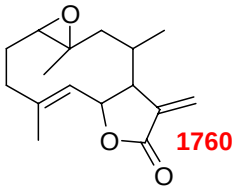
②



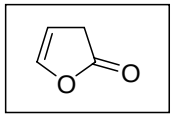
higher in frequency

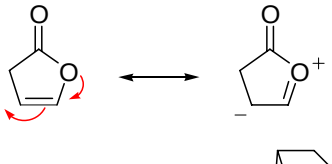


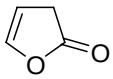


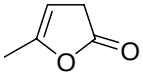


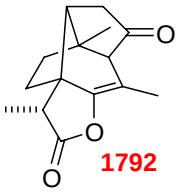
③ Stronger inductive effect gives higher ν(C=O): 1800−1790 cm^{-1}

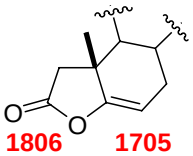


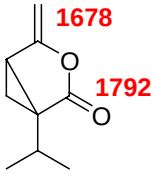




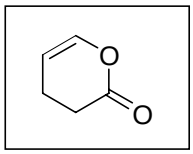


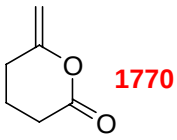


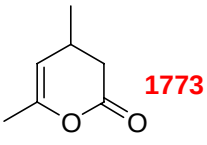


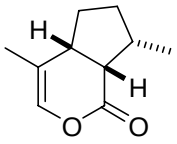


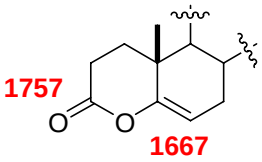
④

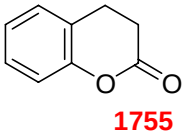


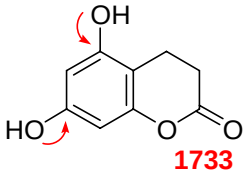




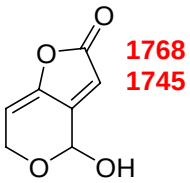


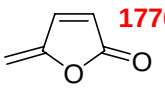


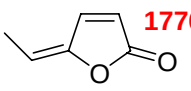


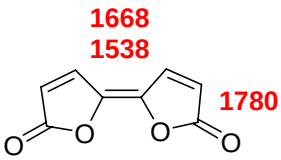


⑤ αβ,γδ-Unsaturated γ-lactones: ν(C=O) is close to that of saturated γ-lactones

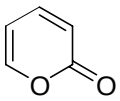




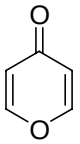




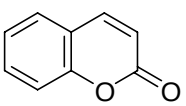
⑥ Pyrones

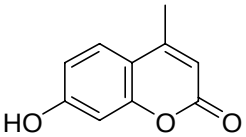


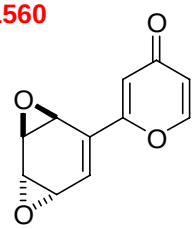
C=O 1730-1720
C=C 1650-1620
1570-1540

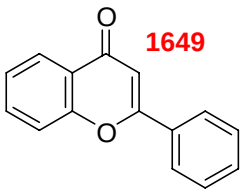


C=O 1670-1650
C=C 1650-1600
1590-1560



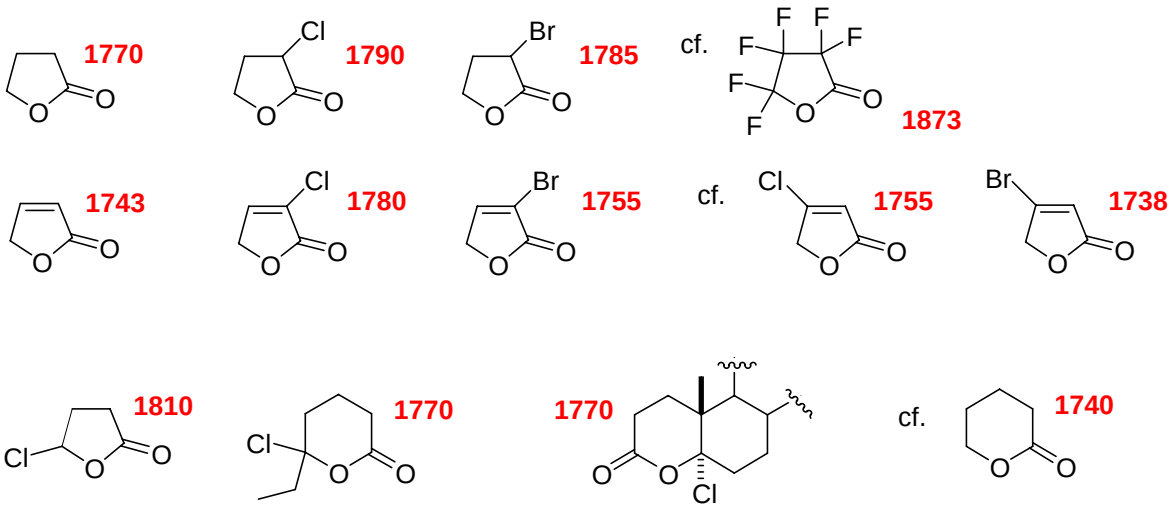




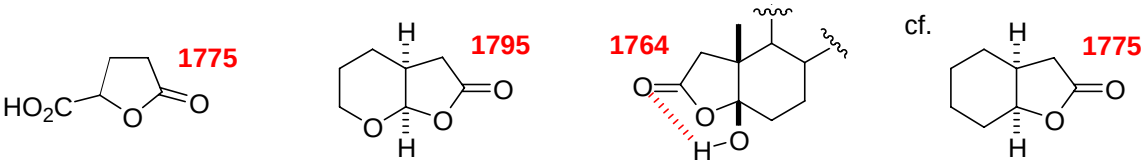


C. Polar effect (Inductive effect and dipole-dipole interactions)

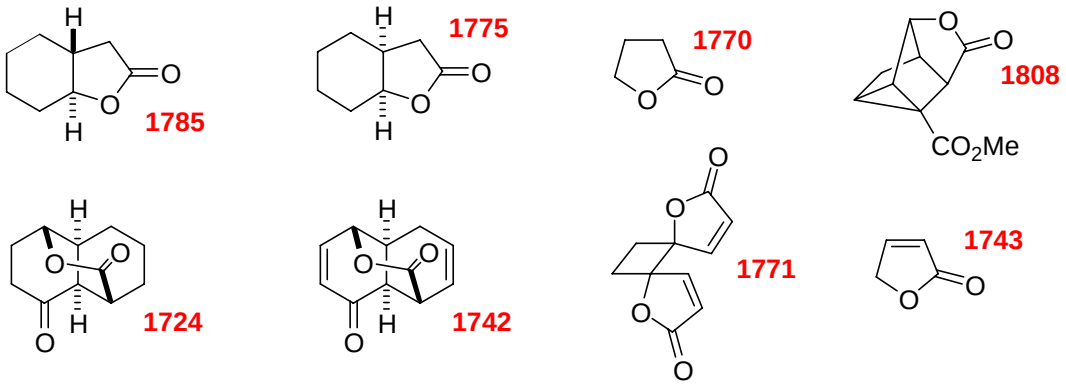
① Halogens



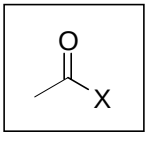
② Oxygens



D. Steric effects



▶ Acid halides



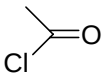
ν(C=O): 1815−1770 cm^{-1} for chlorides

Stronger inductive effect by X induces the increase of ν(C=O).

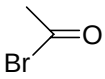
Splitting into doublet (Fermi resonance) is frequently observed.

Small changes in ν(C=O) between gas and condensed phase, and even smaller changes among various solvents.

1840 (liq)

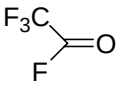


1806 (liq)
1799 (CCl_4)

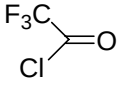


1814 (liq)
1818 (CCl_4)

1928 (gas)

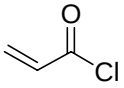


1905 (liq)
1901 (gas)



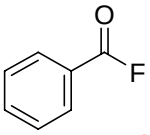
1810 (gas)

① Conjugated Acid Halides: **1780–1750 cm^{-1} for chlorides**

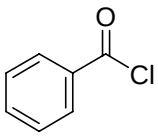


1762 (CCl_4)

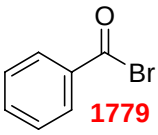
② Aroyl Halides



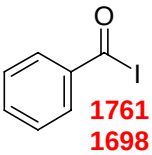
1812 (CCl_4)



1773
1736 (CCl_4)
1773
1736 (CS_2)



1779
1701 (CS_2)

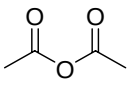


1761
1698 (CS_2)

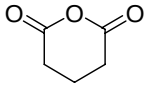
▶ Acid anhydrides

Asymmetric: 1820 cm^{-1}

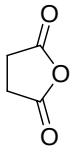
Symmetric: 1750 cm^{-1} **Δν ~ 60–70**



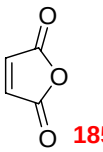
1833 (s-as)
1767 (w-s) (CCl_4)



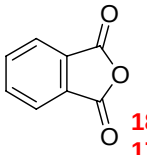
1802 (w)
1761 (s) (CCl_4)



1872
1796 (CCl_4)



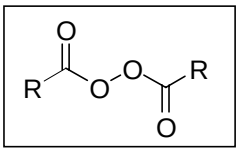
1856
1784 (CCl_4)



1853
1793 (CCl_4)
1779

※Higher frequency band is more intense for acyclic anhydride, whereas the lower frequency band is stronger for cyclic anhydride.

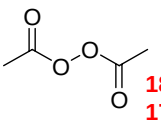
▶ Diacylperoxides



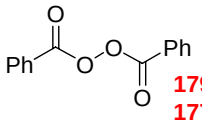
Aliphatic: 1820–1811 (as), 1796–1784 (s), Δν ~25 cm^{-1}

Aromatic: 1805–1780 (as), 1794–1769 (s), Δν ~25 cm^{-1}

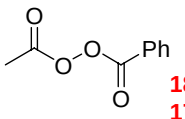
Mixed aliphatic and aromatic: Two bands



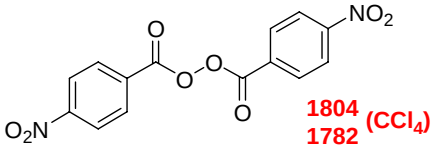
1820
1796 (CCl_4)



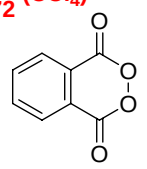
1792
1772 (CCl_4)



1811
1779 (CCl_4)

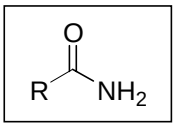


1804
1782 (CCl_4)



1805
1783 (nujol)

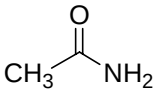
▶ Amides

A 

Amide–I band: ν (C=O) 1690(free)–1650(H–bonded).
Amide–II band: δ (NH_2–deformation) and ν(C–N) 1640–1600
Amide–III band: ν (C–N) 1420–1405.
ν(N–H) asymmetric free amide: 3550–3420, symmetric free amide: 3450–3320, H–bonded amide: 3200–3050

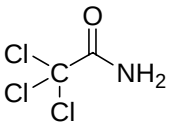
Note

① Amide–I band: Gas phase 1720–1715; Dilute solution 1700; Liquid 1659



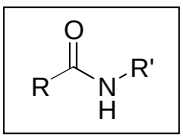
1684 (KBr)
1675 ($CHCl_3$), 1690 (dioxane), 1670 (MeOH)
1714 (CCl_4)

② Halogen shift (Inductive effect)



1732 ($CHCl_3$)

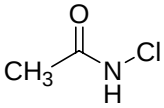
③ Amide–II band:
Straight chain alkane amides: 1590–1588 (dilute solution in $CHCl_3$, monomer)
New band at 1608 cm^{-1} appears on higher concentration
1650–1620 (in solid, dimer and trimer etc.)

B 

Amide–I band: ν (C=O) 1680 (free), 1655 (H–bonded).
Amide–II band: mainly δ (N–H) 1530(free), 1550(associated)
Amide–III band: δ (N–H) 1260 (free), 1300 (associated).
ν(N–H) 3440 (free amide), 3300 (associated), 3070 (unknown origin).

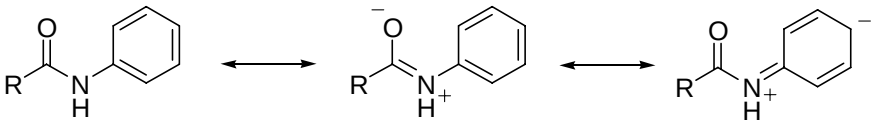
Note

① Amide–I band: 1640 (solid phase), 1680 (in dioxane)

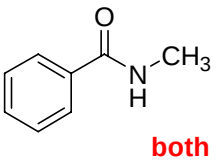


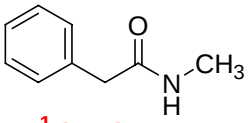
Electron-withdrawing group on nitrogen gives a band of higher frequency.
1680 (solid), 1705 ($CHCl_3$)

Anilide: ~1700 cm-1



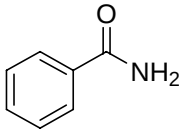
Very little effect by conjugation with benzene ring



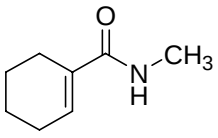


both at 1649 cm^{-1} (KBr)

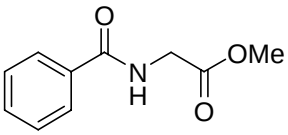
cf.



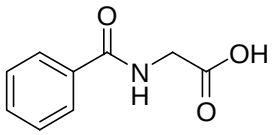
1656 cm^{-1} (KBr)



1640 cm^{-1} (KBr)



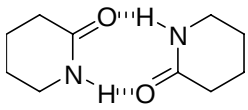
1640



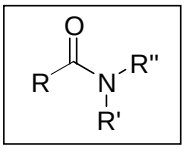
1597 (H-bonding)

② Amide–II band: band at 1530–1550 (weak) disappears upon changing to N–D. 1550 (solid), 1533 ($CHCl_3$), 1540–1520 (dioxane)

③ ν (N–H): In cyclic lactams, 3440 (free), 3175 (dimer), and 3070 (associated)

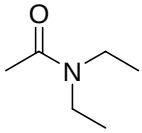


C

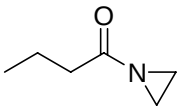


Amide–I band: 1650 cm^{-1}

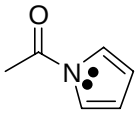
Solvent effect:



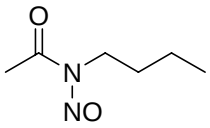
1645 (liq)
1628 ($CHCl_3$)
1650 (CCl_4)



1701
1644 (liq)



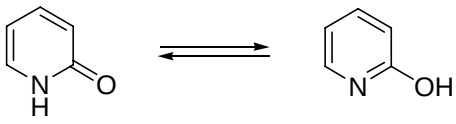
1732 (KBr)

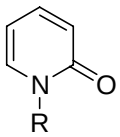


1739 (CCl_4)
1515

▶ Pyridones

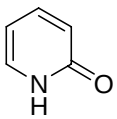
α-pyridones



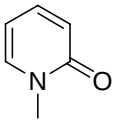


ν(C=O) 1650 cm^{-1}

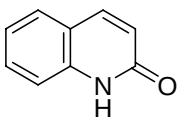
close to saturated amide



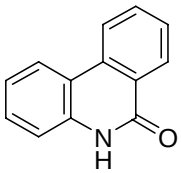
1654
($CHCl_3$)



1665
($CHCl_3$)

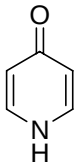


1656
($CHCl_3$)

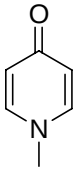


1653
(nujol)

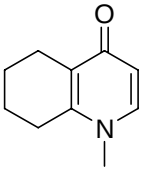
γ-pyridones



1638
($CHCl_3$)

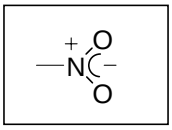


1664
1575
($CHCl_3$)



1639
1577
($CHCl_3$)

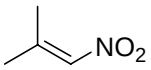
▶ Nitro group



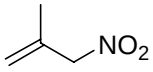
ν (N–O) 1570–1560 (s) asymmetric

ν (N–O) 1380–1350 (s) symmetric

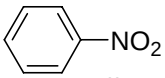
Conjugation gives lower frequency



1515
1350



1555
1366

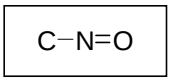


1527 ± 16, 1348 ± 11 cm^{-1}

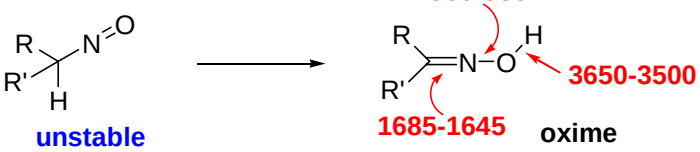
effected by a substituent on the phenyl group

▶ Nitroso group

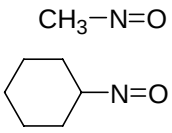
ν (N=O): 1600–1500 cm^{-1}



A. Secondary Nitroso Compounds



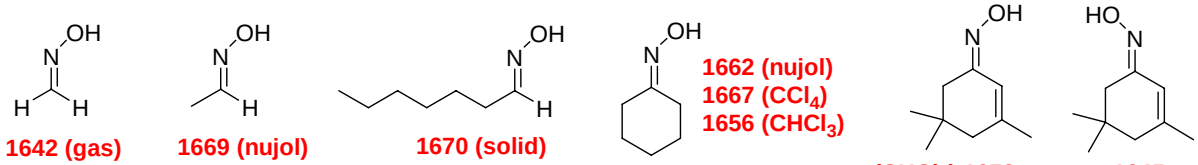
960-930
3650-3500
1685-1645
unstable
oxime



1560
(vapor)
1588

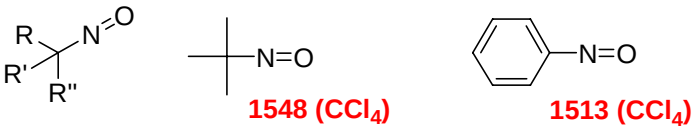
These bands disappear quickly

cf. oximes



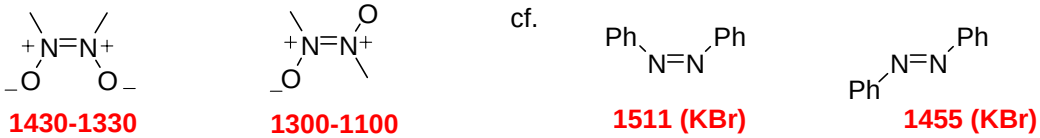
1642 (gas)
1669 (nujol)
1670 (solid)
1662 (nujol)
1667 (CCl_4)
1656 ($CHCl_3$)
($CHCl_3$) 1673
1645

B. Tertiary Nitroso Compound



1548 (CCl_4)
1513 (CCl_4)

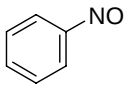
The majority of nitroso compounds associate in solution to give a mixture of the cis and trans dimers



1430-1330
1300-1100
cf.
1511 (KBr)
1455 (KBr)

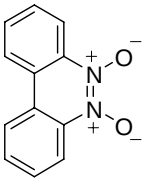
cis dimer **1426**
1370 (KBr)
1323

trans dimer **1222 (KBr)**
1134



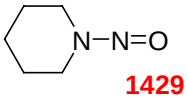
dimer **1409 (KBr)**
1397

cf.

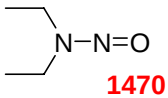


1399 (KBr)
1342

C. Nitrosamines (lower then any other ν N=O)



1429 ($CHCl_3$)



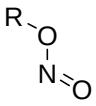
1470 (CCl_4)

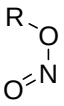
D. Nitrites (R–O–N=O)

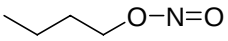
ν (N=O) 1680–1610 (s) asymmetric; 1300–1250 (s) symmetric

Two bands due to s-trans and s-cis conformations

trans (higher) cis (lower)

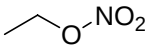




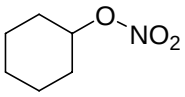


1650 trans (CCl_4)
1608 cis (CCl_4)

E. Nitrates



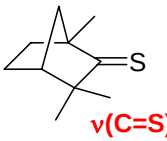
1634
1282 **(liq)**



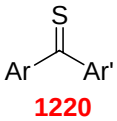
1626
1277 **(liq)**

▶ Sulfur compounds

A. Thiones

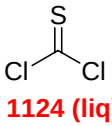


ν(C=S) 1188

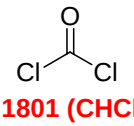


1220

$\frac{\nu(C=O)}{\nu(C=S)}$ **= 1.6 ~ 1.14**

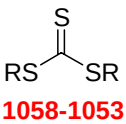


1124 (liq)

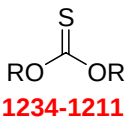


1801 ($CHCl_3$)

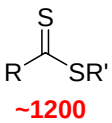
CS_2: 1522, 650 cm^{-1}.



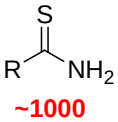
1058-1053



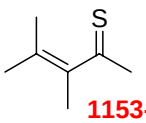
1234-1211



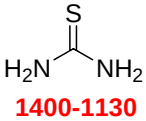
~1200



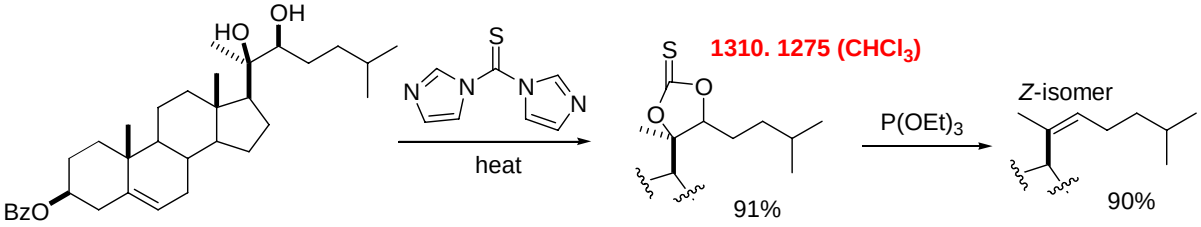
~1000



1153-1143



1400-1130

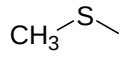


1310. 1275 ($CHCl_3$)

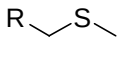
B. Thiols (C–SH) and Sulfides (R–S–R')

ν (S–H) 2600–2550 cm^{-1} (weak)

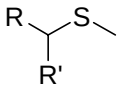
ν (C–S) 700–600 m^{-1} (medium or weak)



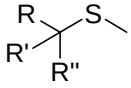
708-685 cm^{-1}



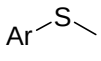
660-630 cm^{-1}



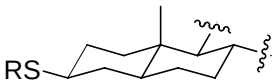
630-600 cm^{-1}



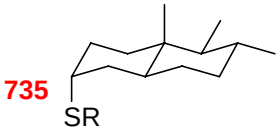
600-570 cm^{-1}



702-673 cm^{-1}

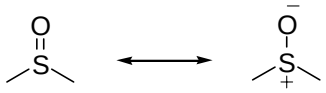


760



735

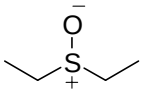
C. Sulfoxides



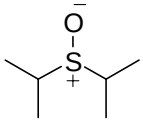
more important

ν (S=O) 1070–1045 cm^{-1} (very strong)

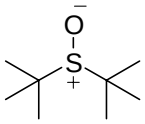
1072 (CCl_4)
1055 ($CHCl_3$)
1057 (liq)



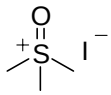
1020 ($CHCl_3$)



1012 ($CHCl_3$)

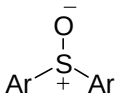


1012 ($CHCl_3$)

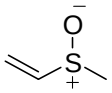


1232 (KBr)
1231 (nujol)

1045 ($CHCl_3$)



1041 ($CHCl_3$)



1070 (liq)

D. Sulfones

ν (S=O) 1350–1300 cm^{-1} (very strong) asymmetric

ν (S=O) 1160–1120 cm^{-1} (very strong) symmetric