Characteristic Group Vibrations of Organic Molecules II

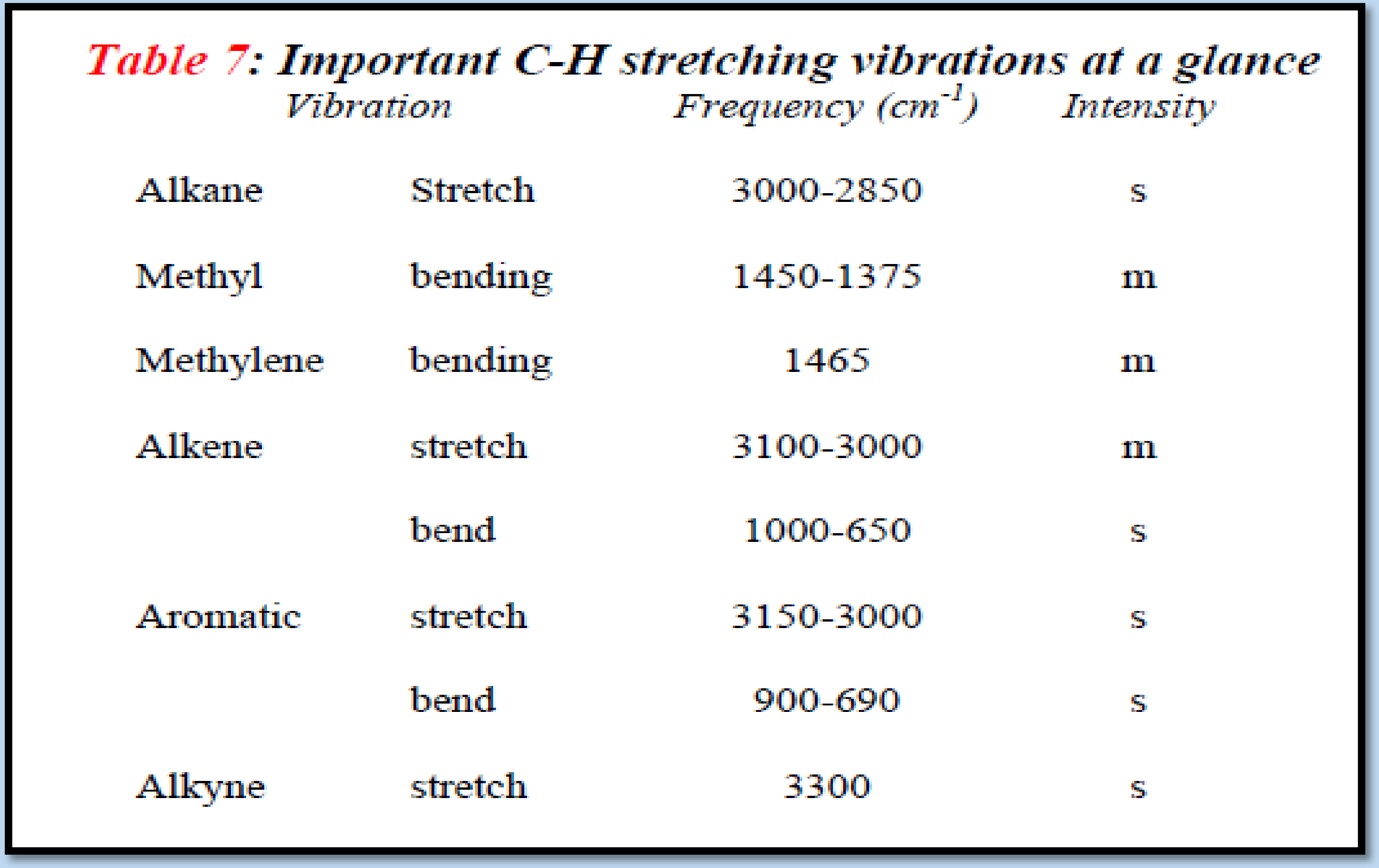
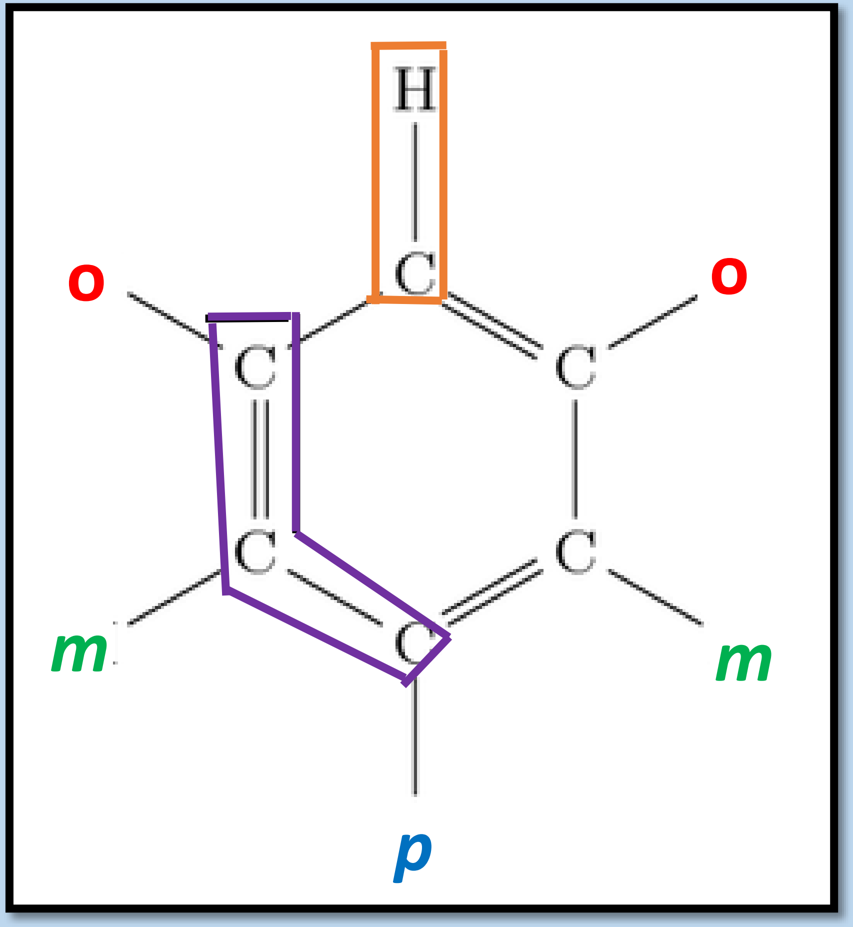


Table 7: Important C-H stretching vibrations at a glance

Vibration		*Frequency (cm^{-1})*	*Intensity*
Alkane	Stretch	3000-2850	s
Methyl	bending	1450-1375	m
Methylene	bending	1465	m
Alkene	stretch	3100-3000	m
	bend	1000-650	s
Aromatic	stretch	3150-3000	s
	bend	900-690	s
Alkyne	stretch	3300	s

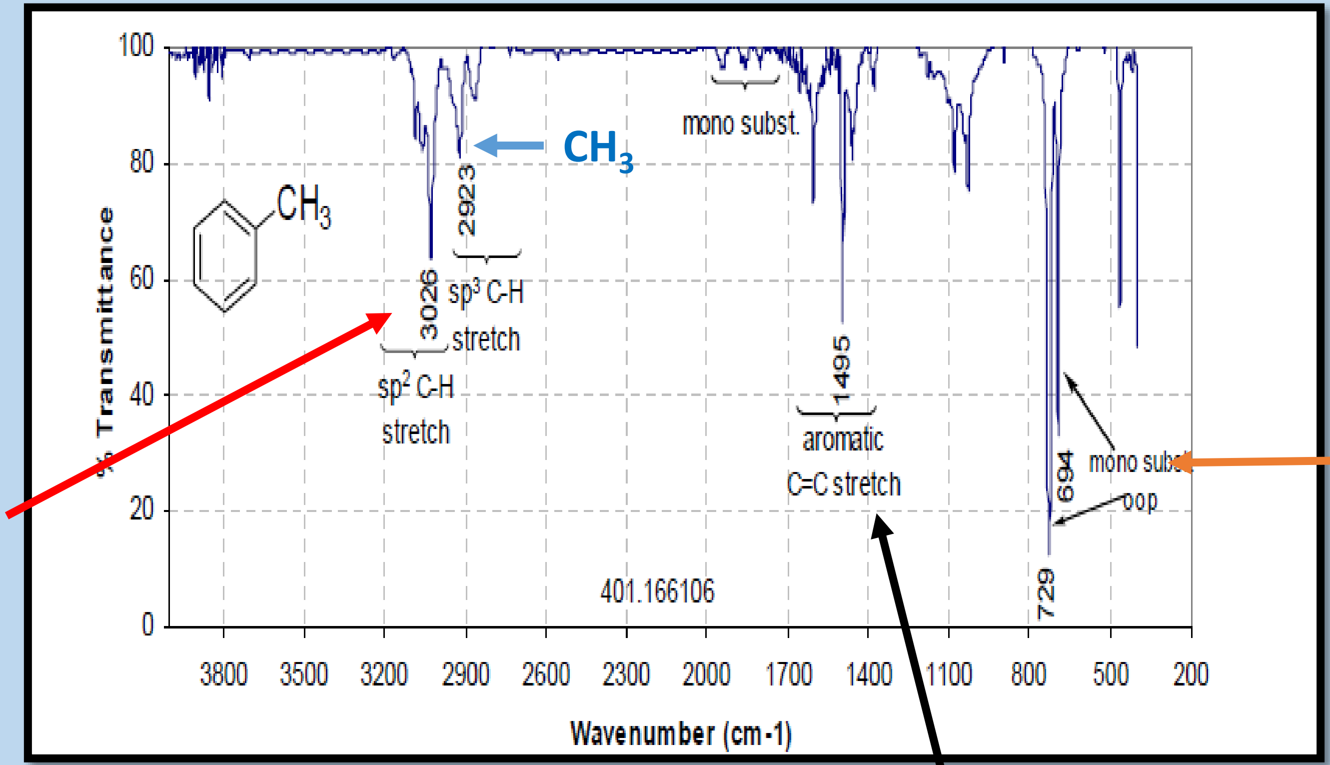
Aromatic Hydrocarbons



Aromatic (C-H) stretching	(3130-3030) cm^{-1}
Aromatic (C-H) bending	(900-650) (1225-950) cm^{-1}
Aromatic (C=C-C)	(1615-1580) (1510-1450) cm^{-1}
Monosubstitution	(710-690) cm^{-1}
Disubstitution (ortho)	(770-730) cm^{-1}
(meta)	(810-750) (900-860) cm^{-1}
(para)	(860-800) cm^{-1}
Aromatic ring	(1600-1500) cm^{-1}

Aromatic Hydrocarbons

Monosubstituted aromatic ring

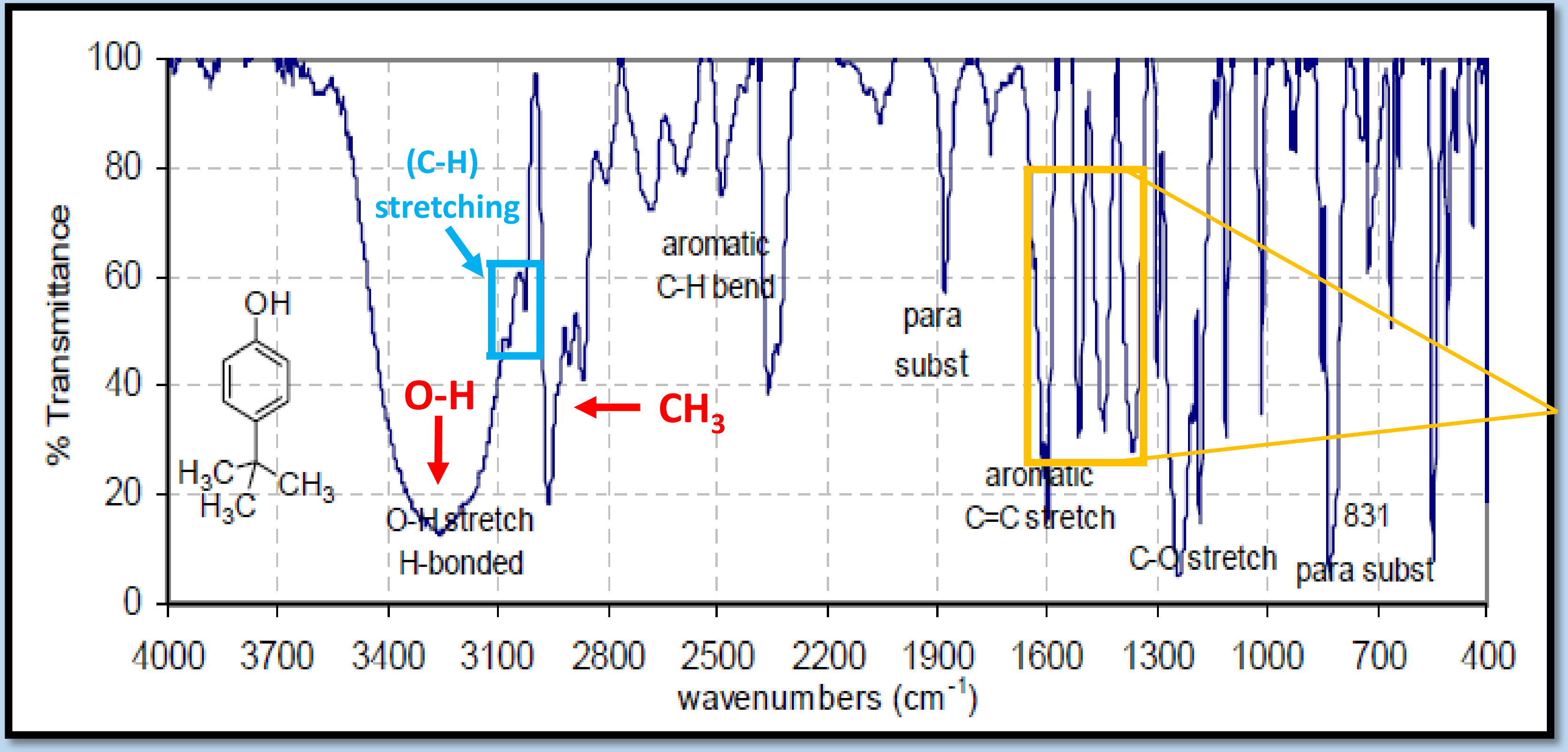


Aromatic (C-H) stretching
(3130-3030) cm^{-1}

Monosubstitution
(710-690) cm^{-1}

Aromatic (C=C-C)
(1510-1450) cm^{-1}

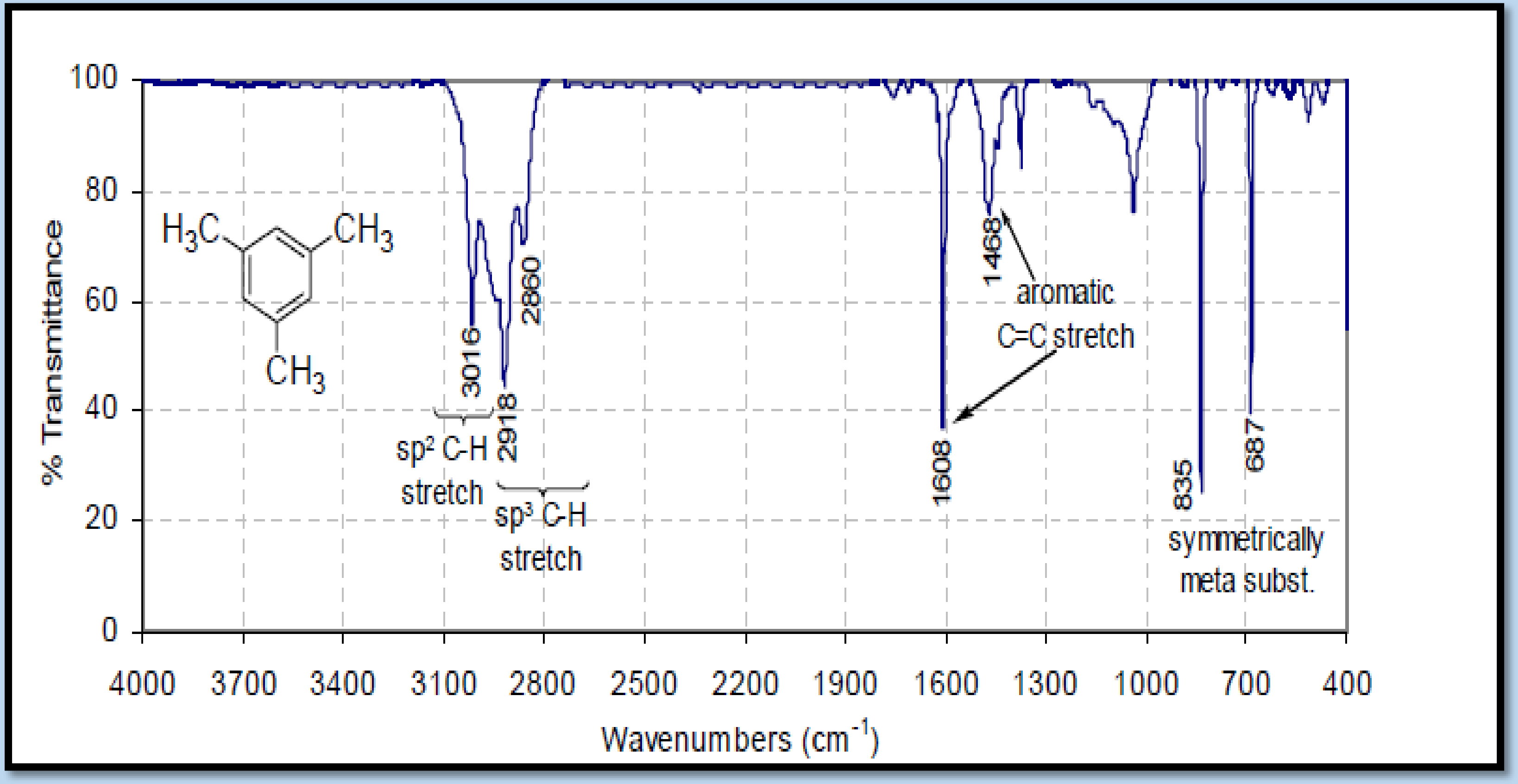
Disubstituted aromatic ring (para)



1650-1400 cm^{-1}

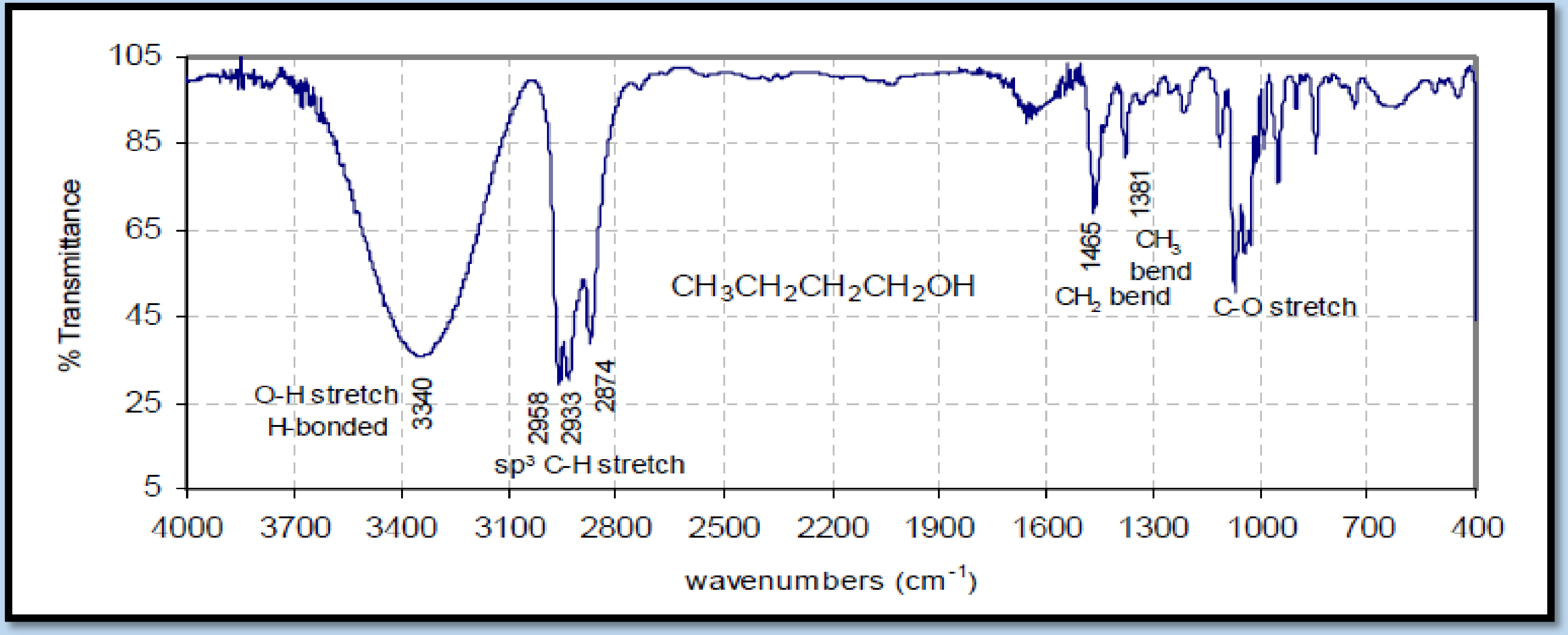
(C=C) in-plane

The combination and overtone bands in 2000-1650 cm^{-1} region are also characteristics of aromatic rings. Moreover, they are **very weak** and are **observed only in the case of concentrated solutions of highly symmetric benzene derivatives**.



Alcohols and Phenols

- The **(C-O)** and **(O-H)** absorption bands can be recognised from **3700 to 3400 cm^{-1}**
- The presence of **(N-H)** or moisture causes similar results.
- The exact position and shape of this band depends largely on **the degree of H-bonding**.
- A strong and sharp peak in the region as higher **3700 cm^{-1}** **in gaseous or extremely dilute solutions represents unbounded or free OH group(s).**



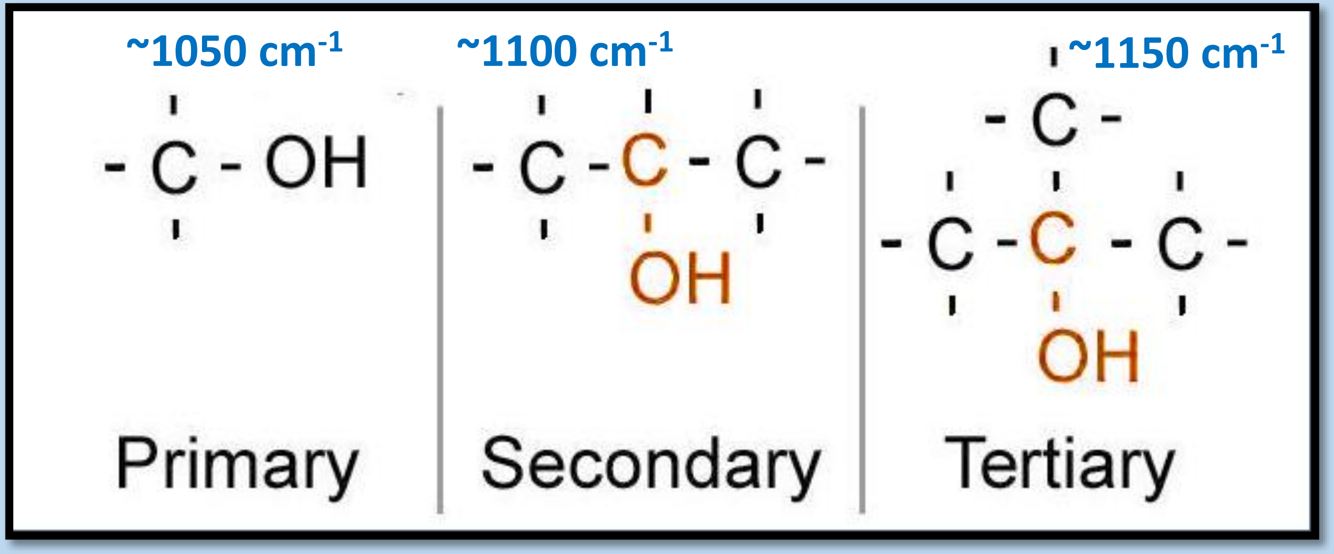
Alcohols and Phenols

- ***Alcohols and phenols*** in condensed phases (bulk liquid, KBr discs, concentrated solution etc.) are strongly hydrogen bonded, usually in the form of dynamic polymeric association; dimmers, trimers, tetramers etc., and cause broadened bands at lower frequencies.

- H-bonding involves a **lengthening** of the original **(O-H)** bond. This bond is consequently **weakened**, force constant is **reduced** and so the stretching frequency is **lowered**.

- **(C-O) stretching (1250-1000)** cm^{-1}

- **(C-O)** with **(C-C)** stretching mode



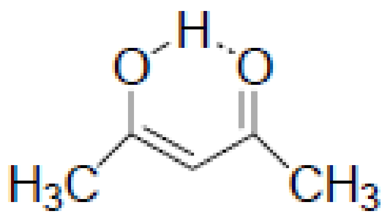
These two bands can differentiate the types of alcohols and phenols

Enols and Chelates

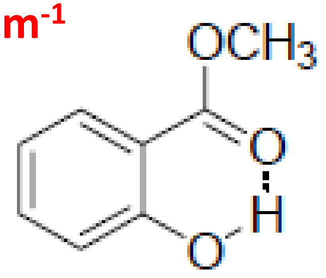
- Since these bonds are not easily broken on dilution by an inert solvent, free **(O-H)** may not be seen at ***low concentrations***.
- In structures, such as 2,6-di -t-butylphenol, in which ***steric hindrance*** prevents hydrogen bonding, no bounded O-H band is observed, not even in spectra of neat samples.

alkene alcohol = enol

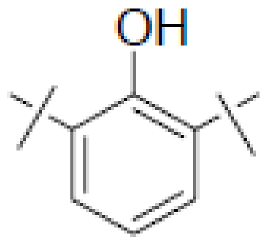
O-H stretching **2880 cm^{-1}**



acetyl acetone



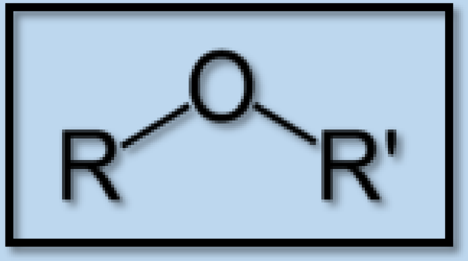
methyl salicylate



NO bounded O-H

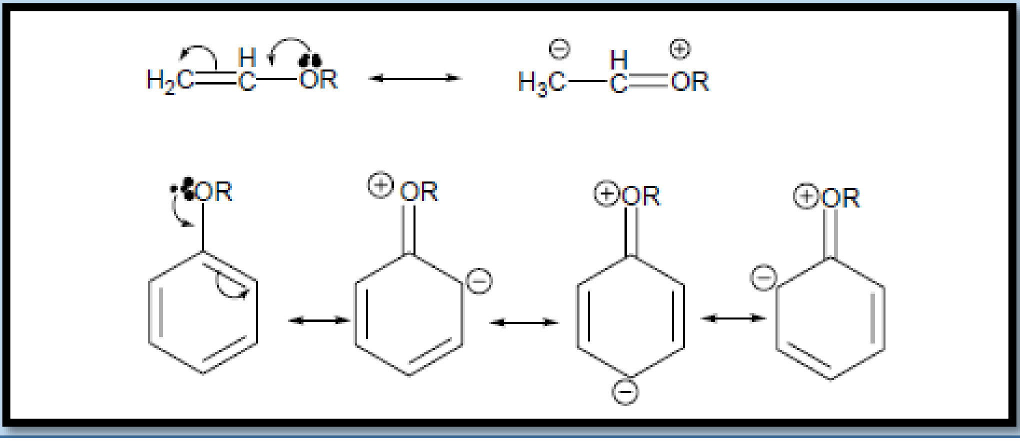
2,6-di-tert.-butylphenol

Ethers and Epoxides

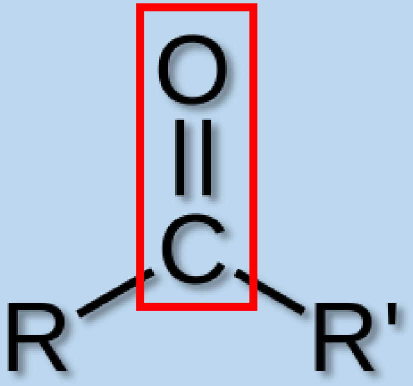


- **Asymmetric (C-O-C) stretching 1150-1000 cm^{-1}**
- But a band in this region is also observed in other oxy compounds like **alcohols, aldehydes, ketones**, and **acids** etc. ***Therefore***, we consider the possibility that a compound is ether or an epoxide ***only if*** the unknown oxy compound shows **no absorption bands** in **(O-H) (3750-3000 cm^{-1})** or **carbonyl (1850-1550 cm^{-1})** regions. ***((How can you recognize ether from other carbonyl groups?))***

- The conjugation of ether with **(C=C)** bond or phenyl ring ***shifts*** the **(C-O-C)** symmetric stretching to **~1250 cm^{-1}**. The resonance ***increases*** the bond order from single to partial double bond and **so higher the force constant and higher the absorption frequency**.



Carbonyl compounds



- The absorption peak for **(C=O)** stretching in the region **1870 to 1600 cm^{-1}** is perhaps the easiest band to recognize in IR spectrum and is extremely useful in analysis of carbonyl compounds.

- The changes in **(C=O)** stretching frequency in ***various carbonyl compounds*** can be explained by considering:

1. ***Electronic and mass effects of neighboring substituents***
2. ***Resonance effects (both C=C and heteroatom lone pair)***
3. ***Hydrogen bonding (inter and intramolecular)***
4. ***Ring strain etc.***

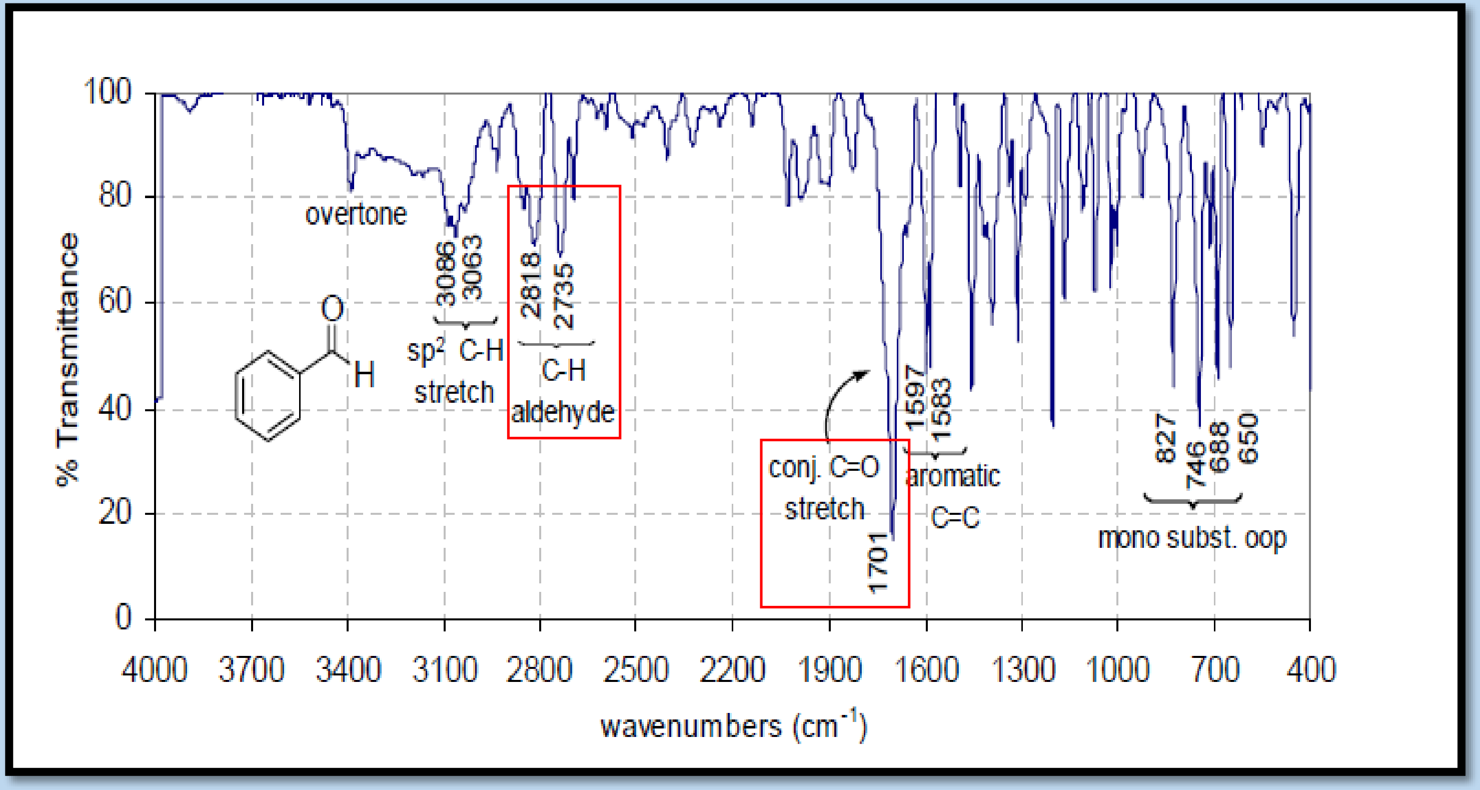
- It is customary to refer to the absorption frequency of a saturated aliphatic ketone at **1715 cm^{-1}**

a. Aldehydes and Ketones

Aliphatic aldehydes show strong **(C=O)** stretching in the region of **1740 – 1725 cm^{-1}**.

- **The conjugation** of an aldehyde to a **(C=C)** or a phenyl group **lowers** **(C=O)** stretching by **~ 30 cm^{-1}**.

- This effect is seen in benzaldehyde in which aryl group is attached directly to the carbonyl group and shifts **(C=O)** stretch to **1701 cm^{-1}**.

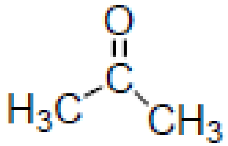


- The higher **(C-H)** stretching band **(2860-2800 cm^{-1})** of aldehyde is often buried under aliphatic C-H band. **But the lower C-H band at 2760-2700 cm^{-1} is usually used to *distinguish* aldehydes from ketones. The C-H bending vibrations appear between 945-780 cm^{-1}.**

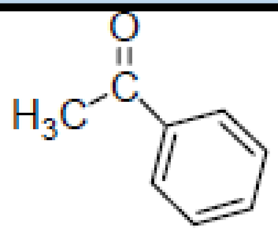
a. Aldehydes and Ketones

C=O Streching

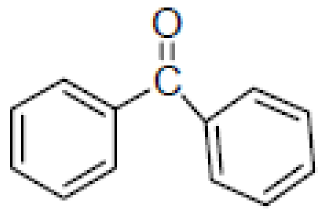
1720-1700 cm^{-1}



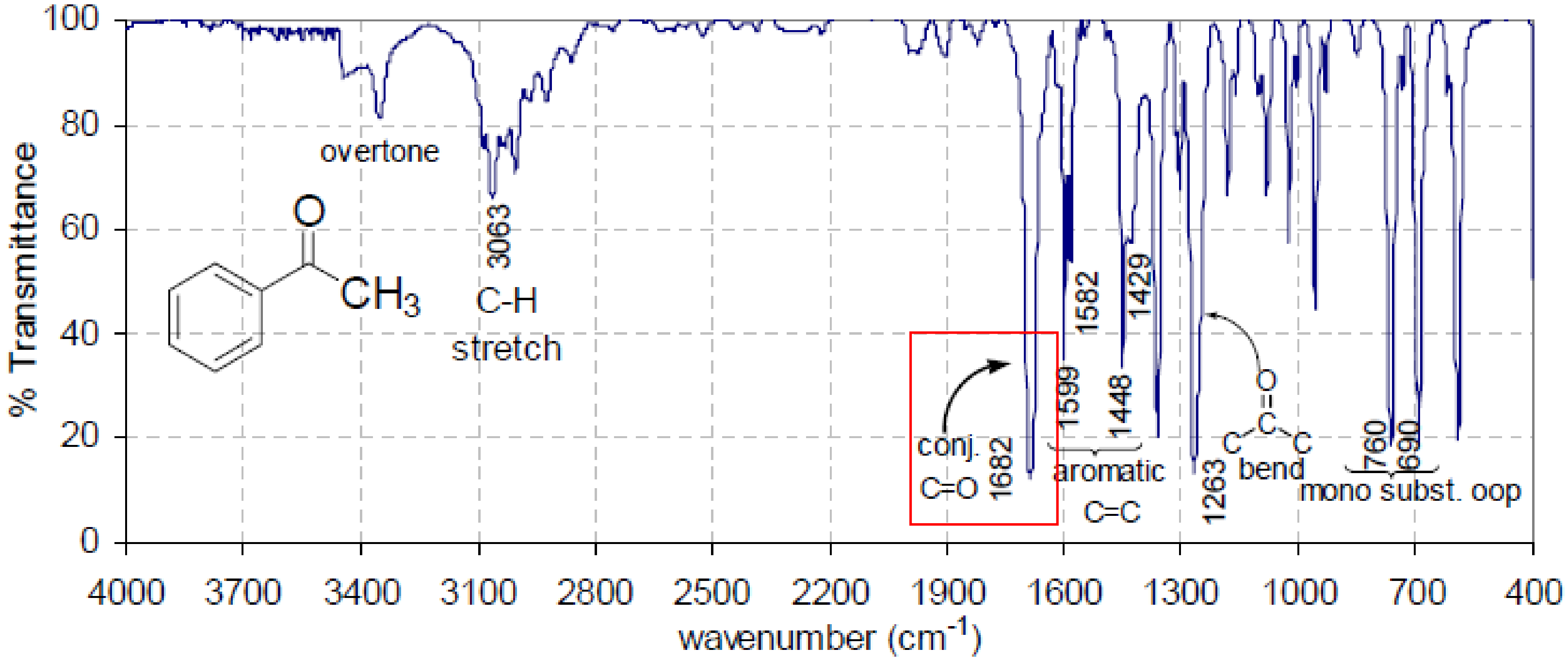
1715 cm^{-1}



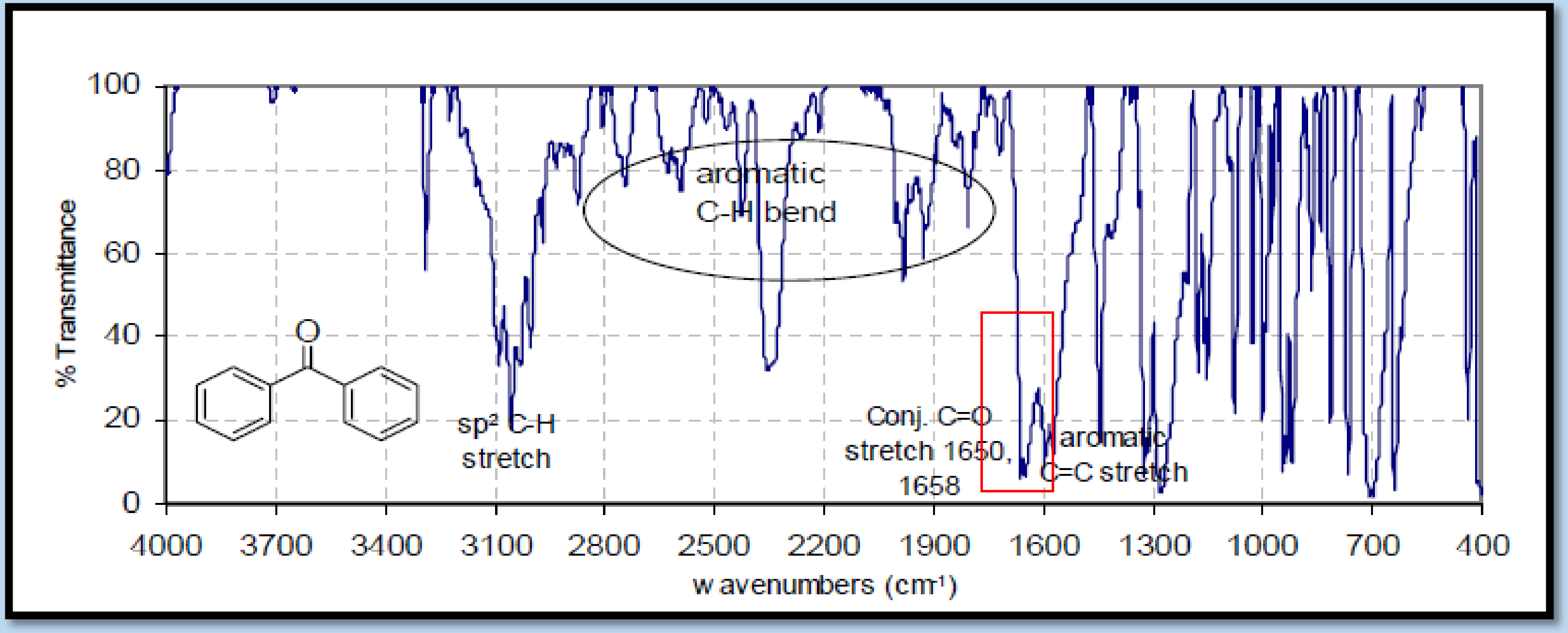
1682 cm^{-1}



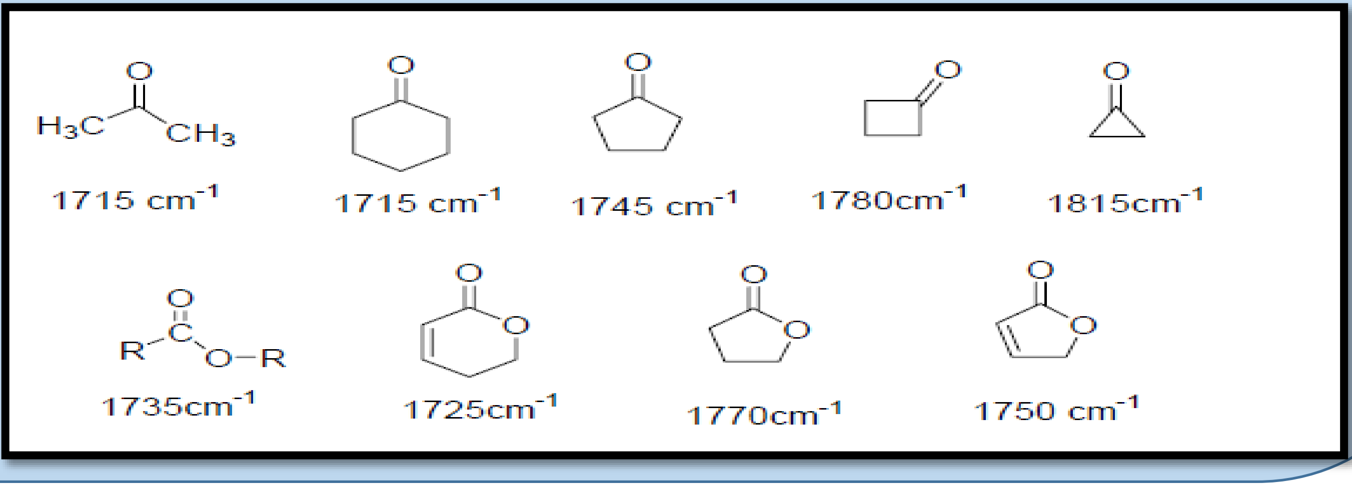
1658 cm^{-1}



a. Aldehydes and Ketones

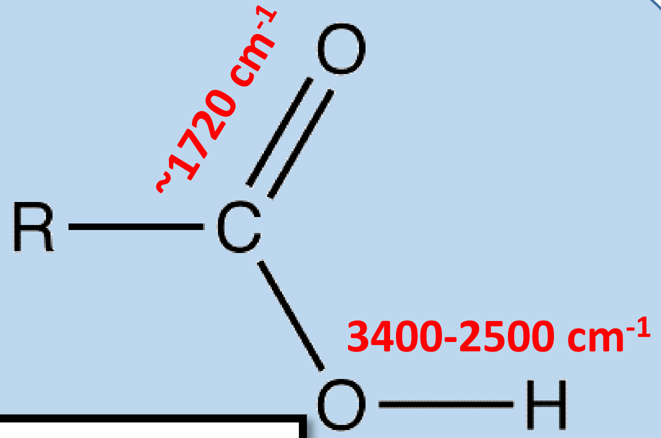


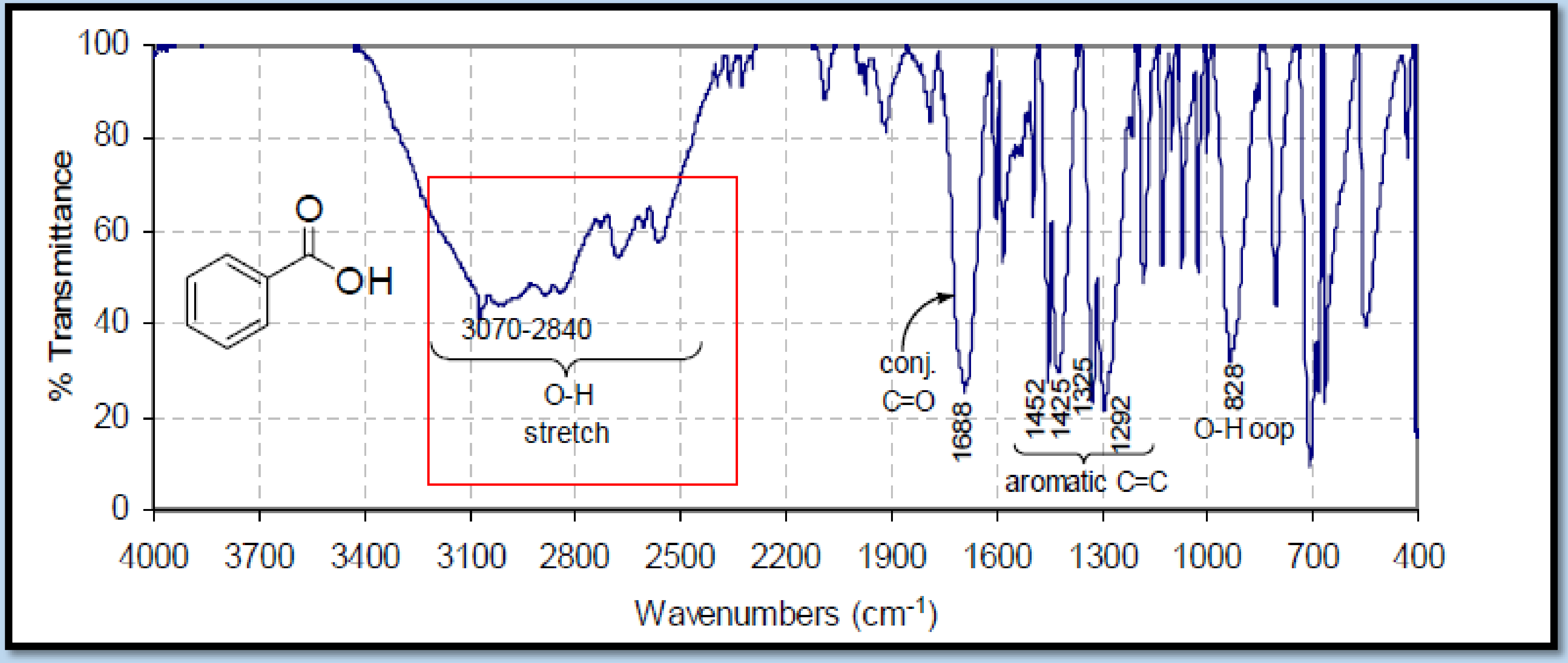
In case of cyclic ketones, the coupling between (C=O) stretching and C(=O)-C single bond causes increase in C=O stretching frequency as the C-C(=O) angle decreases.



b. Carboxylic Acids, Esters and Carboxylates

In case of carboxylic acids, the appearance of strong **(C=O)** stretching along with broad hydroxyl peak centered at **~ 3000 cm^{-1}** in an IR spectrum certainly shows the presence of carboxylic acid. In addition a medium intensity **(C=O)** stretch appears between **1320 – 1260 cm^{-1}**. ***In dilute solutions***, the carboxylic acids attain monomeric structures and the *inductive effect* of oxygen shifts the **(C=O)** absorption band to higher values **1760 – 1730 cm^{-1}** than observed in **ketones (1710 cm^{-1})**.





b. Carboxylic Acids, Esters and Carboxylates

In case of α,β-unsaturated or aryl carboxylic acids esters, the esters of due to conjugation absorb at **lower frequency**.

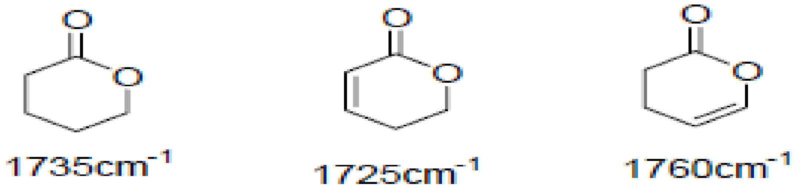
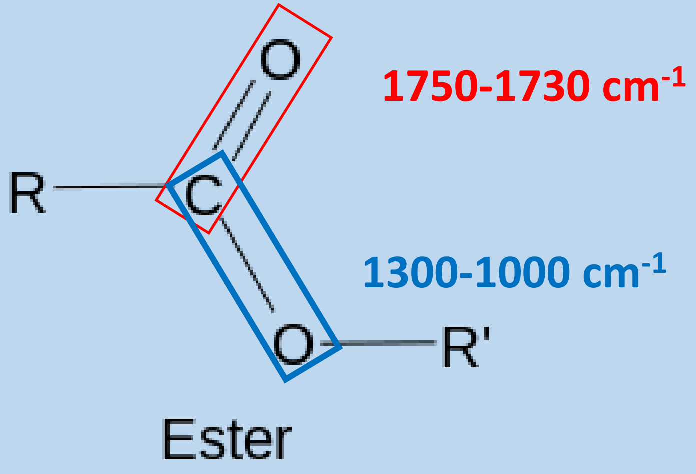


Figure 34 : Effect of conjugation in cyclic esters



If in an ester, **(C-O)** oxygen bears ***electron-withdrawing group*** like **vinyl, Ph** etc., then the **(C=O)** stretching is shifted to ***higher*** values **(~1770 cm^{-1})** This increases the electron-withdrawing ability of oxygen causing increase in carbonyl double bond character.

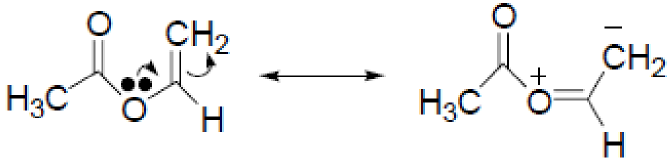


Figure 35 : Resonance effects in vinyl esters

In cyclic esters (lactones) **(C=O)** stretching is shifted to ***higher frequency with decreasing ring size***. Because of ring strain.

In salts of carboxylic acids, expected due to partial **(C=O)** bond character, the **C=O** stretching frequency is shifted to ***lower*** frequencies at **~ 1600 cm^{-1}**.

c. Acid Chlorides and Anhydrides

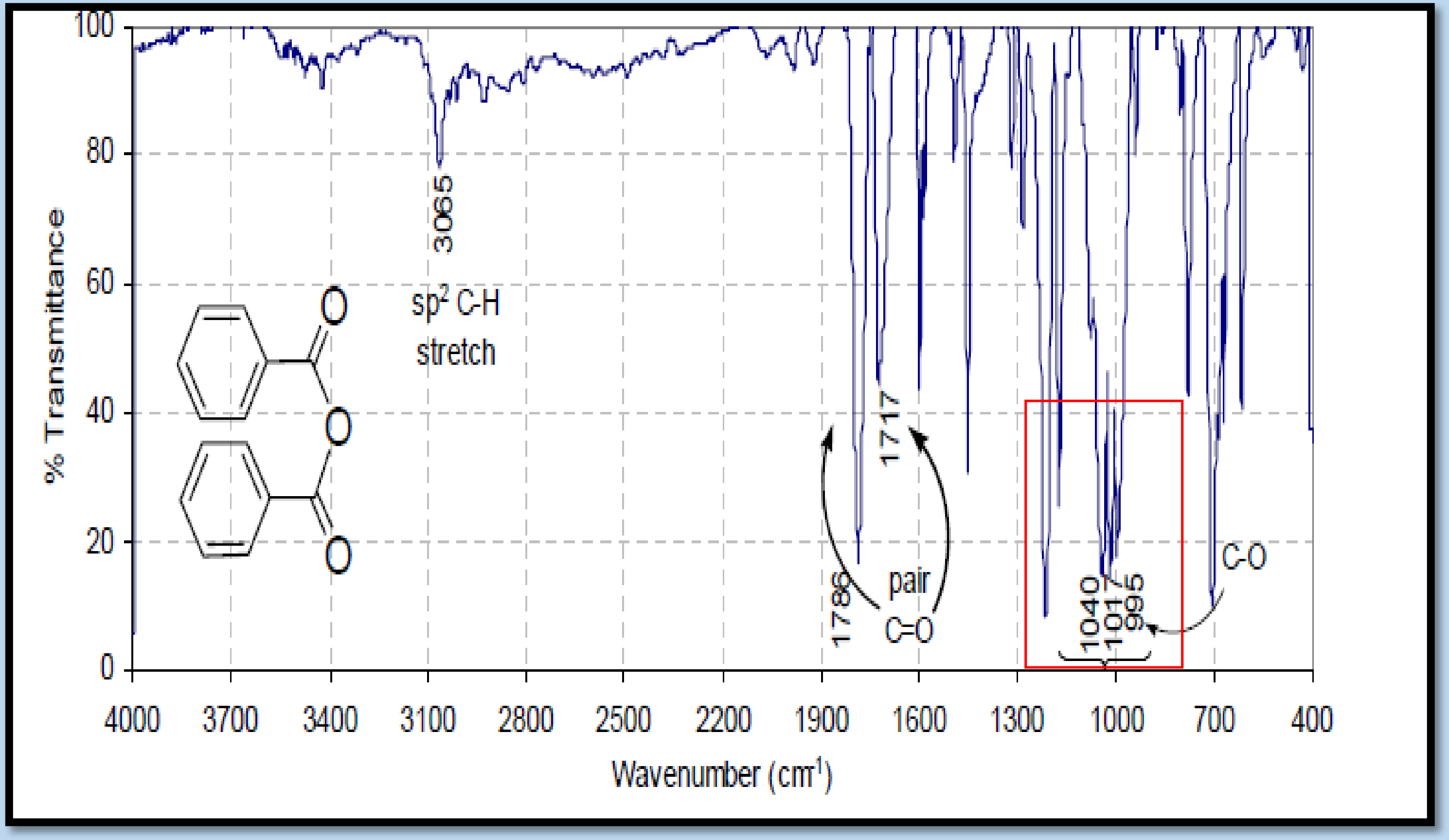
- **Both carboxylic acid halides and anhydrides** show strong **(C=O)** absorptions at frequencies **> 1800 cm^{-1} ,** and are easily differentiated form other carbonyl compounds.

- **The acid anhydrides** show **two** absorption bands in carbonyl region at **1820 cm^{-1} due to symmetric and at 1760 cm^{-1} due to asymmetric stretching vibrations**.

- ***In case of anhydrides of conjugated carboxylic acids***, the frequencies due to these bands are shifted to **1775 and 1720 cm^{-1}**.

c. Acid Chlorides and Anhydrides

- **The effect of conjugation** is clearly visible in IR spectrum of benzoyl anhydride. The strong and broad **(C-O)** stretching vibrations appear in the region **1300 – 900 cm^{-1}**.



- *__In case of acid chlorides__*, the **(C=O)** stretching frequencies appear at **1810-1790 cm^{-1}** which is attributed to high electronegativity of chlorine

d. Amides

- In case of amides strong resonance participation of lone pair of electrons by amide nitrogen ***weakens*** the carbonyl bond, Consequently:

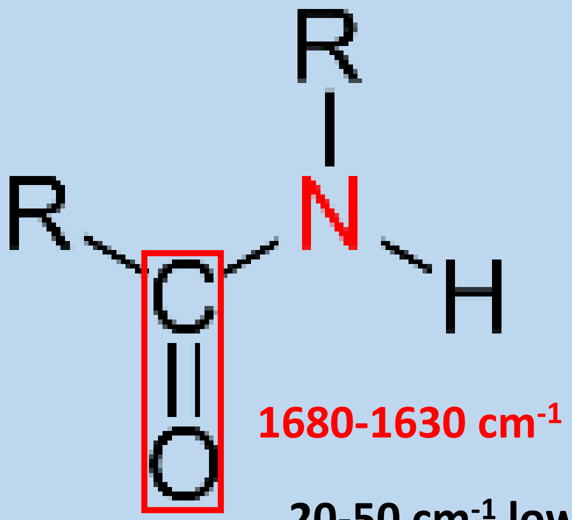
(C=O) amide **<** (C=O) ketone

- The **(C=O)** stretching band in IR spectra of amide is called amide I band.

- ***In primary and secondary amides***, **(N-H)** deformation band appears in the region **1655 - 1595 cm^{-1}** and is called amide II band.

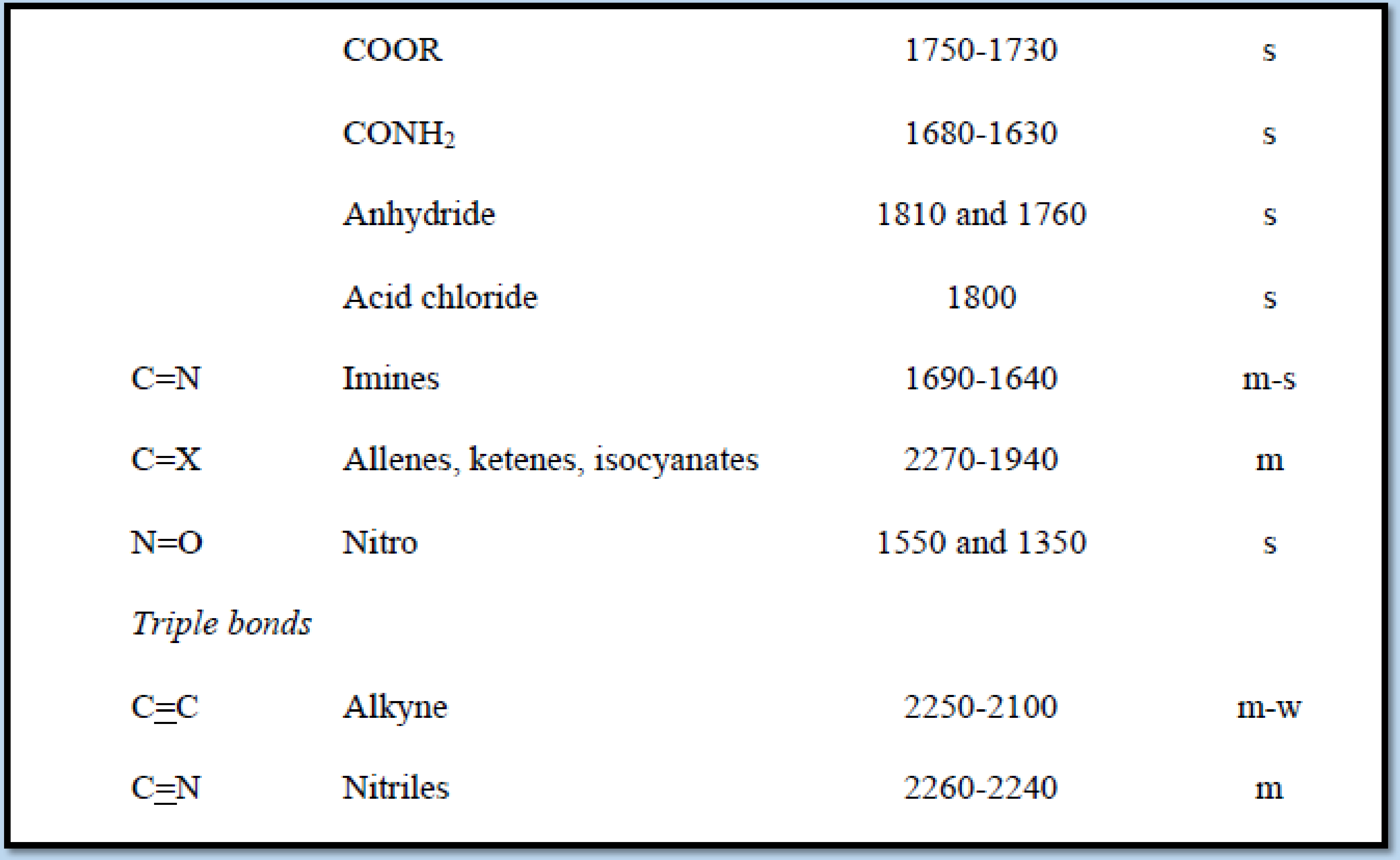
- In the solid or pure liquid state, ***primary amides***, which are highly hydrogen bonded, **exhibit two N-H stretching bands, one at 3550 cm^{-1} due to N-H asymmetric stretching and other at 3180 cm^{-1} due to N-H symmetric stretching.**

- ***In dilute solutions***, due to **lowering in degree of hydrogen bonding**, the absorption bands **shift to higher** frequencies at **3500 and 3400 cm^{-1}** , respectively. The secondary amides show only one **(N-H)** band at **~ 3300 cm^{-1}**.



1680-1630 cm^{-1}

20-50 cm^{-1} lower than ketones



	COOR	1750-1730	s
	$CONH_2$	1680-1630	s
	Anhydride	1810 and 1760	s
	Acid chloride	1800	s
$C=N$	Imines	1690-1640	m-s
$C=X$	Allenes, ketenes, isocyanates	2270-1940	m
$N=O$	Nitro	1550 and 1350	s
Triple bonds			
$C\equiv C$	Alkyne	2250-2100	m-w
$C\equiv N$	Nitriles	2260-2240	m

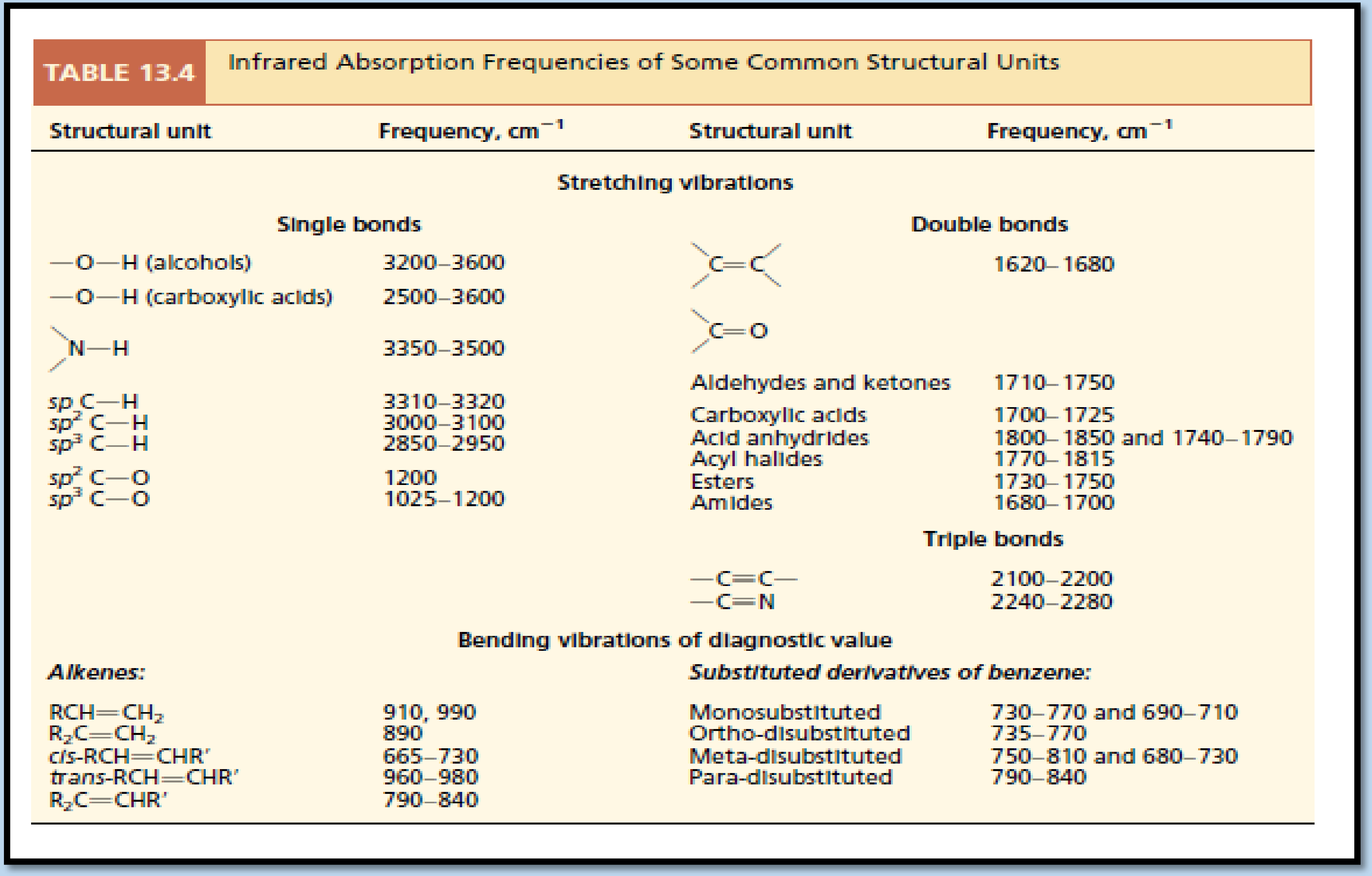


TABLE 13.4 Infrared Absorption Frequencies of Some Common Structural Units

Structural unit	Frequency, cm^{-1}	Structural unit	Frequency, cm^{-1}
Stretching vibrations			
Single bonds		**Double bonds**	
—O—H (alcohols)	3200–3600	$C{=}C$	1620–1680
—O—H (carboxylic acids)	2500–3600		
N—H	3350–3500	$C{=}O$	
sp C—H	3310–3320	Aldehydes and ketones	1710–1750
sp^2 C—H	3000–3100	Carboxylic acids	1700–1725
sp^3 C—H	2850–2950	Acid anhydrides	1800–1850 and 1740–1790
sp^2 C—O	1200	Acyl halides	1770–1815
sp^3 C—O	1025–1200	Esters	1730–1750
		Amides	1680–1700
		Triple bonds	
		$—C{\equiv}C—$	2100–2200
		$—C{\equiv}N$	2240–2280
Bending vibrations of diagnostic value			
Alkenes:		***Substituted derivatives of benzene:***	
$RCH{=}CH_2$	910, 990	Monosubstituted	730–770 and 690–710
$R_2C{=}CH_2$	890	Ortho-disubstituted	735–770
cis-$RCH{=}CHR'$	665–730	Meta-disubstituted	750–810 and 680–730
trans-$RCH{=}CHR'$	960–980	Para-disubstituted	790–840
$R_2C{=}CHR'$	790–840		