**Infrared spectra:** It is important to remember that the absence of an absorption band can often provide more information about the structure of a compound than the presence of a band. Be careful to avoid focusing on selected absorption bands and overlooking others. Use the examples linked to the table to see the profile and intensity of bands.

Look for absorption bands in decreasing order of importance:

1.the C-H absorption(s) between 3100 and 2850 cm-1. An absorption above 3000 cm-1 indicates C=C, either alkene or aromatic. Confirm the aromatic ring by finding peaks at 1600 and 1500 cm-1 and C-H out-of-plane bending to give substitution patterns below 900 cm-1. Confirm alkenes with an absorption generally at 1640-1680 cm-1. C-H absorption between 3000 and 2850 cm-1 is due to aliphatic hydrogens.

2. the carbonyl (C=O) absorption between 1690-1760cm-1; this strong band indicates either an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide. The an aldehyde may be confirmed with C-H absorption from 2840 to 2720 cm-1.

3. the O-H or N-H absorption between 3200 and 3600 cm-1. This indicates either an alcohol, N-H containing amine or amide, or carboxylic acid. For -NH2 a doublet will be observed.

4.the C-O absorption between 1080 and 1300 cm-1. These peaks are normally rounded like the O-H and N-H peak in 3. and are prominent. Carboxylic acids, esters, ethers, alcohols and anhydrides all containing this peak.

5.the CC and CN triple bond absorptions at 2100-2260 cm-1 are small but exposed.

6.structure of aromatic compounds may also be confirmed from the pattern of the weak overtone and combination tone bands found from 2000 to 1600 cm-1.

Table 11.2 S	Structural Units of	and Absorption Frequence	oles
BOND		TYPE OF COMPOUND	FREQUENCY (CM <sup>-1</sup> )
	(stretch)	Alkane	2800–3000
=C-H	(stretch)	Alkenes, aromatics	3000-3100
≡C—H	(stretch)	Alkynes	3300
—О—Н	(stretch)	Alcohols, phenols	3600–3650 (free) 3200–3500 (H-bonded) (broad)
—OH	(stretch)	Carboxylic acids	2500-3300
–N–H O	(stretch)	Amines	3300–3500 (doublet for $NH_2$ )
Щ —С—-Н	(stretch)	Aldehyde	2720 and 2820
	(stretch)	Alkenes	1600–1680
-C = C - C	(stretch)	Aromatic	1500 and 1600
C≡=C 0	(stretch)	Alkynes	2100–2270
∥ —C—	(stretch)	Aldehydes, ketones	1680–1740
—C≡N	(stretch)	Nitriles	2220-2260
CN	(stretch)	Amines	1180–1360
—С—Н	(bending)	Alkane	1375 (methyl)
—С—Н	(bending)	Alkane	1460 (methyl and methylene)
—С—Н	(bending)	Alkane	1370 and 1385 (isopropyl split)
—С—Н	(bending)	$R \rightarrow CH = CH_2$	1000–960 and 940–900
—C—H	(bending)	$R_2C = CH_2$	915–870
—С—Н	(bending)	cis RCH==CHR	790–650
—С—-Н	(bending)	trans RCH=CHR	990940
—С—Н	(out-of-plane bending)	mono subst. benzene	770–730 and 710–690
—С—Н	(out-of-plane bending)	o-subst. benzene	770–735
—С—Н	(out-of-plane bending)	m-subst. benzene	810–750 and 710–690
—С—Н	(out-of-plane bending)	<i>p</i> -subst. benzene	860800
C0	(stretch)	Primary alcohol	1050–1085
CO	(stretch)	Secondary alcohol	1085–1125
CO	(stretch)	Tertiary alcohol	1125–1200
C0	(stretch)	Phenol	1180–1260

#### **Unconjugated Alkenes** LOD • C=C-H: - stretch: $\geq 3000 \text{ cm}^{-1}$ • linear alkenes: - C=C stretch: moderate to weak absorption at 1667-1640 cm<sup>-1</sup> 5D alkene **C-H stretch** 3049 cm-1 1640 cm<sup>-1</sup>, moderate moderate 1650 cm<sup>-1</sup>, moderate 1670 cm<sup>-1</sup> weak alkane C-H weak stretches Alkynes 2800-3000 cm-1 4000 3000 LOD stretch: weak absorption at 2260-2100 cm<sup>-1</sup> - not observed for symmetrical alkynes (v. weak for 'pseudo' symmetric alkynes 5D - terminal alkynes (R-C $\equiv$ C-H) absorptions are stronger than Alkyne internal (R-C = C-R) absorptions C=C stretch 2119 cm-1 • C=C-H stretch: alkane C-H Alkyne - 3333-3267 cm<sup>-1</sup> C-H stretch stretches 3310 cm-1 2800-3000 cm<sup>-1</sup> - strong, narrow (as compared to OH or NH) 3000 4000 2000 examples of C=C. C≡C stretches OH 2240 1650 cm<sup>-1</sup> (as) 1647 2120 2080 1650 (weak) 1970 $1600 \text{ cm}^{-1}$ (s) 1611 1650

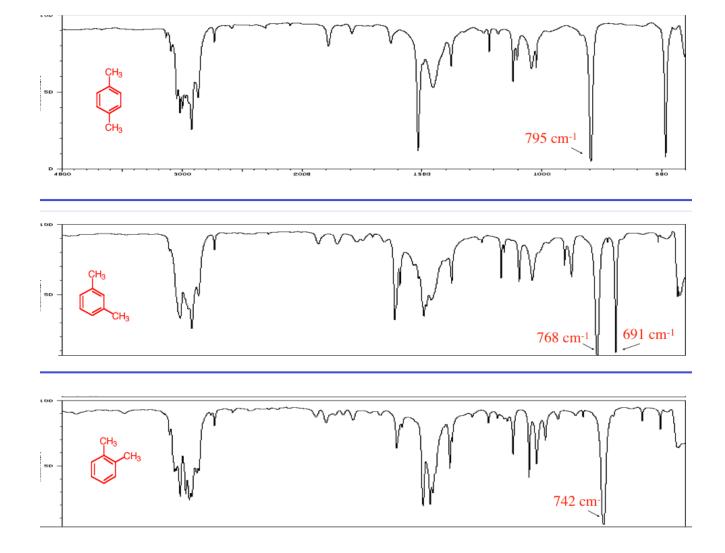
#### **Mononuclear Aromatic Hydrocarbons (benzene)**

- $\bullet$  Out of plane bending of aromatic C-H bonds: most informative 900–675  $cm^{-1}$ 
  - intense bands, strongly coupled to adjacent hydrogens on the ring
  - position and number of bands gives information about the substitution pattern (particularly useful for alkyl substituted aromatics. Substitution of polar groups can give rise to exceptions)

- C=C-H stretch: 3100-3000 cm<sup>-1</sup>
- C-C stretch: 1600-1585; 1500-1400 cm<sup>-1</sup>
- C—C out of plane ring bending: 600-420 cm<sup>-1</sup>

#### disubstituted benzenes

Out of plane bending of aromatic C-H bonds used to distinguish para, meta, ortho isomers



#### Alcohols

**CH stretch** typically occurs as a broad peak centered @ 3300 cm<sup>-1</sup> (spanning 3550-3200 cm<sup>-1</sup>). This peak is broad due to H-bonding

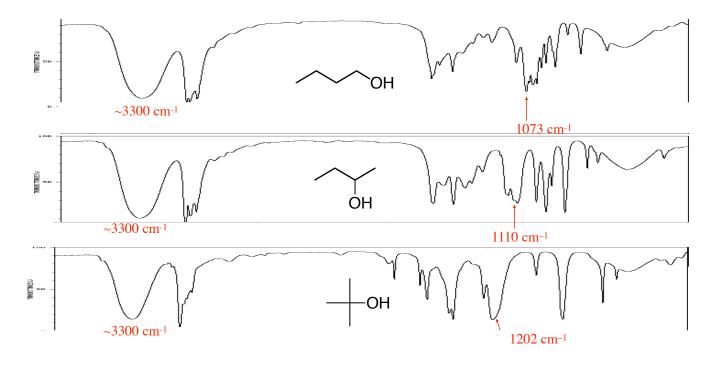
In rare cases where H-bonding is not present, the peak is sharp and at higher frequency

#### **C–O stretching Vibrations**

• Alcohols (1260-1000 cm<sup>-1</sup>)

• Phenols (1800-1260 cm<sup>-1</sup>)

primary alcohol: 1050-1085 cm<sup>-1</sup> secondary alcohol: 1085-1125<sup>-1</sup> tertiary alcohol: 1125-1200 cm<sup>-1</sup>



## **Ketones** C=O stretch (see tables)

- aliphatic: 'normal' position of a neat aliphatic ketone is 1715 cm<sup>-1</sup>
- conjugation: shifts position to lower frequency alkene or phenyl group causes absorption in the 1685-1666 cm<sup>-1</sup> region. For  $\alpha$ , $\beta$ -unsaturated carbonyls, 2 absorptions may be observed
- cyclic ketones The bond angle influences the absorption frequency of the C=O  $r^{\circ}$

## Aldehydes

C=O stretch (see tables)

- Aliphatic aldehydes: C=O stretch at 1740-1720 cm<sup>-1</sup>
- Electron withdrawing groups shift to higher frequency
- Conjugative groups shift to lower frequency (1710-1685 cm<sup>-1</sup>)

#### C-H stretch

2830–2695 cm<sup>-1</sup> Often, two bands are observed

## **Carboxylic Acids**

OH stretch in the 3300–2500 cm<sup>-1</sup> region centered near 3000 cm<sup>-1</sup>

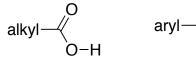
#### C=O stretch

- 1720-1705 for aliphatic acids
- 1710–1680 for conjugated acids

# 1788 1750 1715



1730

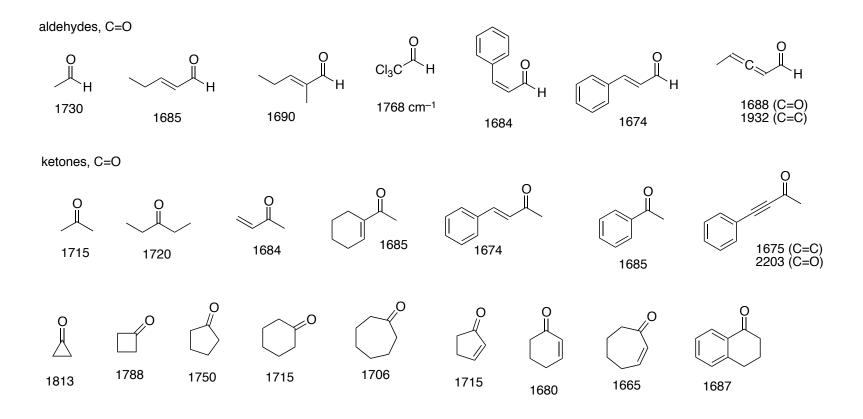




1720–1706 cm<sup>-1</sup>

1710-1680 cm<sup>-1</sup>

#### C=O stretch tables



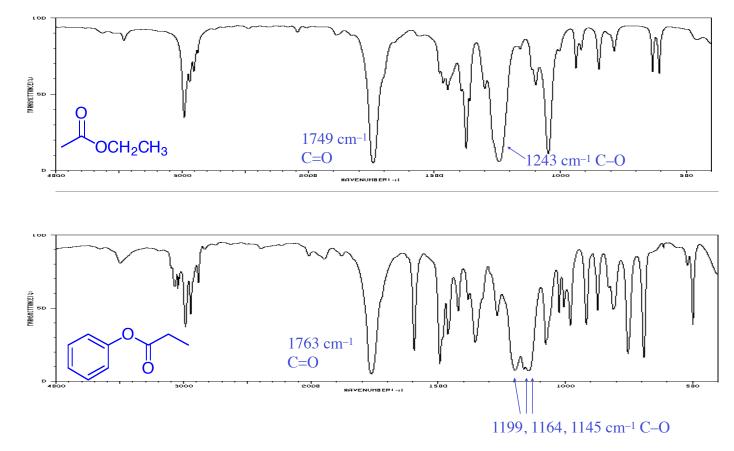
## **Esters**

### C=O stretch

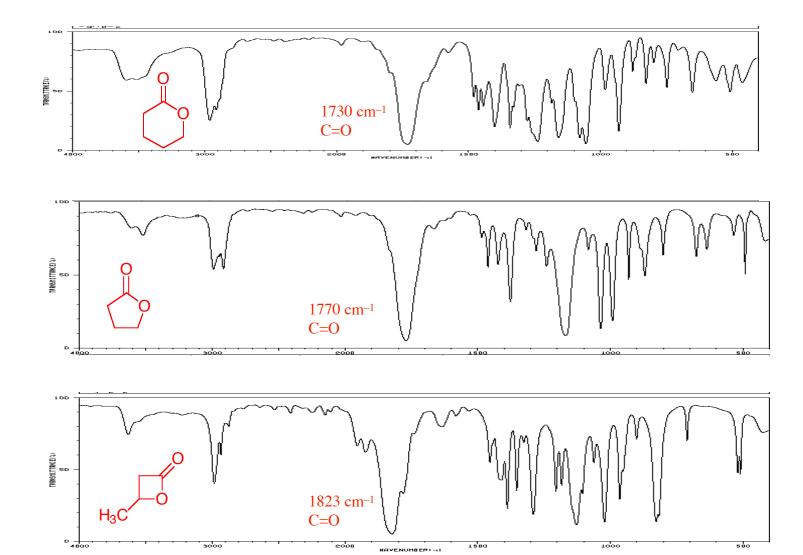
- saturated aliphatic esters: C=O: 1750–1735 cm<sup>-1</sup>
- formates,  $\alpha$ , $\beta$ -unsaturated, and benzoate esters: 1730-1715 cm<sup>-1</sup>
- phenyl or vinyl esters: 1770-1780 cm<sup>-1</sup>

C–O stretches (strong absorptions; asymmetrical coupled vibrations)

- saturated aliphatic esters (except acetates): C–O: 1210–1163 cm<sup>-1</sup>
- acetates: 1240 cm<sup>-1</sup>
- $\alpha$ , $\beta$ -unsaturated esters: 1300–1160 cm<sup>-1</sup>
- benzoate esters: 1310–1250 cm<sup>-1</sup>



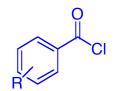




HAVENUMBER !---



1815–1785 cm<sup>-1</sup>



#### Anhydrides

3000

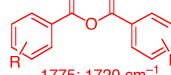
• Two carbonyl stretches (symmetrical and asymmetrical)

1500





2000



500

1000

1865; 1782 cm<sup>-1</sup>

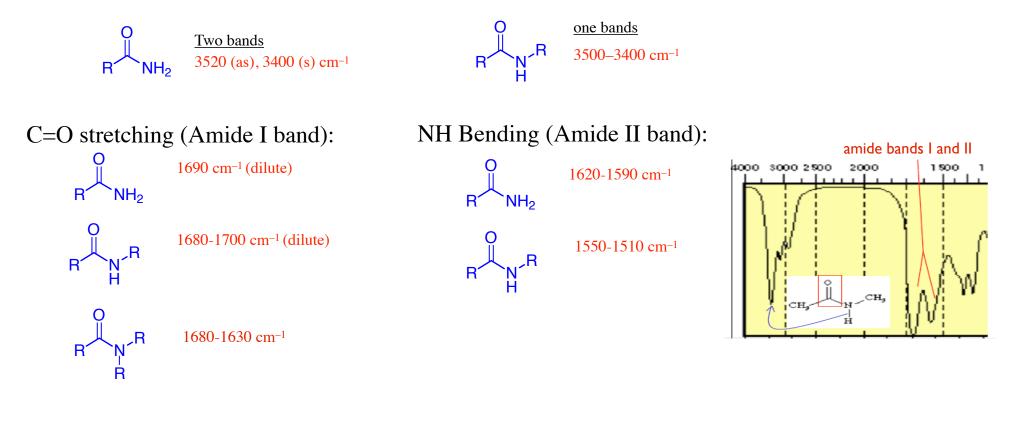
1800–1770 cm<sup>-1</sup>

1818; 1750 cm<sup>-1</sup>

1775; 1720 cm<sup>-1</sup>

## amides

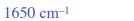
NH stretch(es): Primary amides produce two N-H stretch absorptions, secondary amides only one, and tetriary none.



## Lactams







1750-1700 cm<sup>-1</sup>

1760-1730 cm<sup>-1</sup>

- NH stretching
  - primary amines (RNH<sub>2</sub>) display <u>two</u> bands, near 3500 and 3400 cm<sup>-1</sup>. These represent 'free' asymmetrical and symmetrical stretches.
  - secondary amines ( $R_2NH$ ) display <u>one</u> band near 3350-3310 cm<sup>-1</sup>.
  - weaker and sharper than OH

#### **Nitriles**

alkyl—C≡N C=N  $2260-2240 \text{ cm}^{-1}$   $2240-2222 \text{ cm}^{-1}$ 

Nitro compounds

 2 bands from the asymmetrical and symmetrical stretching of the N=O bond

 $alkyINO_2$ 

NO<sub>2</sub>

1550 cm<sup>-1</sup> and 1372 cm<sup>-1</sup>

 $1550-1500 \text{ cm}^{-1}$  and  $1360-1290 \text{ cm}^{-1}$