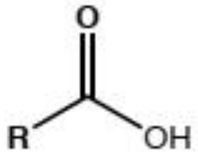
INFRA-RED SPECTROSCOPY

Characteristic Group Vibrations of Organic Molecules

5

2022-2023

IR for Functional Groups

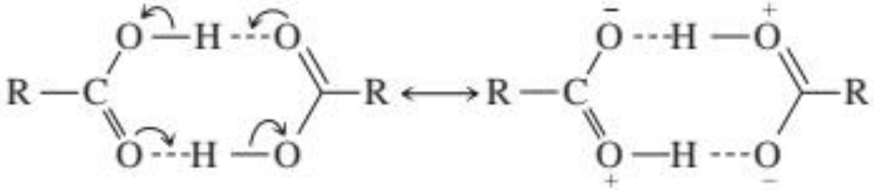


Carboxylic Acids

- **Carboxylic Acids**

- Free hydroxyl stretching vibration (near 3520 cm^{-1}) is observed only in very dilute solution in nonpolar solvents or in the vapor phase.

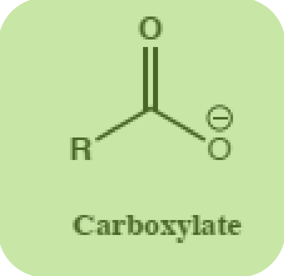
- Carboxylic acid dimers display very broad, intense O—H stretching absorptions in the region of **3300-2500 cm^{-1}** . The band is usually centered near **3000 cm^{-1}** .



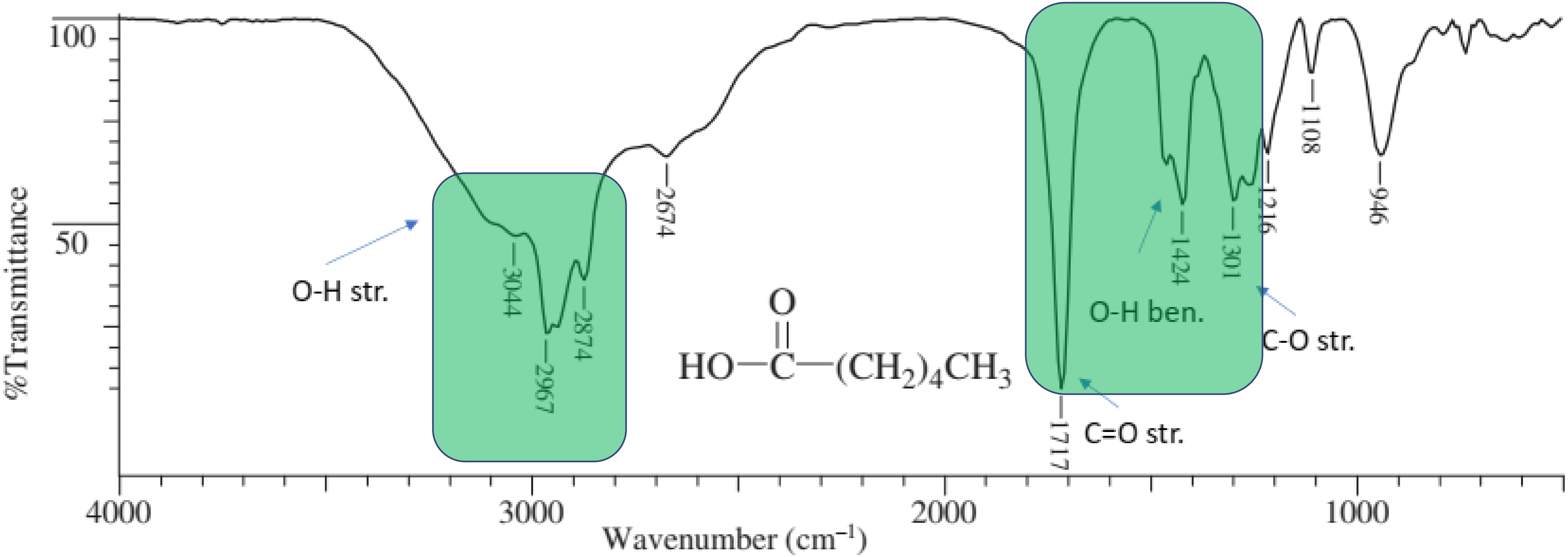
- ***C=O Stretching Vibrations.*** The C=O stretching bands of acids are considerably **more intense** than ketonic C=O stretching bands and it absorbs at **1730-1700 cm^{-1}**.

IR for Functional Groups

- **Carboxylic Acids**
- ***C—O Stretching and O—H Bending Vibrations.*** Two bands arising from C—O stretching and O—H bending appear in the spectra of carboxylic acids near **1320-1210 cm^{-1}** and **1440-1395 cm^{-1}**, respectively.


Carboxylate

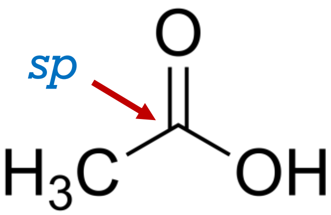
- **Carboxylate Anion**
- The carboxylate anion has two strongly coupled C=O bonds with bond strengths intermediate between C=O and C—O.
- The carboxylate ion gives rise to **two bands**: **a strong asymmetrical stretching** band near **1650-1550 cm^{-1}** and **a weaker symmetrical stretching** band near **1400 cm^{-1}**.
- The O—H stretching band disappears.



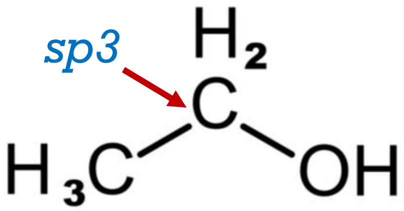
$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4CH_3$$

IR SPECTRUM OF CARBOXYLIC ACIDS AND ALCOHOLS

Carboxylic acid



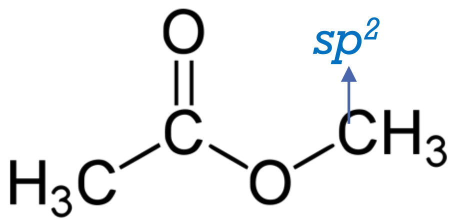
Alcohol



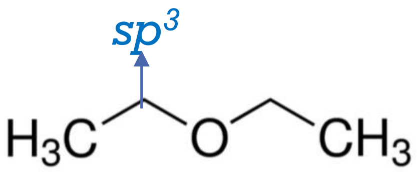
(2500-3300 cm^{-1})	O-H	(3200-3500 cm^{-1})
(1700 cm^{-1})	C=O	✗
(1210-1320 cm^{-1})	C-O	(1000-1150 cm^{-1})

IR SPECTRUM OF ESTERS AND ETHERS

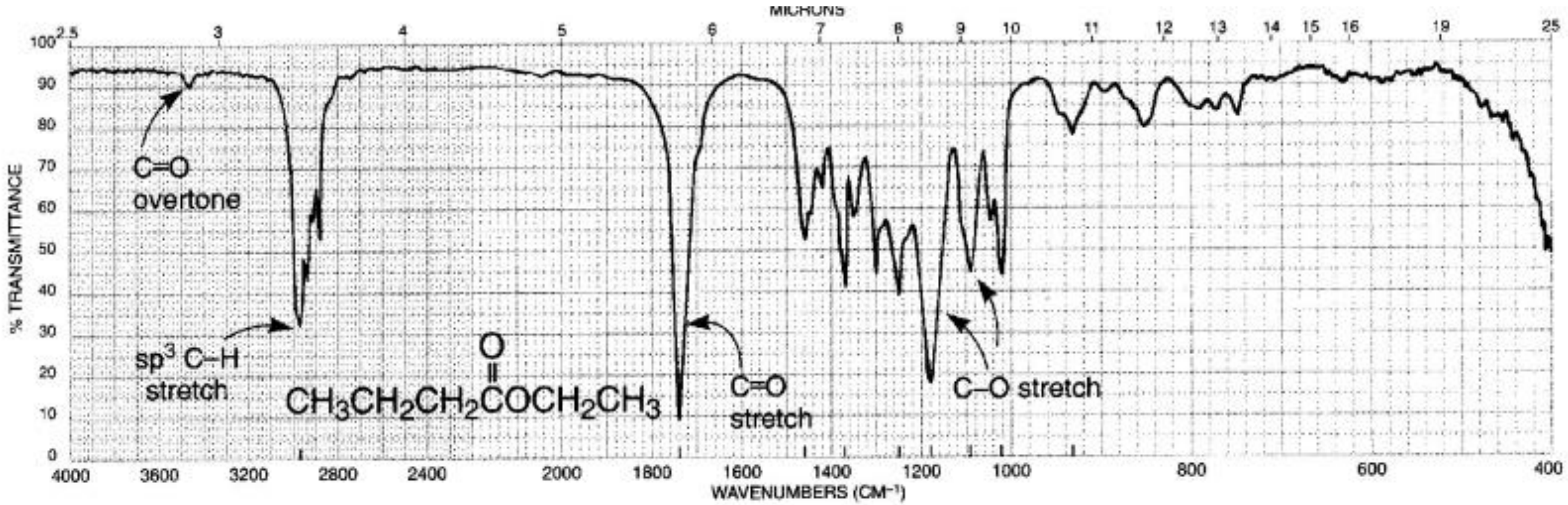
Ester

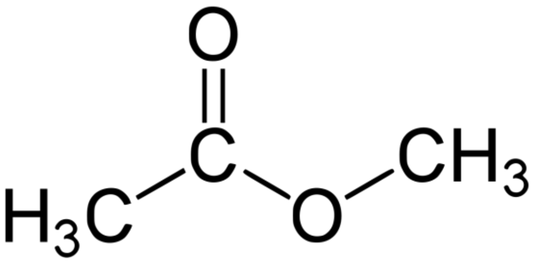


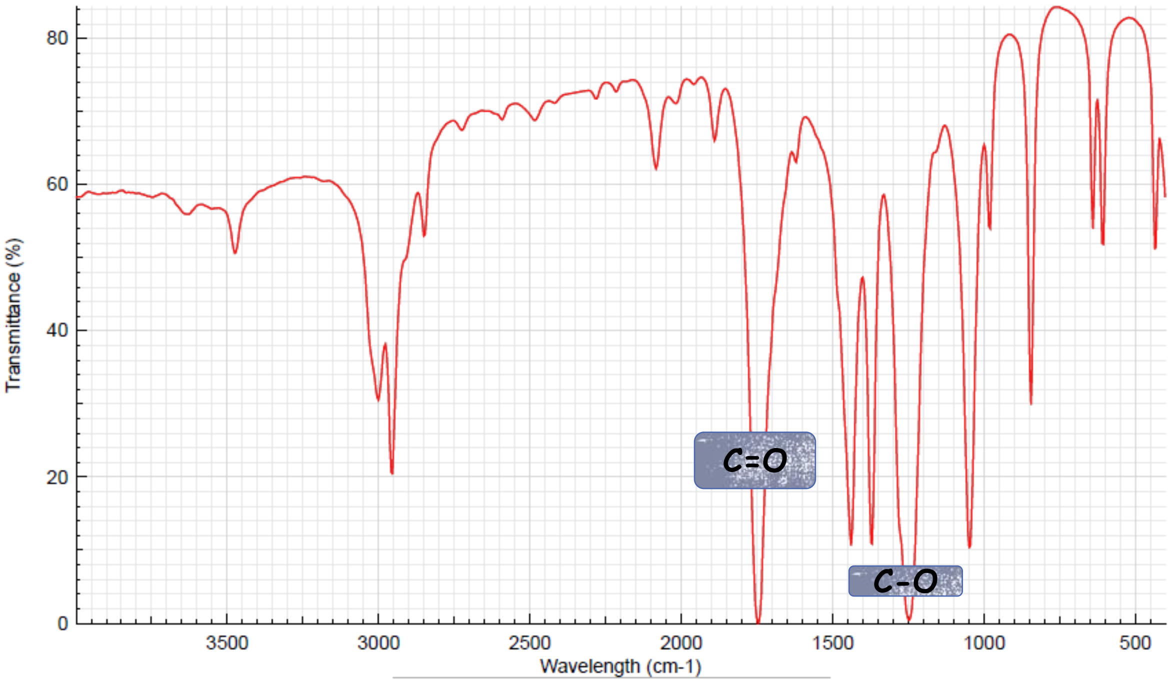
Ether

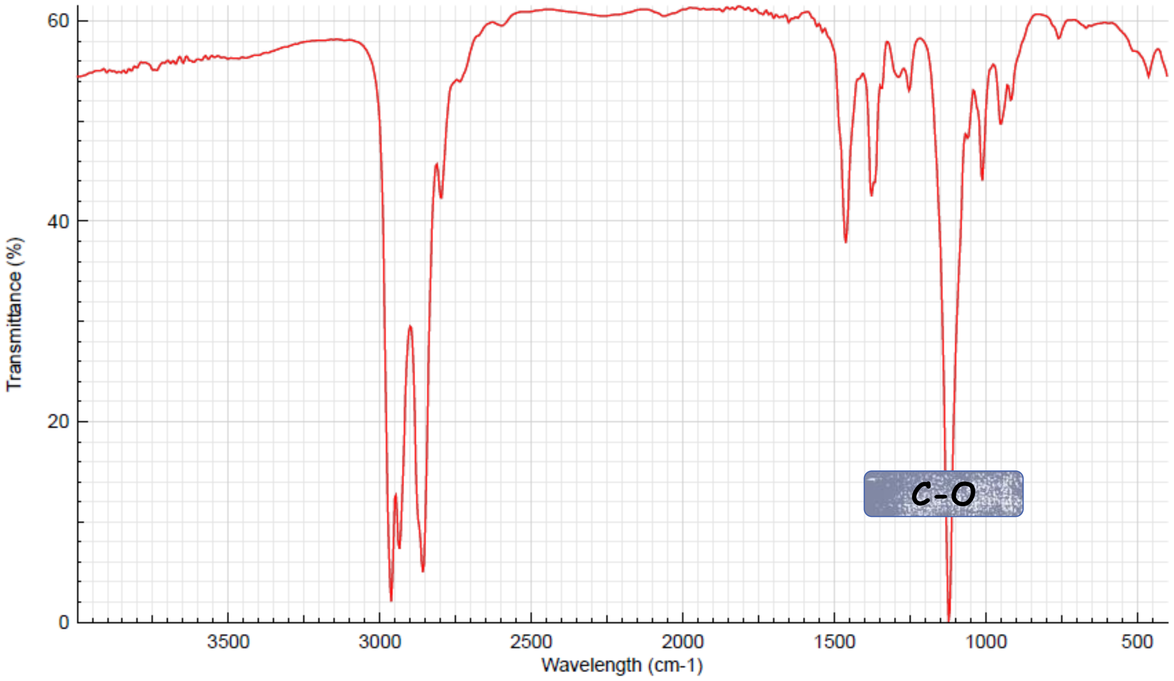


(1000-1300 cm^{-1}) two bands	C-O	(1000-1150 cm^{-1})
(1735-1750 cm^{-1})	C=O	✗

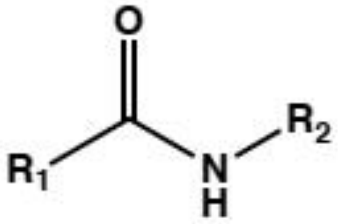




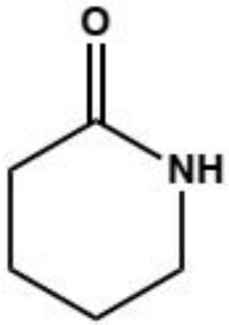

Transmittance (%)
80
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C=O
C-O


Transmittance (%)
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C-O

IR for Functional Groups



Amides



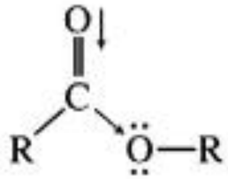
Lactames

- **Amides and Lactams**
- ***C=O Stretching Vibrations (Amide I Band).*** The C=O absorption of amides occurs at lower frequencies than “normal” carbonyl absorption at **1680-1630 cm^{-1}** due to the resonance effect.
- The ***N—H* stretching** is observed in the range of **3350–3180 cm^{-1}**,
- ***N—H Bending Vibrations (Amide II Band).*** All primary amides show a sharp absorption band in dilute solution (amide II band) resulting from N—H bending at a somewhat lower frequency than the C=O band at **1620-1590 cm^{-1}**, and normally is separated from the amide I band.

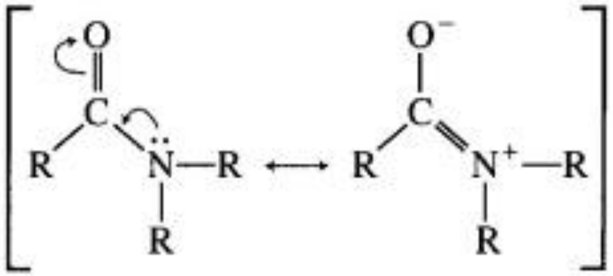
Ester vs Amide

More electron withdrawing element (higher frequency) see ester
Resonance (lower frequency) see amide

Ester



Amide

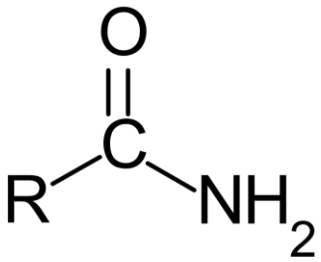


← cm^{-1} →

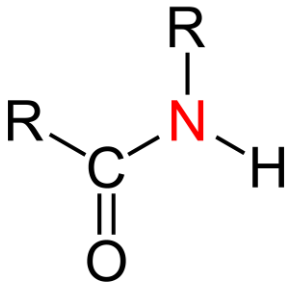
1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

IR SPECTRUM OF AMIDES

1° amide

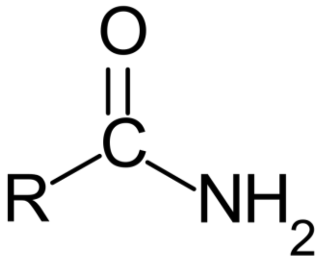


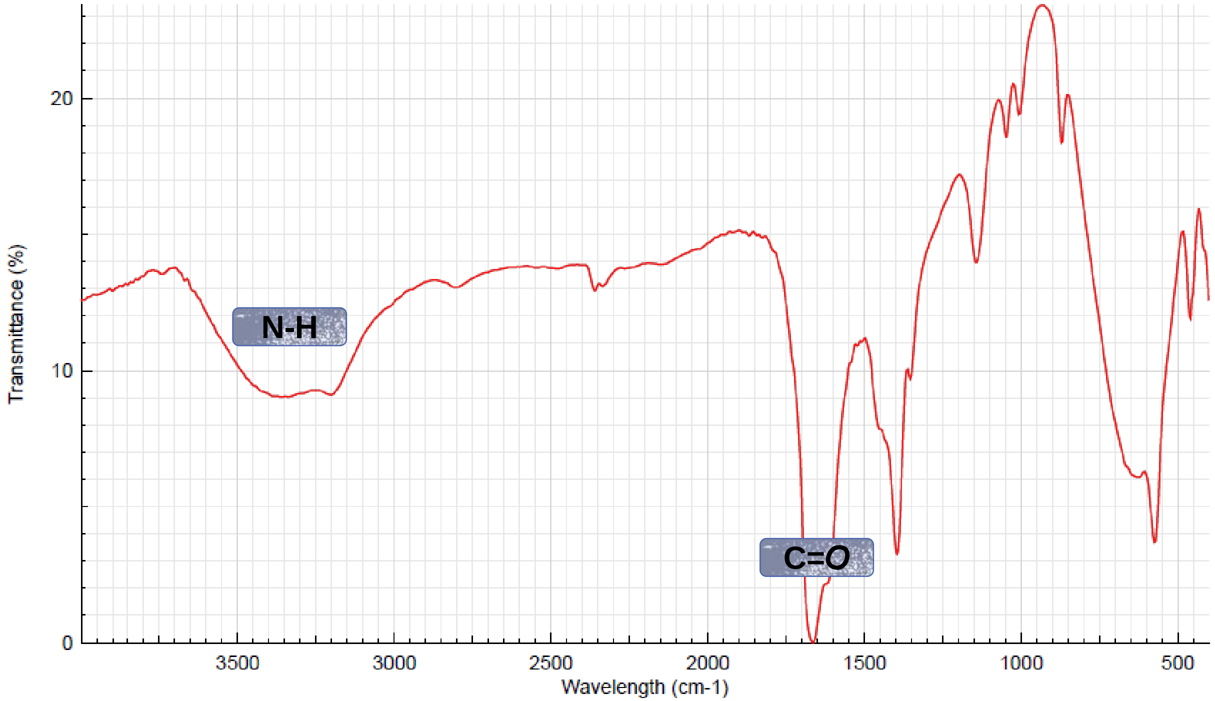
2° amide

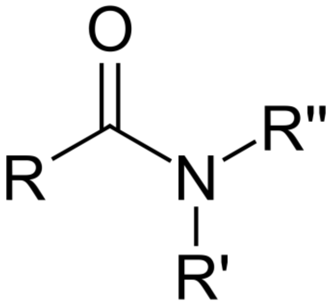


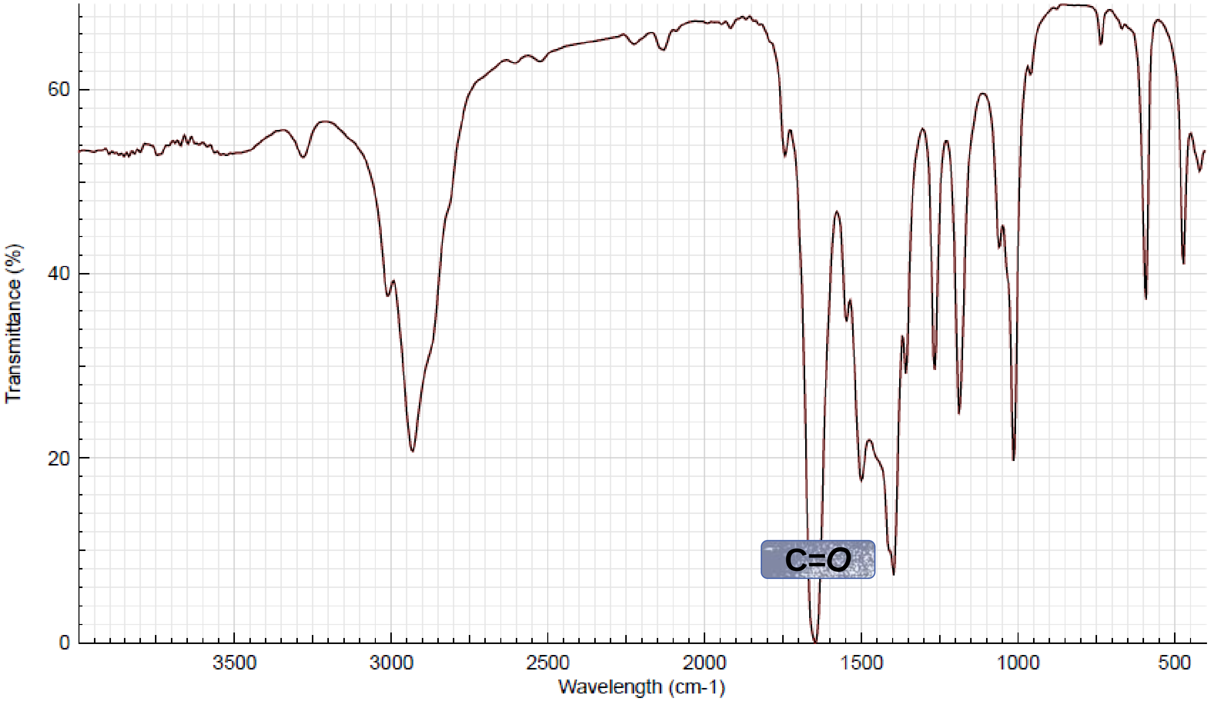
1° amide		2° amide
(1630-1680 cm^{-1})	C=O	(1630-1680 cm^{-1})
(3350 and 3180 cm^{-1})	(N-H) stretching	~ (3300 cm^{-1})

In 3° amide, there is no (N-H) stretching


O
C
R
NH2

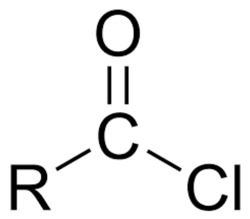

N-H
C=O
Transmittance (%)
20
10
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)


O
R
N
R''
R'

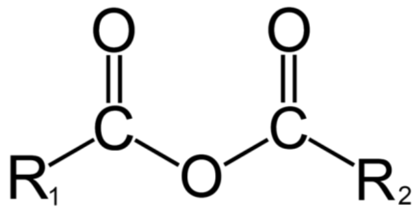

C=O
Transmittance (%)
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

IR SPECTRUM OF ACID CHLORIDE AND ANHYDRIDE

Acid chloride

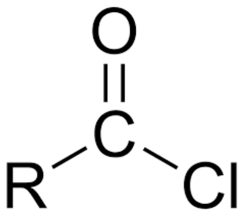


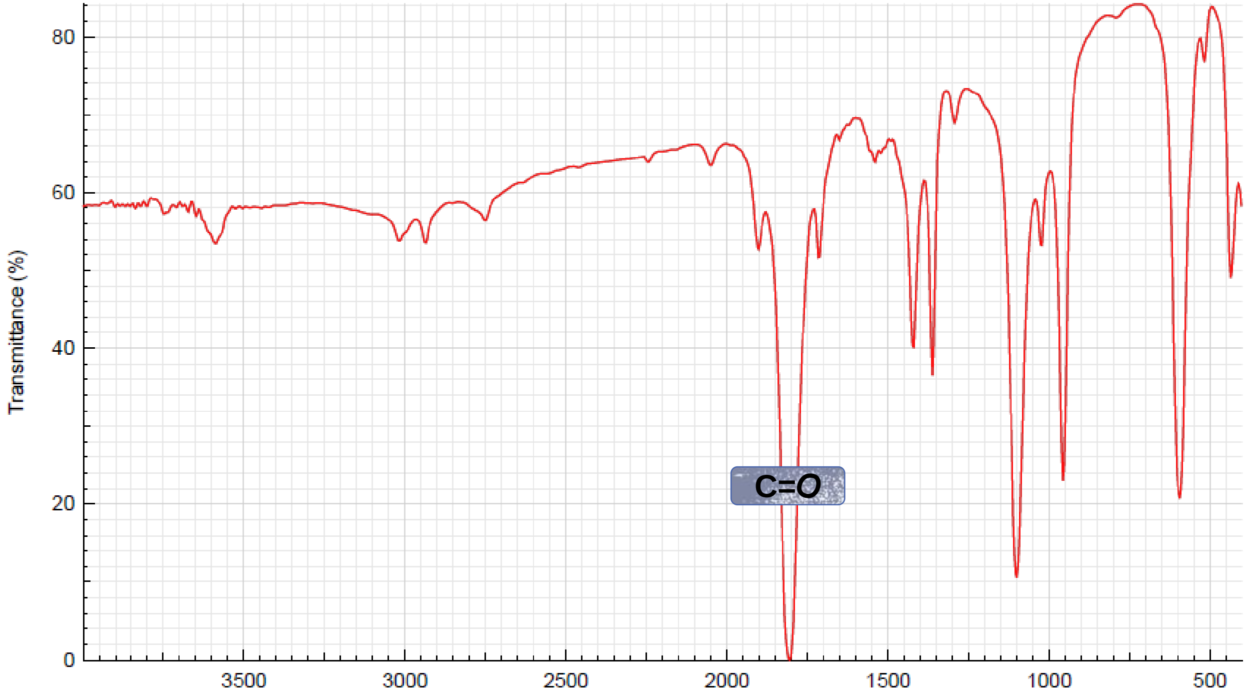
Anhydride



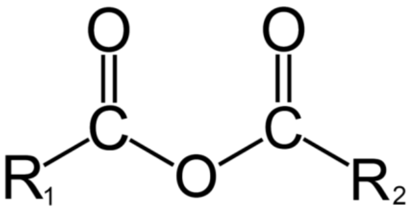
(1790-1810 cm^{-1})	C=O	(1750-1800 cm^{-1})
✗	C-O	(900-1300 cm^{-1})

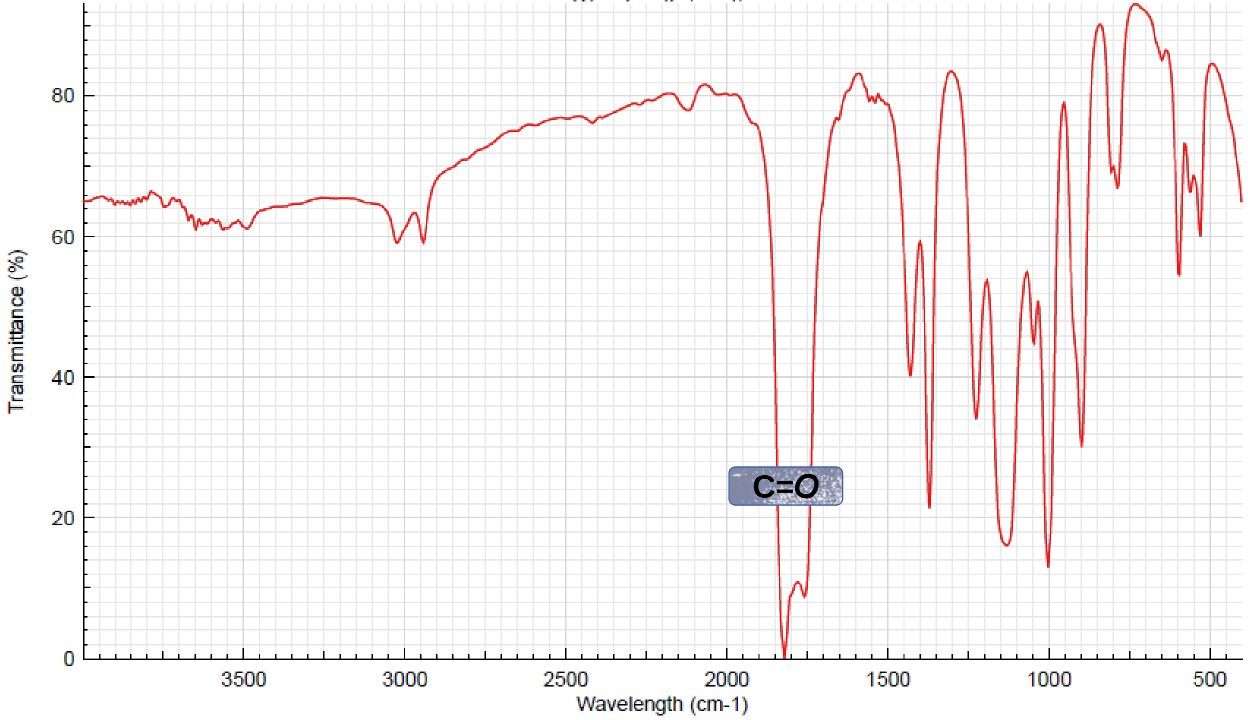
- ❑ In case of **acid chlorides**, the (C=O) stretching frequencies appear at 1810-1790 cm^{-1} which is attributed to high electronegativity of chlorine
- ❑ In case of **anhydrides of conjugated carboxylic acids**, the frequencies due to these bands are shifted to 1775 and 1720 cm^{-1}.





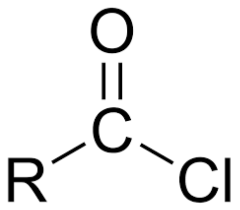
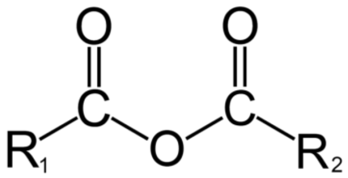
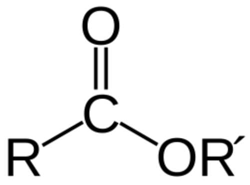
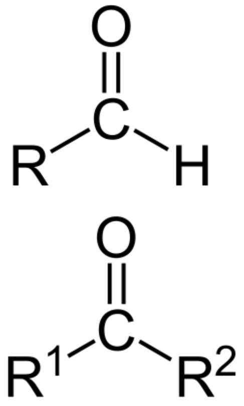
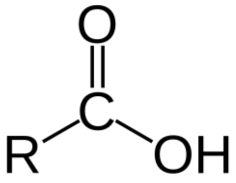
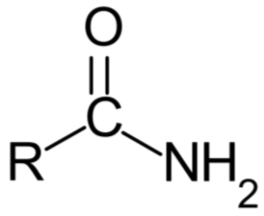
Transmittance (%)
80
60
40
20
0
3500
3000
2500
2000
1500
1000
500
C=O



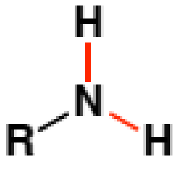


Transmittance (%)
80
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C=O

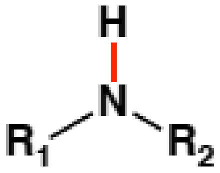
(C=O) stretching values (in cm^{-1}) of carbonyl compounds

					
1800	**1750-1800**	**1730- 1750**	**1710-1750**	**1700-1725**	**1650-1690**

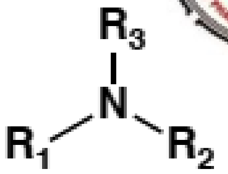
IR for Functional Groups



primary amine



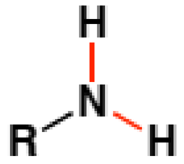
secondary amine



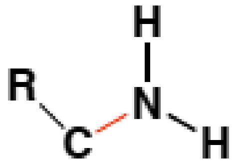
tertiary amine

- **Amines**
- ***N—H Stretching Vibrations.***
- Primary amines, display **two weak** absorption bands: one at **3400-3300 cm^{-1}** and the other at **3330-3250 cm^{-1}**.
- **Aromatic primary amines** absorb at slightly **higher wavenumbers than aliphatic primary amines**.
- Secondary amines show a **single weak** band in the **3350-3310 cm^{-1}** region.
- These bands are shifted to **longer wavelengths by hydrogen bonding**. The associated N—H bands are **weaker** and frequently **sharper than the corresponding O—H bands**.
- In the primary and secondary amines, a **shoulder** appears on the **low-frequency side of the N-H stretching band**, arising from the **overtone** of the NH bending band intensified by **Fermi resonance**.
- **Tertiary amines** do not absorb in this region.

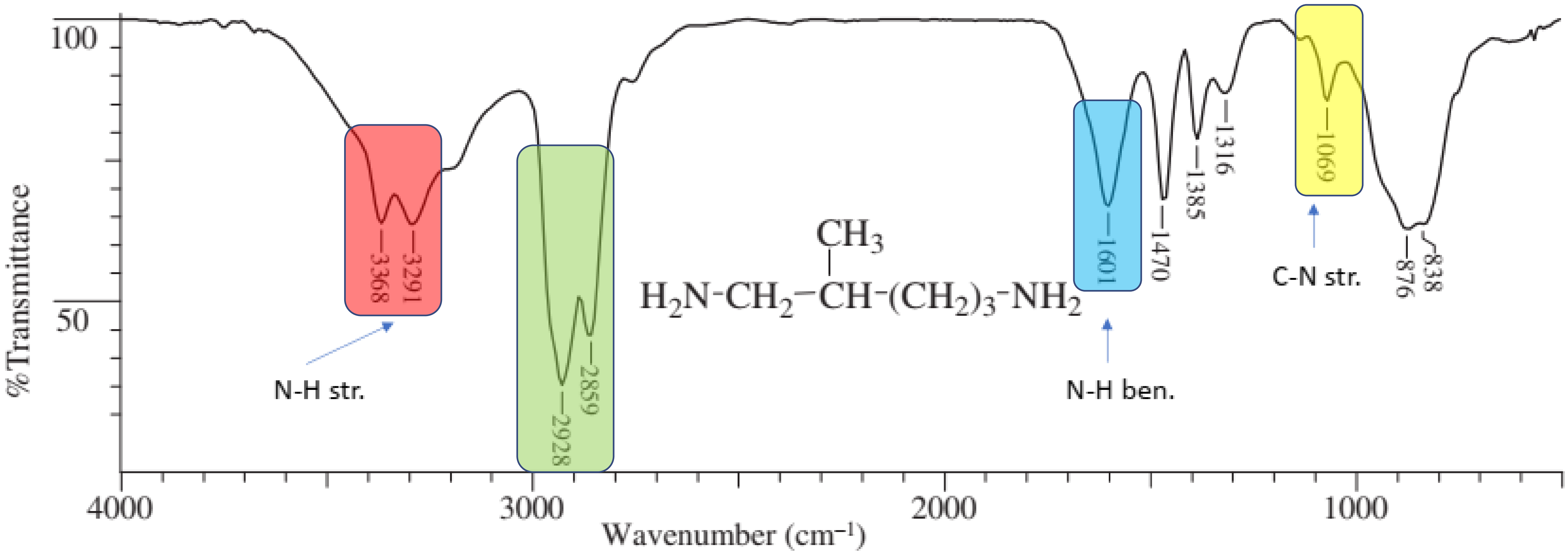
IR for Functional Groups



- **Amines**
- ***N—H Bending Vibrations.*** The N—H bending (scissoring) vibration of primary amines is observed in the **1650-1580 cm^{-1}** region of the spectrum.
- ***C—N Stretching Vibrations.*** Medium absorption bands for the unconjugated C—N linkage in primary, secondary, and tertiary aliphatic amines appear in the region of **1250-1020 cm^{-1}**.



- Aromatic amines display strong C—N stretching absorption in the **1342-1266 cm^{-1}** region. It is higher than the corresponding absorption of aliphatic amines because the force constant of the C—N bond is increased by resonance with the ring.


100
50
% Transmittance
4000
3000
2000
1000
Wavenumber (cm⁻¹)
3368
3291
2928
2859
1601
1470
1385
1316
1069
876
838
N-H str.
N-H ben.
C-N str.
CH₃
H₂N-CH₂-CH-(CH₂)₃-NH₂

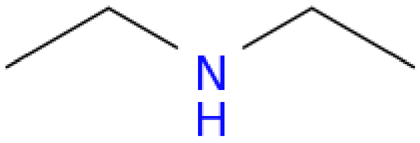
IR SPECTRUM OF AMINE

1° amine

TWO peaks

(N-H) (3300-3500 cm^{-1})

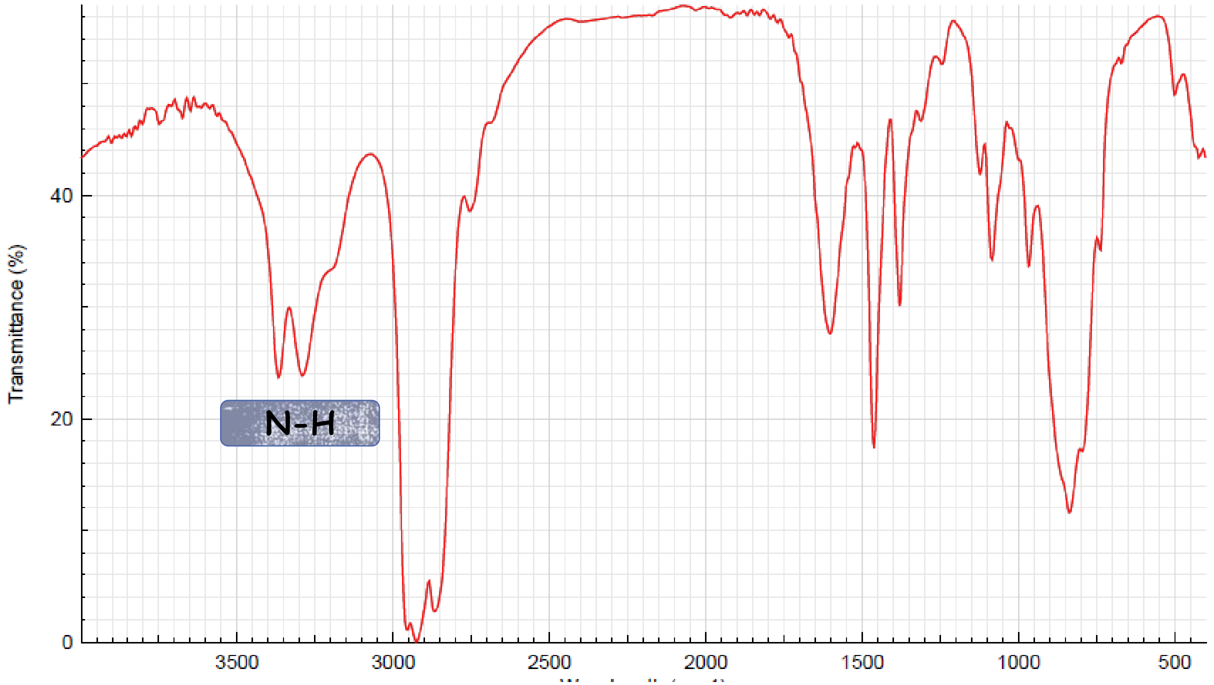
2° amine

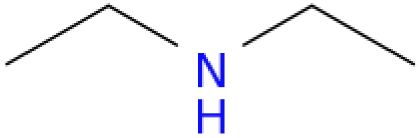


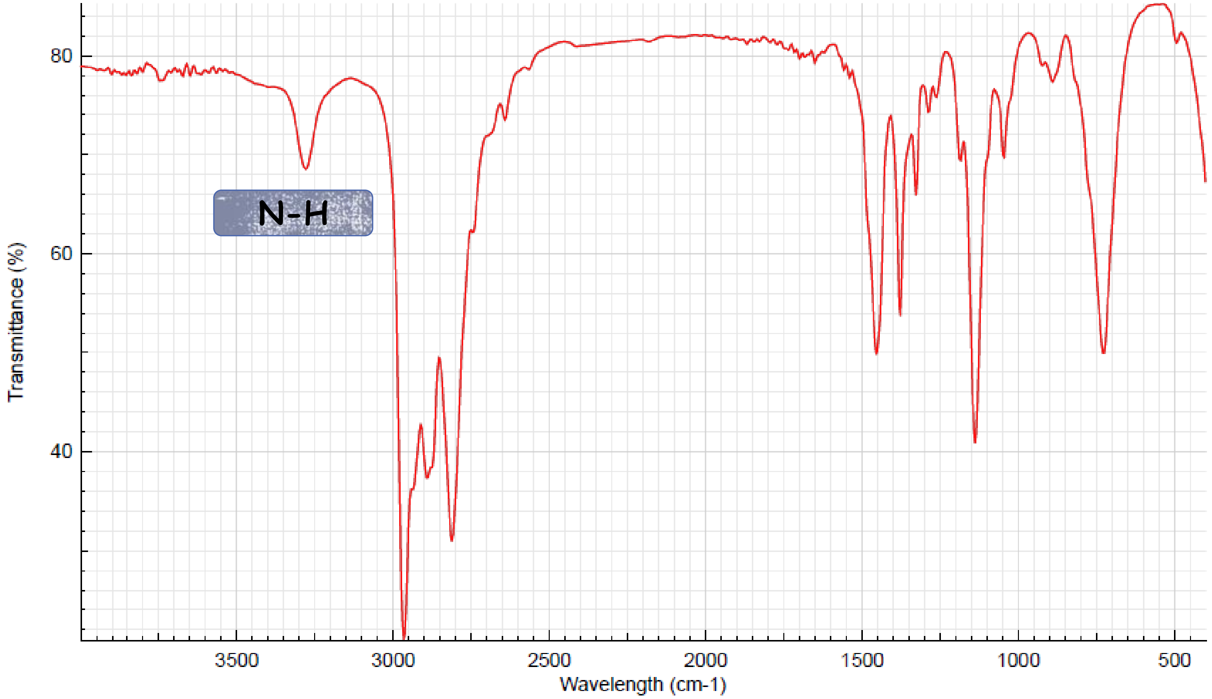
ONE peak

- ❑ **NOTE**: N-H signal in amines is broad BUT it is not broader than O-H signal in alcohols

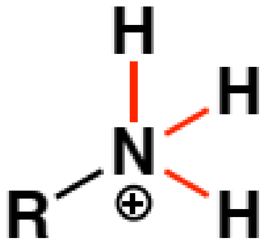

NH2


Transmittance (%)
0
20
40
3500
3000
2500
2000
1500
1000
500
N-H


N
H


Transmittance (%)
40
60
80
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
N-H

IR for Functional Groups

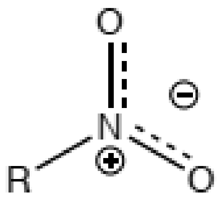


amine salt

- **Amine Salts**
- ***N—H Stretching Vibrations.*** The ammonium ion gives a strong, broad absorption in the **3300-3030 cm^{-1}** region because of N—H stretching vibrations. There is also a band in the **2000-1709 cm^{-1}** region.
- ***N—H Bending Vibrations.*** The ammonium ion displays a strong, broad bending band near **1429 cm^{-1}**.

IR for Functional Groups

- **Nitriles (cyano group)** $-C\equiv N$
- The spectra of nitriles ($-C\equiv N$) are characterized by weak-to-medium absorption in the triple-bond stretching region of the spectrum. Aliphatic nitriles absorb at **2260-2240 cm^{-1}**.
- Conjugation, such as occurs in aromatic nitriles, reduces the wavenumber of absorption to **2240-2222 cm^{-1}** and enhances the intensity.



nitro

- **Nitro compounds,** show absorption caused by **asymmetrical** and **symmetrical** stretching of the **NO_2 group**.
- Asymmetrical absorption results in a strong band in the **1661-1499 cm^{-1}** region; while the symmetrical absorption occurs in the region between **1389-1259 cm^{-1}**.
- Conjugation lowers the wavenumbers of both bands.

Organic Sulfur Compounds

- ***S—H Stretching Vibrations: Mercaptans.*** Aliphatic mercaptans and thiophenols show S—H stretching absorption in the range of **2600-2550 cm^{-1}**.
- The **S—H stretching** band is characteristically **weak** and may go **undetected** in the spectra of dilute solutions. However, since few other groups show absorption in this region, it is useful in detecting S—H groups.
- **C=S *Stretching Vibration***
- The **C=S group** is **less polar** than the **C=O group** and has a weaker bond. So, the **band is not intense**, and it **falls at lower frequencies** at a region of **1250-1020 cm^{-1}**.

IR for Functional Groups

- **Compounds Containing Sulfur—Oxygen Bonds**
- ***S=O Stretching Vibrations.***
- **Sulfoxides** show strong absorption in the **1070-1030 cm^{-1}** region. This absorption occurs at **1050 cm^{-1}** for DMSO.
- The hydrogen bonding shifting the absorption to slightly lower frequencies.
- **Sulfones** Spectra of sulfones show strong absorption bands at **1350-1300 cm^{-1}** and **1160-1120 cm^{-1}**. These bands arise from asymmetric and symmetric SO_2 stretching, respectively.
- **Sulfonamides** absorb strongly at **1370-1335 cm^{-1}** and **1170-1155 cm^{-1}**.
- Primary sulfonamides show strong N—H stretching bands at **3390-3330 cm^{-1}** and **3300-3247 cm^{-1}** in while secondary sulfonamides absorb near **3265 cm^{-1}**.

IR for Functional Groups

- **Organic Halogen Compounds**
- The strong absorption of halogenated hydrocarbons arises from the stretching vibrations of the **carbon–halogen bond**.
- Fluoro- compounds in **1400-1000 cm^{-1}** region.
- Aliphatic C—Cl absorption is observed in the broad region between **850-550 cm^{-1}**.
- Brominated compounds absorb in the **690-515 cm^{-1}** region.
- Iodo- compounds in the **600-500 cm^{-1}** region.
- A strong CH_2 wagging band is observed for the CH_2X (X = Cl, Br, and I) group in the **1300-1150 cm^{-1}**.

IR for Functional Groups

- **Phosphorus Compounds**
- ***P-H, P-C, and P=O Vibrations.***
- The P—H bond has **stretching vibrations** in the region of **2350-2440 cm^{-1}** and **bending vibrations** at **1120-950 cm^{-1}**.
- The stretching vibrations of P—C bonds in aliphatic phosphine oxides appear in the range of **650-750 cm^{-1}**.
- In the phosphoryl group (P=O), unlike for C=O, the oxygen atom bonds with the phosphorus in a highly polar bond that is frequently designated as a ($P^{+}-O^{-}$) group. The phosphoryl stretching absorption occurs at a range of **1310-1150 cm^{-1}**.