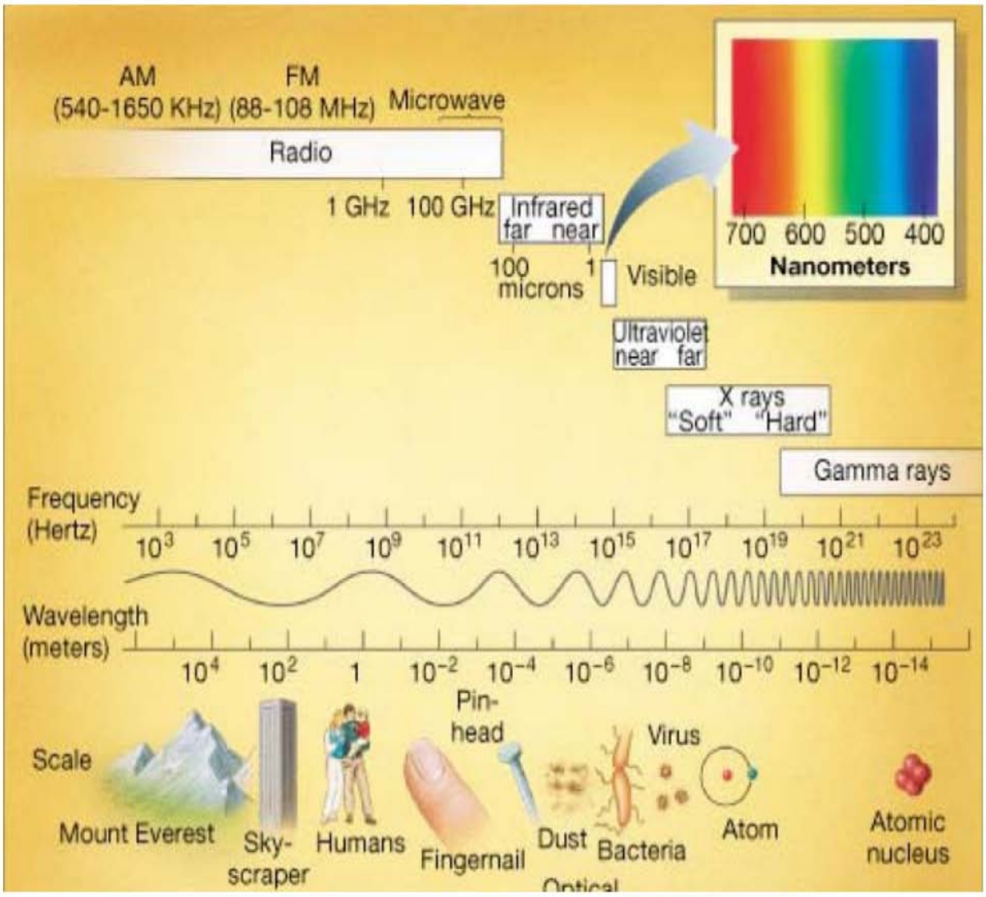
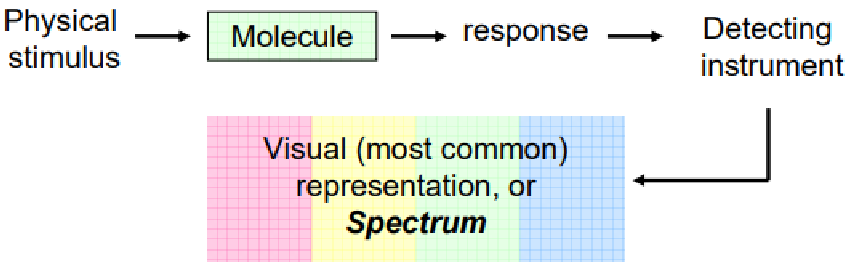
Spectroscopy

Infrared radiation

$$E=h\nu = hc/\lambda$$



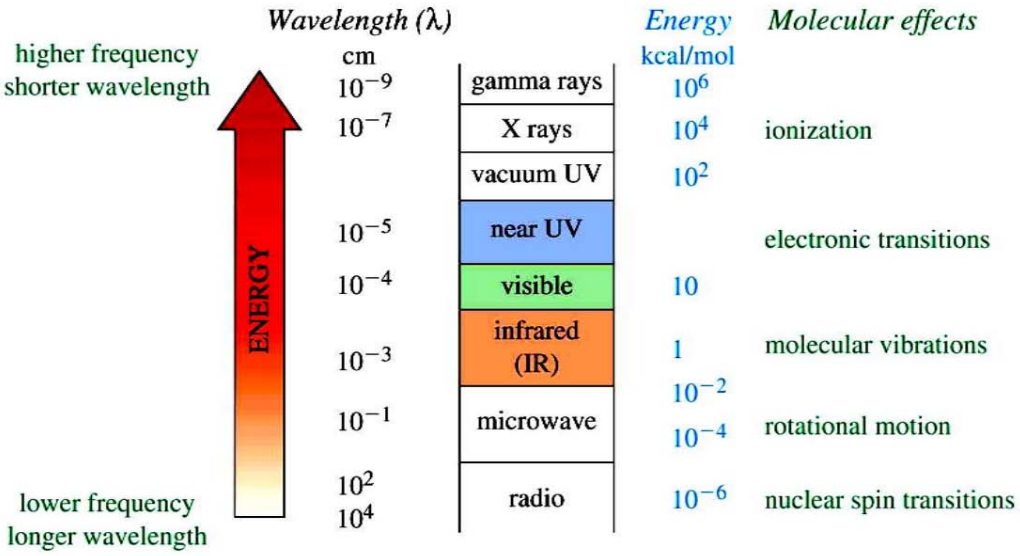


Introduction

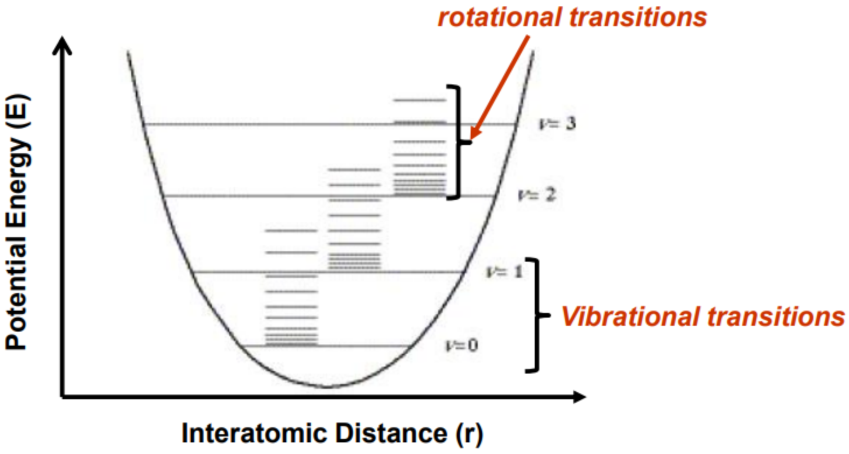
• IR refers to the part of electromagnetic spectrum between the visible and microwave (mw) regions.

•The useful range of IR for an organic chemist is between 4000-625 cm^{-1}.

• Many functional groups have vibration frequencies, characteristic of that functional group, within well-defined regions of this range.



Infrared (IR) spectroscopy: based on IR absorption by molecules as undergo vibrational and rotational transitions. Absorption of radiation in this region by a typical organic molecule results in the excitation of vibrational, rotational and bending modes, while the molecule itself remains in its electronic ground state.



The unit used on an IR spectrum is Wavenumbers

$$\bar{\nu} = \text{wavenumbers } (\text{cm}^{-1}) = \frac{1}{\lambda}$$

wavelength (cm)

$$\nu = \text{frequency} = \bar{\nu}\, c$$

C = speed of light
= 3 x 10^{10} cm/sec

or

$$\nu = \left(\frac{1}{\lambda}\right) c = \frac{c}{\lambda}$$

$$\frac{\text{cm/sec}}{\text{cm}} = \frac{1}{\text{sec}}$$

wavenumbers are directly proportional to frequency

IR is most useful in providing information about the presence or absence of specific **functional groups**.

Range of IR

• Near IR:

0.8 to 2.5μm (12000cm^{-1} –4000cm^{-1})

- Analyzing mixtures of aromatic amines
- Determination of protein, fat, moisture, oil content.

• Middle IR:

2.5 to 15μm (4000cm^{-1} – 667cm^{-1})

- Also known as vibration- rotation region.
- This region is divided into:

1. Group frequency region: 4000cm^{-1} – 1500cm^{-1}
2. Fingerprint region: 1500cm^{-1} – 667cm^{-1}

• Far IR:

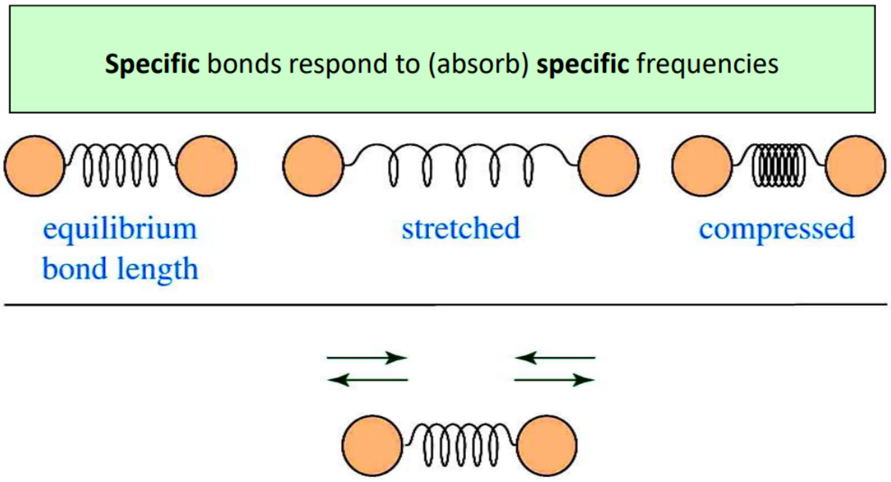
15 to 1000μm (667cm^{-1} –10cm^{-1})

- Study of inorganic or organometallic compounds
- Sensitive to changes in overall structure of the molecule.

MOLECULES
|
|
v
ATOMS
|
|
v
CONTINOUS MOTION
OR
NATURAL VIBRATIONS
|
|
v
APPLIED IR FREQUENCY = NATURAL FREQUENCY
⇓
ABSORPTION OR IR
⇓
VIBRATIONS AT MANY RATES
⇓
⇓
IR SCPECTRA
↓
CHARACTERISTIC FUNCTIONAL GROUPS &
BONDS (FINGERPRINT OF A MOLECULE)

Principle – IR Spectroscopy

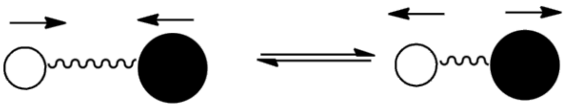
Infrared radiation is largely thermal energy. It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses, or atoms.



- IR radiation in the range from about 10,000-100 cm^{-1} is absorbed and converted into energy of molecular vibration.

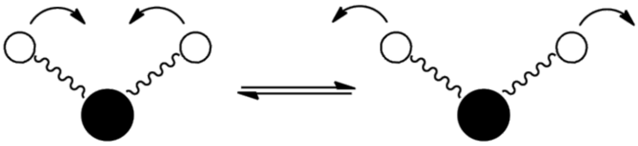
- This absorption is quantized but vibrational spectra appear as bands rather than lines.
- These bands in IR spectra presented as wavenumber ($\bar{v}$).
- There are two types of molecular vibrations:

- Stretching



stretching vibrations

- Bending



bending vibrations

Types of stretching vibrations

i) Symmetric stretching vibration: In this case both the atoms stretched or compressed in same direction.

ii) Asymmetric stretching vibration: In this vibration one atom undergoes stretching and other atom undergoes compression and vice versa.

Types of bending vibrations

1) In plane bending vibrations:

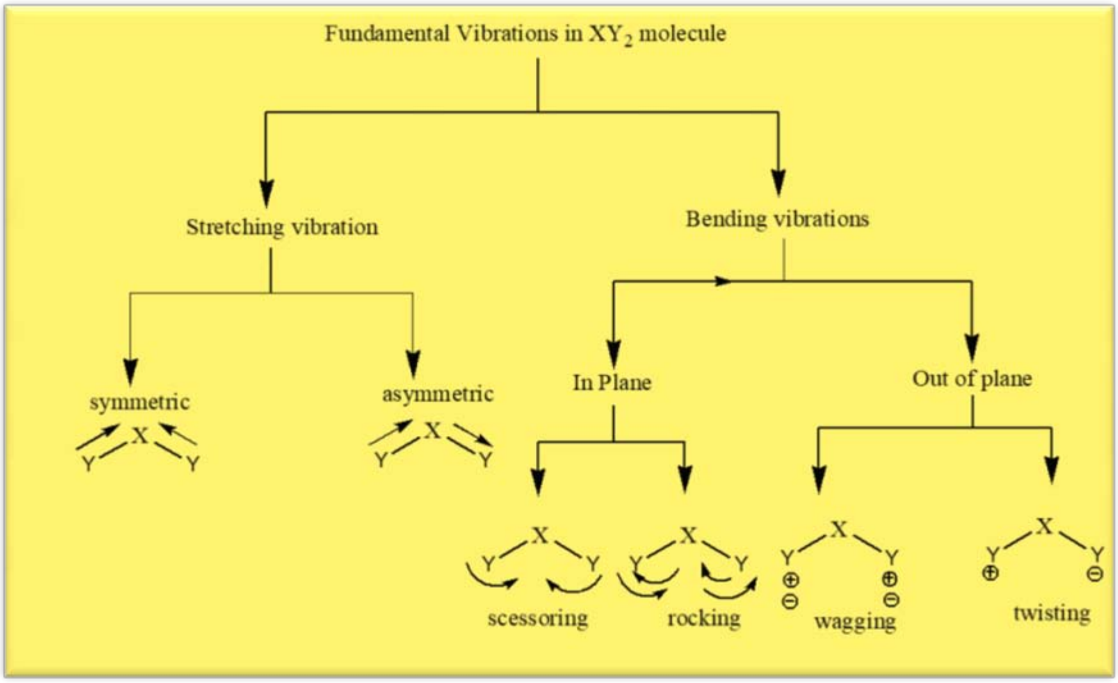
i) Scissoring: both the atom move towards each other just like scissor.

ii) Rocking: both the atoms move in same direction, either in left side or right side.

2) Out of plane bending vibrations:

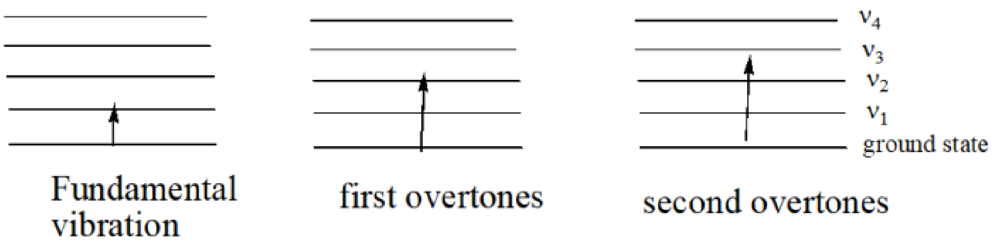
i) Wagging: both the atom move up and down with respect to central atom.

ii) Twisting: one atom move up and other atom move down with respect to central atom.



OVERTONES AND COMBINATION BANDS

When molecule absorbed electromagnetic radiation in IR region, and then molecule promoted from ground state to second, third or even fourth vibrational excited state. These bands are known as Overtones. The intensity of these bands is very weak. It is helpful in characterization of aromatic compounds.



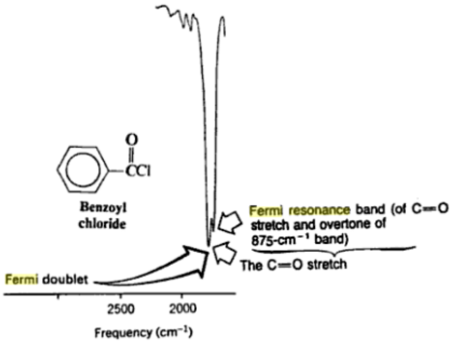
When two fundamental vibrational frequencies (ν1 + ν2) in a molecule couple to give rise to a new vibrational frequency within the molecule, it is known as combination band.

COUPLED VIBRATIONS

The coupled vibrations are observed in group like –CH2, NH2 etc. In these groups same atoms are attached to the central atom. When –CH2 undergoes vibration by the absorption of IR radiation, due to internal perturbation, energy of one C-H bond is transfer to neighboring C-H bond which enhance its vibrational frequency. Therefore two stretching vibrational frequencies for –CH2 group is observed at 2950 cm^{-1} (asymmetric stretching) and 2860 cm^{-1} (symmetric stretching).

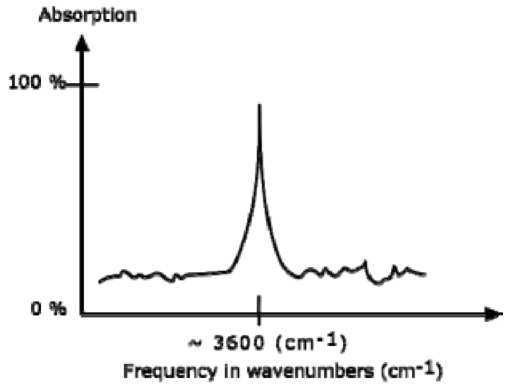
FERMI RESONANCE

When fundamental vibration coupled with overtones or combination band, the coupled vibration is called Fermi resonance or when molecule absorb IR radiation then it transfers its energy or intensity from fundamental vibration to overtones, then Fermi resonance is observed. As we know that the intensity of overtones band is very weak as compare to fundamental vibrations. But, due to transfer of energy, the strong band is observed for overtones along with the fundamental frequency. Fermi resonance is generally observed in carbonyl groups. For example, in benzoyl chloride –C=O stretching vibration observed at 1790 cm^{-1} and 1745 cm^{-1} . The lower frequency band at 1745 cm^{-1} is observed due to combination of overtones of CH bending vibration at 875 cm^{-1} with the fundamental vibration of C=O stretching.



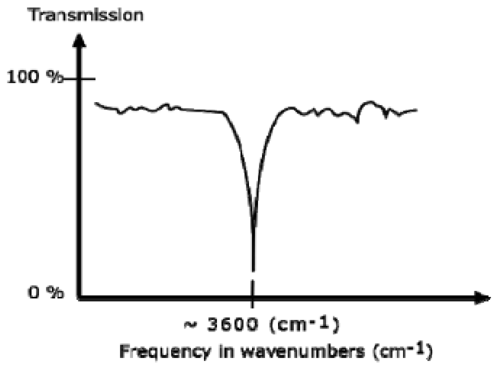
AN IR SPECTRUM IN ABSORPTION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the x-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the y-axis in percentage units.



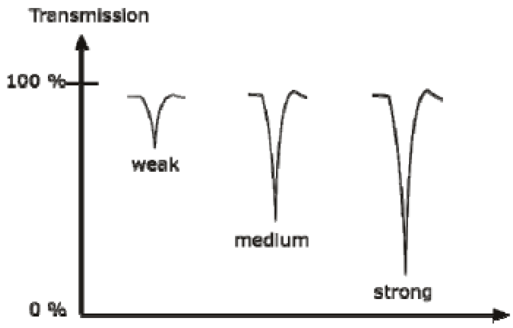
AN IR SPECTRUM IN TRANSMISSION MODE

This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation



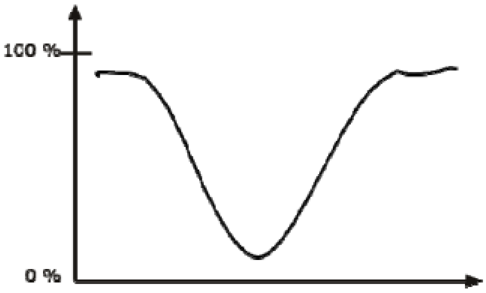
CLASSIFICATION OF IR BANDS

IR bands can be classified as strong (s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.



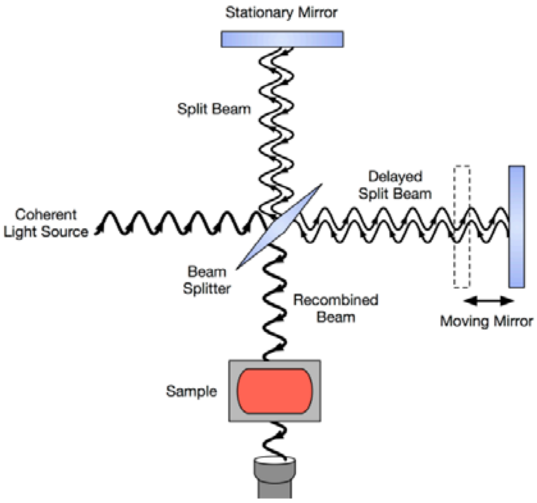
INFRARED BAND SHAPES

Infrared band shapes come in various forms. Two of the most common are narrow and broad. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother. A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



Instrumentation

- IR spectrometers composed of:
- IR source
- Monochromator (interferometer)
- Detector
- Recorder



Sample preparation

- Compounds may be examined:
- In vapour phase
- As a liquid
- In solution
- In the solid state.

- The natural frequency of vibration of a bond is given by the equation:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

- Where the reduced mass (μ) is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

- From the previous equations, two things should be noticed:

1. Stronger bonds have a larger force constant K and vibrate at higher frequencies than weaker bonds

C≡C	C=C	C–C
~2000 cm^{-1}	~1600 cm^{-1}	~1200 cm^{-1}

←

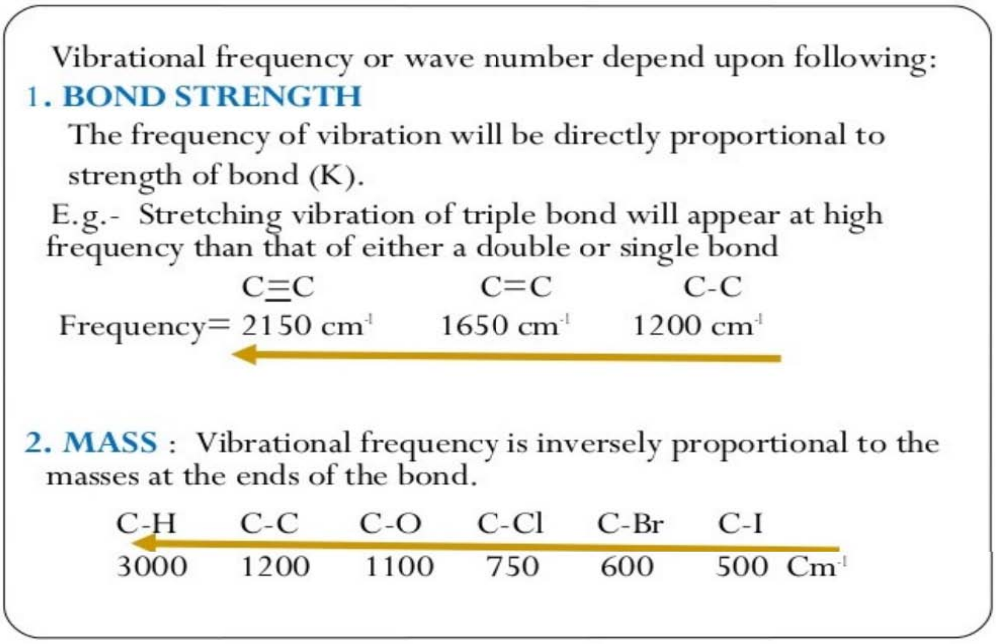
Increasing K

2. Heavier atoms vibrate at lower frequencies than bonds between lighter atom, i.e. larger μ values

C–H	C–C	C–O	C–Cl	C–Br	C–I
~3000 cm^{-1}	~1200 cm^{-1}	~1000 cm^{-1}	~750 cm^{-1}	~600 cm^{-1}	~500 cm^{-1}

→

Increasing K



Vibrational frequency or wave number depend upon following:

1. BOND STRENGTH

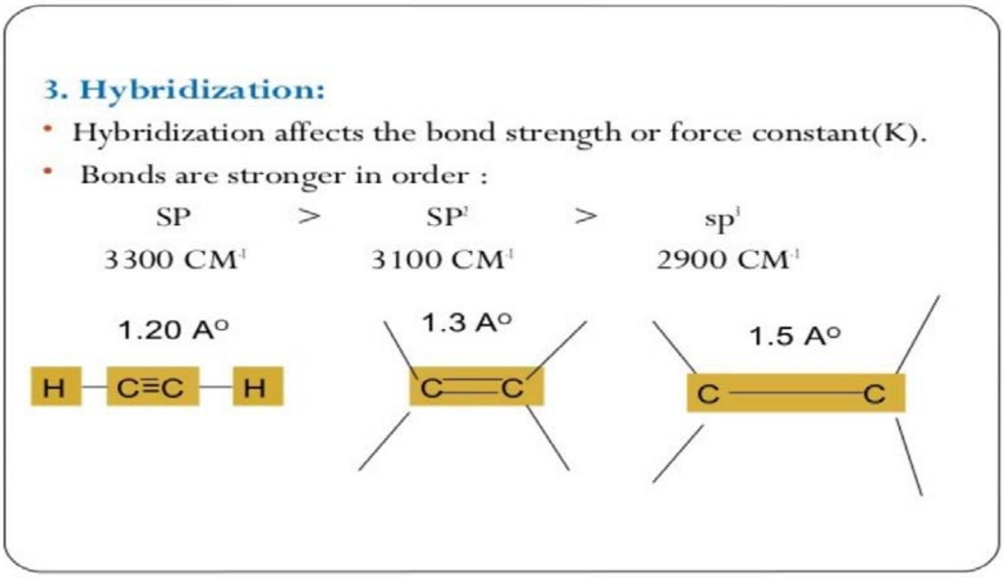
The frequency of vibration will be directly proportional to strength of bond (K).

E.g.- Stretching vibration of triple bond will appear at high frequency than that of either a double or single bond

	C≡C	C=C	C-C
Frequency=	2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

2. MASS : Vibrational frequency is inversely proportional to the masses at the ends of the bond.

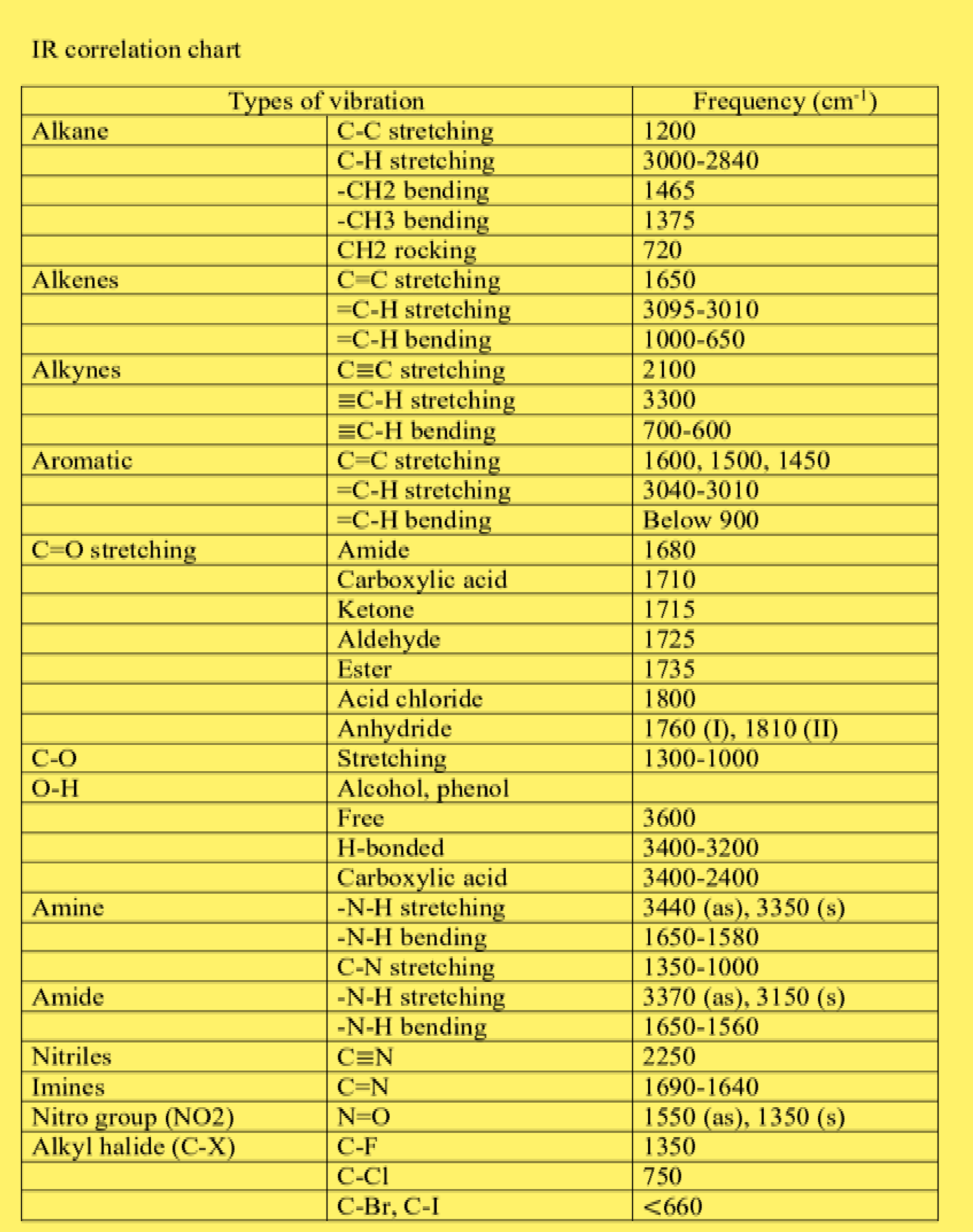
C-H	C-C	C-O	C-Cl	C-Br	C-I
3000	1200	1100	750	600	500 Cm^{-1}



3. Hybridization:

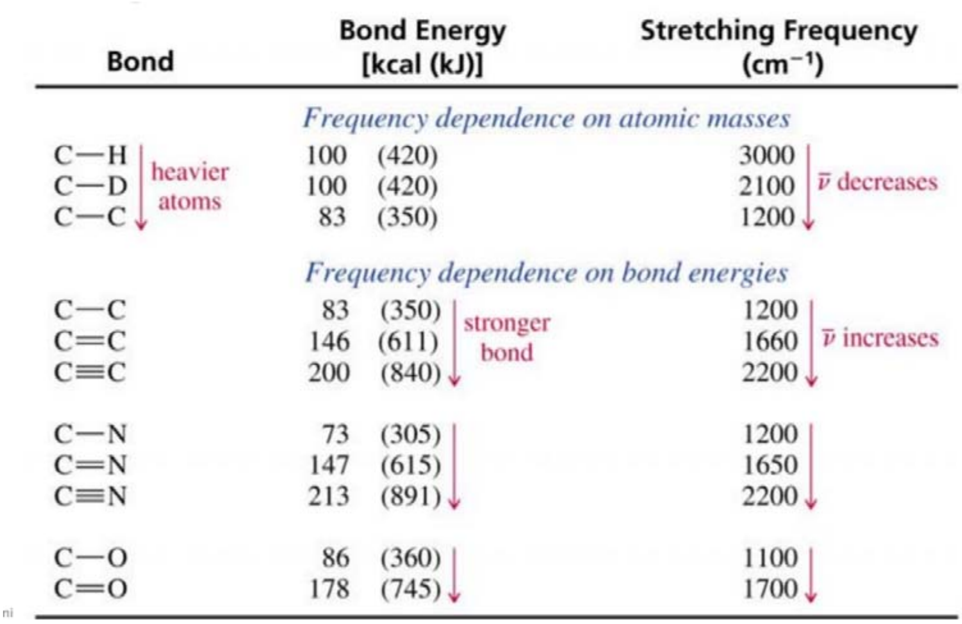
- Hybridization affects the bond strength or force constant(K).
- Bonds are stronger in order :

SP	>	SP^2	>	sp^3
3300 CM^{-1}		3100 CM^{-1}		2900 CM^{-1}



IR correlation chart

Types of vibration		Frequency (cm^{-1})
Alkane	C-C stretching	1200
	C-H stretching	3000-2840
	-CH2 bending	1465
	-CH3 bending	1375
	CH2 rocking	720
Alkenes	C=C stretching	1650
	=C-H stretching	3095-3010
	=C-H bending	1000-650
Alkynes	C≡C stretching	2100
	≡C-H stretching	3300
	≡C-H bending	700-600
Aromatic	C=C stretching	1600, 1500, 1450
	=C-H stretching	3040-3010
	=C-H bending	Below 900
C=O stretching	Amide	1680
	Carboxylic acid	1710
	Ketone	1715
	Aldehyde	1725
	Ester	1735
	Acid chloride	1800
	Anhydride	1760 (I), 1810 (II)
C-O	Stretching	1300-1000
O-H	Alcohol, phenol	
	Free	3600
	H-bonded	3400-3200
	Carboxylic acid	3400-2400
Amine	-N-H stretching	3440 (as), 3350 (s)
	-N-H bending	1650-1580
	C-N stretching	1350-1000
Amide	-N-H stretching	3370 (as), 3150 (s)
	-N-H bending	1650-1560
Nitriles	C≡N	2250
Imines	C=N	1690-1640
Nitro group (NO2)	N=O	1550 (as), 1350 (s)
Alkyl halide (C-X)	C-F	1350
	C-Cl	750
	C-Br, C-I	<660

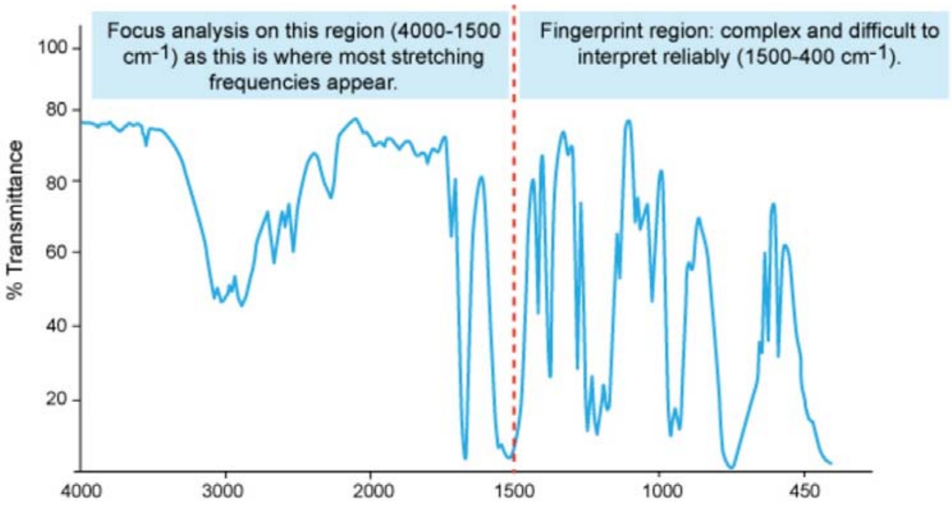


Bond		Bond Energy [kcal (kJ)]		Stretching Frequency (cm^{-1})	
		Frequency dependence on atomic masses			
C—H	heavier atoms ↓	100 (420)		3000	$\bar{\nu}$ decreases ↓
C—D		100 (420)		2100	
C—C		83 (350)		1200	
		Frequency dependence on bond energies			
C—C		83 (350)	stronger bond ↓	1200	$\bar{\nu}$ increases ↓
C=C		146 (611)		1660	
C≡C		200 (840)		2200	
C—N		73 (305)	↓	1200	↓
C=N		147 (615)		1650	
C≡N		213 (891)		2200	
C—O		86 (360)	↓	1100	↓
C=O		178 (745)		1700	

Interpretation of IR spectra

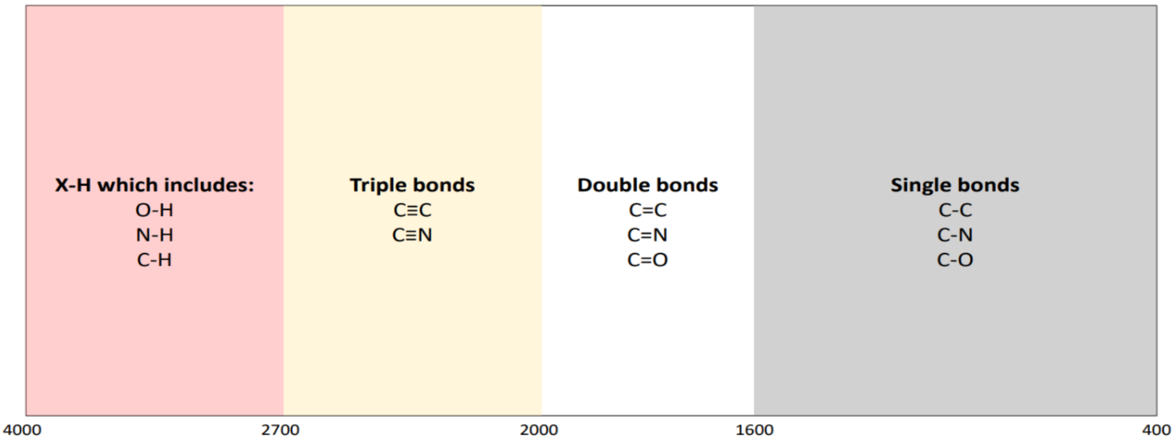
- IR spectrum can be divided into two regions:

1. Functional group region (4000-1500 cm^{-1})
2. Fingerprint region (1500-400 cm^{-1})



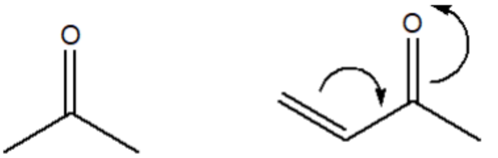
Wave number cm-1

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the 600 - 1400 cm^{-1} range is called the fingerprint region. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1}.



Factor affecting vibrational frequency

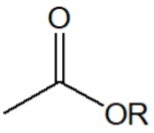
a) Conjugation: As the conjugation increase, stretching frequency decreases, because force content decrease due to conjugation.



C=O (s) = 1720 cm^{-1} C=O (s) = 1680 cm^{-1}

b) Inductive effect and resonance effect:

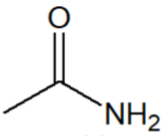
Oxygen is more electronegative than nitrogen, therefore nitrogen easily donate electron or lone pair of nitrogen undergoes delocalization with C=O bond. Due to delocalization double bond of C=O changes into partial double bond therefore force constant decreases which decrease the C=O stretching frequency.



ester

C=O (s) = 1735 cm^{-1}

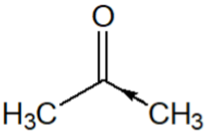
-I effect of -OR



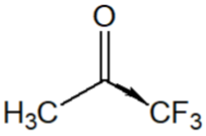
amide

C=O (s) = 1690 cm^{-1}

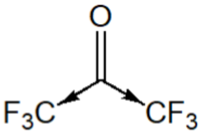
+R effect of -NH2



1720 cm^{-1}
+I effect



1760 cm^{-1}
-I effect

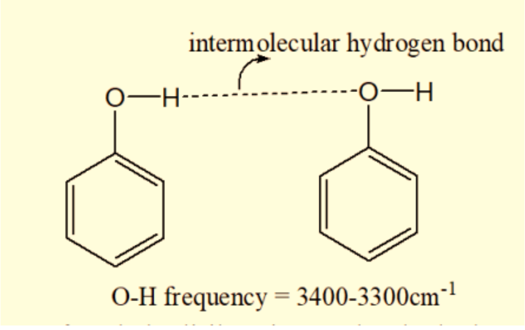


1790 cm^{-1}
-I effect

c) Hydrogen bonding:

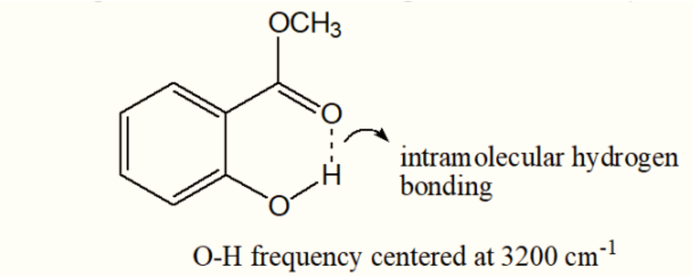
Intermolecular hydrogen bonding weakens the O-H bond, thereby shifting the band to lower frequency.

For example, in neat solution O-H stretching vibration of phenol observed in the range from 3400-3300 cm-1 . When solution is dilute then O-H frequency shifted towards higher frequency at 3600 cm^{-1} .



O-H frequency = 3400-3300cm^{-1}

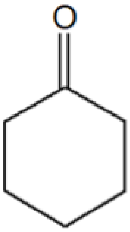
Whereas in case of methyl salisilate, intramolecular hydrogen bonding lower down the stretching frequency of O-H at 3200 cm-1 . Intramolecular hydrogen bonding does not change its frequency even in very dilute solution because upon dilution structure of compound does not change.



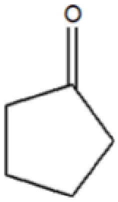
O-H frequency centered at 3200 cm^{-1}

d) Ring strain:

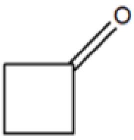
As the size of the ring decrease, vibrational frequency of C=O increase. For example.



1710 cm^{-1}



1745 cm^{-1}



1780 cm^{-1}

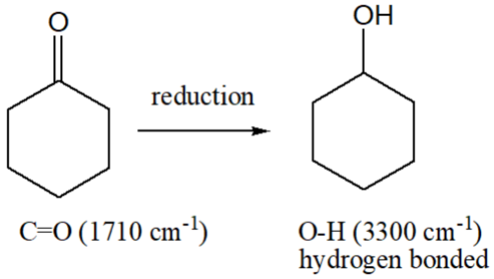
Applicationof IR Spectroscopy

a) Identification of different functional group.

b) Distinction between intermolecular and intra-molecular hydrogen bonding

. c) Identification of purity of the compound, if compound is impure then additional peaks are observed in the IR spectrum.

d) Study of chemical reaction:

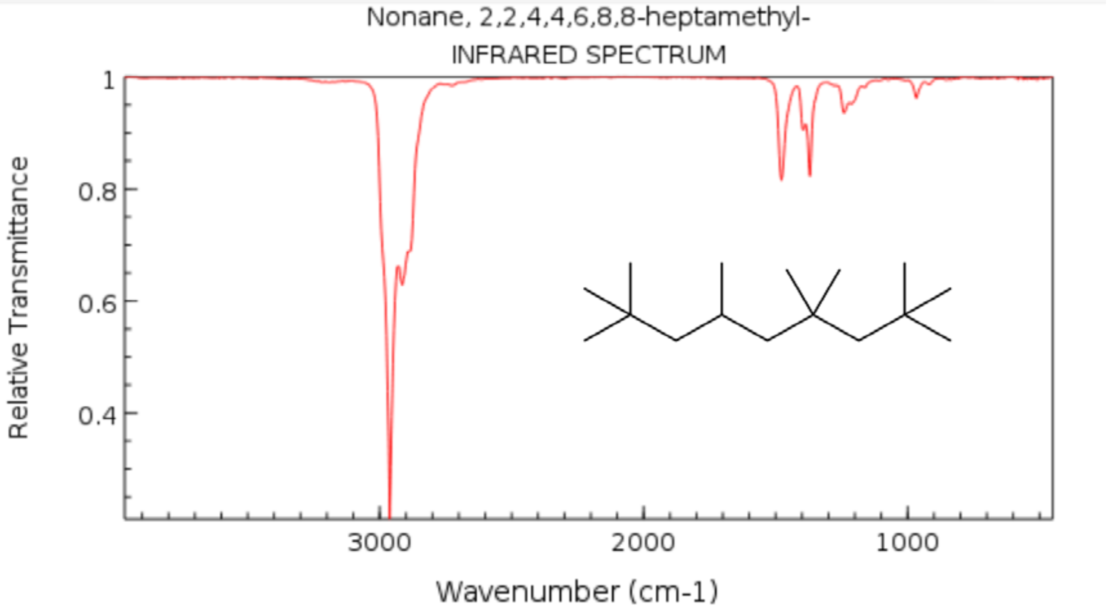


e) Identification of geometrical isomers (cis-trans).

Interpretation of IR spectra: 1. Alkanes

- C-H stretching in the alkanes occurs in the general region of 3000- 2800 cm^{-1}.

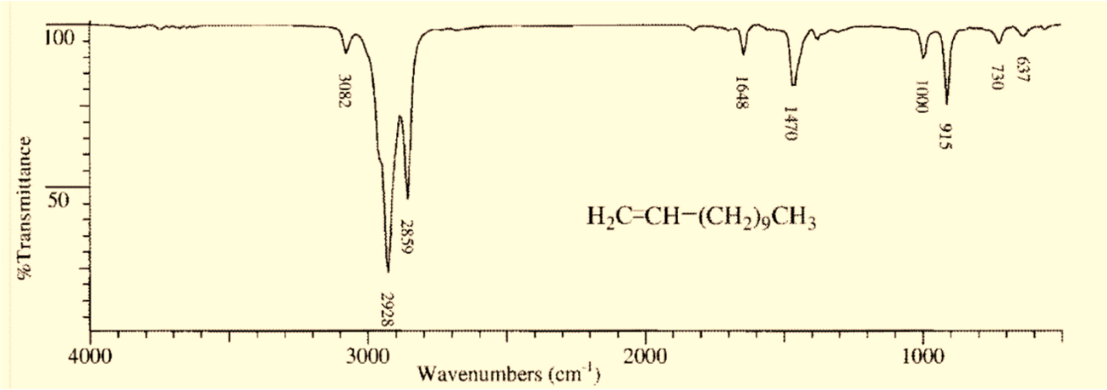
- C-C stretching vibrations are weak and appear in the broad region of 1200-800 cm^{-1} (fingerprint region).



Interpretation of IR spectra: 2. Alkenes

- Any C-H stretching bands above 3000 cm^{-1} result from aromatic, heteroaromatic, alkyne, or alkene C-H stretching.

- C=C absorb in the range 1680-1620 cm^{-1}.



- C=C-H stretch: 3082 cm^{-1}

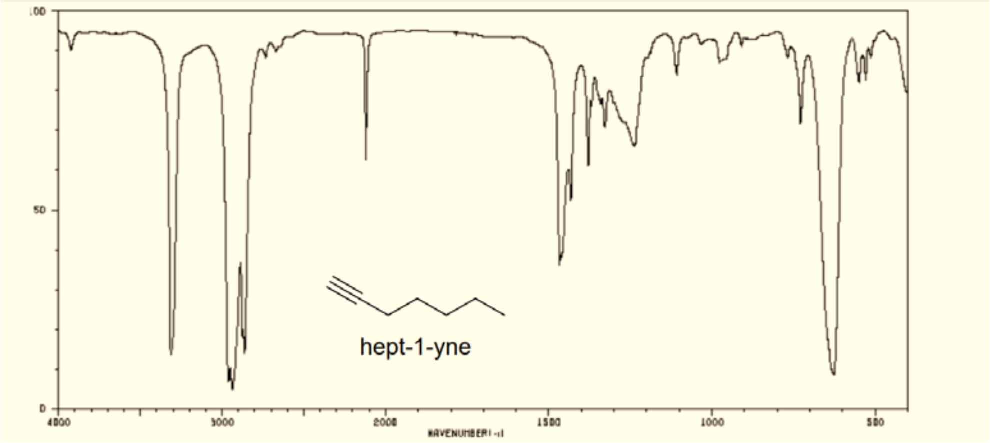
- C=C stretch: 1648 cm^{-1}

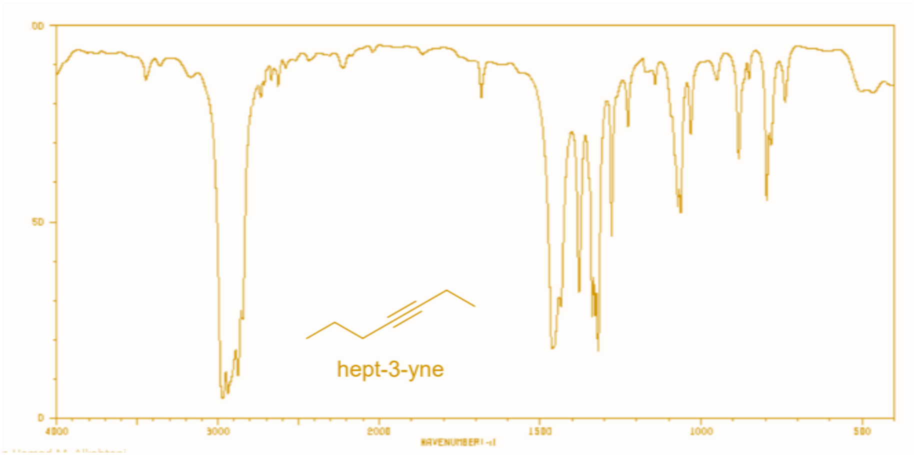
Interpretation of IR spectra: 3. Alkynes

- C≡C stretching vibrations occur in the region of 2260-2100 cm^{-1}.

- Terminal C≡C shows stronger band than internal one.

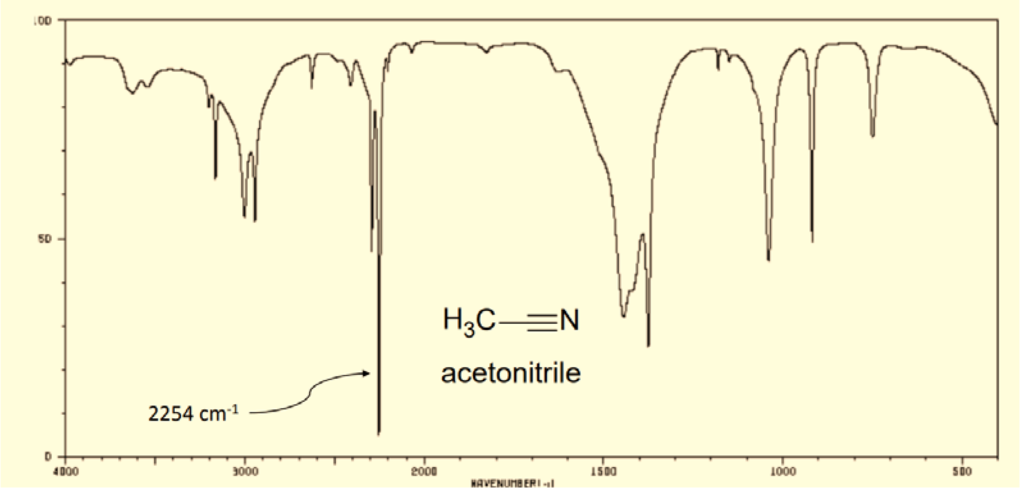
- C≡C-H stretching vibrations occur in the general region of 3333-3267cm^{-1} (This is a strong band and is narrower than the hydrogen bonded OH and NH bands occurring in the same region).

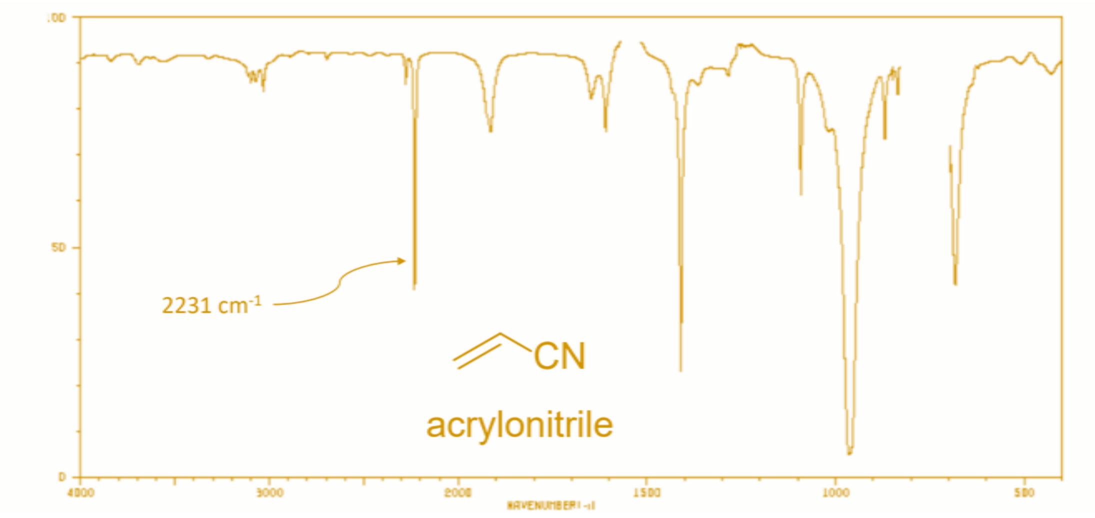


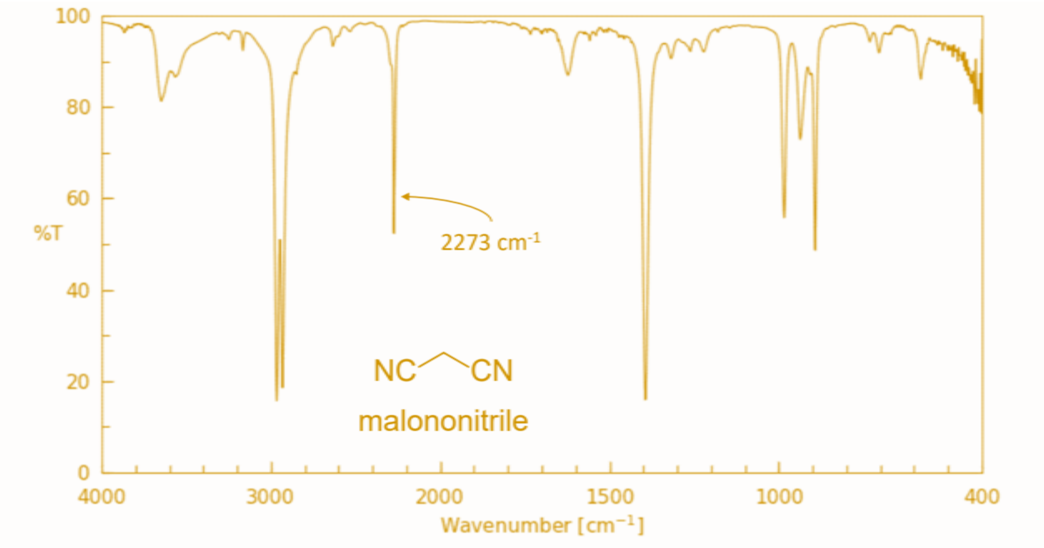


Interpretation of IR spectra: 4. Nitriles

- Nitriles absorb in the range 2260–2200 cm^{-1} (weak to medium).
- Conjugation usually reduces frequency and increases intensity.
- EWG groups attached to the a carbon to the C≡N reduce band intensity.

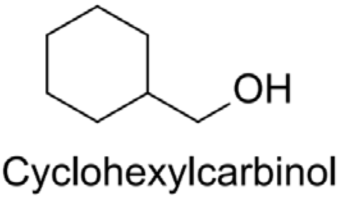




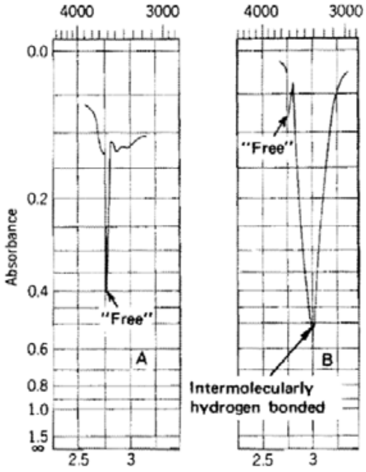


Interpretation of IR spectra: 5. O-H

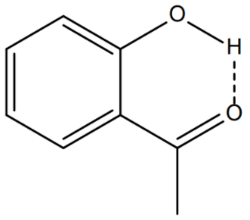
- These vibrations are sensitive to H-bonding.
- The stronger the H-bond the longer O-H bond, the lower the vibration frequency and the broader and the more intense the absorption band.
- The non-H-bonded hydroxyl group of alcohols and phenols absorbs strongly in the 3700-3584 cm^{-1} region.
- Intermolecular H-bonding increases as the concentration of the solution increases, and additional bands start to appear at lower frequencies, 3550-3200 cm^{-1}.



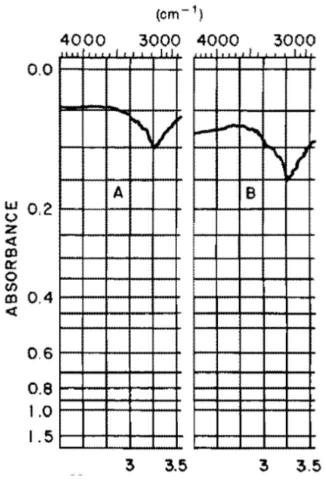
IR spectrum of the O-H stretching region of cyclohexylcarbinol in CCl_4: **A** at 0.03 M and **B** at 1.00 M



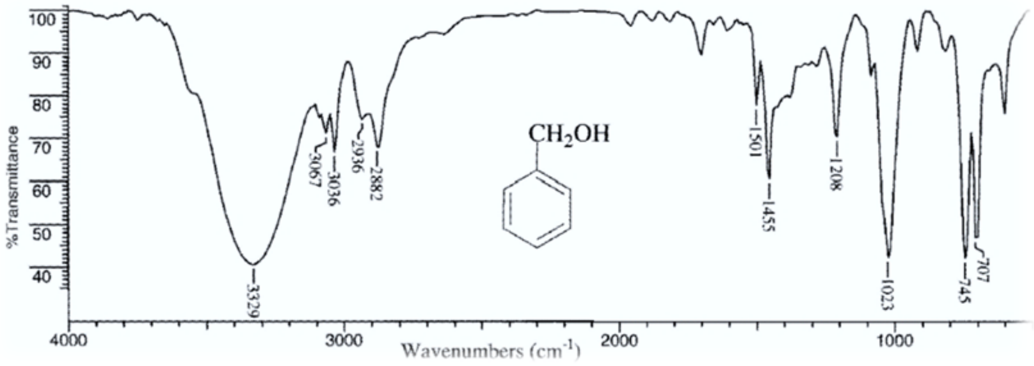
- Strong intramolecular H-bonding occurs in o-hydroxyacetophenone. The resulting absorption at 3077 cm^{-1} is broad, shallow, and independent of concentration.

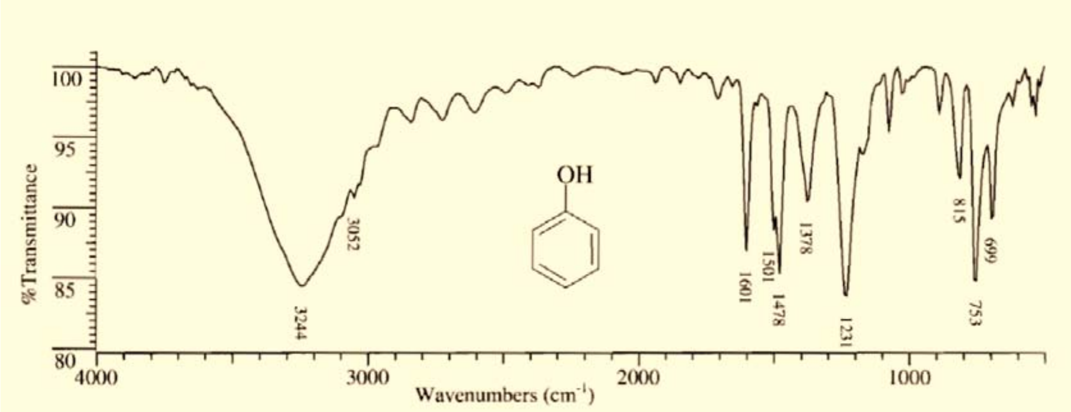


o-Hydroxyacetophenone

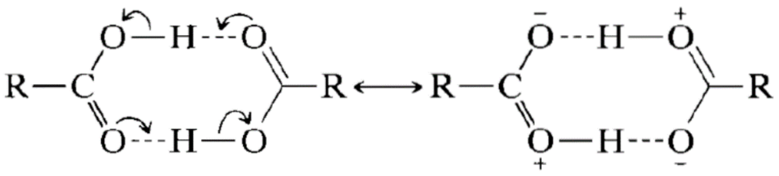


A portion of the IR spectra of *o*-hydroxyacetophenone: **A** at 0.03 M and **B** at 1.0 M



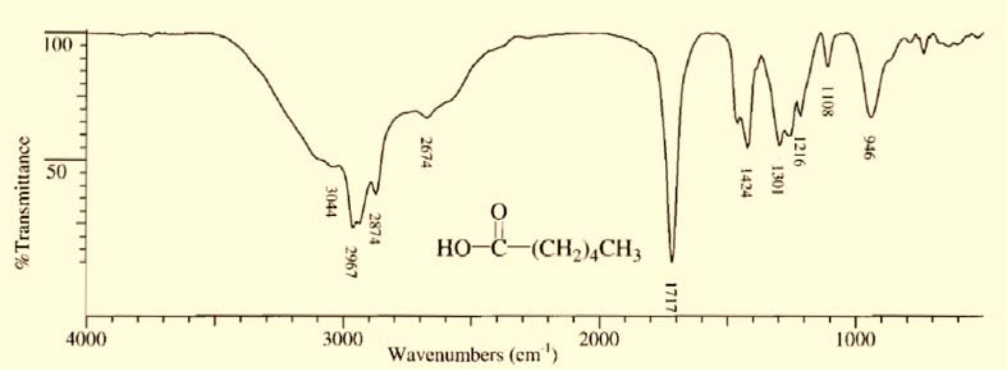


- In the liquid or solid state, and in CCl4 solution at conc. > 0.01 M, carboxylic acids exist as dimers due to strong H-bonding.



- Carboxylic acids dimers display broad and intense O-H stretching absorption in the region of 3200-2500 cm^{-1}.

- Free O-H stretching vibration (near 3520 cm^{-1}) is observed only in very dilute solution in nonpolar solvent or in the vapour phase.



Interpretation of IR spectra: 6. N-H

- The stretching frequencies of the N-H bonds of amines are typically in the range 3500-3300 cm^{-1}.

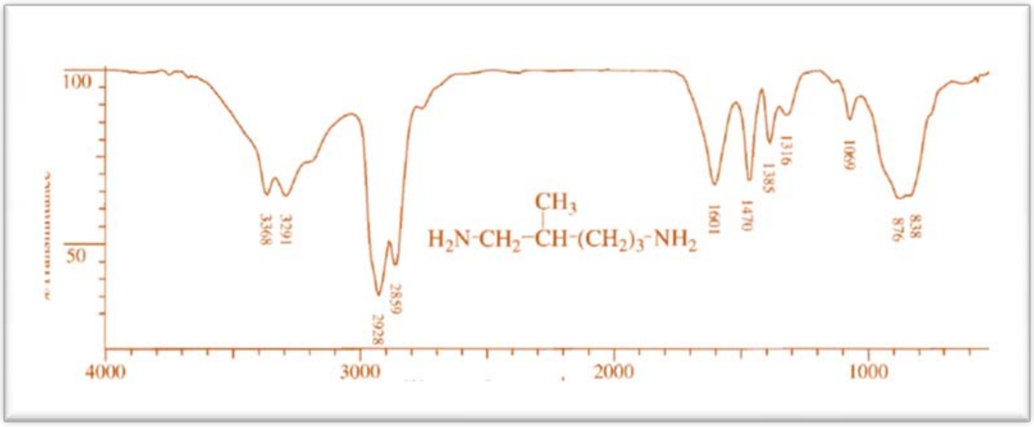
- They are less intense than O-H stretching.

- Because an N-H has a weaker tendency to form a H-bond, its absorption is often sharper.

- Primary amines display two peaks: one near 3500 cm^{-1} and the other near 3400 cm-$^{1.}$

- This is because asymmetric and symmetric stretching modes, respectively.

- Secondary amines show a single weak band in 3350-3310 cm^{-1} region.



Interpretation of IR spectra: 8. C=O

- Carbonyl bands are always strong with the following order of strength: RCOOH > RCOOR’ > RCOR’ or RCHO

- The precise position of C=O absorption is governed by the following factors:

a. Electronegativity

b. H-bonding

c. Conjugation

d. Ring strain.

a-Electronegativity

- The more electronegative the group X in the system R-CO-X, the higher is the frequency.

- Therefore:

RCO-F > RCO-Cl > RCO-Br

b. H-bonding

- H-bonding to C=O results in absorption at lower frequencies.

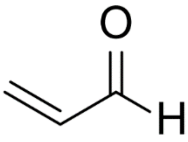
- H-bonding reduces absorption by ~40-60 cm^{-1}.

- C=O of acids and amides show this effect clearly.

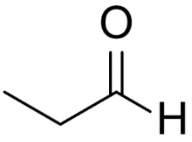
c. Conjugation

- α,β-unsaturation causes a lowering frequency of 15-40 cm^{-1}.

- This effect is similar to that of amides.



1696 cm^{-1}

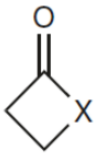


1739 cm^{-1}

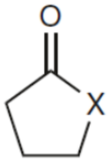
d. Ring strain

- Ring strain in cyclic compounds causes a relatively large shift to higher frequency.
- Therefore, this provides a reliable test of ring size.

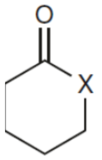
1813



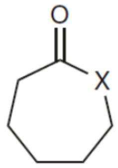
X=CH_2 1775
X=O 1841
X=NH 1750



X=CH_2 1750
X=O 1774
X=NH 1717



CH_2 1715
O 1750
NH 1673

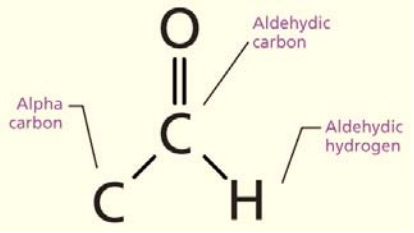


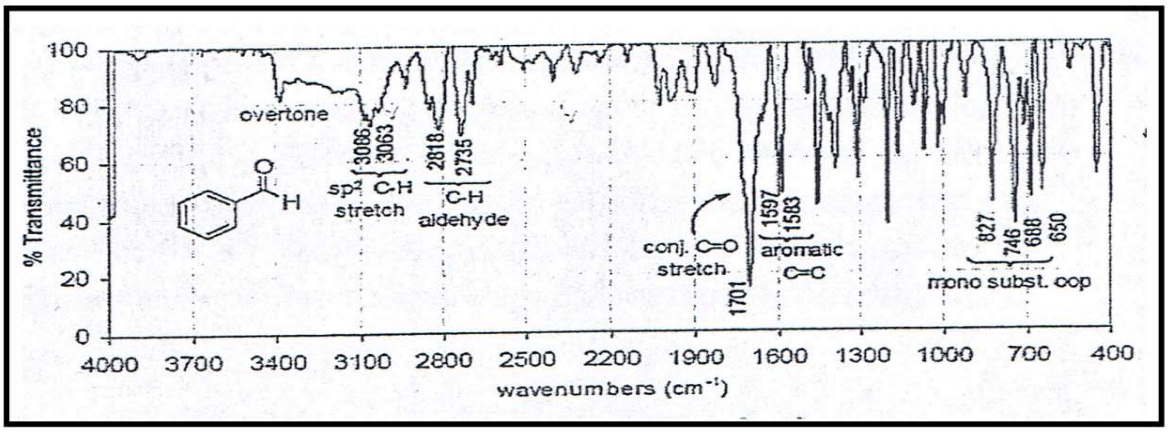
X=CH_2 1710
X=O 1727
X=NH 1669

Aldehydes and ketones

the stretching vibration of the carbonyl group has a strong infrared absorption between 1710 and 1740 cm^{-1}. Conjugation of C=O bond with a double bond or phenyl ring lowers the stretching frequency.

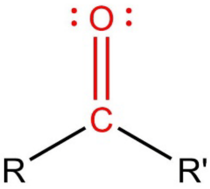
the C-H stretch fundamental and the first overtone of the aldehydic C-H bend both fall near 2800 cm^{-1}, and when they are of the same symmetry they frequently Fermi resonate, giving rise to two peaks between 2850 and 2700 cm^{-1} rather than one.

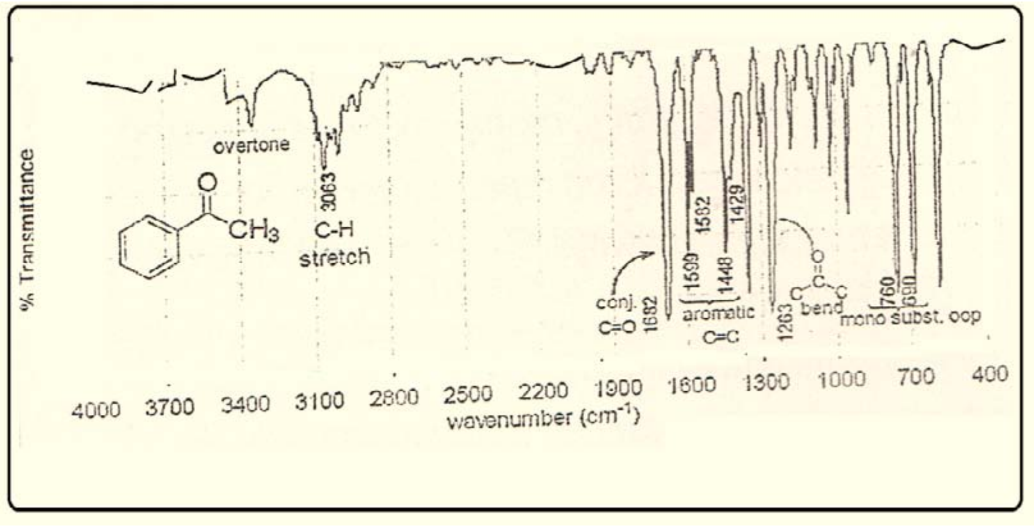




FTIR of benzaldehyde

in ketones, due to the presence of the +I effect of the methyl group, the strength of the carbonyl group decreases but is less in aldehydes which has one hydrogen atom attached to the carbonyl carbon that does not show inductive effect. Hence, the ketones absorbs at a lower wavenumber than an aldehyde carbonyl group.





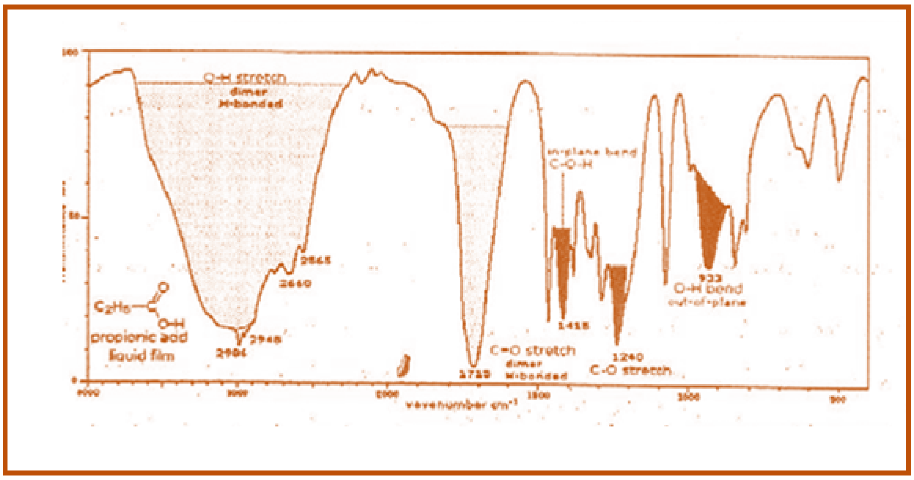
FTIR of acetophenone

Carboxylic acid and derivatives

A carboxylic acid functional group combines the features of alcohols and ketones because it has both the O-H bond and the C=O bond.

Therefore carboxylic acids show a very strong and broad band covering a wide range between 2800 and 3500 cm^{-1} for the O-H stretch.

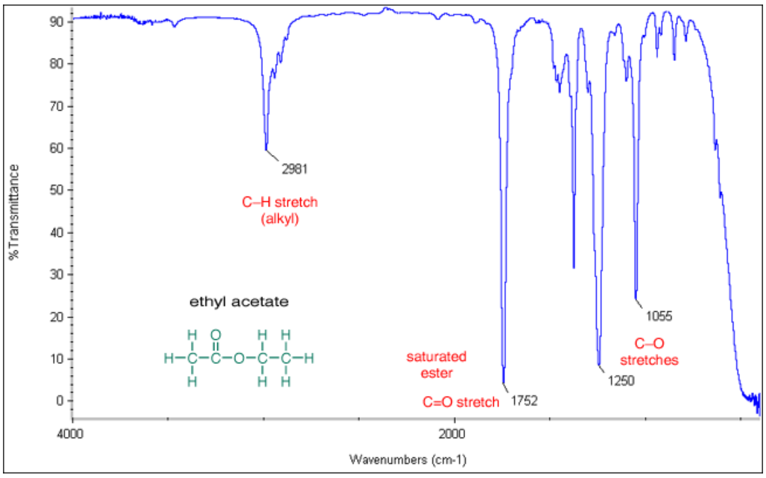
the stretching vibrational frequency, $\nu_{C=O}$, indicates the protonation state of the carboxylic group (i.e., 1690–1750 cm^{-1} for COOH, and1540–1650 and ∼1300–1420 cm^{-1} for the asymmetric and symmetric stretching modes of COO^{-}, respectively).



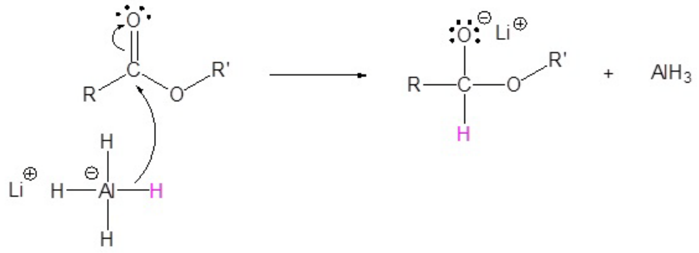
FTIR of Benzoic acid

Esters

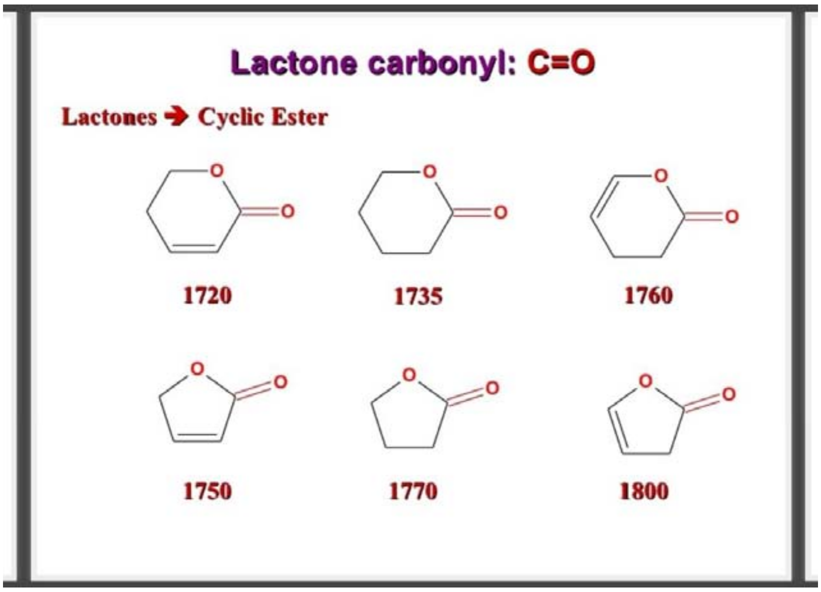
The carbonyl stretch C=O. of aliphatic esters appears from 1750-1735 cm^{-1}; that of α, β-unsaturated esters appears from 1730-1715 cm^{-1}.



Esters have pretty good resonance stabilization from the heteroatom attached to the carbonyl carbon. They are less reactive than are aldehydes and ketones,Esters are less reactive than acyl halides and acid anhydridesbecause the alkoxide group is a poor leaving group with its negative charge fully localized on a single oxygen atom.

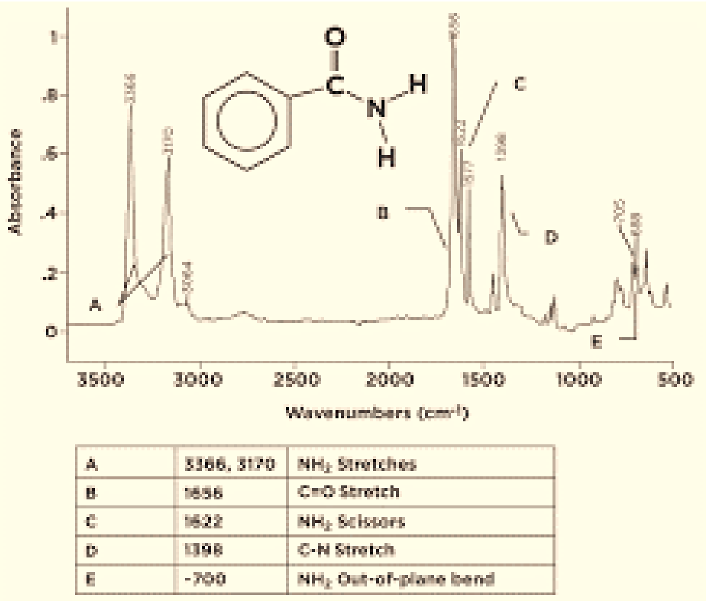


Ring strain in cyclic esters causes a relatively large shift to higher frequency, show in the following figure:



Amides

The amide functional group combines the features of amines and ketones because it has both the N-H bond and the C=O bond. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between 3100 and 3500 cm^{-1} for the N-H stretch .The C=O. stretch in Figure is seen at 1656 cm^{-1}.

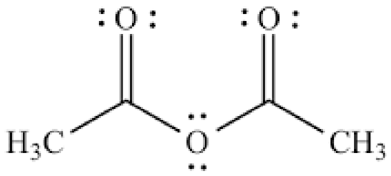


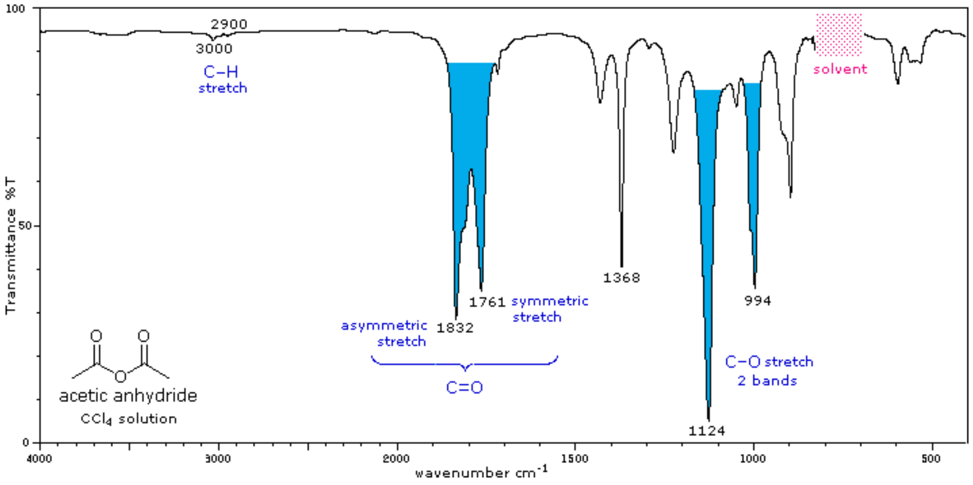
A	3366, 3170	NH_2 Stretches
B	1656	C=O Stretch
C	1622	NH_2 Scissors
D	1398	C-N Stretch
E	-700	NH_2 Out-of-plane bend

Anhydrides

Anhydride (acid anhydride): A functional group characterized by two acyl groups joined by an oxygen atom. When the R groups in the general structure shown below are not the same (i.e., when the anhydride is derived from two different carboxylic acids) it is called a mixed anhydride .

The carbonyl stretching frequencies for an acid anhydride are approximately 1820 cm^{-1} and 1760 cm^{-1}. These are both higher frequencies than a simple ketone owing to the electron withdrawing capability of the adjacent group.





There are two types of stretching vibrations. In symmetric stretching, two or more bonds vibrate in and out together. In asymmetric stretching, some bonds are getting shorter at the same time as others are getting longer. Bending vibrations change the angle between two bonds.

Acyl chloride

Like most carbonyl compounds, infrared spectroscopy reveals a band near 1810 cm^{-1}. The simplest stable acyl chloride is acetyl chloride; formyl chloride is

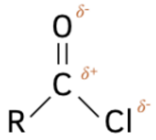
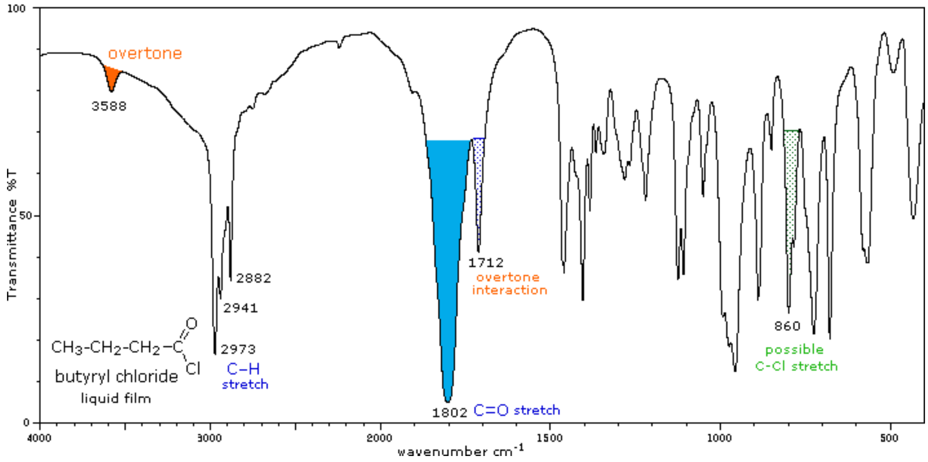


Fig 5. Dipole on an Acyl Chloride Group.



Ethers and epoxides

Ethers and epoxides typically have a strong C-O stretch between 1000 and 1300 1/cm. Because this absorption appears in the fingerprint region of the IR is can be difficult to assign. In addition to the C-O peak, it is helpful to note if an IR spectrum has no C=O

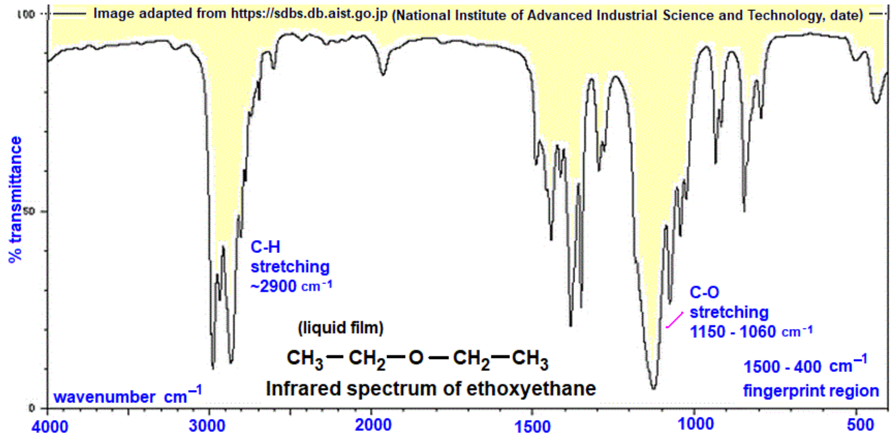
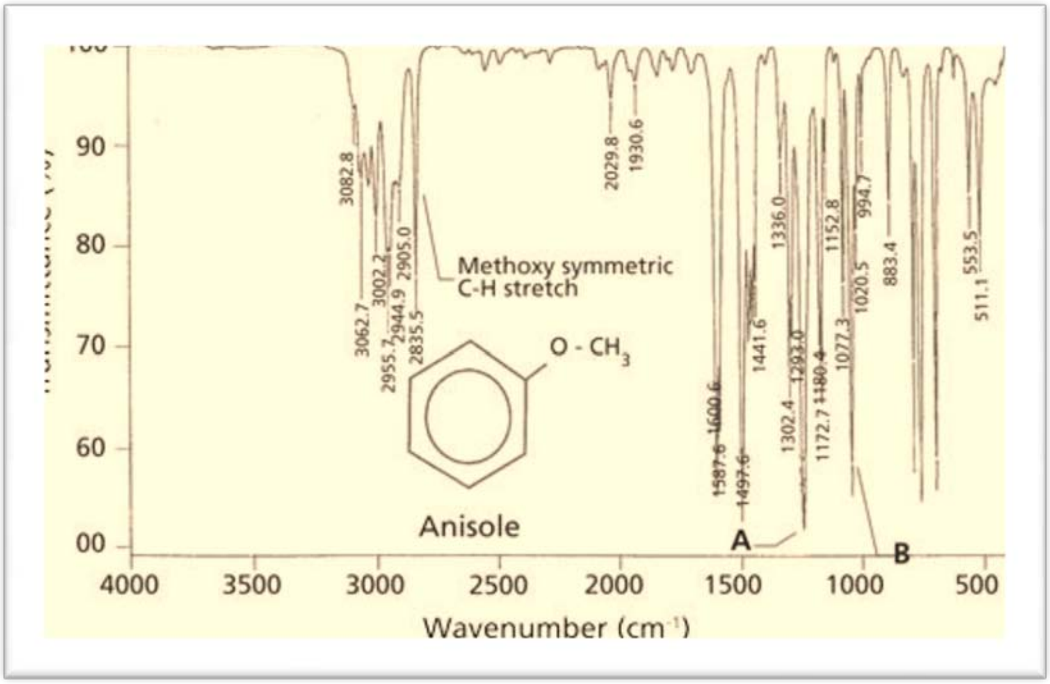


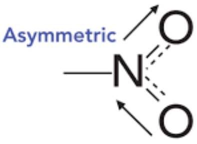
Image adapted from https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, date)

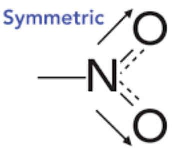
While Aromatic ethers of the type aryl-O—CH_2 usually have strong IR bands at 1310–1210 cm^{-1} (aryl-O) and 1050–1010 cm^{-1} (O—CH_2 or O—CH_3)

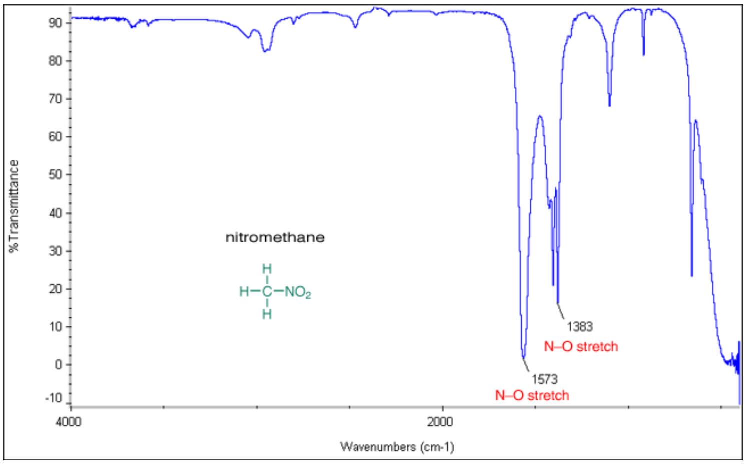


Nitro compounds

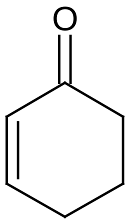
The N–O stretching vibrations in nitroalkanes occur near 1550 cm^{-1} (asymmetrical) and 1365 cm^{-1} (symmetrical), the band at 1550 cm^{-1} being the stronger of the two.

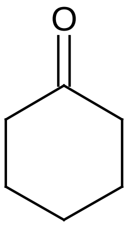


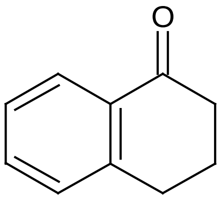


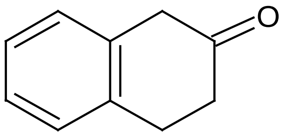


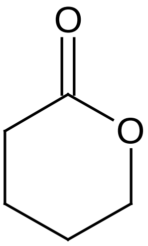
How can distinguish between pairs compounds by using FTIR technique?





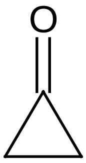


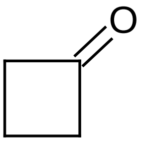


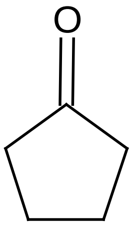


CH3 - CH2 - COOCH3

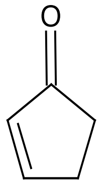
Rearrangement the following compounds according the increase the frequency of carbonyl band?

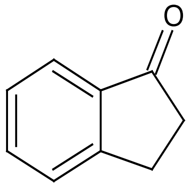


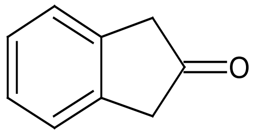




CH3 - COCl CH3 - COOH CH3 - CHO







Q Give the chemical structure for the following molecular formula

1- (**C_7H_9N**) shows the following bands in IR Spectrometery

3070, 1600&1550 , 3400 & 3200, , 2800&2940, 854 cm^{-1}

<u>solution</u>

from theformation above observed the following:

1-3400 cm^{-1},3200 cm^{-1} refers to the stretching vibration of NH_2Asymmetrical and symmetrical .

2-3070 cm^{-1} refers to the stretching vibration of C-H Aromatic.

3-2940 cm^{-1} refers to the stretching vibration Asymmetrical of C-H Alkane&2800cm^{-1}erfers to the stretching vibration symmetrical of C-H alkane.

4-1600 &1550 cm^{-1} refers to the stretching vibration Asymmetrical of C=C band for aromatic ring.

5-854cm^{-1} refers to the substitution of aromatic ring in para postion.

So the structure is

2- (**$C_5H_{10}O_2$**) shows the following bands in IR Spectrometery

2950, 1200, 1735 cm^{-1}

The spectrum is for a substance with an empirical formula of C3H5N. What is the compound?