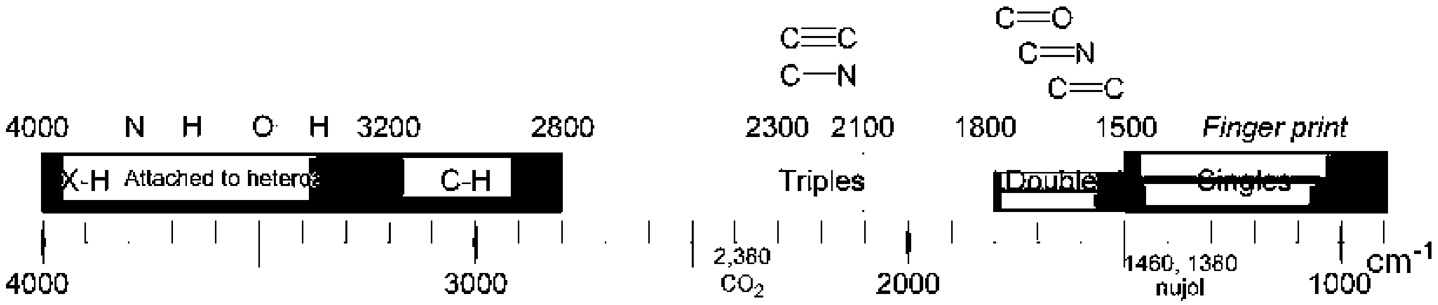
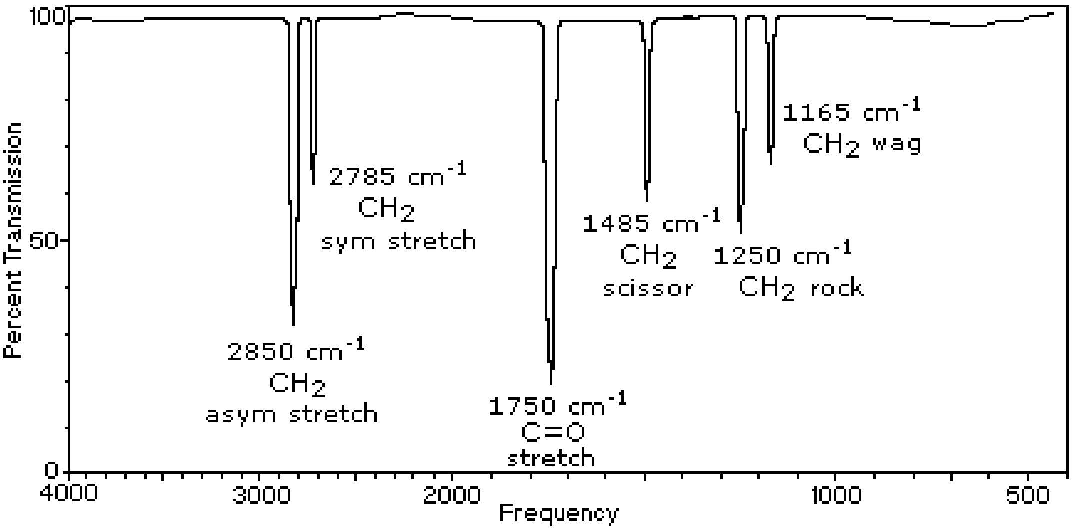
- **Infrared spectroscopy** (IR Spectroscopy) is a type of absorption spectroscopy that uses the Infrared portion of the electromagnetic spectrum. As with all spectroscopic techniques, it can be used to investigate the composition of a sample.
- In IR spectrophotometer, infrared radiations of successively increasing wavelength is passed through the sample of the compound and percentage transmittance is measured.
- An IR spectrum is a graph of percentage transmittance versus either increasing wavelength (units in mμ) or decreasing frequency (units of cm^{-1}).
- The infra red radiations broadly refer to that part of th4 electromagnetic spectrum between the visible and microwave regions. Of greatest practical use to the organic chemist is the limited portion between 4000 cm^{-1} and 666 cm^{-1}. Recently there has been some interest in the near infrared region 14,290 – 4000 cm^{-1} and the far IR region, 700 – 200 cm^{-1}.
- Although the IR spectrum is characteristic of the entire molecule, there are certain groups of atoms that give rise to bands at or near the same frequency regardless of the structure of the molecule.



Molecular vibrations

- In their vibrations covalent bonds behave as if they were tiny springs connecting the atoms.
- Atoms in a molecule do not remain at fixed positions with respect to each other but actually vibrate but actually vibrate back and forth about an average value of the inter atomic distance.
- Molecular vibrations lead to a change in the dipole moment of the molecule, giving rise to IR absorption bands. These depend upon
  - Masses of the atoms present in the molecule
  - Strength of the bond
  - Arrangement of atoms within the molecule
- There are two kinds of fundamental vibrations, **Stretching** and **Bending**.
  - In **stretching** the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.
    - **Symmetrical Stretching**: Molecules move in the same direction with respect to a central atom
    - **Asymmetrical Stretching**: one atom approaches the central atom while the other moves away from it.
  - In **Bending** vibration the position of the bond axis changes with respect to the original bond axis. Since more energy is required for the bending motion than for the stretching motion, the bending movements absorb at higher energy. There are four types of bending motions
    - **Scissoring**: the two atoms approach each other
    - **Rocking**: movement of atoms takes place in the same direction'
    - **Wagging**: the two atoms move above and below the plane with respect to the central atom
    - **Twisting**: One atom moves above the plane while the other moves below the plane with respect to the central atom.



Some General Trends:

- **i)** Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)
- **ii)** Bonds to hydrogen have higher stretching frequencies than those of heavier atoms.
- **iii)** Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds.

(Except for bonds to hydrogen).

Hookes Law

- The frequency of IR absorptions due to stretching or bending vibrations by a molecule depends on the following factors
  - Relative masses of the atoms
  - Force constant of the bonds
  - Environment or gemetry of the atoms
- Hookes law is used to calculate the general region where vibration will occur.
- This law is derived from the motion of springs.
- This law states ***"the frequency of vibration is directly proportional to the square root of the force constant of the bond".***
- The force constant is particular to and characteristic of a given bond and may be linked to the stiffness.
- The frequency is inversely proportional to the square root of the reduced mass **$(m_1 + m_2)/ m_1 m_2$** of the system. Therefore:
  - Greater the mass, lower the frequency of absorption.
  - Stronger the bond greater will be the frequency of absorption.

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}} = \frac{1}{2\pi c}\left[\frac{f}{\mu}\right]^{1/2}$$

$\bar{\nu}$ = vibrational frequency in cm^{-1} (wave number)

c = velocity of light in cm sec^{-1}

m_1 = mass of atom 1 in g

m_2 = mass of atom 2 in g

f = force constant in dyne cm^{-1}

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

μ is the reduced mass

Vibration frequency thus depends upon

1. Bond strength
2. Reduced mass

Increasing bond strength ↓

	Absorption cm^{-1}		**Absorption cm^{-1}**
$C-C$	1200	$C-N$	1050
$C=C$	1650	$C=N$	1650
$C\equiv C$	2200	$C\equiv N$	2250

Inference of Hookes Law

1. The vibrational frequency of a bond is expected to increase as the strength of the bond increases and also when the reduced mass of the system decreases. It may therefore be predicted that C=C and C=O stretching will have higher frequencies thab C – C and C – O stretchings respectively.
2. C – H and O – H stretchings occur at higher frequencies than C – C and C – O stretchings.
3. O – H stretching occurs at higher frequency than O – D stretching.

Questions

Calculate the vibrational absorption frequency of C=O group if the force constant for the double bond is 1 X 10^6 dynes cm^{-1}

$$\text{Mass of oxygen atom} = \frac{16}{6.023 \times 10^{23}} = 2.65 \times 10^{-23}\,g$$

$$\text{Mass of carbon atom} = \frac{12}{6.023 \times 10^{23}} = 2.00 \times 10^{-23}\,g$$

$$\bar{\nu} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \left[\frac{1 \times 10^6 (2.65 \times 10^{-23} + 2.00 \times 10^{-23}\,g)}{2.65 \times 10^{-23} \times 2.00 \times 10^{-23}\,g}\right]^{1/2}$$

$$= 1581\ cm^{-1}$$

Degree of Freedom

Polyatomic exhibit more that one fundaments vibrational absorption bands. This depends upon the number of degrees of freedom. A molecule composed of n-atoms has

- 3n degrees of freedom = **translational + rotational + vibrational**
- There are 3 **transitional** degrees of freedom
- There are 3 **rotational** degrees of freedom (2 for linear molecules)
- There are **3n-6 vibrational** degrees of freedom(3n-5 if the molecule is linear).

	CO_2	C_6H_6
No of atoms	3	12
Total degrees of freedom	9	36
Translational	3	3
Rotational	2	3
Vibrational	4	30
No of theoretical bands	**4**	**30**

Factors influencing the number of bands

The fundamental number of bands are seldom observed because of overtones and other reasons some of which are

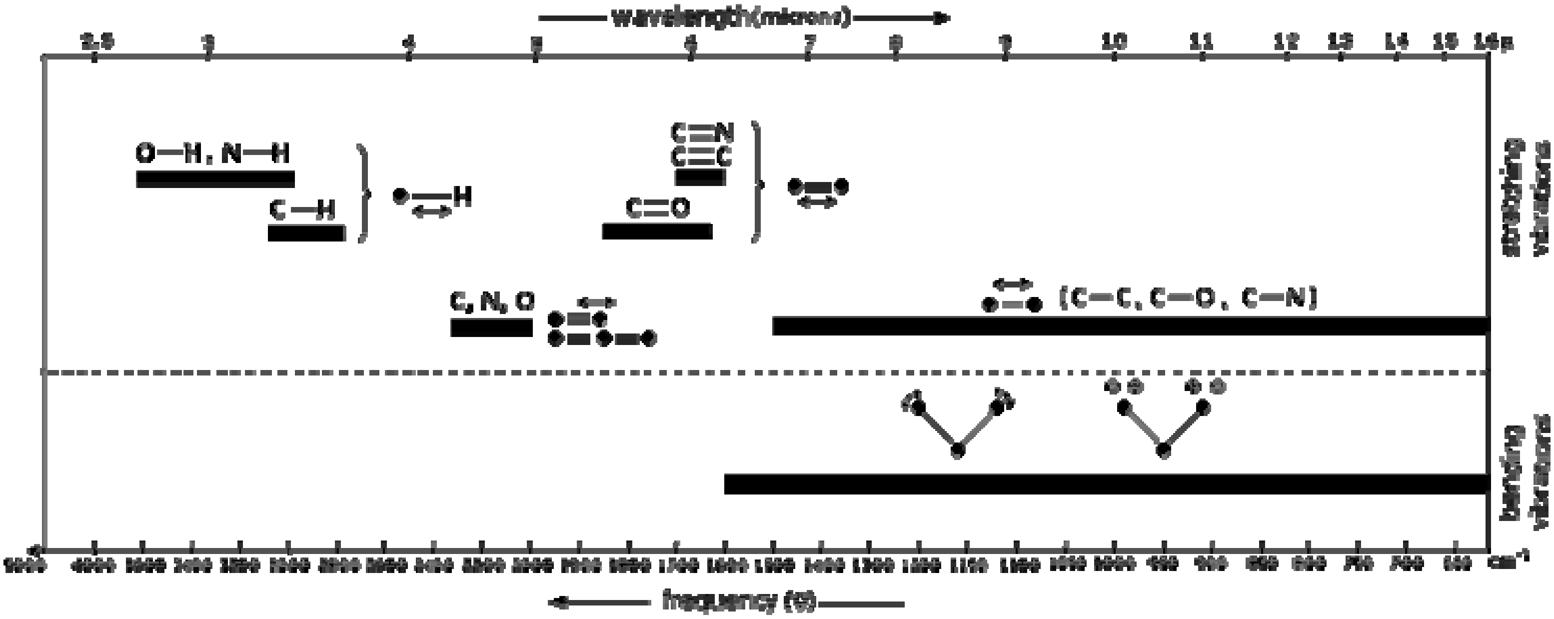
1. Fundamental frequencies fall outside the region
2. Fundamental bands are too weak to be observed
3. Fundamental vibrations are so close that they coalesce

- Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The six fundamental vibrations (12 minus 6) in formaldehyde have been assigned to the spectrum absorptions.
- The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms.
- In practice, infrared spectra do not normally display separate absorption signals for each of the 3n-6 fundamental vibrational modes of a molecule.
- The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact.
- Molecular symmetry, spectrometer limitations, and spectroscopic selection rules may decrease the number of observed absorptions.

One selection rule that influences the intensity of infrared absorption's, is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.

Fingerprint Region

- The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in the following chart. The complexity of infrared spectra in the 1450 to 600 cm^{-1} region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region.
- Absorption bands in the 4000 to 1450 cm^{-1} region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.
- Many of the vibrational modes in the finger print region depend on complex vibrations involving the entire molecule. It is impossible for any two different molecules (except enantiomers) to have precisely the same IR spectrum.



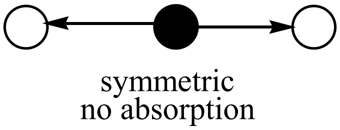
Factors influencing vibrational frequencies

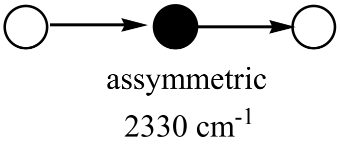
Coupling interactions (also known as Fermi resonance)

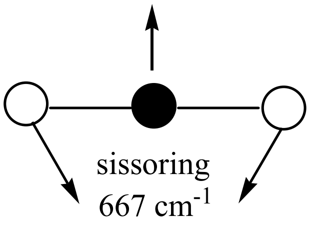
1. Strong coupling between stretching vibrations occurs only when the two vibrations have a common atom
2. Interaction between bending vibrations occurs when a common bond is present between the vibrating groups
3. Coupling between a stretching and a bending vibration can occur if stretching bond forms one side of the angle that varies in the bending vibrations
4. Interaction is greatest when the coupled groups have individual energies that are approximately equal.
5. If groups are separated by two or more bonds, little or no interaction occurs.
6. Coupling occurs when vibrations are of the same symmetric species.

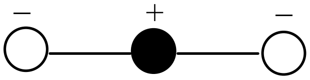
e.g. CO_2 (aliphatic ketone 1700 cm^{-1})

- Symmetric vibrations - no change in dipole moment – no band
- Assymmetric vibrations - change in dipole moment - 2330 cm^{-1}
- Bending vibrations – equal energy – 667 cm^{-1}









C-O stretching coupled to adjacent C-H and C-C couplings

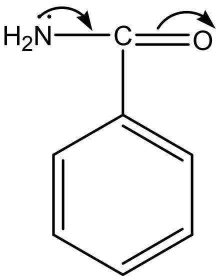
methanol	(CH_3OH)	1034 cm^{-1}
ethanol	(CH_3CH_2OH)	1053 cm^{-1}

Electronic effects

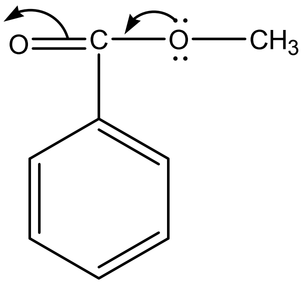
Changes in the absorption frequencies for a particular group takes place when the substitutents in the neighboring group are changed. The frequency shifts are due to the electronic effects which include **inductive effect, mesomeric effect** and **field effects** etc.

+I effect causes in weakening of bond		**-I effect** increases the bond order	
formaldehyde	1750 cm^{-1}	Acetone	1715 cm^{-1}
Acetaldehyde	1745 cm^{-1}	Chloro acetone	1725 cm^{-1}
acetone	1715 cm^{-1}	Di chloro acetone	1740 cm^{-1}

In those cases where lone pairs are involved the mobility of the lone pair matters. e.g. on comparing benzamide and phenyl acetate we find that nitrogen being less electronegative that oxygen, the electron pair in the former is more labile. As a consequence the carbonyl absorption in benzamide is at 1693 cm^{-1}while that in phenyl acetate is at 1730 cm^{-1}.



benzamide
1693 cm^{-1}



phenyl acetate
1730 cm^{-1}

In di-substituted aromatic compounds both inductive effect and mesomeric effects have effect while in meta substituted products only inductive effect is considered. Ortho substituted products are also influenced by stearic interactions. Here lone pairs present on the substituents cause electrostatic repulsion’s leading to absorption at higher wavelengths.

Hydrogen bonding

- Hydrogen bonding brings about a remarkable downfield shift. Stronger the hydrogen bonding greater is the absorption shift towards the lower wave number.
- Intermolecular hydrogen bonding gives broad bands while intra molecular hydrogen bonding gives sharp ones.
- Intermolecular hydrogen bonds are concentration dependent.
- Hydrogen bonding in amines is weaker that I alcohols thus the frequency shifts are less dramatic.
  - Amines show N – H stretching at 3500 cm^{-1} in dilute solutions while in condensed phase spectra the absorption occurs at 3300 cm^{-1}.
  - In aliphatic alcohols a sharp band appears at 3650 cm^{-1} in dilute solutions while a broad band is seen at 3350 cm^{-1} due to hydrogen bond.

Detailed absorptions table of bonds in organic molecules

Bond	**Type of bond**	**Specific type of bond**	**Absorption range and intensity**
C-H	alkyl	methyl	1380 cm^{-1} (weak), 1460 cm^{-1} (strong) and 2870, 2960 cm^{-1} (both strong to medium)
		methylene	1470 cm^{-1} (strong) and 2850, 2925 cm^{-1} (both strong to medium)
		methyne	2890 cm^{-1} (weak)
	vinyl	$C=CH_2$	900 cm^{-1} (strong) and 2975, 3080 cm^{-1} (medium)
		C=CH	3020 cm^{-1} (medium)
		monosubstituted alkenes	900, 990 cm^{-1} (both strong)
		cis-disubstituted alkenes	670-700 cm^{-1} (strong)
		trans-disubstituted alkenes	965 cm^{-1} (strong)
		trisubstituted alkenes	800-840 cm^{-1} (strong to medium)
	aromatic	benzene/sub. benzene	3070 cm^{-1} (weak)
		monosubstituted benzene	700-750 cm^{-1} (strong) and 700±10 cm^{-1} (strong)
		ortho-disub. benzene	750 cm^{-1} (strong)
		meta-disub. benzene	750-800 cm^{-1} (strong) and 860-900 cm^{-1} (strong)
		para-disub. benzene	800-860 cm^{-1} (strong)
	alkynes		3300 cm^{-1} (medium)
	aldehydes		2720, 2820 cm^{-1} (medium)
C-C	acyclic C-C	monosub. alkenes	1645 cm^{-1} (medium)
		1,1-disub. alkenes	1655 cm^{-1} (medium)
		cis-1,2-disub. alkenes	1660 cm^{-1} (medium)
		trans-1,2-disub. alkenes	1675 cm^{-1} (medium)
		trisub., tetrasub. alkenes	1670 cm^{-1} (weak)
	conjugated C-C	dienes	1600, 1650 cm^{-1} (strong)
		with benzene ring	1625 cm^{-1} (strong)

		with C=O	1600 cm^{-1} (strong)
	aromatic C=C		1450, 1500, 1580, 1600 cm^{-1} (strong to weak) - always ALL 4!
	triple C-C	terminal alkines	2100-2140 cm^{-1} (weak)
		disubst. alkines	2190-2260 cm^{-1} (very weak, sometimes not visible)
C=O	aldehyde/ketone	saturated aliph./cyclic 6-membered	1720 cm^{-1}
		α,β-unsaturated	1685 cm^{-1} (goes for aromatic ketones as well)
		cyclic 5-membered	1750 cm^{-1}
		cyclic 4-membered	1775 cm^{-1}
		aldehydes	1725 cm^{-1} (influence of conjugation like with ketones)
	carboxylic acids/derivates	saturated carboxylic acids	1710 cm^{-1}
		unsat./aromatic carb. acids	1680-1690 cm^{-1}
		esters and lactones	1735 cm^{-1} (influence of conjugation and ring size like with ketones)
		anhydrides	1760 and 1820 cm^{-1} (both!)
		halogenides	1800 cm^{-1}
		amides	1650 cm^{-1} (associated amides)
		carboxylates (salts)	1550-1610 cm^{-1} (goes for aminoacid zwitterions as well)
O-H	alcohols, phenoles		3610-3670 cm^{-1} (concentrating samples broadens the band and moves it to 3200-3400 cm^{-1})
	carboxylic acids		3500-3560 cm^{-1} (concentrating samples broadens the band and moves it to 3000 cm^{-1})
N-H	primary amines		doublet between 3400-3500 cm^{-1} and 1560-1640 cm^{-1} (strong)
	secondary amines		above 3000 cm^{-1} (medium to weak)
	ammonium ions		broad bands with multiple peaks between 2400-3200 cm^{-1}
C-O	alcohols	primary	1050±10 cm^{-1}
		secondary	around 1100 cm^{-1}
		tertiary	1150-1200 cm^{-1}
	phenoles		1200 cm^{-1}
	ethers	aliphatic	1120 cm^{-1}
		aromatic	1220-1260 cm^{-1}
	carboxylic acids		1250-1300 cm^{-1}
	esters		1100-1300 cm^{-1} (two bands - distinction to ketones, which do not posess C-O!)
C-N	aliphatic amines		1020-1220 cm^{-1} (often overlapped)
	C=N		1615-1700 cm^{-1} (similar conjugation effects to C=O)
	nitriles (triple C-N bond)		2210-2260 cm^{-1} (unconjugated 2250, conjugated 2230 cm^{-1})

C-X (X=F, Cl, Br, I)	fluoroalkanes	ordinary	1000-1100 cm^{-1}
		trifluromethyl	two strong, broad bands between 1100-1200 cm^{-1}
	chloroalkanes		540-760 cm^{-1} (medium to weak)
	bromoalkanes		below 600 cm^{-1}
	iodoalkanes		below 600 cm^{-1}
N-O	nitro compounds	aliphatic	1550 cm^{-1} (stronger band) and 1380 cm^{-1} (weaker band) - ALWAYS BOTH!
		aromatic	1520, 1350 cm^{-1} (conjugation usually lowers the wave number)