INFRA-RED SPECTROSCOPY

Introduction

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2022-2023

- Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light .

- **Near-infrared**; 14000–4000 cm^{-1} (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations.

- **Mid-infrared**; 4000–400 cm^{-1}(2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure.

- **Far-infrared**, 400–10 cm^{-1} (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

Introduction

- Three typical spectral regions for IR spectroscopy:

1. **Near-IR**: excites overtones or harmonics of fundamental vibrations (multiple level transition).
2. **Mid-IR**: excites the fundamental vibrations (single level transition). This region is the most widely used for IR spectroscopy, because it generates spectral fingerprints in which most of organic molecules.
3. **Far-IR**: excites low-energy vibrations and higher energy rotations. The far-IR is a difficult spectral region for IR spectroscopy, and thus has few analytical uses.

Region	Energy (kJ/mol)	Wavenumber (cm^{-1})	Wavelength (µm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-400	2.5-25
Far IR	2.5-0.1	400-10	25-1000

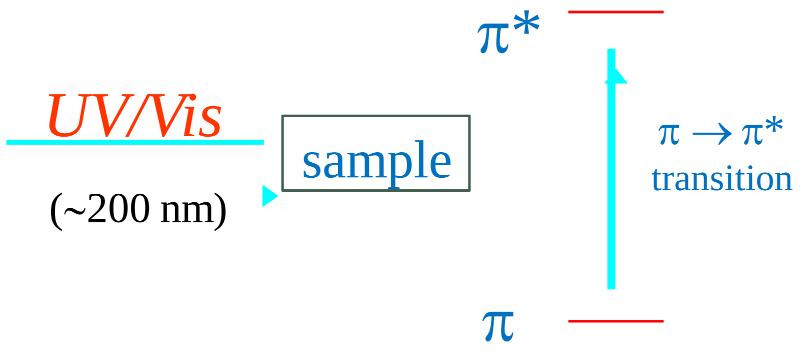
- **Higher wavenumber** corresponds to a **higher energy** absorption

Introduction

- Spectroscopy provide the information about **molecular structure**. As IR is very useful in identifying **functional groups**.
- A **peak-by- peak correlation** is excellent evidence for identity. Any two compounds, except enantiomers, are unlikely to give exactly the same IR spectrum.
- IR spectra usually used in **conjunction with other spectral data** in order to determine or confirm molecular structure.
- Even a very simple molecule can give an extremely complex spectrum.

- What happens when a sample absorbs UV/Vis energy?

❑ Excitation of ground state electrons (typically π and *n* electrons) $E_{electronic}$ increases momentarily



UV/Vis

(~200 nm)

sample

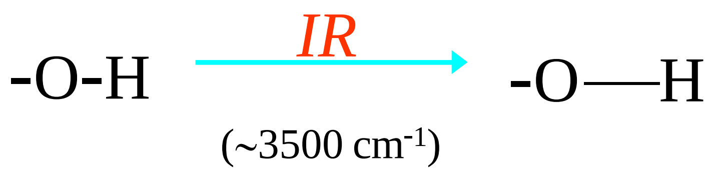
π^*

$\pi \rightarrow \pi^*$ transition

π

- What happens when a sample absorbs IR energy?

❑ Stretching and bending of bonds (typically covalent bonds) $E_{vibration}$ increases momentarily



-O-H $\xrightarrow{IR}$ -O—H

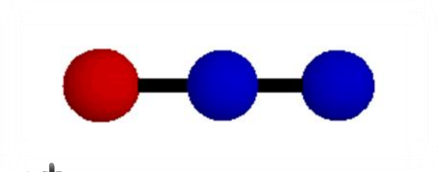
(~3500 cm^{-1})

(IR) measures the bond vibration frequencies in a molecule and is used to determine the functional group

MOLECULAR VIBRATIONS

What is a vibration in a molecule?

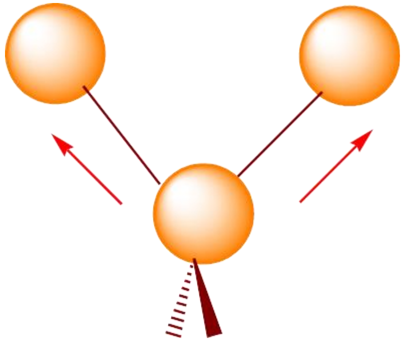
Any change in shape of the molecule- stretching of bonds, bending of bonds, or internal rotation around single bonds



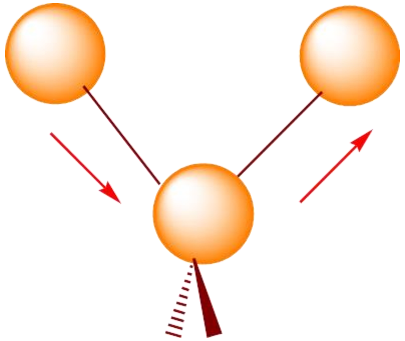
There are two main vibrational modes :

1. Stretching - change in bond length (higher frequency) Occurs at

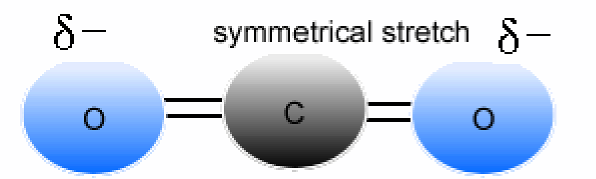
   higher energy: 4000-1250 cm^{-1}

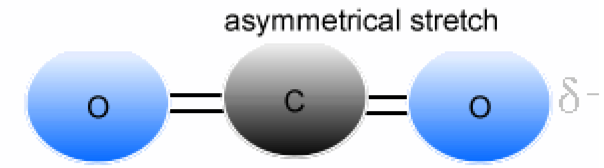


Symmetric



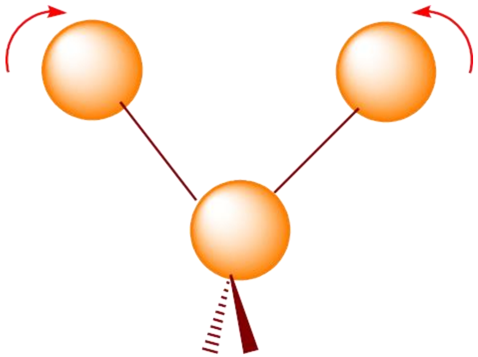
Asymmetric



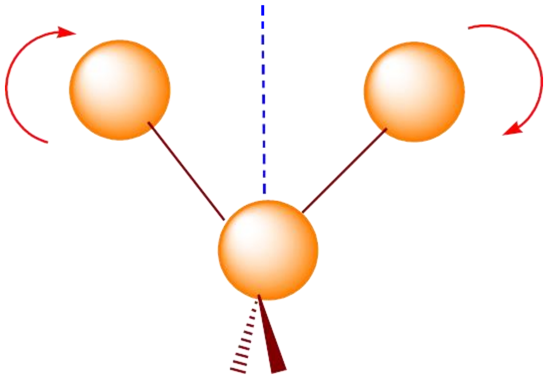


2. Bending - change in bond angle (lower frequency)

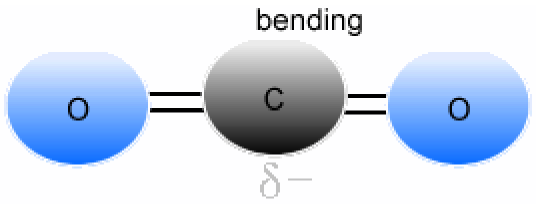
Occurs at lower energy: 1400-666 cm^{-1}.



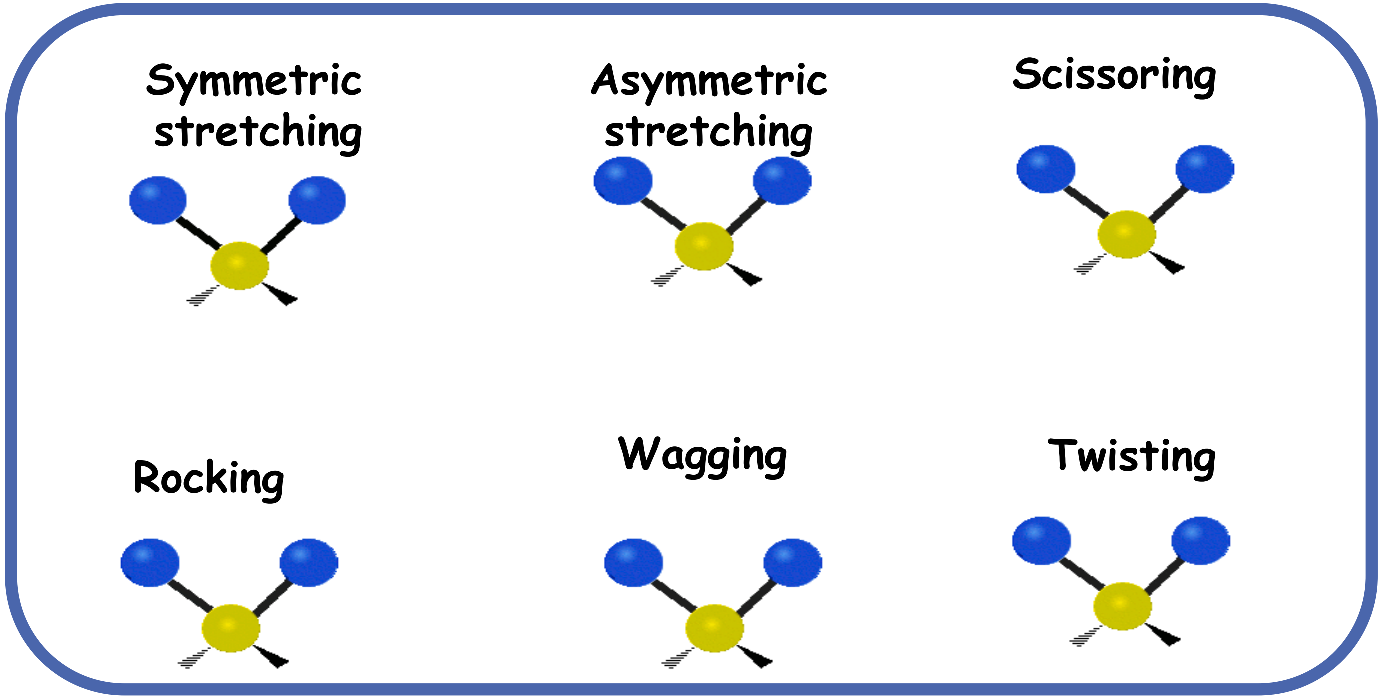
In-plane (Scissoring)



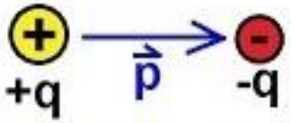
Out-plane (Twisting)



More complex types of stretching and bending vibrations are possible



Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment.



(Dipole moment)

Can a vibration change the dipole moment of a molecule?

- Infrared active vibrations (those that absorb IR radiation) must result in a change of dipole moment
- Asymmetrical stretching/bending are IR active.
- Symmetrical stretching/bending is not IR active

Question: Which of the following atoms or molecules will absorb IR radiation and WHY?:

[✓ $I{-}Cl$] H_2 N_2 Cl_2

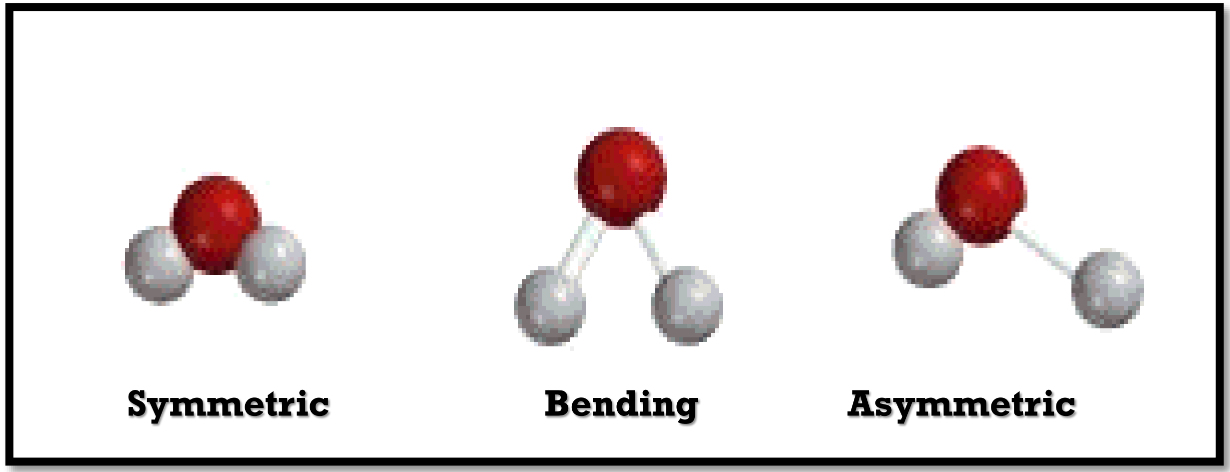
Number of vibrational modes

- A molecule can vibrate in many ways, and each way is called a vibrational mode.
- In order for a vibrational mode in a sample to be "IR active", it must be associated with changes in the dipole moment.

Example H_2O, will have (3 × 3 – 6 = 3) degrees of vibrational freedom, or modes.

- For molecules with *N* number of atoms,

1. Linear molecules have *3N – 5* degrees of vibrational modes
2. Nonlinear molecules have *3N – 6* degrees of vibrational modes (also called vibrational degrees of freedom).



Factors affect the *NUMBER* of IR bands

1) Degeneracy of bands from several absorptions of the same frequency
2) Lack of change in molecular dipole moment during vibration
3) Fall of frequencies outside the 4000-400 cm^{-1} region

All of above factors decrease the number of bands

- What are the reasons that affect (reduced or increase) the number of theoretical fundamental vibrations in IR spectroscopy?

Theory

- The the observed vibrations might be **larger** than the theoretical number of fundamental vibrations because of **overtones**.
- The following will **reduce** the number of observed bands:

1. Fundamental wavenumbers that fall **outside of the 4000 cm^{-1} to 400 cm^{-1} region**.
2. Fundamental bands that are **too weak** to be observed.
3. Fundamental vibrational wavenumbers that are so close that the **bands coalesce**.
4. The occurrence of a **degenerate band** from several absorptions of the same frequency in highly **symmetrical molecules**.
5. The failure of certain fundamental vibrations to appear in the IR because of the **lack of change in molecular dipole**.

HOOKE'S LAW

- Bonds can be thought like a spring, and wavenumbers can be approximated by Hooke's law

a) The electronegativity (force constant of the bond)

b) The relative masses of the atoms

c) Their geometry vibrate at different types

$$\boxed{\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}}$$

$$\boxed{\mu = \frac{M_x \bullet M_y}{M_x + M_y}}$$

c = speed of light (3×10^{10} cm/s)
k = force constant
μ = reduced mass of the atoms
M_x = mass of atom x in kg
M_y = mass of atom y in kg

Hooke's law-Example

Calculate the predicted vibrational frequency (in cm^{-1}) for C- H bond, knowing that: The force constant for single bond is $5x\ 10^5$ dyne/ cm, the velocity of light is $3\ X\ 10^8$ cm/s, the mass of carbon atom is $20\ x10^{-24}$g, the mass of hydrogen is $1.6\ x\ 10^{-24}$ g.

$$\boxed{\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}}$$

$$\therefore \quad \bar{\nu} = \frac{7}{2 \times 22} \times \frac{1}{3 \times 10^{8}} \sqrt{\frac{5 \times 10^{5}}{(20 \times 10^{-24})(1.6 \times 10^{-24})/(2.0 + 1.6)10^{-24}}}$$

$$= \sim 3100\ cm^{-1}$$

The relationship between wave number (v), bond strength and mass

The vibrational frequency of a bond would increase with the increase in bond strength.

Consequently, we can expect that

$$\bar{v} \;\; \alpha \;\; \sqrt{K}$$

C=C and C=O > C-C and C-O, respectively

The vibrational frequency of a bond would increase with the decrease in reduced mass of the system.

$$\bar{v} \;\; \alpha \;\; \sqrt{\frac{1}{\mu}}$$

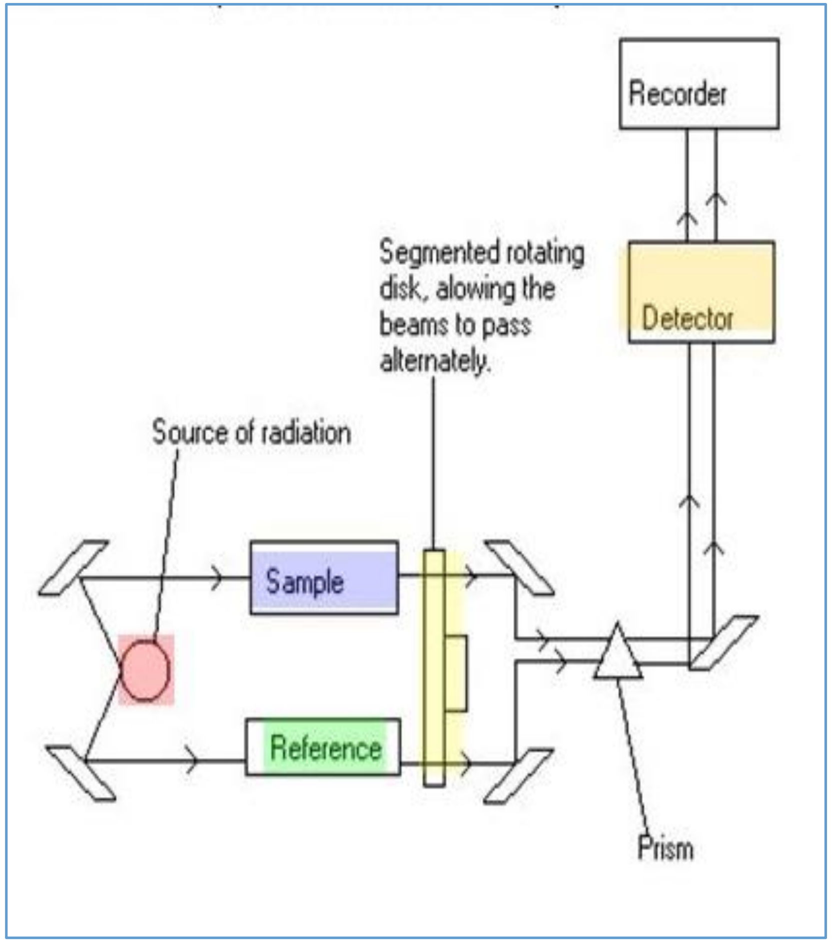
C-H and O-H > C-C and C-O, respectively

Similarly,

O-H > O-D

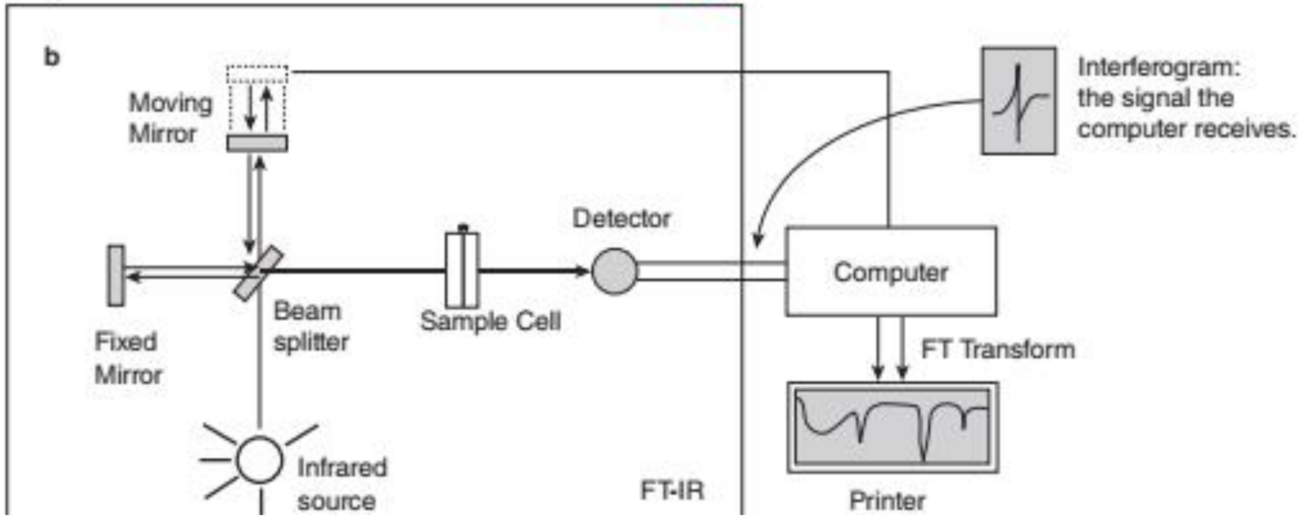
Instrumentation IR spectroscopy

- source of energy
- Sampling area
- Photometer
- Grating (monochromator)
- Detector



IR Instrumentation

- **Fourier-Transform Infrared** (**FT-IR**) instrument uses a system called an **interferometer**.
- The interferometer consists of a **source**, **beam-splitter**, **two mirrors**, and a **detector**.
- This interferogram goes from the beam-splitter to the sample, the energy either **absorbed** or **transmitted**. Then the transmitted portion reaches the detector.
- The detector reads information about every wavelength in the infrared range.
- The detector signal is sent to the computer, and an algorithm called a **Fourier transform** is performed on the **interferogram** to convert it into a **single beam spectrum**.



Sample preparation

Infrared spectra may be obtained for **gases**, **liquids**, or **solids**.

- **Gases fill cell**

  (a) transparent windows (NaCl/KBr)

  (b) long pathlength (10 cm) - few molecules

- **Liquids fill cell**

  (a) solute in transparent solvent - not water (attacks windows)

  (b) short pathlength (0.1-1 mm) - solvents absorb

  (c) Solvent may be used is CCl_4

  (d) (NaCl/AgCl) used as diluents

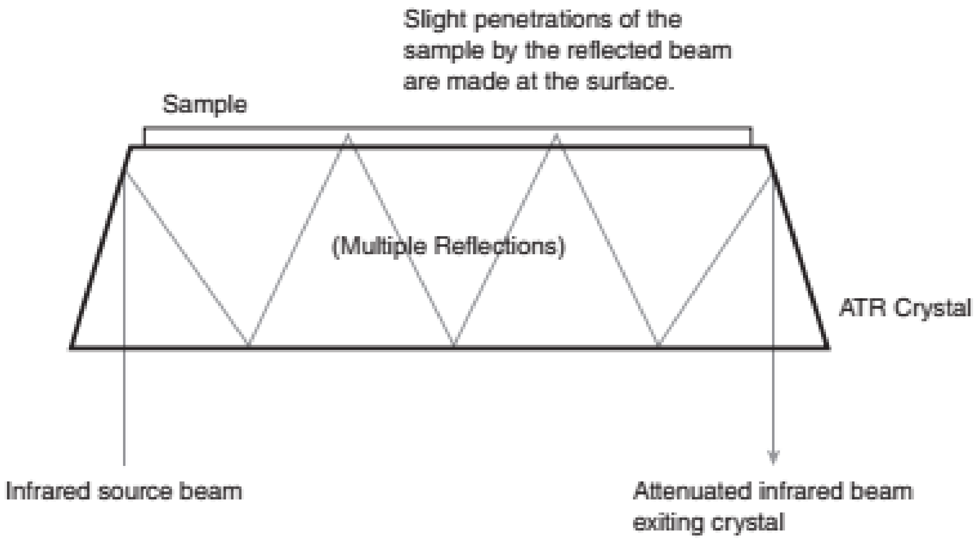
Sample preparation

- **Solids**

(a) make semi-transparent pellet with KBr

(b) grind and mix with Nujol (hydrocarbon oil) to form mull. One drop between NaCl plates.

- The best method of determining a spectrum of samples is to make use of an **Attenuated Total Reflectance (ATR) accessory**.
- The ATR method provides a powerful sampling technique that virtually eliminates sample preparation with both liquids and solids, thus leading to rapid analysis of samples.



Solvents in IR spectroscopy

Properties of solvents

1. Pure solvent is placed in the **reference**
2. The spectrum thus obtained is that of the solute **except** in the region in which the solvent absorbs strongly .
3. The solvent selected **must be dry and transparent** in interest .

Types of solvents

- Solvent, like **carbon tetrachloride (CCl_4)** a is relatively free of absorption at frequencies above 1333 cm $^{-1}$,
- **carbon disulfide (CS_2)** shows little absorption below 1333cm^{-1}

Solvent and solute combinations that react ***must be avoided*** **. For example** :-

1. CS_2 cannot be use as a solvent for primary or secondary amine
2. Amino alcohol react slowly with **CS_2 & CCl_4**

- **Chloroform ($CHCl_3$) shows absorption at all wavelength but its absorption is so high ,so avoid it and used analyses dissolving solvent than neglected**

Factors affect IR frequencies

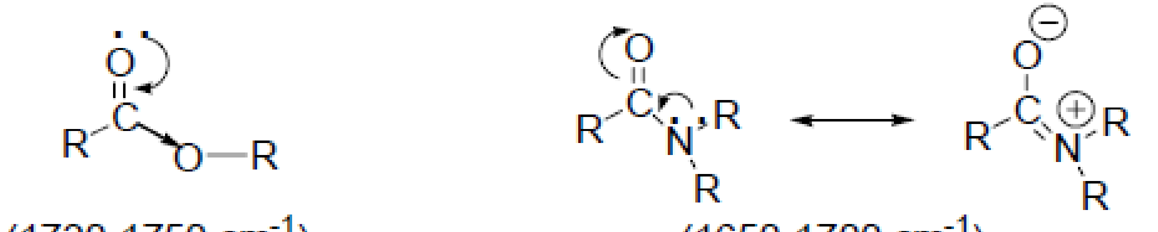
Inductive and Resonance Effects

Conjugation Effects

Ring size effects

Hydrogen bonding

- The replacement of an alkyl group of the saturated aliphatic ketone by a heteroatom (O, N) **shifts** the C=O stretching frequencies due to inductive and resonance effects.
- **In esters**, the oxygen due to inductive effect **withdraws** the electrons from carbonyl group and *increases* the C=O bond strength and thus the frequency of absorption.



(1720-1750 cm^{-1})
Ester

(1650-1700 cm^{-1})
Amide

Factors affect IR frequencies

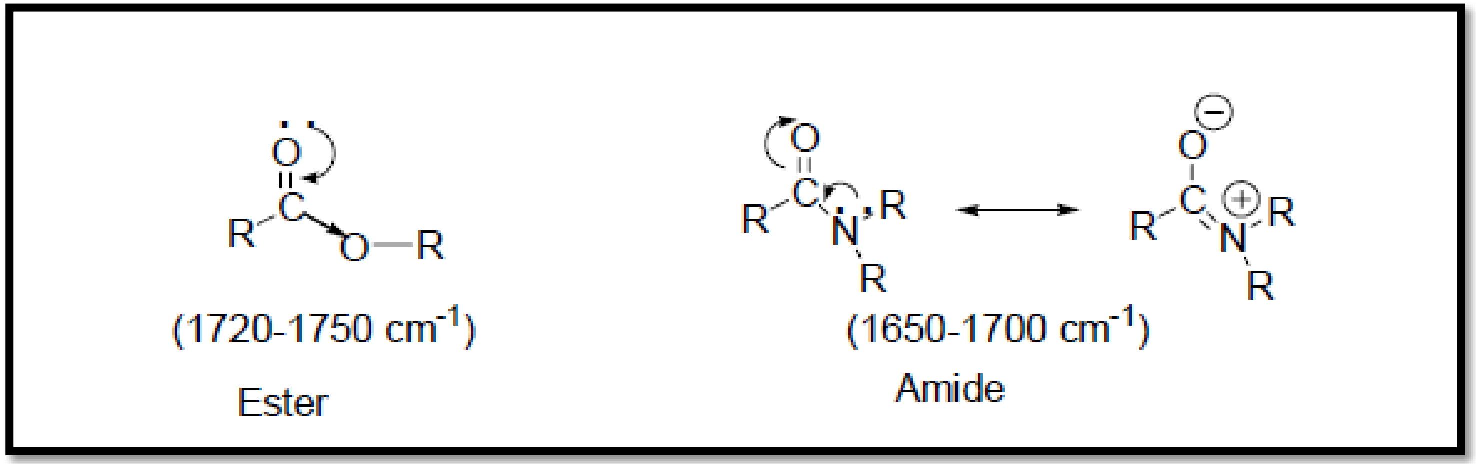
Inductive and Resonance Effects

Conjugation Effects

Ring size effects

Hydrogen bonding

- ☐ **In amides**, due to the conjugation of lone pair of electrons on nitrogen atom, the resonance effect increases the C=O bond length and reduces the C=O absorption frequency. Therefore, C=O absorption frequencies due to resonance effects in amides are lowered but due to inductive effect in esters are increased than those observed in ketones.



What is the effect of inductive and resonance effect at the at Vibration frequencies?

Factors affect IR frequencies

Inductive and Resonance Effects

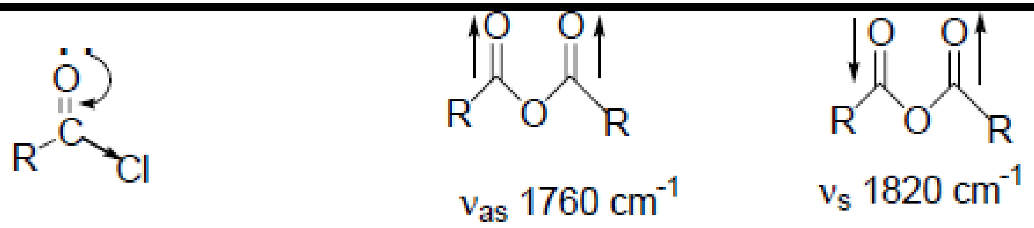
Conjugation Effects

Ring size effects

Hydrogen bonding

- ❑ **In acid chlorides**, the halogen atom strengthens the C=O bond through inductive effect and shifts the C=O stretching frequencies even higher than are found in esters.

- ❑ **The acid anhydrides** give two bands in C=O stretching frequency region due to symmetric (~1820 cm^{-1}) and asymmetric (~1760 cm^{-1}) stretching vibrations.



Acid chloride

Acid anhydrides

What is the effect of inductive and resonance effect at the at Vibration frequencies?

Factors affect IR frequencies

Inductive and Resonance Effects

Conjugation Effects

Ring size effects

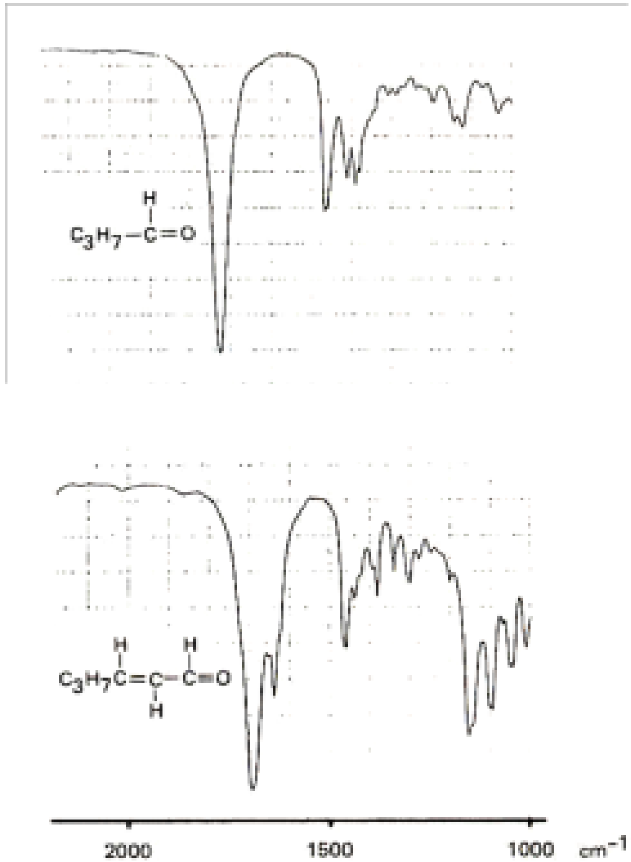
Hydrogen bonding

- ❑ The C=O stretching frequencies for C=C conjugated systems are generally lower by 25-45 cm^{-1} than those of corresponding non-conjugated compounds.
- ❑ The delocalization of π-electrons in the C=O and C=C bonds lead to partial double bond character in C=O and C=C bonds and lowers the force constant.
- ❑ Greater is the ability of delocalization of electrons, the more is lowering in C=O stretching frequency.

Factors Affecting Group Frequencies

Electronic Effects - Effect of Conjugation

- Effects due to the **change in the distribution of electrons** in a molecule produced by a substituent atom or group can often be detected in vibrational spectra. Include **inductive** and **resonance effects** as well as **conjugation** of double bonds.
- **Conjugation** tends to **lower the double bond character** and **increase the bond order** of the intervening single bond.
- As a consequence, the C=O stretching frequency is **lowered by 20-30 cm^{-1}** in this conjugated aldehyde.



Factors affect IR frequencies

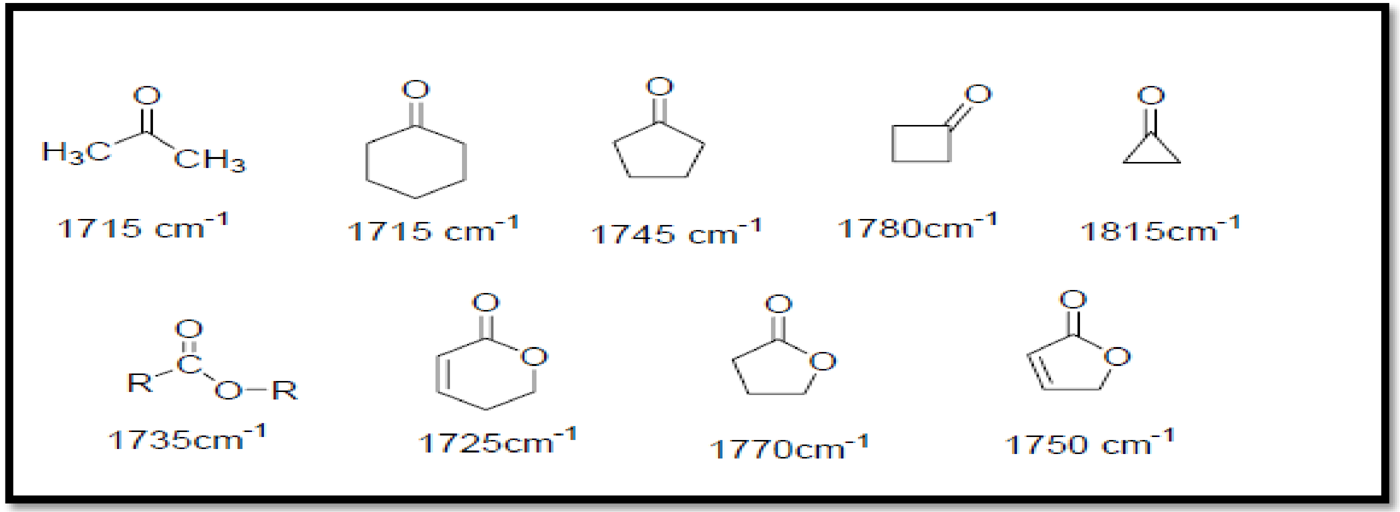
Inductive and Resonance Effects

Conjugation Effects

Ring size effects

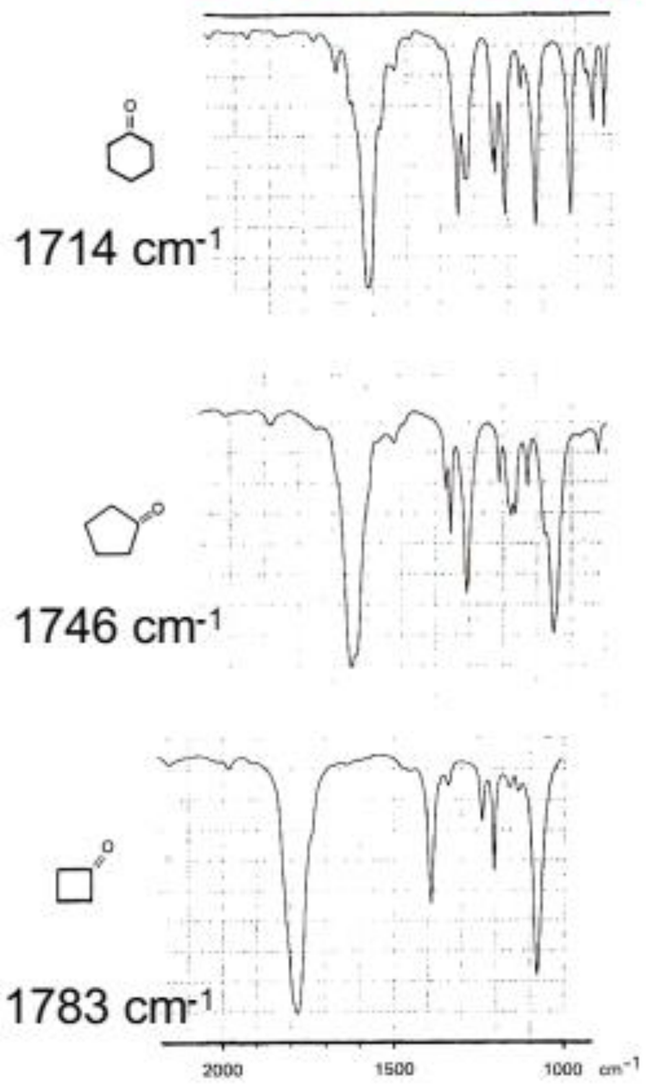
Hydrogen bonding

- Decrease in ring size increases the C=O stretching frequency.
- This gives more s character to the C=O sigma bond and thus results in strengthening of C=O double bond.
- The comparison of C=O stretching frequencies of various compounds shows that in ketones and esters, ~ 30 cm^{-1} increase in frequency occurs on moving to one carbon lower ring.



Factors Affecting Group Frequencies

Effect of Ring Strain



- Increasing ring strain causes a shift in the carbonyl stretching to higher wave numbers.
- This increase in frequency with increasing angle strain is observed for exocyclic double bonds.

Factors affect IR frequencies

Inductive and Resonance Effects

Conjugation Effects

Ring size effects

Hydrogen bonding

- The strength of Hydrogen bonding decreases as the distance between X & Y increase. Hydrogen bonding alters the force constant of both groups ,thus, the frequencies of both stretching and bending vibrations are altered
- The X-H stretching band move to lower frequencies (longer wavelength)usually with increase intensity and band widening
- The stretching frequency of the acceptor group ,for , C=O is also reduced but to a lesser degree than the proton donor group

Factors Affecting Group Frequencies

Hydrogen Bonding

- Hydrogen bonding takes place between a hydrogen atom bonded to an electronegative element and an atom with a non-bonding electron pair.
- X-H....Y
- The effect of hydrogen bonding is to cause **increasing the intensities**, **broadening peaks** and a **shift peaks to lower frequencies** in IR.

Factors affect hydrogen bonding

A. Temperature since when temp. increases, the H- bonding decreases

B. Concertation have different affect on both H-bonding result from intermolecular bonding disappear at low conc. While intramolecular bonding has internal effect & so it persist at very low conc.

C. The relative acidity and basicity of the proton donor and acceptor groups affect the strength of bonding.

D. Ring strain

E. Molecular geometry

Factors affect position of C=O stretching band

A. The physical state

B. Electronic and mass effect of neighbouring group

C. The relative acidity and basicity of the proton donor and acceptor groups affect the strength of bonding.

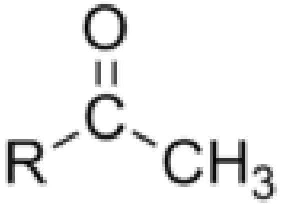
D. Ring strain

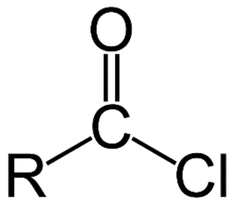
E. Conjugation effect

F. Hydrogen bonding effect

G. Inductive effect

Example: The carbonyl stretching frequency in **$RCOCH_3$** (~1720 cm^{-1}) is lower than acid chloride **RCOCl** (1750-1820 cm^{-1}).





This change in frequency of the C=O stretching may be arising due to:

a. Difference in mass between CH_3 and Cl
b. The inductive or mesomeric influence of Cl on the C=O bond
c. Coupling interactions between C=O and C -Cl bonds
d. Change in bond angles arising due to steric factors etc.