

# INFRARED SPECTROSCOPY

- Almost any compound having covalent bonds, whether organic or inorganic, absorbs various frequencies of electromagnetic radiation in the infrared region of the electromagnetic spectrum. For chemical purposes, we are interested in the vibrational portion of the infrared region.
- It includes radiation with wavelengths ( $\lambda$ ) between 2.5  $\mu\text{m}$  and 25  $\mu\text{m}$  (1  $\mu\text{m}$  =  $10^{-6}$  m). Although the more technically correct unit for wavelength in the infrared region of the spectrum is the micrometer ( $\mu\text{m}$ ), you will often see the micron ( $\mu$ ) used on infrared spectra.

TYPES OF ENERGY TRANSITIONS IN EACH REGION OF THE ELECTROMAGNETIC SPECTRUM	
Region of Spectrum	Energy Transitions
X-rays	Bond breaking
Ultraviolet/visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radiofrequencies	Nuclear spin (nuclear magnetic resonance) Electronic spin (electron spin resonance)

- IR examines the transitions between the vibrational quantum levels of molecules. Some of the functional groups in the molecule can be detected. Vital information about the structures of organic molecules can be understood.
- Molecules absorb IR radiation (wavelength between 0,78 – 1000  $\mu$ ) and IR is based on measurement of the stimulation of molecules to vibration and rotational energy levels. (It is based on the measurement of the vibrational and rotational energy levels after stimulation with IR radiation.)
- Infrared radiation is between VISIBLE REGION and MICROWAVE in the electromagnetic spectrum.

0,78 - 2,5  $\mu$   $\Rightarrow$  Near IR

2,5-15  $\mu$  (4000-667  $\text{cm}^{-1}$ )  $\Rightarrow$  IR

15 – 1000  $\mu$   $\Rightarrow$  Far IR

not useful in  
organic structure  
analysis

Radiation in near infrared region  vibrational, rotational energies

Radiation in far infrared region  rotational energies

In the region between 2.5 and 15  $\mu$  (In the range 2,5-15  $\mu$ ) , the bands are observed as a result of the absorption of the beams which are required for the vibrational rotational energy change.

Wavelength of bands depends on;

- The mass of atoms,
- Force constant for bonds,
- The geometry of atoms.

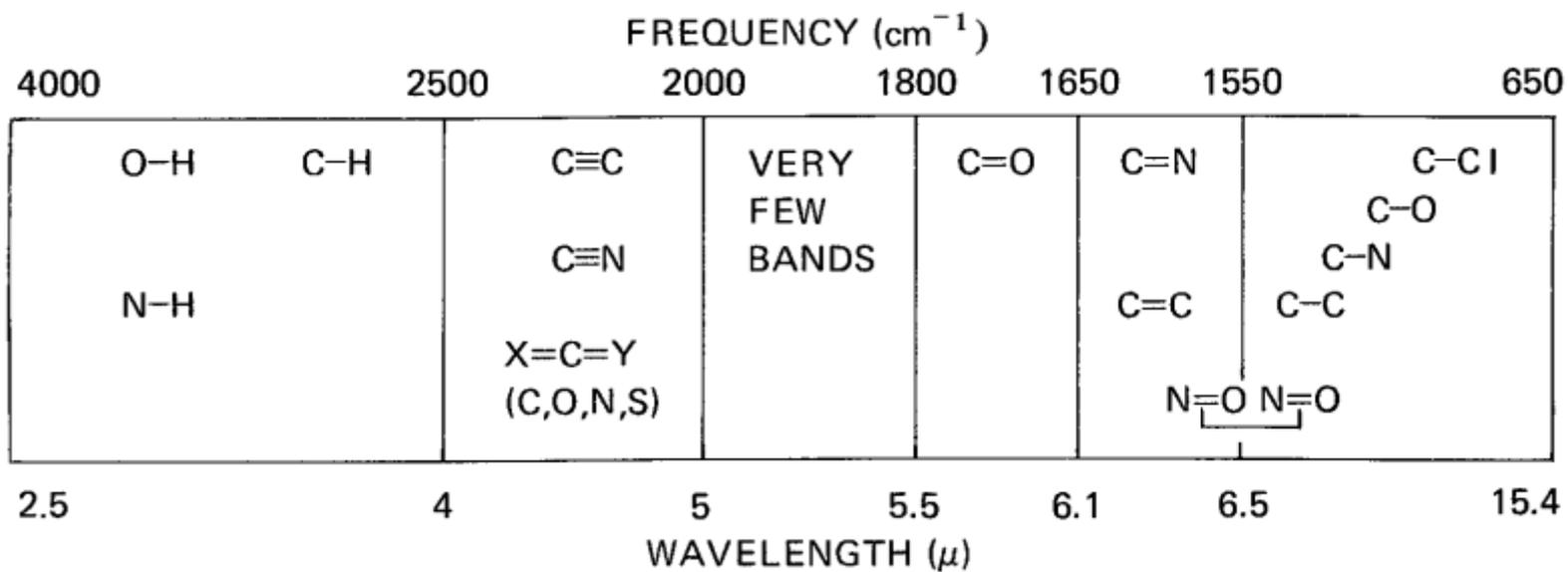
- By infrared spectroscopy;

1- Functional groups in the structure of organic compounds can be found.

2- It is understood whether two organic compounds are the same.

3- It is also used for quantitative analysis.

- Although some of the frequencies absorbed in the two cases might be the same, in no case of two different molecules will their infrared spectra (the patterns of absorption) be identical. Thus, the infrared spectrum can be used for molecules much as a fingerprint can be used for humans.
- The absorptions of each type of bond (N-H, C-H, O-H, C-X, C=O, C-O, C-C, C=C, C≡C, C≡N, and so on) are regularly found only in certain small portions of the vibrational infrared region. A small range of absorption can be defined for each type of bond.
- Homonuclear molecules such as N<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub> do not absorb the IR radiation. All organic molecules except these molecules absorb the IR radiation.



- Wavenumbers are expressed as reciprocal centimeters ( $\text{cm}^{-1}$ ) and are easily computed by taking the reciprocal of the wavelength expressed in centimeters. Convert a wavenumber  $\bar{\nu}$  to a frequency  $\nu$  by multiplying it by the speed of light (expressed in centimeters per second).
- The radiation refer in the vibrational infrared region of the electromagnetic spectrum in terms of a unit called a wavenumber ( $\bar{\nu}$ ) ( $\text{cm}^{-1}$ ), rather than wavelength ( $\mu$  or  $\mu\text{m}$ ).

$$E = h\nu = \frac{hc}{\lambda} = h \cdot \bar{\nu} \cdot c$$

E= energy

h= planck constant =  $6,62 \times 10^{-27}$  erg/sn

$\nu$ = frequency

c= light speed

$\bar{\nu}$ = wavenumber

$$\bar{\nu} (\text{cm}^{-1}) = \frac{10^4}{\lambda (\mu\text{m})}$$

The intensity of the bands is indicated as transmittance (T) or absorbance (A) as in ultraviolet ( $A = \log_{10} 1/T$ )

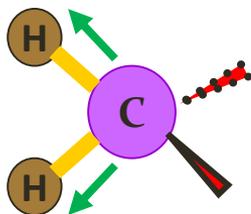
- As with other types of energy absorption, molecules are excited to a higher energy state when they absorb infrared radiation. The absorption of infrared radiation is, like other absorption processes, a quantized process. A molecule absorbs only selected frequencies (energies) of infrared radiation.
- Radiation in this energy range corresponds to the range encompassing the stretching and bending vibrational frequencies of the bonds in most covalent molecules.
- In the absorption process, those frequencies of infrared radiation that match the natural vibrational frequencies of the molecule in question are absorbed, and the energy absorbed serves to increase the **amplitude** of the vibrational motions of the bonds in the molecule. Note, however, that not all bonds in a molecule are capable of absorbing infrared energy, even if the frequency of the radiation exactly matches that of the bond motion. Only those bonds that have a **dipole moment** that changes as a function of time are capable of absorbing infrared radiation.
- Symmetric bonds, such as those of  $\text{H}_2$  or  $\text{Cl}_2$ , do not absorb infrared radiation. A bond must present an electrical dipole that is changing at the same frequency as the incoming radiation for energy to be transferred. The changing electrical dipole of the bond can then couple with the sinusoidally changing electromagnetic field of the incoming radiation. Thus, a symmetric bond that has identical or nearly identical groups on each end will not absorb in the infrared. For the purposes of an organic chemist, the bonds most likely to be affected by this restraint are those of symmetric or pseudosymmetric alkenes ( $\text{C}=\text{C}$ ) and alkynes ( $\text{C}\equiv\text{C}$ ).

- The motions that create the basis for the absorption of the rays in the IR region and create energy requirements are the vibration movements.

The simplest types, or **modes**, of vibrational motion in a molecule that are **infrared active**—those, that give rise to absorptions—are the stretching and bending modes. However, other, more complex types of stretching and bending are also active. The following illustrations of the normal modes of vibration for a methylene group introduce several terms. In general, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations; also, stretching vibrations occur at higher frequencies than bending vibrations. The terms **scissoring**, **rocking**, **wagging**, and **twisting** are commonly used in the literature to describe the origins of infrared bands.

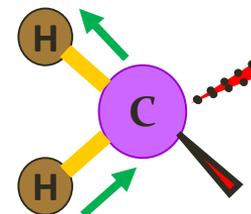
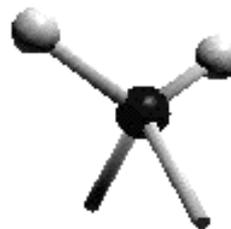
 **Stretching Vibrations:** It is a movement of two atoms approaching and moving away.

*symmetric*



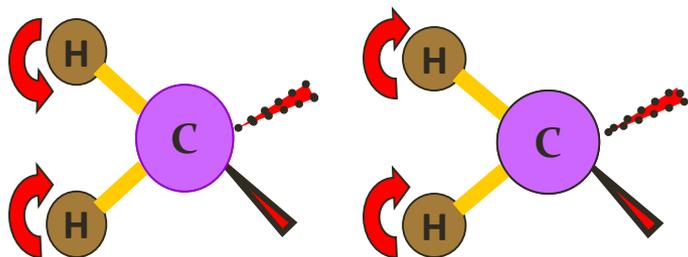
Copyright © 1997 Charles B. Abrams

*asymmetric*



Copyright © 1997 Charles B. Abrams

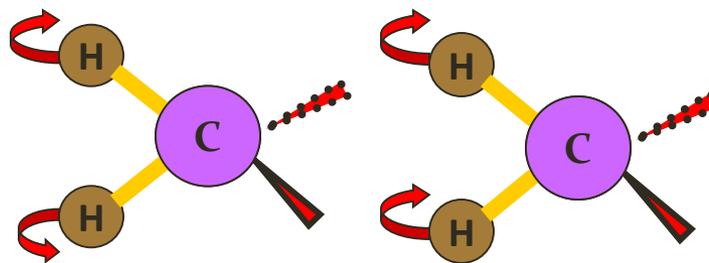
▣ **Bending Vibrations** : It is caused by the change of bond angles between atoms.



*scissoring*

*rocking*

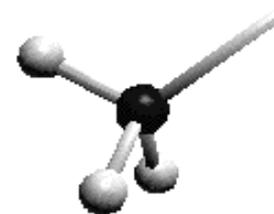
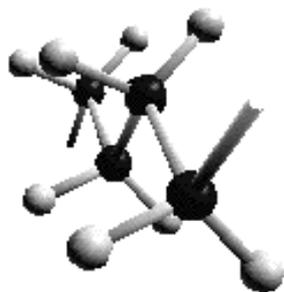
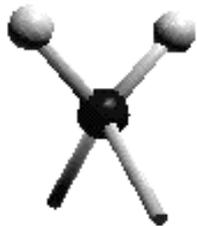
in-plane



*twisting*

*wagging*

Out-of-plane



## Finding Vibration Numbers of Molecules

For a non-linear molecule containing N atoms;

$$3N-6$$

For a linear molecule containing N atoms;

$$3N-5$$

- $\text{H}_2\text{O}$  (nonlinear molecule)  
 $3N-6 = 3 \times 3 - 6 = 3$  main vibration
- $\text{HCN}$ ,  $\text{CO}_2$  (linear molecule)  
 $3N-5 = 3 \times 3 - 5 = 4$  main vibration
- $\text{HCl}$   
 $3N-5 = 3 \times 2 - 5 = 1$  main vibration

The vibrations we have been discussing are called **fundamental absorptions**. They arise from excitation from the ground state to the lowest-energy excited state. Usually, the spectrum is complicated because of the presence of weak overtone, combination, and difference bands.

### Reasons for the presence of more than expected absorption band:

- **Combination tone:** When two vibrational frequencies ( $\bar{\nu}_1$  and  $\bar{\nu}_2$ ) in a molecule couple to give rise to a vibration of a new frequency within the molecule, and when such a vibration is infrared active, it is called a **combination band**. This band is the sum of the two interacting bands ( $\bar{\nu}_{\text{comb}} = \bar{\nu}_1 + \bar{\nu}_2$ ). Not all possible combinations occur. The rules that govern which combinations are allowed are beyond the scope of our discussion here.
- **Overtone: Overtones** result from excitation from the ground state to higher energy states, which correspond to integral multiples of the frequency of the fundamental ( $n$ ). For example, you might observe weak overtone bands at  $2\bar{\nu}$ ,  $3\bar{\nu}$ , . . . . Any kind of physical vibration generates overtones. If you pluck a string on a cello, the string vibrates with a fundamental frequency. However, less-intense vibrations are also set up at several overtone frequencies. An absorption in the infrared at  $500 \text{ cm}^{-1}$  may well have an accompanying peak of lower intensity at  $1000 \text{ cm}^{-1}$ —an overtone.
- **Difference tone: Difference bands** are similar to combination bands. The observed frequency in this case results from the difference between the two interacting bands ( $\bar{\nu}_{\text{diff}} = \bar{\nu}_1 - \bar{\nu}_2$ ).

## Reasons for the presence of less than expected absorption band:

- If the main frequency is outside the range 2.5-15  $\mu$ ,
- If the main band does not have enough intensity to be seen in the spectrum,
- If the two main vibrations are very close and the bands are joined together,
- In symmetric molecules, if there are impaired bands corresponding to the absorbances at the same frequency,
- If some essential vibrations are weakened due to lack of necessary changes in the dipole momentum of molecule

## Finding the Frequency of a Bond (calculation)

The natural frequency of vibration of a bond is given by the equation which is derived from **Hooke's Law** for vibrating springs.

Two things should be noticeable immediately. One is that stronger bonds have a larger force constant  $K$  ( $f$ ) and vibrate at higher frequencies than weaker bonds. The second is that bonds between atoms of higher masses (larger reduced mass,  $m$ ) vibrate at lower frequencies than bonds between lighter atoms.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{\frac{M_x \cdot M_y}{M_x + M_y}}}$$

$\bar{\nu}$ : wavenumber ( $\text{cm}^{-1}$ )

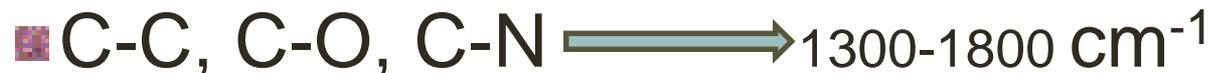
$c$ : speed of light ( $3 \times 10^{10}$  cm/sec)

$f$ : force constant

(single bonds :  $5 \times 10^5$  dynes/cm, for double bonds are twice those of single bonds, for triple bonds are three times those of single bonds)

$M_x$  ve  $M_y$ : masses of the atoms (g)

Calculations with Hooke's Law give the following general values:



- In general, triple bonds are stronger than double or single bonds between the same two atoms and have higher frequencies of vibration (higher wavenumbers).
- Bending motions occur at lower energy (lower frequency) than the typical stretching motions because of the lower value for the bending force constant  $K$ .
- Hybridization affects the force constant  $K$ , also. Bonds are stronger in the order  $sp > sp^2 > sp^3$ , and the observed frequencies of -C-H vibration illustrate this nicely.

# Factors that Influence the Frequency and Shape of Bands

## *Physical state of matter:*

The effect of the hydrogen bond or solvent changes the position of the band.

**Gas:** short thick band as a result of free vibration and rotational movement

In liquids or solids, the fine structure is usually blended together into a broad, smooth curve

**Liquid:** narrow and symmetrical bands as a result of their inability to rotate for a long time

**Solid:** Vibrational absorption bands are often divided, new bands have emerged. complex and sharp bands

Of the three physical states, most preferred are liquid and solid states. The spectra of liquids can be more easily interpreted, as well as the increased complexity of the spectrum of solids may provide an advantage for some qualitative analysis.

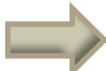
- *Physical state of matter:*
- The effect of heat on the absorption frequency is usually not much. Fluid structures generally give sharper bands at higher temperatures. The bands can also be sharpened by reducing the heat in solids.



## Factors that Influence the Frequency and Shape of Bands

The vibrational coupling type interaction between the two equivalent bands which must be overlapped by the equivalent groups causes this band to split into a doublet.

3497-3077  $\text{cm}^{-1}$   -NH peaks of  $-\text{NH}_2$   
in primary amines and  
primary amide groups

1818-1720  $\text{cm}^{-1}$   carbonyl stretching bands for  
-CO-O-CO- and -CO-NH-CO-  
groups

## Factors that Influence the Frequency and Shape of Bands

### *Electrical effects:*

The force constant (bond strength) between atoms depends on the distribution of electrons in the molecule and can be changed by **conjugation**, **resonance** and **inductive effects**.

- **Conjugation:** The introduction of a C=C bond adjacent to a carbonyl group results in delocalization of the p electrons in the C=O and C=C bonds. This conjugation increases the single-bond character of the C=O and C=C bonds in the resonance hybrid and hence lowers their force constants, resulting in a lowering of the frequencies of carbonyl and double-bond absorption.

### **C=C stretching frequencies;**

is seen at lower frequencies up to  $20\text{-}40\text{ cm}^{-1}$  from isolated double bonds

### **C-C stretching frequencies;**

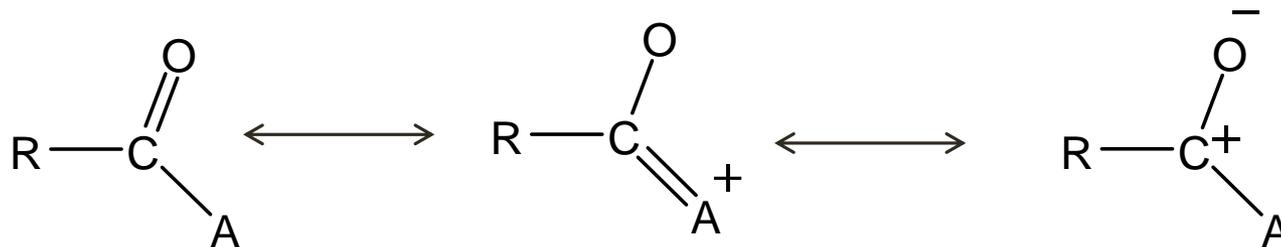
is seen at high frequencies.

**If conjugation is between C = C and C = O groups;**

both bands slip down to low frequencies.

# Factors that Influence the Frequency and Shape of Bands

- **Resonance:** Resonance has the effect of reducing the force constant  $K$ , and the absorption moves to a lower frequency.



A	Formula	C=O absorption
-OH	R-CO-OH	1650 $\text{cm}^{-1}$
-NH <sub>2</sub>	R-CO-NH <sub>2</sub>	1670 $\text{cm}^{-1}$
-R'	R-CO-R'	1700 $\text{cm}^{-1}$
-OR'	R-CO-OR'	1735 $\text{cm}^{-1}$
-Cl	R-CO-Cl	1800 $\text{cm}^{-1}$

- **Inductive effects:** The electron withdrawing or pushing power of an atom or atom group is caused by inductive effects. This effect affects the frequency of absorption

# Factors that Influence the Frequency and Shape of Bands

## ■ *Hydrogen-Bonding Effects:*

Hydrogen bonding to a carbonyl group lengthens the C=O bond and lowers the stretching force constant  $K$ , resulting in a lowering of the absorption frequency. Examples of this effect are the decrease in the C=O frequency of the carboxylic acid dimer and the lowering of the ester C=O frequency in methyl salicylate caused by intramolecular hydrogen bonding.

It may be intramolecular and intermolecular, and may be between solvent and solute.

The stretching bands of a proton donor group; slides down to the lower frequency with increased absorption intensity and band expansion.

-COOH, -OH, -NH<sub>2</sub>

The stretching frequency of a proton acceptor group slides down to low frequency. (but less than the proton donor group)

-X, -O, -N, ethylenic bonds

## Factors that Influence the Frequency and Shape of Bands

### ■ *Fermi resonance:*

When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called Fermi resonance. Fermi resonance is often observed in carbonyl compounds. It causes two bands to form in the region where the main band is expected.

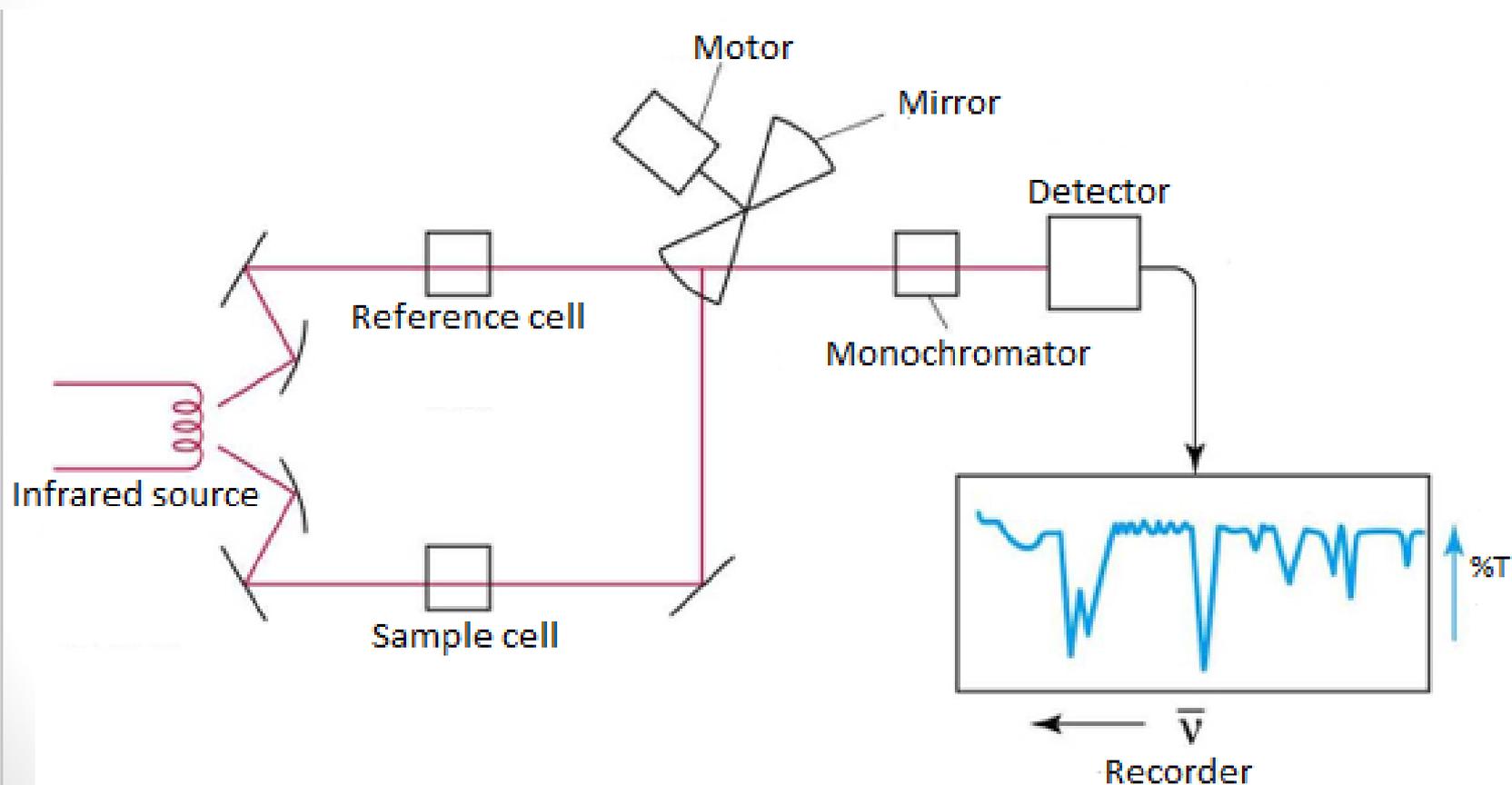
Aldehyde;

C-H Stretching band  a characteristic doublet is observed between 2700-2900  $\text{cm}^{-1}$  while a singlet expected to be observed at 2800  $\text{cm}^{-1}$

Overtone of C-H bending vibrations (1400  $\text{cm}^{-1}$ )

# THE INFRARED SPECTROMETER

The instrument that determines the absorption spectrum for a compound is called an infrared spectrometer or, more precisely, a spectrophotometer.



Two types of infrared spectrometers are in common use in the organic laboratory: single beam and double beam. A modern double beam instrument consists of 5 parts, a source of radiation, a photometer, a monochromator, a detector system and a recorder.

### ■ **Radiation Source :**

When heated by electric current (1200-1800 ° C), it is the object that continuously radiates the desired radiation.

Nernst lamp



Zirconium oxide,  
thorium oxide,  
cerium oxide

Globalar



Silicon carbide

The radiation from the light source is divided into two equal light beams by mirrors. One of them passes from the reference cell and the other from the sample cell.

### ■ **Photometer:**

The beams passing through the reference and sample come into the photometer field, whereby the reference and sample beams are converted into a single beam by means of the regulatory mirror.

### ■ **Monochromator:**

The beams then pass into the monochromator, which disperses each into a continuous spectrum of frequencies of infrared light. The monochromator consists of a rapidly rotating sector (beam chopper) that passes the two beams alternately to a diffraction grating (a prism in older instruments).

### ■ **Detector and Recorder:**

The detector senses the ratio between the intensities of the reference and sample beams. In this way, the detector determines which frequencies have been absorbed by the sample and which frequencies are unaffected by the light passing through the sample. After the signal from the detector is amplified, the recorder draws the resulting spectrum of the sample on a chart.

There are two types of detectors: Photon and Thermal

# INFRARED DEVICES

are divided into three in terms of commercial use.

- **Dispersive Infrared Spectrometers**

Qualitative measurement

- **Fourier Transform Infrared Spectrometers (FT-IR)**

Qualitative and quantitative measurements

- **Non Dispersive Infrared Spectrometers (ND-IR)**

Quantitative measurement

# PREPARATION OF SAMPLES FOR INFRARED SPECTROSCOPY

- The matter that will be determine IR spectrum should contain no water. Because water molecules absorb IR light at 3700 and 1596  $\text{cm}^{-1}$ .

There are at least three common methods for preparing a solid sample for spectroscopy.

- The first method involves mixing the finely ground solid sample with powdered potassium bromide (or sodium bromide) and pressing the mixture under high pressure. Under pressure, the potassium bromide melts and seals the compound into a matrix. The result is a **KBr pellet** that can be inserted into a holder in the spectrometer. The main disadvantage of this method is that potassium bromide absorbs water, which may interfere with the spectrum that is obtained. If a good pellet is prepared, the spectrum obtained will have no interfering bands since potassium bromide is transparent down to 400  $\text{cm}^{-1}$ .
- The second method, a **Nujol mull**, involves grinding the compound with mineral oil (Nujol) to create a suspension of the finely ground sample dispersed in the mineral oil. The thick suspension is placed between salt plates. The main disadvantage of this method is that the mineral oil obscures bands that may be present in the analyzed compound. Nujol bands appear at 2924, 1462, and 1377  $\text{cm}^{-1}$ .
- The third common method used with solids is to **dissolve the organic compound in a solvent**, most commonly carbon tetrachloride ( $\text{CCl}_4$ ). Again, as was the case with mineral oil, some regions of the spectrum are obscured by bands in the solvent. Although it is possible to cancel out the solvent from the spectrum by computer or instrumental techniques, the region around 785  $\text{cm}^{-1}$  is often obscured by the strong C-Cl stretch that occurs there.

# Use of IR Spectroscopy

- **Structure determination:** The IR spectrum gives characteristic peaks for many groups. Thus, in the matter which characteristic groups are, therefore, contributes to the analysis of the structure of matter. In addition, it is important for us to shift the characteristic group peaks with the change of the molecular structure. For example, the C = O group gives a peak in IR between  $1900\text{-}1600\text{ cm}^{-1}$ , but the location of the peak in this region depends on the structure of the molecule.
- **Qualitative analysis:** The IR spectrum is characteristic for each substance and so far thousands of substances were drawn up in the IR spectrum and catalogs were prepared. The spectrum of matter can be determined by comparing the spectra in these catalogs.
- **Determination of hydrogen bond:** Characteristic group peaks shift to higher wavelengths if hydrogen bond is present in the molecule. For example, while the O-H group normally absorbs at  $3600\text{-}3650\text{ cm}^{-1}$ , this absorption shifts to  $3500\text{-}3600\text{ cm}^{-1}$  when it is hydrogen bonded. This is an important feature for understanding the hydrogen bond in the molecule.

- **Determination of bond lengths and angles between atoms:** As we have seen in the IR theory, the frequency of vibration movement is proportional to the force constants. It is possible to calculate bond lengths and angles between bonds by means of force constants.
- **Purity control and use in industry:** In case of impurities, the spectrum will be different from the pure substance spectrum. Some peaks will disappear or some new peaks will be observed. For example; a carbonyl group will be converted to the carboxylic acid group by the oxidation reaction or to the alcohol group by the reduction reaction and the bands of these groups will be observed in the spectrum. Thus, the purity of the substance and the state of the reaction can be determined.
- **Quantitative analysis:** We can also use IR spectroscopy for quantitative analysis. Analysis can be carried out in two ways;
  - According to the Lambert-Beer Law: It is necessary to know the thickness of the cell in order to be able to account in such an application. The measurement of this is both very difficult and not very sensitive.
  - By drawing a calibration curve: This method is a more sensitive but time-consuming method. In this method, solutions of several different concentrations are prepared from the substance and the absorbance observed for each concentration at a characteristic peak of this substance is plotted against the concentration. The absorption of the solution (unknown concentration) at the same frequency gives us the concentration of this substance through the graph.

## Structure Evaluation in IR Spectra

While there are not certain valid rules in the evaluation of IR spectra, there are some points that must be observed and taken into consideration ;

- The substance must be pure.
- The spectrophotometer must be adjusted completely and correctly.
- Care must be taken in preparing the substance for analysis, KBr or solvent used should be very pure. If it is to be worked in a solvent, it should be noted that the solvent should not interact with the substance. also it should be indicate the concentration of the solution and the thickness of the cuvette used.
- The substance to be analyzed in IR should not be in a complex structure.
- It should be known that the positive results of the spectra to be taken are related to the physical state of the substance.

## Places of Specific Regions and Groups in IR Spectrum

2,5-8  $\mu$  (4000-1250  $\text{cm}^{-1}$ )  functional group region

Characteristic stretching band of the functional groups like -OH, -NH, C=O are in this region

8-15  $\mu$  (1250-667  $\text{cm}^{-1}$ )  fingerprint region

is related to the structure of the molecule and is characteristic for the molecule. All peaks of the substances claimed to be identical must be exactly the same in this region.

Region of H bond	Region of unsaturation			Fingerprint region
O-H, N-H, C-H	Triple bonds	Double bonds	Single bonds	Skeletal Vibrations

3750  $\text{cm}^{-1}$

2500  $\text{cm}^{-1}$

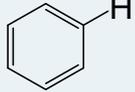
2000  $\text{cm}^{-1}$

1540  $\text{cm}^{-1}$

1250  $\text{cm}^{-1}$

600  $\text{cm}^{-1}$

## Region of H bond :

3750-3300 $\text{cm}^{-1}$	-O-H	R-OH
		Ar-OH
		-CO-OH (2500-3300 $\text{cm}^{-1}$ ) (intermolecular H bond)
	-N-H	$\text{NH}_2$ dublet
3300-2700 $\text{cm}^{-1}$	-C-H	$\text{—C}\equiv\text{C—H}$ $=\text{C—H}$ Ar-H  $\longrightarrow$ 3030 $\text{cm}^{-1}$
3000-2700 $\text{cm}^{-1}$	-C-H	$\text{—CH}_3$ $\text{—CH}_2$ $\text{—CH}$ $\text{—C—H} \longrightarrow$ Fermi resonance $\text{O}$ $\text{  }$ $\text{O}$ (2900-2700 $\text{cm}^{-1}$ )

## Region of unsaturation :

2260-2150 $\text{cm}^{-1}$	Triple bonds	$-\text{C}\equiv\text{C}-$ $-\text{C}\equiv\text{N}$
1900-1650 $\text{cm}^{-1}$	$\begin{array}{c} \text{---C---H} \\    \\ \text{O} \end{array}$	$\text{R-CO-OH} \rightarrow 1650 \text{ cm}^{-1}$ $\text{R-CO-NH}_2 \rightarrow 1670 \text{ cm}^{-1}$ $\text{R-CO-R} \rightarrow 1715 \text{ cm}^{-1}$ $\text{R-CO-H} \rightarrow 1720 \text{ cm}^{-1}$ $\text{R-CO-OR}' \rightarrow 1735 \text{ cm}^{-1}$ $\text{R-CO-O-CO-R} \rightarrow 1750-1830 \text{ cm}^{-1}$
1675-1500 $\text{cm}^{-1}$	Double bonds	$-\text{C}=\text{C}-$ $-\text{C}=\text{N}-$ $-\text{N}=\text{N}-$

} aromatic and aliphatic

## Region of single bond:

1310-1085 $\text{cm}^{-1}$	C-O	R-O-R Ar-O-R Ar-O-Ar
----------------------------	-----	----------------------------

## Fingerprint region:

1250-600 $\text{cm}^{-1}$	C-H Fingerprint region
Substituted benzene	Mono substituted benzene: 750-700 $\text{cm}^{-1}$ Orto di substituted benzene: 750 $\text{cm}^{-1}$ Meta di substituted benzene: 810-780 $\text{cm}^{-1}$ Para di substituted benzene: 850-800 $\text{cm}^{-1}$