Bonga university

Instrumental Analysis II (Chem.2052)

Chapter 6

Infrared spectroscopy

2012 E.C

The Electromagnetic Spectrum

Visible

X-Rays

Microwave

Gamma
Rays

UV

IR

Radio

meters								
10^{-13}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}	10

cm								
10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}	10	10^{3}

Wavelength

nm								
10^{-4}	10^{-2}	10^{0}	10^{2}	10^{4}	10^{6}	10^{7}	10^{9}

Frequency Hz

10^{21}	10^{19}	10^{17}	10^{15}	10^{13}	10^{11}	10^{9}	10^{7}

Energy kcal

10^{8}	10^{6}	10^{4}	10^{2}	10^{0}	10^{-2}	10^{-4}	10^{-6}
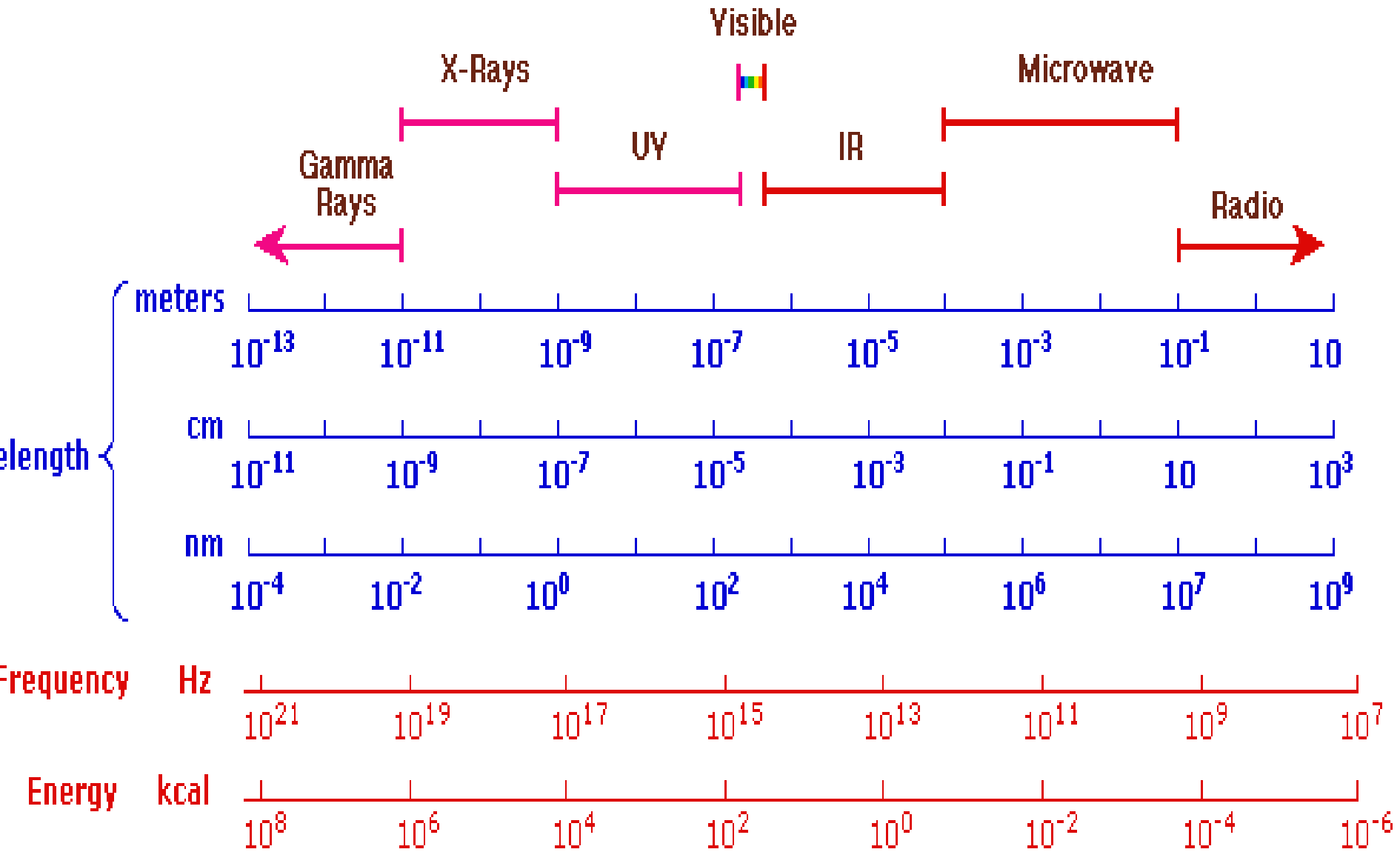
3.1 Introduction

❖ Absorption of electromagnetic radiation in the infrared region of the spectrum resulting in changes in the vibrational energy of molecules.

❖ This region covers approximately between 750 and 3000 nm. Thus, there are three sub regions in the IR region.

Region	Wavelength (μm)	Wave number (cm^{-1})	Energy (KJ/mol)
Near IR	0.78 – 2.5	12, 800 - 4000	150 - 50
Mid IR	2.5 – 50	4000-200	50 – 2.5
Far IR	50 – 1000	200 – 10	2.5 – 0.1

❖ Usually the IR region is expressed in terms of wavenumber instead of λ b/c wavenumber is directly related with frequency, wavenumber is read as frequency in IR region (It is not exactly frequency $\upsilon \neq \bar{\upsilon}$).

❖ IR radiation is not energetic enough to bring about the kind of electronic transition that we have encountered in UV-Vis. Thus, the transitions responsible for IR bands are due to molecular vibrations and rotations, i.e. to periodic motions involving stretching or bending of bonds.

❖ EMR of IR is absorbed by a molecule with a non-zero change in dipole moment during vibration. It is absorption of IR radiation due to the interaction of oscillating dipole moment of vibrating molecules and oscillating field of the IR radiation (i.e. molecule electric field (dipole moment) interacts with IR photon electric field).
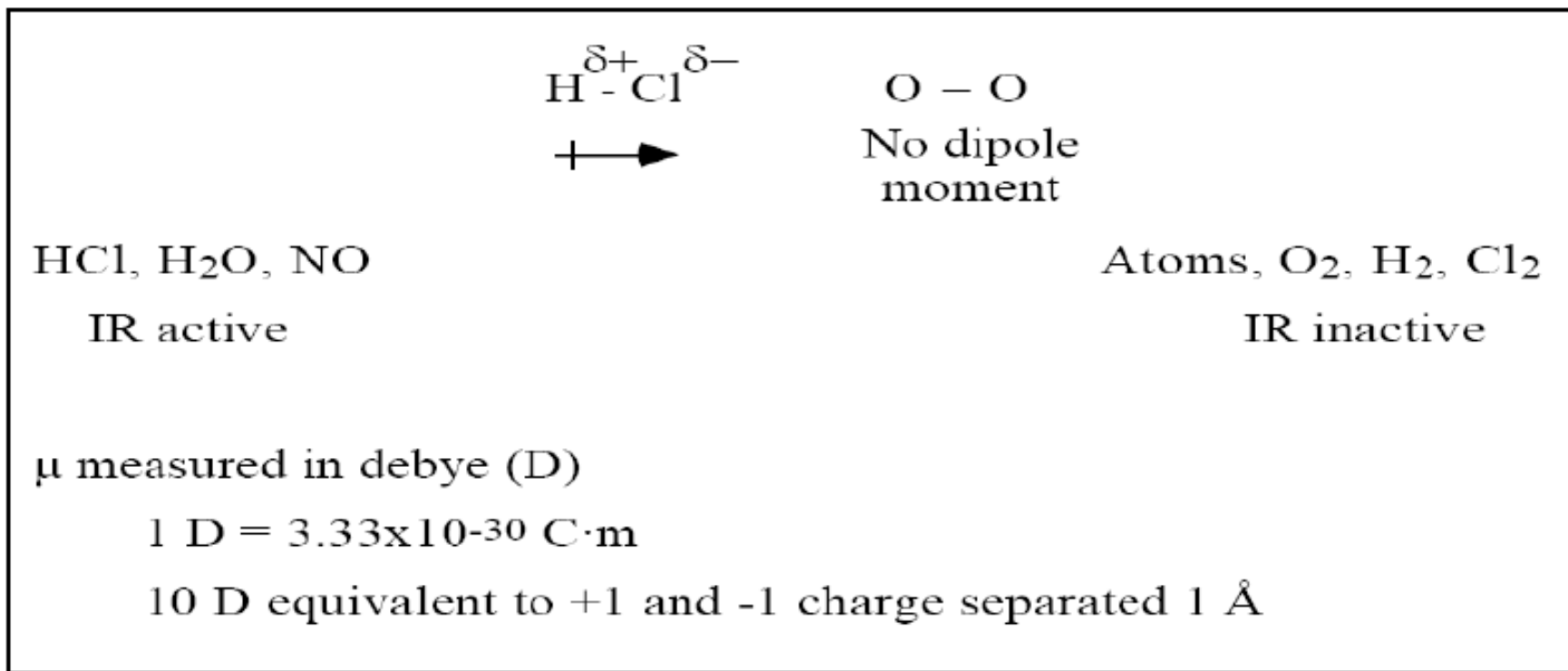
➢ Thus, homodiatomic molecules (homonuclear molecules) don't interact with the IR for net dipole change vibration.
  Examples: H_2, N_2, O_2, F_2, Cl_2, Br_2 and I_2

▪ Polar bonds are associated with strong IR absorptions while symmetrical bonds may not absorb at all. The magnitude of a dipole moment is determined by charge and separation of charge. Vibration or rotation causes varying separation of atoms in a molecule.
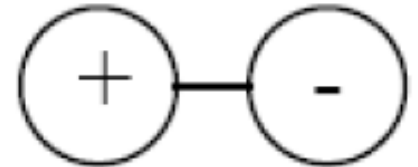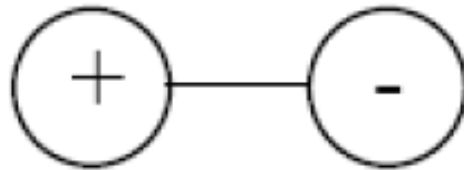
❖ Molecule must have change in dipole moment due to vibration or rotation to absorb IR radiation. Molecules with permanent dipole moments (μ) are IR active.
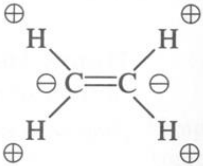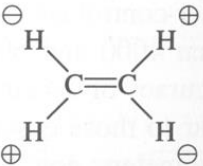
$$H \overset{\delta+}{-} Cl \overset{\delta-}{} \qquad O - O$$

$$\longmapsto \qquad \text{No dipole moment}$$

HCl, H$_2$O, NO   Atoms, O$_2$, H$_2$, Cl$_2$

   IR active   IR inactive

μ measured in debye (D)

    1 D = 3.33x10^{-30} C·m

    10 D equivalent to +1 and -1 charge separated 1 Å
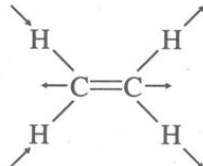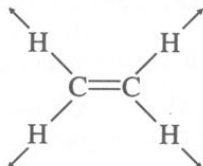
❖ IR spectrum is Absorption versus frequency.

Vibrational Modes: Examples

- **IR-activity requires dipole changes during vibrations!**

- **For example, this is Problem 16-3 from Skoog (6th edition):**

Molecule	Motion	
(a) CH_3—CH_3	C—C stretching	Inactive
(b) CH_3—CCl_3	C—C stretching	Active
(c) SO_2	Symmetric stretching	Active
(d) CH_2=CH_2	C—H stretching:	Active
(e) CH_2=CH_2	C—H stretching:	Inactive
(f) CH_2=CH_2	CH_2 wag:	Active
(g) CH_2=CH_2	CH_2 twist:	Inactive

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3.2. Energy levels in vibrating and rotating molecules

Types of Molecular Vibrations

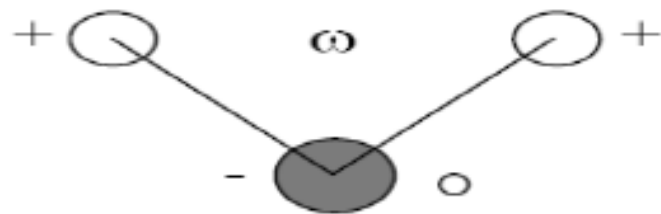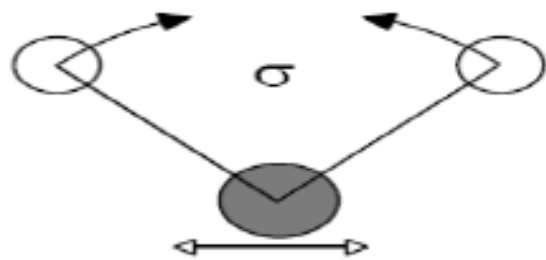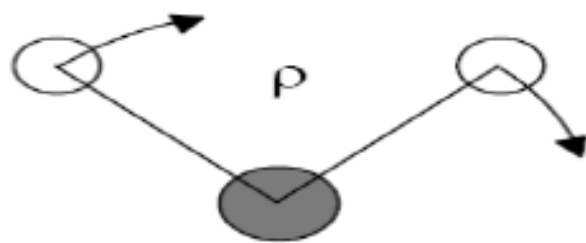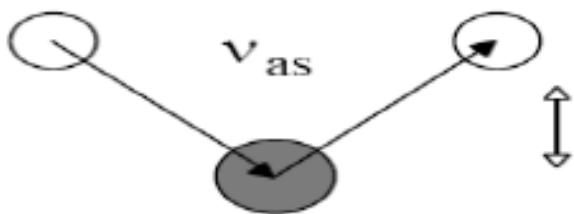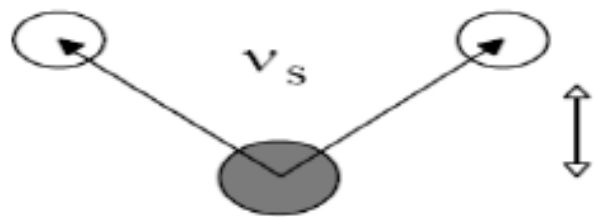There are two major vibration types. These are:

1. Stretching: involves change in bond length (bond angle is constant)
 ⬜ Symmetric
 ⬜ Asymmetric

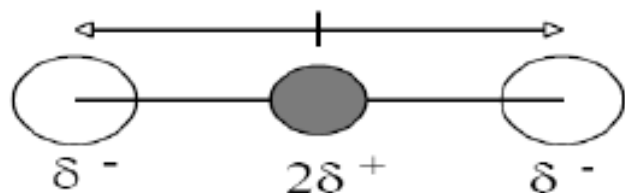2. Bending: involves change in bond angle (bond length is constant)
 ⬜ Rocking (in - plane)
 ⬜ Scissoring (in - plane)
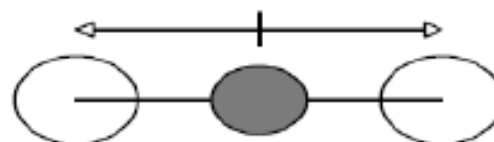 ⬜ Wagging (out – of - plane)
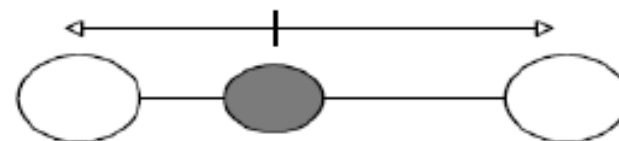 ⬜ Twisting/
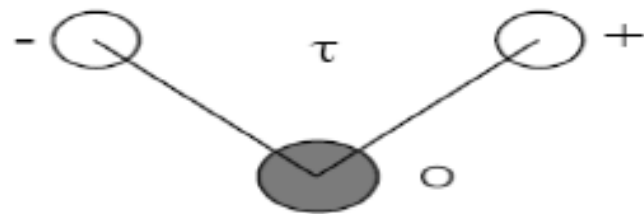
Only some modes may be IR active:

Example CO_2 $O=C=O$ linear

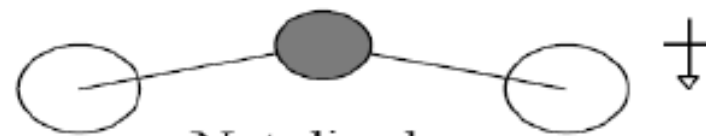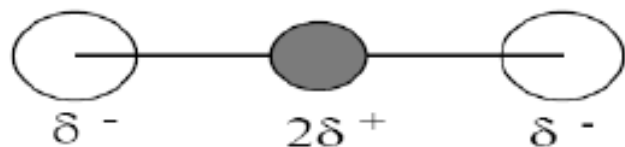δ^- $2\delta^+$ δ^-

No net dipole moment change

δ^- $2\delta^+$ δ^-

Net dipole moment change

δ^- $2\delta^+$ δ^-
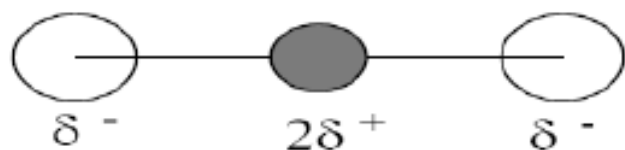
Net dipole moment change

ν_s not IR active ν_{as}, bend IR active

❖ Which needs more energy for stretching? The asymmetric because it increase the net dipole moment.

N.B	$E_{asy.stre}$	>	$E_{sym.stre}$	>	$E_{deformation}$

Example:
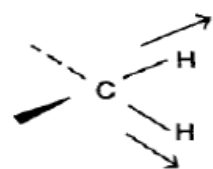
Symmetric stretch
(~2853 cm⁻¹)

Scissoring
(~1450 cm⁻¹)

Wagging
(~1250 cm⁻¹)

Asymmetric stretch
(~2926 cm⁻¹)
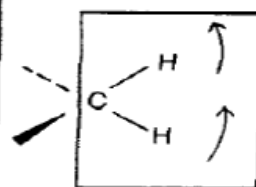
Rocking
(~720 cm⁻¹)

Twisting
(~1250 cm⁻¹)

IN-PLANE
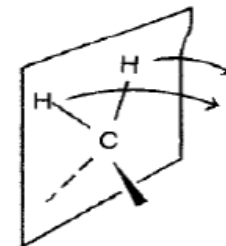
OUT-OF-PLANE
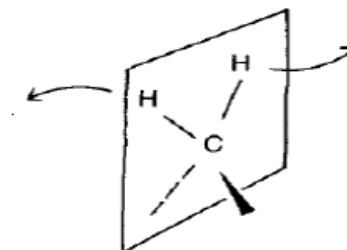
STRETCHING VIBRATIONS

BENDING VIBRATIONS

Molecular vibration

- Molecules are not rigid assemblage of atoms

- The common molecular vibrations that are excited by IR radiation are stretching vibrations and bending vibrations. These are called modes of vibration.

- Stretching involves a change in bond lengths

- Bending involves a change in bond angle
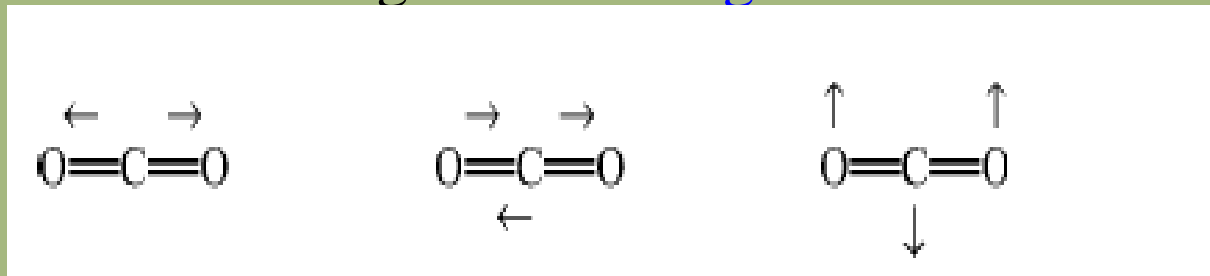
- The CO_2 molecule on the left is undergoing a symmetric stretch, the one in the middle an asymmetric stretch and the one on the right an in-plane bend. The symmetric

- For polyatomic molecules, the spectra are usually recorded as liquids, solids or in solution, the complexity of the spectrum increases rapidly with the number of atoms *N in the molecule.*

- The number of fundamentals or *normal modes of vibration is given by **3N – 6 and 3N – 5** for non linear and linear molecules respectively. A normal mode of vibration is defined as the movement of all the atoms of the molecule in phase. In the case of polyatomics, the number of fundamentals includes both stretching and bending vibrations.*

- **Example: How many vibrational modes?**

  2 atoms (H_2) - 1 vibration (stretch)

  3 atoms (H_2O) - 3 vibrations (v_s, v_{as}, σ)

  3 atoms (CO_2) - 4 vibrations (v_s, v_{as}, σ, ω)

  4 atoms (H_2CO) - 6 vibrations (v_s, v_{as}, σ, ω, $\rho(CH_2)$ v (C=O))

Harmonic oscillator and Hook's low

- The stretching frequency of a bond can be approximated by Hooke's Law.

- this approximation, two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring:

- According to Hooke's law, the frequency of the vibration of the spring is related to

- the mass and the force constant of the spring, k , by the following formula:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

where k is the force constant; m is the mass; υ is the frequency of the vibration

Bond Properties and Absorption trends
i. Force constant of the bond

❖As for any harmonic oscillator, when a bond vibrates its energy of vibration is continuously periodically changing from kinetic energy to Potential energy and back again.

❖ The classical analogy of a vibrating diatomic molecule is that of two weights connected by a spring.

❖ Force required to displace m is

$$F = -k \times y \qquad \text{Hooke's Law}$$

K = spring constant (N/m)

❖ Energy is force x distance

$$dE = -Fdy$$

$$dE = kydy$$

❖ Total energy is given by:

$$\int_0^E dE = k \int_0^y ydy$$

❖ Fig. Parabolic E vs. displacement curve of harmonic oscillator

Classical vibrational motion:

Mass m

Displacement y

-y

+y
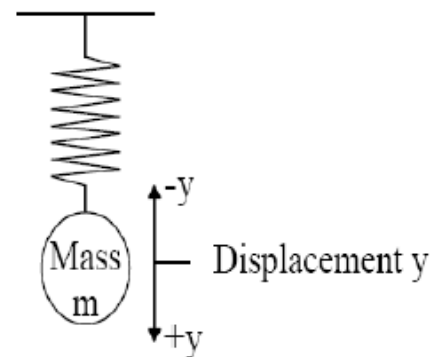
$$E = \frac{1}{2}ky^2$$

❖ Classical vibrational frequency for two atoms with masses m_1 and m_2 is given by:

$$v_{classical} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{or} \qquad \bar{v} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m1.m2}{m1+m2} \quad \text{(reduced mass)},$$

Where: $k \Rightarrow$ the force constant of the bond.

$\mu \Rightarrow$ reduced mass

$c \Rightarrow$ speed of light

- The following formula has been derived from Hooke's law. For the case of a diatomic molecule

$$E = h\nu = \frac{hc}{\lambda}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}}$$

where $\bar{\nu}$ is the vibrational frequency (cm^{-1})
  m_1 and m_2 are the mass of atoms 1 and 2, respectively, in g
  c is the velocity of light (cm/s)

f= force constant of the bond (dyne/cm)

How does the mass influence the vibration?

H_2

I_2

MM =2 g/mole

MM =254 g/mole
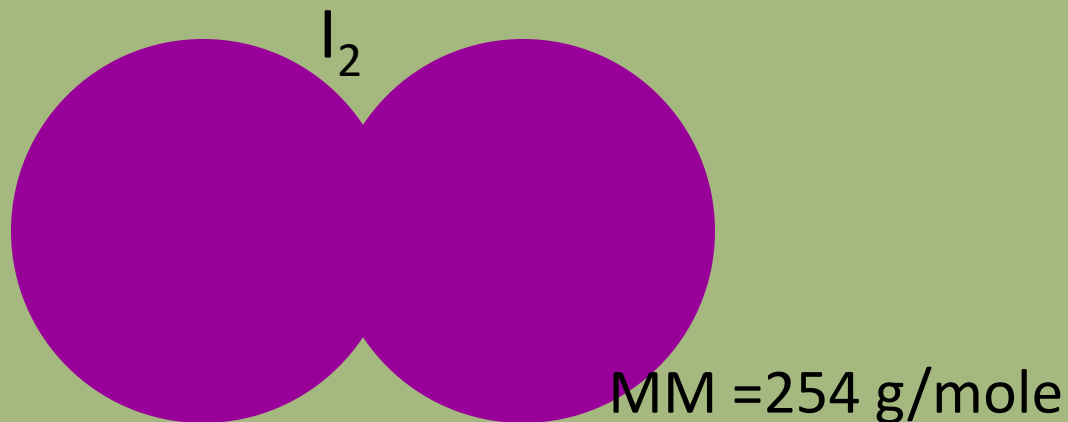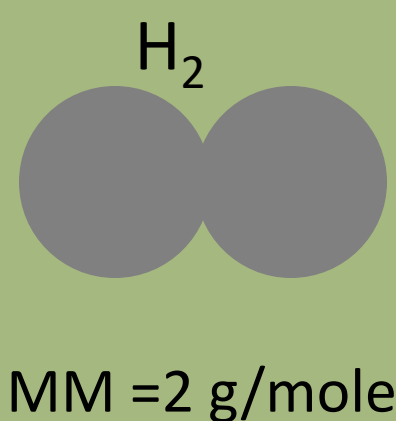
➢ **The greater the mass - the lower the wavenumber**

- the vibrational frequency of a bond would increase with the decrease in reduced mass of the system. It implies that C-H and O-H stretching absorptions should appear at higher frequencies than C-C and C-O stretching frequencies

- As the force constant increases, the vibrational frequency (wavenumber) also increases.

Examples of stretching frequencies and correlations with bond strengths (bond order)

	Bond strength*	Bond order	ν
C-C	350	1	1000 cm^{-1}
C=C	600	2	1600 cm^{-1}
C≡C	840	3	2200 cm^{-1}

*In kJ/mol

For same reduced mass!

The requirements for the absorption of IR radiation by molecules can be summarized as follows:

1. The natural frequency of vibration of the molecule must equal the frequency of the incident radiation.

2. The frequency of the radiation must satisfy $\Delta E = h\nu$, where ΔE is the energy difference between the vibrational states involved.

3. The vibration must cause a change in the dipole moment of the molecule.

• Some molecular vibrations may not give rise to absorption bands b/c

A. their frequency may fall out side the normal IR region (if heavy atom is present

B. some of vibration may have the same frequency and overlap

C. some vibration may not cause change is dipole moment of the molecule and some may give week band at normal conc.

- In addition to fundamental vibrations, other frequencies can be generated. Like overtones

- Over tone bands results in weak absorption

- Overtone bands appear at integral multiples of fundamental vibrations. Therefore, the strong absorptions at say 800 cm^{-1} and 1750 cm^{-1} will also give rise to weaker absorptions at 1600 cm^{-1} and 3500 cm^{-1}, respectively.

- In the IR spectra of benzaldehyde and acetophenone, due to C=O stretching vibration a weak overtone can be seen at 3400 and 3365 cm^{-1}, respectively.
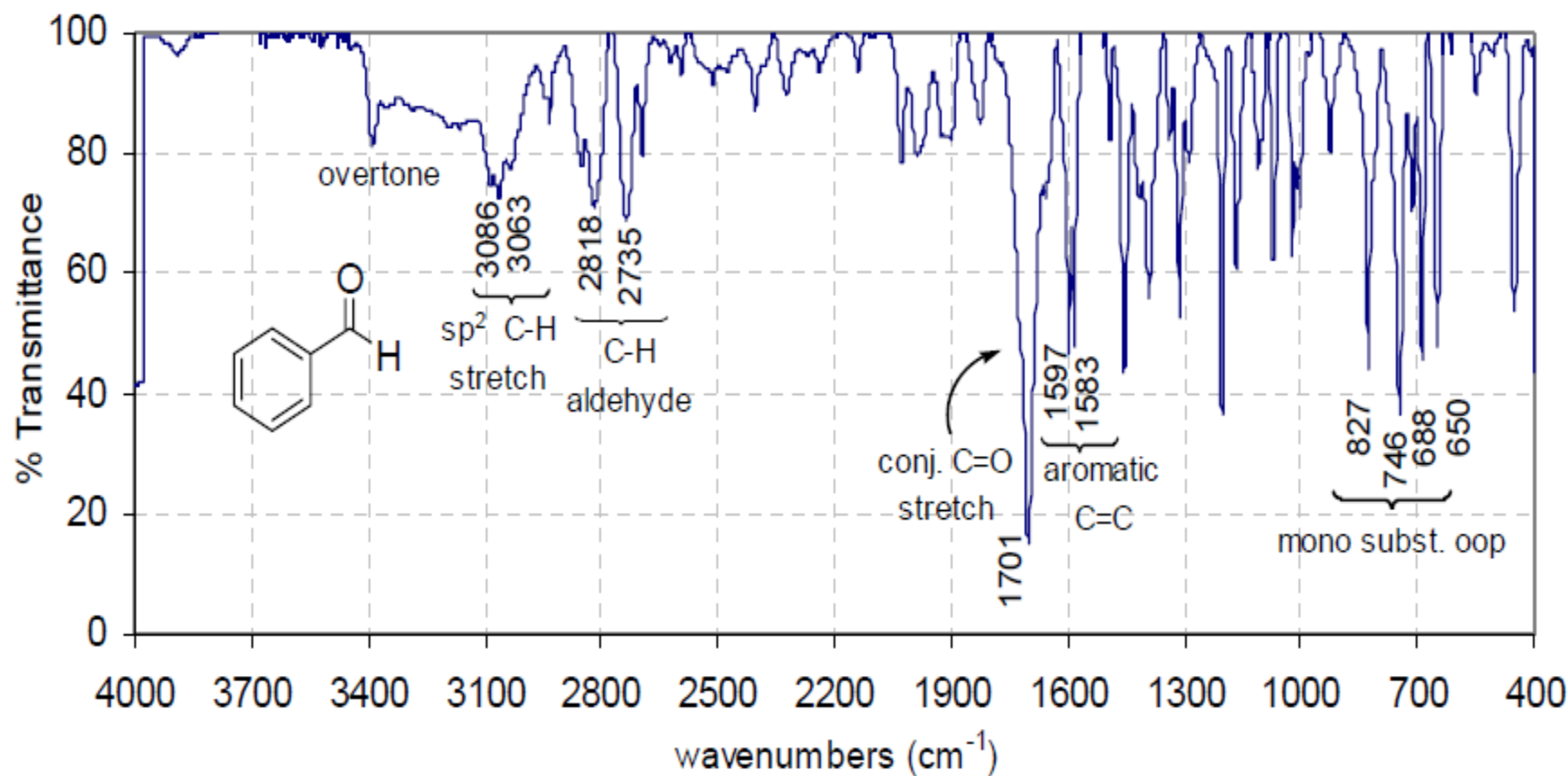
Figure 30 : The infrared spectrum of benzaldehyde (neat liquid)
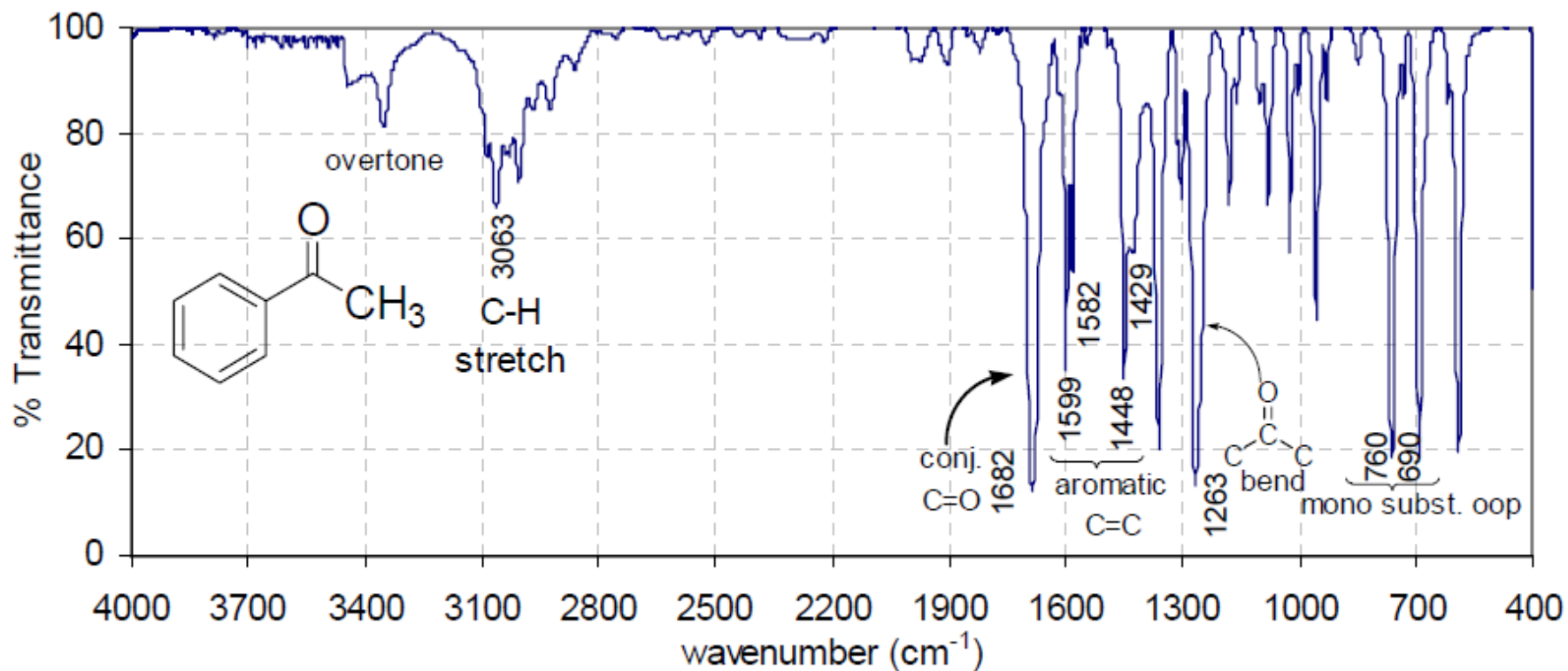
Figure 31 : The infrared spectrum of acetophenone (neat liquid)

- One interesting phenomenon which is occasionally occur when a fundamental frequency is near an overtone from some other frequency . The result is an increase in the intensity of the overtone and and decrease in the fundamental (fermi resonance)

- Vibrational coupling which complicates the spectra

- ** stretching absorption of a bond appears at higher frequency in the IR spectrum than bending absorption frequency of the same bond.

- ** assymetric stretching appears at higher enegry

- The vibrational frequency of a bond, being part of a molecule, is significantly affected by the electronic and steric factors of the surroundings, in addition to the bond strength and atomic masses discussed above.

- 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 (i) difference in mass between CH_3 and Cl (ii) the inductive or mesomeric influence of Cl on the C=O bond (iii) coupling interactions between C=O and C-Cl bonds (iv) change in bond angles arising due to steric factors etc.

Cyclohexanol
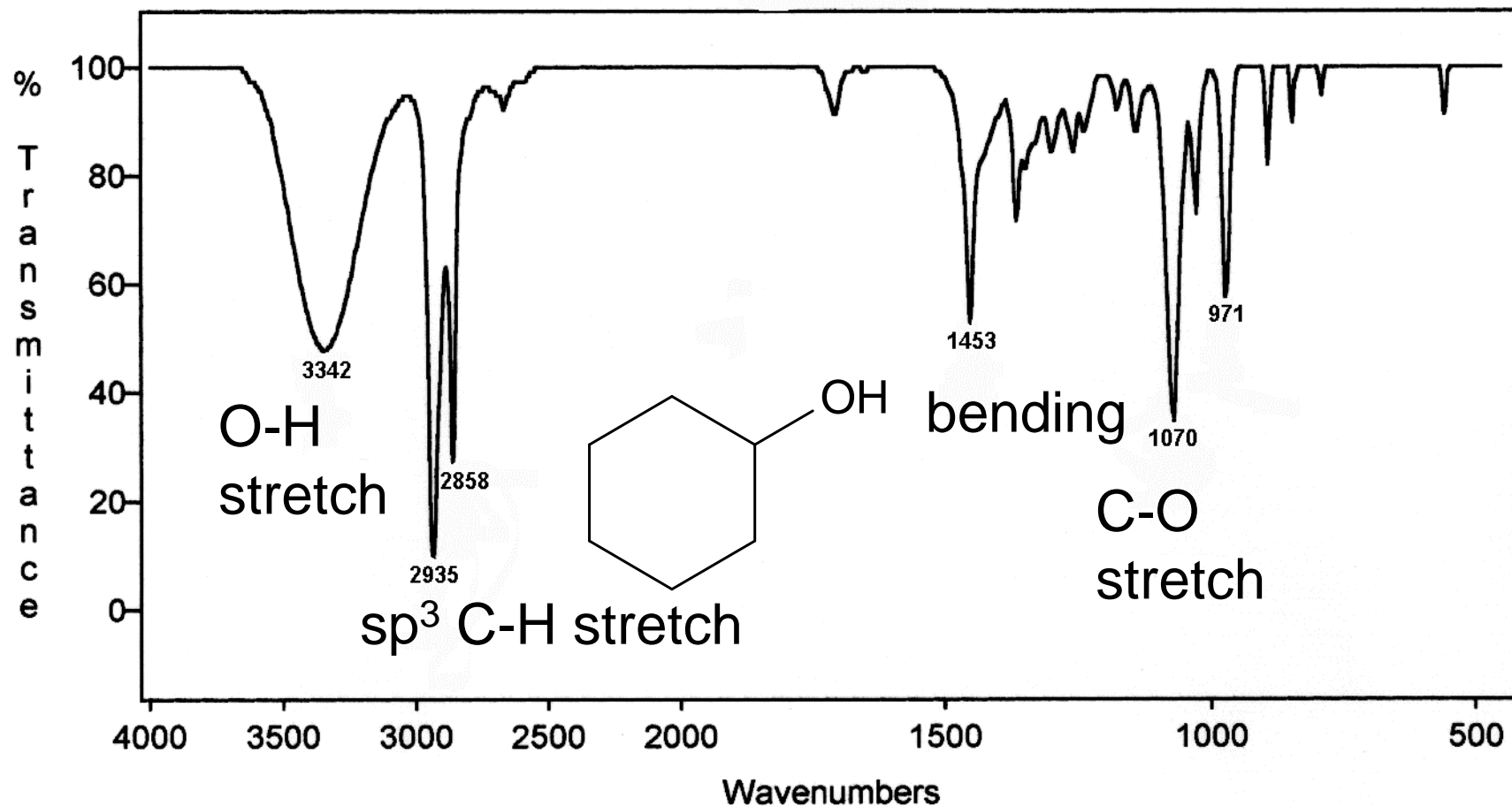
The "Fingerprint" Region:

- Small differences in the structure and constitution of a molecule result in significant changes in the distribution of absorption peaks in this region of the spectrum that extends from about 1200 to 700 cm^{-1}.

- As a consequence, a close match between two spectra in this fingerprint region constitutes strong evidence for the identity of compounds yielding the spectra.

- Exact interpretation of spectra in this region is seldom possible because of the complexity of the spectra. But it is unique and thus is "fingerprint" of a compound that is unlikely to be found even in other quite similar cpds. The use of this region to confirm the identity of a compound with the authentic sample is considerably more reliable

Application of IR spectroscopy

1. Establishing conclusively the identity of two samples that have identical spectra when determined in the same media

- Using the finger print region

2. Peaks in the functional group region (4000-1300 cm-1) are characteristics of a particular functional group such as –OH, -CH, -NH, -SH, C=O, C=C-H, and CΞC-H

3. Existence of strong peak in the region of 910-650 cm-1 indicates that the compound may aromatic . No compound is aromatic if there is no strong peak in this region

Quantification

Characteristic Vibrational Frequencies for Common Functional Groups

Frequency (cm^{-1})	Functional Group	Comments
3200-3500	alcohols (O-H)	Broad
	amine, amide (N-H)	Variable
	alkynes (C≡C-H)	Sharp
3000	alkane (C-C-H)	
	alkene (C=C-H)	
2100-2300	alkyne (C≡C-H)	
	nitrile (C≡N-H)	
1690-1760	carbonyl (C=O)	ketones, aldehydes, acids
1660	alkene (C=C)	Conjugation lowers amide frequency
	imine (C=N)	
	amide (C=O)	
1500-1570 1300-1370	nitro (NO$_2$)	
1050-1300	alcohols, ethers, esters, acids (C-O)	

Instrumentation of IR

TENSOR 27 and HYPERION 2000

- **Dispersive instruments**: with a monochromator to be used in the mid-IR region for spectral scanning and quantitative analysis.

- **Fourier transform IR (FTIR) systems**: widely applied and quite popular in the far-IR and mid-IR spectrometry.

- **Nondispersive instruments**: use filters for wavelength selection or an infrared-absorbing gas in the detection system for the analysis of gas at specific wavelength.

Instrumentation for Vibrational Spectroscopy

- **Two IR Absorption methods:**

    – **Dispersive methods:** Scanning of wavelengths using a grating (common examples are double-beam, like a spectrometer discussed in the optical electronic spectroscopy lecture).

| Radiation Source | → | Sample | → | Wavelength Selector | → | Detector (transducer) |
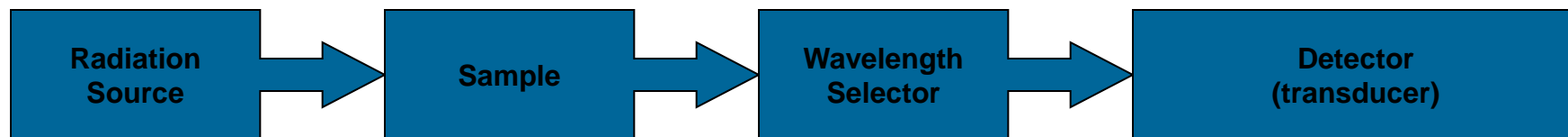
    – **Fourier-transform methods:** based on interferometry, a method of interfering and modulating IR radiation to encode it as a function of its frequency.

| Radiation Source | → | Interferometer | → | Sample | → | Detector (transducer) |
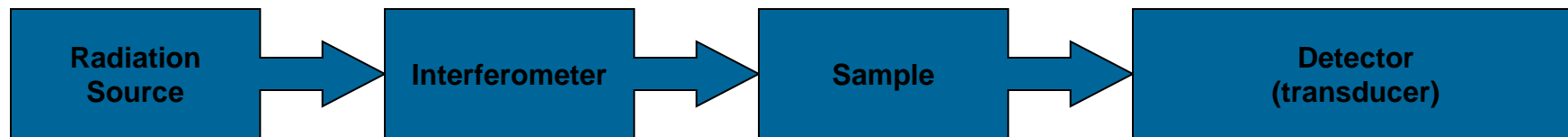
IR Emission Spectroscopy

- Emission is seldom used for chemical analysis

- The sample must be heated to a temperature much greater than its surroundings (destroying molecules)

- IR emission is widely used in astronomy and in remote sensing applications on heated materials.

Fourier Transform IR Spectroscopy: Rationale

- Advantages of FT methods:
  - The Jacqinot (throughput) advantage: FT instruments have few slits, or other sources of beam attenuation
  - Resolution/wavelength accuracy (Connes advantage): achieved by a colinear laser of known frequency
  - Fellgett (multiplex) advantage: all frequencies detected at once, signal averaging occurs and thermal noise grows more slowly than signal (good with IR detectors)
- These advantages are critical for IR spectroscopy
- The need for FT instruments is rooted in the detector
  - There are no transducers that can acquire time-varying signals in the 10^{12} to 10^{15} Hz range – they are not fast enough!
- Why are FT instruments not used in UV-Vis?
  - The multiplex disadvantage (shot noise) adversely affects signal averaging – it is better to multiplex with array detectors (such as the CCD in ICP-OES)
  - In some cases, there are technical challenges to building interferometers with tiny mirror movements

Inteferometers for FT-IR and FT-Raman

- The Michelson interferometer, the product of a famous physics experiment:
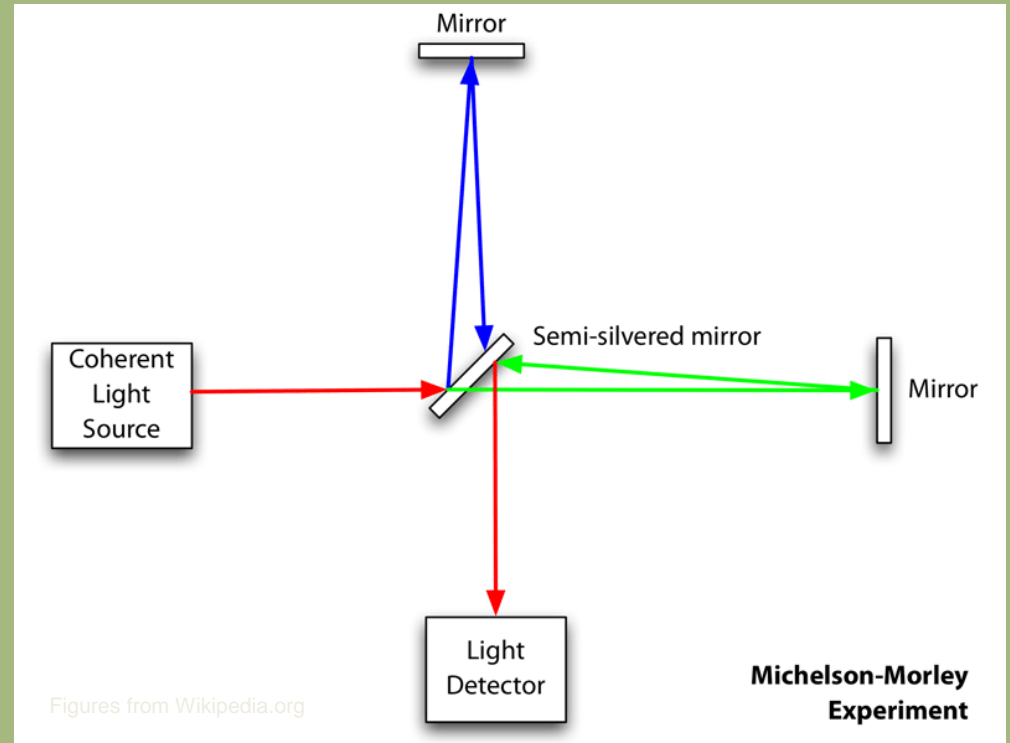
- Produces interference patterns from monochromatic and white light
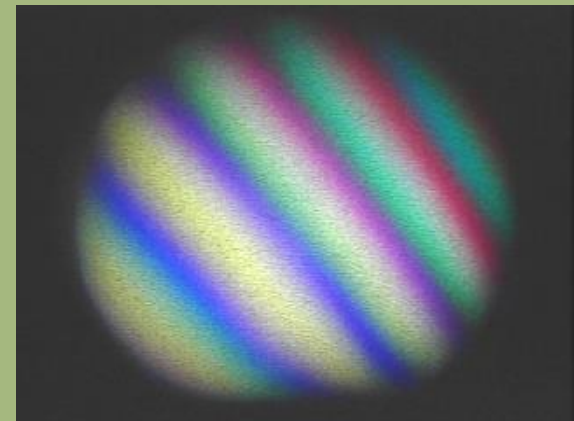
Inteferometers

- For monochromatic radiation, the interferogram looks like a cosine curve

- For polychromatic radiation, each frequency is encoded with a much slower amplitude modulation
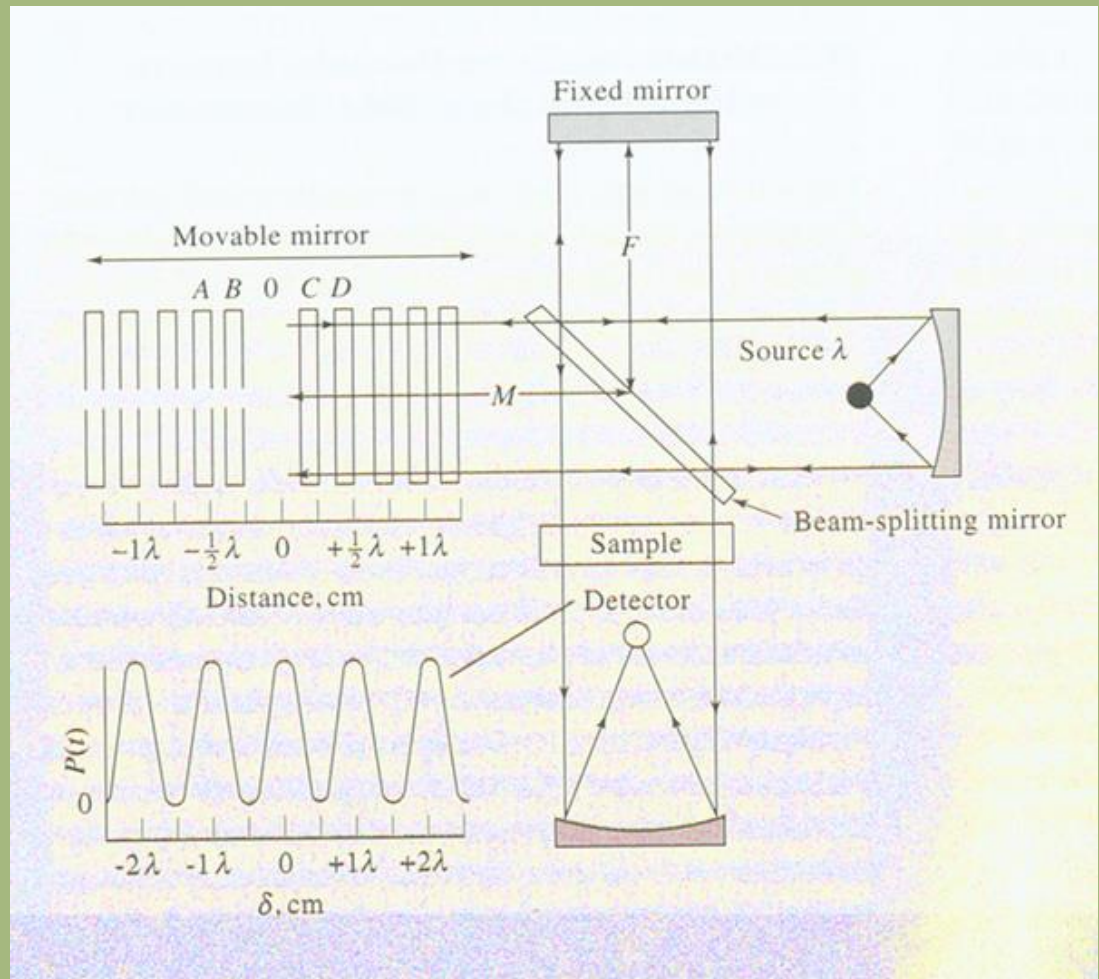
- The relationship between frequencies:

$$f = \frac{2v_M}{c} v$$

Where:
v is the frequency of the radiation
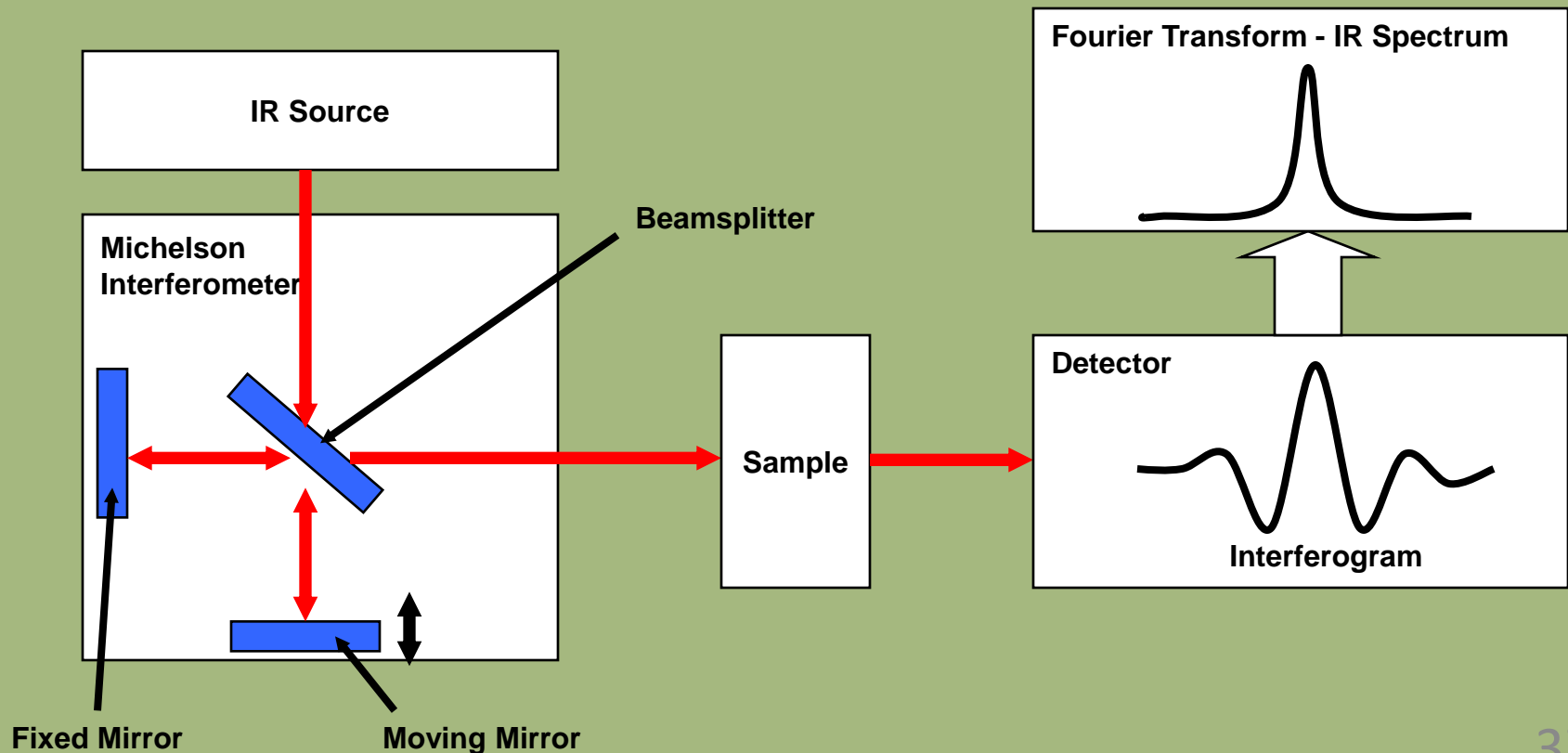c is the speed of light in cm/s
v_m is the mirror velocity in cm/s

- Example: mirror rate = 0.3 cm/s modulates 1000 cm^{-1} light at 600 Hz
- Example: mirror rate = 0.2 cm/s modulates 700 nm light at 5700 Hz

FTIR Spectrometer Design

- It is possible to build a detector that detects multiple frequencies for some EM radiation (ex. ICP-OES with CCD, UV-Vis DAD)

- FTIR spectrometers are designed around the Michelson interferometer, which modulates each IR individual frequency with an additional unique frequency well suited to the time response of IR detectors:

Fourier Transform - IR Spectrum

IR Source

Michelson Interferometer

Beamsplitter
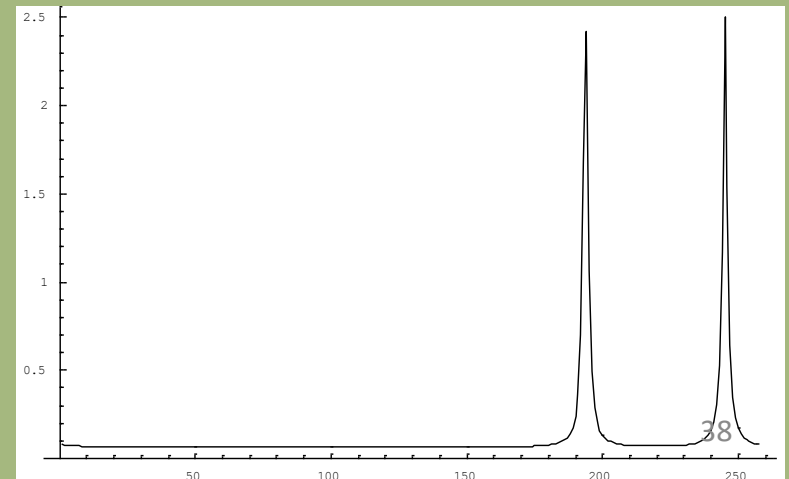
Sample

Detector

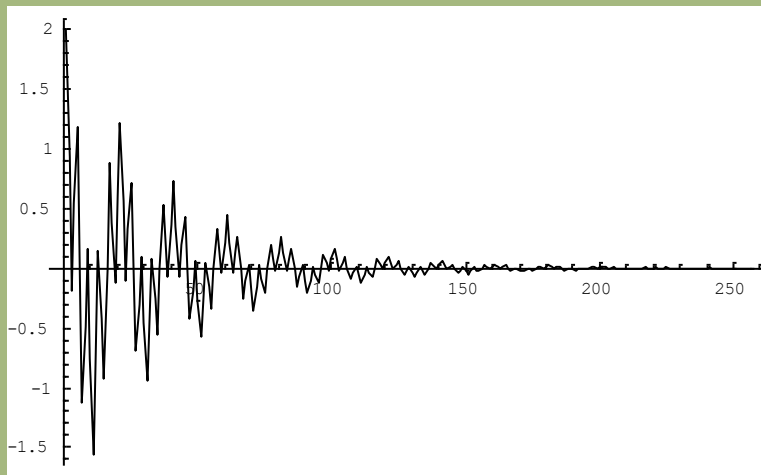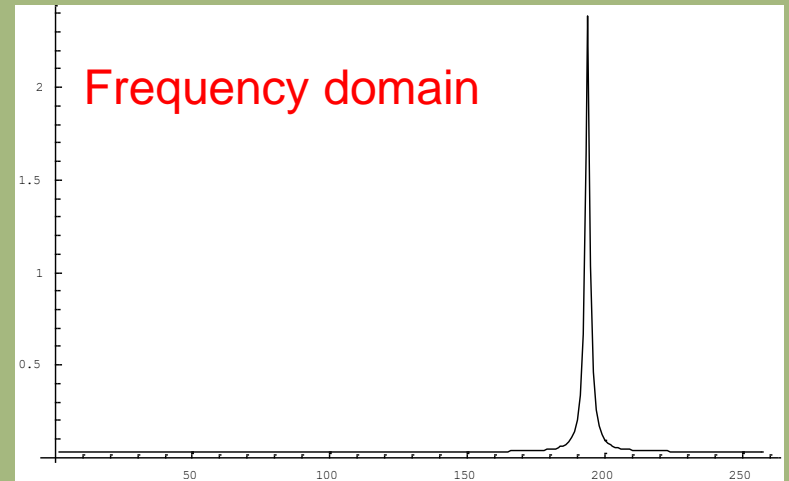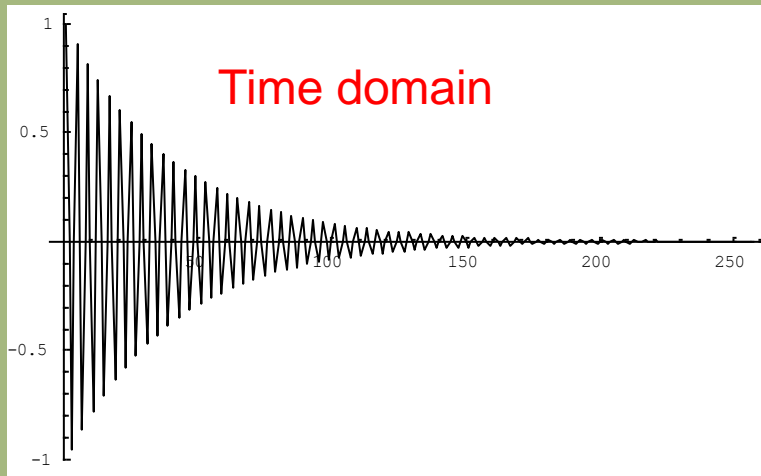Interferogram

Fixed Mirror

Moving Mirror

The Basics of the Fourier Transform

- The conversion from time- to frequency domain:

Continuous: $g(\omega) = \int\limits_{a}^{b} K^{-1}(\omega,t) f(t) d\omega \quad K(\omega,t) = \exp(-i\omega t)$

Discrete: $f_n = \dfrac{1}{\sqrt{N}} \sum\limits_{k=0}^{N-1} d_k e^{-2\pi i k n / N}$

Time domain

Frequency domain

FT

FT

IR source

Nernst Glower	A rod or cylinder made from several grams of rare earth oxides, heated to 1200-2200K by an electric current.	1-50 μm (mid- to far-IR)
Globar	Similar to the Nernst glower but made from silicon carbide SiC, electrically heated. Better performance at lower frequencies.heated	1-50 μm (mid- to far-IR)
Tungsten (W) filament lamp	Heated to 1100 K	0.78-2.5 μm (Near-IR)
Hg arc lamp	High-pressure mercury vapor tube, electric arc forms a plasma.	50 - 300 μm (far-IR)
CO_2 laser	High-intensity, tunable radiation used for quantitation of specific analytes	9-11 μm

Sample Handling

No good solvents exist that are transparent throughout the region of interest.

- As a consequence, sample handling is frequently the most difficult and time-consuming part of an infrared spectrometric analysis.

- For recording an IR spectrum, the sample may be gas, a liquid, a solid or a solution of any of these. The samples should be perfectly free of moisture, since cell materials (NaCl, KBr, CsBr etc.) are usually spoiled by the moisture.

Solvents:

- No single solvents is transparent throughout the entire mid-infrared region.

- Water and alcohols are seldom employed, not only because they absorb strongly, but also because they attack alkali-metal halides, the most common materials used for cell windows

Common IR Solvents
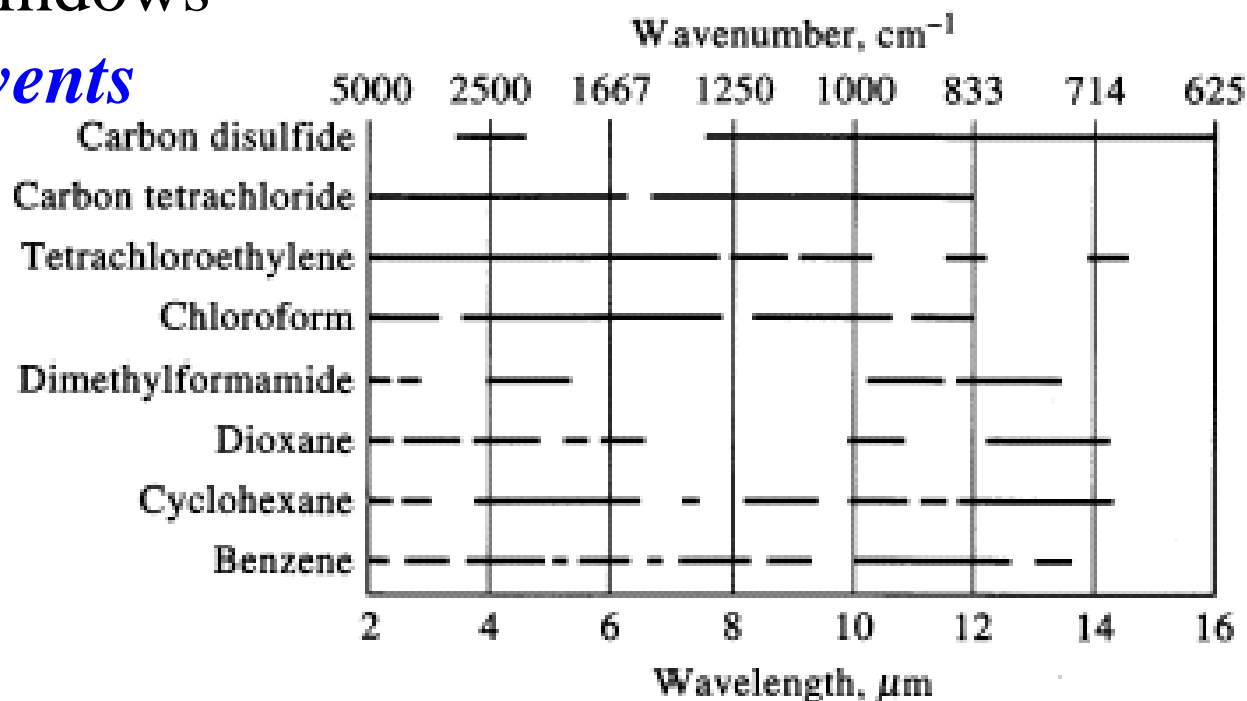
➢ The horizontal lines indicate regions where solvent transmits at least 25% of the incident radiation in a 1 mm cell.

Gas samples analysis

- A gas sample cell consists of a cylinder of glass or sometimes a metal. The cell is closed at both ends with an appropriate window materials (NaCl/KBr) and equipped with valves or stopcocks for introduction of the sample.

Liquid samples

- Liquids are studied neat or in solution. In case of neat liquid, a thin film of < 0.01 mm thickness is obtained by pressing the liquid between two sodium chloride plates and plates are subjected to IR beam.

- Spectra of solutions are obtained by taking 1-10 % solution of the sample in an appropriate solvent in cells of 0.1-1 mm thickness. A compensating cell, containing pure solvent is placed in the reference beam of the instrument. The choice of solvent depends on the solubility of the sample and its own minimal absorption in IR region. Carbon tetrachloride, chloroform and carbon disulfide are preferred solvents.

Solid samples

• Spectra of solids are obtained as alkali halide discs (KBr), mulls (e.g. Nujol, a highly refined mixture of saturated hydrocarbons) and films (solvent or melt casting)

Alkali halide discs:

1. A milligram or less of the fine ground sample mixed with about 100 mg of dry KBr powder in a mortar or ball mill.

2. The mixture compressed in a die to form transparent disc.

Mulls

1. Grinding a few milligrams of the powdered sample with a mortar or with pulverizing equipment. A few drops of the mineral oil added (grinding continued to form a smooth paste).

2. The IR of the paste can be obtained as the liquid sample.

IR Detectors

- **Thermal transducers**
  - Response depends upon heating effects of IR radiation (temperature change is measured)
    - Slow response times, typically used for dispersive instruments or special applications

- **Pyroelectric transducers**
  - **Pyroelectric:** insulators (dielectrics) which retain a strong electric polarization after removal of an electric field, while they stay below their Curie temperature.
  - **DTGS (deuterated triglycine sulfate):** Curie point ~47°C
    - Fast response time, useful for interferometry (FTIR)

- **Photoconducting transducers**
  - **Photoconductor:** absorption of radiation decreases electrical resistance. Cooled to LN_2 temperatures (77K) to reduce thermal noise.
  - **Mid-IR:** Mercury cadmium telluride (MCT)
  - **Near-IR:** Lead sulfide (NIR)

Plan of attack (plan of analyzing IR spectra)

❖ When analyzing the spectrum of an unknown compound concentrate your first effort on determining the presence or absence of important and common functional groups like C=O, **O–H,** -C≡N, C≡C-, etc. Thus it is very important to find the degree of unsaturation.

Degree of unsaturation = ring + double bond
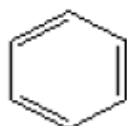
$$r + db = n - \frac{m}{2} + \frac{t}{2} + 1$$

Where n – number of tetravalent atoms

m – number of monovalent atom

t - number of trivalent atom

➤ The r+ db gives almost 20 % to 30 % unsaturation. The degree of unsaturation is at least 4. If the molecular formula is given, it is possible to find r+ db if not from the given spectrum we can determine it.

Example:

1 ring + 4 double bond = 4

Interpretation of IR Sprctra

- **Step 1**
  - Look first for the carbonyl C=O band.
  - Look for a strong band at 1820-1660 cm^{-1}.

  This band is usually the most intense absorption band in a spectrum. It will have a medium width. If you see the carbonyl band, look for other bands associated with functional groups that contain the carbonyl by going to step 2.
  - If no C=O band is present, check for alcohols and go to step 3.

- **Step 2**
  - If a C=O is present you want to determine if it is part of an acid, an ester, or an aldehyde or ketone. At this time you may not be able to distinguish aldehyde from ketone.

47

- **ACID**
  - Look for indications that an O-H is also present.
  - It has a broad absorption near 3300-2500 cm^{-1}.
  - This actually will overlap the C-H stretch. There will also be a C-O single bond band near 1100-1300 cm^{-1}.
  - Look for the carbonyl band near 1725-1700 cm^{-1}.
- **ESTER**
  - Look for C-O absorption of medium intensity near 1300-1000 cm^{-1}.
  - There will be no O-H band.

- **ALDEHYDE**
  - Look for aldehyde type C-H absorption bands. These are two weak absorptions to the right of the C-H stretch near 2850 cm^{-1} and 2750 cm^{-1} and are caused by the C-H bond that is part of the CHO aldehyde functional group.
  - Look for the carbonyl band around 1740-1720 cm^{-1}.
- **KETONE**
  - The weak aldehyde CH absorption bands will be absent. Look for the carbonyl CO band around 1725-1705 cm^{-1}.
- **Step 3**
  - If no carbonyl band appears in the spectrum, look for an alcohol O-H band.
- **ALCOHOL**
  - Look for the broad OH band near 3600-3300 cm^{-1} and a C-O absorption band near 1300-1000 cm^{-1}.

- **Step 4**
  - If no carbonyl bands and no O-H bands are in the spectrum, check for double bonds, C=C, from an aromatic or an alkene.
- **ALKENE**
  - Look for weak absorption near 1650 cm^{-1} for a double bond. There will be a CH stretch band near 3000 cm^{-1}.
- **AROMATIC**
  - Look for the benzene, C=C, double bonds which appear as medium to strong absorptions in the region 1650-1450 cm^{-1}. The CH stretch band is much weaker than in alkenes.

  - Also check the region of 950-650 cm-1 and around 3030 cm-1 (the –CH stretching)

C-H stretching region

- Alkanes C-H sp^3 stretch < 3000 cm^{-1}
- Alkenes C-H sp^2 stretch > 3000 cm^{-1}
- Alkynes C-H sp stretch ~ 3300 cm^{-1}
- **C-H Bending region**
- CH$_2$ bending ~ 1460 cm^{-1}
- CH$_3$ bending (asym) appears near the same value
- CH$_3$ bending (sym) ~ 1380 cm^{-1}

- **Step 5**
  - If none of the previous groups can be identified, you may have an alkane.
- **ALKANE**
  - The main absorption will be the C-H stretch near 3000 cm^{-1}. The spectrum will be simple with another band near 1450 cm^{-1}.
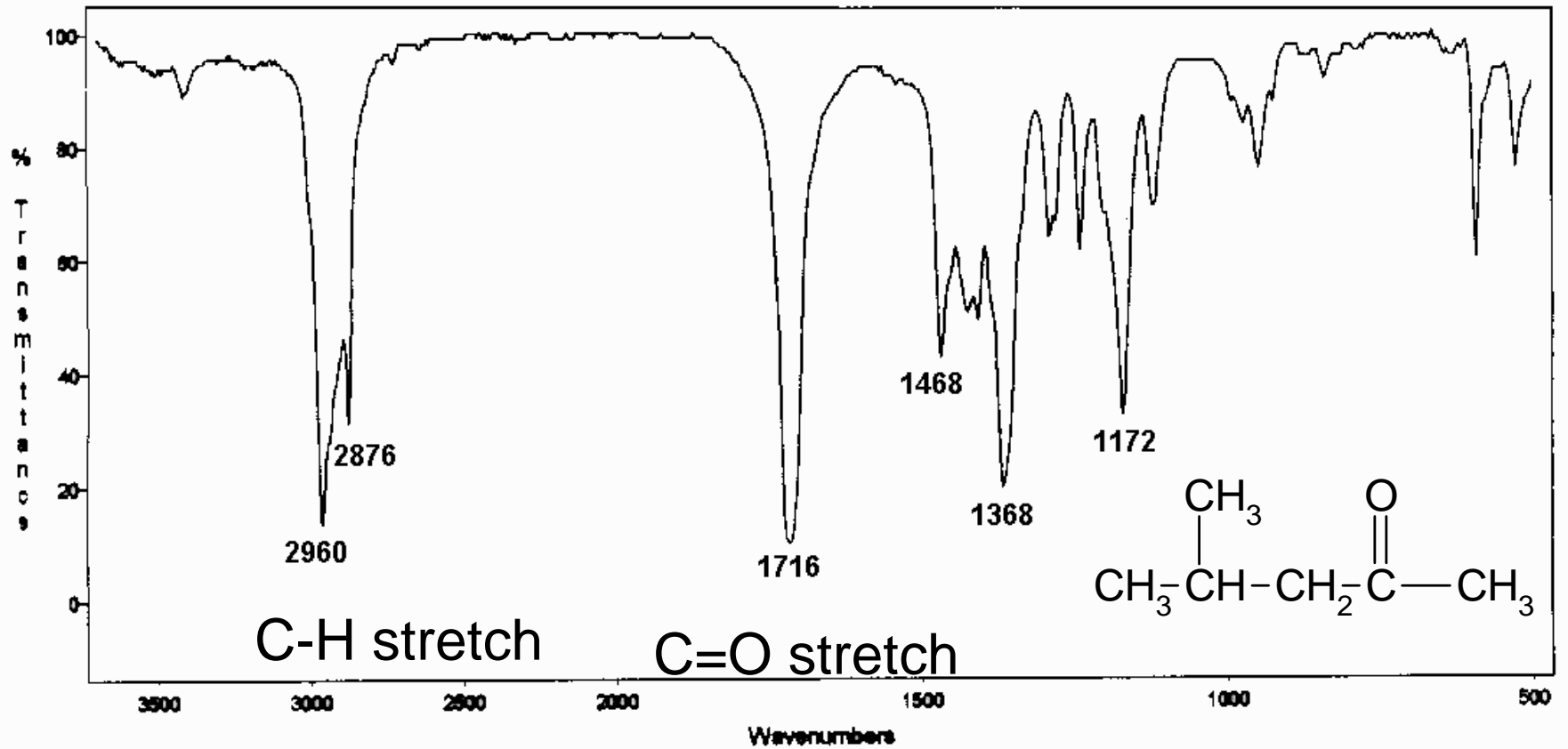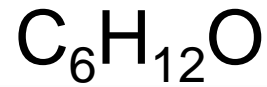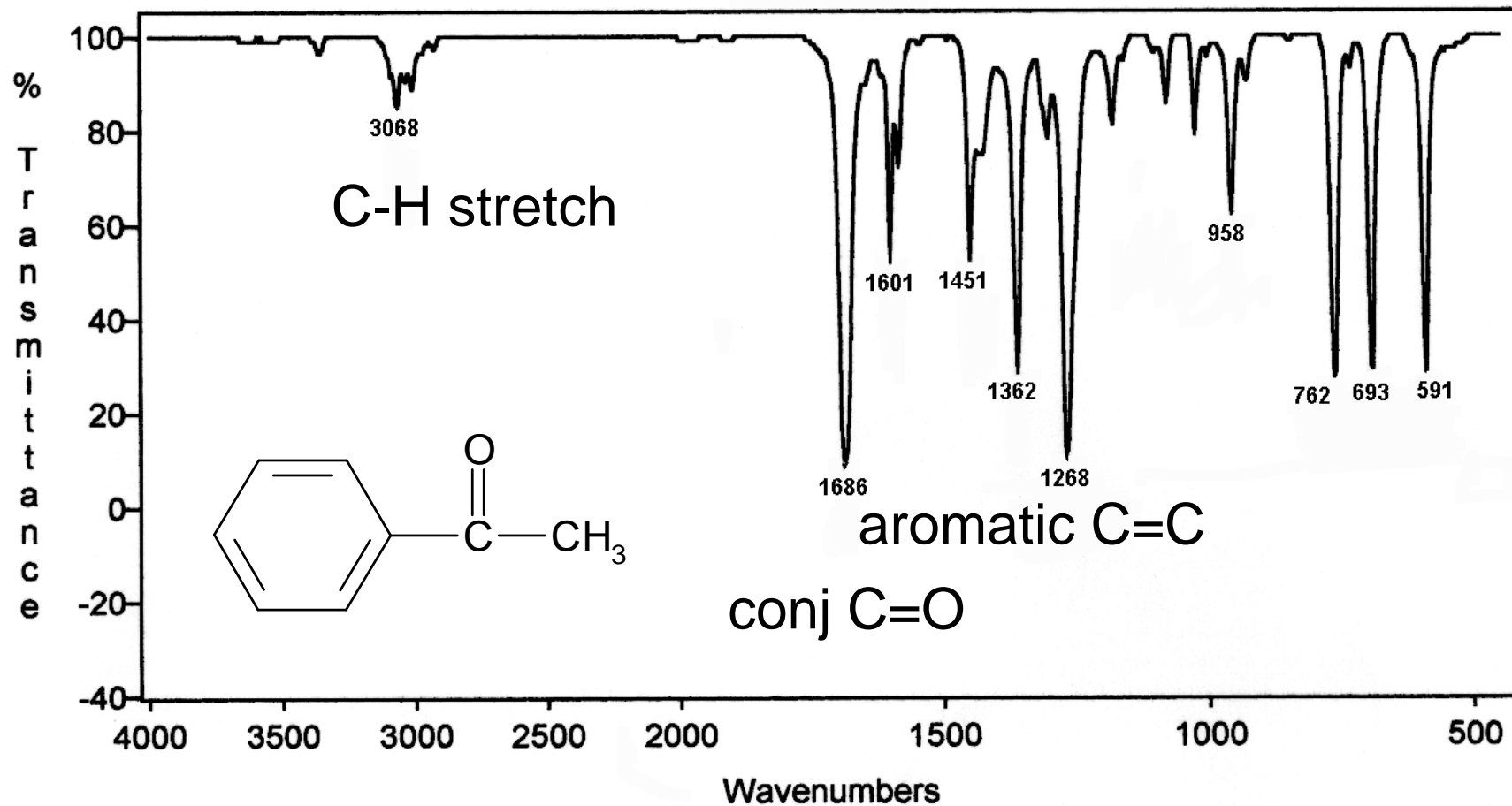- **Step 6**
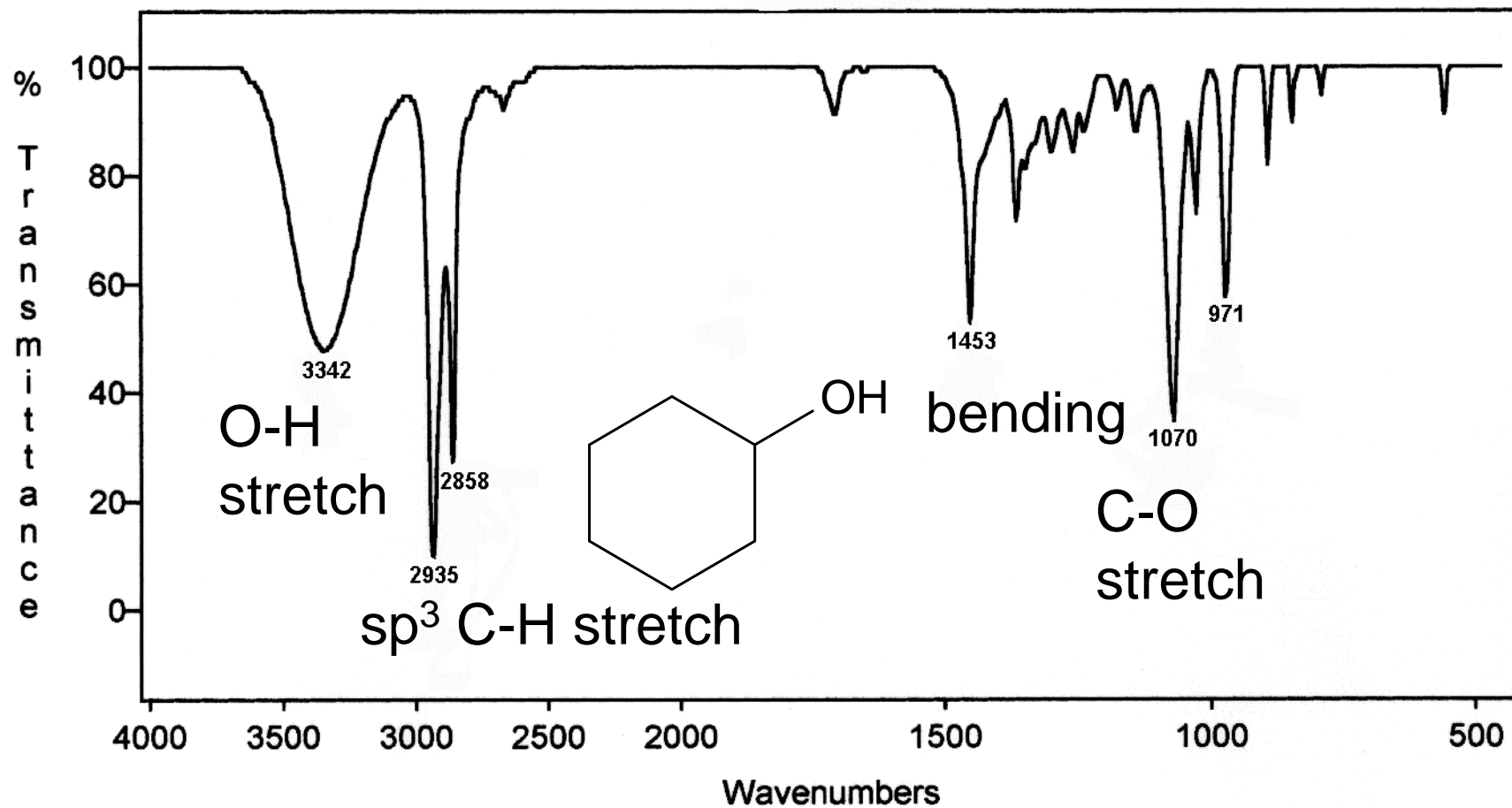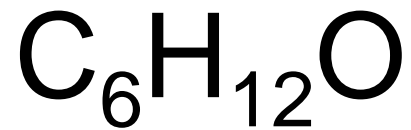 - If the spectrum still cannot be assigned you may have an alkyl halide.
- **ALKYL BROMIDE**
  - Look for the C-H stretch and a relatively simple spectrum with an absorption to the right of 667 cm^{-1}.

Examples

$C_6H_{12}O$

C-H stretch   C=O stretch

C_8H_8O

$C_6H_{12}O$

Thank You !