

## Infrared Spectrometry (Chapter 16 & 17)

~750-3000 nm

Region	Energy (kJ/mol)	Wavenumber (cm <sup>-1</sup> )	Wavelength (μm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-200	2.5-50
Far IR	2.5-0.1	200-10	50-1000

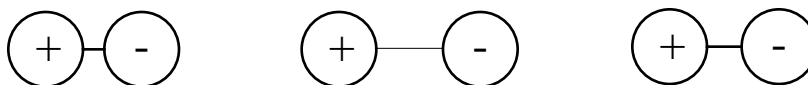
Energy of IR photon insufficient to cause electronic excitation but can cause **vibrational** or **rotational** excitation

Molecule electric field (dipole moment) interacts with IR photon electric field (**both dynamic**)

Magnitude of dipole moment determined by

- (i) charge
- (ii) separation of charge

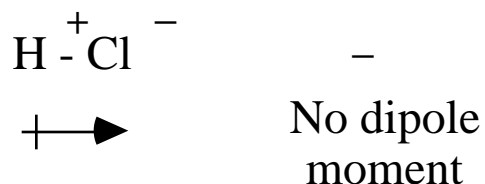
Vibration or rotation causes varying separation



Molecule must have change in dipole moment due to vibration or rotation to absorb IR radiation

Absorption causes increase in vibration amplitude/rotation frequency

Molecules with permanent dipole moments ( $\mu$ ) are IR active



HCl, H<sub>2</sub>O, NO

IR active

Atoms, O<sub>2</sub>, H<sub>2</sub>, Cl<sub>2</sub>

IR inactive

$\mu$  measured in debye (D)

$$1 \text{ D} = 3.33 \times 10^{-30} \text{ C}\cdot\text{m}$$

10 D equivalent to +1 and -1 charge separated 1 Å

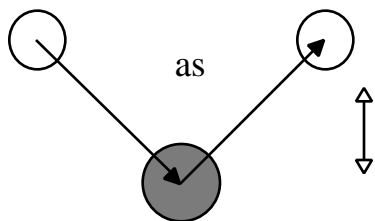
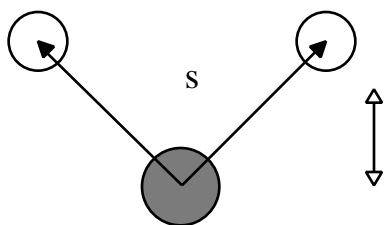
# Types of Molecular Vibrations:

## Stretch

change in bond length

symmetric

asymmetric



## Bend

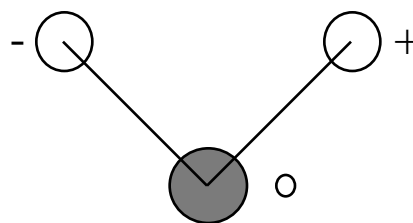
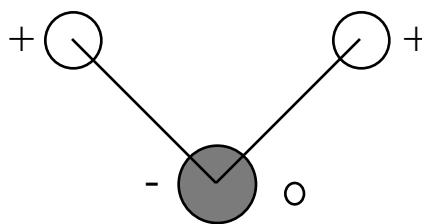
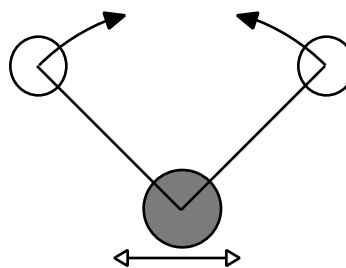
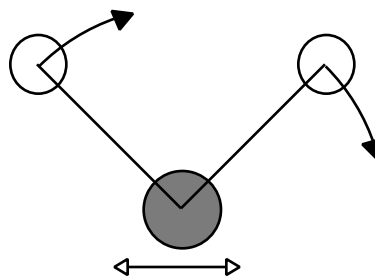
change in bond angle

scissoring

wagging

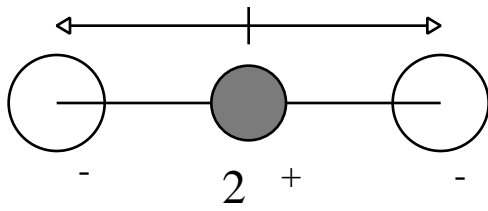
rocking

twisting/torsion

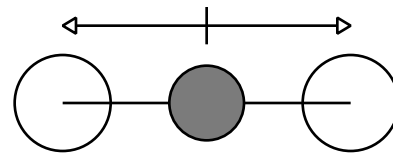


Only some modes may be IR active:

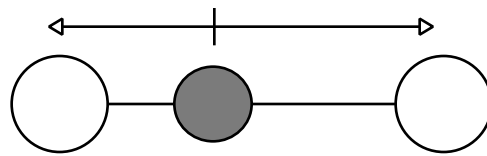
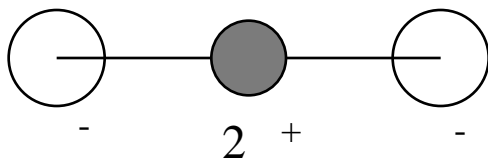
Example CO<sub>2</sub>



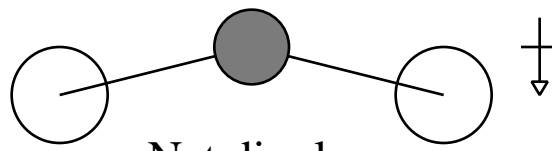
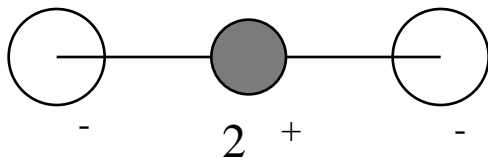
O=C=O linear



No net dipole moment change



Net dipole moment change

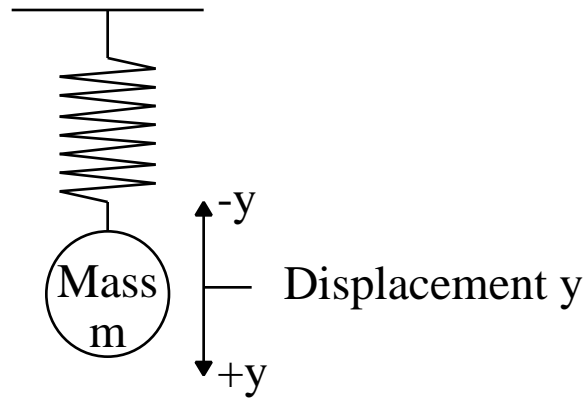


Net dipole moment change

s not IR active

as, bend IR active

## Classical vibrational motion:



Force required to displace  $m$  is

$$F = -k y$$

Hooke's Law

spring constant (N/m)

Energy is force  $\times$  distance

$$dE = -Fdy$$

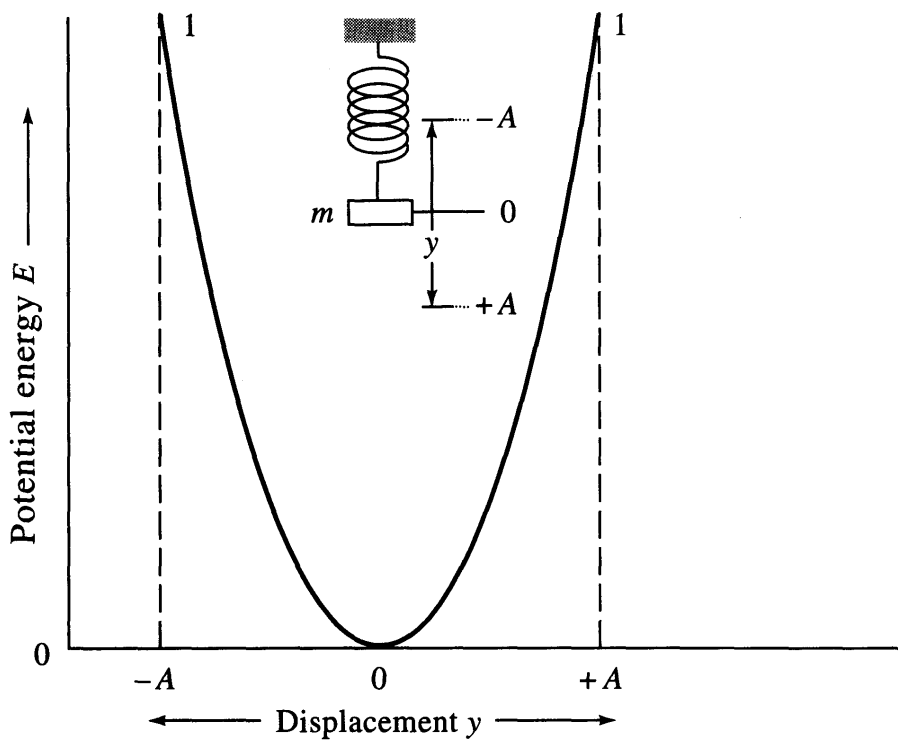
$$dE = kydy$$

Total Energy

$$E = \int_0^y ky dy$$

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

Parabolic E vs. displacement curve of **harmonic oscillator**



(Fig 16-3)

## Classical vibrational frequency:

$$\text{classical} = \frac{1}{2} \sqrt{\frac{k}{m}} \quad \text{independent of energy}$$

Two masses?

$$\text{classical} = \frac{1}{2} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}$$

What about quantum mechanics?

$$(1) \quad E = \left( n + \frac{1}{2} \right) \frac{h}{2} \sqrt{\frac{k}{\mu}} = \left( n + \frac{1}{2} \right) h \quad \text{classical}$$

Vibrational quantum number (0, 1, 2... )

$$E_0 = \frac{1}{2} h \quad \text{classical} \quad \text{Ground vibrational state ( } n = 0 \text{)}$$

$$E_1 = \frac{3}{2} h \quad \text{classical} \quad \text{First excited state ( } n = 1 \text{)}$$

$$E = h \quad \text{classical}$$

Calculated  $E$  often agrees quite well with experiment

$$\text{calculated (C=O)} = 1600 \text{ cm}^{-1} \quad \text{experiment (C=O)} = 1600\text{-}1800 \text{ cm}^{-1}$$

See example 16-1

$$(2) \quad \Delta n = \pm 1 \quad \text{Vibrational Selection Rule}$$

Since levels equally spaced - should see one absorption frequency

## Anharmonic oscillator:

Must modify harmonic oscillator potential for

- (i) electron repulsion (steeper at small distances)
- (ii) dissociation (bond breaks at large distances)

New E-y curve:

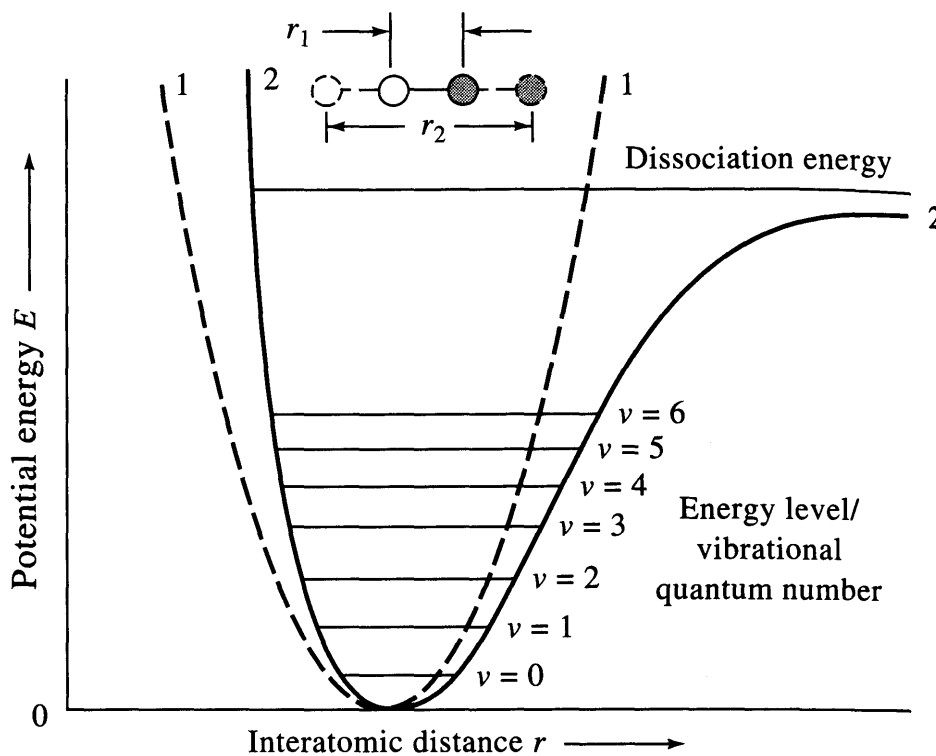


Fig 16-3

Three consequences

- (1) Harmonic at low
- (2)  $E$  becomes smaller at high (broadens band)
- (3) Selection rule fails  $= \pm 1$  and  $= \pm 2 \dots$  (overtones)



## How many vibrational modes?

2 atoms (H<sub>2</sub>) - 1 vibration (stretch )

3 atoms (H<sub>2</sub>O) - 3 vibrations ( s, as, )

3 atoms (CO<sub>2</sub>) - 4 vibrations ( s, as, , )

4 atoms (H<sub>2</sub>CO) - 6 vibrations ( s, as, , , (CH<sub>2</sub>) (C=O))

5 atoms ...

3N - 6 Non-linear molecule

3N - 5 Linear molecule

"Normal modes"

**Coupling** of different vibrations shifts frequencies

Coupling **likely** when:

- (1) common atom in stretching modes
- (2) common bond in bending modes
- (3) common bond in bending+stretching modes
- (4) similar vibrational frequencies

Coupling **not likely** when

- (1) atoms separated by two or more bonds
- (2) symmetry inappropriate

Example	(C-O) in	methanol	1034 cm <sup>-1</sup>
		ethanol	1053 cm <sup>-1</sup>
		butanol	1105 cm <sup>-1</sup>

## Instrumentation:

### Sources

Nernst Glower	heated rare earth oxide rod (~1500 K)	1-10 $\mu\text{m}$
Globar	heated SiC rod (~1500 K)	1-10 $\mu\text{m}$
W filament lamp	1100 K	0.78-2.5 $\mu\text{m}$
Hg arc lamp	plasma	>50 $\mu\text{m}$
CO <sub>2</sub> laser	stimulated emission lines	9-11 $\mu\text{m}$

### Transducers

Thermocouple	thermoelectric effect - dissimilar metal junction	cheap, slow, insensitive
Bolometer	Ni, Pt resistance thermometer (thermistor) at 1.5 K	highly sensitive <400 $\text{cm}^{-1}$
Pyroelectric	triglycine sulfate piezoelectric material	fast and sensitive (mid IR)
Photoconducting	PbS, HgCdTe light sensitive resistance thermometer at 77 K	fast and sensitive

IR beam  $10^{-7}$ - $10^{-9}$  W, T at transducer mK- $\mu\text{K}$

## Dispersive Grating IR Instruments:

Similar to UV-Vis spectrophotometer

BUT sample after source and before monochromator in IR (sample after monochromator in UV-Vis - less incident light)

Grating 10-500 lines per mm

Single beam and double beam (in time and space)

much more useful

eliminates atmospheric gas interference

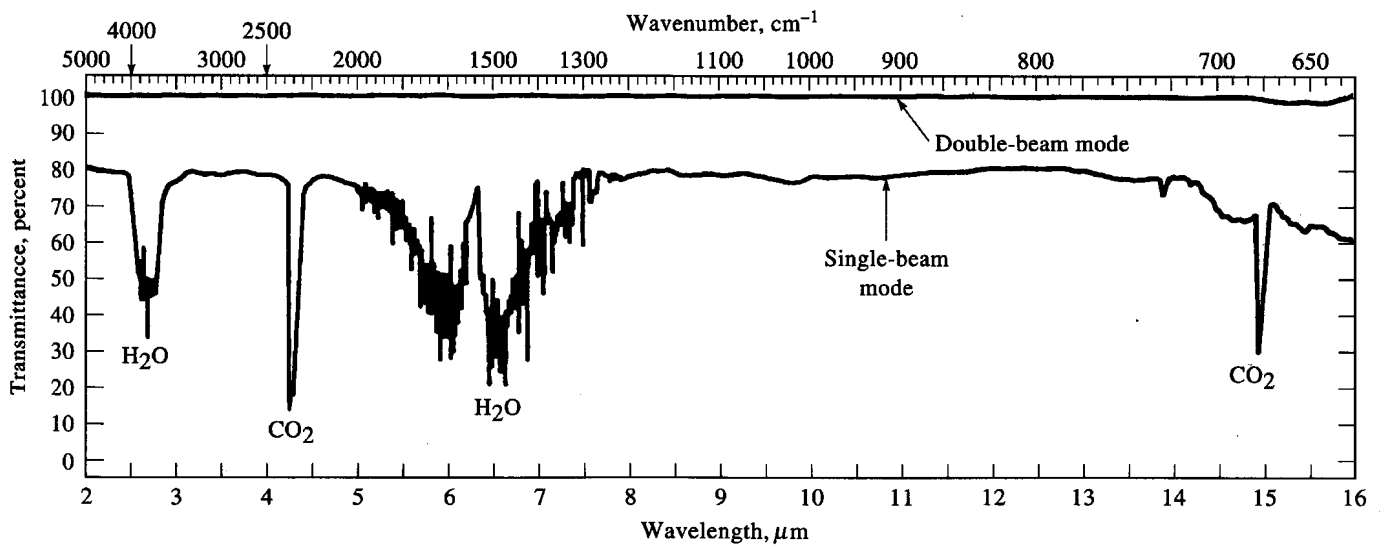


Fig 16-9

**Fourier Transform Instruments** (Section 7-I) have two advantages:

- (1) **Jaquinot** or **throughput** advantage. Few optics, no slits mean high intensity

Usually to improve resolution decrease slit width but less light makes spectrum "noisier" - **signal to noise ratio (S/N)** (p. 107-108)

average signal

$$\frac{S}{N} = \sqrt{n} \frac{\bar{S}}{\sqrt{(\bar{S} - S_i)^2}} = \frac{\bar{S}}{N} \sqrt{n} \quad \# \text{ scans}$$

average noise

S/N improves with more scans (noise is random, signal is not!)

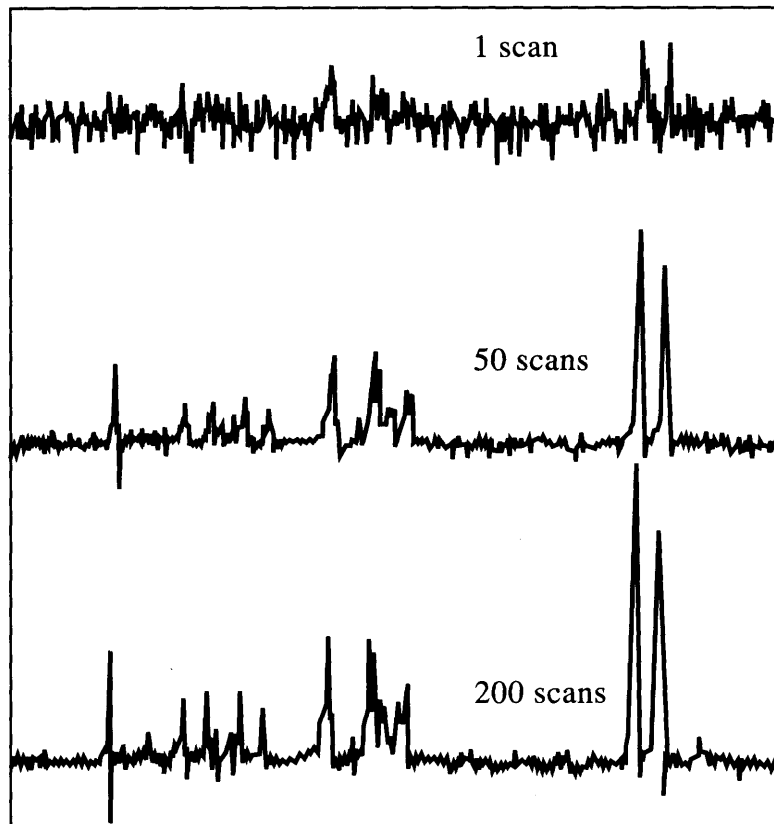
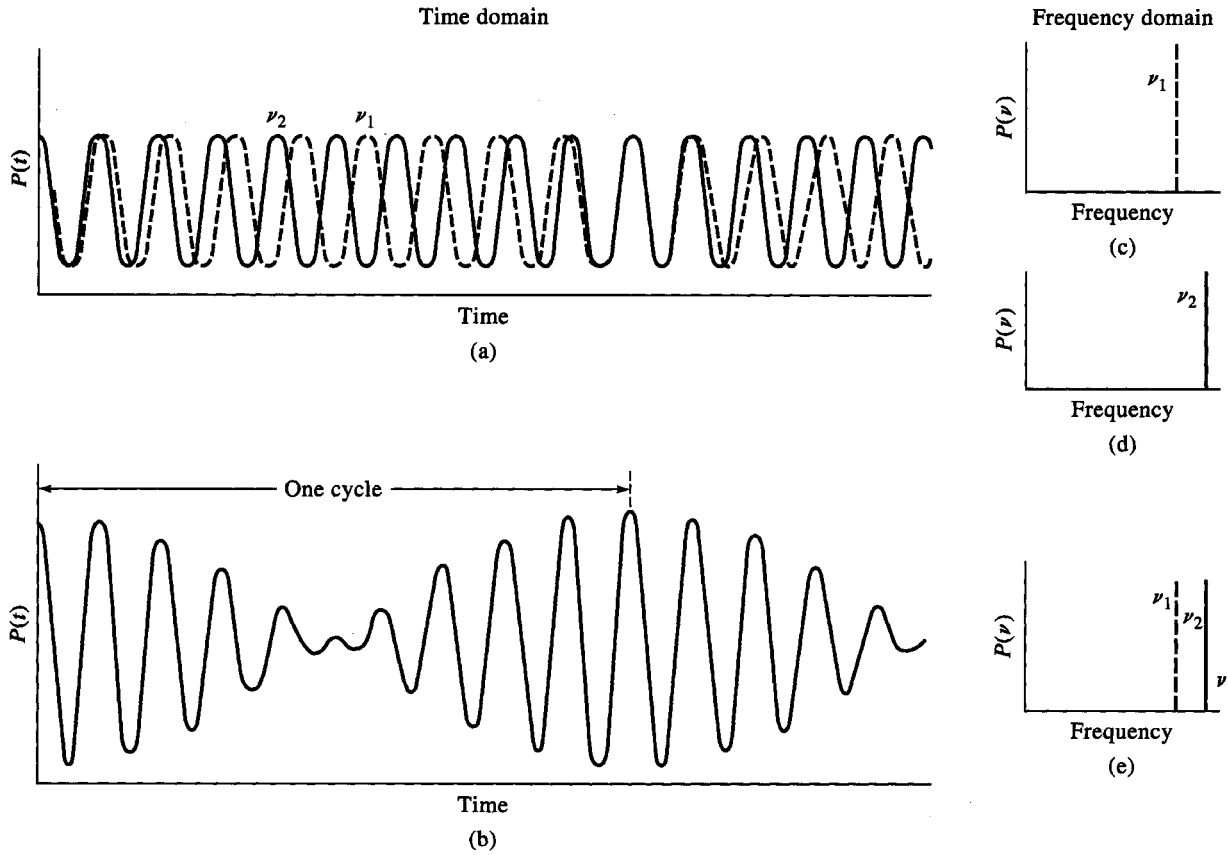


Fig 5-10

- (2) **Fellget** or **multiplex** advantage. Simultaneously measure all spectrum at once saves time

(Fig 7-40)



Unfortunately, no detector can respond on  $10^{-14}$  s time scale

Use **Michelson interferometer** to measure signal proportional to time varying signal

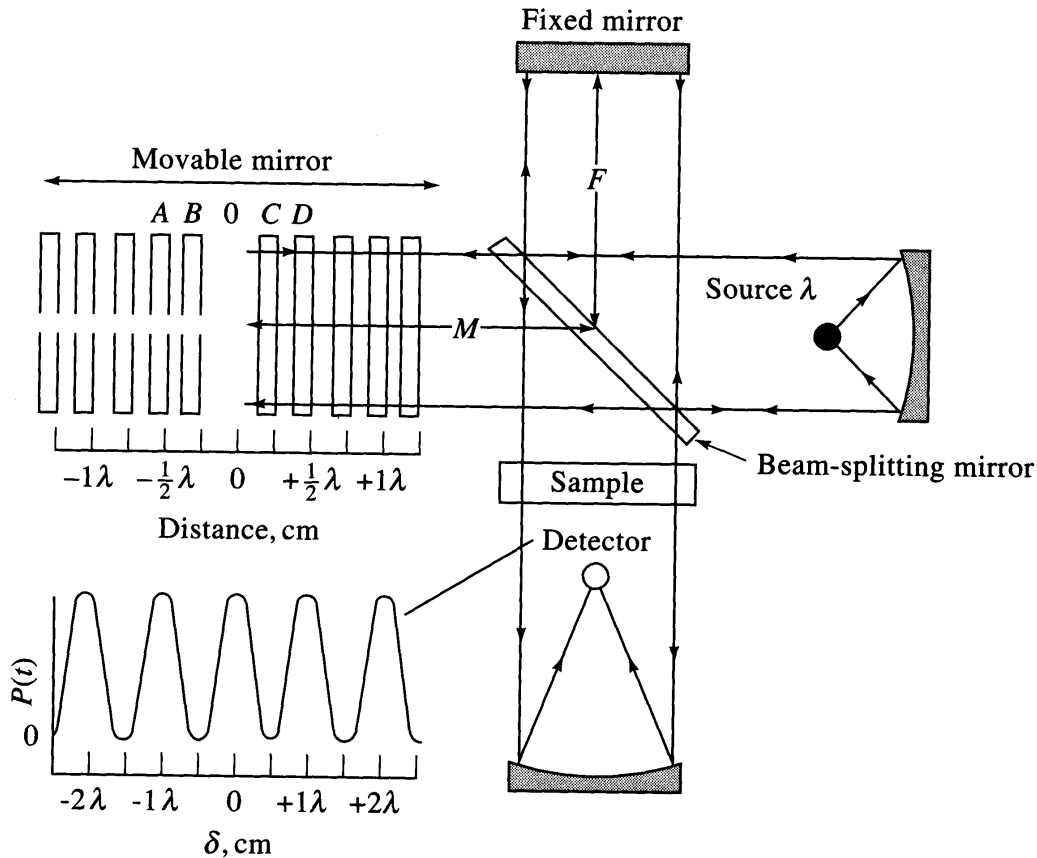


Fig 7-42

If moving mirror moves  $1/4$  ( $1/2$  round-trip) waves are out of phase at beam-splitting mirror - no signal

If moving mirror moves  $1/2$  ( $1$  round-trip) waves are in phase at beam-splitting mirror - signal

...

Difference in pathlength called **retardation**  $\delta$

Plot vs. signal - cosine wave with frequency proportional to light frequency but *signal varies at much lower frequency*

One full cycle when mirror moves distance  $\lambda/2$  (round-trip =  $\lambda$ )

velocity of moving mirror

$$\frac{\lambda}{2} = v_{MM} t$$

time to move  $\lambda/2$

Frequency of signal

$$f = \frac{1}{t} = \frac{v_{MM}}{\lambda/2} = \frac{2v_{MM}}{\lambda}$$

Substituting  $\lambda = c/f$

$$f = \frac{2v_{MM}}{c}$$

If mirror velocity is 1.5 cm/s

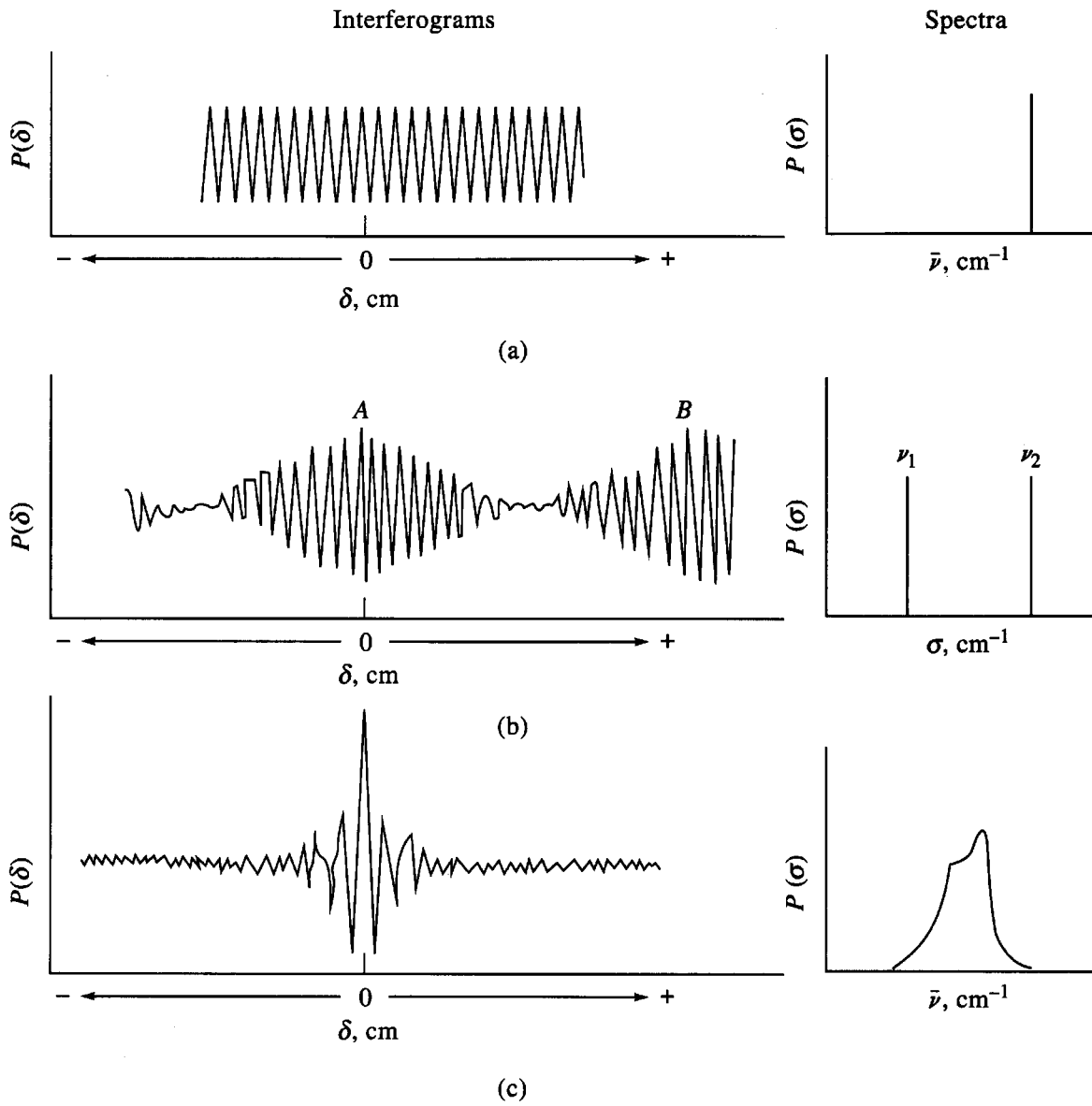
$$f = \frac{3 \text{ cm/s}}{3 \times 10^{10} \text{ cm/s}} \quad f = 10^{-10}$$

Bolometer, pyroelectric, photoconducting IR detectors can "see" changes on  $10^{-4}$  s time scale!

Computer needed to turn complex **interferogram** into **spectrum**

Time  $\xrightarrow{\text{FT}}$  Frequency  $\xleftarrow{\text{IFT}}$  Frequency  $\xrightarrow{\text{IFT}}$  Time

(Fig 7-43)





## Resolution?

Two closely spaced lines only separated if one complete "beat" is recorded. As lines get closer together, must increase.

$$(\text{cm}^{-1}) = \frac{1}{\text{}}$$

Mirror motion is 1/2

Resolution governed by distance MM travels

## Applications: (Chapter 17)

FTIR single-beam, dispersive IR double-beam, but FTIR advantages include

- High S/N ratios - high throughput
- Rapid (<10 s)
- Reproducible
- High resolution (<0.1 cm<sup>-1</sup>)
- Inexpensive

IR (especially FTIR) very widely used for

- qualitative
- quantitative

analysis of

- gases
- liquids
- solids

Most time-consuming part is **sample preparation**

**Gases** fill gas cell

(a) transparent windows (NaCl/KBr)

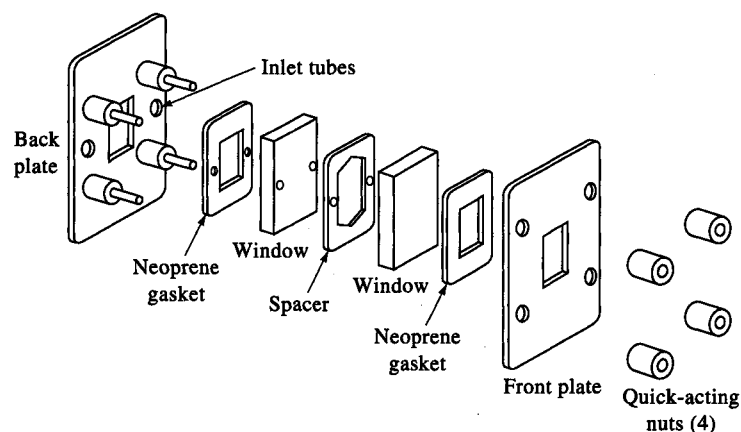
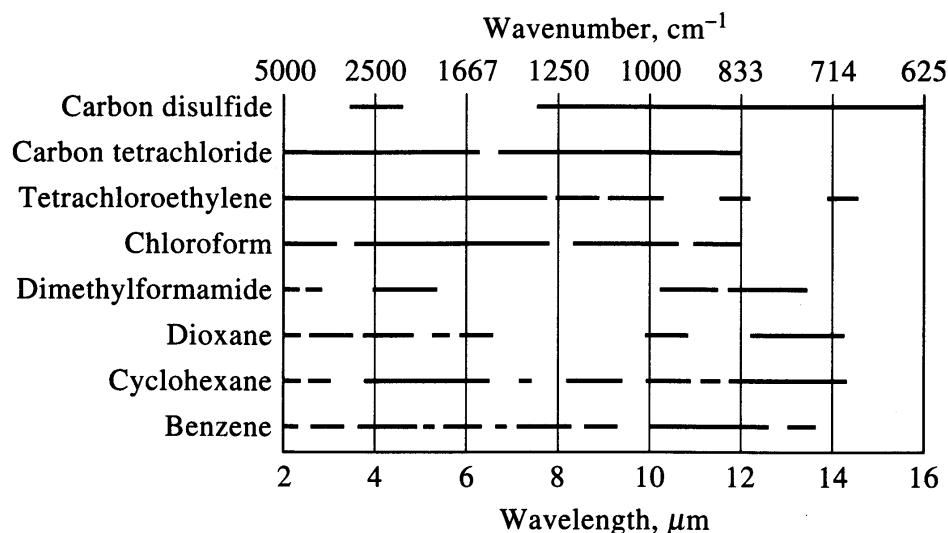
(b) long pathlength (10 cm) - few molecules

**Liquids** fill liquid cell

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

(b) short pathlength (0.015-1 mm) - solvents absorb

(Fig. 17-1, 17-2)



## Solids

(a) make semi-transparent pellet with KBr

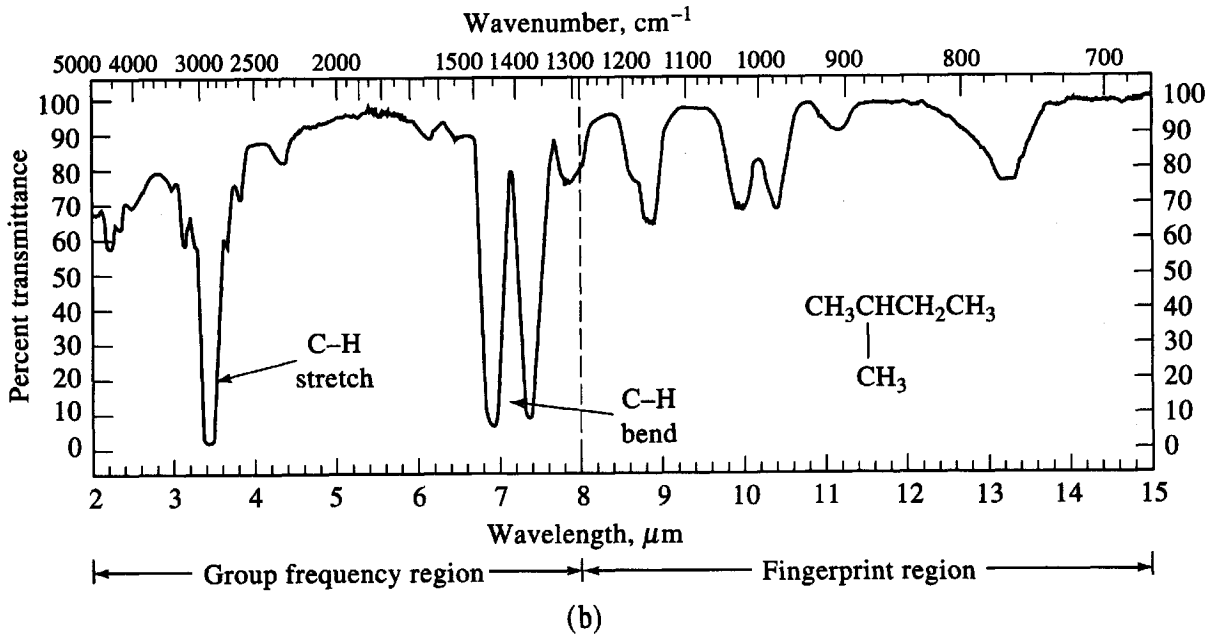
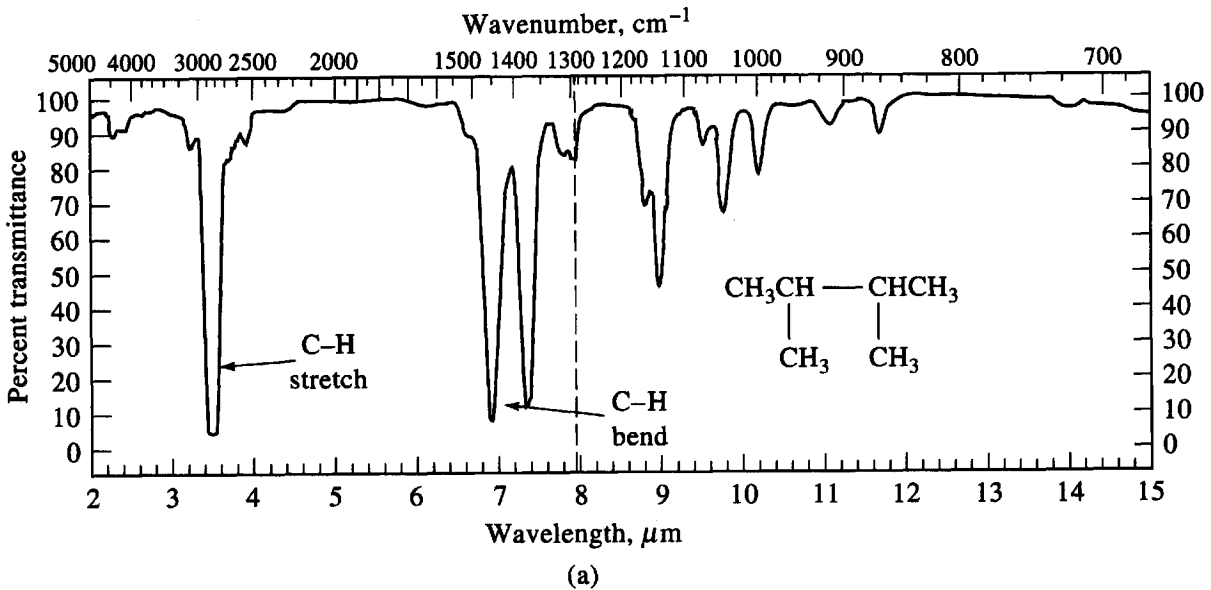
(b) grind and mix with Nujol (hydrocarbon oil) to form mull. One drop between NaCl plates.

## Qualitative Analysis:

Step One Identify **functional groups** (group frequency region)

Step Two **Compare with standard spectra** containing these functional groups (fingerprint region)

Fig 17-4



## Group Frequencies:

- Approximately **calculated** from masses and spring constants
- Variations due to **coupling**
- Compared to **correlation charts/databases**

**TABLE 17-2** Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, $\text{cm}^{-1}$	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes $\left( \begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array} \begin{array}{c} \text{H} \\ \diagup \\ \diagdown \end{array} \right)$	3010–3095	Medium
		675–995	Strong
C—H	Alkynes ( $\text{—C}\equiv\text{C—H}$ )	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO <sub>2</sub>	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

## **Quantitative Analysis:**

IR more difficult than UV-Vis because

- narrow bands (variation in )
- complex spectra
- weak incident beam
- low transducer sensitivity
- solvent absorption

IR mostly used for rapid qualitative but not quantitative analysis