1   Theory of IR

1.1 Introduction

1.1.1 Energy of IR photon

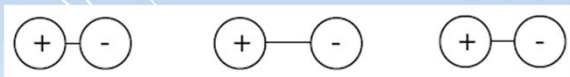|	
Near IR	12,800-4000 cm⁻¹
Mid IR	4000-200 cm⁻¹
Far IR	200-10 cm⁻¹

$$\bar{v}(cm^{-1}) = \frac{1}{\lambda} = \frac{v}{c}$$

Energy of IR photons is insufficient to cause electronic excitation but can excite vibrational or rotational modes
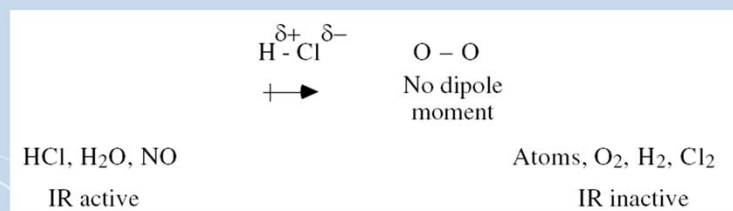
1.1.2 Prerequisite for IR-active vibrations

Magnitude of dipole moment determined by

a. charge

b. separation (vibrational or rotation causes varying separation)

*   **Molecule must have change in dipole moment due to vibration or rotation to absorb IR radiation** (only in this case the alternating E field can interact with the molecule and causes change in the amplitude of one of its motions)

Molecule with permanent dipole moment is IR active

$$\overset{\delta+}{H} - \overset{\delta-}{Cl} \qquad O - O$$

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

HCl, H_2O, NO   Atoms, O_2, H_2, Cl_2

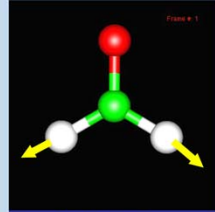IR active   IR inactive
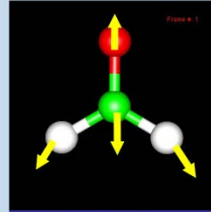
1.1.3 Types of molecular vibrations
- **stretching**: change in bond length, symmetric or asymmetric
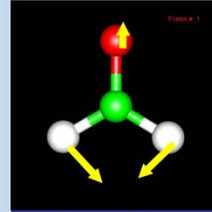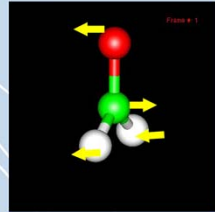- **bending**: change in the angle, scissoring, wagging, rocking, twisting/torsion

H_2CO

$\nu_1 = 2790 \text{ cm}^{-1}$
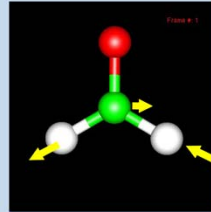CH_2 sys stretch
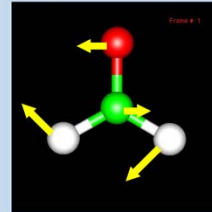
$\nu_2 = 1756 \text{ cm}^{-1}$
CO stretch

$\nu_3 = 1482 \text{ cm}^{-1}$
CH_2 scissors

$\nu_4 = 1165 \text{ cm}^{-1}$
out-of-plane wagging

$\nu_5 = 2846 \text{ cm}^{-1}$
aym CH stretch

$\nu_6 = 1221 \text{ cm}^{-1}$
in-plane CH_2 rock

1.1.4 Vibrational modes

	Translation	Rotation	Vibration
Non-Linear	3	3	3N - 6
Linear	3	2	3N - 5

Only some vibrational modes are IR active

Example CO_2 O=C=O linear

No net dipole moment change

Net dipole moment change

Net dipole moment change

v_s not IR active $v_{as.}$ bend IR active
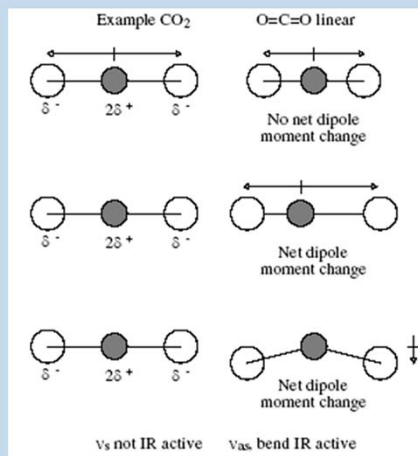
1.1.5 Classical vibrational motion

$$\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad k \text{ is force constant}$$

A system of two masses connected by a spring?

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

1.1.6 Quantum treatment

$$E = (\nu + \frac{1}{2})\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = (\nu + \frac{1}{2})h\nu_m$$

Fig. 16-3 (p433)

$E_0 = 1/2\ h\nu_m$ ground vibrational state ($\nu = 0$)
$E_1 = 3/2\ h\nu_m$ first excited vibrational state ($\nu = 1$)

Vibrational selection rule: $\Delta\nu = \pm 1$ and $\Delta E = h\nu_m$
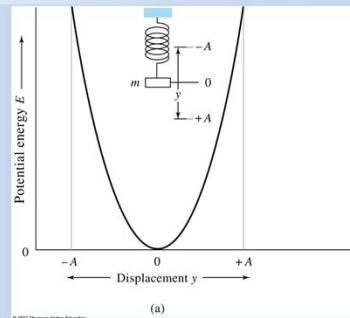since levels are equally spaced- should see one absorption frequency

2 Instrumentation for IR

2.1 FT-IR

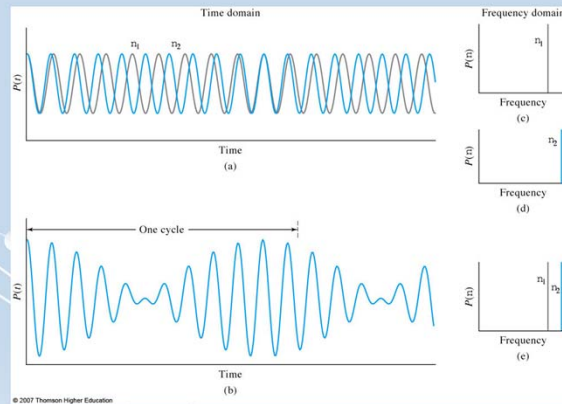**2.1.1 Time-domain spectroscopy - changes in radiant power with *time***

Fig. 7-41 (p207)

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

2.1.2 Michelson interferometer

Use Michelson interferometer to measure signal proportional to time varying signal

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

- If moving mirror moves $1/2\lambda$ (1λ round-trip) waves are out of phase at beam-splitting mirror –signal

Difference in path lengths called retardation δ
Plot δ vs. signal – cosine wave with frequency proportional to light frequency but signal varies at much lower frequency
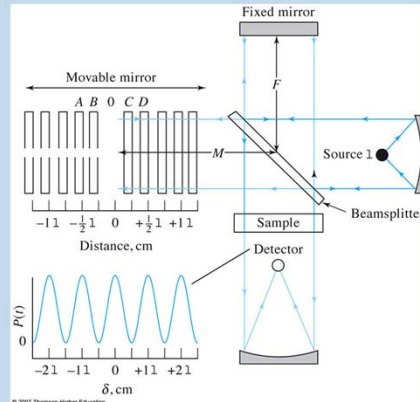

Fig. 7-43 (p208)

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

The velocity of moving mirror v_M

time for mirror to move $\lambda/2$ $\quad \tau = \dfrac{\lambda}{2v_M}$

frequency of signal at the detector $\quad f = \dfrac{1}{\tau} = \dfrac{2v_M}{\lambda}$

optical frequency of radiation $= \dfrac{c}{\lambda}$

$v_M = 1.5\,\text{cm/s}$

frequency of signal at the detector $= 10^{-10} \times$ optical frequency of radiation

Bolometer, photoconducting IR detector, etc. can "see" changes on 10^{-4} s

Time-domain signal → frequency-domain signal

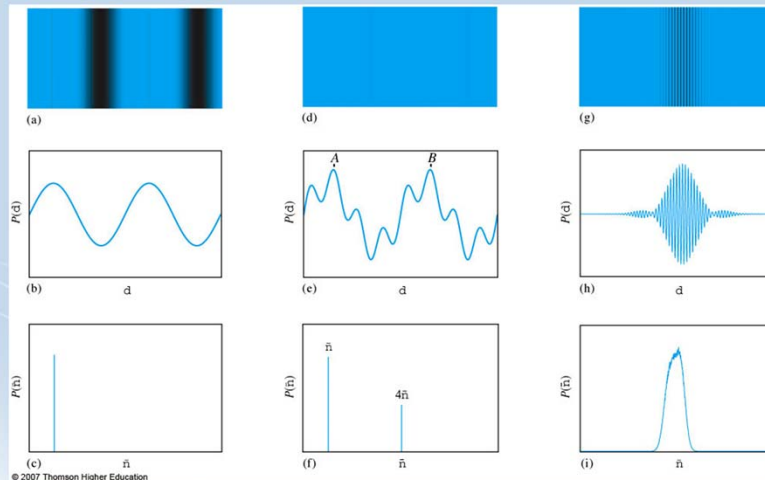Fig. 7-44 (p210)

2.1.3 Resolution

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

$$\Delta\overline{v}(cm^{-1}) = \frac{1}{\delta}$$

Mirror motion is $1/2\delta$, resolution is governed by distance moving mirror travels.

2.1.4 Advantages of FT-IR (reading assignment)

2.2 IR sources
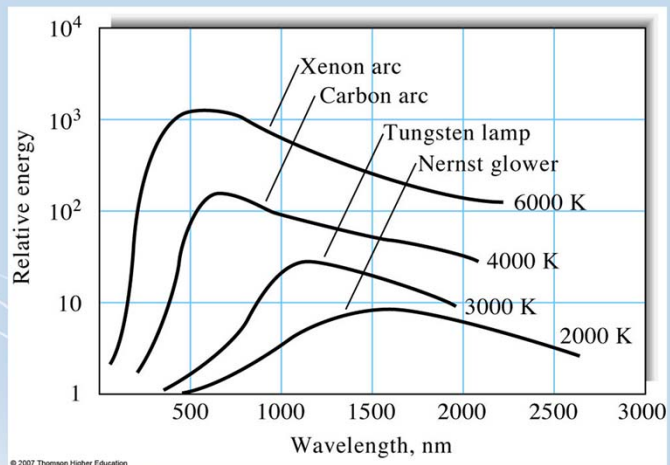
Fig. 6-22 (p153)

2.3 IR transducer

Pyroelectric - TGS (Triglycine sulfate)
    based on pyroelectric effect (temperature dependent capacitance)
    fast enough for FT-IR (but less sensitive than thermocouple)
    most common detector for FT-IR

Photoconducting
    semiconductors (e.g., PbS, MCT, etc.)
    resistance decreases with increase photon flux (promotion of electrons to conduction band)
    MCT (mercury telluride-cadmium telluride) about x100 sensitive than TGS, cooled to N2(liquid) temp to reduce thermal noise.

2.4 Diffuse-reflection spectrometry

• Advantages (powdered samples)

• Instrumentation

(an adapter fitting into the cell

component of FT-IR)

$f(R'_\infty) = \frac{(1-R'_\infty)^2}{2R'_\infty} = \frac{k}{s}$

$f(R'_\infty)$: relative reflectance intensity of powder

$k = 2.303\varepsilon c$

$R'_\infty = \dfrac{\text{reflected intensity of the sample}}{\text{that of non-absorbing standard KCl}}$

Ellipsoidal mirror

Sample cup

From interferometer
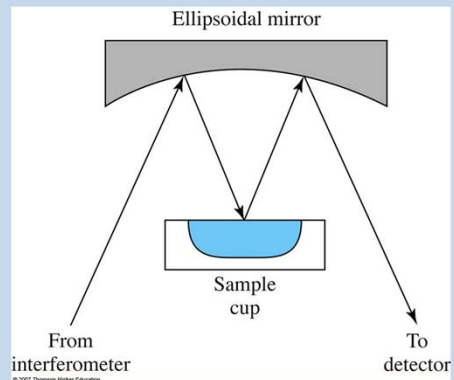
To detector

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Fig. 17-11 (p471)
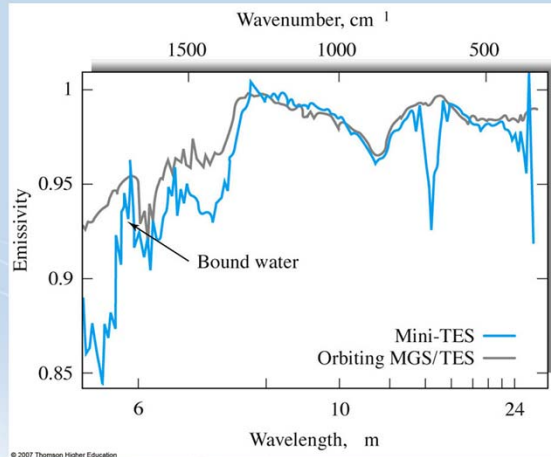
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2.5 IR emission spectrometry

Fig. 17-18 (p477)

— Orbiting Mars Global Surveyor-Thermal Emission Spectra, providing measurement of the Martian Surface and atmosphere

— mini thermal-emission spectrometer measured by the Mars rover Spirit, indicating composition of nearly soils and rocks

http://upload.wikimedia.org/wikipedia/commons/thumb/d/d8/NASA_Mars_Rover.jpg

Spirit, also known as Mars Exploration Rover, is a robotic rover on Mars, active from 2004 to 2010. rovers of NASA's ongoing Mars Exploration Rover Mission. It landed successfully on Mars at 04:35 Ground UTC on January 4, 2004, three weeks before its twin, Opportunity, landed on the other side of the planet. Its name was chosen through a NASA-sponsored student essay competition. The rover became stuck in late 2009, and its last communication with Earth was sent on March 22, 2010.

Mars Global Surveyor (MGS)

- MGS was a US spacecraft developed by NASA's Jet Propulsion Laboratory and launched November 1996. Mars Global Surveyor was a global mapping mission that examined the entire planet, from the ionosphere down through the atmosphere to the surface. As part of the larger Mars Exploration Program, Mars Global Surveyor performed atmospheric monitoring for sister orbiters during aerobraking, and it helped rovers and lander missions by identifying potential landing sites and relaying surface telemetry.

- It completed its primary mission in January 2001 and was in its third extended mission phase when, on 2 November 2006, the spacecraft failed to respond to messages and commands. A faint signal was detected three days later which indicated that it had gone into safe mode. Attempts to recontact the spacecraft and resolve the problem failed, and NASA officially ended the mission in January 2007.

3   Applications of IR Absorption

3.1 Qualitative Analysis by IR absorption

(1) Identify functional groups (group frequency region, 3600-1250 cm^{-1})

(2) Compare with standard spectra containing these functional groups (fingerprint region, 1200 – 600 cm^{-1})

- use computerized spectral search engines

- use IR assignments in conjunction with other info (e.g., chemical, physical, spectroscopic)

Group frequencies

- Approximately calculated from masses and spring constants
- Variation due to coupling
- Compared to correlation charts/database (Table 17-6, p 462-463)

TABLE 17-3 Abbreviated Table of Group Frequencies for Organic Functional Groups

| Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes (>C=C<^{H})	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡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_2	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

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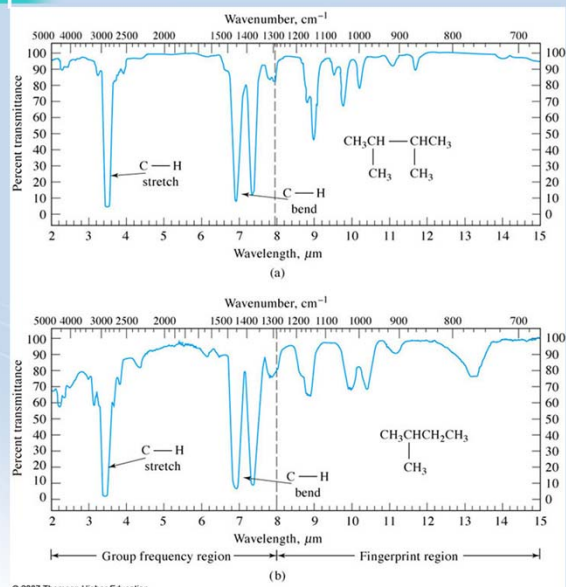
Fig. 17-5 (p460)

3.2 Quantitative analysis of IR absorption (Beer's Law)

IR more difficult than UV-Vis because
(1) narrow bands (variation in ε)

(2) complex spectra

(3) weak incident beam

(4) low transducer sensitivity

(5) solvent absorption

IR mostly used for rapid qualitative but not quantitative analysis

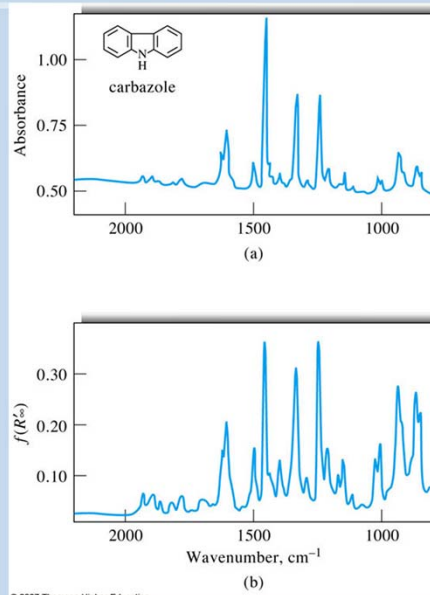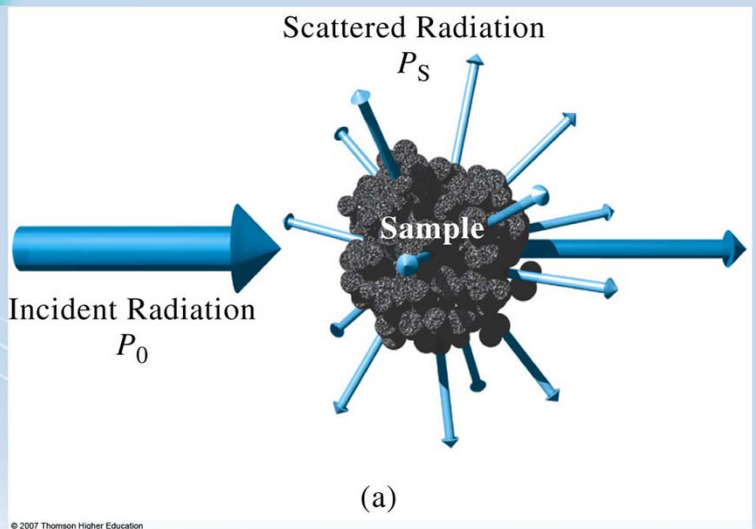Comparison of the absorbance spectrum (a) for carbazole with its diffuse-reflectance spectrum (b)

Fig. 17-12 (p471)

Theory for Raman Spectroscopy

4

Scattered Radiation P_S

Incident Radiation P_0

Sample

(a)

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### 4.1 Elastic scattering and inelastic scattering

EMR induces oscillating electric field
in the electron cloud around the molecule-
which is then re-emitted as a photon

- **Elastic scattering (Rayleigh scattering):**
  no change in energy of light

- **Inelastic scattering:**
  Scattered photon will be at an energy either greater than or
  lower than the original energy by an amount equal to the energy of the
  vibration.

  (only about 1 molecule in 10^8-10^9 will inelastically scatter photons)

Excited State

j ---------------------- "Virtual" State

Ground State
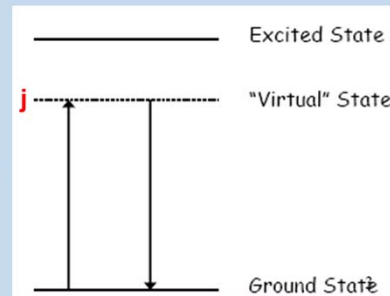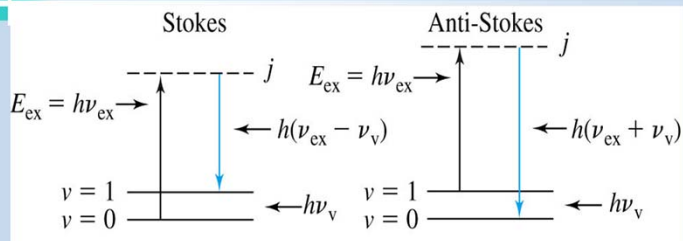
Stokes Lines: longer wavelength (more intense)

Anti-stokes Lines: shorter wavelength

$\Delta \nu = \nu_{Raman}$

The intensity ratio of Stokes vs. Anti-Stokes may be used to spectroscopically measure The temperature of sample

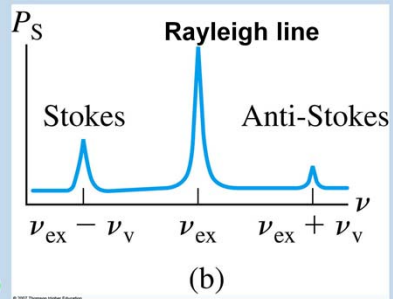Fig. 18-1 (p482)

4.2 Wave model

$E = E_0 \cos(2\pi v_{ex} t)$

E interacts with an electron cloud of a bond, induced dipole moment

$m = \alpha E = \alpha E_0 \cos(2\pi v_{ex} t)$

a : polarizability

$a = a_0 + (r - r_{eq})(\dfrac{\partial a}{\partial r})$

$r - r_{eq} = r_m \cos(2\pi v_{vib} t)$

$m = a_0 E_0 \cos(2\pi v_{ex} t) + E_0 r_m (\dfrac{\partial a}{\partial r}) \cos(2\pi v_{vib} t) \cos(2\pi v_{ex} t)$

$(\text{note} : \cos x \cos y = [\cos(x+y) + \cos(x-y)]/2)$

$m = a_0 E_0 \cos(2\pi v_{ex} t) + $ — Rayleigh scattering

$\quad \dfrac{E_0}{2} r_m (\dfrac{\partial a}{\partial r}) \cos[2\pi (v_{ex} - v_{vib}) t] + $ — Stokes line

$\quad \dfrac{E_0}{2} r_m (\dfrac{\partial a}{\partial r}) \cos[2\pi (v_{ex} + v_{vib}) t]$ — Anti-Stokes line

25

Selection rule

1.There is a change in polarizability during the vibration
   (**Polarizability:** a term describes a molecule properties having to do
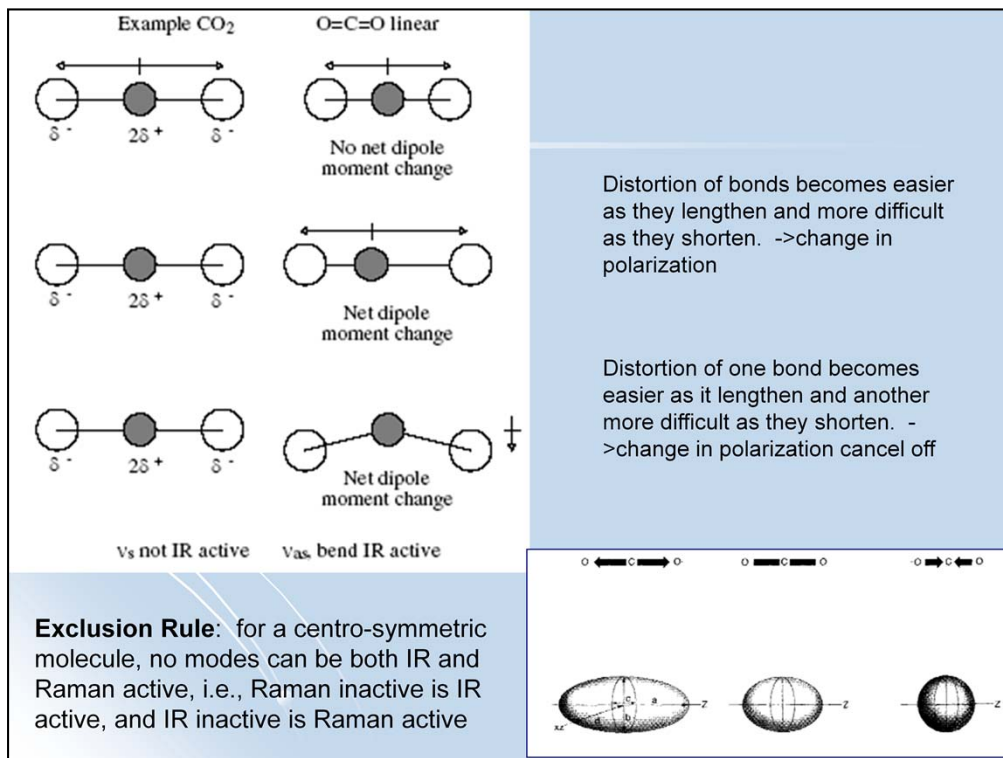   with the deformability of a bond)

2. $\Delta v = \pm 1$

For comparison, IR
1. There is a change in dipole moment
2. $\Delta v = \pm 1$

Example CO_2 O=C=O linear

No net dipole moment change

Net dipole moment change

Net dipole moment change

v_s not IR active v_{as} bend IR active

Exclusion Rule: for a centro-symmetric molecule, no modes can be both IR and Raman active, i.e., Raman inactive is IR active, and IR inactive is Raman active

Distortion of bonds becomes easier as they lengthen and more difficult as they shorten. ->change in polarization

Distortion of one bond becomes easier as it lengthen and another more difficult as they shorten. ->change in polarization cancel off

4.3 Intensity of Raman bands

-proportional to concentration

-directly to source intensity

- $1/\lambda^4$, Source wavelength

Instrumentation for Raman

5.1 Block diagram

Sample
cell

Wavelength
selector

Radiation
transducer

Computer
data system

Double grating
monochromator,
Michelson
interferometer

PMT,
Cooled germanium
photoconductor,
CCD

Laser
source

High intensity,
Monochromatic,
Chosen carefully, avoid
Solvent absorption

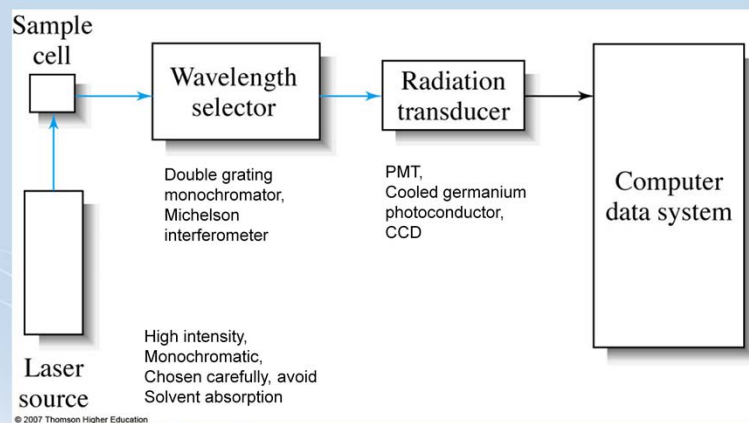© 2007 Thomson Higher Education

Fig. 18-6 (p487)

5.2 Sample handling

(p 488-490), simpler than for IR spectroscopy

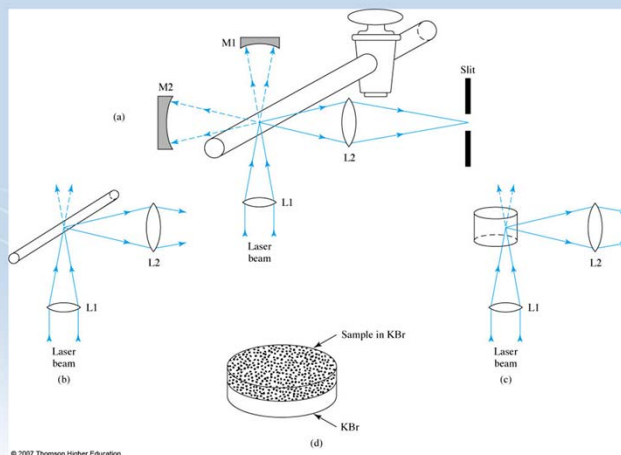glass can be used for windows, and can use aqueous solutions

Fig. 18-8 (p489)

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5.3 Raman properties

Get vibrational spectrum
-Complementary with IR
-Aqueous solution are accessible to study

Problem:
-Low efficiency of effect = poor sensitivity
-Competition from fluorescence for high fluorescence species

Solving problems:
-Resonance Raman (selectivity and detectability)
-Surface-enhanced Raman (sensitivity and detectability)
-Multi-channel detection (detectability)
-Near-IR excitation (fluorescence rejection)

Resonance Raman

➤ If $\lambda_{incident}$ corresponds to a strong absorption band, I_{Raman} **enhanced by** $10^2 - 10^6$ x

• *Enhancement only for vibrational modes associated with portion of molecule involved in electronic transition.*

$\nu_{incident}$ ν_{stokes}
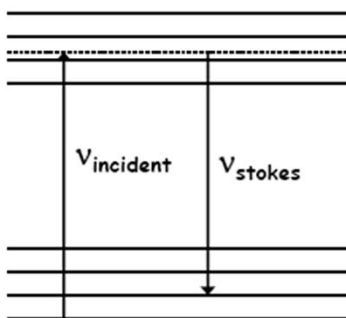
How does this differ from fluorescence?

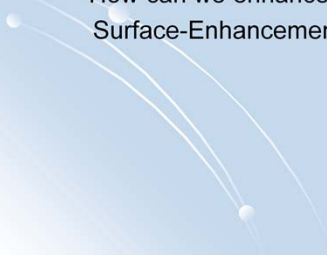**Surface enhanced Raman spectroscopy (SERS)**

- Raman signal enhancement occurs if sample is on
  an "active metal" surface
  - Active metal = Ag, Au, Cu, and others
  - A generalizable phenomenon (SEIRA)

- For ultimate in detectability (near unity "Raman Quantum Yield"),
  couple with
  - Resonance enhancement
  - Sample adsorbed onto metal nano-particles

Near-IR excitation

- Can eliminate fluorescence background by using low energy excitation λ
  Use λ = 1.06 μm (Nd: YAG Laser)
  Problem: I_{Raman} depends on λ^{-4}
               16 x decrease in signal from 500 nm

- How can we enhance S/N to make measurement possible?
  Surface-Enhancement

6   Comparison of IR and Raman

IR	Raman
1. Result of absorption of light by vibrating molecules	due to scattering of light by vibrating molecules
2. Change in dipole moment	Change in polarizability
3. Relatively inexpensive	More expensive
4. Cannot use with aqueous solutions	Able to use aqueous solutions
5. Elaborate sample prep	Molecules can be used in any state As sensitive as fluorescence and more selective