Chapter 16 - Infrared Spectrometry

Read: pp.430-452 Problems: 16-1,2,4,7,8

Excitation of vibrations and rotations in a molecule. Transitions from one vibrational state to another.

2.5 to 50 μm or 4000 to 200 cm^{-1} (mid-IR)

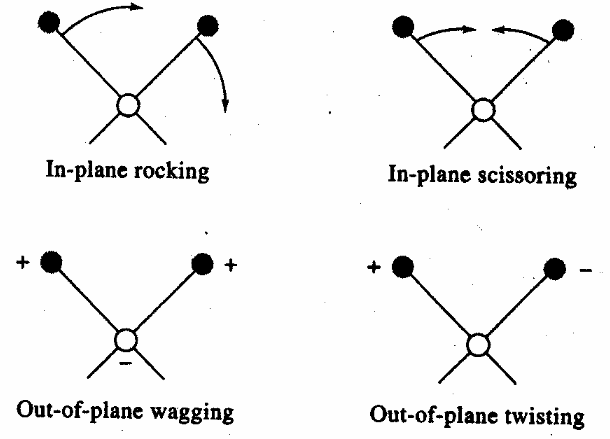
Much lower in energy than electonic excitation!

530 nm = 3.75 x 10^{-19} J/photon or 226 kJ/mol

4.3 μm = 4.6 x 10^{-20} J/photon or 27 kJ/mol

Types of Vibrations

(a) Stretching vibrations



(b) Bending vibrations

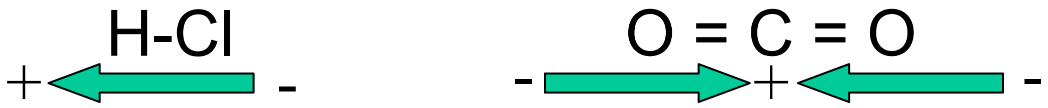
Figure 16-2 Types of molecular vibrations. Note: + indicates motion from the page toward the reader; − indicates motion away from the reader.

Dipole Changes During Vibrations and Rotations

A molecule must undergo a **net** change in dipole moment as a consequence of its vibrational and rotational motion in order to absorb IR radiation. Only then can the alternating electric field of the radiation interact with the molecule and produce a change in the **amplitude** of one of its motions.

When two charges, q and q-, are separated by a distance, R, then a dipole moment exists. Directed from negative toward positive end.

$$\mathbf{p = (Debye,\ C\text{-}m) = \Delta q \bullet R}$$



Classical and Quantum Mechanical Picture of Two Atoms in a Bond Vibrating

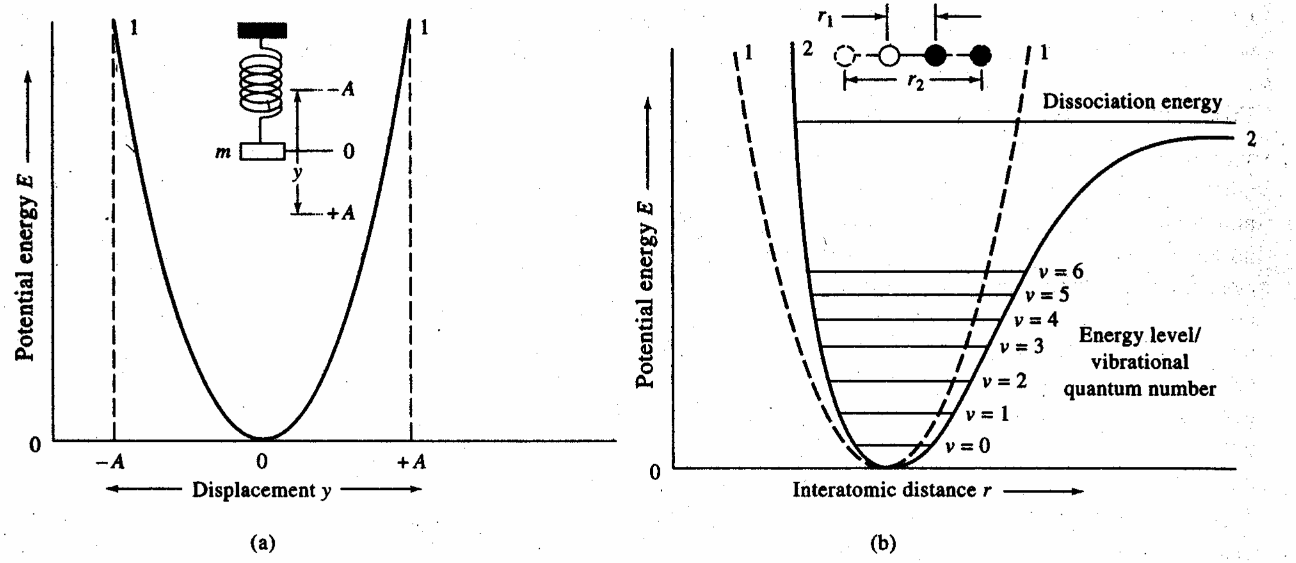


Figure 16-3 Potential energy diagrams. Curve 1, harmonic oscillator. Curve 2, anharmonic oscillator.

$$\boxed{\Delta E = h\upsilon_m = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}}$$

$F = -ky$

$E = (1/2)ky^2$

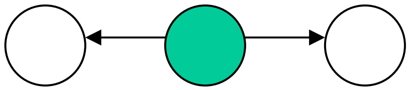
$$\upsilon_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

An Absorption Example

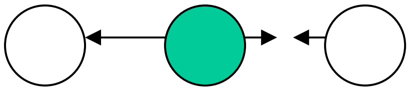
O = C = O A linear, symmetric molecule!

Predicted # of vibrations for a linear molecule = 3N-5
Predicted # of vivbrations for a non-linear molecule = 3N-6

$CO_2 \longrightarrow 3 \times 3 - 5 = \underline{4}$ normal modes



Symmetric (inactive)



Asymmetric (2330 cm^{-1} (4.3 μm))

Degenerate bending motions (667 cm^{-1} (15 μm))

Instrumentation

Sources (weakly intense!!)

1. Nernst glower (rare earth oxides
2. Glowbar (SiC rod)

Detectors (must be stable, have fast response time and be highly sensitive)

1. Thermal transducers (temperature changes)
2. Thermocouples (junction of two metals with a resistance that changes with temperature)
3. Pyroelectric (changes in temperature cause polarization in material to change
4. Photoconductors (incident photons cause charge separation internally)

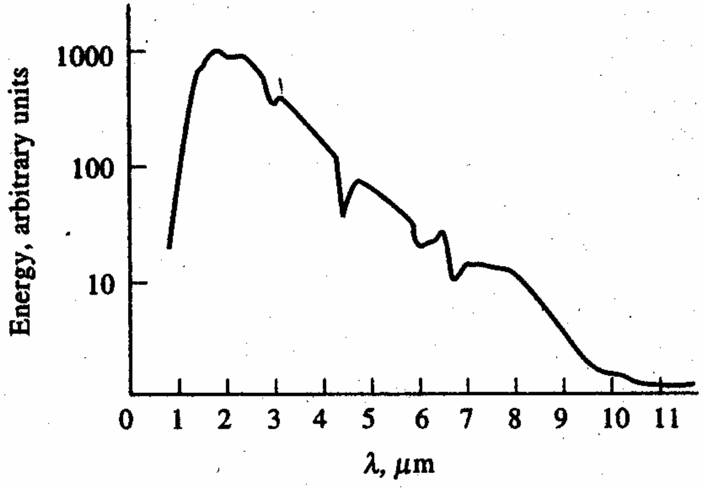


Figure 16-4 Spectral distribution of energy from a Nernst glower operated at approximately 2200 K.

Instruments must have good focusing and collection optics!!

Go back and read pp. 206-212!!

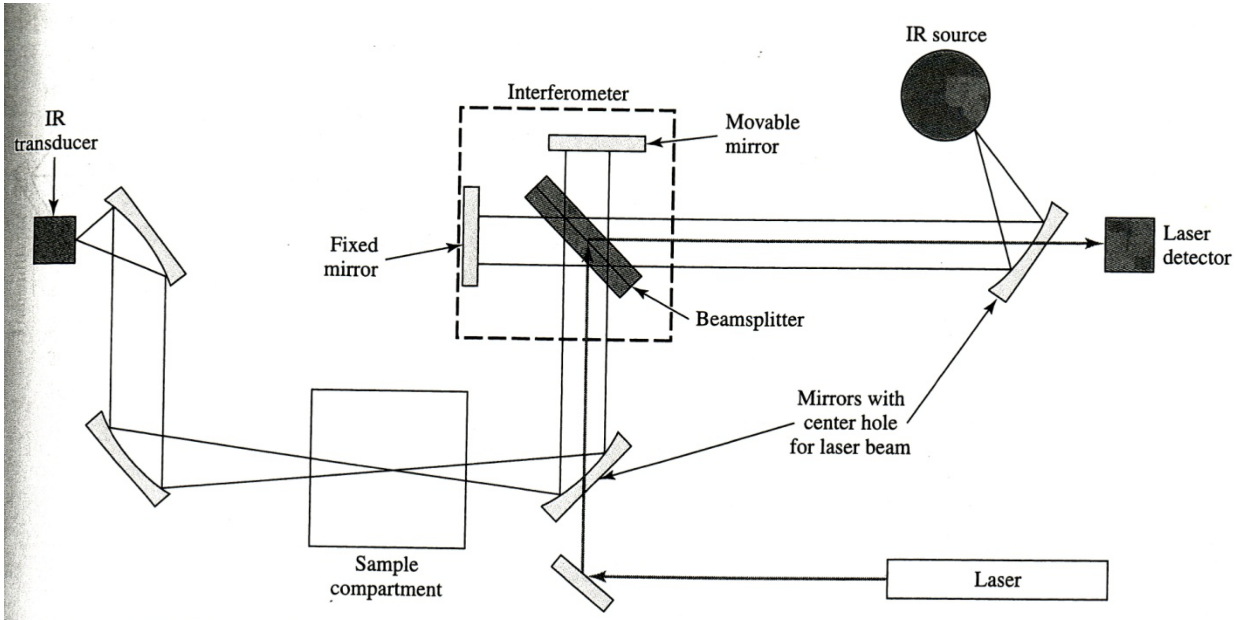


FIGURE 16-8 Single-beam FTIR spectrometer. In one arm of the interferometer, the IR source radiation travels through the beamsplitter to the fixed mirror, back to the beamsplitter, and through the sample to the IR transducer. In the other arm, the IR source radiation travels to the beamsplitter, is reflected to the movable mirror, and travels back through the beamsplitter to the sample and to the transducer. When the two beams meet again at the beamsplitter, they can interfere with each other if the phase difference (path difference) is appropriate. A plot of the signal versus mirror displacement is the interferogram. The interferogram contains information about all the frequencies present. The spectrum, intensity versus wavenumber, is the FT of the interferogram. It can be calculated with a computer from the signal versus mirror displacement. An empty sample compartment allows the reference spectrum to be calculated. Next, the sample is placed in the sample compartment and the sample spectrum is obtained. The absorbance is then calculated at each wavenumber from the ratio of the sample intensity to the reference intensity.

Wavelength Selector - Interferometer

Remember: Dispersion instruments were used in the past but they were slow (slow scanning) and highly susceptible to noise (poor sensitivity). FT instruments now used!!

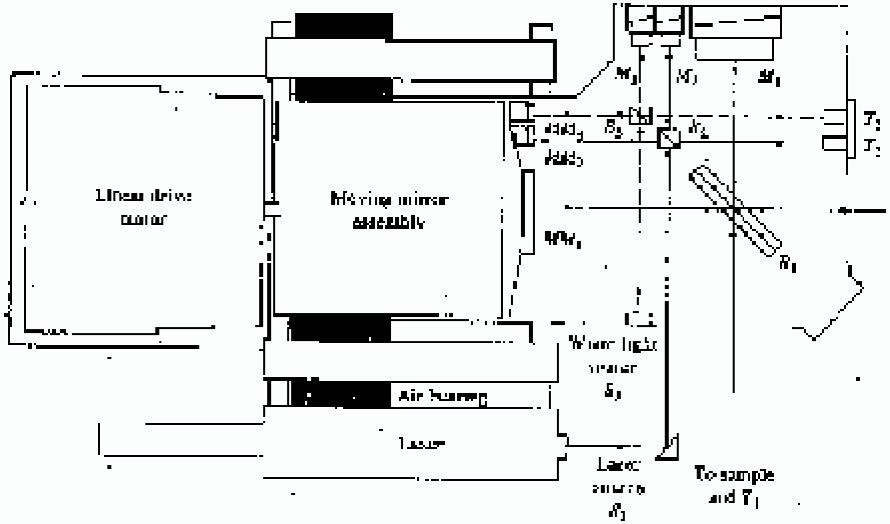


Figure 16-6 Interferometers in an infrared Fourier transform spectrometer. Subscript 1 defines the radiation path in the infrared interferometer; subscripts 2 and 3 refer to the laser and white-light interferometers, respectively. (Courtesy of Nicolet Analytical Instruments, Madison, Wis.)

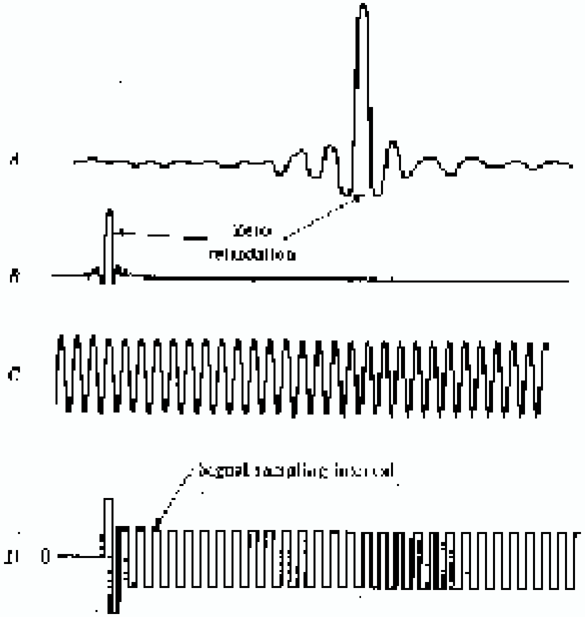


Figure 16-7 Time domain signals for the three interferometers contained in a Fourier transform infrared instrument. Curve A: infrared signal; curve B: white-light signal; curve C: laser-fringe reference signal; curve D: square-wave electrical signal formed from the laser signal. (From P. R. Griffiths, Chemical Infrared Fourier Transform Spectroscopy, p. 102. New York: Wiley, 1975. Reprinted by permission of John Wiley & Sons, Inc.)

Advantages of Fourier Transform Spectrometers

- Very high light throughput (fewer optical components) = *Jaquinot advantage*.
- High resolution (<0.01 cm^{-1}).
- All wavelengths of light reach the detector simultaneously = *multiplex advantage*.
- Fast speed and improved sensitivity (S/N ratios).

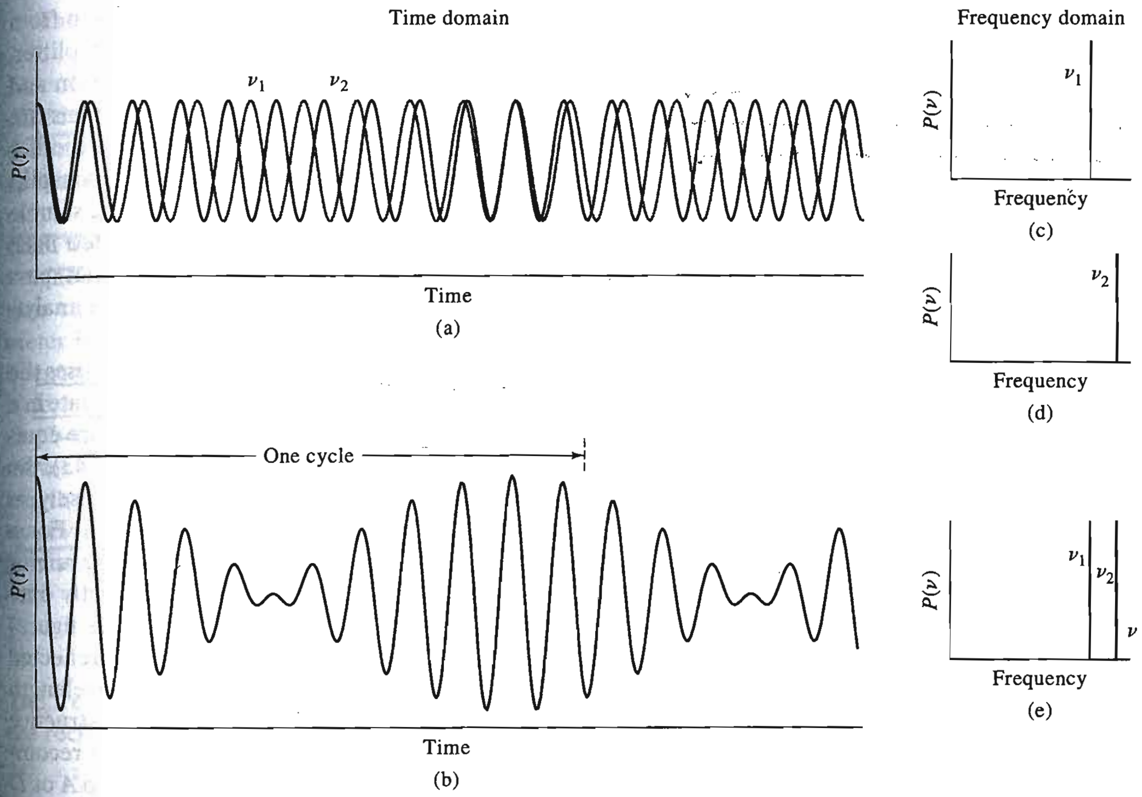


FIGURE 7-41 (a) Time-domain plot of two slightly different frequencies of the same amplitude ν_1 and ν_2. (b) Time-domain plot of the sum of the two waveforms in (a). (c) Frequency-domain plot of ν_1. (d) Frequency-domain plot of ν_2. (e) Frequency-domain plot of the waveform in (b).

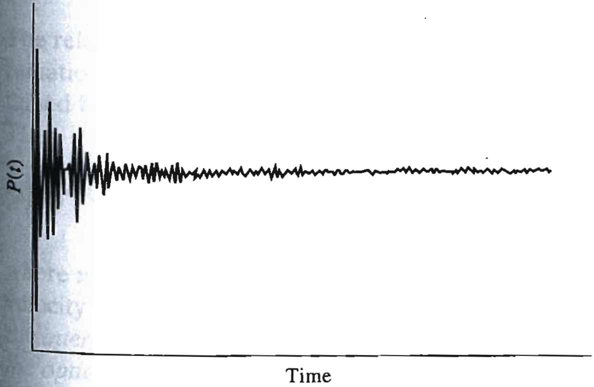


FIGURE 7-42 Time-domain signal of a source made up of many wavelengths.

meters.

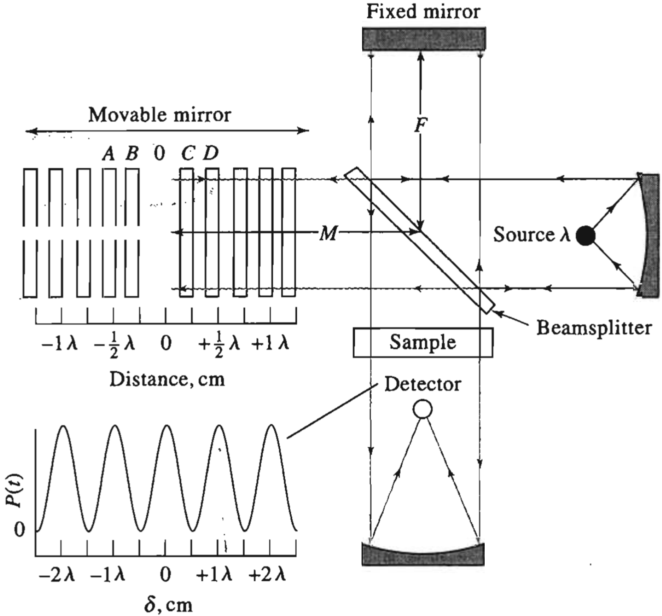


FIGURE 7-43 Schematic of a Michelson interferometer illuminated by a monochromatic source.

Typical FTIR Spectrometer

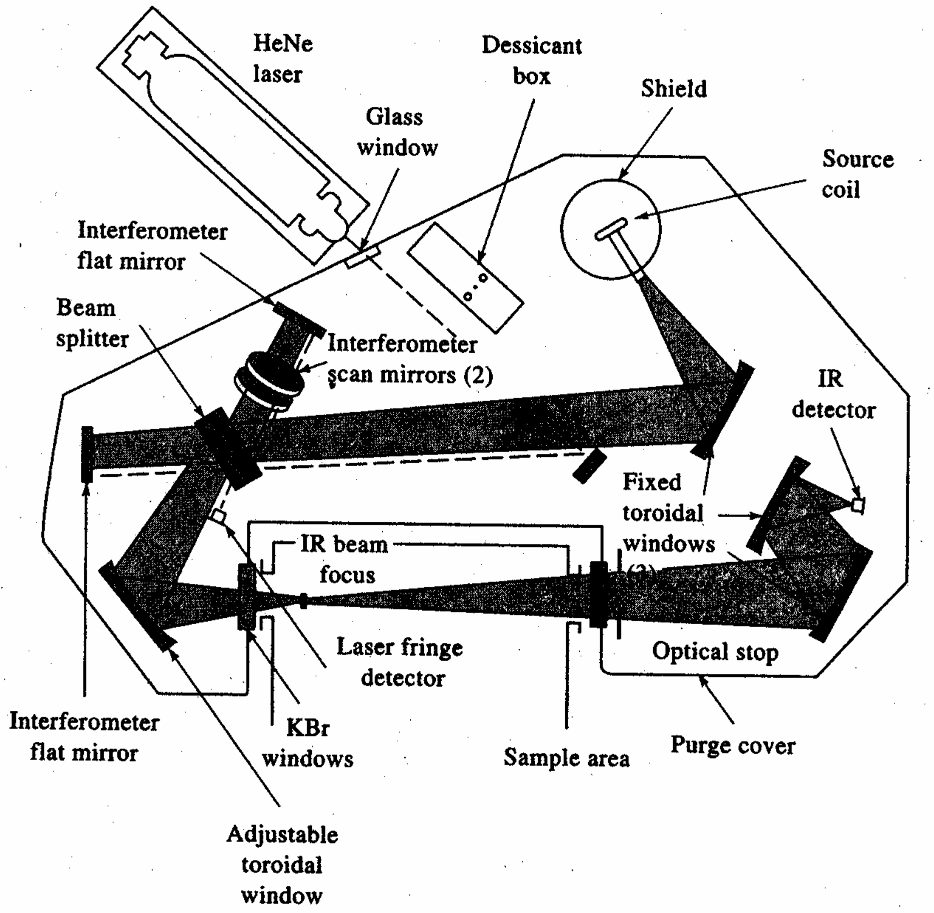


Figure 16-8 A single-beam FTIR spectrometer. *(Courtesy of Perkin-Elmer, Norwalk, CT.)*

Typical Background Spectrum of Air

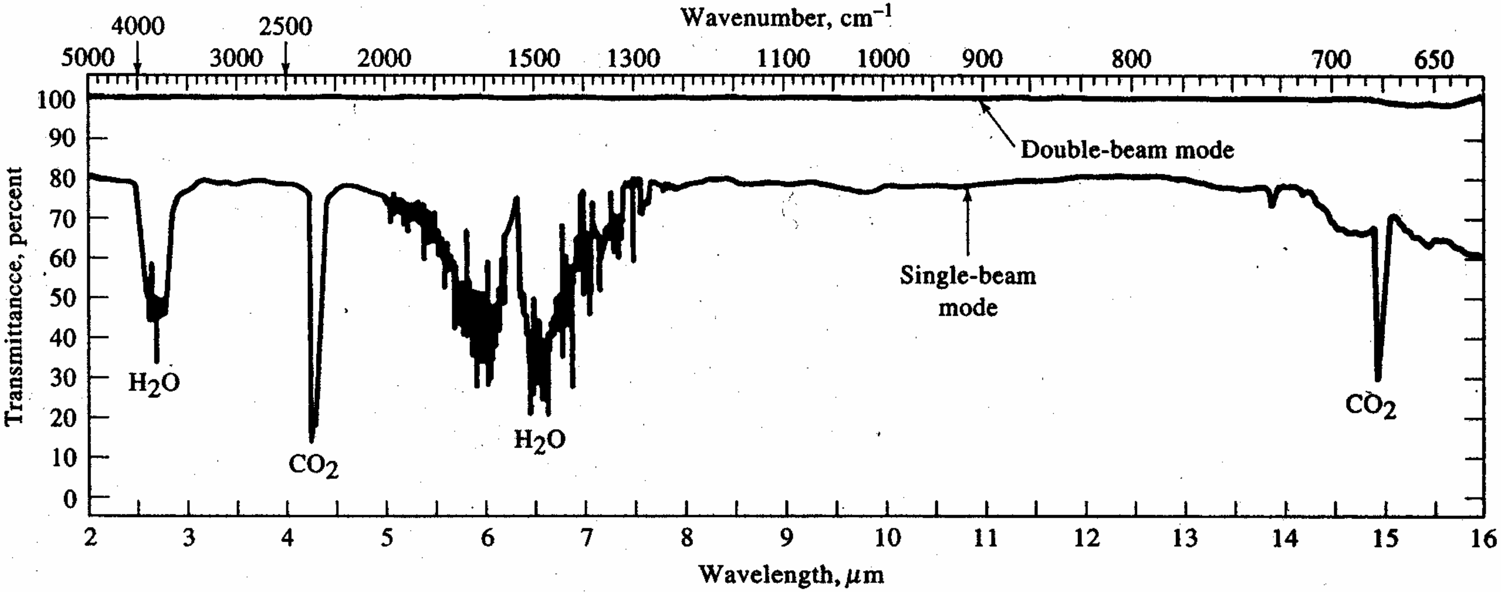
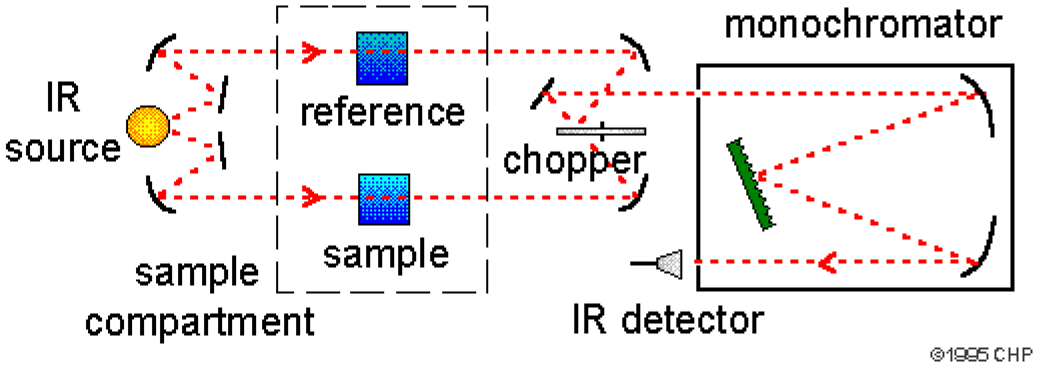
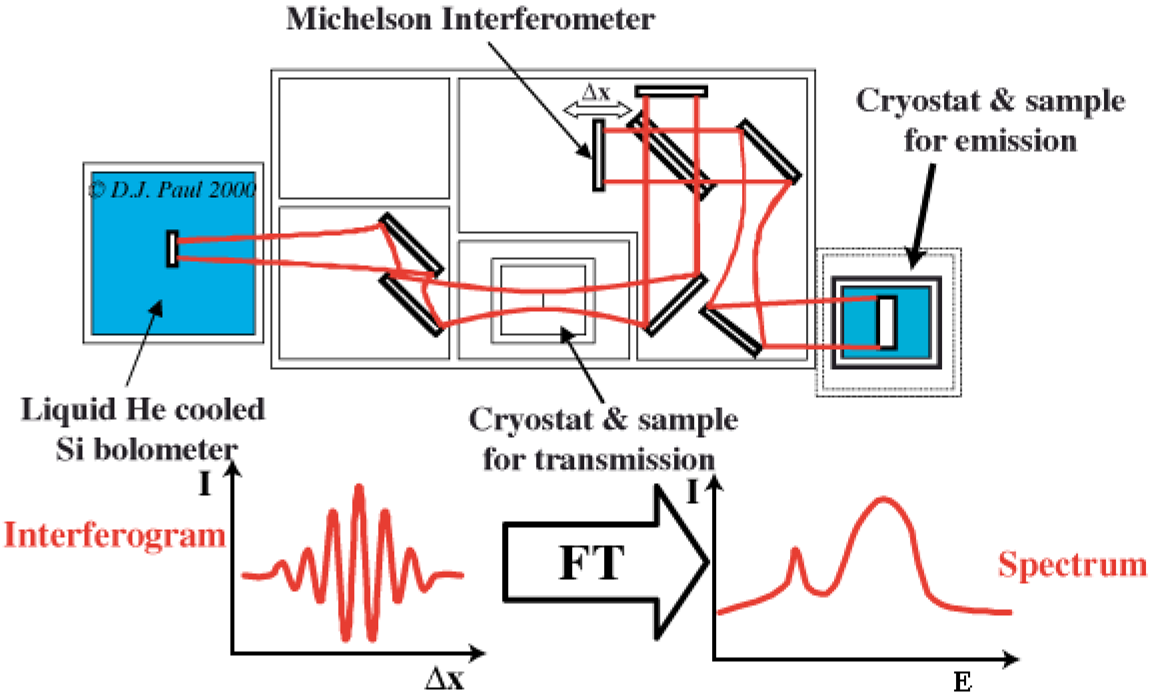


Figure 16-9 Single- and double-beam spectra of atmospheric water vapor and CO_2. In the lower, single-beam trace, the absorption of atmospheric gases is apparent. The top, double-beam trace shows that the reference beam compensates nearly perfectly for this absorption and allows a stable 100% *T* baseline to be obtained. *(From J. D. Ingle Jr. and S. R. Crouch,* Spectrochemical Analysis, *p. 409. Englewood Cliffs, NJ: Prentice-Hall, 1988. With permission.)*

Dispersive vs. FTIR Instruments





Chapter 17: Applications of Infrared Spectroscopy

Read: pp. ~~404-421~~ Problems: none

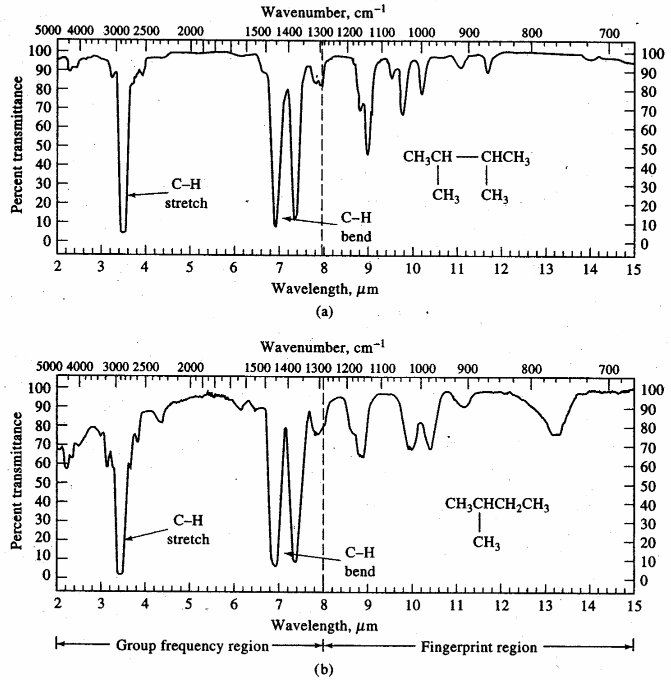


Figure 17-4 Group frequency and fingerprint regions of the mid-infrared spectrum. *(From R. M. Roberts, J. C. Gilbert, L. B. Rodewald, and A. S. Wingrove,* Modern Experimental Organic Chemistry, *4th ed. Philadelphia: Saunders College Publishing, 1985. With permission.)*

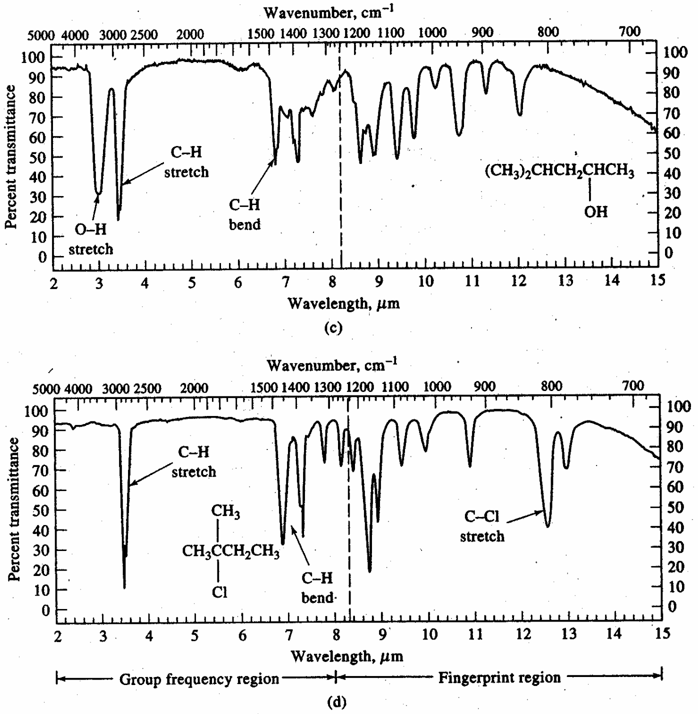


Figure 17-4 *Continued*

Structural identification of molecules + quantitative information!

Identification of Structural Features

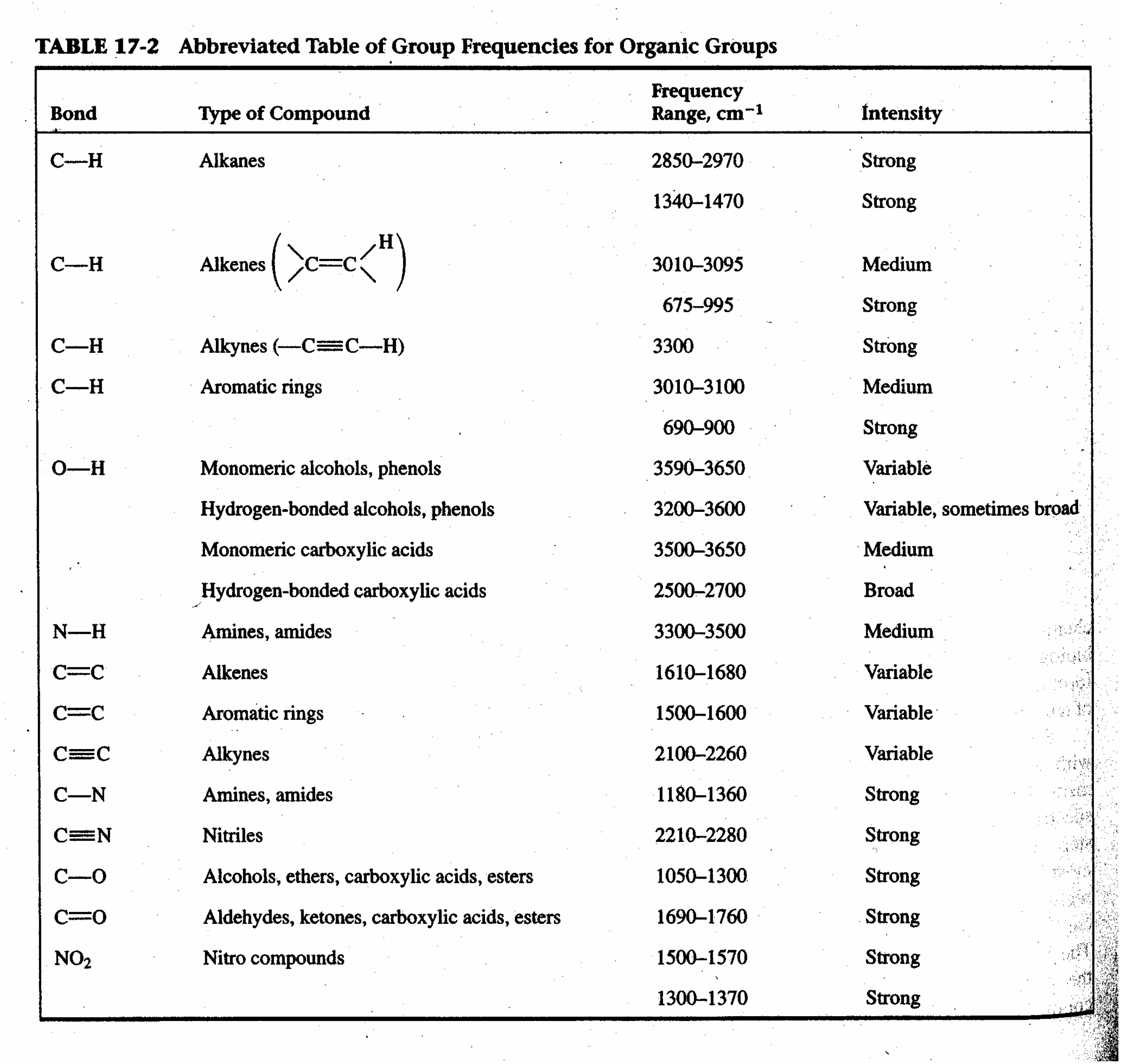


TABLE 17-2 Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes	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

Quantitative Information

Wider slit widths leads to wider bandwidths.

This results in nonlinear Beer’s Law behavior

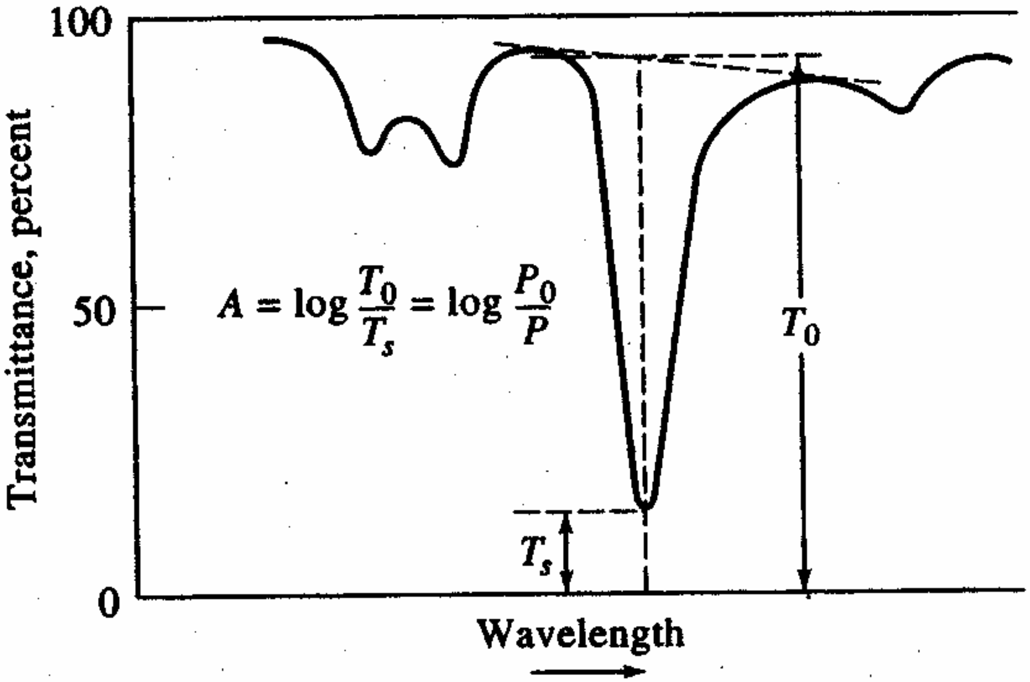


Figure 17-7 Baseline method for determination of absorbance.

$$\boxed{A = \varepsilon bC = \log P_{solvent}/P_{solution}}$$

Sample Handling

- **Solvents** = water and alcohol are seldom used as they absorb strongly and attack cell window materials. No solvent is transparent through-out the entire mid-IR region.
- **Cells** = NaCl or KBr often used as a transparent material – sample holder.
- **Samples** = gases, liquids or solids. Pelleting (1 part sample: 1 parts KBr, press to make a transparent pellet) and mulls (dispersing solid in mineral oil)

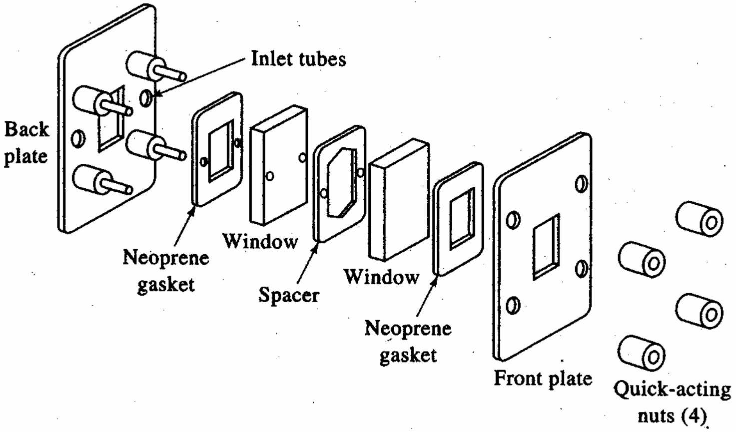


Figure 17-2 Expanded view of a demountable infrared cell for liquid samples. Teflon spacers ranging in thickness from 0.015 to 1 mm are available. *(Courtesy of Perkin-Elmer, Norwalk, CT.)*

Diffuse Reflectance Mode

Useful for the study of the surface chemistry of powder samples

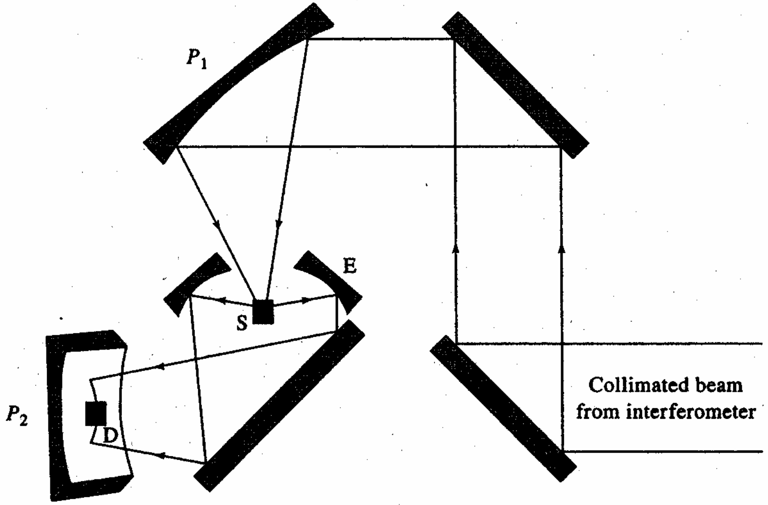


Figure 17-9 A diffuse reflectance attachment for a Fourier transform spectrometer. *(From M. P. Fuller and P. R. Griffiths,* Anal. Chem., *1978,* 50, *1907. With permission.)*

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

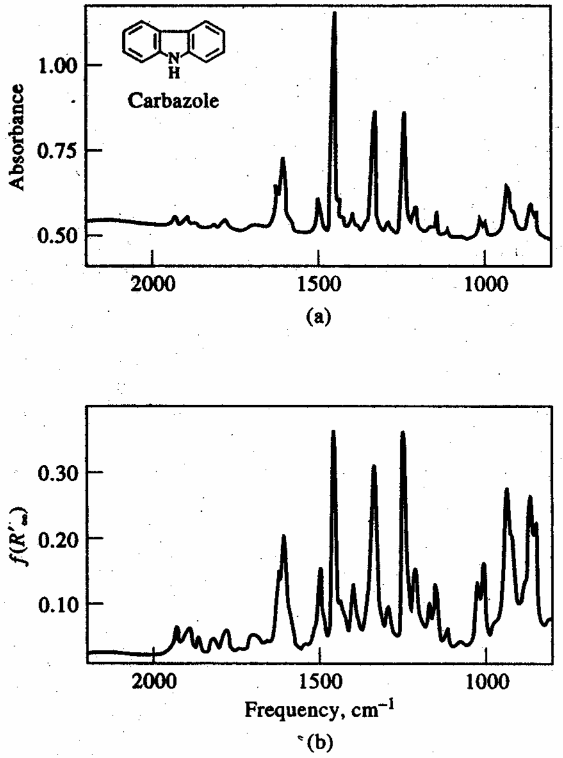


Figure 17-10 Comparison of the absorption spectrum (a) for carbazole with its diffuse reflectance spectrum (b).

Attenuated Total Reflectance

Useful for solids of limited solubility, films, threads, pastes, etc.

Total internal reflection

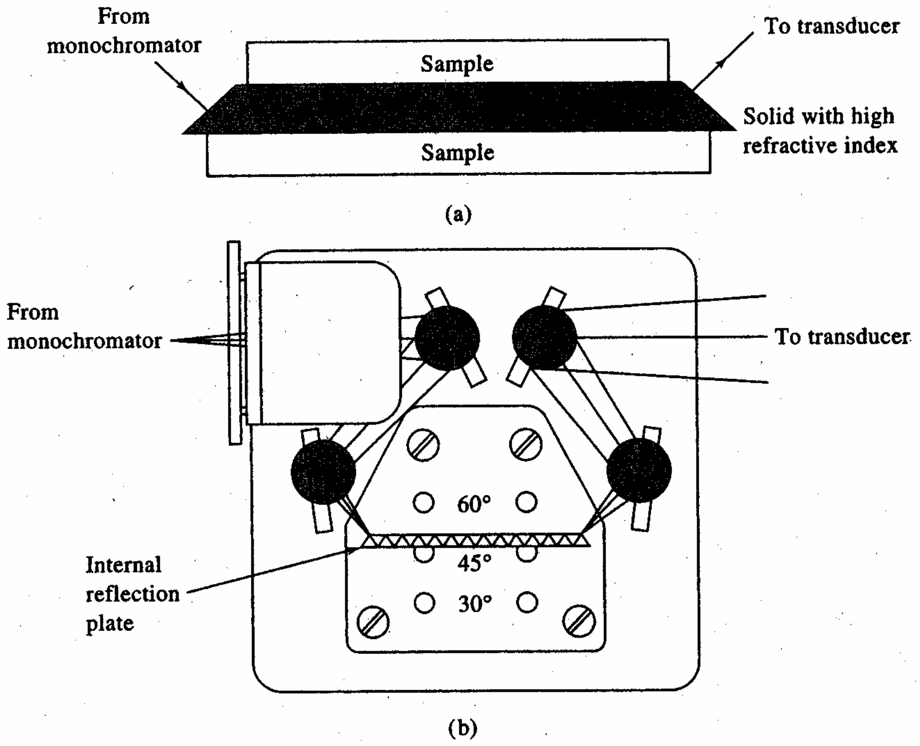
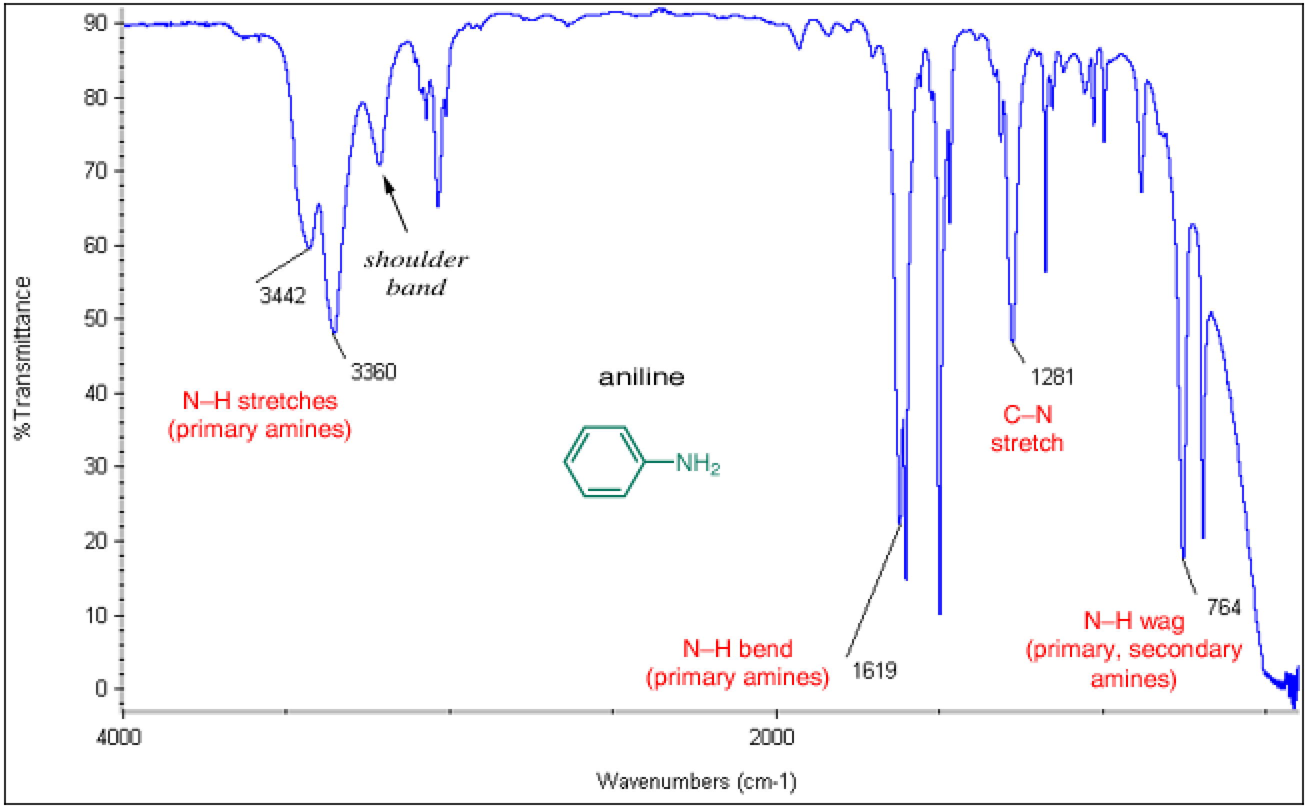


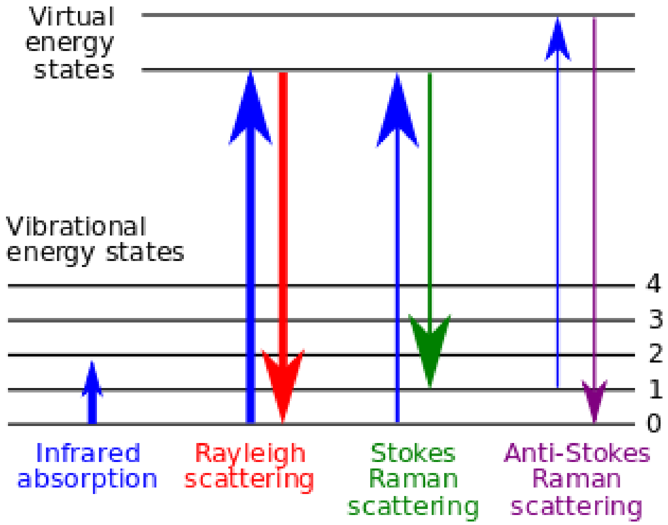
Figure 17-11 Attenuated total reflectance apparatus. (a) Sample mounted on reflection plate; (b) internal reflection adapter. *(Courtesy of The Foxboro Company, Foxboro, MA.)*

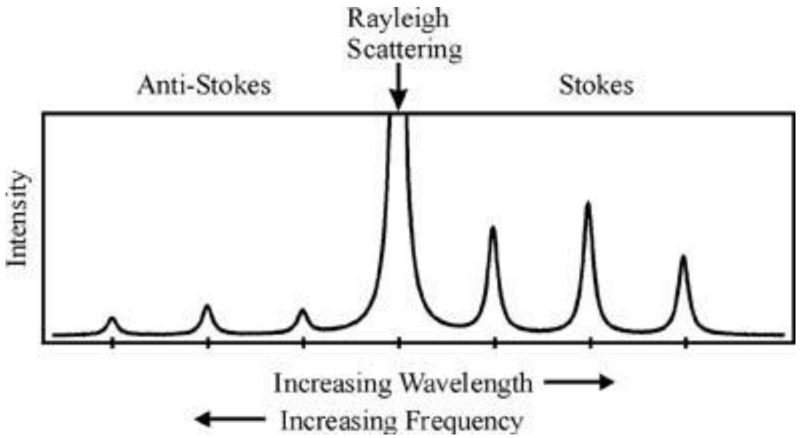
https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/Spectrpy/InfraRed/infrared.htm



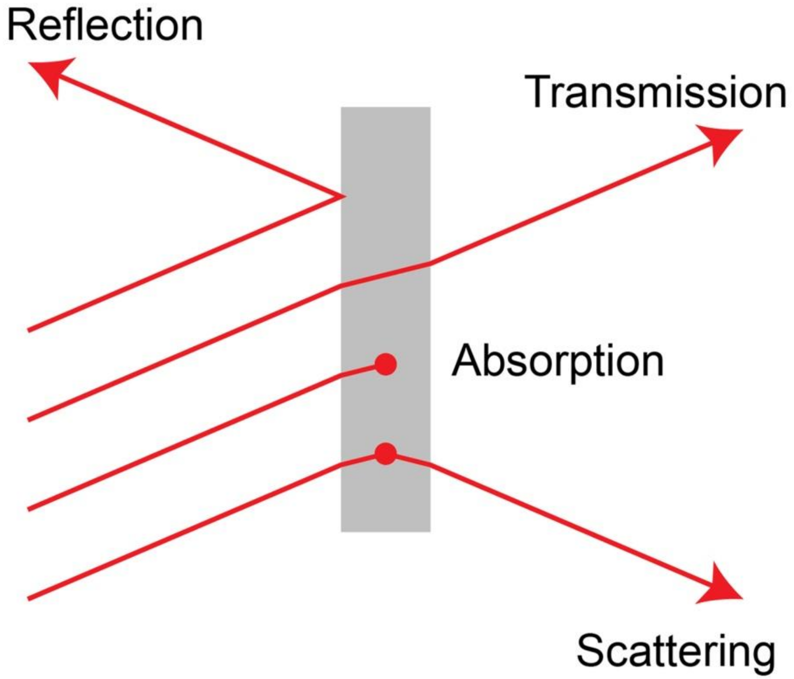
Raman Spectroscopy

A spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system.[1] It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.





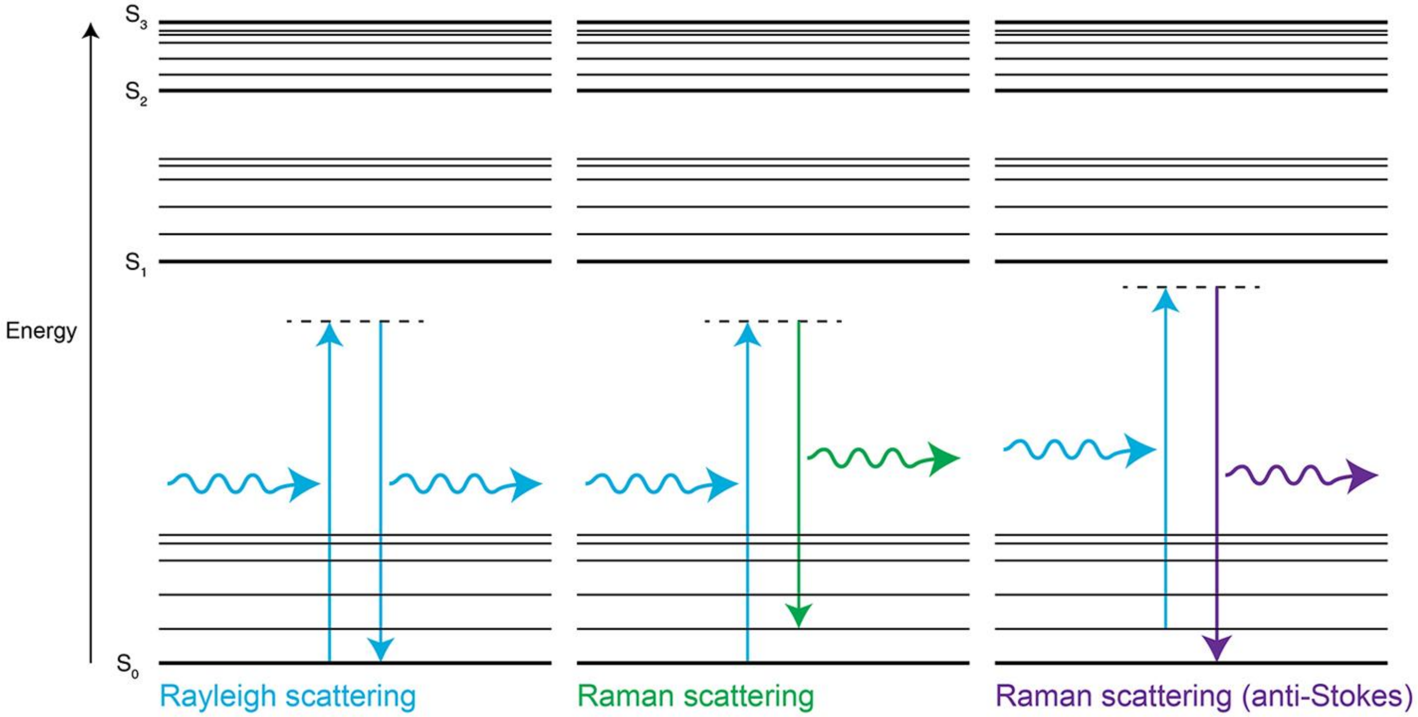
Light Interacting With Matter - Spectroscopy



- •Reflection - *Change in light direction at a fixed angle*
- •Transmission - *Passage of light through the material, without loss of energy*
- •Absorption - *Transfer of light radiation to energy within a material*
- •Scattering - *Change in light direction*

Raman Effect

Most of the light that scatters off is unchanged in energy ('Rayleigh scattered'). A minute fraction—perhaps 1 part in 10 million—has lost or gained energy ('Raman scattered'). This Raman shift occurs because photons (particles of light) exchange part of their energy with molecular vibrations in the material.



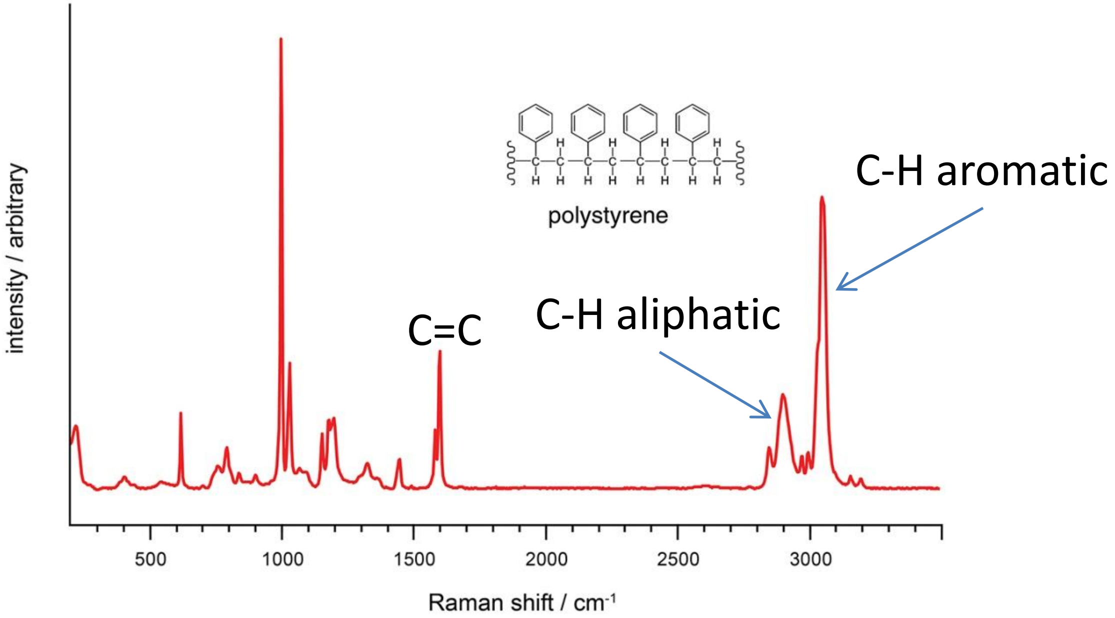
Renishaw Instruments

Application Areas

- Life Sciences (cells, tissues, micro-organisms)
- Materials Sciences (carbon and nanotechnology, semiconductors, catalysts)
- Chemical Sciences (pharmaceuticals, polymers, chemicals)
- Earth Sciences (geology, gemmology)
- Analytical Sciences (art, forensics, contaminants)

Example Spectrum

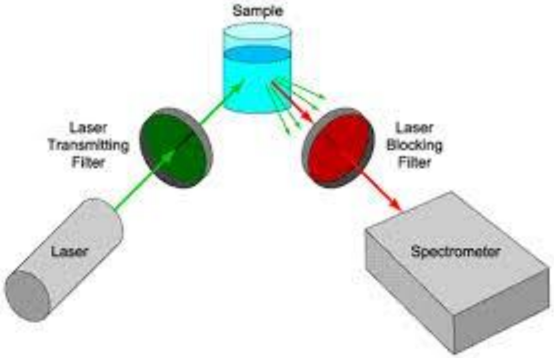
One plots the intensity of the scattered light (y-axis) for each energy (frequency) of light (x-axis). The frequency is traditionally measured in a unit called the wavenumber (number of waves per cm, cm^{-1}). We plot the x-axis frequencies relative to that of the laser as it is the shift in energy of the light that is of particular interest.



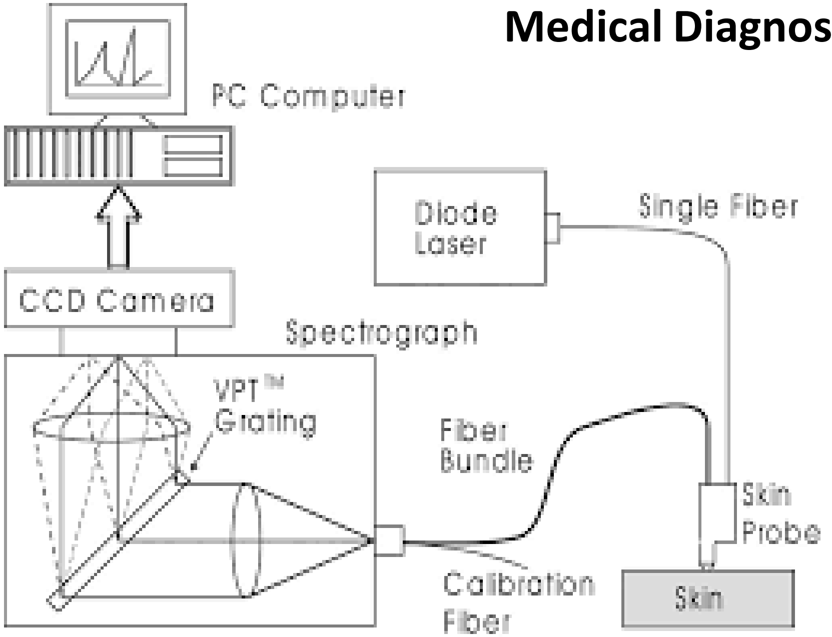
- High frequency carbon-hydrogen (C-H) vibrations in the polystyrene spectrum at about 3000 cm^{-1}. The low frequency carbon-carbon (C-C) vibrations are at around 800 cm^{-1}.
- Vibrations of two carbon atoms linked by strong double bonds (C=C) at around 1600 cm^{-1}. This is at a higher frequency than two carbon atoms lined by a weaker single bond (C-C, 800 cm^{-1}).

Different Types of Raman Instruments

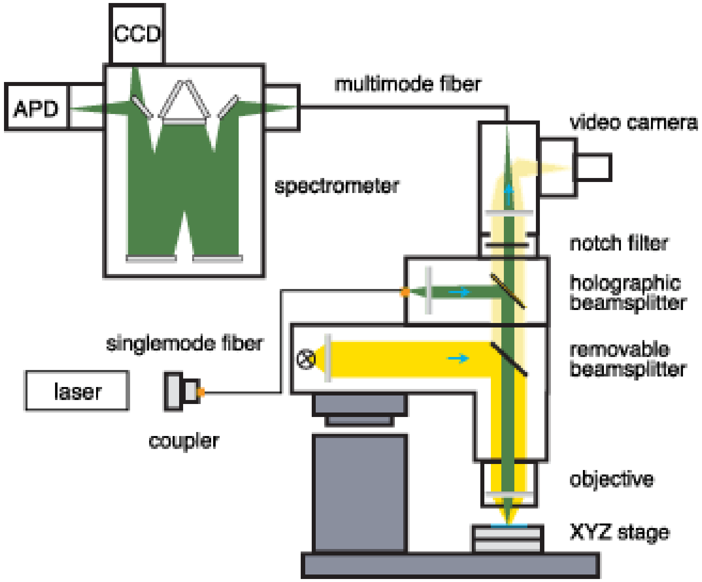
Process Control



Medical Diagnostics

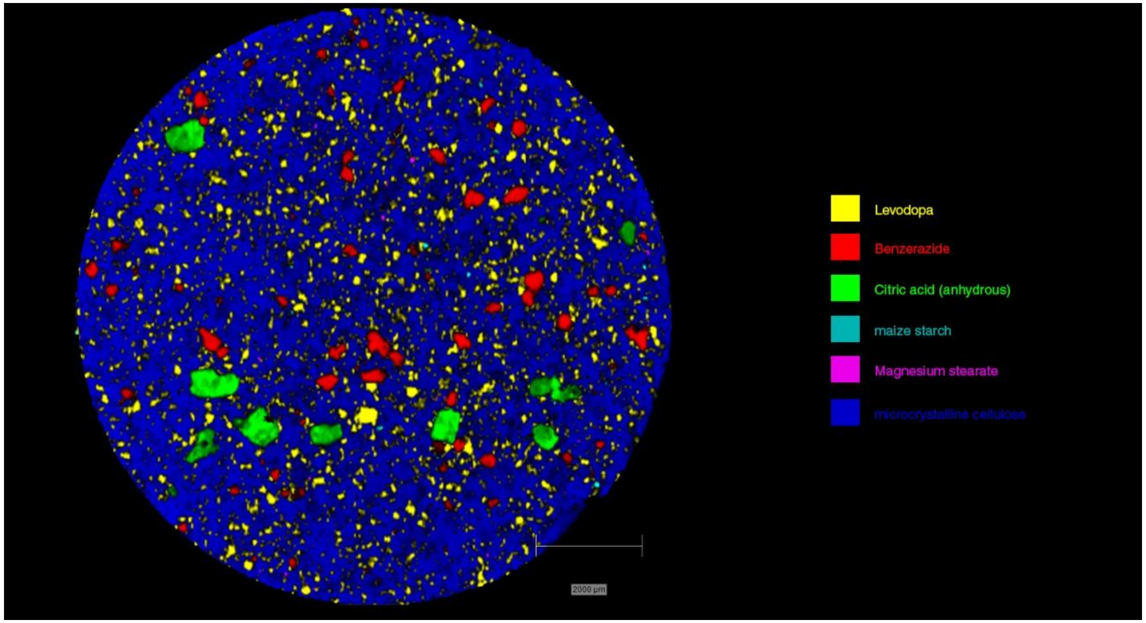


Raman Microscope and Imaging



Images from Internet

Why Use Raman Imaging?



Raman image of tablet used for the treatment of Parkinson's disease.

Renishaw Instruments

You can determine:

- if a specific material or species is present
- if any unknown materials are present in the sample
- the variation in a parameter of a material, such as crystallinity or stress state
- the distribution of the material or species
- the size of any particles or domains
- the thickness and composition of layered materials
- the relative amounts of materials or species

Raman Spectroscopy

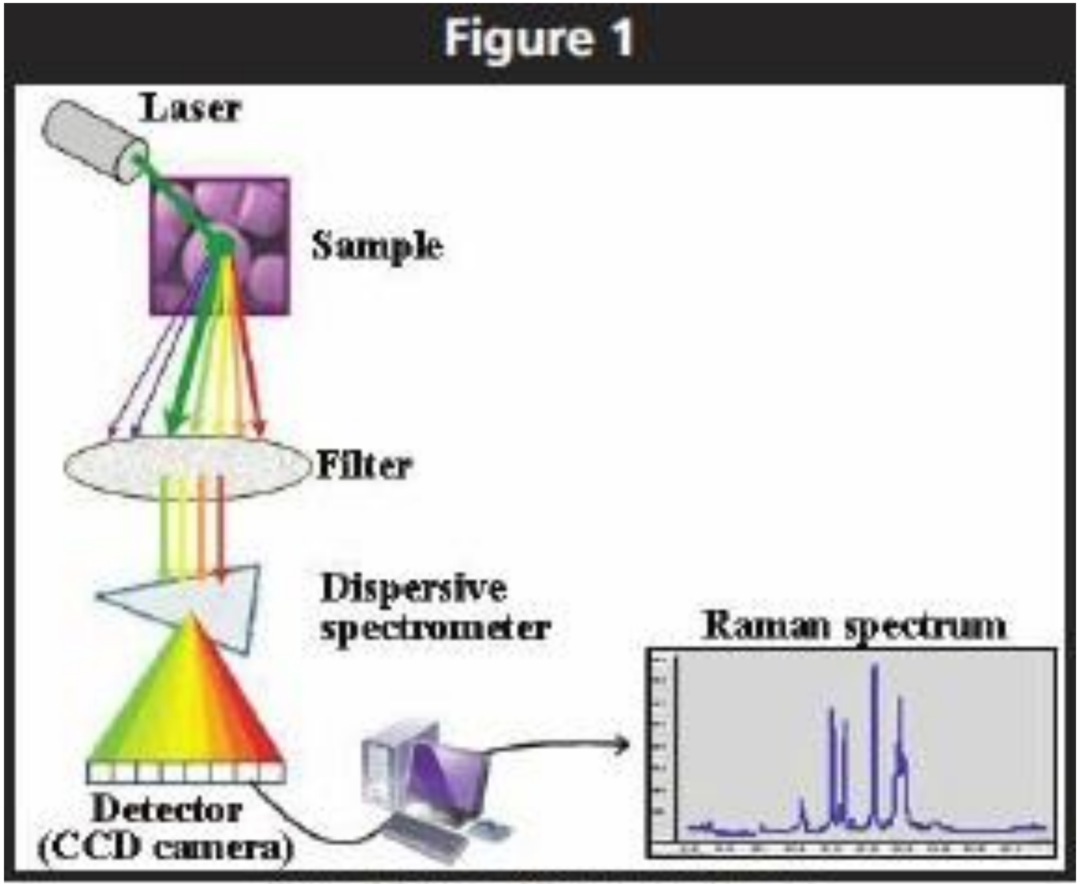


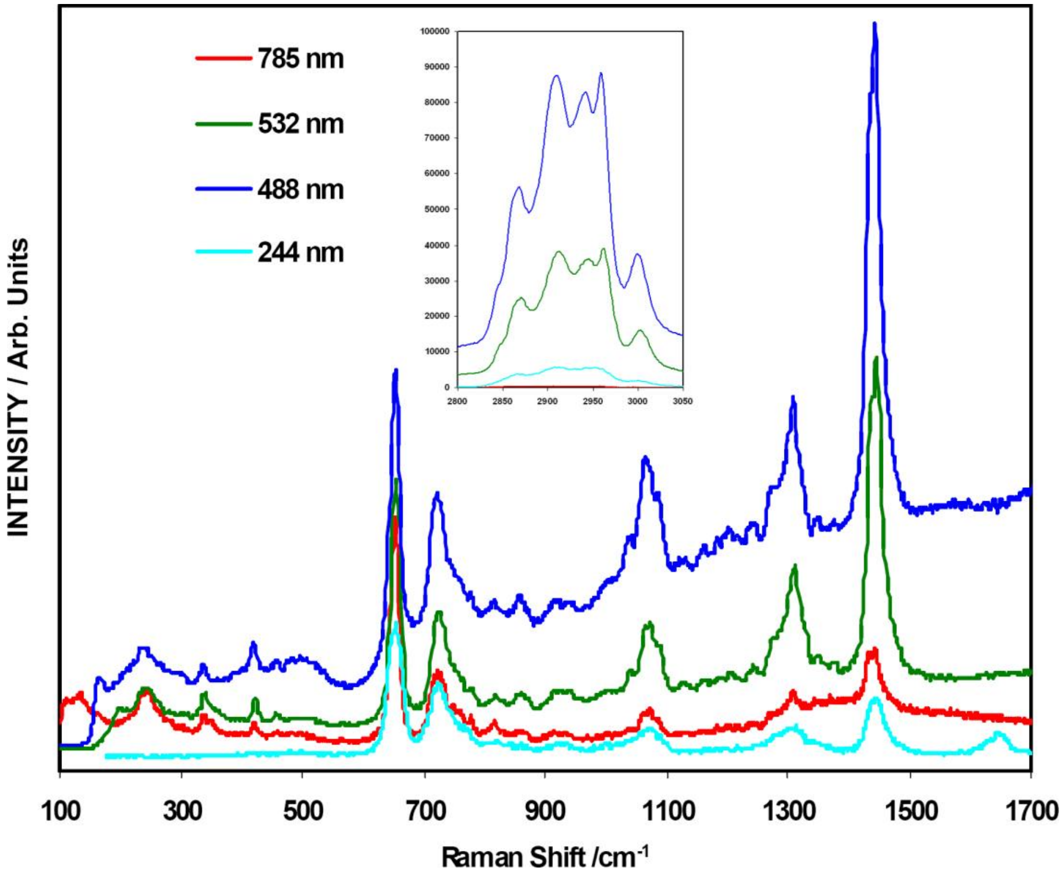
Figure 1: Schema of Raman spectroscopy

Raman Scattering Depends on the Excitation Wavelength

$$I_R = \text{(Parameters)}\, P_o\, \beta\, N_d\, d\, \lambda^{-4}$$

IR (photons $sr^{-1}\, s^{-1}$), P_o (photons s^{-1}), β ($cm^2\, sr^{-1}$ molecule^{-1}), N_d (molecules cm^{-3}), d (cm), λ (cm)

1,6-dichlorohexane



Surfaced Enhanced Raman Spectroscopy

Raman signals are inherently weak, especially when using visible light excitation and so a low number of scattered photons are available for detection. One method to amplify weak Raman signals is to employ surface-enhanced Raman scattering (SERS). SERS uses nanoscale roughened metal surfaces typically made of gold (Au) or silver (Ag). Laser excitation of these roughened metal nanostructures resonantly drives the surface charges creating a highly localized (plasmonic) light field. When a molecule is absorbed or lies close to the enhanced field at the surface, a large enhancement in the Raman signal can be observed.