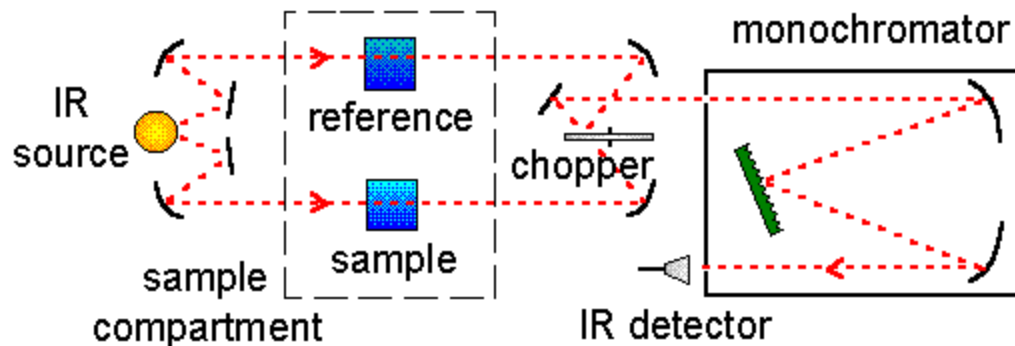
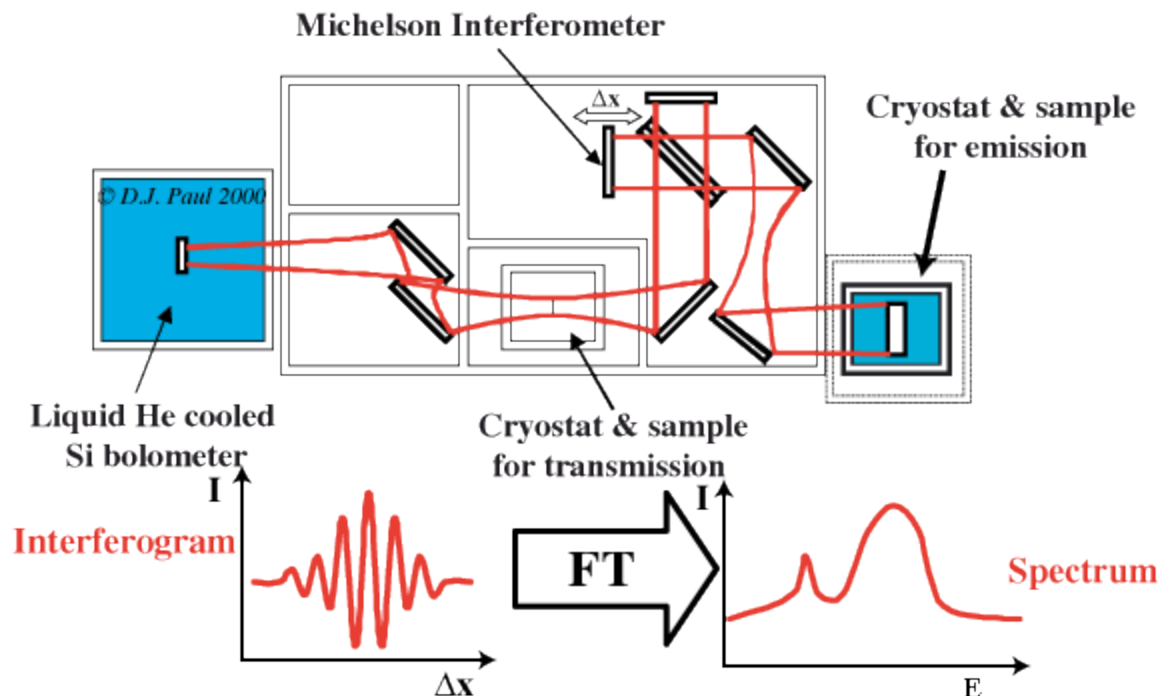


Dispersive vs. FTIR Instruments



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Chapter 17: Applications of Infrared Spectroscopy

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

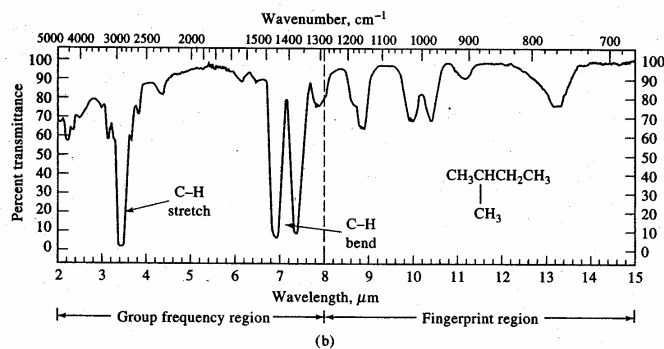
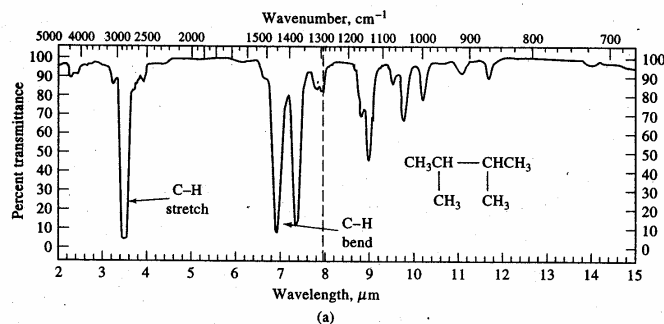


Figure 17-4 Group frequency and fingerprint regions of the mid-infrared spectrum. (From R. M. Roberts, J. C. Gilbert, L. B. Rodewald, and A. S. Wingrove, *Modern Experimental Organic Chemistry*, 4th ed. Philadelphia: Saunders College Publishing, 1985. With permission.)

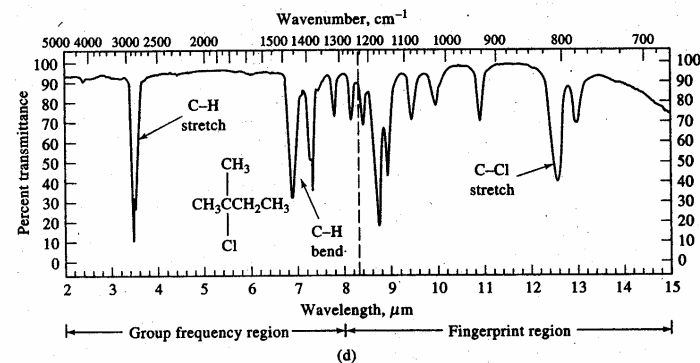
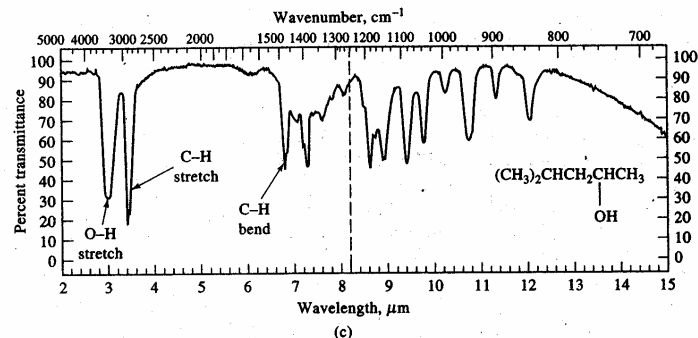


Figure 17-4 Continued

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 (>C=C<H)	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 $\equiv$ C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C $\equiv$ 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

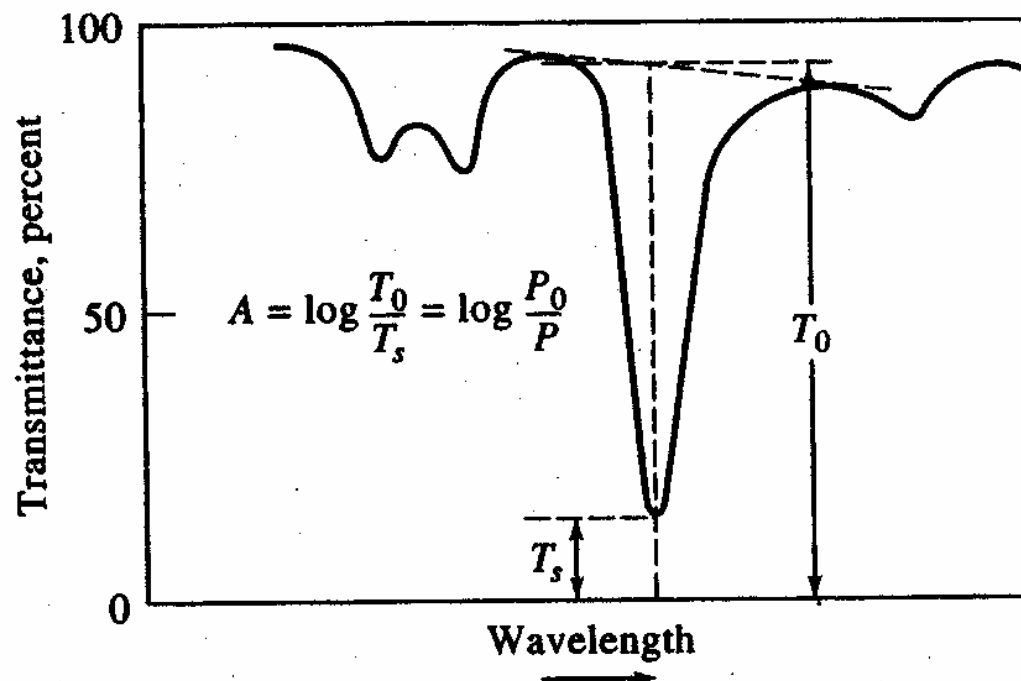


Figure 17-7 Baseline method for determination of absorbance.

$$A = \epsilon b C = \log P_{\text{solvent}} / P_{\text{solution}}$$

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)

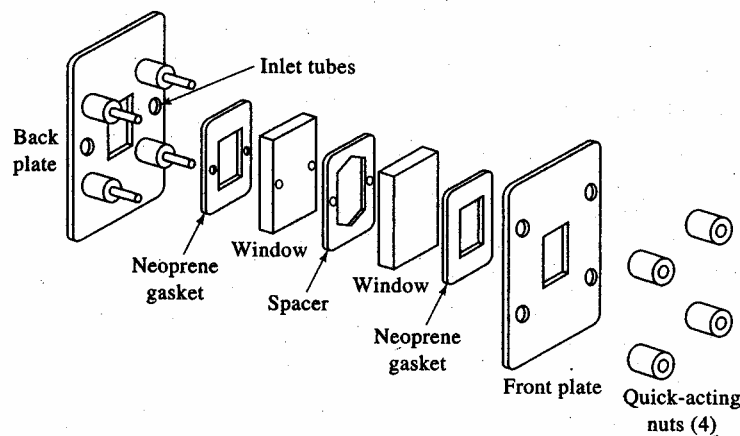


Figure 17-2 Expanded view of a demountable infrared cell for liquid samples. Teflon spacers ranging in thickness from 0.015 to 1 mm are available. (Courtesy of Perkin-Elmer, Norwalk, CT.)

Diffuse Reflectance Mode

Useful for the study of the surface chemistry of powder samples

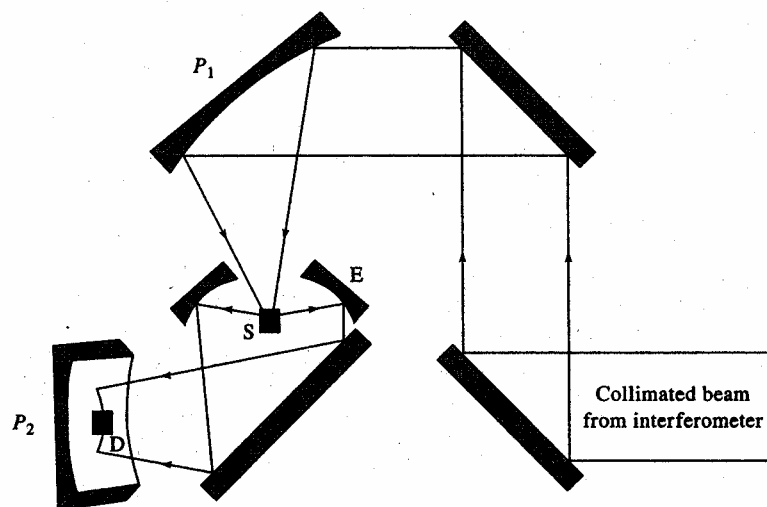


Figure 17-9 A diffuse reflectance attachment for a Fourier transform spectrometer. (From M. P. Fuller and P. R. Griffiths, *Anal. Chem.*, 1978, 50, 1907. With permission.)

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

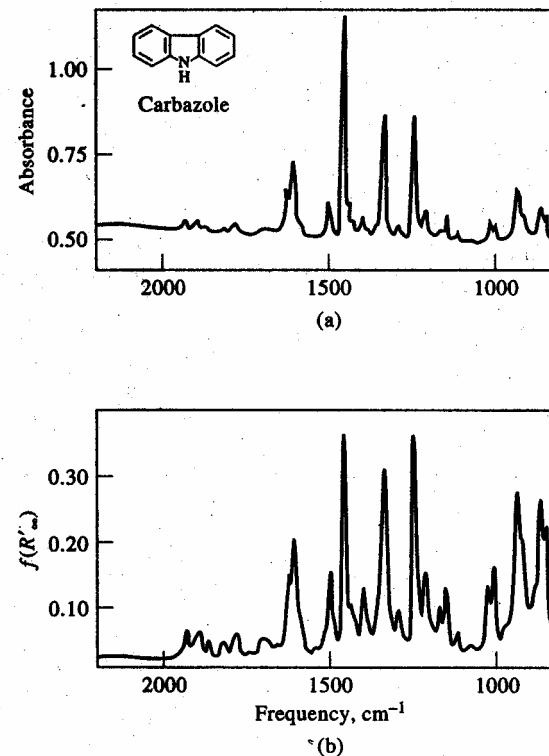


Figure 17-10 Comparison of the absorption spectrum (a) for carbazole with its diffuse reflectance spectrum (b).

Attenuated Total Reflectance

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

Total internal reflection

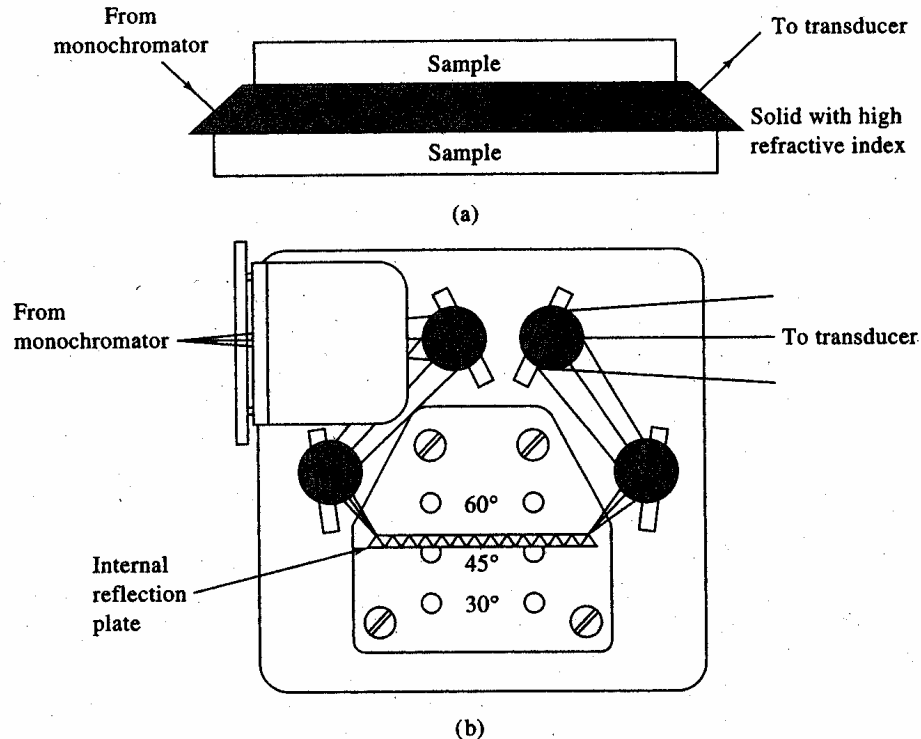
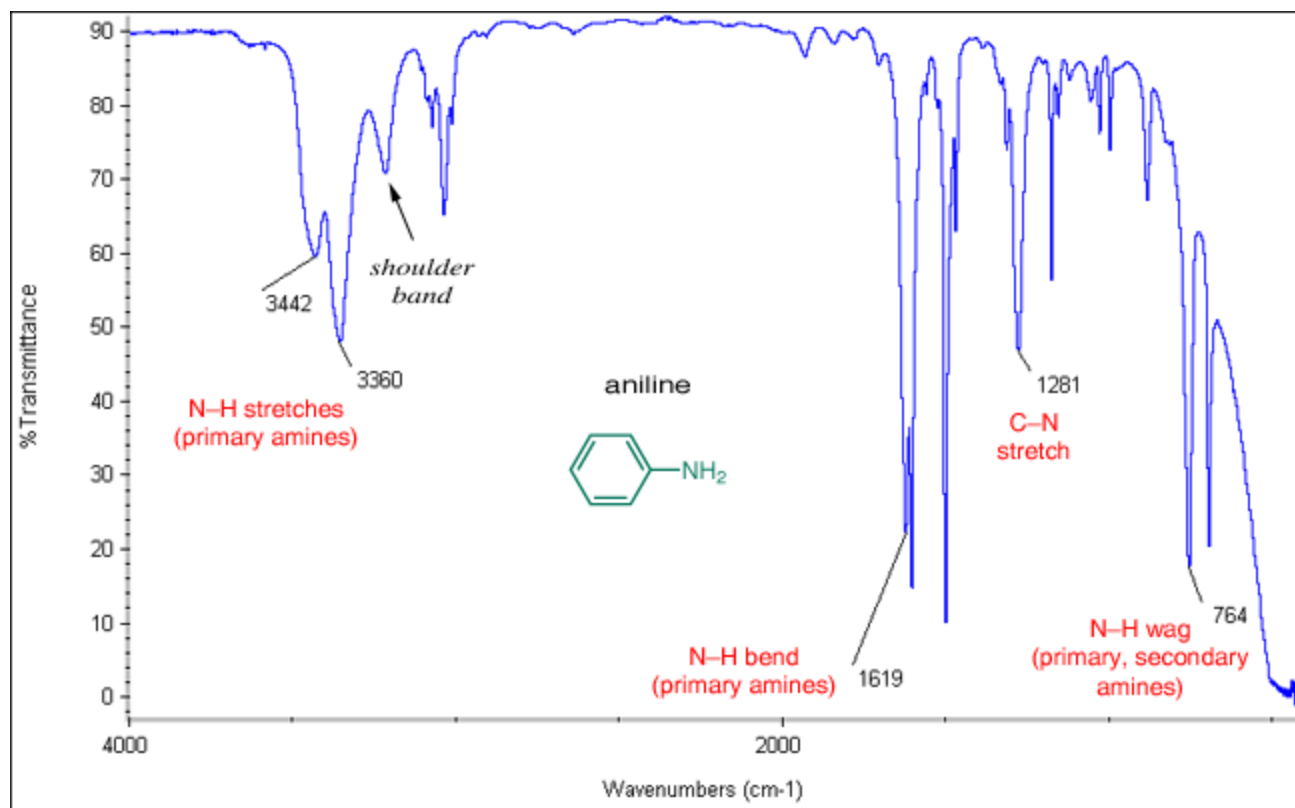


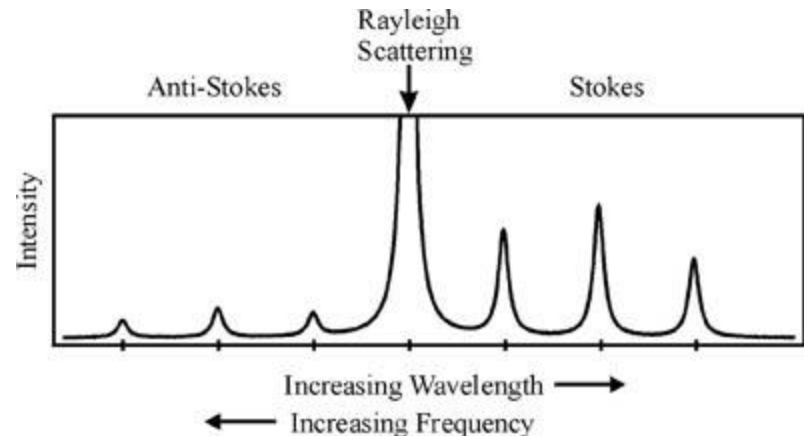
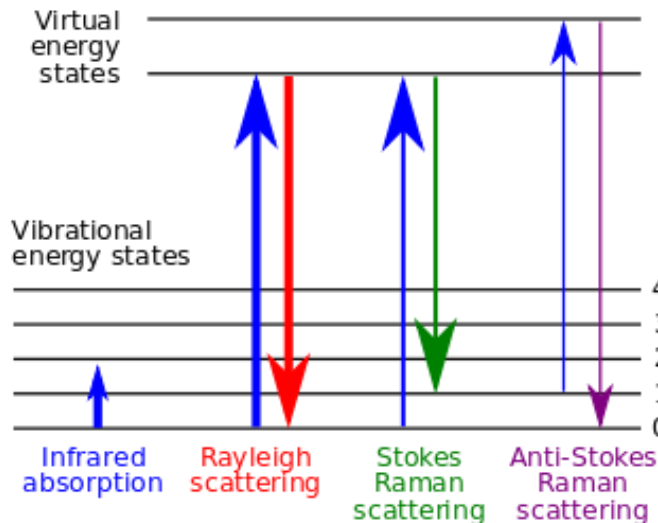
Figure 17-11 Attenuated total reflectance apparatus. (a) Sample mounted on reflection plate; (b) internal reflection adapter. (Courtesy of The Foxboro Company, Foxboro, MA.)

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

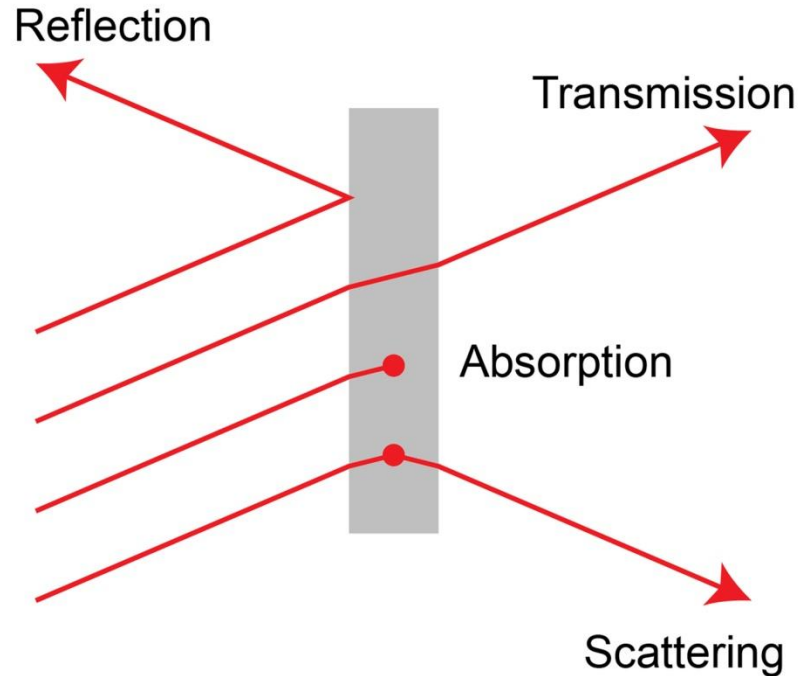


Raman Spectroscopy

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.



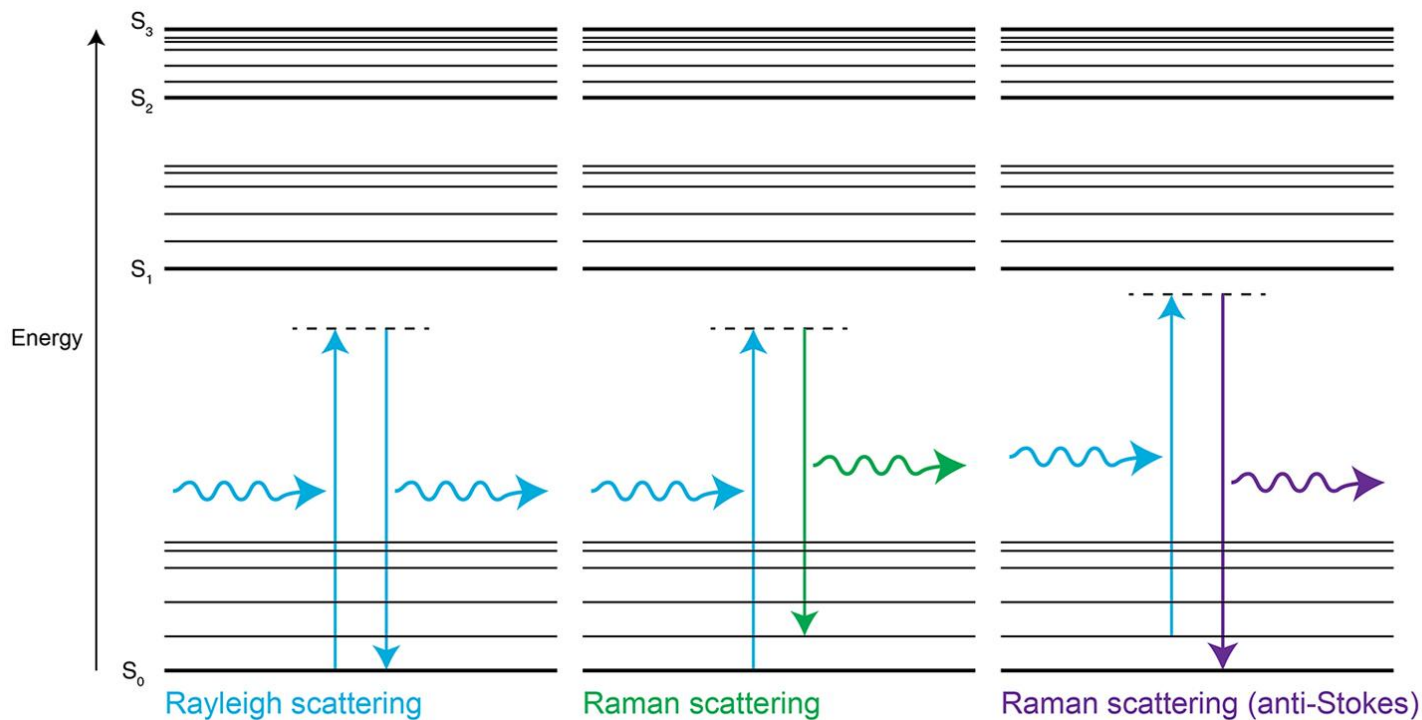
Light Interacting With Matter - Spectroscopy



- 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.

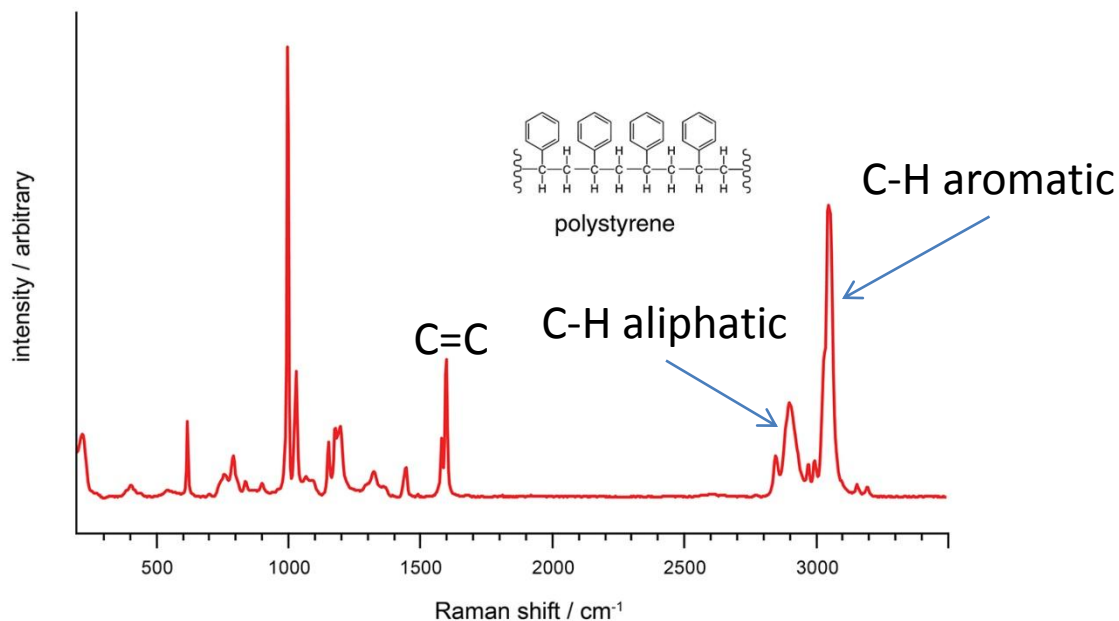


Application Areas

- 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

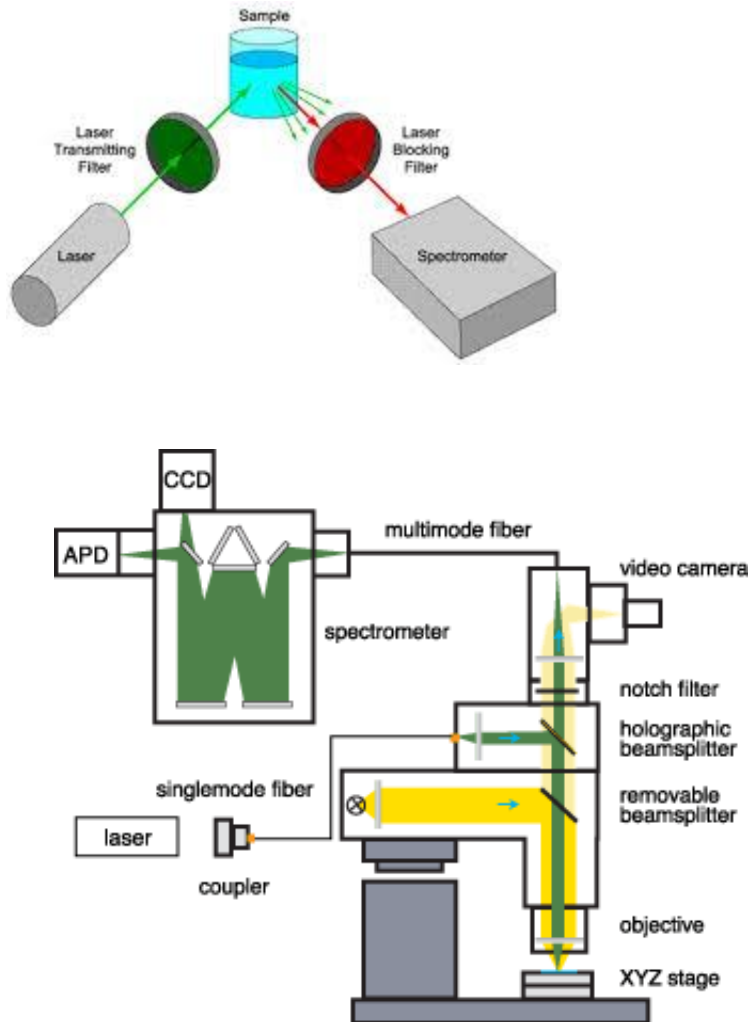
One plots the intensity of the scattered light (y-axis) for each energy (frequency) of light (x-axis). The frequency is traditionally measured in a unit called the wavenumber (number of waves per cm, cm^{-1}). We plot the x-axis frequencies relative to that of the laser as it is the shift in energy of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



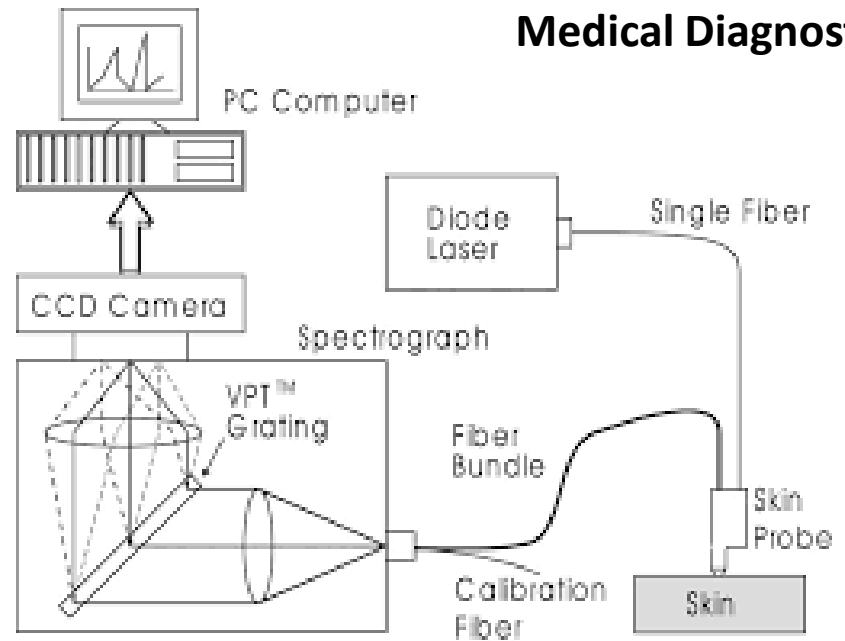
- High frequency carbon-hydrogen (C-H) vibrations in the polystyrene spectrum at about 3000 cm^{-1} . The low frequency carbon-carbon (C-C) vibrations are at around 800 cm^{-1} .
- Vibrations of two carbon atoms linked by strong double bonds (C=C) at around 1600 cm^{-1} . This is at a higher frequency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

Different Types of Raman Instruments

Process Control



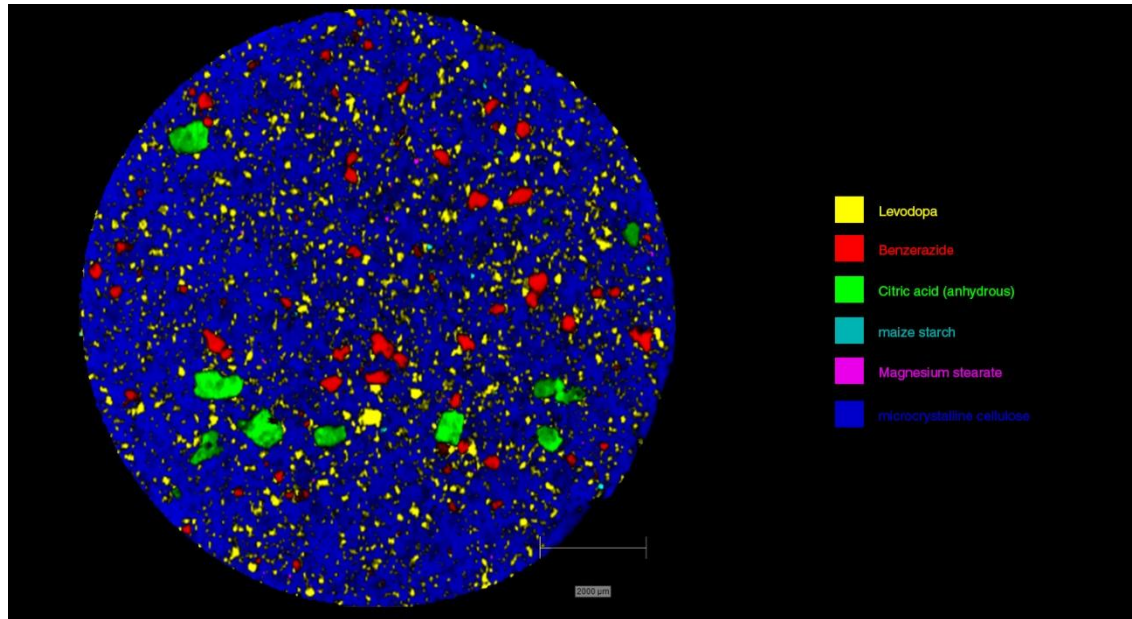
Medical Diagnostics



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

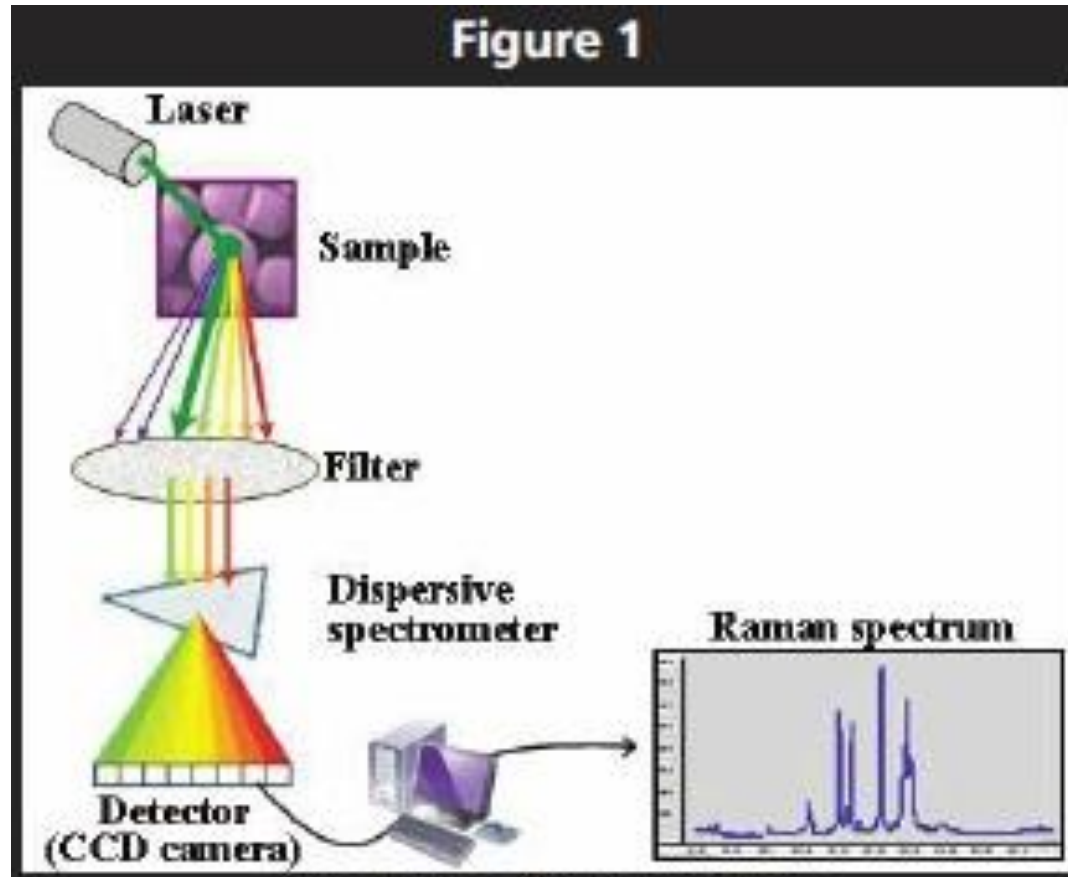


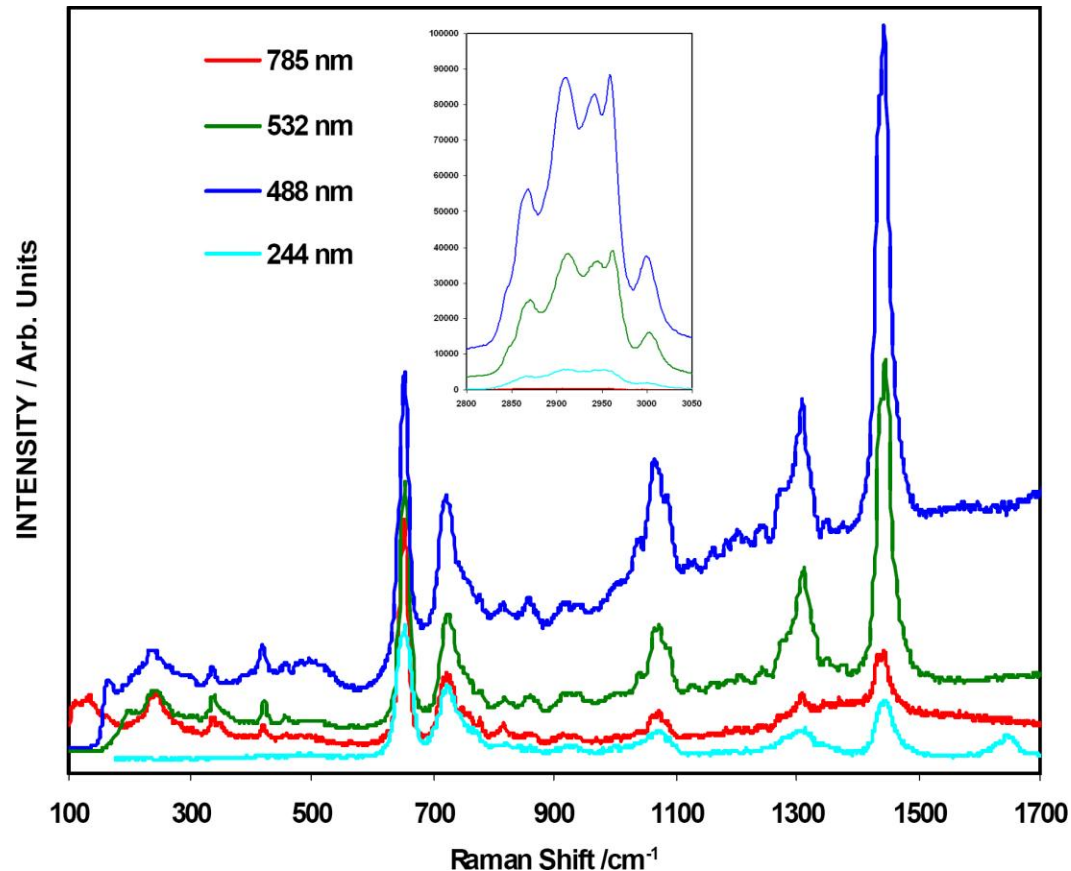
Figure 1: Schema of Raman spectroscopy

Raman Scattering Depends on the Excitation Wavelength

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

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

1,6-dichlorohexane



Surface 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.

