# 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 $\mu$m or 4000 to 200 cm$^{-1}$ (mid-IR)

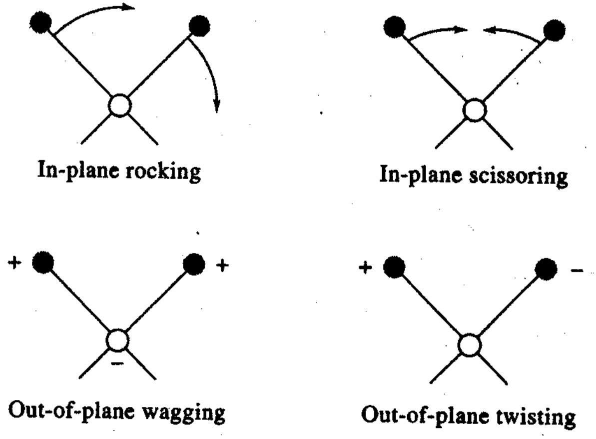
Much lower in energy than electonic excitation!

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

4.3 $\mu$m = 4.6 x 10$^{-20}$ J/photon or 27 kJ/mol

## Types of Vibrations

(a) Stretching vibrations



(b) Bending vibrations

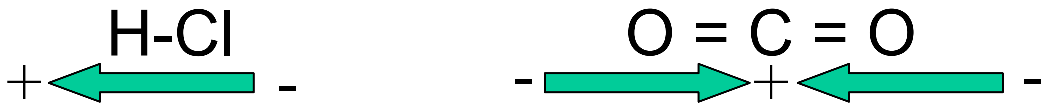
**Figure 16-2** Types of molecular vibrations. Note: + indicates motion from the page toward the reader; – indicates motion away from the reader.

# 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.

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



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

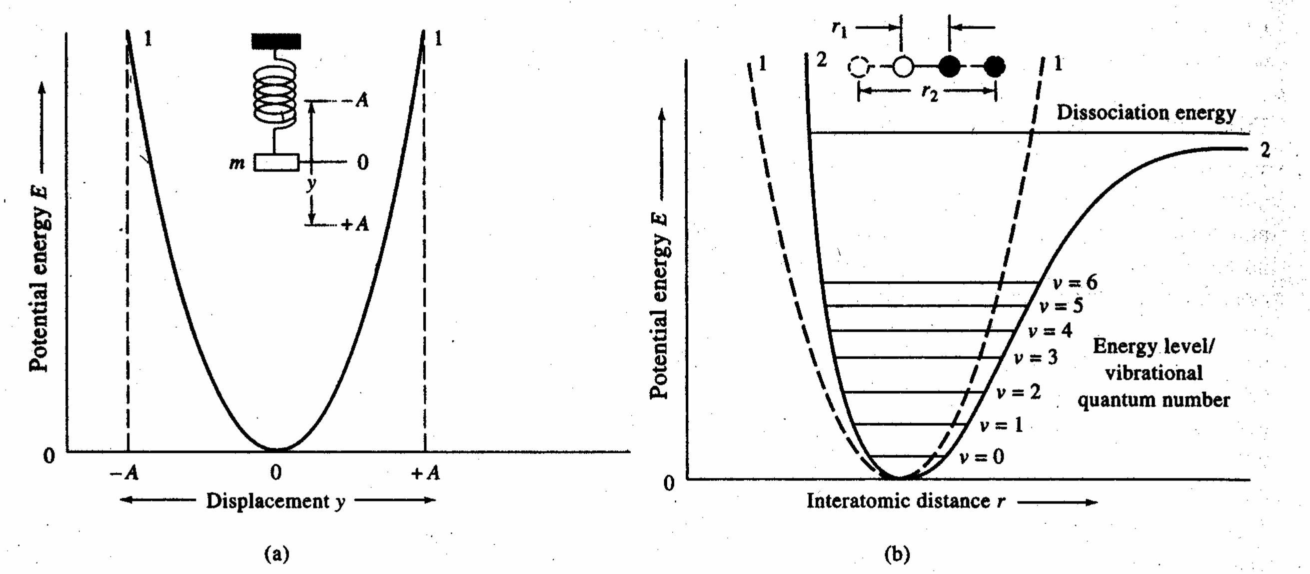


**Figure 16-3** Potential energy diagrams. Curve 1, harmonic oscillator. Curve 2, anharmonic oscillator.

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

F = -ky

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

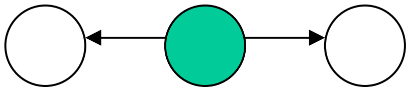
$$\upsilon_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1m_2}}$$

# An Absorption Example

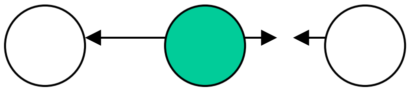
O = C = O A linear, symmetric molecule!

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 $\mu$m))

Degenerate bending motions (667 cm$^{-1}$ (15 $\mu$m))

# 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)

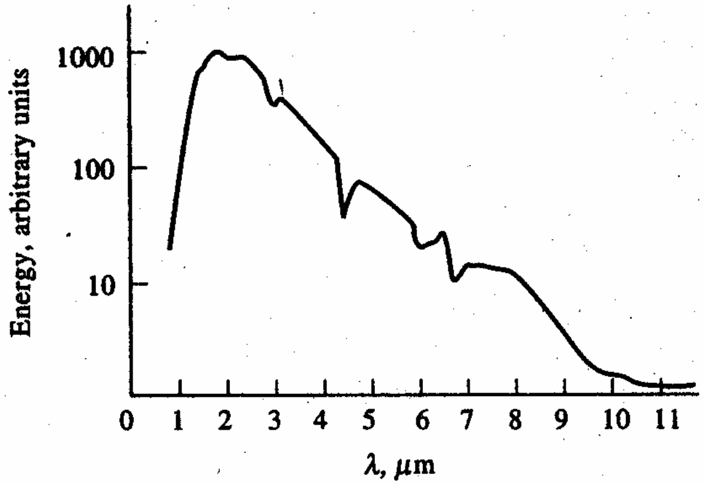


**Figure 16-4** Spectral distribution of energy from a Nernst glower operated at approximately 2200 K.

Instruments must have good focusing and collection optics!!

Go back and read pp. 206-212!!

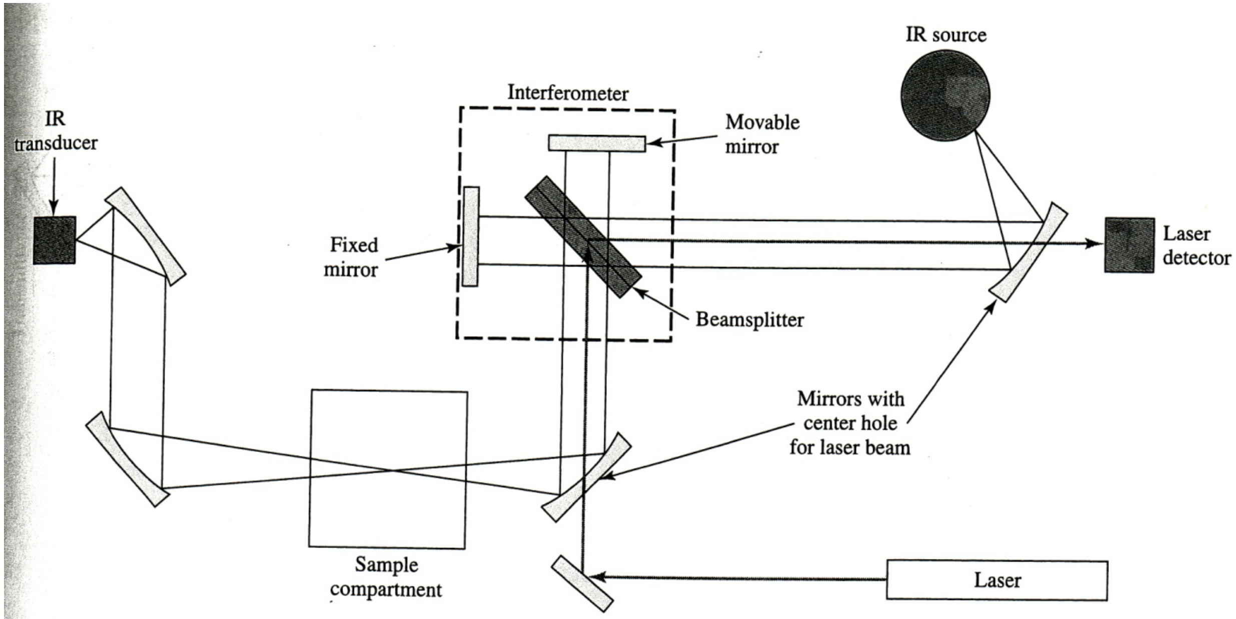


**FIGURE 16-8** Single-beam FTIR spectrometer. In one arm of the interferometer, the IR source radiation travels through the beamsplitter to the fixed mirror, back to the beamsplitter, and through the sample to the IR transducer. In the other arm, the IR source radiation travels to the beamsplitter, 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.

# Advantages of Fourier Transform Spectrometers

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

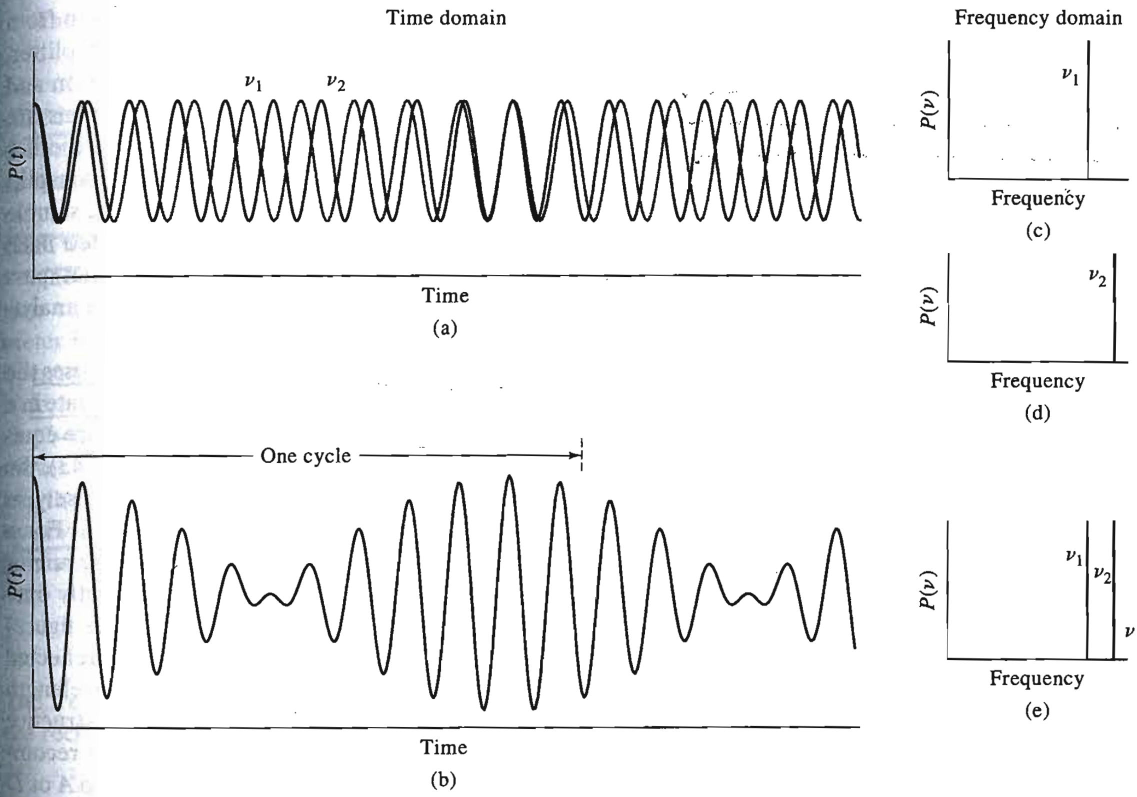


**FIGURE 7-41** (a) Time-domain plot of two slightly different frequencies of the same amplitude $\nu_1$ and $\nu_2$. (b) Time-domain plot of the sum of the two waveforms in (a). (c) Frequency-domain plot of $\nu_1$. (d) Frequency-domain plot of $\nu_2$. (e) Frequency-domain plot of the waveform in (b).

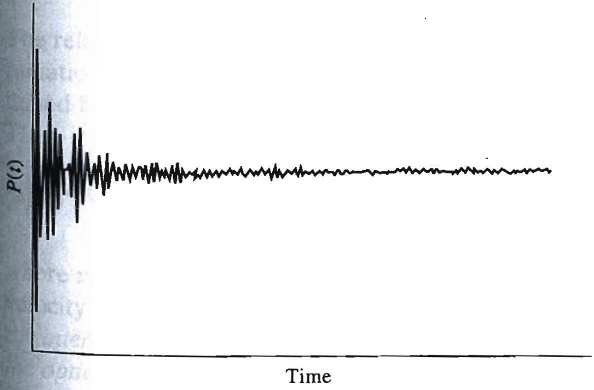


**FIGURE 7-42** Time-domain signal of a source made up of many wavelengths.

**meters.**

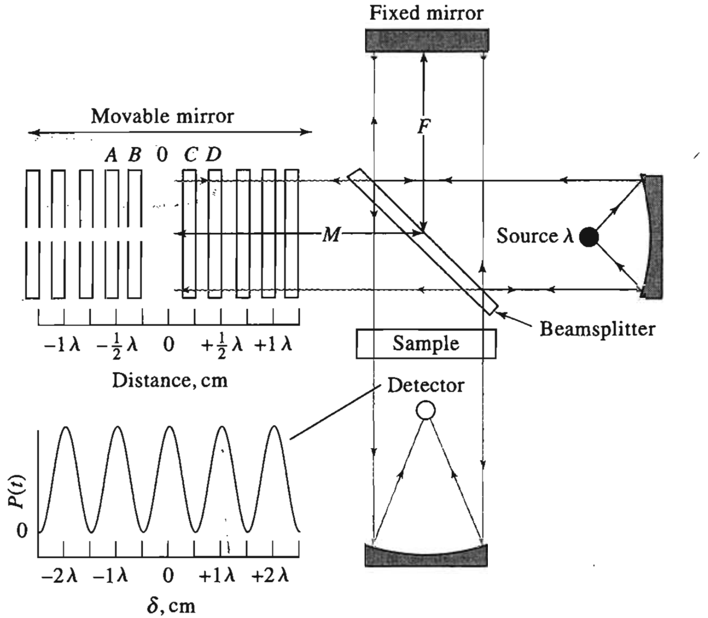


**FIGURE 7-43** Schematic of a Michelson interferometer illuminated by a monochromatic source.

# Typical FTIR Spectrometer

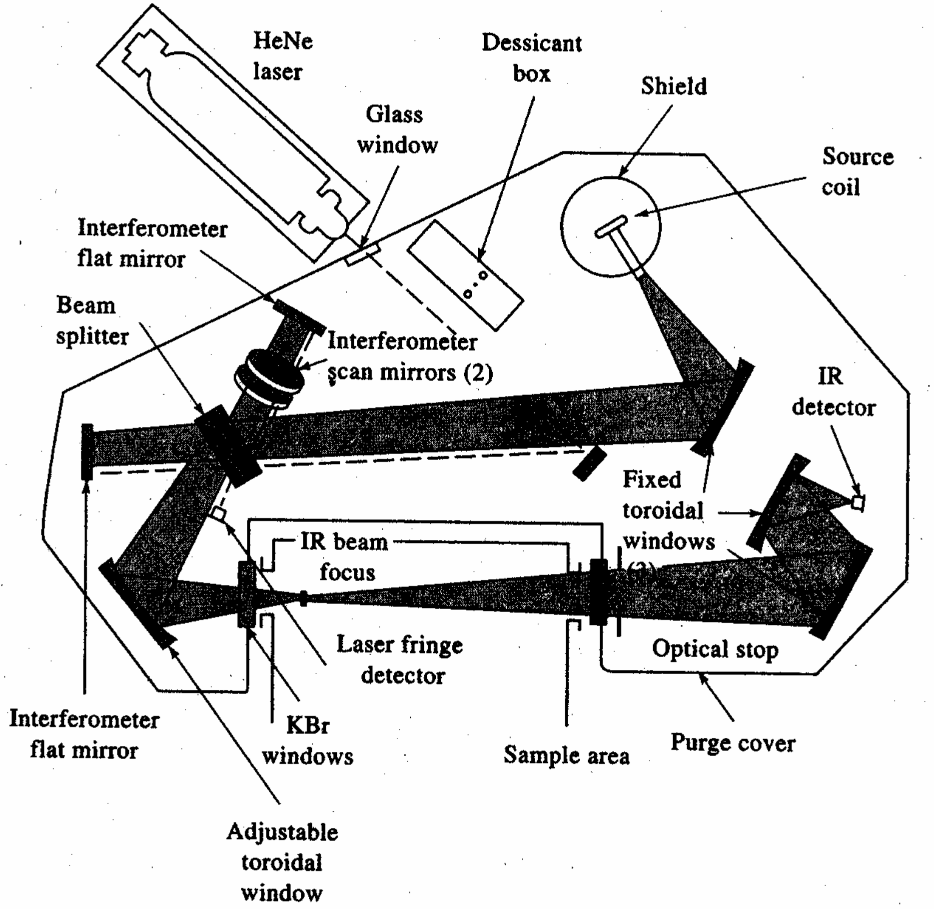


**Figure 16-8** A single-beam FTIR spectrometer. *(Courtesy of Perkin-Elmer, Norwalk, CT.)*

# Typical Background Spectrum of Air

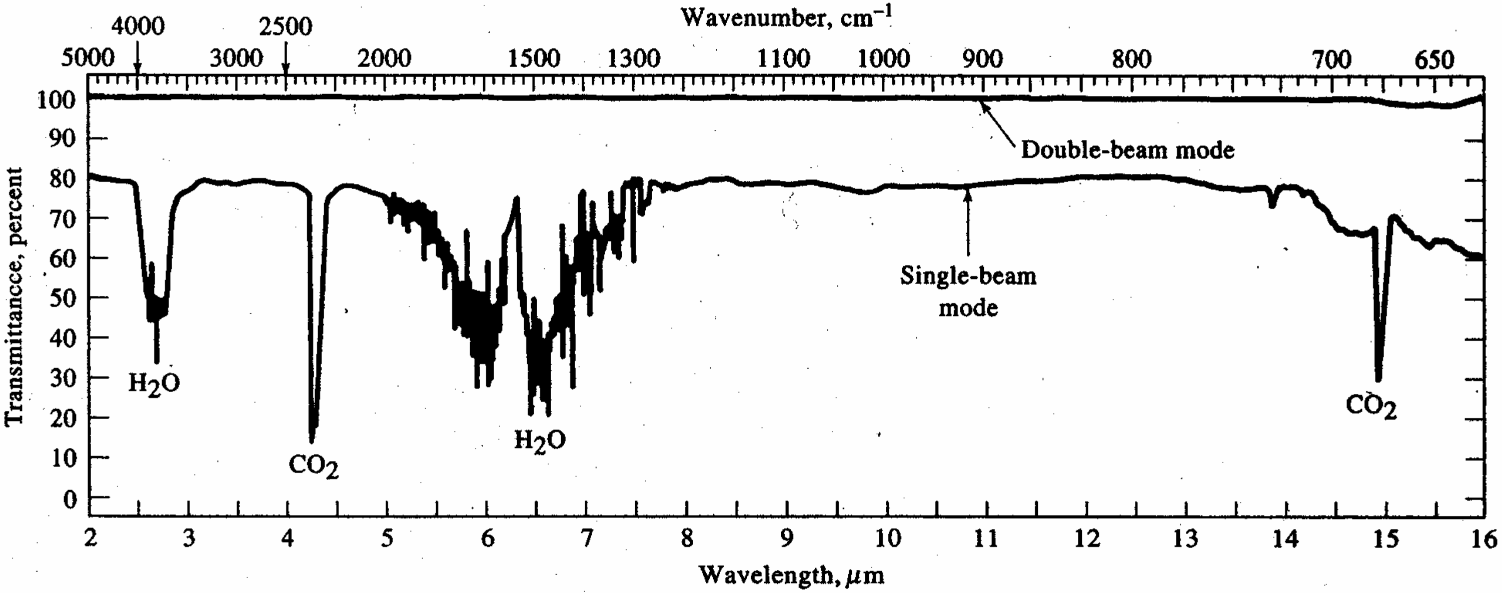


**Figure 16-9** Single- and double-beam spectra of atmospheric water vapor and $CO_2$. In the lower, single-beam trace, the absorption of atmospheric gases is apparent. The top, double-beam trace shows that the reference beam compensates nearly perfectly for this absorption and allows a stable 100% *T* 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.)*

# Chapter 17: Applications of Infrared Spectroscopy

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

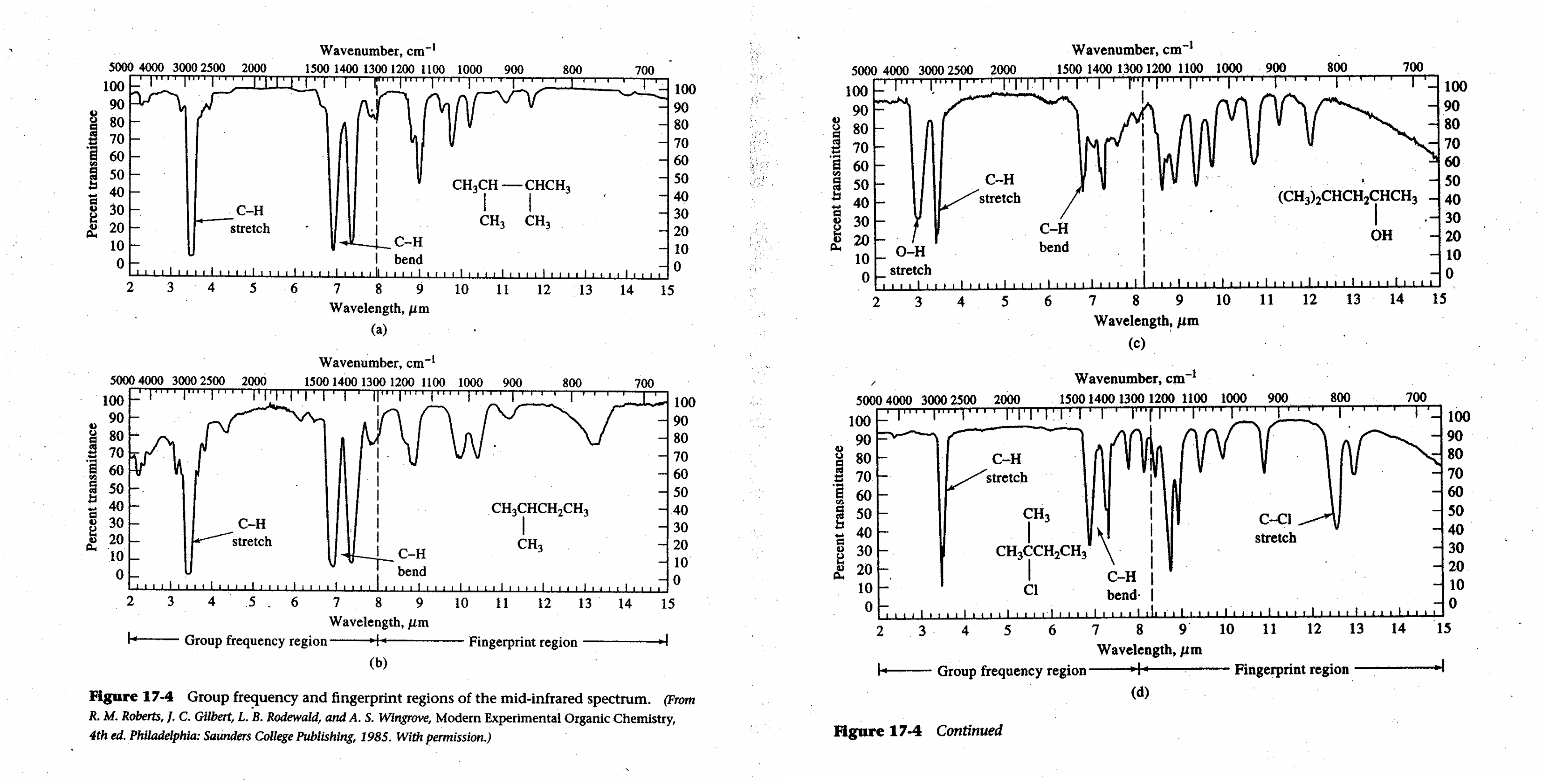


**Figure 17-4** Group frequency and fingerprint regions of the mid-infrared spectrum. *(From R. M. Roberts, J. C. Gilbert, L. B. Rodewald, and A. S. Wingrove,* Modern Experimental Organic Chemistry, *4th ed. Philadelphia: Saunders College Publishing, 1985. With permission.)*

**Figure 17-4** *Continued*

Structural identification of molecules + quantitative information!

# Identification of Structural Features

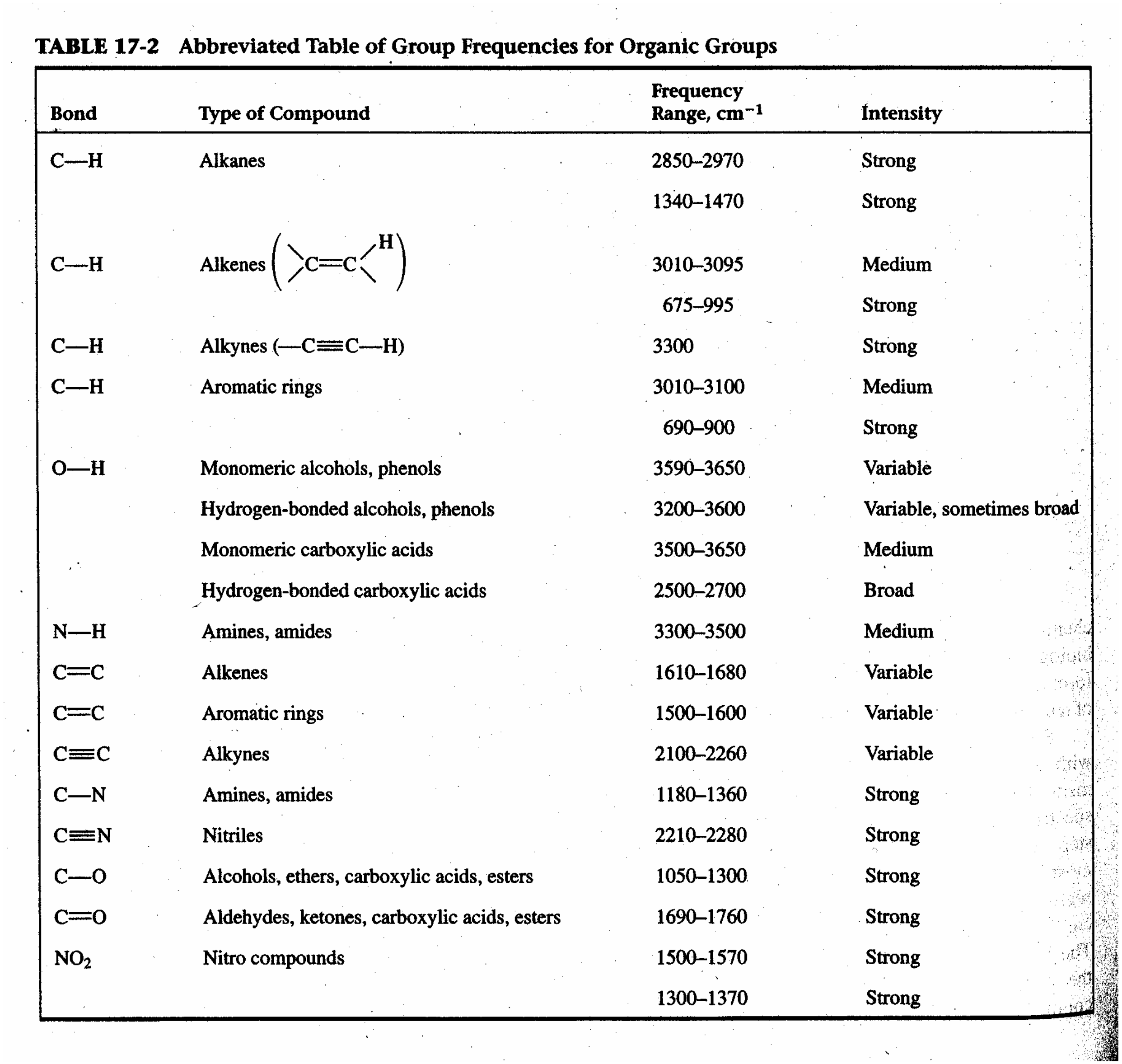


**TABLE 17-2** Abbreviated Table of Group Frequencies for Organic Groups

| 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 (—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

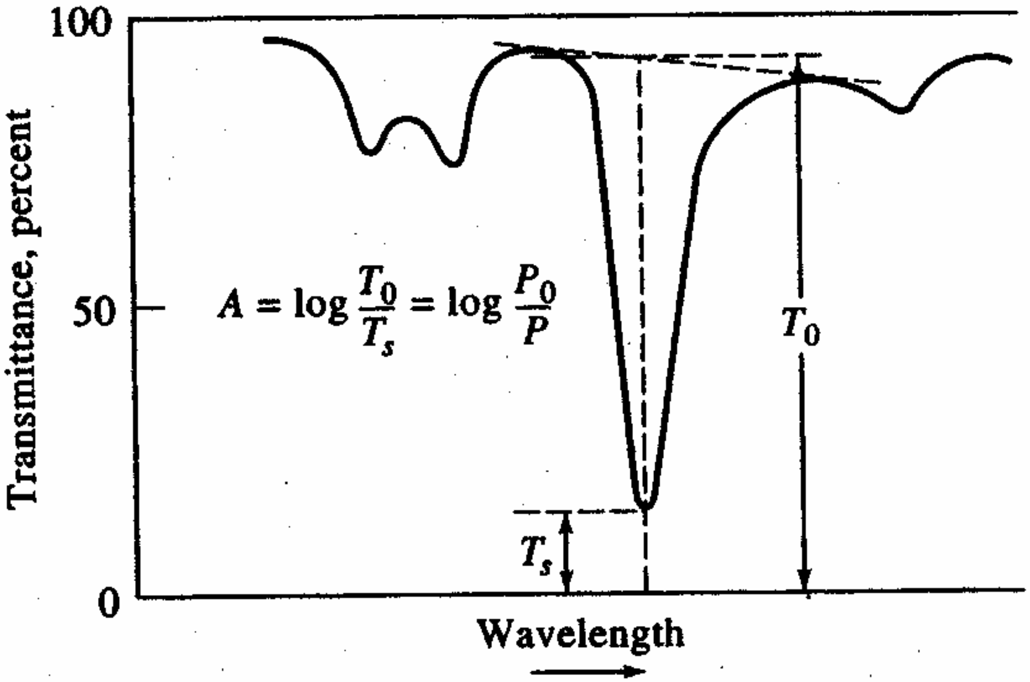


**Figure 17-7** Baseline method for determination of absorbance.

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

# 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)

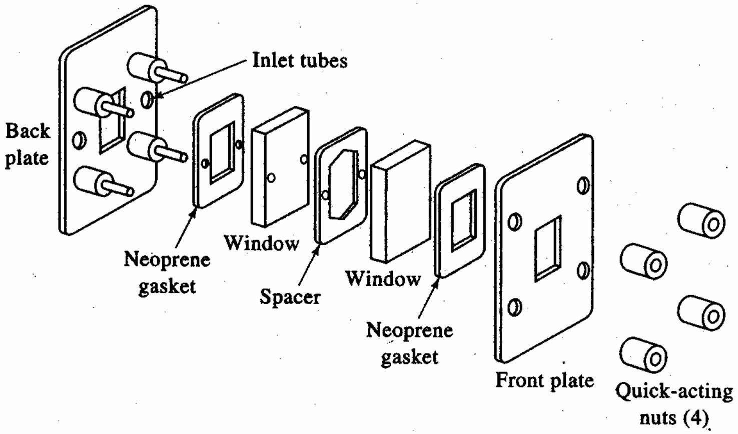


**Figure 17-2** Expanded view of a demountable infrared cell for liquid samples. Teflon spacers ranging in thickness from 0.015 to 1 mm are available. *(Courtesy of Perkin-Elmer, Norwalk, CT.)*

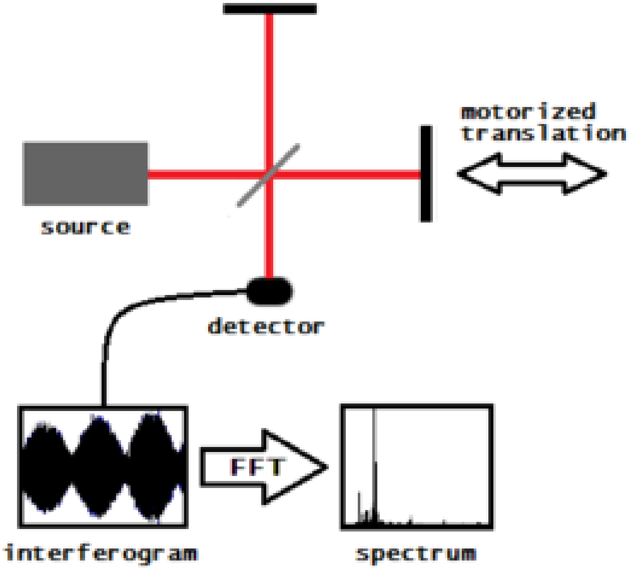
# Principles of FTIR Spectroscopy

▪ In FTIR analyses, Infrared light from the light source passes through a Michelson interferometer along the optical path.

The Michelson interferometer comprises a beam splitter, moving mirror, and fixed mirror. The light beam split into two by the beam splitter is reflected from the moving mirror and fixed mirror, before being recombined by the beam splitter.

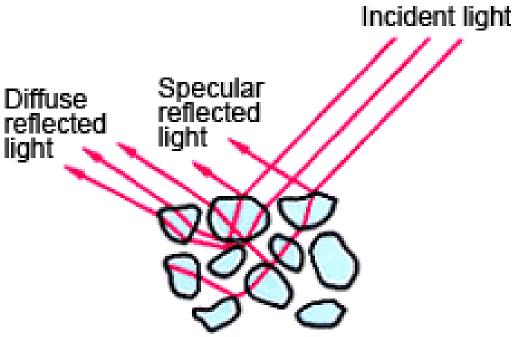
▪As the moving mirror makes reciprocating movements, the optical path difference to the fixed mirror changes, such that the phase difference changes with time. The light beams are recombined in the Michelson interferometer to produce interference light.

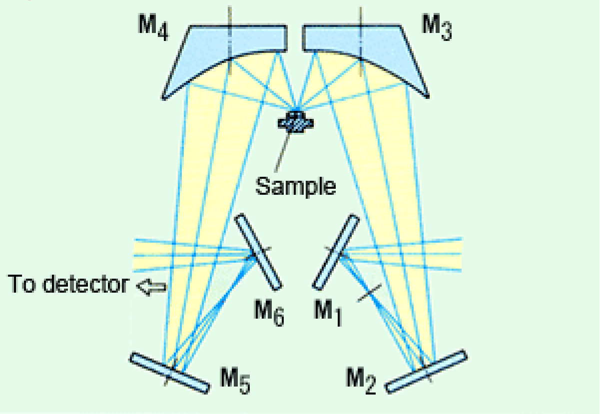
▪The intensity of the interference light is recorded in an interferogram, with the optical path difference recorded along the horizontal axis.



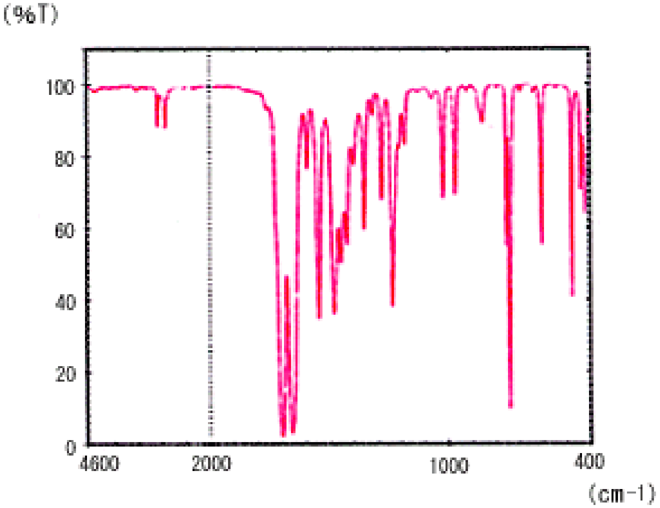
# Principles of Diffuse Reflectance Method

## Measurement of chemicals adhering to a surface - Powders



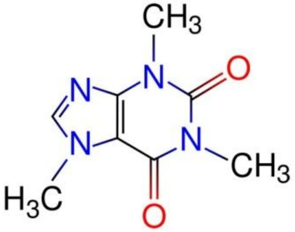


$r_\infty = \frac{r_\infty(\text{Sample})}{r_\infty(\text{Standard powder})}$ is measured, and $f(r_\infty) = \frac{(1-r_\infty)^2}{2r_\infty} = \frac{K}{S}$ is determined.



K is the absorption coefficient, and S is the scattering coefficient. In practice, the comparative reflectance $r_\infty$ with respect to a standard powder such as KBr or KCl, of which K is near zero (0) in the actual measurement range

Spectrum of solid caffeine



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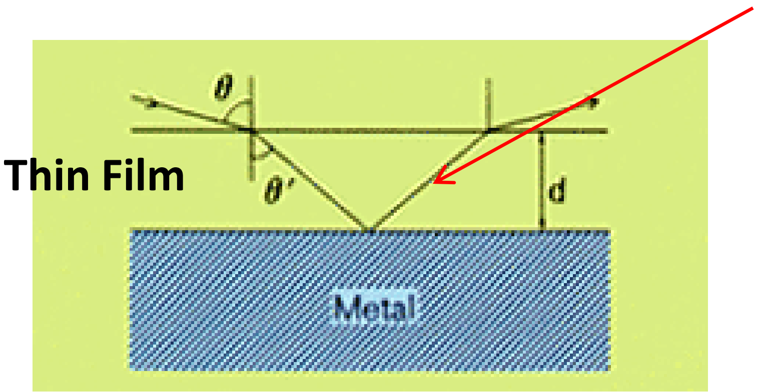
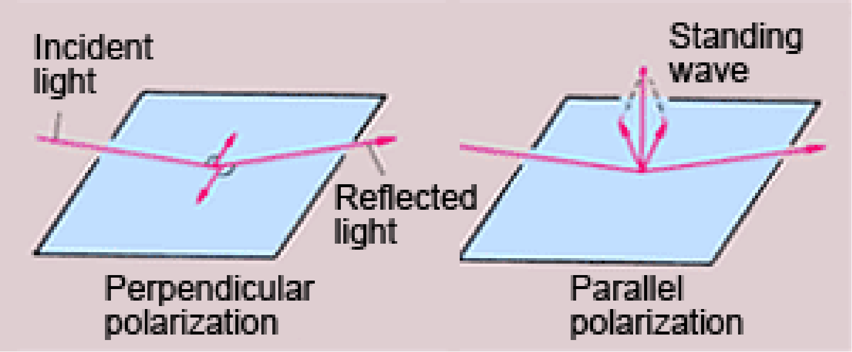
# High Sensitivity Reflection Measurement

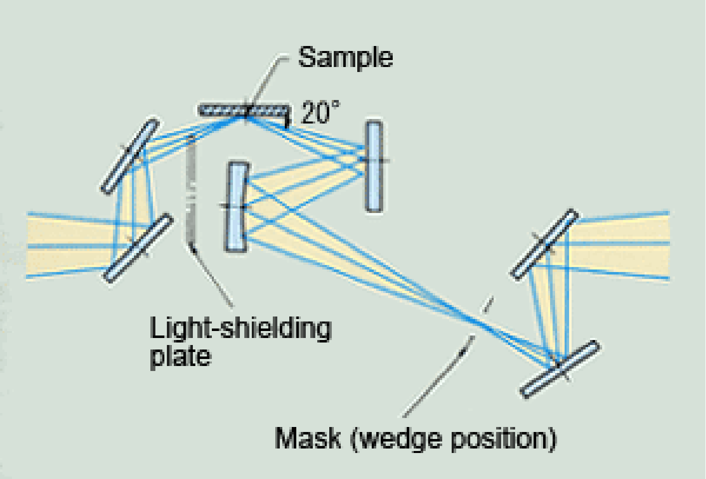
**A reflection method is required to measure substances adhered to or applied to a material that does not permit light transmission, such as a metal sheet.**

Path length





Only the parallel polarized light affects the absorption by the sample so using a polarizer for measurements increases the apparent peak size. Information on the sample orientation can also be acquired, as only functional groups with a perpendicular dipole moment with respect to the metal sheet are measured. However, such increases in sensitivity are available only with a metal substrate.



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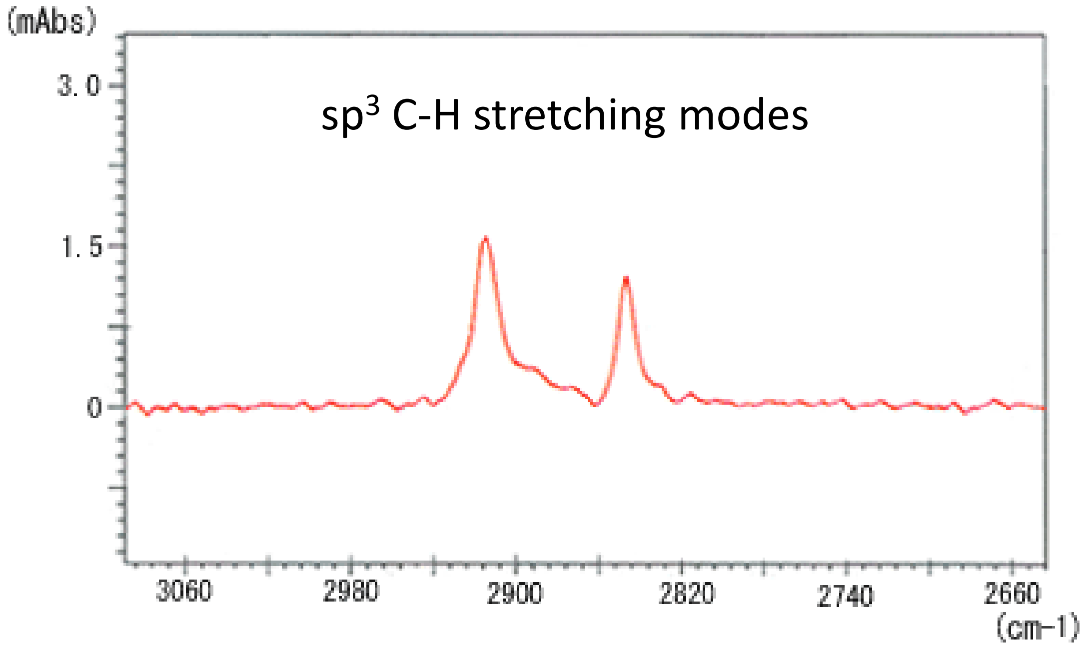

**Spectrum of a 25 Å-thick organic film on a Au surface.**

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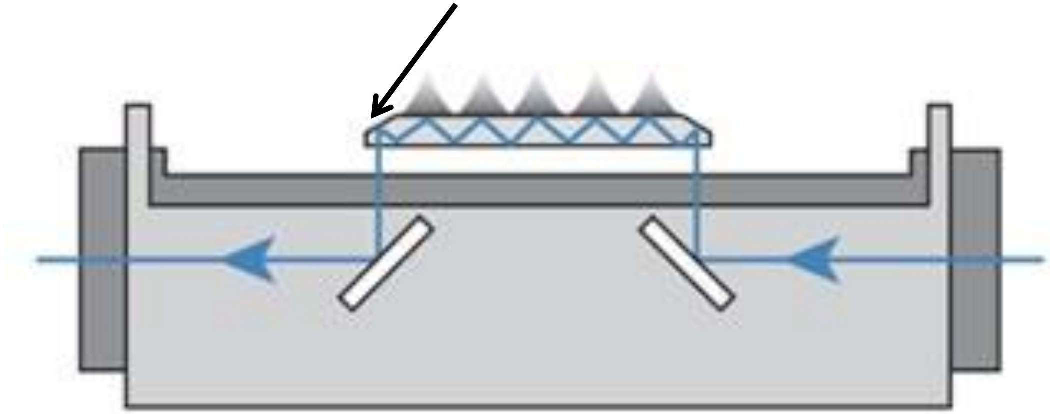
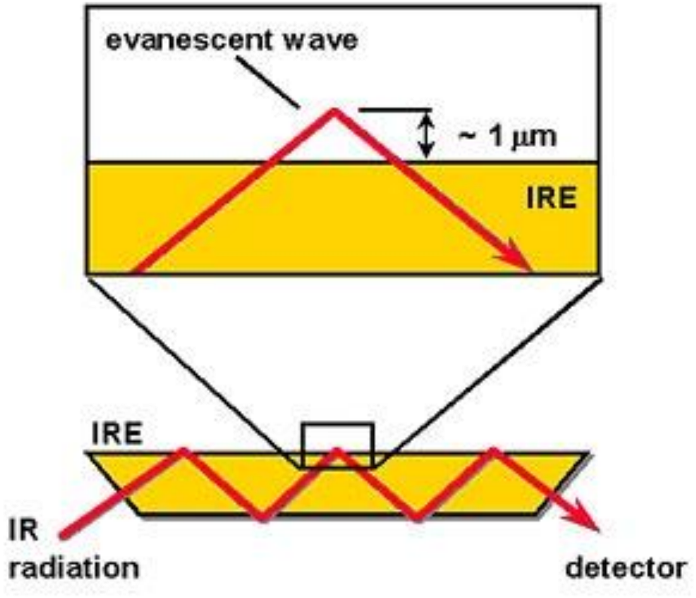
# Attenuated Total Reflectance

Enables samples to be examined directly in the solid or liquid state without further preparation.



Diamond, Si, Ge (high refractive index)

Penetration depth = 0.5-2 µm



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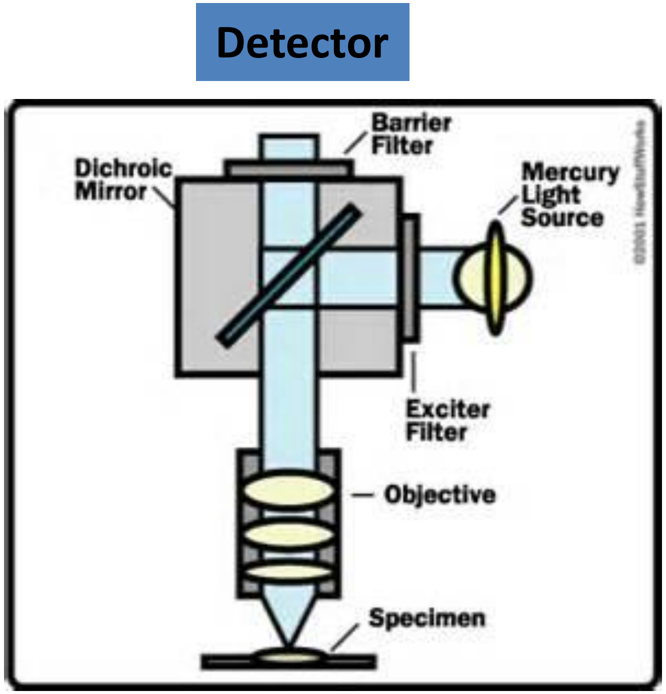
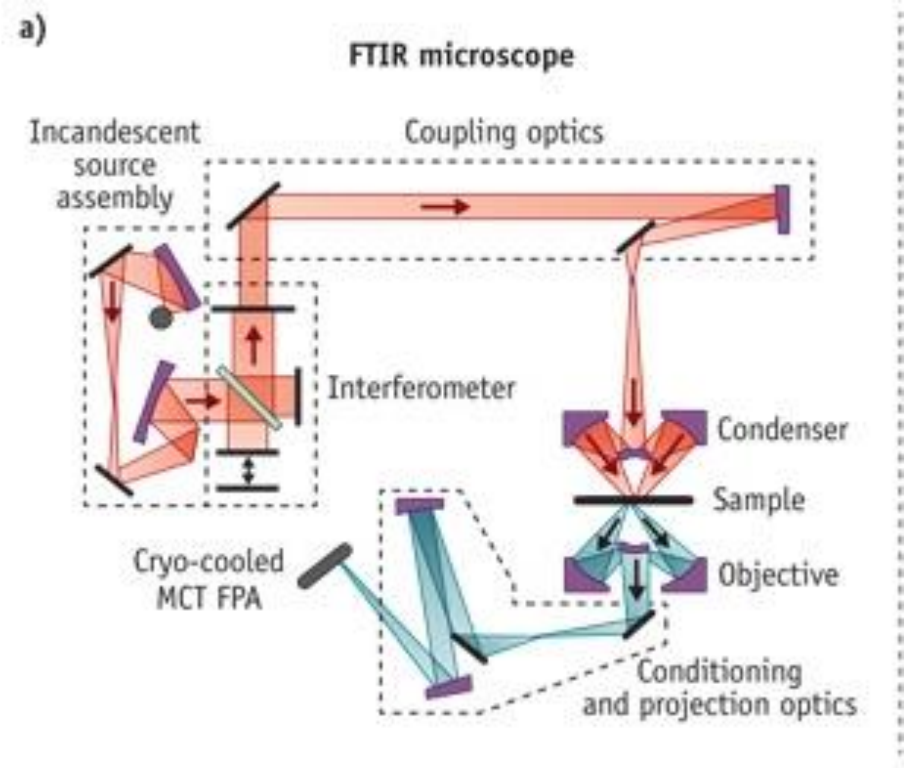
# Fluorescence and FTIR Microscopy





Useful for generating spatial maps of “vibrational modes”. For example, tissue analysis, polymer homogeneity, pharmaceutical quality, forensics.

Jasco website