

FUNDAMENTAL INFRARED SPECTROSCOPY

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Principle of Infrared Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation with a chemical substance. The nature of the interaction depends upon the properties of the substance. When radiation passes through a sample (solid, liquid or gas), certain frequencies of the radiation are absorbed by the molecules of the substance leading to the molecular vibrations. The frequencies of absorbed radiation are unique for each molecule which provide the characteristics of a substance.

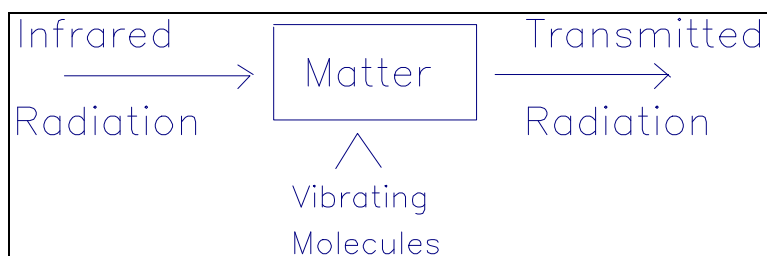


Figure 1. Interaction of radiation with matter.

The electromagnetic spectrum covers an immense range of wavelengths. The infrared regions are classified as follows:

Near Infrared	12500 to 4000cm ⁻¹ (0.8 to 2.5μm)
Mid Infrared	4000 to 200cm ⁻¹ (2.5 to 50μm)
Far Infrared	200 to 12.5cm ⁻¹ (50 to 800μm)

Either the wavelength (μm) or wavenumber (cm^{-1}) is used to measure the position of an infrared absorption. The absorption bands for most organic and inorganic compounds are found in the infrared region. The table of characteristic IR absorptions of functional groups can be found in most chemistry text books. Any absorption band can be characterized by two parameters: the wavelength at which maximum absorption occurs and the intensity of absorption at this wavelength. In an absorption spectrum, the y-axis measures the intensity of the band which is proportional to the number of molecules observed. This principle consequently leads to quantitative analysis.

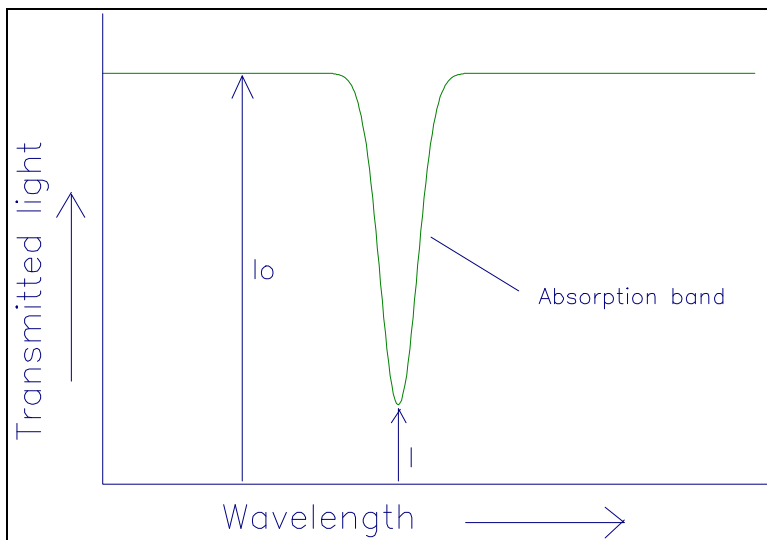


Figure 2. Schematic absorption spectrum.

Intensity of IR Absorption

$$\text{Transmittance } T = I/I_0$$

$$\begin{aligned} \text{Absorbance } A &= \log(1/T) = \log(I_0/I) \\ &= e c L \end{aligned}$$

- I_0 = Intensity of incident radiation
- I = Intensity of transmitted radiation
- e = molar extinction coefficient
- c = concentration (mole/l)
- L = sample pathlength (cm)

For diatomic molecules, the absorption frequency can be calculated.

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 * m_2}}$$

m_1, m_2 = masses of vibrating atoms, g
 c = velocity of light, 3×10^{10} cm/sec
 ν = wavenumber, cm^{-1}
 k = force constant (bond strength), dynes/cm
 $P = 3.1416$ (π)

Bond Strength

For a single bond $k = 5 \times 10^5$ dynes/cm
 double bond $k = 10 \times 10^5$ dynes/cm
 triple bond $k = 15 \times 10^5$ dynes/cm

Example: Calculate the fundamental frequency expected in the infrared absorption spectrum for the C-O stretching frequency.

$$\nu = \frac{\sqrt{\frac{(5 \times 10^5)(12 + 16)(6.023 \times 10^{23})}{(12) \times (16)}}}{2(3.1416)(3 \times 10^{10})}$$

$$= 1110 \text{ cm}^{-1}$$

* Avogadro's number = 6.023×10^{23} atoms/mole

Fundamental Vibrations of Molecules

Each molecule has certain natural vibrational frequencies. When infrared light is incident on the molecule, the frequency which matches the natural vibrational frequency is absorbed by the molecule resulting in molecular vibrations. Consequently, a change in dipole moment of the molecule occurs.

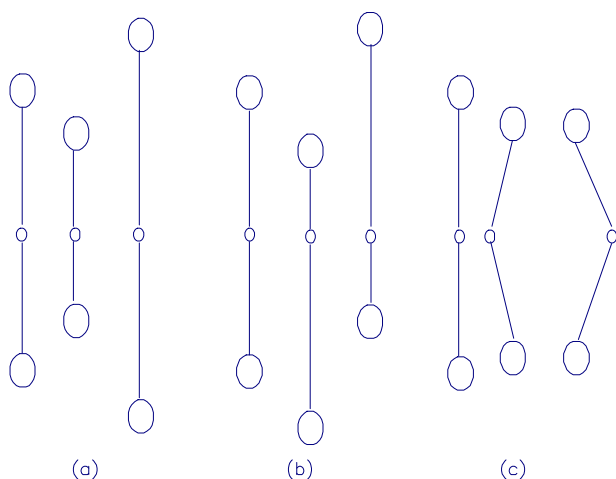
Modes of vibration:

Stretching - distance between 2 atoms increases or decreases.

Bending - position of the atom changes relative to the original bond axis.

The CO_2 molecule is a typical example that illustrates these vibration modes, as shown in the following figure. A symmetrical vibration along the axis produces no change in the center and therefore is infrared inactive. The unsymmetrical stretching gives a charge separation and thus is capable of interacting with radiation of the same frequency. Bending motions can also occur.

Example: Carbon dioxide molecule depicted in vibration modes.



- (a) symmetrical stretching
- (b) asymmetrical stretching
- (c) bending

Factors Influencing Number of Absorption Bands

Infrared absorption occurs as a result of vibrational and rotational transitions within the molecule. Because only a few compounds exhibit pure rotational bands, the vibrational absorption bands are of more practical interest. There are other factors influencing the number of absorption bands.

Factors limiting the number of absorption bands:

- * No change in dipole moment due to symmetry.
- * Degeneracy: Vibrational frequencies located too closely.
- * Weak absorptions.

Factors increasing the number of absorption bands:

- * Overtone bands: Absorption at frequencies representing the fundamental frequencies at the multiples of the fundamentals.
- * Combination bands: Two fundamental vibrations interact and are influenced by radiation at the combined frequency.
- * Vibrational-Rotational bands: The single vibrational band is accompanied by a series of subsidiary bands both at lower and higher frequencies. Gas spectra are commonly characterized by very complex vibration-rotation systems.
- * Harmonic coupling bands: Interaction from adjacent groups of nearly identical oscillation frequencies produces a series of bands quite apart from those normally expected. This phenomenon is relatively uncommon.

Interferometry

The main component in the Fourier Transform Infrared (FTIR) spectrometer is an interferometer. This device splits and recombines a beam of light such that the recombined beam produces a wavelength-dependent interference pattern or an **interferogram**. The Michelson interferometer is most commonly used.

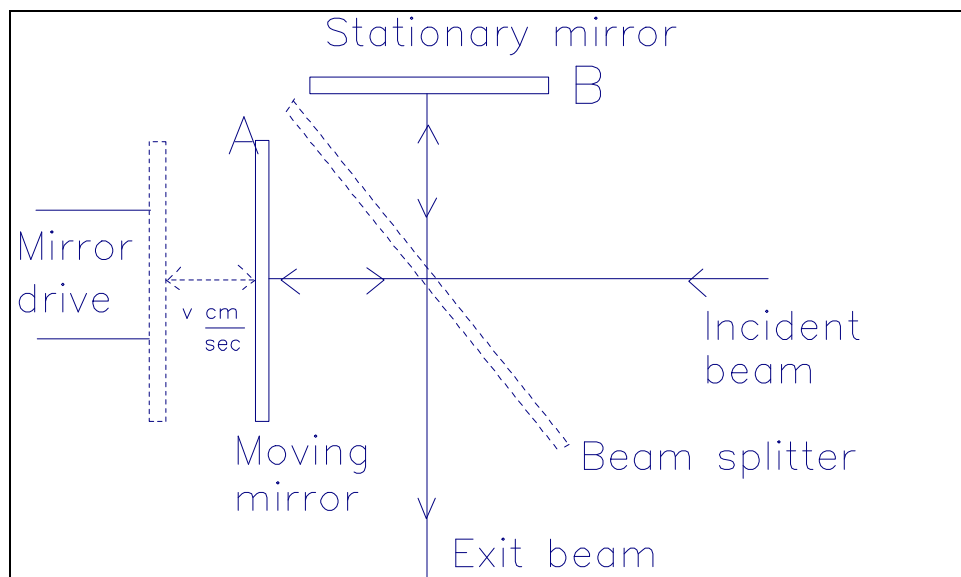


Figure 3. Optical schematic of a Michelson interferometer.

A Michelson interferometer consists of two mirrors and a beamsplitter positioned at an angle of 45 degrees to the mirrors. A KBr beamsplitter coated with Germanium is typically used for mid IR region. Incident light strikes the beamsplitter so that half of the light is transmitted through the beamsplitter and half is reflected to the mirrors. The two components are then reflected back and recombined at the beamsplitter with half of the light passing on toward the sampling areas and half travelling back toward the source. The signal at the detector is a cosine wave.

In general, the function of the interferometer is to disperse the radiation provided by the IR source into its component frequencies.

With polychromatic light (radiation with more than a single wavelength), the output signal is the sum of all the cosine waves which is the Fourier Transform of the spectrum or an **interferogram**. Figure 4 presents a simplified interferogram from an incident wave consisting of three discrete frequencies. This signal is the sum of the three cosine wave signals from each frequency separately. The interferogram contains the basic information on frequencies and intensities characteristic of a spectrum but in a form that is not directly interpretable. Thus, the information is converted to a more familiar form, a spectrum, using Fourier Transform methods.

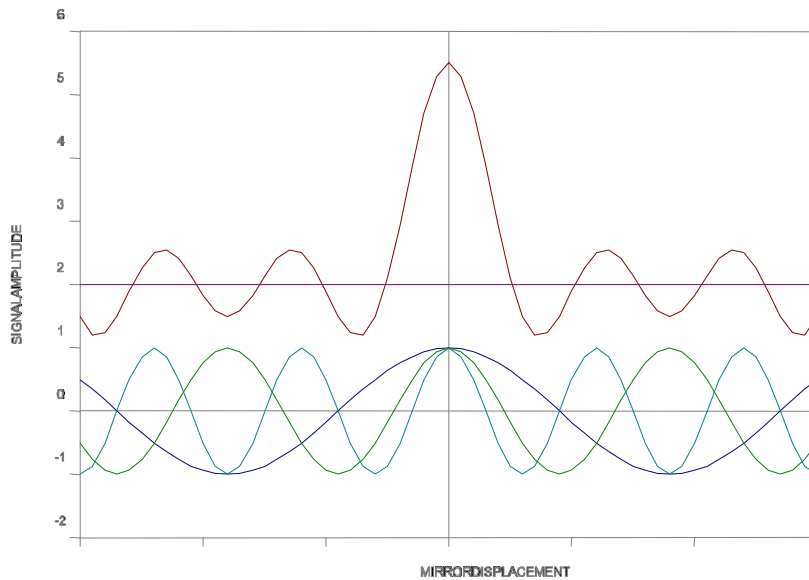
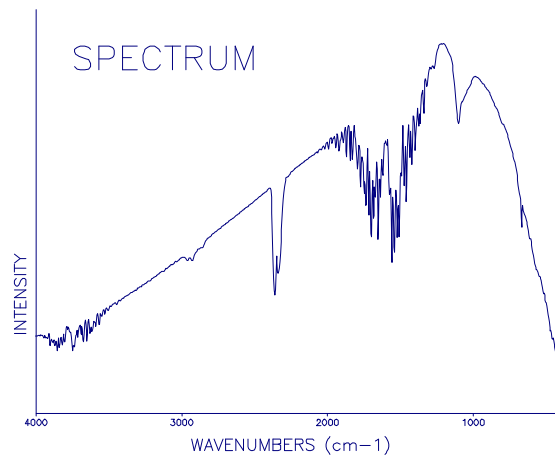
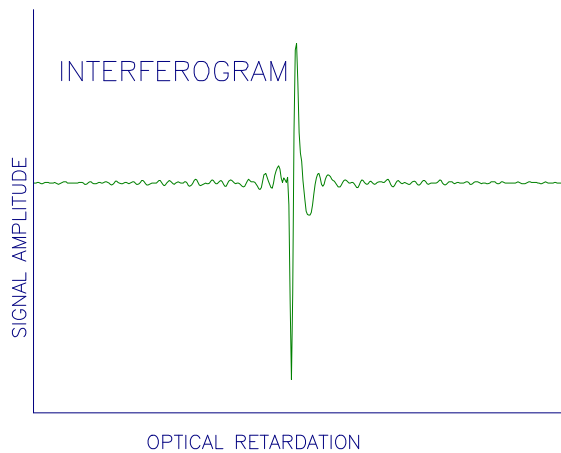


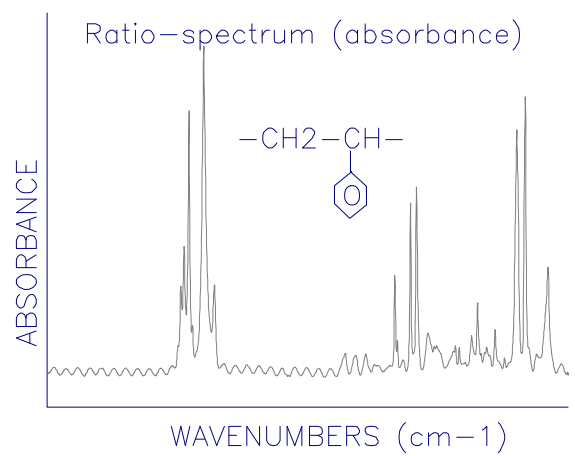
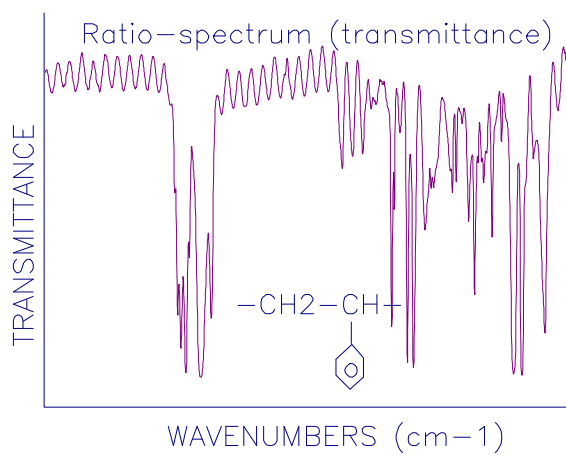
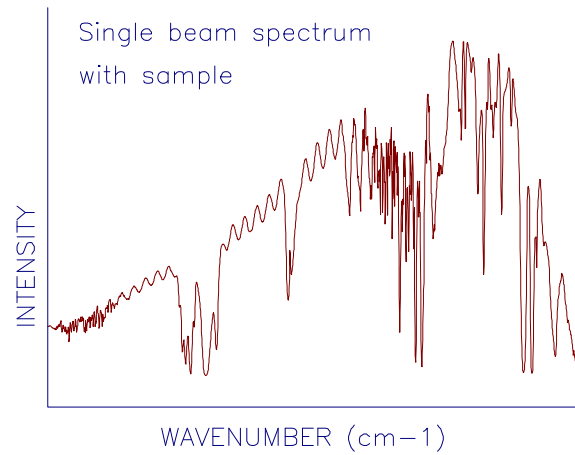
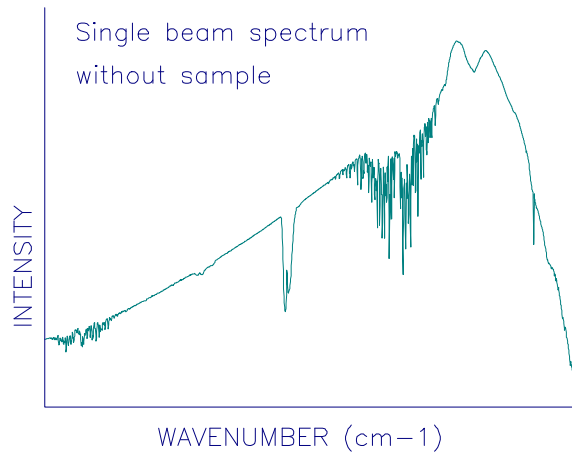
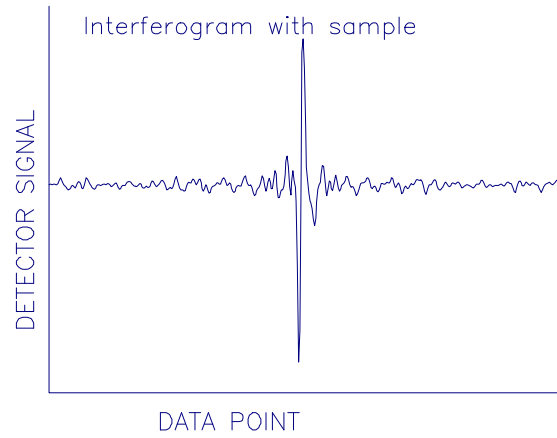
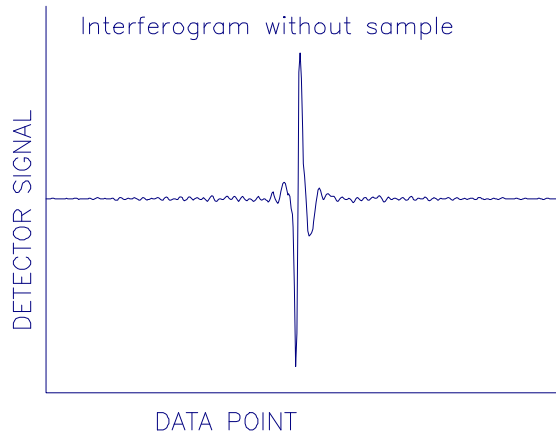
Figure 5. A simplified interferogram (offset by 2 units) from a light wave consisting of three discrete frequencies. This signal is the sum of the 3 cosine waves separately.

The interferogram is a function of time domain and the spectrum is a function of frequency domain. A **spectrum** is calculated from the interferogram by computing the cosine Fourier Transform of the interferogram.

===== **FOURIER TRANSFORM** =====>>



Intermediate steps of data acquisition of the IR spectrum of polystyrene



Instrumentation

The basic components of an infrared spectrometer are shown in block diagram form on Figure 3. The system consists of an interferometer, a computer, a data station, and a printer and/or plotter for data output.

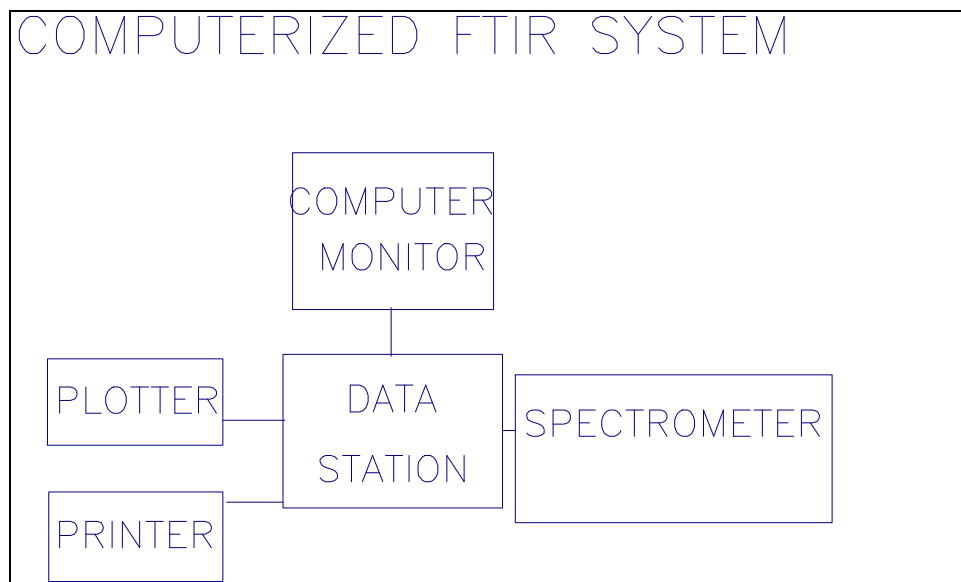


Figure 4. Basic components of a computerized spectrometer system.

With an infrared data station, the computer acquires, processes, stores and retrieves spectral data. Many commercial software packages including spectral enhancement, quantitation and searching are available for infrared spectroscopy.