

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 electronic excitation!

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

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

Types of Vibrations

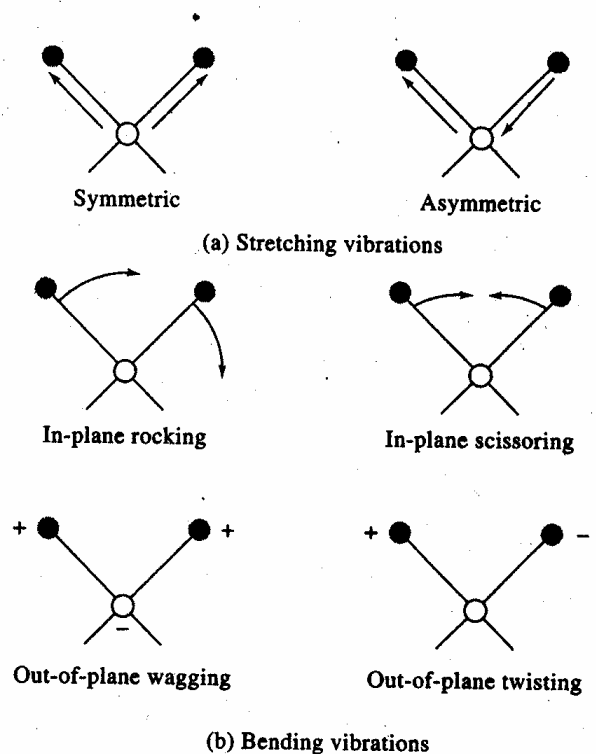


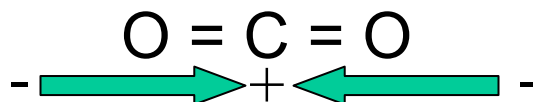
Figure 16-2 Types of molecular vibrations. Note: + indicates motion from the page toward the reader; - indicates motion away from the reader.

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.

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



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

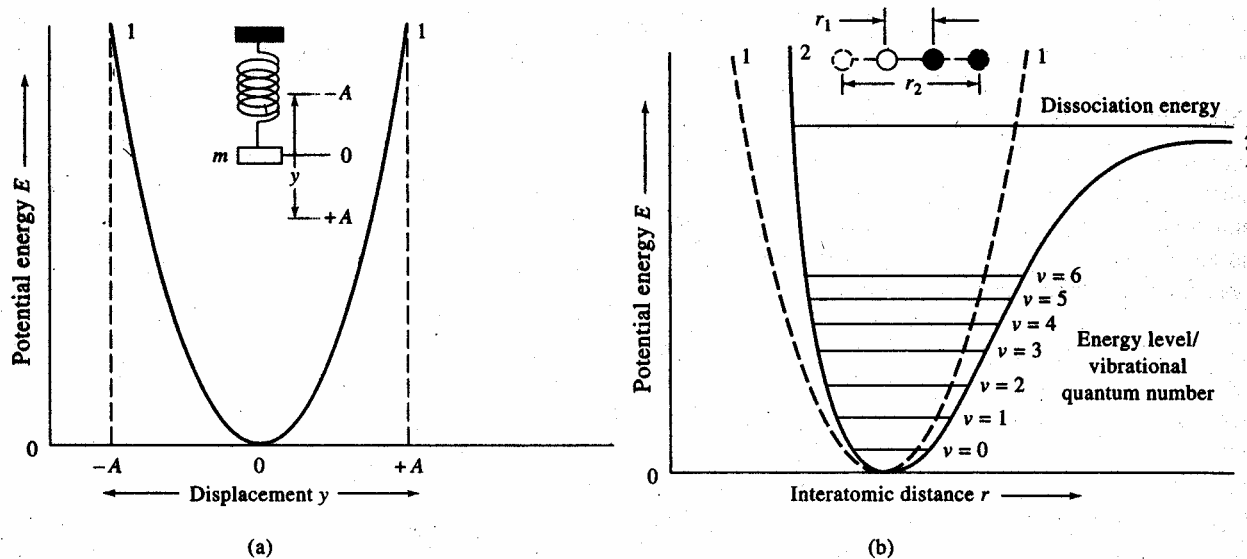


Figure 16-3 Potential energy diagrams. Curve 1, harmonic oscillator. Curve 2, anharmonic oscillator.

$$F = -ky$$

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

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

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

An Absorption Example

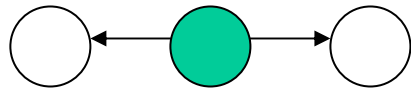


A linear, symmetric molecule!

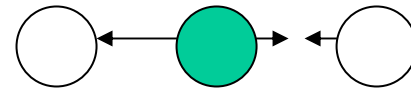
Predicted # of vibrations for a linear molecule = $3N-5$

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

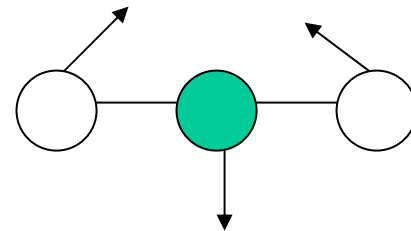
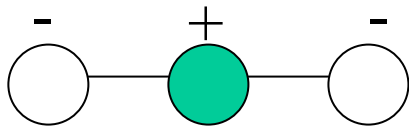
$$\text{CO}_2 \longrightarrow 3 \times 3 - 5 = \underline{4} \text{ normal modes}$$



Symmetric (inactive)



Asymmetric (2330 cm^{-1} ($4.3 \mu\text{m}$))



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

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)

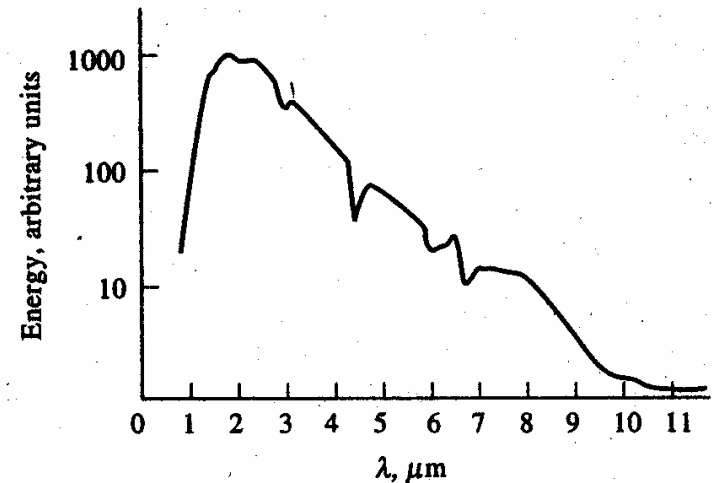


Figure 16-4 Spectral distribution of energy from a Nernst glower operated at approximately 2200 K.

Instruments must have good focusing and collection optics!!

Go back and read pp. 206-212!!

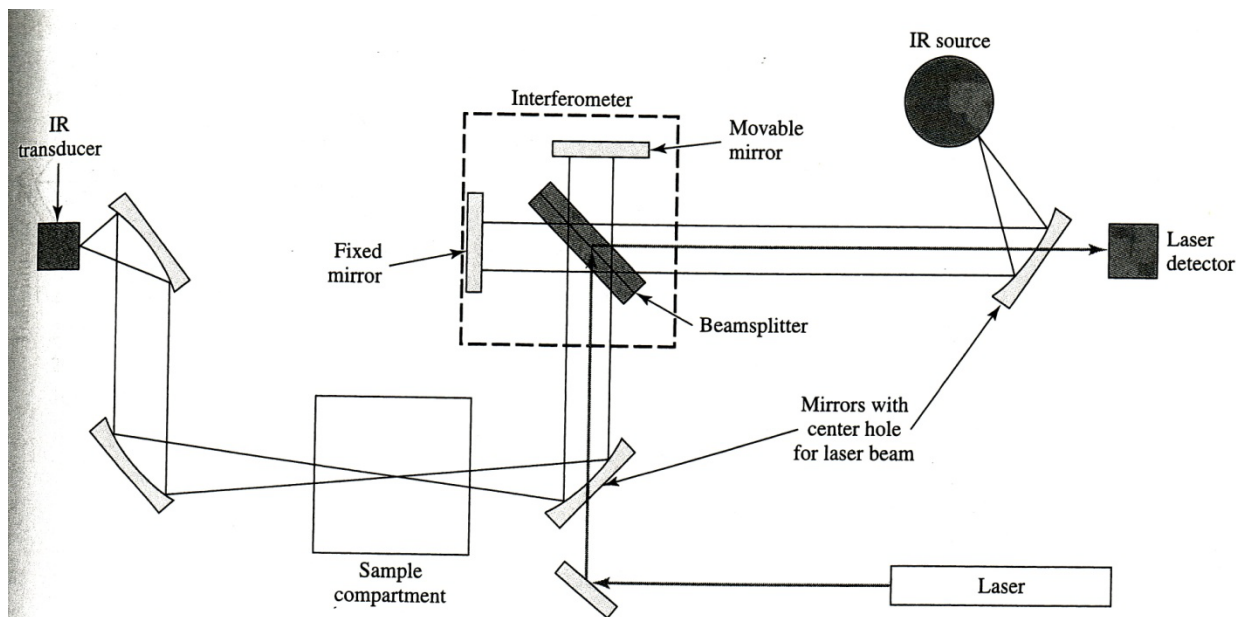


FIGURE 16-8 Single-beam FTIR spectrometer. In one arm of the interferometer, the IR source radiation travels through the beamsplitter to the fixed mirror, back to the beamsplitter, and through the sample to the IR transducer. In the other arm, the IR source radiation travels to the beamsplitter, is reflected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

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!!

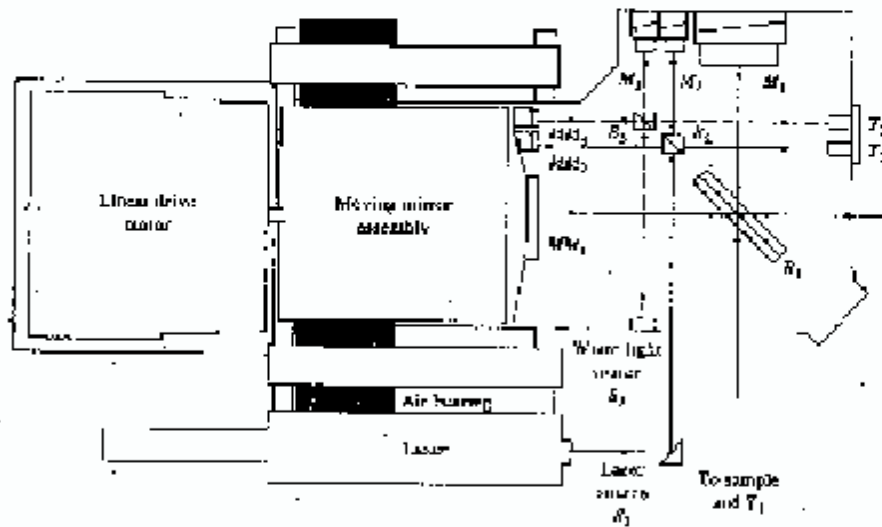


Figure 16-6 Interferometer for an infrared Fourier transform spectrometer. Subscript 1 defines the reflection path in the infrared interferometer; subscripts 2 and 3 refer to the laser and white light interferometers, respectively. (From *Journal of Analytical Instrumentation*, Middlebrook)

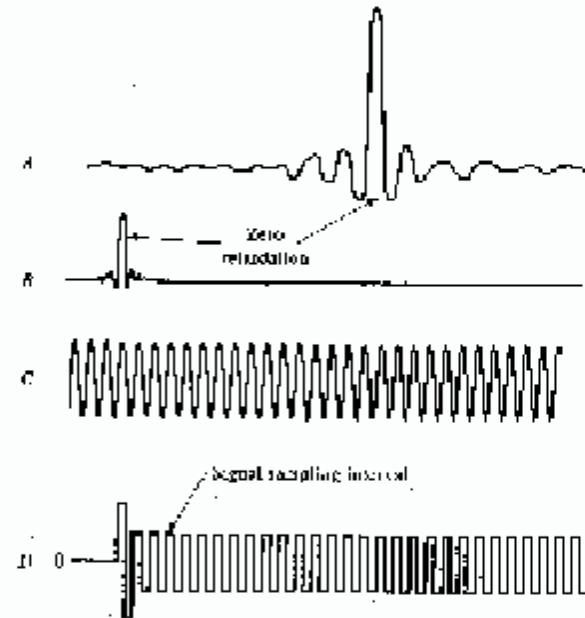


Figure 16-7 Time domain signals for the three interferometers converted to a Fourier transform infrared instrument. Curve A: infrared signal; curve B: white-light signal; curve C: laser-light reference signal; curve D: square-wave electrical signal derived from the laser signal. (From E. B. G. Gillis, *Chemical Infrared Fourier Transform Spectroscopy*, p. 102, New York: Wiley, 1978. Reprinted by permission of John Wiley & Sons, Inc.)

Advantages of Fourier Transform Spectrometers

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

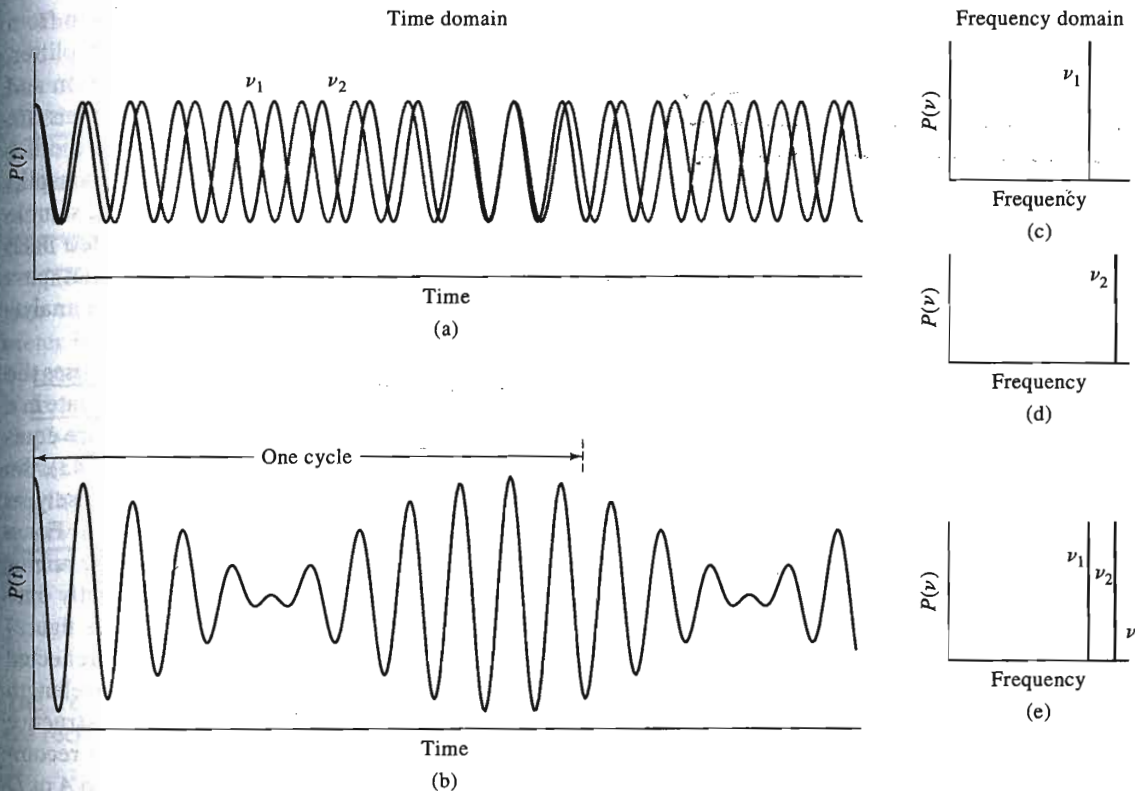


FIGURE 7-41 (a) Time-domain plot of two slightly different frequencies of the same amplitude ν_1 and ν_2 . (b) Time-domain plot of the sum of the two waveforms in (a). (c) Frequency-domain plot of ν_1 . (d) Frequency-domain plot of ν_2 . (e) Frequency-domain plot of the waveform in (b).

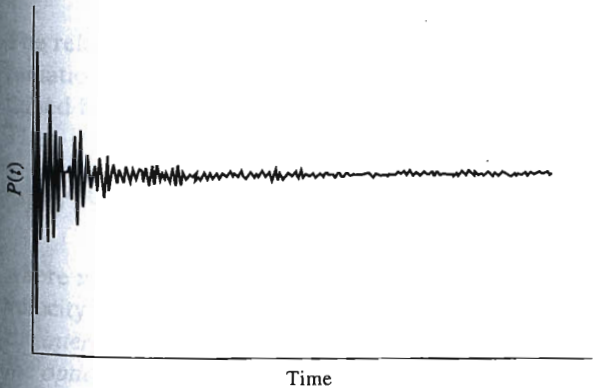


FIGURE 7-42 Time-domain signal of a source made up of many wavelengths.

meters.

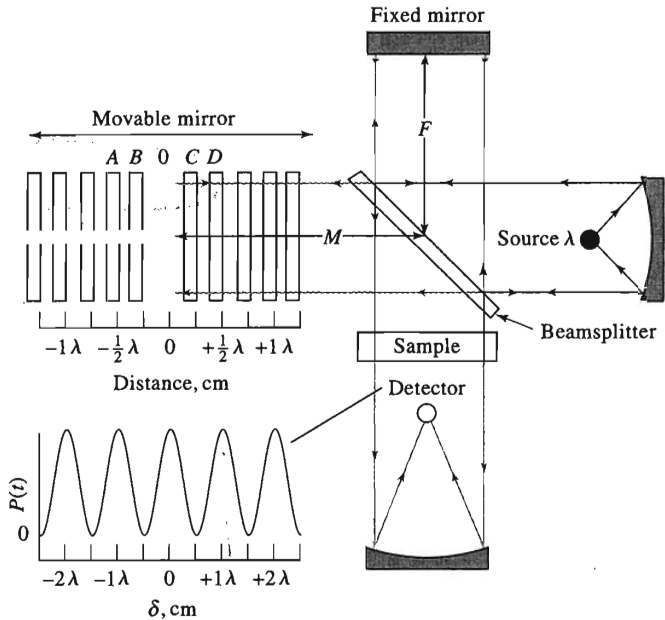


FIGURE 7-43 Schematic of a Michelson interferometer illuminated by a monochromatic source.

Typical FTIR Spectrometer

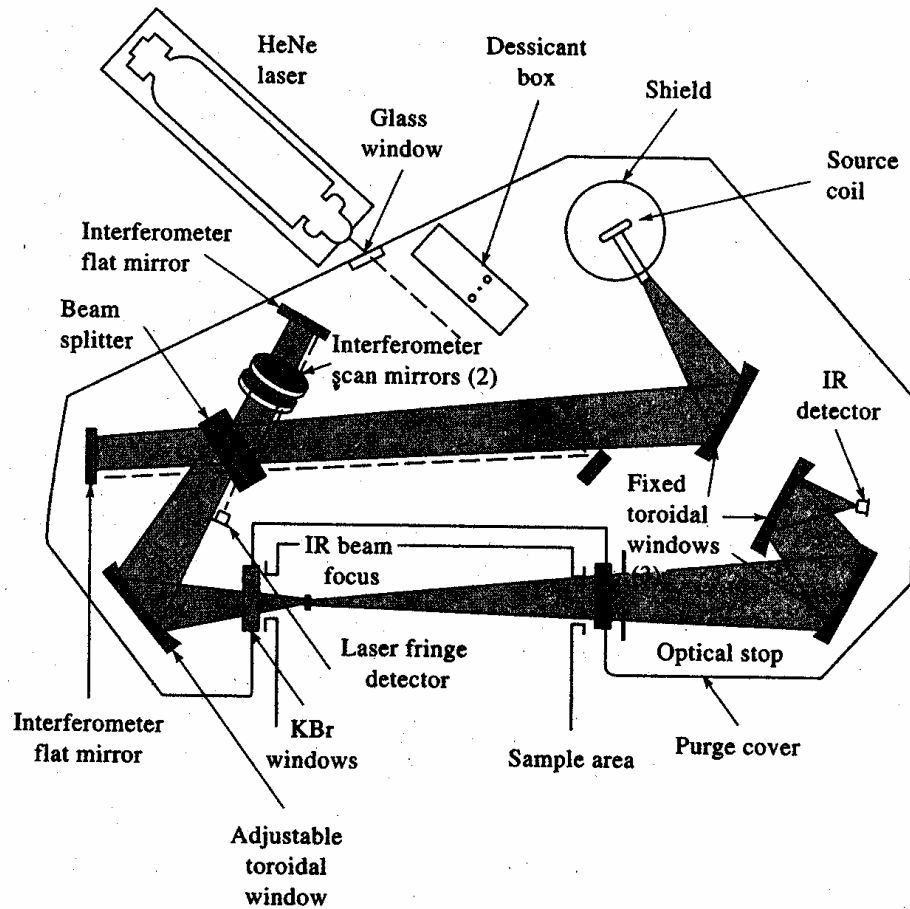


Figure 16-8 A single-beam FTIR spectrometer. (Courtesy of Perkin-Elmer, Norwalk, CT.)

Typical Background Spectrum of Air

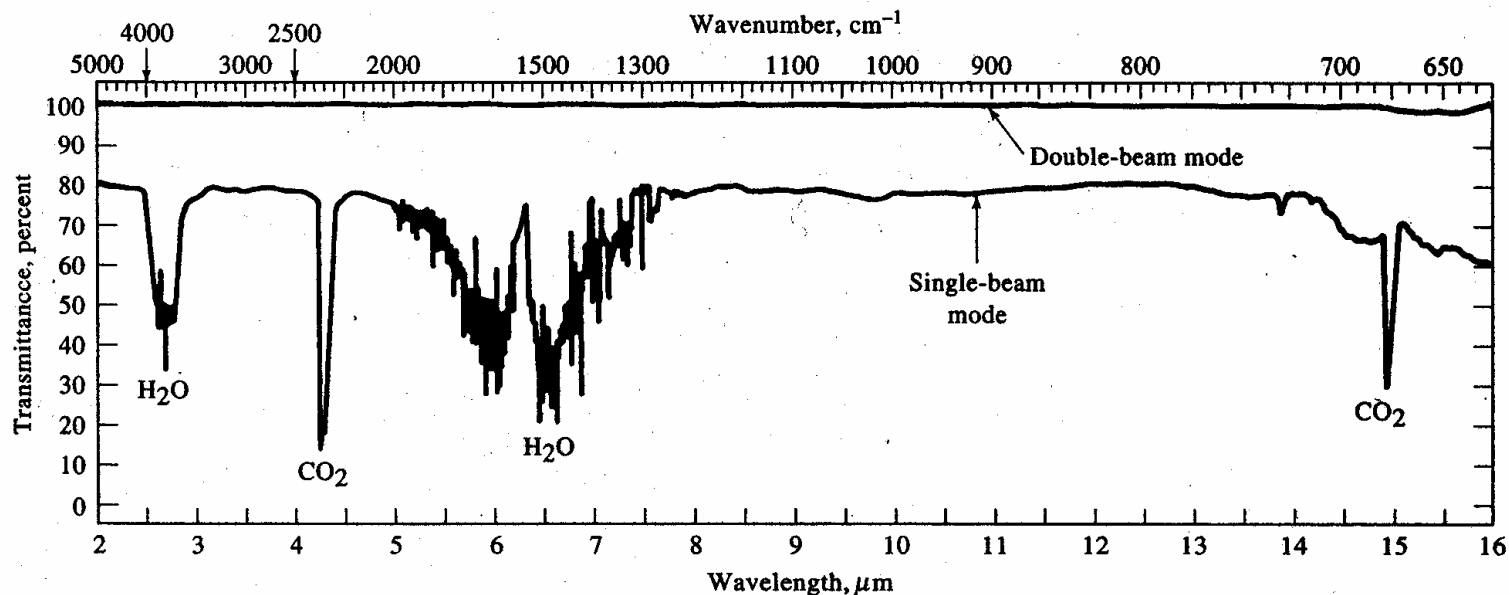


Figure 16-9 Single- and double-beam spectra of atmospheric water vapor and CO₂. In the lower, single-beam trace, the absorption of atmospheric gases is apparent. The top, double-beam trace shows that the reference beam compensates nearly perfectly for this absorption and allows a stable 100% T baseline to be obtained. (From J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, p. 409. Englewood Cliffs, NJ: Prentice-Hall, 1988. With permission.)