Chem 306 Instrumental Analysis II

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Informations given in these slides are, either in part or all, recollection from the following sources, solely for education purposes.

Principles of Instrumental Analysis, 6e/7e by Holler, Skoog & Crouch, 2007

Fundamentals of Analytical Chemistry 9e by Douglas A. Skoog, 2013.

Chapter 16-17

An Introduction and Application to Infrared Spectrometry

The infrared region of the spectrum encompasses radiation with wavenumbers ranging from about 12,800 to 10 cm^{-1} or wavelengths from 0.78 to 1000 μm. The infrared spectrum is divided into **near-, mid-,** and **far-** infrared radiation.

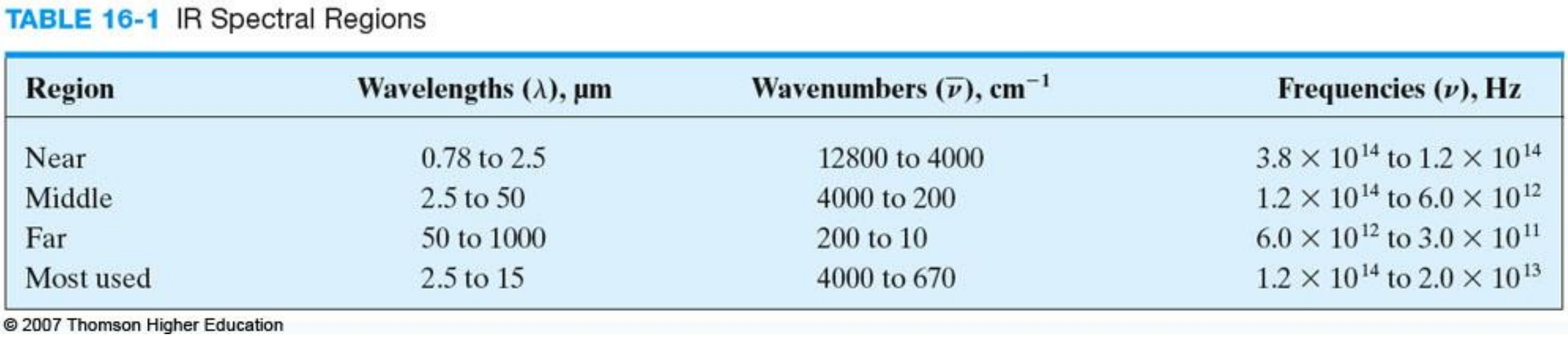


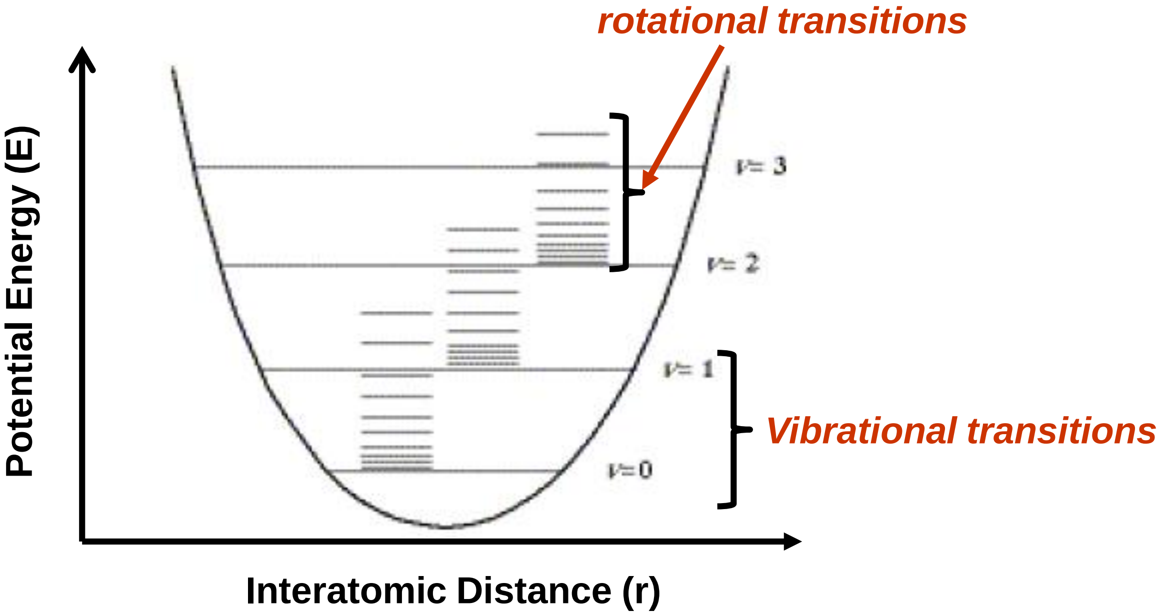
TABLE 16-1 IR Spectral Regions

Region	Wavelengths (λ), μm	Wavenumbers ($\bar{\nu}$), cm^{-1}	Frequencies (ν), Hz
Near	0.78 to 2.5	12800 to 4000	3.8×10^{14} to 1.2×10^{14}
Middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
Far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
Most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

Infrared Spectroscopy

A) Introduction

A) 1.)Infrared (IR) spectroscopy: based on IR absorption by molecules as undergo vibrational and rotational transitions. Absorption of radiation in this region by a typical organic molecule results in the excitation of vibrational, rotational and bending modes, while the molecule itself remains in its electronic ground state.



rotational transitions

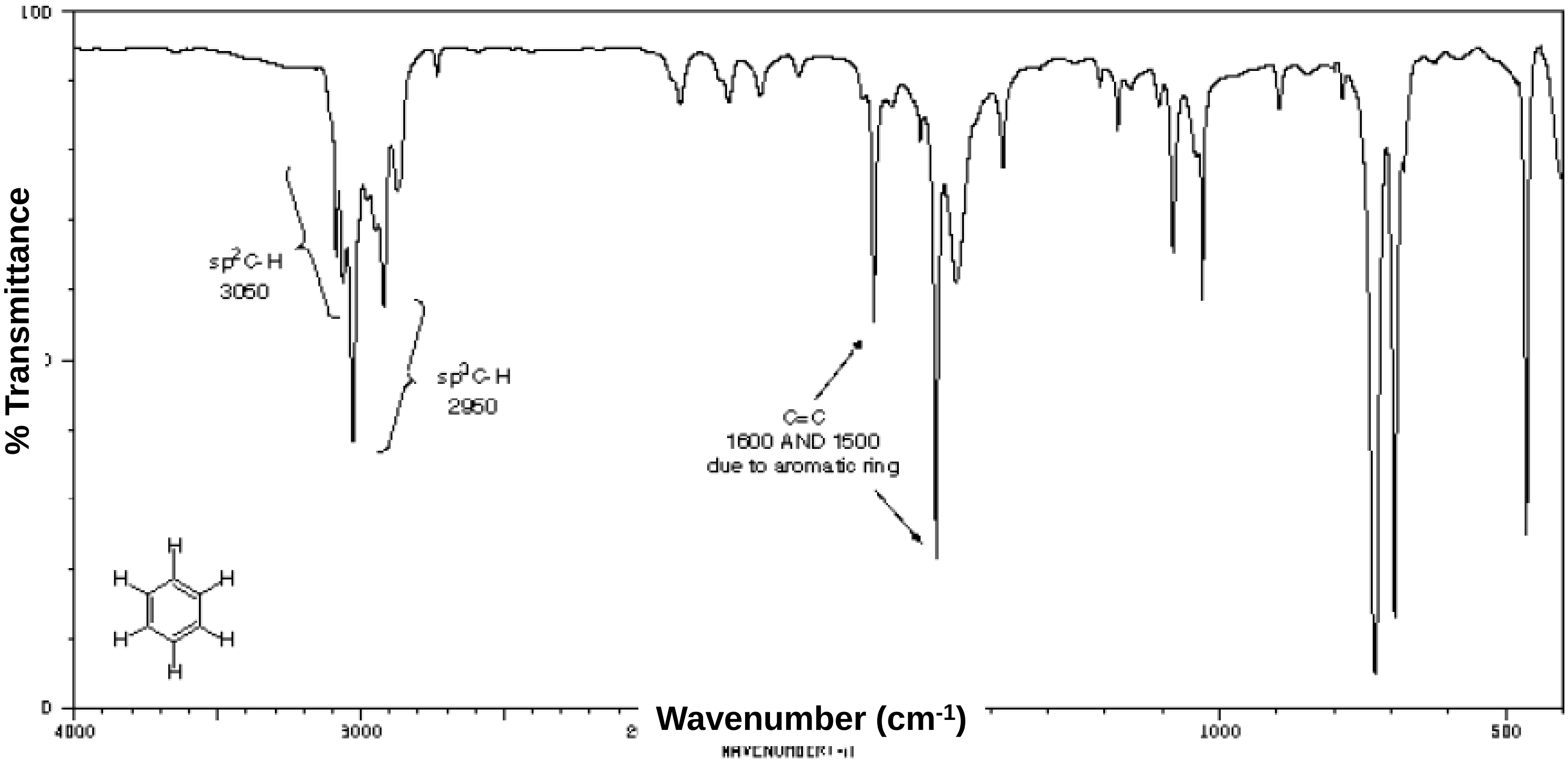
Vibrational transitions

Potential energy resembles classic Harmonic Oscillator

2.) IR radiation is in the range of 12,800 – 10 cm^{-1} or λ = 0.78 – 1000 μm

- rotational transitions have small energy differences
  - ≤ 100 cm^{-1}, λ > 100 μm
- vibrational transitions occur at higher energies
- rotational and vibrational transitions often occur together

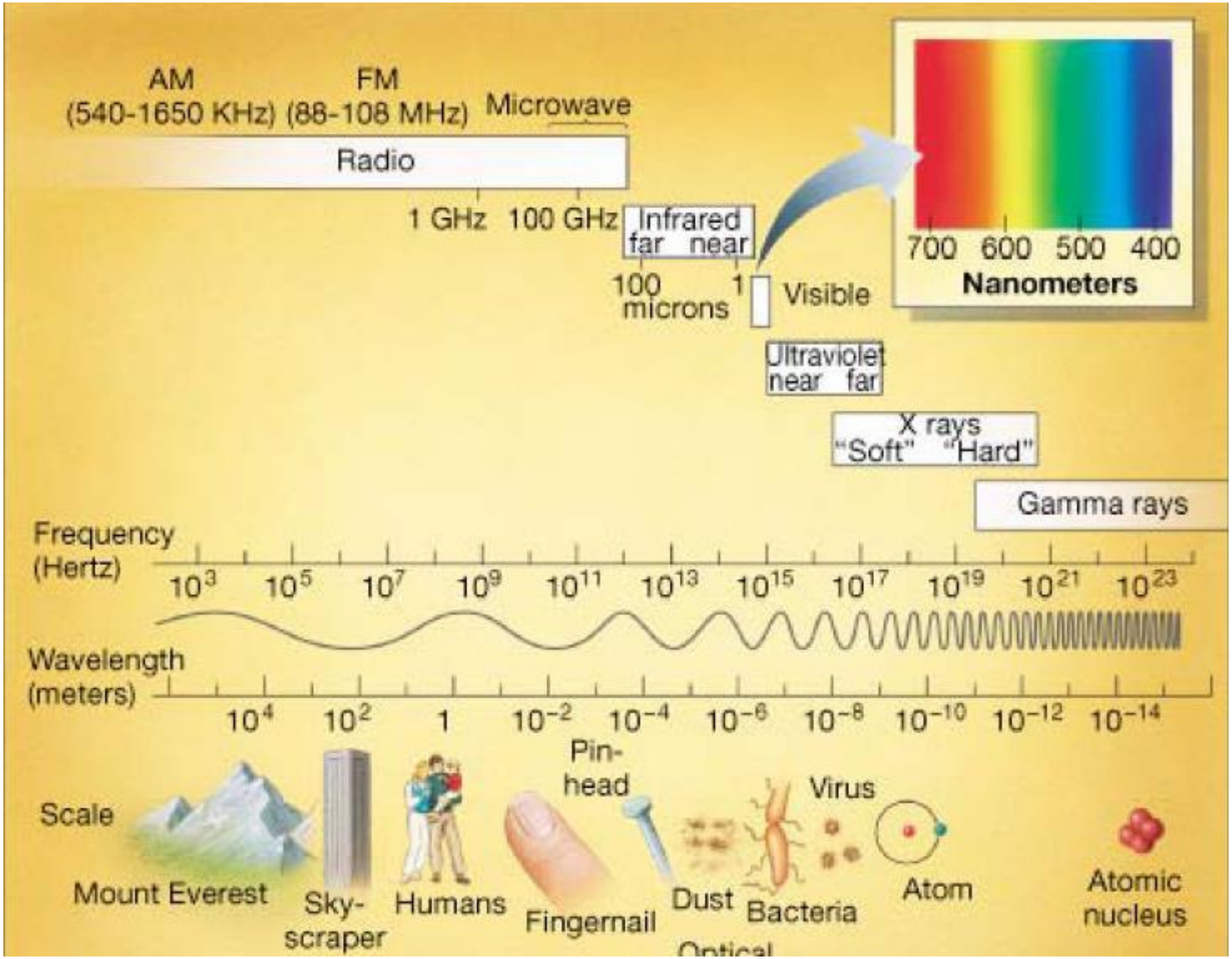
3.) Typical IR spectrum for Organic Molecule



Wide Range of Types of Electromagnetic Radiation in nature.

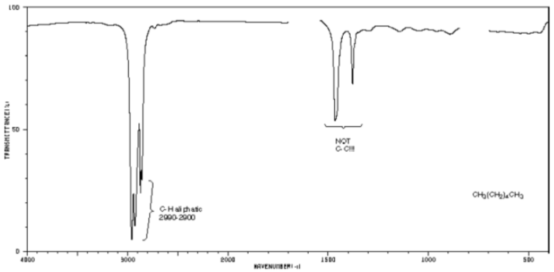
1. Only a small fraction (350-780 nM is visible light).
2. The complete variety of electromagnetic radiation is used throughout spectroscopy.
3. Different energies allow monitoring of different types of interactions with matter.

$$E=h\nu = hc/\lambda$$

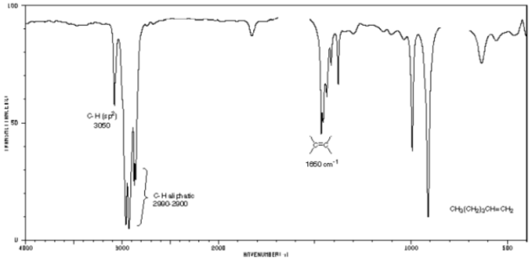


3.) Typical IR spectrum for Organic Molecule

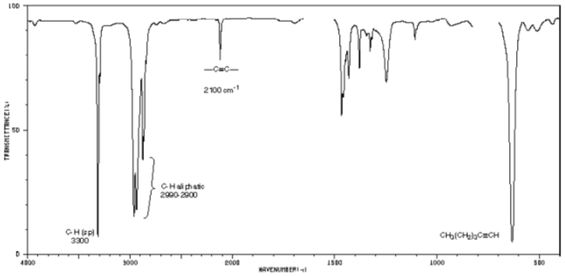
- many more bands then in UV-vis, fluorescence or phosphorescence
- bands are also much sharper
- pattern is distinct for given molecule
  - except for optical isomers
- good qualitative tool
  - can be used for compound identification
  - group analysis
- also quantitative tool
  - intensity of bands related to amount of compound present
- spectra usually shown as percent transmittance (instead of absorbance) vs. wavenumber (instead of λ) for convenience



Hexane



Hexene



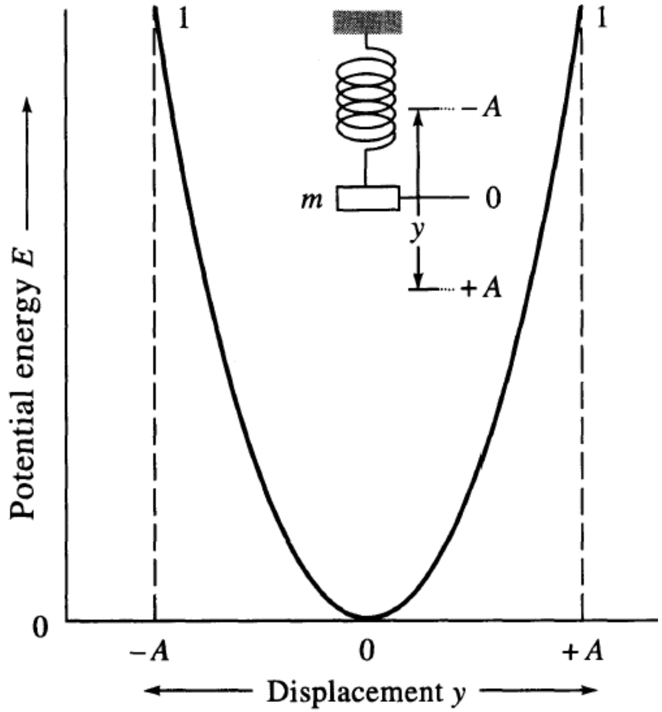
Hexyne

B) Theory of IR Absorption

1.) Molecular Vibrations

i.) Harmonic Oscillator Model:

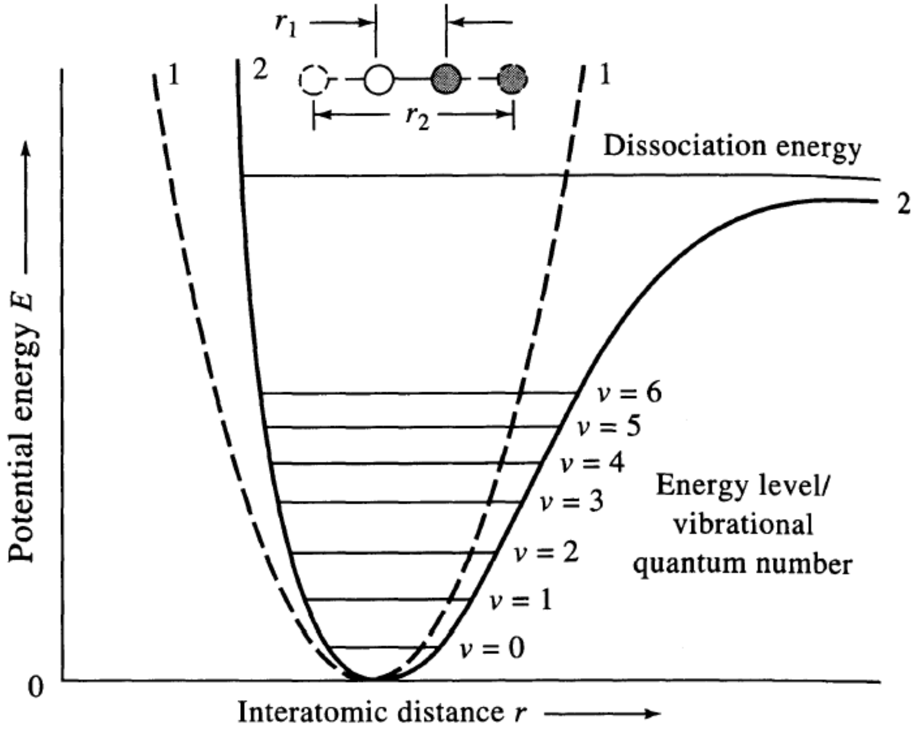
- approximate representation of atomic stretching
- two masses attached by a spring



$$E = \frac{1}{2} k y^2$$

where:

y is spring displacement
k is spring constant



Vibrational frequency given by:

$$\nu = 1/2\pi\sqrt{k/m}$$

where:
ν : frequency
k: force constant (measure of bond stiffness)
μ: reduced mass – m_1m_2/m_1+m_2

If know ν and atoms in bond, can get *k:*

Single bonds:
k ~ $3\text{x}10^2$ to $8\text{ x}10^2$ N/m (Avg ~ $5\text{x}10^2$)

double and triple bonds ~ 2x and 3x *k* for single bond.

$$\nu \propto \sqrt{k}$$

So, vibration ν occur in order:
single < double < triple

EXAMPLE 16-1

Calculate the approximate wavenumber and wavelength of the fundamental absorption due to the stretching vibration of a carbonyl group C═O.

Solution

The mass of the carbon atom in kilograms is given by

$$m_1 = \frac{12 \times 10^{-3}\ \mathrm{kg}/\cancel{\mathrm{mol}}}{6.0 \times 10^{23}\ \cancel{\mathrm{atom}}/\cancel{\mathrm{mol}}} \times 1\ \cancel{\mathrm{atom}}$$

$$= 2.0 \times 10^{-26}\ \mathrm{kg}$$

Similarly, for oxygen,

$$m_2 = (16 \times 10^{-3})/(6.0 \times 10^{23}) = 2.7 \times 10^{-26}\ \mathrm{kg}$$

and the reduced mass μ is given by (Equation 16-9)

$$\mu = \frac{2.0 \times 10^{-26}\ \mathrm{kg} \times 2.7 \times 10^{-26}\ \cancel{\mathrm{kg}}}{(2.0 + 2.7) \times 10^{-26}\ \cancel{\mathrm{kg}}}$$

$$= 1.1 \times 10^{-26}\ \mathrm{kg}$$

As noted earlier, the force constant for the typical double bond is about 1×10^3 N/m. Substituting this value and μ into Equation 16-15 gives

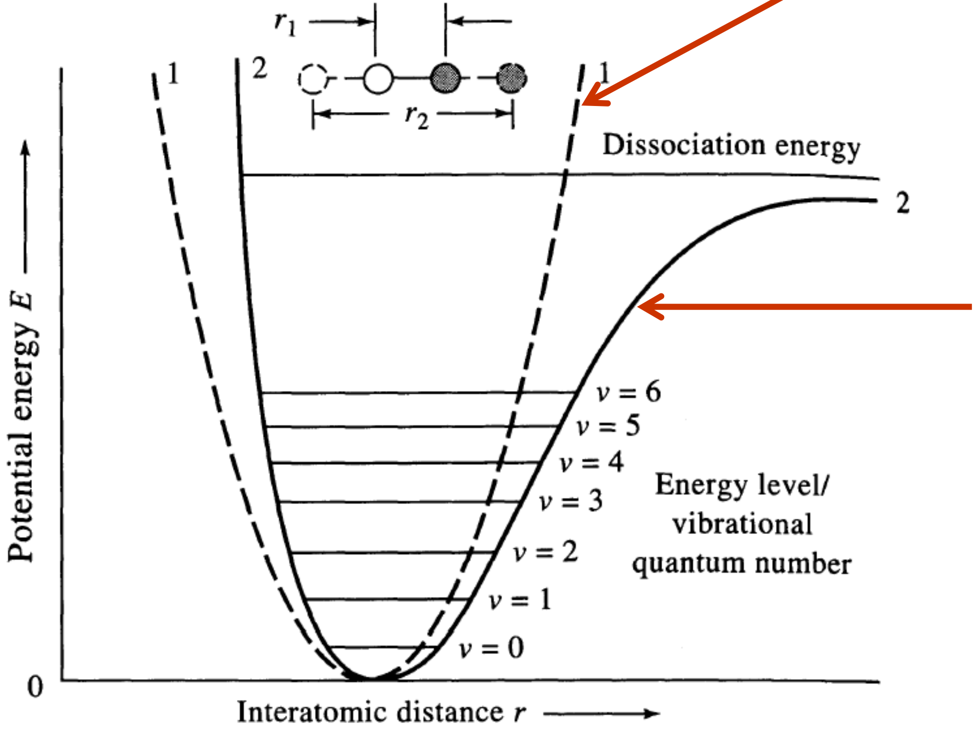
$$\bar{\nu} = 5.3 \times 10^{-12}\ \mathrm{s/cm}\sqrt{\frac{1 \times 10^3\ \mathrm{N/m}}{1.1 \times 10^{-26}\ \mathrm{kg}}}$$

$$= 1.6 \times 10^3\ \mathrm{cm}^{-1}$$

The carbonyl stretching band is found experimentally to be in the region of 1600 to 1800 cm^{-1} (6.3 to 5.6 μm).

ii.) Anharmonic oscillation:

- harmonic oscillation model good at low energy levels (ν_0, ν_1, ν_2, …)
- not good at high energy levels due to atomic repulsion & attraction
  - as atoms approach, coulombic repulsion force adds to the bond force making energy increase greater then harmonic
  - as atoms separate, approach dissociation energy and the harmonic function rises quicker



Harmonic oscillation

Anharmonic oscillation

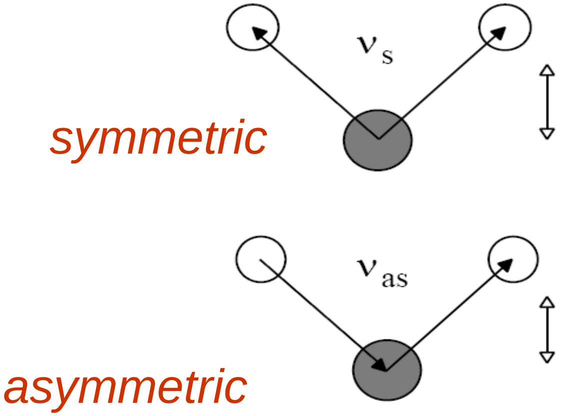
Because of anharmonics: at low ΔE, $\Delta\nu = \pm 2, \pm 3$ are observed which cause the appearance of overtone lines at frequencies ~ 2-3 times the fundamental frequency. Normally $\Delta\nu = \pm 1$

iii.) Types of Molecular Vibrations

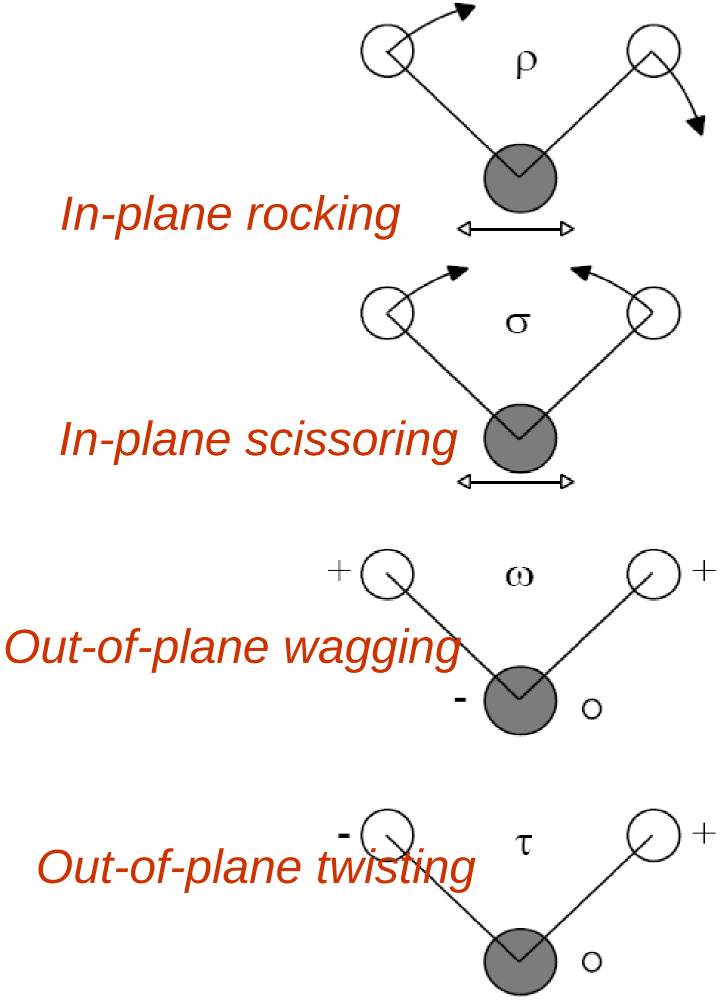
1- Fundamental Vibrations:

Fundamental bands are inherently intense, make up most of the peaks seen in mid-IR spectra, and comprise most of the diagnostically useful peaks for interpretation purposes.

Bond Stretching



Bond Bending



2- Non-fundamental Vibrations

- Overtones, from *v* = 0 to *v* = 2,3,4 or higher

*For fundamentals above 2000 cm^{-1} their overtones will mostly appear above 4000 cm^{-1}

* Since overtones are weak they are generally not diagnostically useful IR features.

- Combination Tones, more than one vibration can be excited at the same time.

Figure 3: The IR spectrum of methyl ethyl ketone, with examples of fundamental and overtone bands marked.

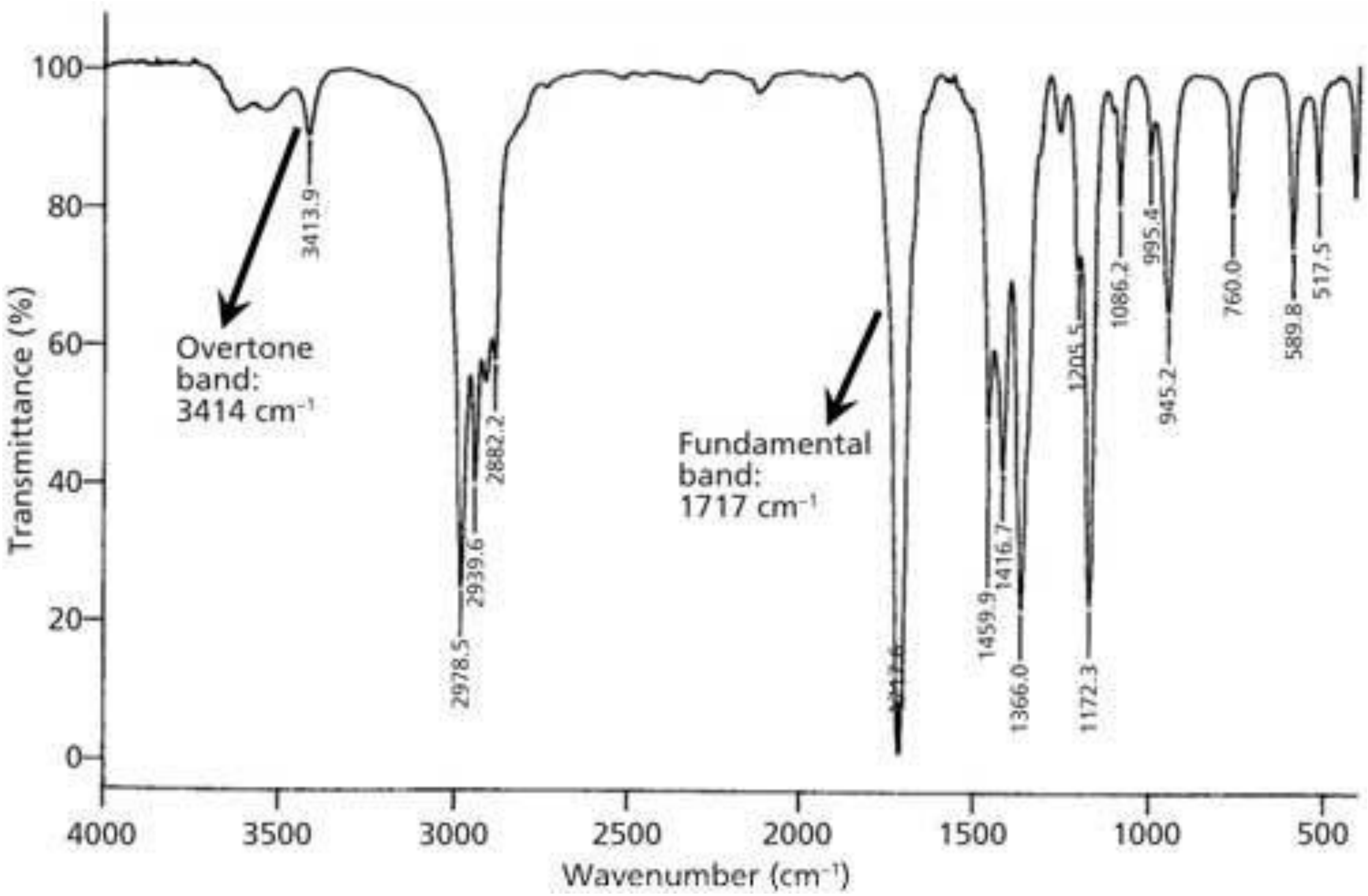
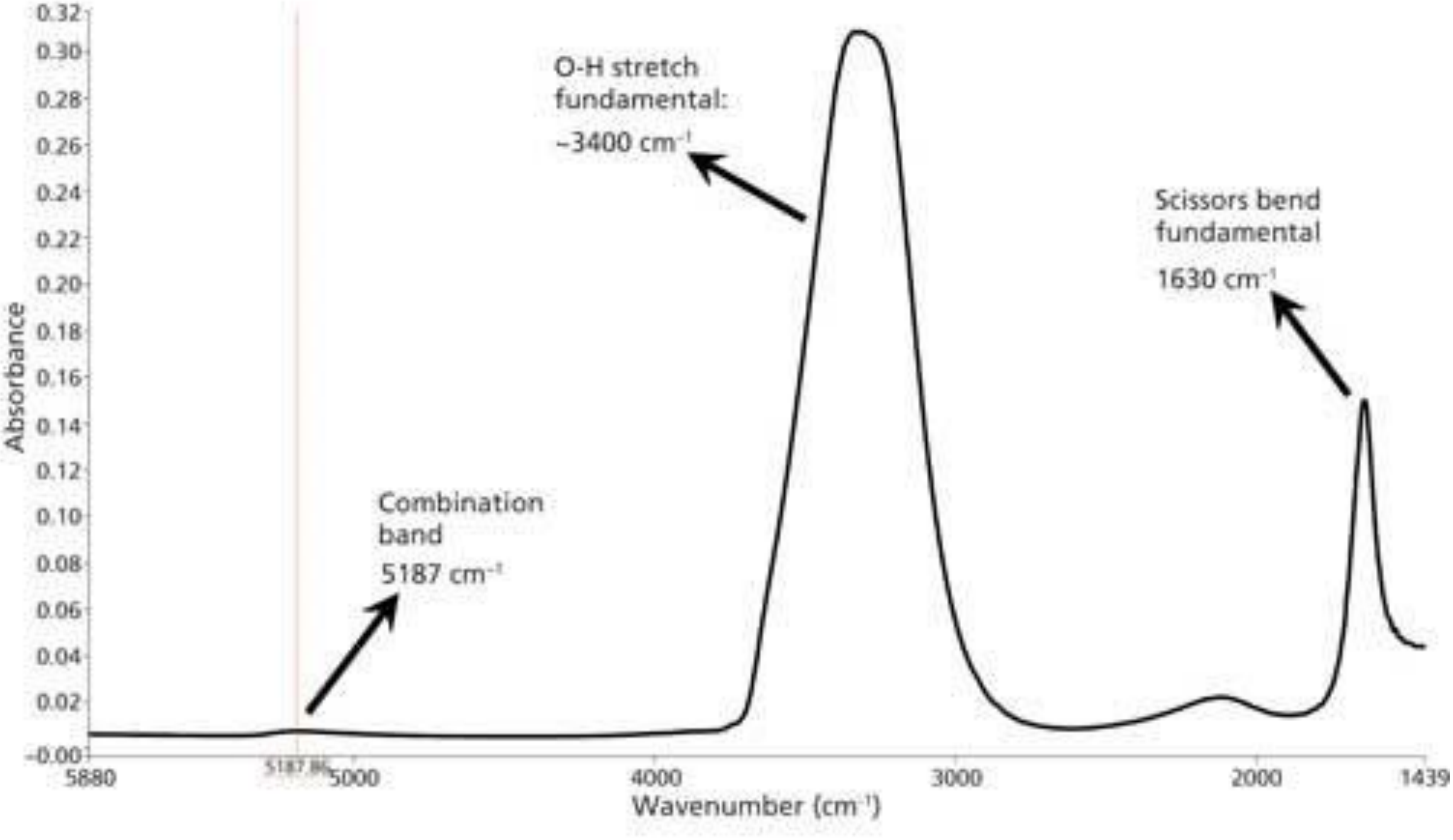
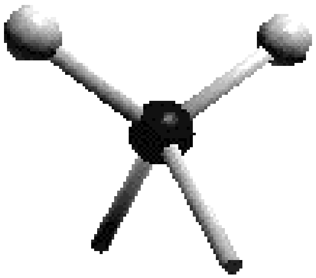
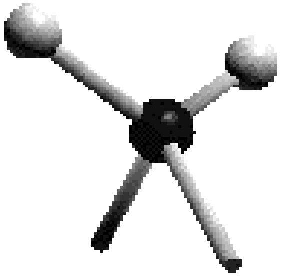


Figure 4: The IR spectrum of liquid water with the scissors vibration, O-H stretch, and combination band marked.

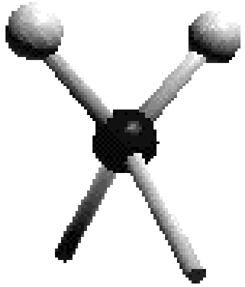




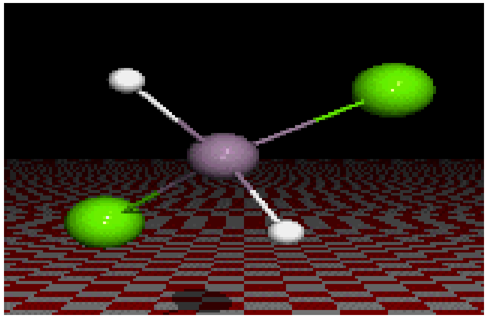
symmetric



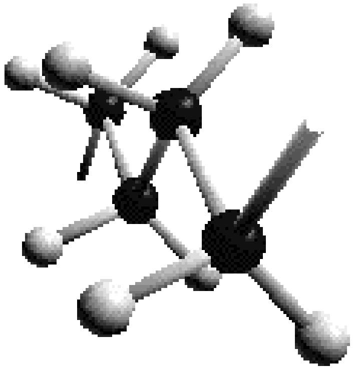
asymmetric



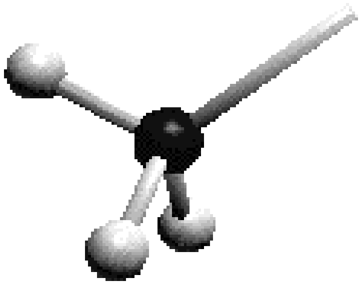
In-plane scissoring



Out-of-plane twisting



In-plane rocking



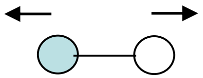
Out-of-plane wagging

iv.) Number of Vibrational Modes:

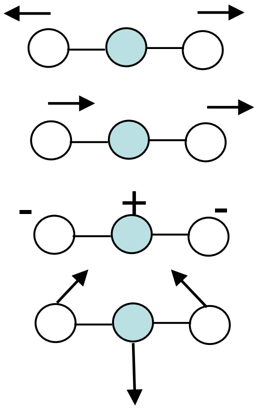
- for non-linear molecules, number of types of vibrations: 3N-6
- for linear molecules, number of types of vibrations: 3N-5
- why so many peaks in IR spectra
- observed vibration can be less then predicted because
  - symmetry (no change in dipole)
  - energies of vibration are identical
  - absorption intensity too low
  - frequency beyond range of instrument

Examples:

1) HCl: 3(2)-5 = 1 mode



2) CO_2: 3(3)-5 = 4 modes



moving in-out of plane

See web site for 3D animations of vibrational modes for a variety of molecules

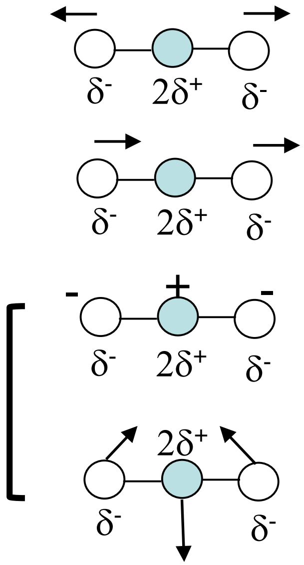
http://www.chem.purdue.edu/gchelp/vibs/co2.html

v.) IR Active Vibrations:

- In order for molecule to absorb IR radiation:
  - vibration at same frequency as in light
  - but also, must have a change in its *net dipole moment* as a result of the vibration

Examples:

1) CO_2: 3(3)-5 = 4 modes



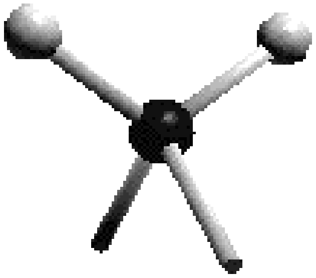
$\mu = 0$; IR inactive

$\mu > 0$; IR active

$\mu > 0$; IR active

$\mu > 0$; IR active

degenerate –identical energy single IR peak



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Example 8: Calculate the absorption frequency for the C-H stretch with a force constant of $k = 5.0\text{x}10^2$ N/m.

16B IR INSTRUMENTATION

Three types of instruments for IR absorption measurements are commonly available:

(1) dispersive spectrophotometers with a grating monochromator, (Until the 1980s)

(2) FT spectrometers employing an interferometer (Section 7I), and

(3) nondispersive photometers using a filter or an absorbing gas that are used for analysis of atmospheric gases at specific wavelengths.

(1) DISPERSIVE INSTRUMENTS

- dispersive instruments are generally ***double-beam*** instruments,

- use reflection gratings for dispersing radiation.

- the double-beam design is less demanding wrto the performance of sources and detectors

— an important characteristic because of the relatively low intensity of IR sources, the low sensitivity of IR transducers, and the resulting requirement for large signal amplifications (see Section 16C).

- An additional reason for the general use of double-beam instruments in the IR region is the elimination of the atmospheric water and carbon dioxide from the spectra.

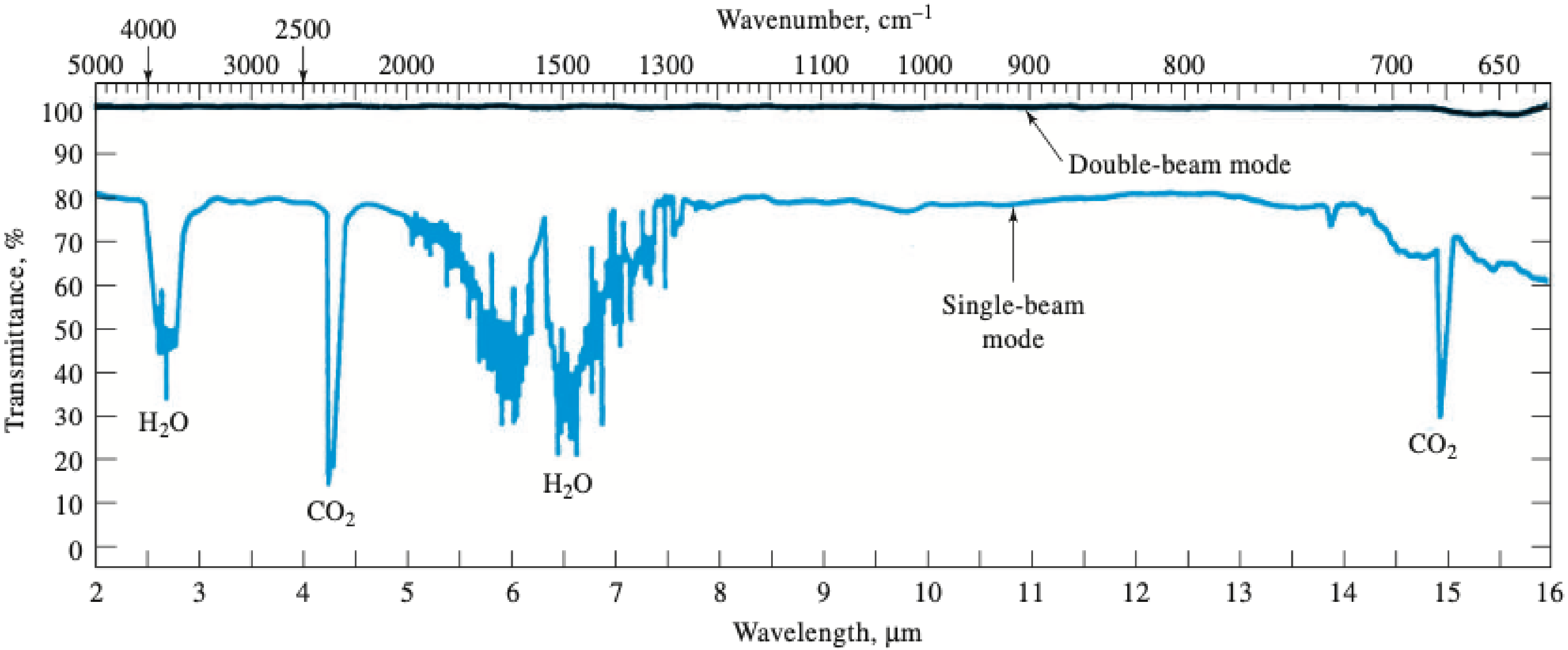


FIGURE 16-10 Single- and double-beam spectra of atmospheric water vapor and CO_2. In the lower, single-beam trace, the absorption of atmospheric gases is apparent. The top, double-beam spectrum shows that the reference beam compensates very well for this absorption and allows for a stable 100% *T* baseline to be obtained. (From J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, p. 409, Upper Saddle River, NJ: Prentice-Hall, 1988. With permission.)

Double-beam instruments

Basic Design: similar to UV-Vis, main differences are light source & detector

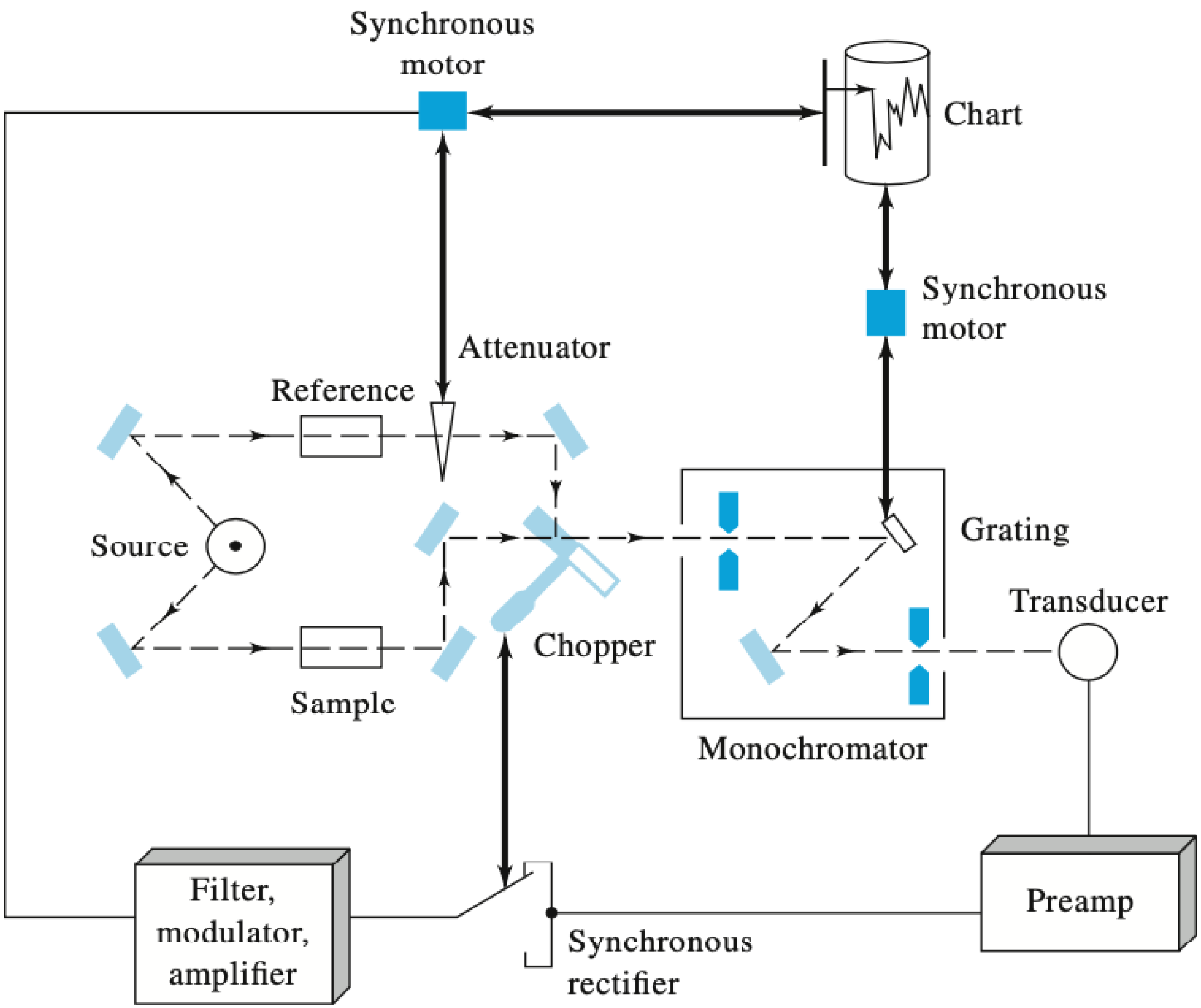


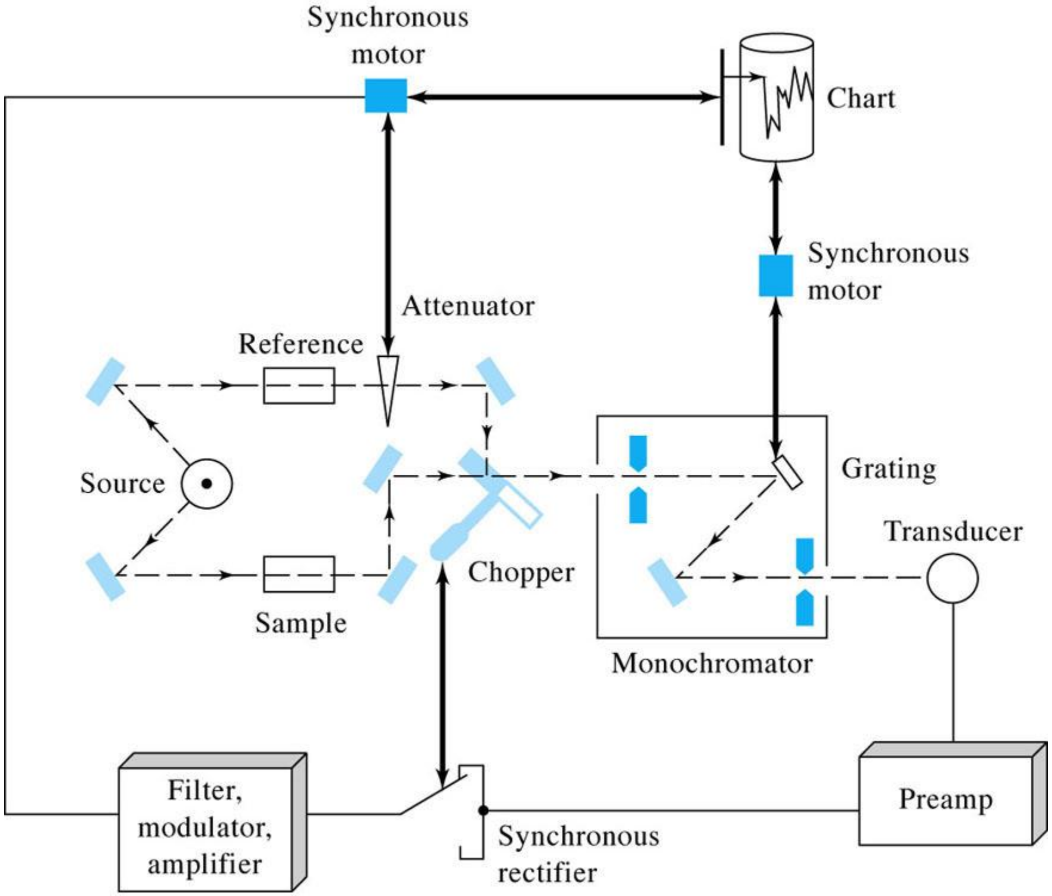
FIgure 11 Schematic diagram of a double-beam, dispersive IR spectrophotometer. The heavy black lines indicate mechanical linkages, and the light lines indicate electrical connections. The radiation path is designated by dashed lines.

- a low-frequency chopper permits the detector to discriminate between the signal from the source and signals from extraneous radiation, such as IR emission from various bodies surrounding the transducer.

the sample and reference compartments located between the source and the MC ;

- IR radiation, in contrast to UV-visible, is not sufficiently energetic, no photochemical decomposition of the sample.
- It is also advantageous that most scattered radiation and IR emission, generated within the cell compartment, is effectively removed by the MC and thus does not reach the transducer.

iv.) Overall Instrument Design



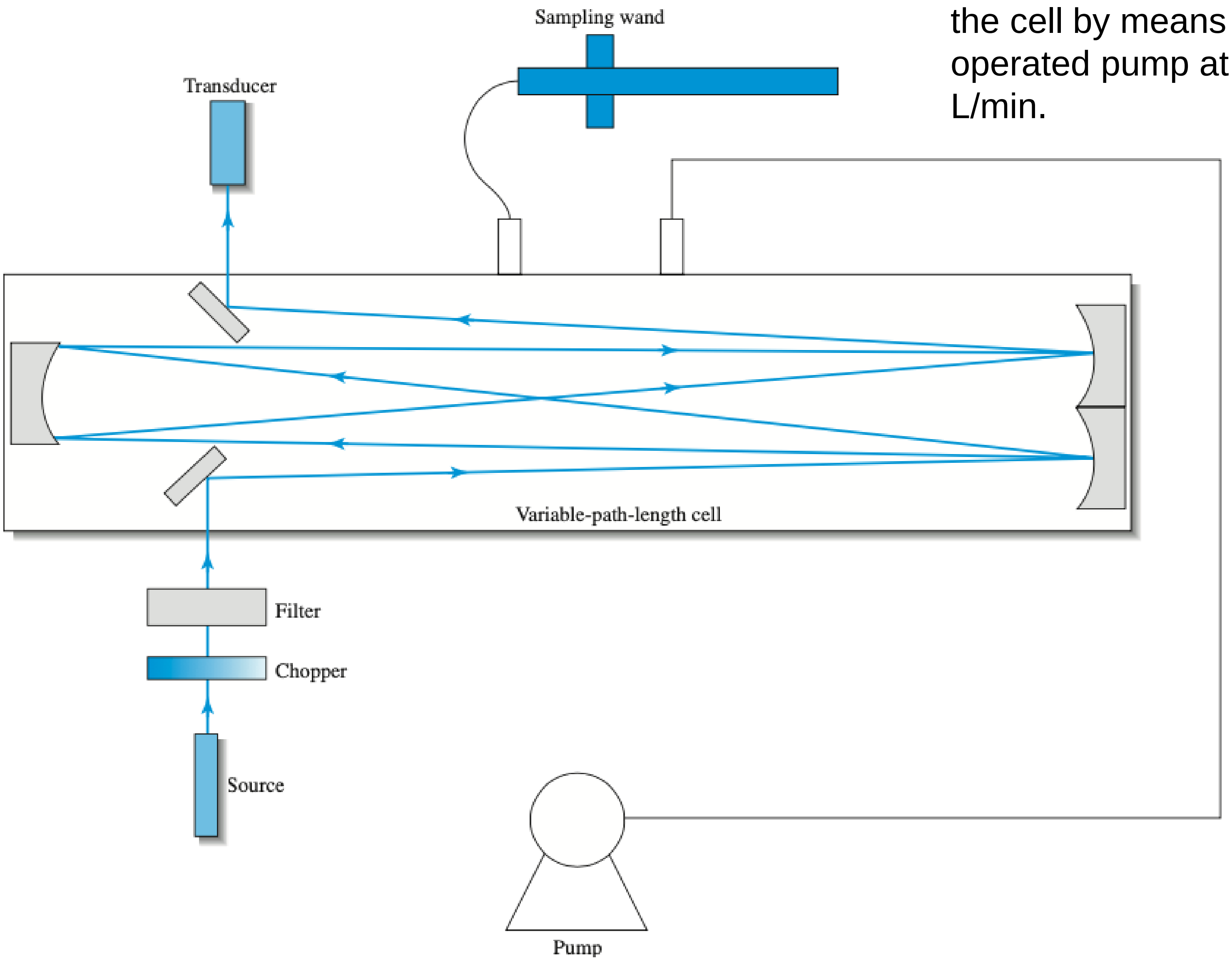
- Need chopper to discriminate source light from background IR radiation
- Monochromator after sample cell
  - Not done in UV-Vis since letting in all hν to sample may cause photdegradation (too much energy)
  - IR lower energy
  - Advantage that allows monochromator to be used to screen out more background IR light
- Problems:
  - Source weak , need long scans
  - Detector response slow – rounded peaks

2) NONDISPERSIVE INSTRUMENTS

- Generally, these instruments are less complex, more rugged, easier to maintain, and less expensive than the instruments we have previously described in this chapter.
- Some are simple filter photometers,
- some use filter wedges in lieu of a dispersing element to provide entire spectra.
- Some gas analyzers use no wavelength-selection device at all.

IR filter photometer designed for quantitative analysis of various substances in the atmosphere.

The gaseous sample is brought into the cell by means of a battery-operated pump at a rate of 20 L/min.



In the cell, three gold-plated mirrors are used in a folded-path-length design. Path lengths of 0.5 m and 12.5 m may be selected. Detection of many gases at sub-parts-per-million levels, particularly with the long-path-length setting, have been reported with this photometer.

FIgure 16-13 A portable IR photometer designed for gas analysis. The sample is introduced into the cell by means of a pump. The path length can be changed by altering the number of mirror reflections

Photometers without Filters

- Widely used to monitor gas streams for a single comp.
- Figure 16-14 to determine CO) in a gaseous mixture
- The reference cell: a non absorbing gas;
- the sample flows through a second cell of similar length.
- The beams chopped simultaneously by the chopper.
- Selectivity is obtained by filling both compartments of the sensor cell with the gas being analyzed, CO in this example.
- The two chambers of the detector are separated by a thin, flexible, metal diaphragm that serves as one plate of a capacitor; the second plate is contained in the sensor compartment on the left.
- In the absence of CO in the sample cell, the two sensor chambers are heated equally by IR radiation from the two sources.
- If the sample contains CO, however, the right-hand beam is attenuated somewhat and the corresponding sensor chamber becomes cooler with respect to its reference counterpart.
- As a result, the diaphragm moves to the right and the capacitance of the capacitor changes. This change in capacitance is sensed by the amplifier system
- The device can be adapted to the determination of any IR-absorbing gas (e.g., CO_2, NO, or H_2S).

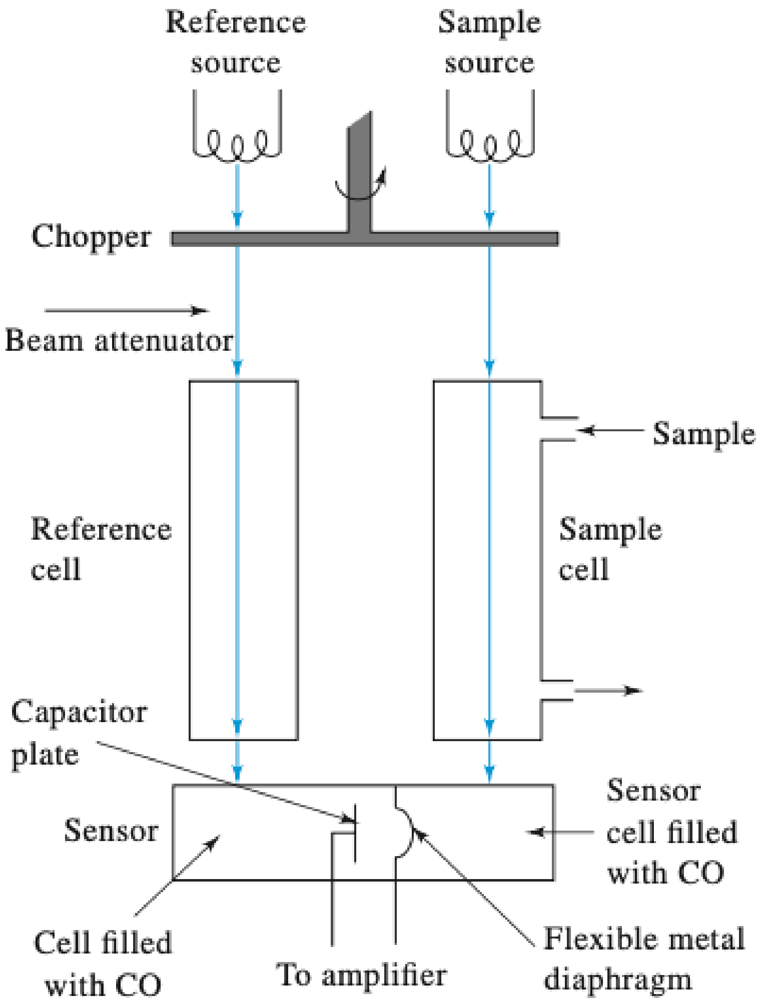
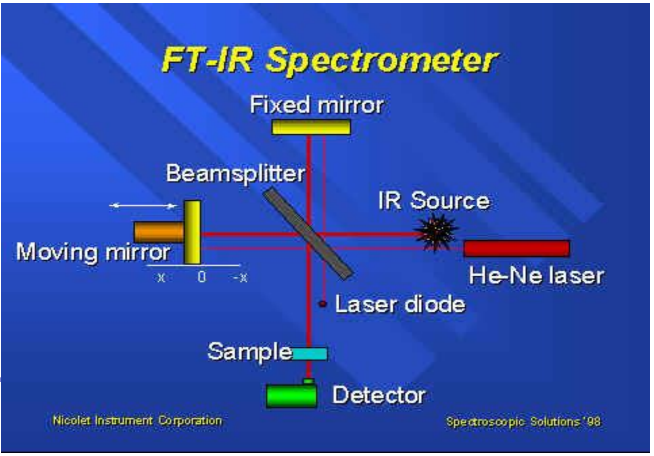


FIgure 16-14 A nondispersive IR photometer for monitoring CO.

3) FOURIER TRANSFORM IR (FTIR)

- alternative to Normal IR
- Based on the Michelson Interferometer that generates an interferogram
- This interferogram data is then mathematically transformed using a Fourier algorithm to obtain an IR spectrum.
- FTIR is much faster and more sensitive than traditional IR spectroscopy.



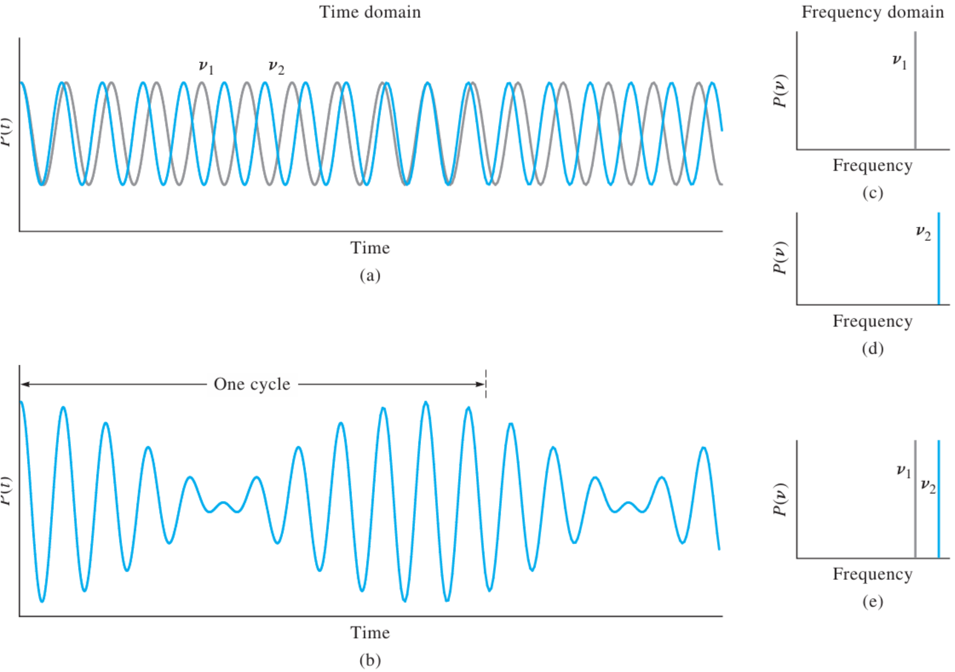


FIGURE 7-41 (a) Time-domain plot of two slightly different frequencies of the same amplitude ν1 and ν2.
(b) Time-domain plot of the sum of the two waveforms in (a).
(c) frequency-domain plot of ν1. (d) frequency-domain plot of ν2.
(e) frequency-domain plot of the waveform in (b).

- Conventional spectroscopy can be termed frequency-domain spectroscopy in that radiant power data are recorded as a function of frequency or wavelength. In contrast, time-domain spectroscopy, which can be achieved by the Fourier transform, is concerned with changes in radiant power with time.
- Time-domain signals, cannot be acquired experimentally with radiation in the frequency range that is associated with optical spectroscopy (10^{12} to 10^{15} Hz),because there are no transducers that will respond to radiant power variations at these high frequencies.

- Acquiring Time-Domain Spectra with a Michelson Interferometer

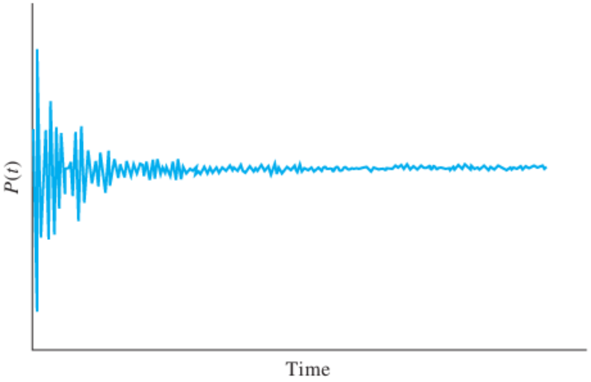


FIGURE 7-42 Time-domain signal of a source made up of many wavelengths.

- A typical transducer yields a signal that corresponds to the average power of a high-frequency signal and not to its periodic variation. To obtain time-domain signals requires, therefore, a method of converting (or modulating) a high-frequency signal to one of measurable frequency without distorting the time relationships carried in the signal; that is, the frequencies in the modulated signal must be directly proportional to those in the original.
- Different signal-modulation procedures are used for the various wavelength regions of the spectrum. The *Michelson interferometer* is used extensively to modulate radiation in the optical region.

1) The *Michelson interferometer* is a device that splits a beam of radiation into two beams of nearly equal power and then recombines them in such a way that intensity variations of the combined beam can be measured as a function of differences in the lengths of the paths of the two beams.

2) The splitted beams go to two other mirrors, one fixed and the other movable, and are reflected to recombine at the central mirror and pass through the sample to the detector

3) The movement of the second mirror enables light to travel different distances in two paths before recombining;

b) constructive & destructive interference occurs

c) as the mirror is moved, get a change in signal

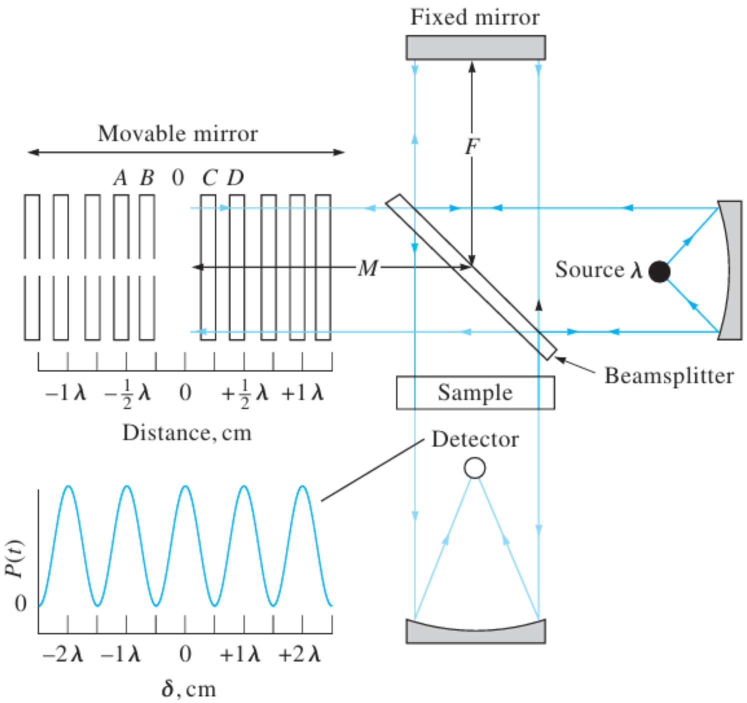
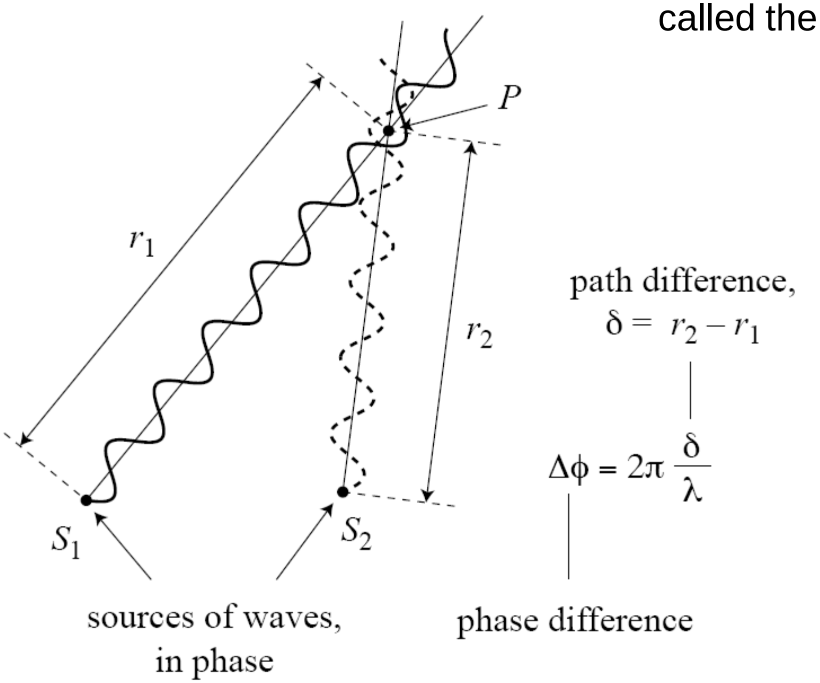


FIGURE 7-43 Schematic of a Michelson interferometer illuminated by a monochromatic source.

Remember

Destructive Interference can be created when two waves from the same source travel different paths to get to a point.

The difference in path lengths for the two beams, in the figure, is called the retardation, δ.



This may cause a difference in the phase between the two waves.

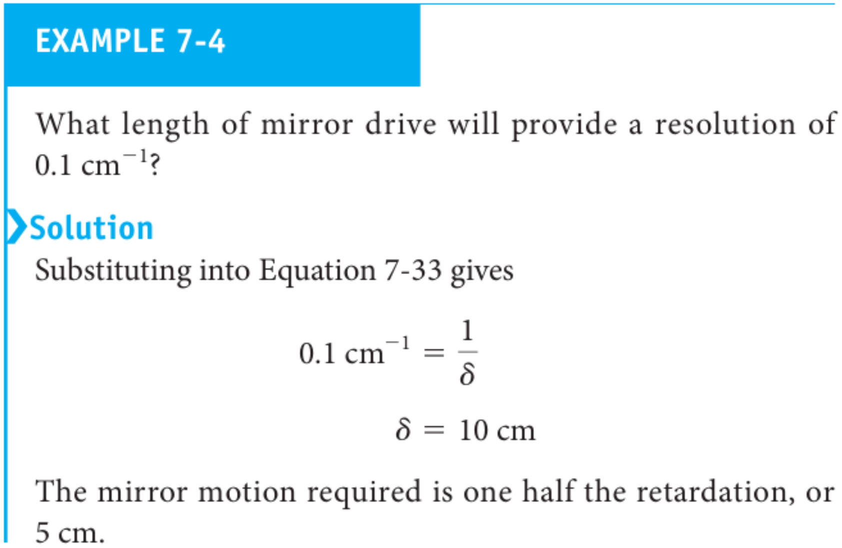
- *If the paths differ by an integer multiple of a wavelength, the waves will also be in phase.*
- *If the waves differ by an odd multiple of half a wave then the waves will be 180 degrees out of phase and cancel out.*

Resolution

The resolution of a Fourier transform spectrometer can be described in terms of the difference in wavenumber between two lines that can be just separated by the instrument.

$$\Delta\bar{\nu} = \bar{\nu}_1 - \bar{\nu}_2 \qquad \boxed{\Delta\bar{\nu} = \bar{\nu}_2 - \bar{\nu}_1 = \frac{1}{\delta}}$$

This equation means that resolution in wavenumbers will improve in proportion to the reciprocal of the distance that the mirror travels.



EXAMPLE 7-4

What length of mirror drive will provide a resolution of 0.1 cm^{-1}?

Solution

Substituting into Equation 7-33 gives

$$0.1\ \text{cm}^{-1} = \frac{1}{\delta}$$

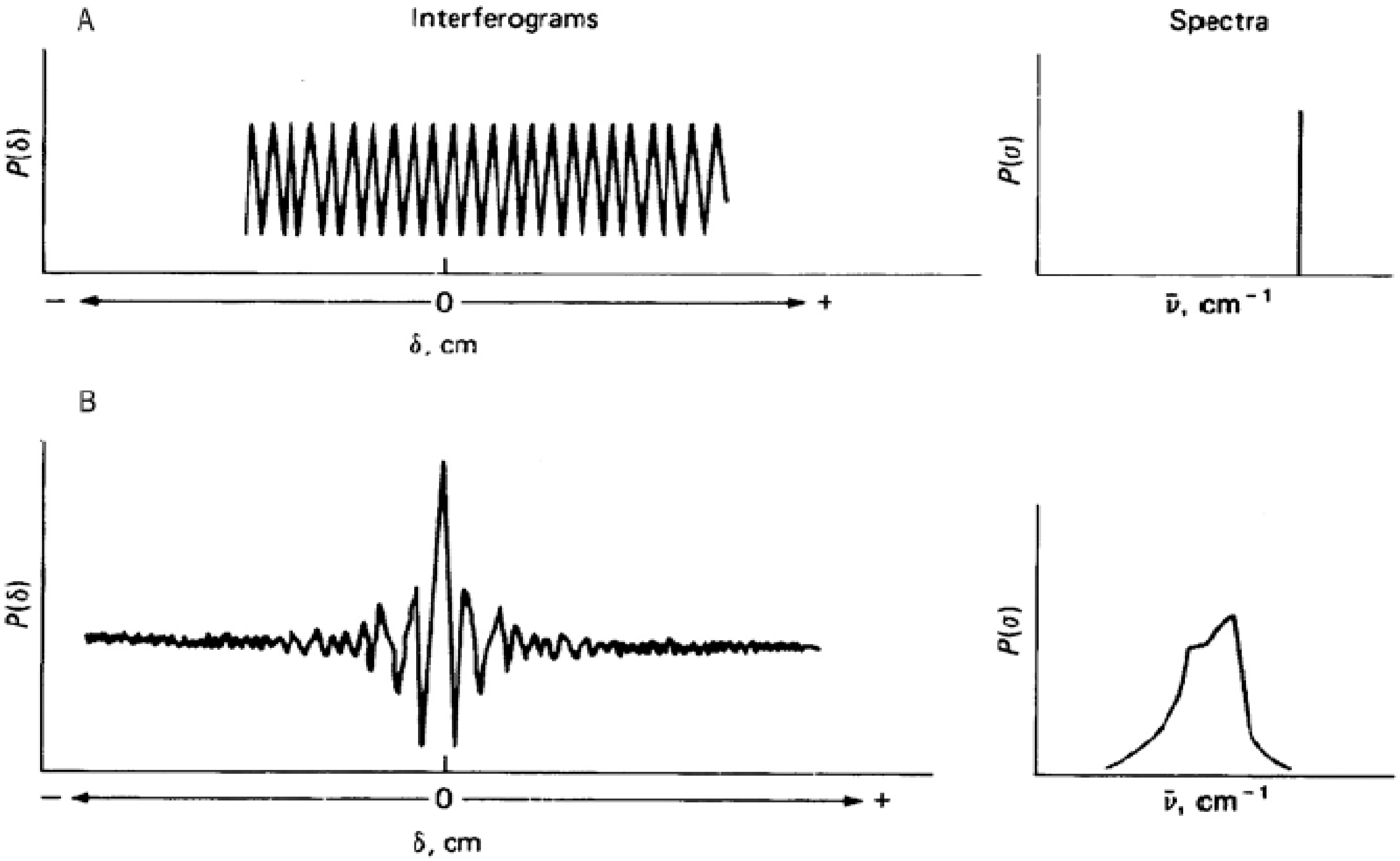
$$\delta = 10\ \text{cm}$$

The mirror motion required is one half the retardation, or 5 cm.

- a plot of Intensity vs. Distance (interferograms)
- convert to the plot of Intensity vs. Frequency by doing a Fourier Transform

$$I(x) = \int_0^{\infty} B(\nu)(1 + \cos 2\pi\nu x)\,d\nu$$

- resolution $\Delta\nu = 1/\Delta\delta$ (interval of distance traveled by mirror)



Fourier transform pairs for (A) a monochromatic source and (B) a broadband source.

Advantages of FTIR compared to Normal IR:

1) The throughput, or Jaquinot, advantage- few optical elements and no slits to attenuate radiation, the radiant power that reaches the detector is much greater than in dispersive instruments, and much greater signal-to-noise ratios are observed.

2) high resolution (<0.1 cm^{-1}); high resolving power and wavelength reproducibility that makes possible the analysis of complex spectra

3) Fellgett, or multiplex, advantage- much faster, seconds vs. minutes- all elements of the source reach the detector simultaneously; all frequencies are collected at once, therefore more data is collected and use of signal averaging to increase signal-to-noise (S/N) is applied.

$$increase\ S/N \propto \sqrt{number\ scans}$$

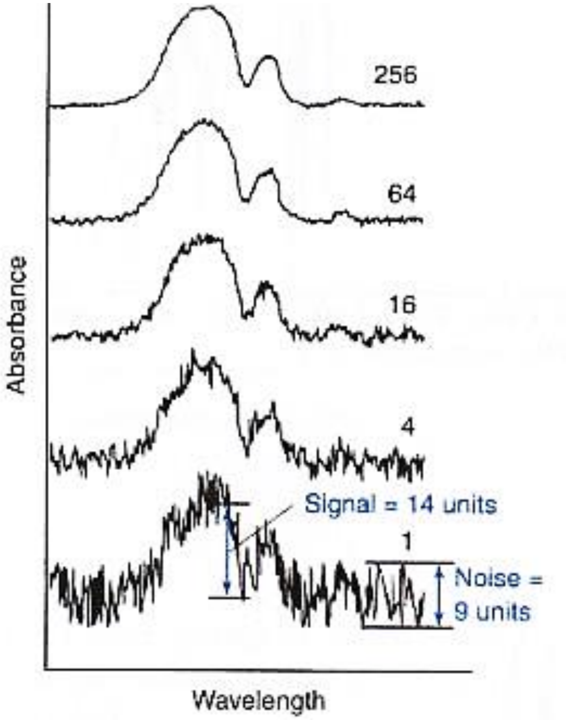
$$\left(\frac{S}{N}\right)_n = \sqrt{n}\left(\frac{S}{N}\right)_i$$

vhere $(S/N)_i$ is the S/N for one measurement.

Disadvantages of FTIR compared to Normal IR:

1) single-beam, requires collecting blank

2) can’t use thermal detectors – too slow

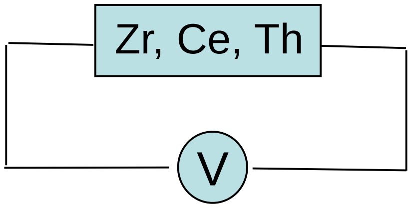


COMPONENTS of IR INSTRUMENTS

i) Light Source:

- must produce IR radiation
- can't use glass since absorbs IR radiation
- several possible types

a) Nernst Glower



- rare earth metal oxides (Zr, Ce, Th) heated electrically
- apply current to cylinder, has resistance to current flow generates heat (1200° – 2200° C).
- causes light production similar to blackbody radiation
- range of use ~ 670 – 10,000cm^{-1}
- need good current control or overheats and damaged

b) Globar

- similar to Nernst Glower but uses silicon carbide rod instead of rare earth oxides
- similar usable range

c) Incandescent Wire Source

- tightly wound nichrome or rodium wire that is electrically heated
- same principal as Nernst Glower
- lower intensity then Nernst Glower or Globar, but longer lifetime

d) CO_2 Laser

- CO_2 laser gas mixture consists of 70% He, 15% CO_2, and 15% N_2
- a voltage is placed across the gas, exciting N_2 to lowest vibrational levels.
- the excited N_2 populate the asymmetric vibrational states in the CO_2 through collisions.
- infrared output of the laser is the result of transitions between rotational states of the CO_2 molecule of the first asymmetric vibrational mode to rotational states of both the first symmetric stretch mode and the second bending mode
- gives off band of ~ 100 cm^{-1}'s in range of 900-1100 cm^{-1}
- small range but can choose which band used & many compounds have IR absorbance in this region
- much more intense than Blackbody sources

e) Others

- mercury arc ($\lambda > 50$ μm) (far IR)
- tungsten lamp (4000 -12,800cm^{-1}) (near IR)

ii.) Detectors:

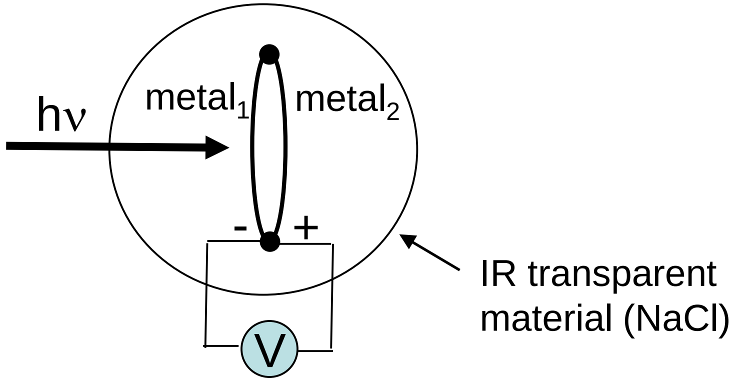
- three main types in common IR instruments

a) Thermal Detectors

b) Photoconducting Detectors

c) Pyroelectric Detectors

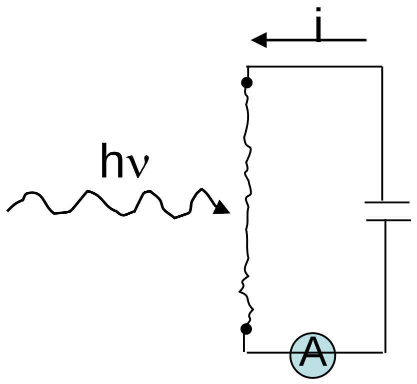
A- Thermal Detectors



1.) Thermocouple

- two pieces of dissimilar metals fused together at the ends
- when heated, metals heat at different rates
- potential difference is created between two metals that varies with their difference in temperature
- usually made with blackened surface (to improve heat absorption)
- placed in evacuated tube with window transparent to IR (not glass or quartz)
- IR “hits” and heats one of the two wires.
- can use several thermocouples to increase sensitivity.

2.) Bolometer



- strips of metal (Pt, Ni) or semiconductor that has a large change in resistance to current with temperature.

- as light is absorbed by blackened surface, resistance increases and current decreases

- very sensitive

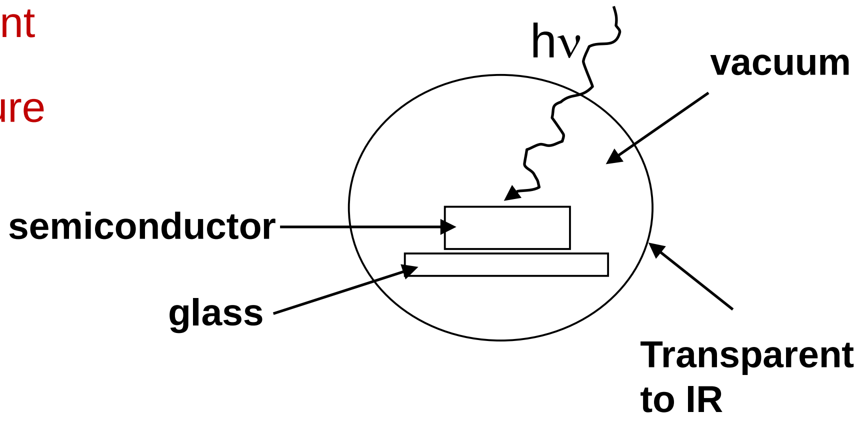
B) PHOTOCONDUCTING DETECTORS

- thin film of semiconductor (ex. PbS) on a nonconducting glass surface and sealed in a vacuum.

- absorption of light by semiconductor moves from non-conducting to conducting state

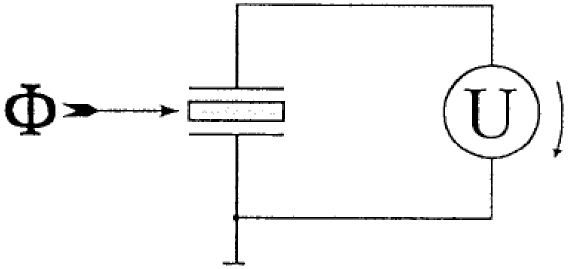
- decrease in resistance → increase in current

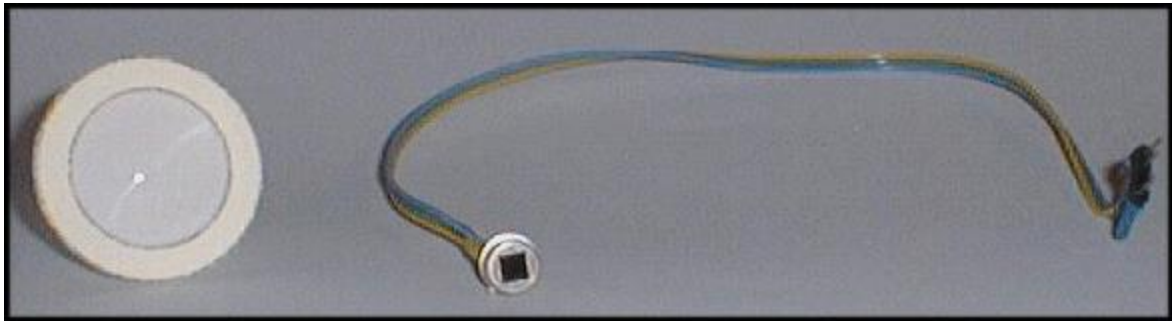
- range: 10,000 -333 cm^{-1} at room temperature



C) PYROELECTRIC DETECTORS

- pyroelectric (ceramic, lithium tantalate) material get polarized (separation of (+) and (-) charges) in presence of electric field.
- temperature dependent polarization
- measure degree of polarization related to temperature of crystal
- fast response, good for FTIR

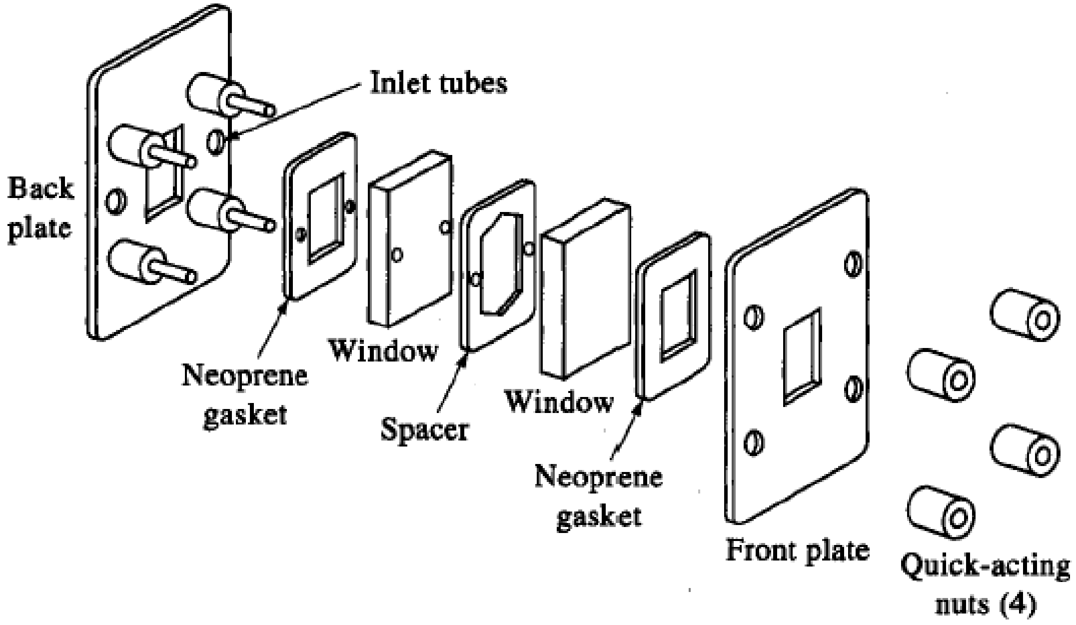




iii.) Other Components

a.) Sample Cell

- must be made of IR transparent material (KBr pellets or NaCl)

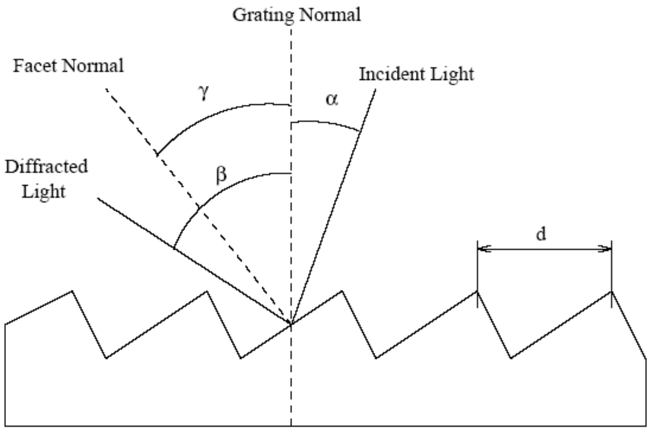


Liguid Sample Holder

NaCl plates

b.) monochromator

- reflective grating is common
- can’t use glass prism, since absorbs IR



Chapter 17 Applications of IR Spectrometry

Mid-IR absorption and reflection spectrometry are major tools for determining the structure of organic and biochemical species. In this section we examine mid-IR absorption applications. Section 17B is devoted to mid-IR reflectance measurements.1

17A-1 Sample Handling

- In UV-Vis, absorbance measurements in the optimal range are obtained by suitably adjusting either the concentration or the cell length.
- Unfortunately, this approach is often not applicable for IR spectroscopy because no good solvents are transparent throughout the region of interest. As a result, sample handling is frequently the most difficult and time-consuming part of an IR spectrometric analysis.
- In this section we outline some of the common techniques for preparation of samples for IR absorption measurements.

Gases:

- The spectrum of a low-boiling-point liquid or gas can be obtained by permitting the sample to expand into an evacuated cylindrical cell equipped with suitable windows.
- For this purpose, a variety of cylindrical cells are available with path lengths that range from a few centimeters to 10 m or more.
- The longer path lengths are obtained in compact cells by providing reflecting internal surfaces, so that the beam makes numerous passes through the sample before exiting the cell

Solutions

-When feasible, a convenient way of obtaining IR spectra is on solutions prepared to contain a known concentration of sample, as is generally done in UV-visible spectrometry. This technique is somewhat limited in its applications, however, by the availability of solvents transparent over significant regions in the IR.

Solvents. no single solvent is transparent throughout the entire mid-IR region.

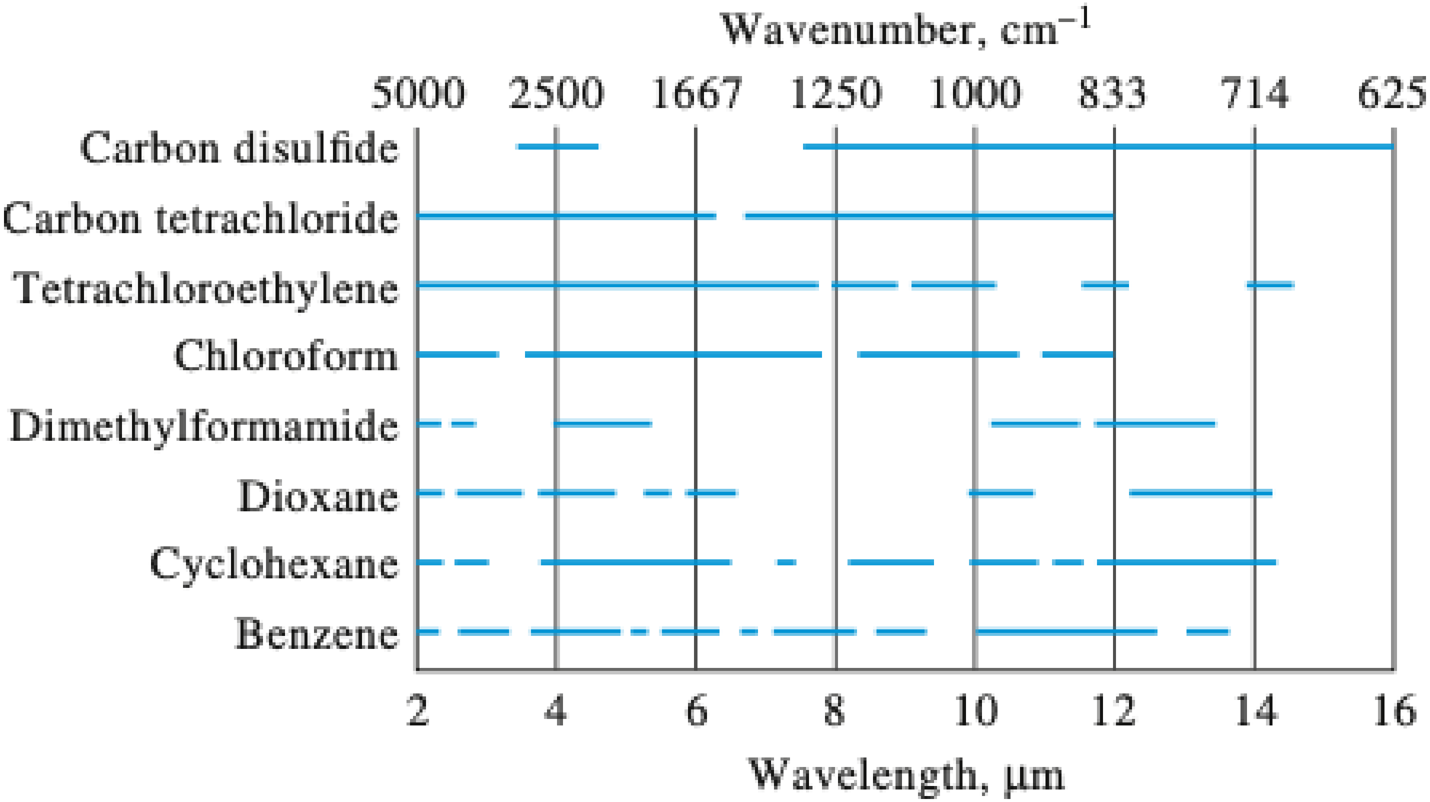


FIGURE 17-1 Solvents for IR spectroscopy. Horizontal lines indicate useful regions.

- Water and the alcohols are difficult to use as solvents in IR spectrometry.
- Water shows several strong absorption bands in the IR region, as can be seen in Figure 17-2.

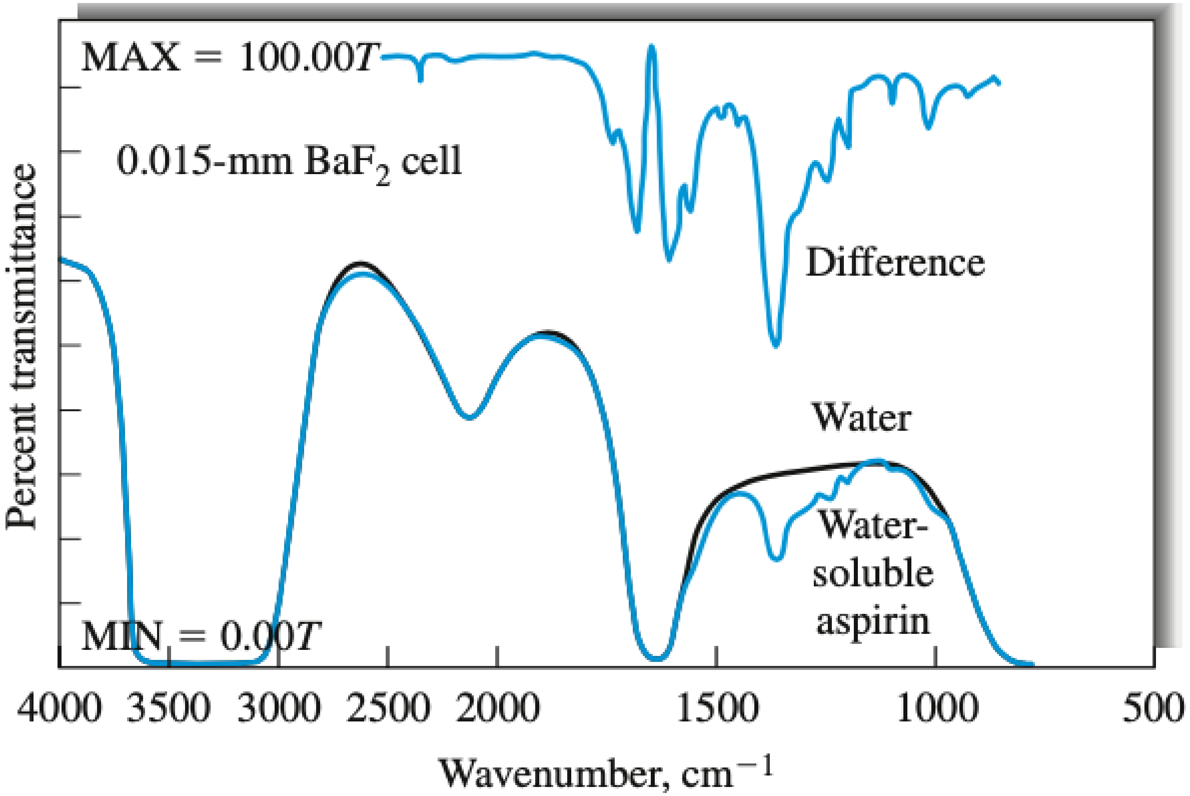


FIGURE 17-2 IR spectra of water and of an aqueous solution containing water-soluble aspirin. The top spectrum shows the computer-generated difference spectrum obtained by subtracting the water spectrum from that of the solution. (From *Practical Sampling Techniques for Infrared Analysis*, P. B. Coleman, ed., Boca Raton, FL: CRC Press, 1993. With permission.)

Water and alcohols also attack alkali-metal halides, the most common materials used for cell windows. Hence, water-insoluble window materials, such as barium fluoride, must be used with such solvents. Care must also be taken to dry the solvents shown in Figure 17-1 before use with typical cells.

Cells.

- Because of the tendency for solvents to absorb IR radiation, IR liquid cells are ordinarily much narrower (0.01 to 1 mm) than those used in the UV and visible regions.
- Often, relatively high sample concentrations (from 0.1% to 10%) are required because of the short path lengths and the low molar absorptivity of IR bands.
- Liquid cells are frequently designed for easy disassembly and use Teflon spacers to allow variation in path length (see Figure 17-3)

Fixed-path-length cells can be filled or emptied with a hypodermic syringe.

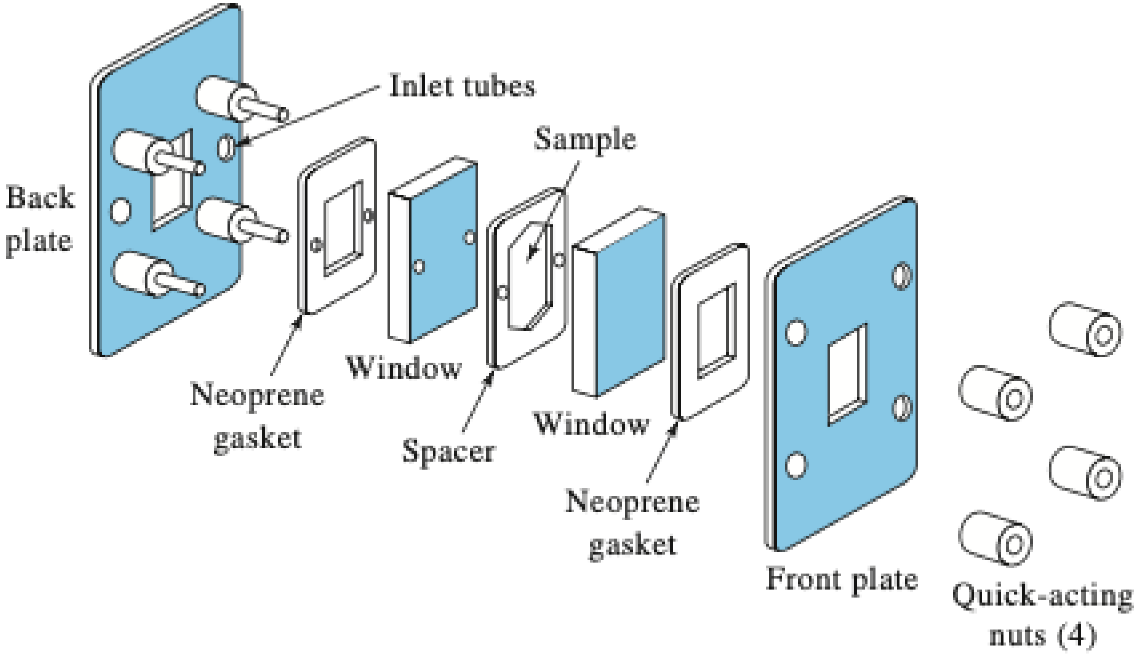
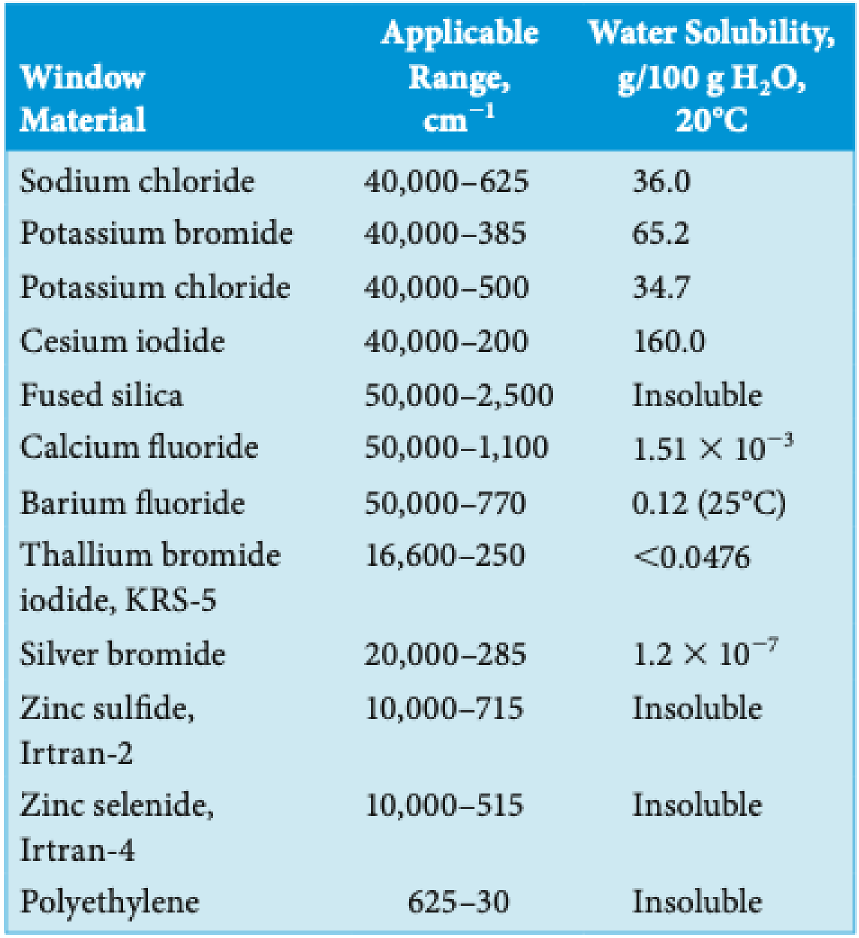


FIGURE 17-3 Expanded view of a demountable IR cell for liquid samples. Teflon spacers ranging from 0.015 to 1 mm thick are available. (Courtesy of Perkin-Elmer Corp., Norwalk, CT.)

- A variety of window materials are available as listed in Table 17-2.
- Window materials are often chosen on the basis of cost, range of transparency, solubility in the solvent, and reactivity with the sample or solvent.
- Sodium chloride and potassium bromide windows are most commonly used and are the least expensive.
- Even with care, however, their surfaces eventually become fogged because of absorption of moisture. Polishing with a buffing powder can, in many cases, return them to their original condition.
- For samples that are wet or aqueous, calcium and barium fluoride are suitable, although neither transmits well throughout the entire mid-IR region. Silver bromide is often used, although it is more expensive, is photosensitive, and is easily scratched.

TABLE 17-2 Common IR Window Materials



Window Material	Applicable Range, cm^{-1}	Water Solubility, g/100 g H_2O, 20°C
Sodium chloride	40,000–625	36.0
Potassium bromide	40,000–385	65.2
Potassium chloride	40,000–500	34.7
Cesium iodide	40,000–200	160.0
Fused silica	50,000–2,500	Insoluble
Calcium fluoride	50,000–1,100	1.51×10^{-3}
Barium fluoride	50,000–770	0.12 (25°C)
Thallium bromide iodide, KRS-5	16,600–250	<0.0476
Silver bromide	20,000–285	1.2×10^{-7}
Zinc sulfide, Irtran-2	10,000–715	Insoluble
Zinc selenide, Irtran-4	10,000–515	Insoluble
Polyethylene	625–30	Insoluble

Liquids

When the amount of a liquid sample is small or when a suitable solvent is unavailable, it is common practice to obtain spectra on the pure (neat) liquid. The thickness of a very thin film of liquid presents a sufficiently short path length to produce satisfactory spectra. Commonly, a drop of the neat liquid is squeezed between two rock-salt plates to give a layer 0.015 mm thick or less. The two plates, held together by capillary action, are then placed in the beam path. This technique does not give particularly reproducible transmittance data, but the resulting spectra are usually satisfactory for qualitative investigations.

Solids

Most organic compounds exhibit numerous absorption bands throughout the mid-IR region, and finding a solvent that does not have overlapping bands is often impossible. Because of this, spectra are often obtained on dispersions of the solid in a liquid or solid matrix. Generally, in these techniques, the solid sample must be ground until its particle size is much less than the wavelength of the radiation to avoid the effects of scattered radiation.

Pelleting. One of the most popular techniques for handling solid samples has been KBr pelleting (other alkali-metal halides have also been used). Halide salts have the property of cold flow, in which they have glasslike transparent or translucent properties when sufficient pressure is applied to the finely powdered materials. In using this technique, a milligram or less of the finely ground sample is intimately mixed with about 100 mg of dried, spectroscopic grade, potassium bromide powder. Mixing can be carried out with a mortar and pestle or, better, in a small ball mill. The mixture is then pressed in a special die at 10,000 to 15,000 pounds per square inch to yield a transparent disk. Best results are obtained if the disk is formed in a vacuum to eliminate occluded air. The disk is then held in the instrument beam for spectroscopic examination. The resulting spectra frequently exhibit bands at 3450 and 1640 cm-1 (2.9 and 6.1 μm) due to absorbed moisture.

KBr

- With many compounds, KBr pelleting produces excellent spectra that appear in many spectral libraries.
- Being ionic, KBr transmits throughout most of the IR region with a lower cutoff of about 400 cm-1
- Although KBr is the most frequently used pelleting salt, materials such as CsI and CsBr are sometimes used. Cesium iodide has greater transparency at low frequencies than KBr.

Mulls.

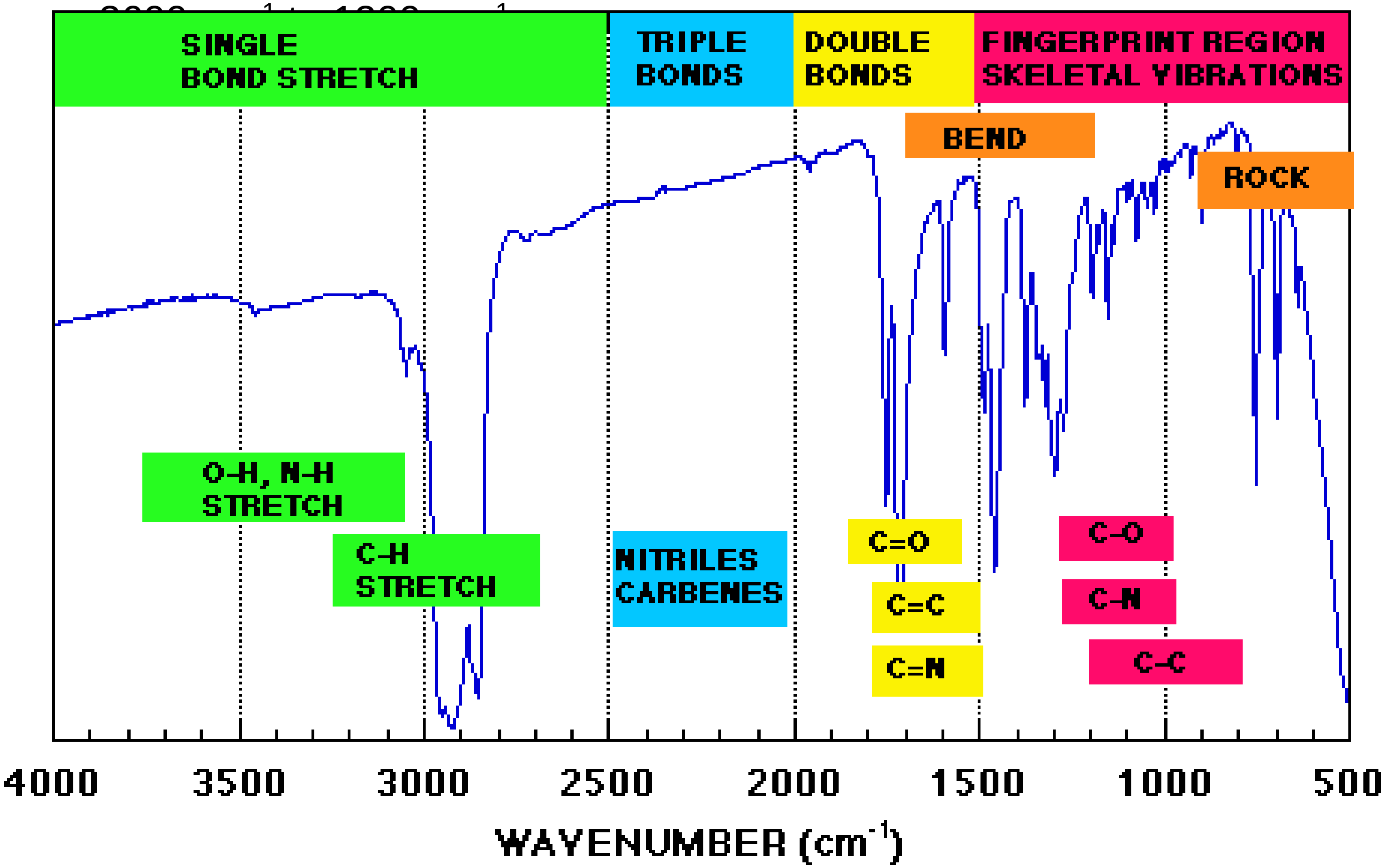
- R spectra of solids that are not soluble in an IR-trans- parent solvent or are not conveniently pelleted in KBr are often obtained by dispersing the analyte in a mineral oil or a fluorinated hydrocarbon *mull*.

Qualitative Analysis (Compound Identification)

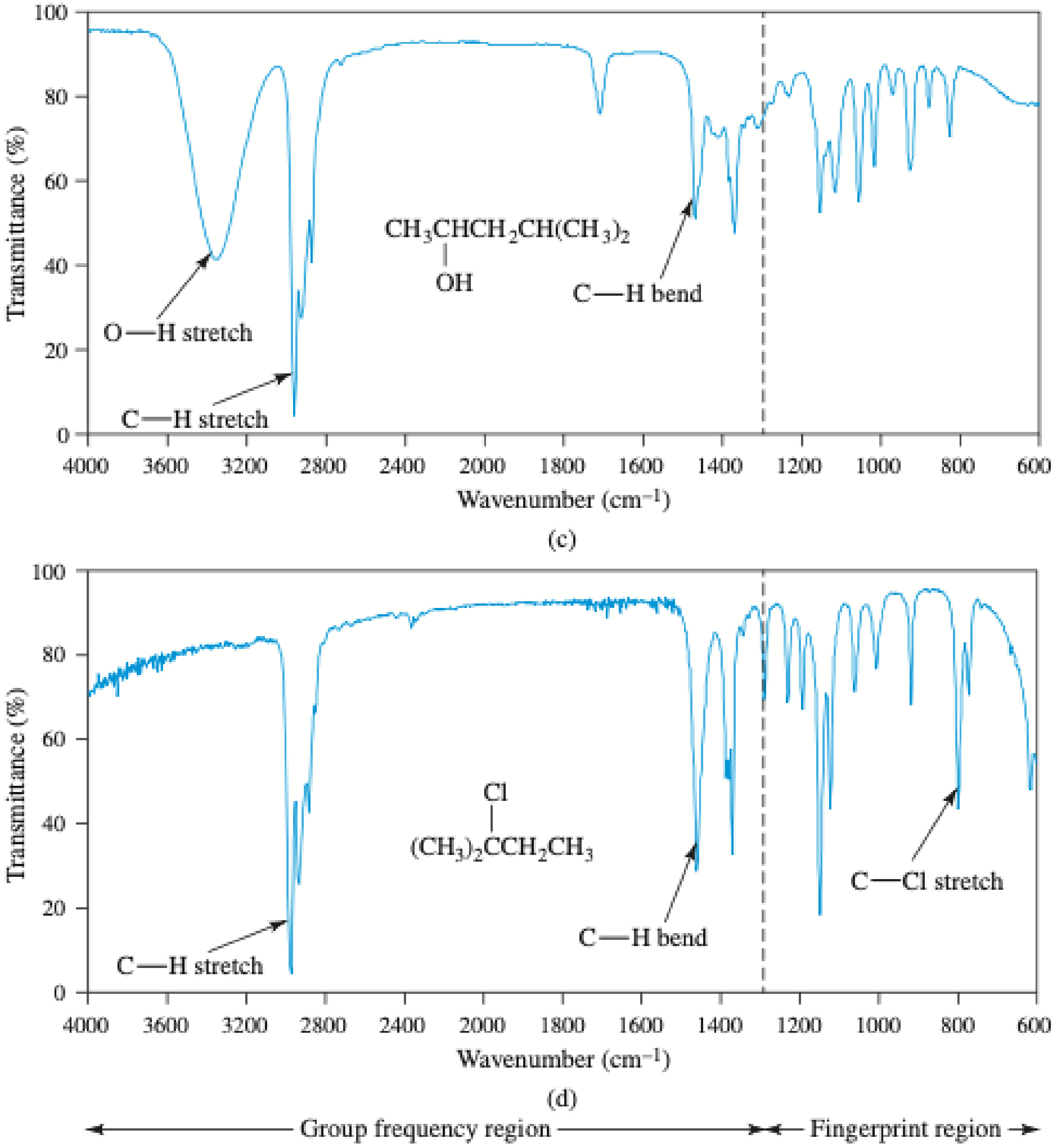
- Use of IR, with NMR and MS, in late 1950’s revolutionized organic chemistry
  - ► decreased the time to confirm compound identification 10- 1000 fold

- Identification of an organic compound from a spectrum of this kind is a two-step process.

1) examine what functional groups are present by looking at group frequency region



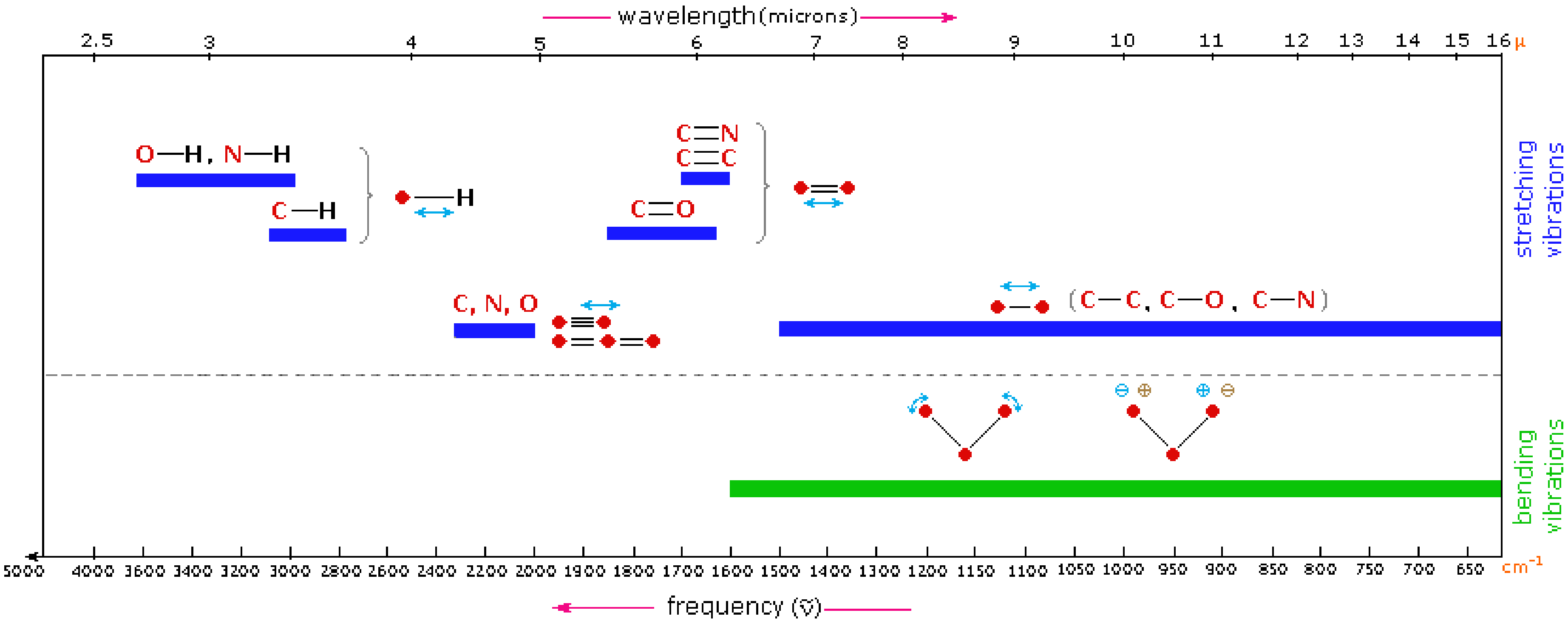
2) A detailed comparison of the spectrum of the unknown with the spectra of pure compounds that contain all of the functional groups found in the first step.



- The fingerprint region, from 1200 to 600 cm-1 is particularly useful here because small differences in the structure and constitution of a molecule result in significant changes in the appearance and distribution of absorption bands in this region.
- Consequently, a close match between two spectra in the fingerprint region (as well as others) constitutes almost certain evidence that the two compounds are identical.

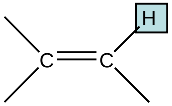
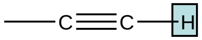
ii.) Group Frequency Region

- approximate frequency of many functional groups (C=O,C=C,C-H,O-H) can be calculated from atomic masses & force constants
- positions changes a little with neighboring atoms, *but* often in same general region
- serves as a good initial guide to compound identity, but not positive proof.



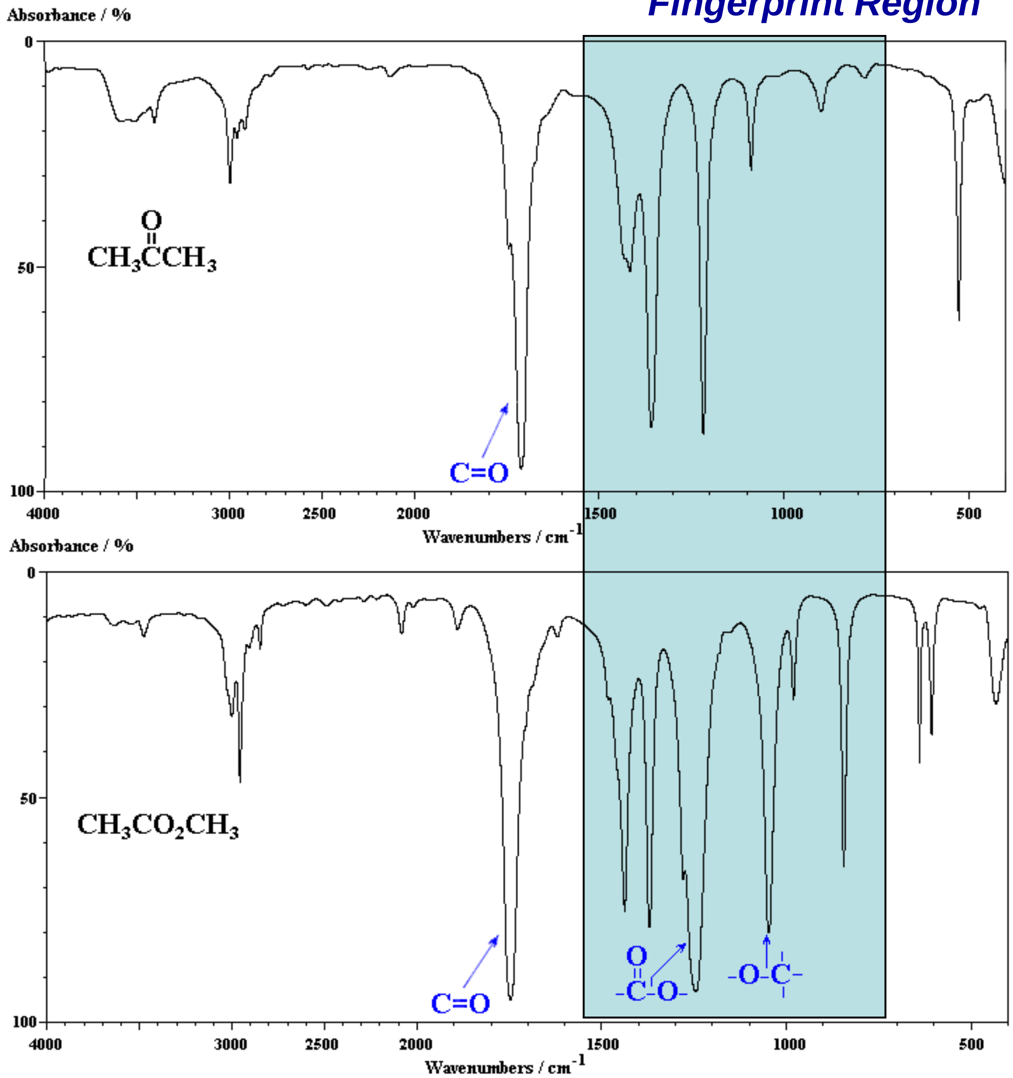
- group frequencies and correlation charts serve as a starting point in the identification process.
- charts permit intelligent guesses as to what functional groups are likely to be present or absent in a molecule.

Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C-H	Alkanes	2850-2970	Strong
C-H	Alkenes 	3010-3095 675-995	Medium strong
C-H	Alkynes 	3300	Strong
C-H	Aromatic rings	3010-3100 690-900	Medium strong
0-H	Monomeric alcohols, phenols Hydrogen-bonded alchohols, phenols Monomeric carboxylic acids Hydrogen-bonded carboxylic acids	3590-3650 3200-3600 3500-3650 2500-2700	Variable Variable, sometimes broad Medium 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 1300-1370	Strong

iii.) Fingerprint Region (1200-700 cm^{-1})

- region of most single bond signals
- many have similar frequencies, so affect each other & give pattern characteristics of overall skeletal structure of a compound
- exact interpretation of this region of spectra seldom possible because of complexity
- complexity → uniqueness



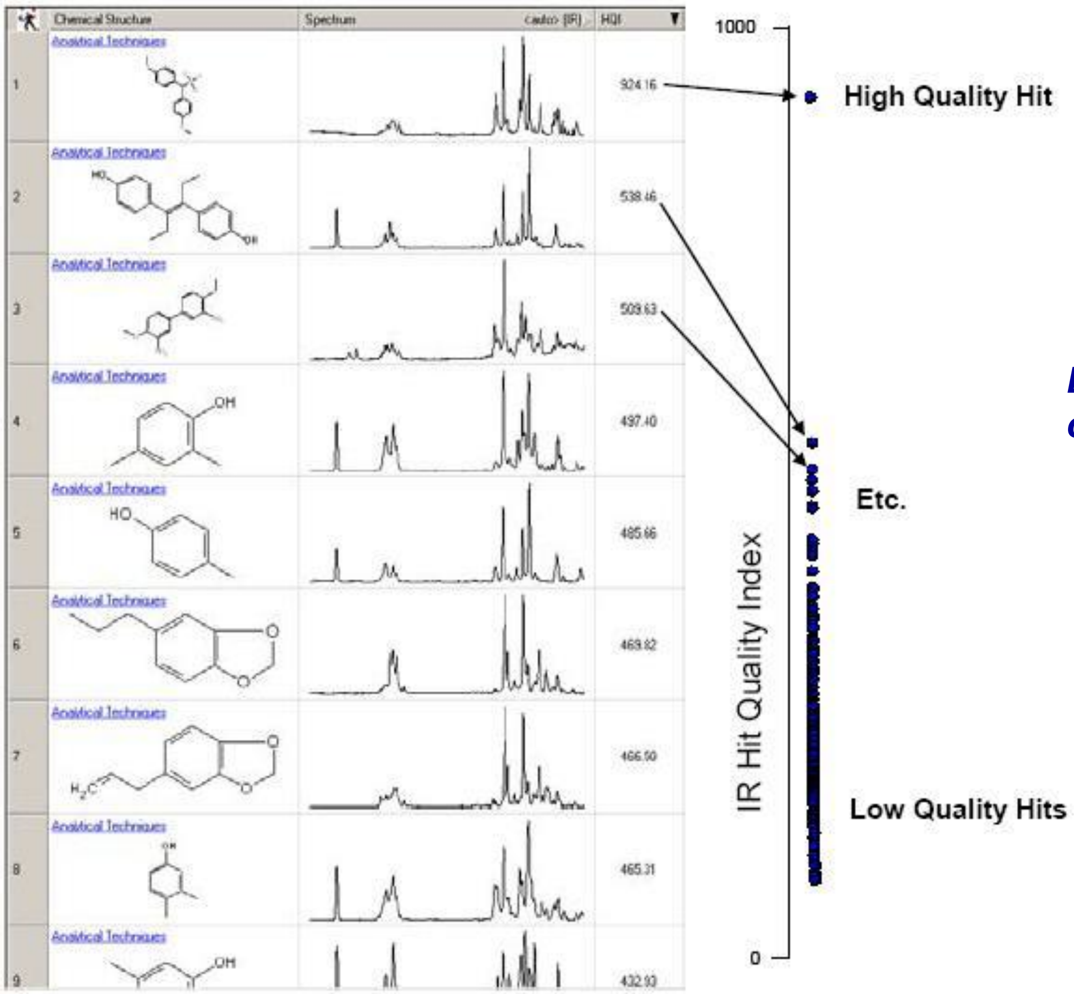
Fingerprint Region

iv.) Computer Searches

- many modern instruments have reference IR spectra on file (~100,000 compounds)
- matches based on location of strongest band, then 2nd strongest band, etc

overall skeletal structure of a compound

- exact interpretation of this region of spectra seldom possible because of complexity
- complexity → uniqueness



	Chemical Structure	Spectrum	<auto> (IR)	HQI
1	Analytical Techniques			924.16
2	Analytical Techniques			538.46
3	Analytical Techniques			509.63
4	Analytical Techniques			497.40
5	Analytical Techniques			485.66
6	Analytical Techniques			469.82
7	Analytical Techniques			466.50
8	Analytical Techniques			465.31
9	Analytical Techniques			432.93

Bio-Rad SearchIT database of ~200,000 IR spectra

2.) Quantitative Analysis

- not as good as UV/Vis in terms of accuracy and precision
  - ► more complex spectra
  - ► narrower bands (Beer's Law deviation)
  - ► limitations of IR instruments (lower light throughput, weaker detectors)
  - ► high background IR
  - ► difficult to match reference and sample cells
  - ► changes in ε ($A=\varepsilon bc$) common
- potential advantage is good selectivity, since so many compounds have different IR spectra
  - ► one common application is determination of air contaminants.

Contaminants	Concn, ppm	Found, ppm	Relative error, %
Carbon Monoxide	50	49.1	1.8
Methylethyl ketone	100	98.3	1.7
Methyl alcohol	100	99.0	1.0
Ethylene oxide	50	49.9	0.2
chloroform	100	99.5	0.5

Baseline method.

- An alternative way of obtaining *P*0 and *T* for a single absorption band is the baseline method. For an instrument that displays transmittance, the solvent transmittance is assumed to be constant or at least to change linearly between the shoulders of the absorption peak, as illustrated in Figure 17-9. The quantities T_0 and T_s are then obtained as shown in the figure.
- For direct absorbance readout, as is shown in Figure 17-7, the absorbance is assumed to be constant or to change linearly under the absorption band. The peak absorbance is then obtained by subtracting the baseline absorbance.

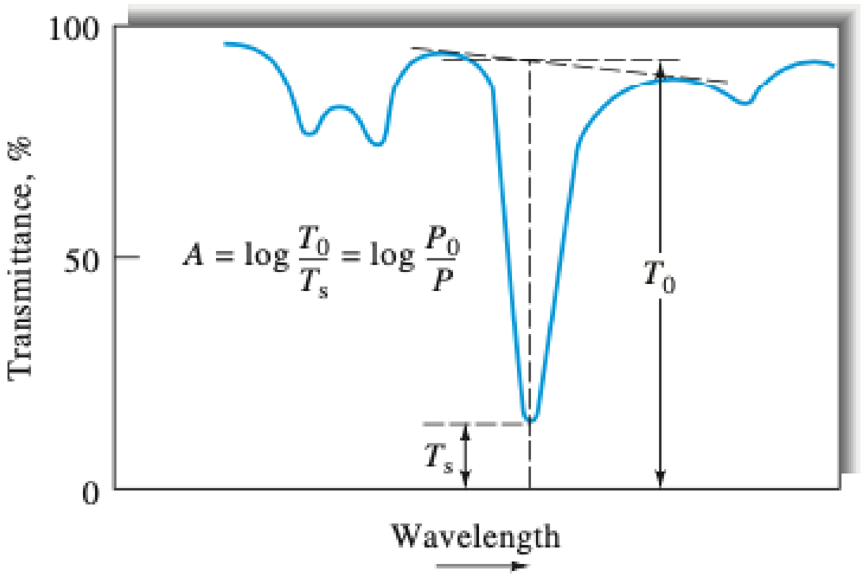


FIGURE 17-9 The baseline method for determining the absorbance of an absorption maximum.

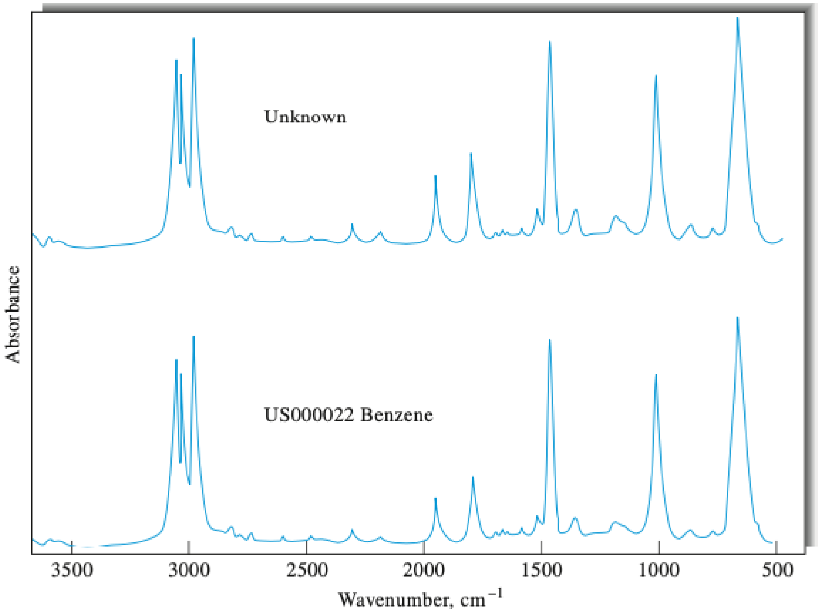
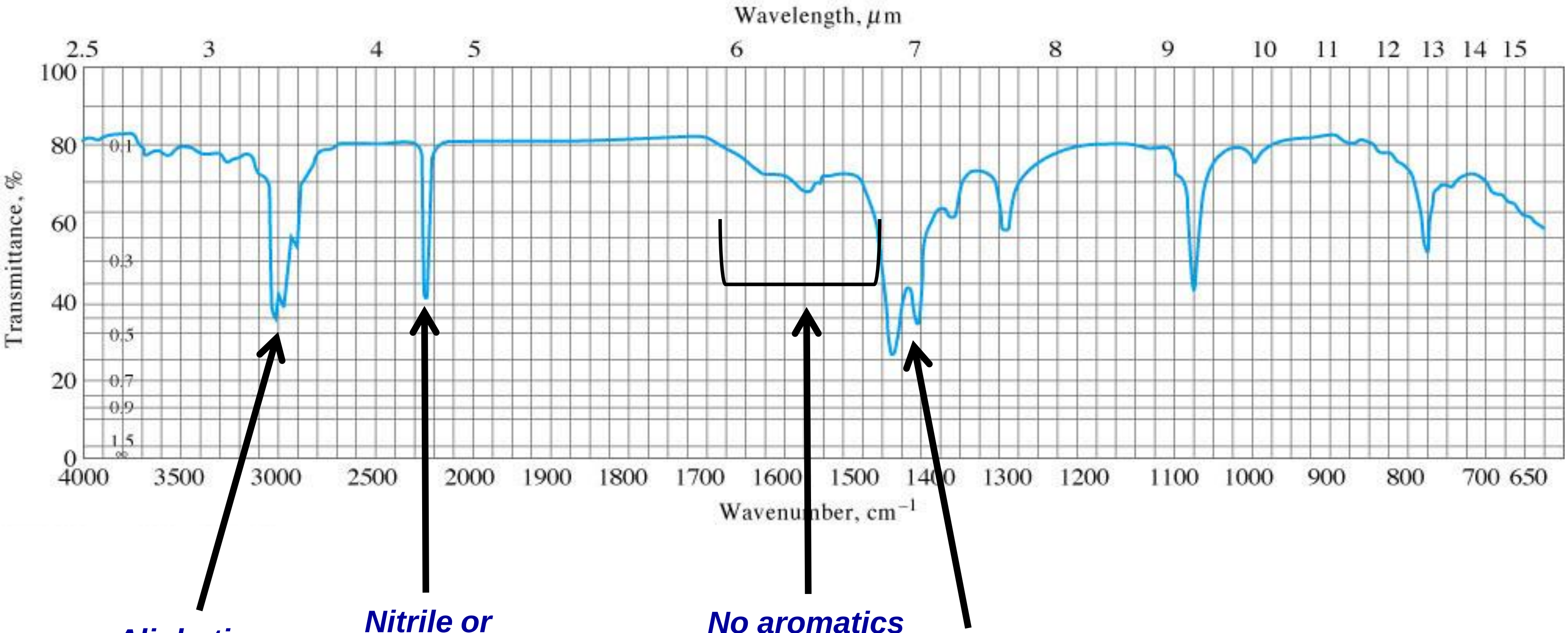


FIGURE 17-7 Plot of an unknown spectrum and the best match from a computer search report. (Courtesy of Informatics/Sadtler Group, Bio-Rad Laboratories, Inc., Philadelphia, PA.)

Example 9: The spectrum is for a substance with an empirical formula of C_3H_5N. What is the compound?



Aliphatic hydrogens

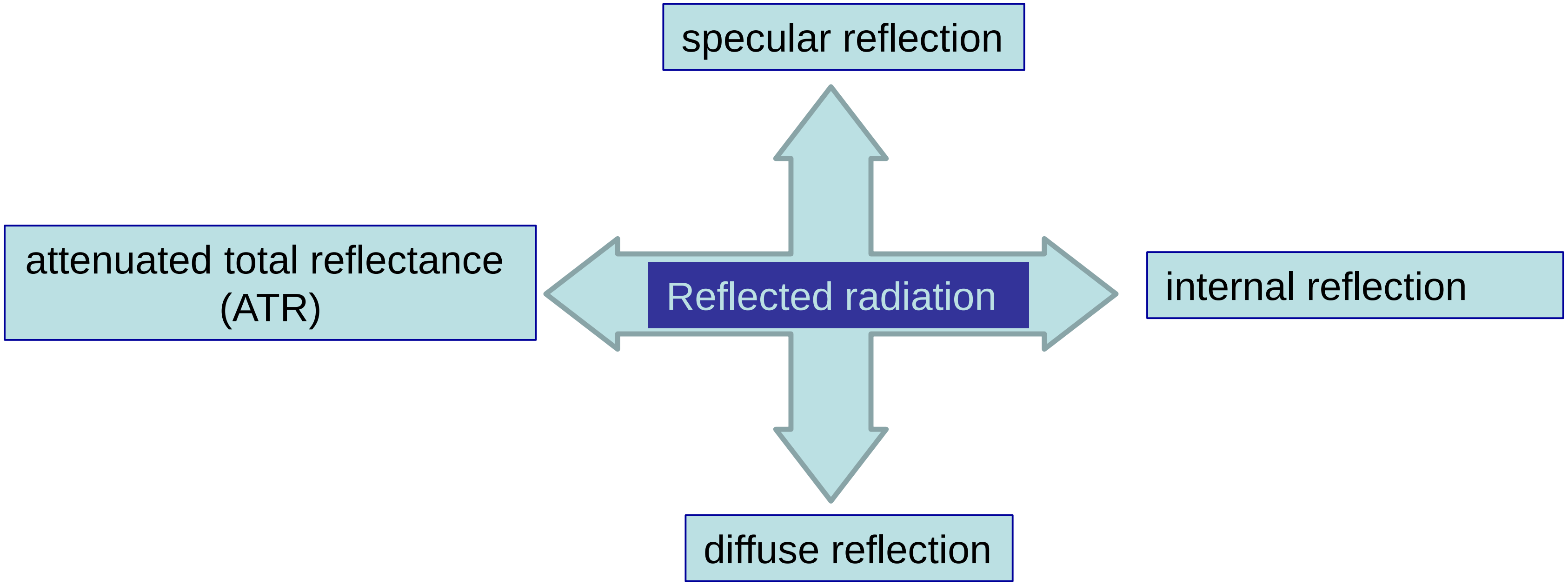
Nitrile or alkyne group

No aromatics

One or more alkane groups

17B MID-IR REFLECTION SPECTROMETRY

- IR reflection spectrometry has found a number of applications, particularly for dealing with;
  - *solid samples that are difficult to handle, e.g. polymer films and fibers, foods, rubber-based materials, agriculture products, and many others.*
- Mid-IR reflection spectra, although not identical to the corresponding absorption spectra, are similar in general appearance and provide the same information as do their absorption counterparts.
- Reflectance spectra can be used for both qualitative and quantitative analysis. Most instrument manufacturers now offer adapters that fit into the cell compartments of IR absorption instruments and make it possible to obtain reflection spectra readily.



Reflected radiation

specular reflection

attenuated total reflectance (ATR)

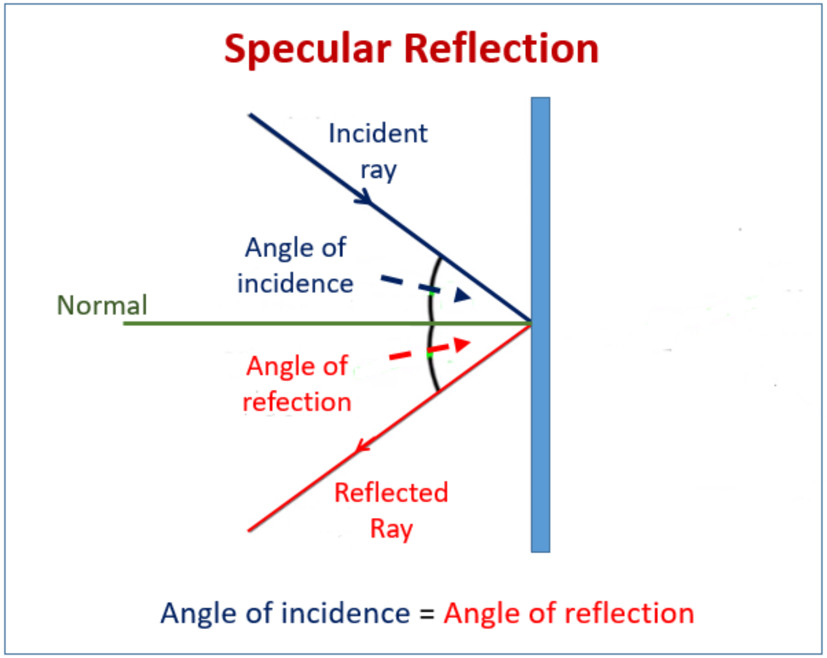
internal reflection

diffuse reflection

Specular Reflection;

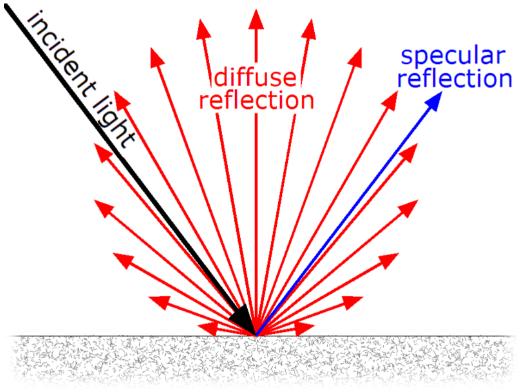
- a smooth polished surface,
- the angle of reflection is identical to the incident angle of the radiation.
- If the surface is made up of an IR absorber, the relative intensity of reflection is less for wavelengths that are absorbed than for wavelengths that are not.
- Thus, a plot of reflectance R, which is the fraction of the incident radiant energy reflected, versus wavelength or wavenumber provides a spectrum for a compound similar in general appearance to a transmission spectrum for the species.
- Specular reflection spectra find some use for examining and characterizing the smooth surfaces of solids and coated solids but are not as widely used as diffuse- and total-reflection spectra. We will, therefore, focus on the latter two types of spectra.

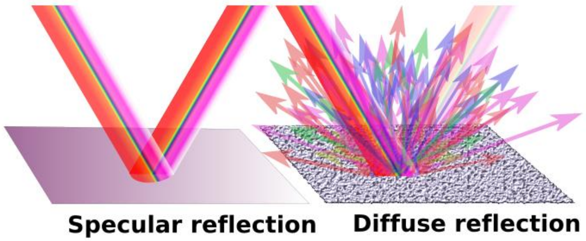
Still water can also exhibit specular reflection.



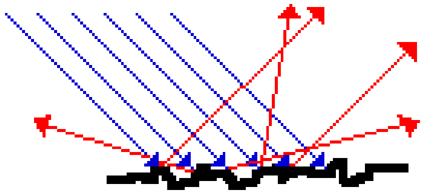
17B-2 Diffuse-Reflectance Spectrometry

- Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials in the mid-IR and NIR spectral ranges with a minimum of sample preparation
- Diffuse reflection is a complex process that occurs when a beam of radiation strikes the surface of a finely divided powder. With this type of sample, specular reflection occurs at each plane surface. However, because there are many of these surfaces and they are randomly oriented, radiation is reflected in all directions. The intensity of the reflected radiation is roughly independent of the viewing angle.
- Diffuse-reflectance IR Fourier transform spectrometry (DRIFTS)

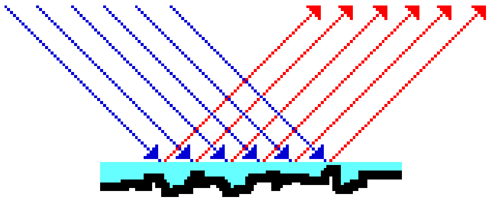




- In addition to saving time in sample preparation, it permits conventional IR spectral data to be gathered on samples not appreciably altered from their original state.

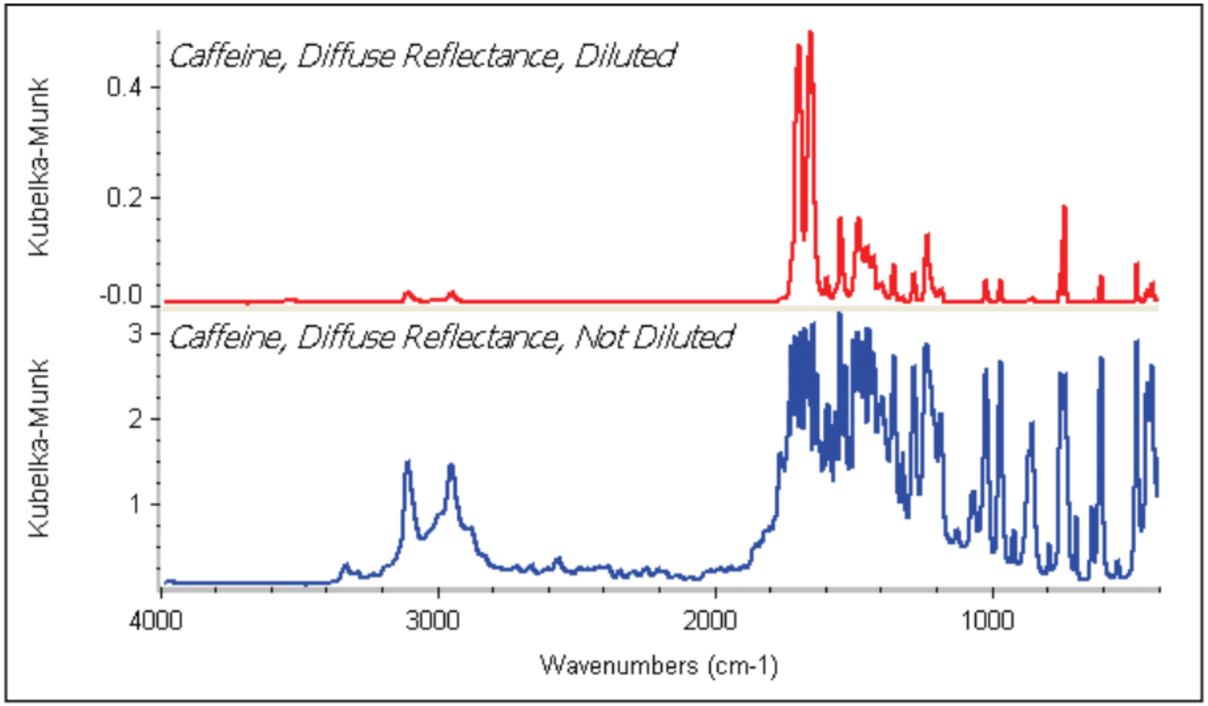


A dry asphalt roadway diffuses incident light.



When wet, water fills in the crevices, resulting in specular reflection and a glare.

- Some powders may be analyzed by diffuse reflectance as neat samples (coal samples, soil samples, diffuse coatings on a reflective base).
- Usually, the sample must be ground and mixed with a non-absorbing matrix such as KBr. The sample to matrix ratio should be between 1 to 5% (by weight). Diluting ensures a deeper penetration of the incident beam into the sample which increases the contribution of the scattered component in the spectrum and minimizes the specular reflection component.



Diffuse reflective spectra showing greatly improved results from sample dilution

Instrumentation:

- Currently, most manufacturers of FTIR instruments offer adapters that fit in cell compartments and permit diffuse-reflectance measurements.
- The collimated beam from the interferometer is directed to an ellipsoidal mirror and then to the sample. The sample is usually ground and mixed with KBr or KCl as a diluent. The mixture is then placed in a sample cup 3–4 mm deep and about 10–15 mm in diameter. A complex combination of reflection, absorption, and scattering occurs before the beam is directed to the detector.

- To obtain a spectrum with a single-beam instrument, the signal for the sample is first stored. A reference signal with a good reflector, such as finely ground KBr or KCl, is then recorded in place of the sample. The ratio of these signals is then taken to give the reflectance.

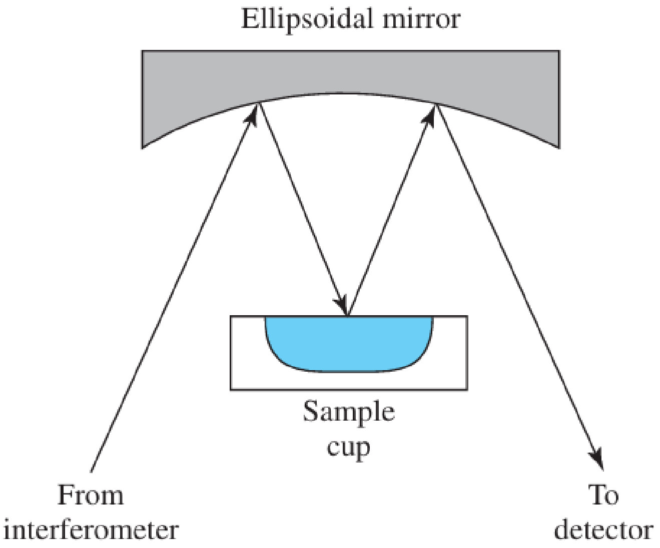


FIGURE 17-11 A diffuse-reflectance attachment for an FTIR spectrometer.

- Even with all these sample preparation practices, the raw diffuse reflectance spectra will appear different from its transmission equivalent (stronger than expected absorption from weak IR bands). A *Kubelka-Munk* conversion can be applied to a diffuse reflectance spectrum to compensate for these differences. This conversion is available in most FTIR software packages.
- The Kubelka-Munk converted spectrum shows excellent comparison with the transmission spectrum and is easily identified using a library search of a transmission spectral data base.
- - Diffuse reflectance can also be used for the analysis of liquid samples. In this application a small amount of the sample is dispensed directly onto the KBr powder and analyzed.

The Kubelka-Munk equation

$$f(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}$$

R is the absolute reflectance
k is the molar absorption coeff.
s is the scattering coefficient

Comparison of Absorption and Reflection Spectra:

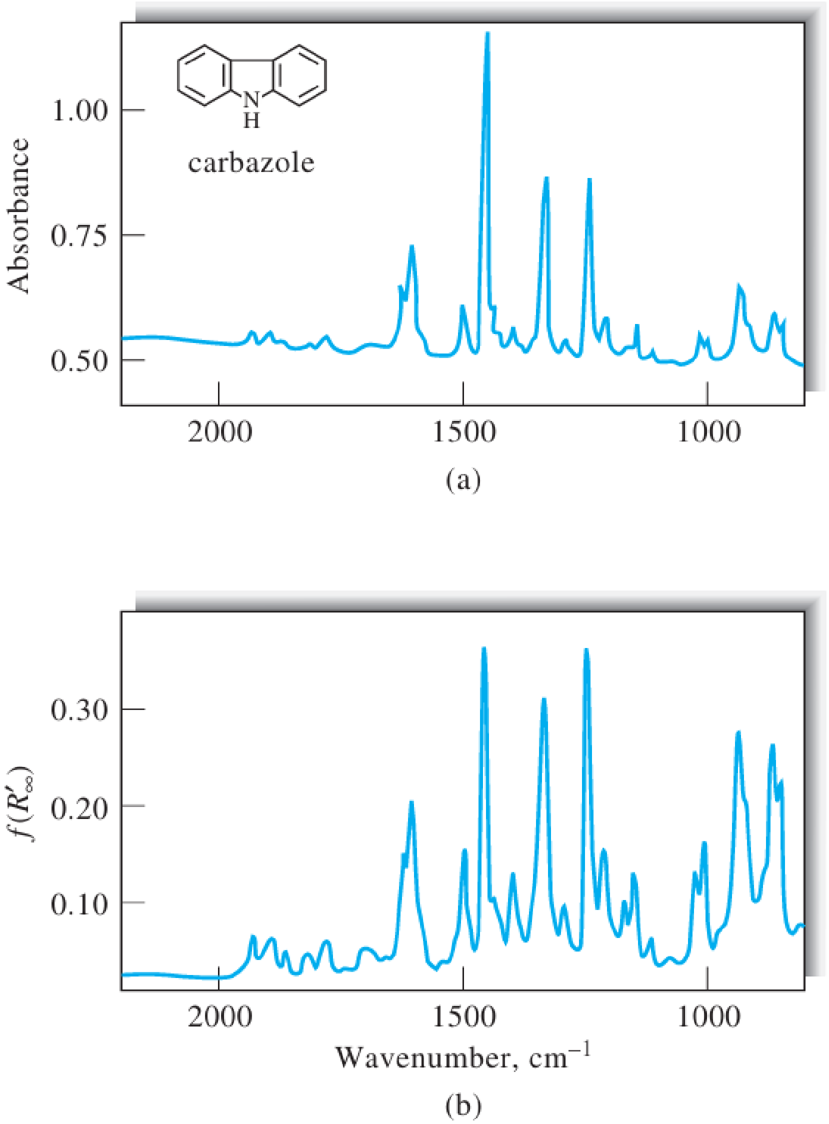
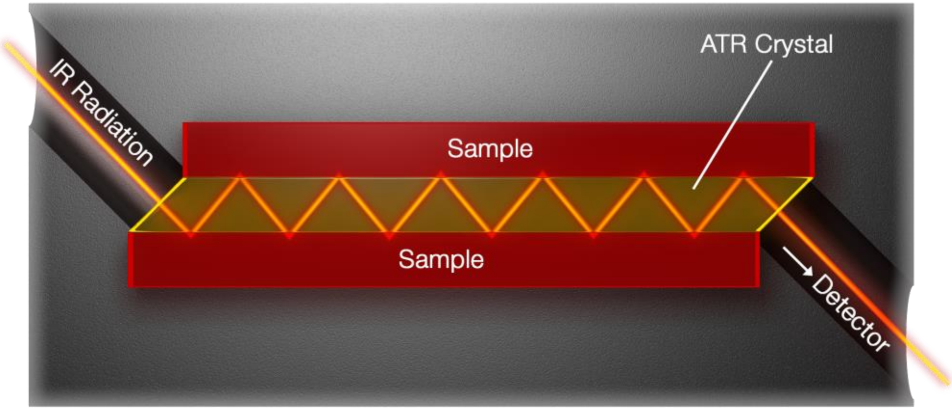


FIGURE 17-12 Comparison of the absorption spectrum (a) for carbazole with its diffuse-reflectance spectrum (b).

Figure 17-12 compares the conventional IR absorption spectrum for carbazole obtained by means of a KBr pellet with the diffuse-reflectance spectrum of a 5% finely ground mixture of carbazole in potassium chloride. Note that the peak locations are the same in the two spectra but that the relative peak heights differ considerably. The differences are typical, with minor peaks generally appearing larger in reflection spectra

17B-3 Attenuated Total Reflection, ATR, Spectrometry

- When a beam of radiation passes from a more dense to a less dense medium, reflection occurs.
- ATR uses a property of total internal reflection resulting in an evanescent wave.
- The fraction of the incident beam reflected increases as the angle of incidence becomes larger; beyond a certain critical angle, reflection is complete



- Internal-reflection spectroscopy is a technique for obtaining IR spectra of samples that are difficult to deal with, such as solids of limited solubility, films, threads, pastes, adhesives, polymers and powders.

- during the reflection process the beam penetrates a small distance into the less dense medium before reflection occurs.
- The depth of penetration, which varies from a fraction of a wavelength up to several wavelengths, depends on the wavelength, the index of refraction of the two materials, and the angle of the beam with respect to the interface.
- The penetrating radiation is called the evanescent wave. At wavelengths where the less dense medium absorbs the evanescent radiation, attenuation of the beam occurs, which is known as attenuated total reflectance, or ATR. The resulting ATR spectrum resembles that of a conventional IR spectrum with some differences.

https://youtu.be/QW2uh1BQuGw

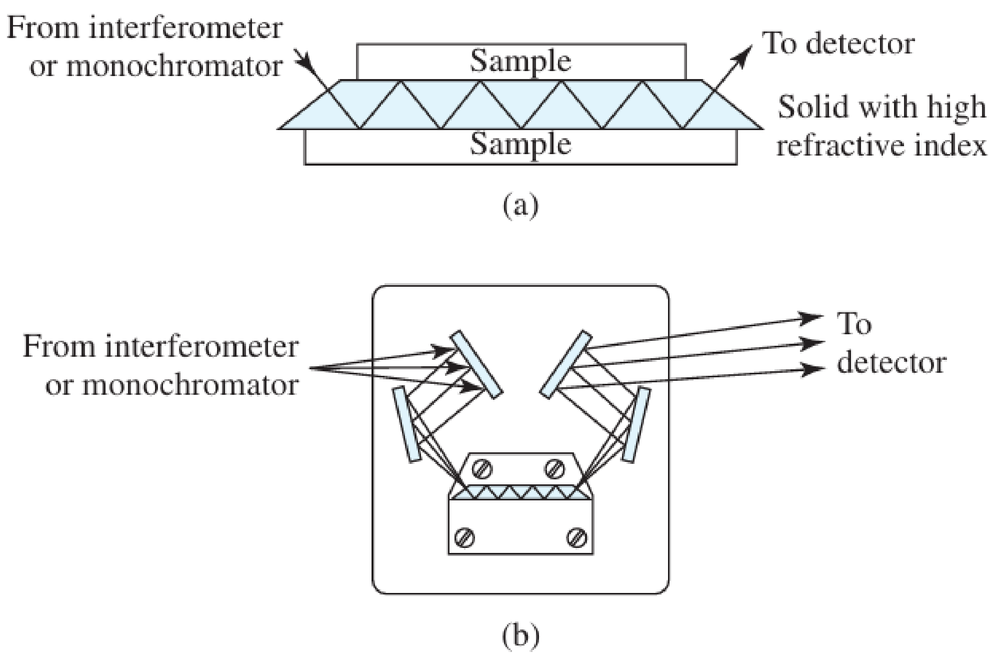


FIGURE 17-13 ATR apparatus. In (a) a solid sample is shown mounted on an internal reflection crystal of high refractive index. The materials used as ATR crystals include KRS-5, AgCl, Ge, Si, and the Irtran materials. Solid samples can be pressed against the crystal to obtain optical contact. In (b), a typical attachment for ATR is shown. With many attachments, the internal reflection plate can be positioned in the holder to provide several incident angles.

17C PHOTOACOUSTİC İR SPECTROSCOPY

NOT INCLUDED

17D NEAR-IR SPECTROSCOPY

The near-IR (NIR) region of the spectrum extends from the upper wavelength end of the visible region at about 770 nm to 2500 nm (13,000 to 4000 cm21).17 Absorption bands in this region are overtones or combinations (Section 16A-4) of fundamental stretching vibrations that occur in the region of 3000 to 1700 cm-1. The bonds involved are usually C-H, N-H, and O-H. Because the bands are overtones or combinations, their molar absorptivities are low and detection limits are on the order of 0.1%.

In contrast to mid-IR spectrometry, the most important uses of NIR radiation are for the routine quantitative determination of species, such as water, proteins, low-molecular-mass hydrocarbons, and fats, in products of the agricultural, food, petroleum, and chemical industries. Both diffuse-reflection and transmission measurements are used, although diffuse reflectance is by far the more widely used.

Instrumentation:

- Grating instruments
- filter instruments
- acousto-optic tunable filter (AOTF) instruments
- Fourier transform spectrometers

- Several commercial UV-visible spectrophotometers are designed to operate from 180 to 2500 nm and can thus be used to obtain NIR spectra.

- use tungsten-halogen lamps with quartz windows.
- Cells for absorption measurements are usually quartz or fused silica transparent up to about 3000 nm.
- Cell lengths vary from 0.1 to 10 cm.
- Detectors range from PbS and PbSe photoconductors to InSb and InAs photodiodes.
- Array detectors, such as InGaAs detectors, have also become available for the region.

17D-2 Data Processing in NIR Spectrometry

- NIR spectral bands are normally broad and often overlapping. There are rarely clean spectral bands that allow simple correlation with analyte concentration. Instead, multivariate calibration techniques are used; partial least squares, principal components regression, and artificial neural networks
- Such calibration involves the development of a calibration model through obtaining results on a “training set” that includes as many of the conditions encountered in the samples as possible.
-

17E FAR-IR SPECTROSCOPY

- The far-IR region is particularly useful for inorganic studies because absorption due to stretching and bending vibrations of bonds between metal atoms and both inorganic and organic ligands generally occurs at frequencies lower than 650 cm-1 (>15 µm).
- For example, heavy-metal iodides generally absorb radiation in the region below 100 cm-1, and the bromides and chlorides have bands at higher frequencies. Absorption frequencies for metal-organic bonds ordinarily depend on both the metal atom and the organic portion of the species.
- Far-IR studies of inorganic solids have also provided useful information about lattice energies of crystals and transition energies of semiconducting materials. Molecules composed only of light atoms absorb far-IR radiation if they have skeletal bending modes that involve more than two atoms other than hydrogen.
- Important examples are substituted benzene derivatives, which generally show several absorption bands. The spectra are frequently quite specific and useful for identifying a particular compound. There are also characteristic group frequencies in the far-IR region. Pure rotational absorption by gases is observed in the far-IR region, provided the molecules have permanent dipole moments. Examples include H_2O, O_3, HCl, and AsH_3.

- Absorption by water is troublesome; elimination of its interference requires evacuation or at least purging of the spectrometer. Prior to the advent of Fourier transform spectrometers, experimental difficulties made it difficult to obtain good far-IR spectra.
- The sources available in this region are quite low in intensity. Order-sorting filters are needed with grating instruments in this region to minimize radiation diffracted from higher grating orders. These reduced the already low throughputs of dispersive spectrometers.
- It is no surprise that Fourier transform spectrometry was first applied in this spectral region. The high throughput of interferometers and the relatively low mechanical tolerances required combine to make it fairly simple to obtain FTIR spectra in the far-IR region with good signal-to-noise ratios.

17F IR EMISSOIN SPECTROSCOPY

- Molecules that absorb IR radiation are also capable of emitting characteristic IR wavelengths when they are heated.
- The principal deterrent to the analytical application of this phenome non has been the poor signal-to-noise characteristics of the IR emission signal, particularly when the sample is at a temperature only slightly higher than its surroundings.
- With interferometry, however, interesting and useful applications have appeared in the literature. An early example of the application of IR emission spectroscopy is found in a paper that describes the use of a Fourier transform spectrometer for the identification of microgram quantities of pesticides.
- Samples were prepared by dissolving them in a suitable solvent followed by evaporation on a NaCl or KBr plate. The plate was then heated electrically near the spectrometer entrance.
- Pesticides such as DDT, malathion, and dieldrin were identified in amounts as low as 1 to 10 µg.
- Equally interesting has been the use of interferometry for the remote detection of components emitted from industrial smokestacks. In one of these applications, an interferometer was mounted on an 8-inch reflecting telescope.25 With the telescope focused on the plume from an industrial plant, CO_2 and SO_2 were readily detected at a distance of several hundred feet.