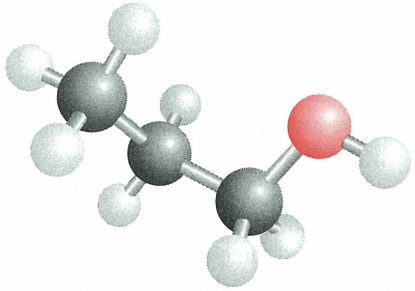
CHAPTER

11



Infrared Spectroscopy

PRELAB EXERCISE: When an infrared (IR) spectrum is run, it is possible that the chart paper is not properly placed or that the spectrometer is not mechanically adjusted. Describe how you could calibrate an IR spectrum.

The types and molecular environment of functional groups in organic molecules can be identified by infrared (IR) spectroscopy. Like nuclear magnetic resonance (NMR) and ultraviolet (UV) spectroscopy, IR spectroscopy is nondestructive. Moreover, the small quantity of sample needed, the speed with which a spectrum can be obtained, the relatively low cost of the spectrometer, and the wide applicability of the method combine to make IR spectroscopy one of the most common structural elucidation tools used by organic chemists.

IR radiation consists of wavelengths that are longer than those of visible light. It is detected not with the eyes but by a feeling of warmth on the skin. When absorbed by molecules, radiation of these wavelengths (typically 2.5–5 μm) increases the amplitude of vibrations of the chemical bonds joining atoms.

2.5–25 μm equals 4000–400 cm^{-1}. Wavenumber(cm^{-1}) is proportional to frequency (c is the speed of light).

$$\bar{\nu}(cm^{-1}) = \frac{\nu}{c}$$

IR spectra are measured in units of frequency or wavelength. The wavelength is measured in micrometers[1] or microns, μm (1 μm = 1×10^{-6} m). The positions of absorption bands are measured in frequency units called wavenumbers ν, which are expressed in reciprocal centimeters, cm^{-1}, corresponding to the number of cycles of the wave in each centimeter.

$$cm^{-1} = \frac{10{,}000}{\mu m}$$

Examine the scale carefully.

Unlike UV and NMR spectra, IR spectra are inverted, with the strongest absorptions at the bottom, and are not always presented on the same scale. Some

1. Although micrometers are also known as microns, the micron is not the official SI unit.

IR spectroscopy easily detects:

Hydroxyl groups	—OH
Amines	—NH_2
Nitriles	—C≡N
Nitro groups	—NO_2

IR spectroscopy is especially useful for detecting and distinguishing among all carbonyl-containing compounds:

Acids —C(=O)—OH

Amides —C(=O)—NH_2

Anhydrides —C(=O)—O—C(=O)—

Aldehydes —C(=O)—H

Ketones —C(=O)—

Esters —C(=O)—O—

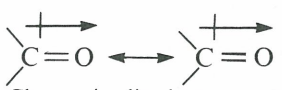
Lactones —C(=O)—O— (cyclic)

spectrometers record the spectra on an ordinate linear in microns, but this compresses the low-wavelength region. Other spectrometers present the spectra on a scale linear in reciprocal centimeters, but linear on two different scales: one between 4000 and 2000 cm^{-1}, which spreads out the low-wavelength region; and the other a smaller one between 2000 and 667 cm^{-1}. Consequently, spectra of the same compound run on two different spectrometers will not always look the same.

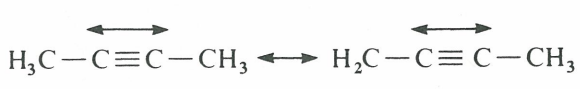
To picture the molecular vibrations that interact with IR light, imagine a molecule as being made up of balls (atoms) connected by springs (bonds). The vibration can be described by Hooke's law from classical mechanics, which says that the frequency of a stretching vibration is directly proportional to the strength of the spring (bond) and inversely proportional to the masses connected by the spring. Thus we find C—H, N—H, and O—H bond-stretching vibrations are high frequency (short wavelength) compared to those of C—C and C—O because of the low mass of hydrogen compared to that of carbon or oxygen. The bonds connecting carbon to bromine and iodine, atoms of large mass, vibrate so slowly that they are beyond the range of most common IR spectrometers. A double bond can be regarded as a stiffer, stronger spring, so we find C=C and C=O vibrations at higher frequency than C—C and C—O stretching vibrations. And C≡C and C≡N stretch at even higher frequencies than C=C and C=O (but at lower frequencies than C—H, N—H, and O—H). These frequencies are in keeping with the bond strengths of single (~100 kcal/mol), double (~160 kcal/mol), and triple bonds (~220 kcal/mol).

These stretching vibrations are intense and particularly easy to analyze. A nonlinear molecule of n atoms can undergo $3n - 6$ possible modes of vibration, which means cyclohexane with 18 atoms can undergo 48 possible modes of vibration. A single CH_2 group can vibrate in six different ways because it is connected to two other atoms. Each vibrational mode produces a peak in the spectrum because it corresponds to the absorption of energy at a discrete frequency. These many modes of vibration create a complex spectrum that defies simple analysis, but even in very complex molecules, certain functional groups have characteristic frequencies that can easily be recognized. Within these functional groups are the above-mentioned atoms and bonds, C—H, N—H, O—H, C=C, C=O, C≡C, and C≡N. Their absorption frequencies are given in Table 11.1.

When the frequency of IR light is the same as the natural vibrational frequency of an interatomic bond, light will be absorbed by the molecule, and the amplitude of the bond vibration will increase. The intensity of IR absorption bands is proportional to the change in dipole moment that a bond undergoes when it stretches. Thus, the most intense bands (peaks) in an IR spectrum are often from C=O and C—O stretching vibrations, whereas the C=C stretching band for a symmetrical acetylene is almost nonexistent because the molecule undergoes no net change of dipole moment when it stretches:



Change in dipole moment



No change in dipole moment

TABLE 11.1 • Characteristic IR Absorption Wavenumbers

Functional Group	Wavenumber (cm^{-1})
O—H	3600–3400
N—H	3400–3200
C—H	3080–2760
C≡N	2260–2215
C≡C	2150–2100
C=O	1815–1650
C=C	1660–1600
C—O	1200–1050

The intensity of absorption is proportional to the change in dipole moment.

Unlike proton NMR spectroscopy, where the area of the peaks is strictly proportional to the number of hydrogen atoms causing the peaks, the intensities of IR peaks are not proportional to the numbers of atoms causing them. Given the chemical shifts and coupling constants, it is not too difficult to calculate a theoretical NMR spectrum that is an exact match to the experimental one. The calculation of all possible stretching and bending frequencies, for larger molecules, requires large amounts of time on a fast computer. Every peak or group of peaks in an NMR spectrum can be assigned to specific hydrogens in a molecule, but the assignment of the majority of peaks in an IR spectrum is usually not possible. Peaks to the right (longer wavelength) of 1250 cm^{-1} are the result of combinations of vibrations that are characteristic not of individual functional groups but of the molecule as a whole. This part of the spectrum is often referred to as the *fingerprint region* because it is uniquely characteristic of each molecule. Although two organic compounds can have the same melting points or boiling points and can have identical UV and NMR spectra, they cannot have identical IR spectra (except, as usual, for enantiomers). IR spectroscopy is thus the final arbiter in deciding whether two compounds are identical.

Analysis of IR Spectra

Only a few simple rules or equations govern IR spectroscopy. Because it is not practical to calculate theoretical spectra, the analysis is done almost entirely by correlation with other spectra. In printed form, these comparisons take the form of lengthy discussions, so detailed analysis of a spectrum is best done with a good reference book at hand.

In a modern analytical or research laboratory, a collection of many thousands of spectra is maintained on a computer. When the spectrum of an unknown compound is run, the analyst picks out five or six of the strongest peaks and asks the computer to list all the compounds that have peaks within a few reciprocal centimeters of the listed peaks. From the printout of a dozen or so compounds, it is often possible to pinpoint all the functional groups in the molecule being analyzed. There may be a perfect match of all peaks, in which case the unknown will have been identified.

For relatively simple molecules, a computer search is hardly necessary. Much information can be gained about the functional groups in a molecule from relatively few correlations.

To carry out an analysis, (1) pay most attention to the strongest absorptions; (2) pay more attention to peaks to the left (shorter wavelength) of 1250 cm^{-1}; and (3) pay as much attention to the absence of certain peaks as to the presence of others. The absence of characteristic peaks will definitely exclude certain functional groups. Be wary of weak O—H peaks because water is a common contaminant of many samples. Because potassium bromide is hygroscopic, water is often found in the spectra of KBr pellets.

The Step-by-Step Analysis of IR Spectra

IR spectra are analyzed as follows:

1. Is there a peak between 1820 cm^{-1} and 1625 cm^{-1}? If not, go to Step 2.
   (a) Is there a strong, wide O—H peak between 3200 cm^{-1} and 2500 cm^{-1}? If so, the compound is a carboxylic acid (Fig. 11.1, oleic acid). If not . . .
   (b) Is there a medium-to-weak N—H band between 3520 cm^{-1} and 3070 cm^{-1}? If there are two peaks in this region, the compound is a primary amide; if not, it is a secondary amide. If there is no peak in this region . . .
   (c) Are there two strong peaks, one in the region 1870 cm^{-1} to 1800 cm^{-1} and the other in the region 1800 cm^{-1} to 1740 cm^{-1}? If so, an acid anhydride is present. If not . . .
   (d) Is there a peak in the region of 2720 cm^{-1}? If so, is the carbonyl peak in the region 1715 cm^{-1} to 1680 cm^{-1}? If so, the compound is a conjugated aldehyde; if not, it is an isolated aldehyde (Fig. 11.2, benzaldehyde). However, if there is no peak near 2720 cm^{-1} . . .
   (e) Does the strong carbonyl peak fall in the region 1815 cm^{-1} to 1770 cm^{-1} and the compound give a positive Beilstein test? If so, it is an acid halide. If not . . .

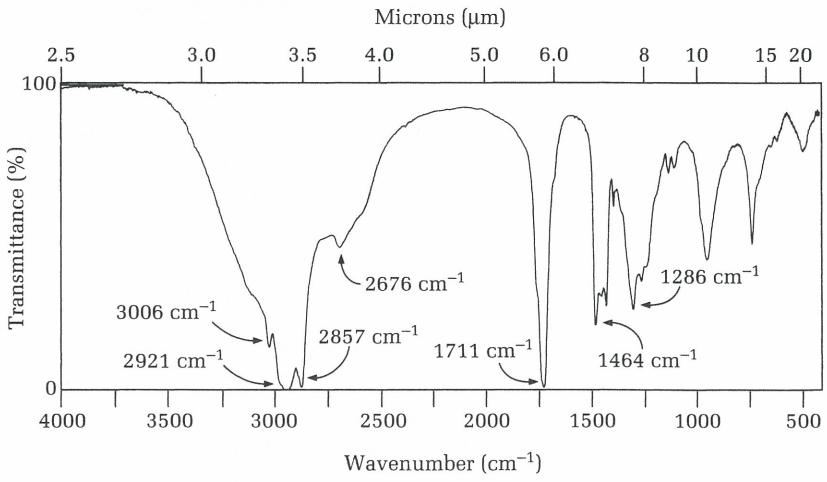


FIG. 11.1
The IR spectrum of oleic acid (thin film).

FIG. 11.2
The IR spectrum of benzaldehyde (thin film).

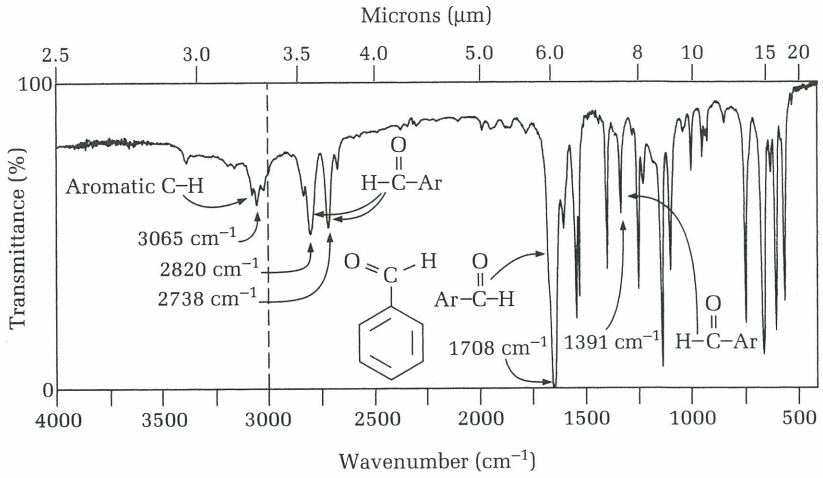
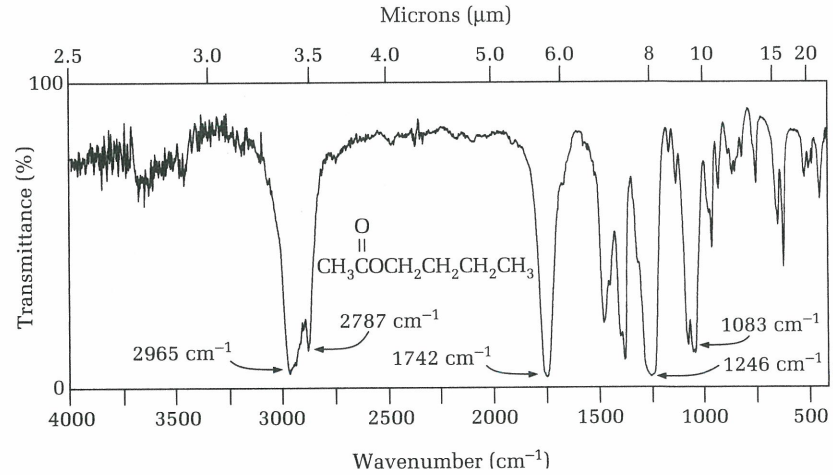


FIG. 11.3
The IR spectrum of *n*-butyl acetate (thin film).



(f) Does the strong carbonyl peak fall in the range 1690 cm^{-1} to 1675 cm^{-1}? If so, the compound is a conjugated ketone. If not . . .

(g) Does the strong carbonyl peak fall in the range 1670 cm^{-1} to 1630 cm^{-1}? If so, the compound is a tertiary amide. If not . . .

(h) Does the spectrum have a strong, wide peak in the range 1310 cm^{-1} to 1100 cm^{-1}? If so, does the carbonyl peak fall in the range 1730 cm^{-1} to 1715 cm^{-1}? If so, the compound is a conjugated ester; if not, the ester is not conjugated (Fig. 11.3, *n*-butyl acetate). If there is no strong, wide peak in the range 1310 to 1100 cm^{-1}, then . . .

(i) The compound is an ordinary nonconjugated ketone.

FIG. 11.4
The IR spectrum of cyclohexanol (thin film).

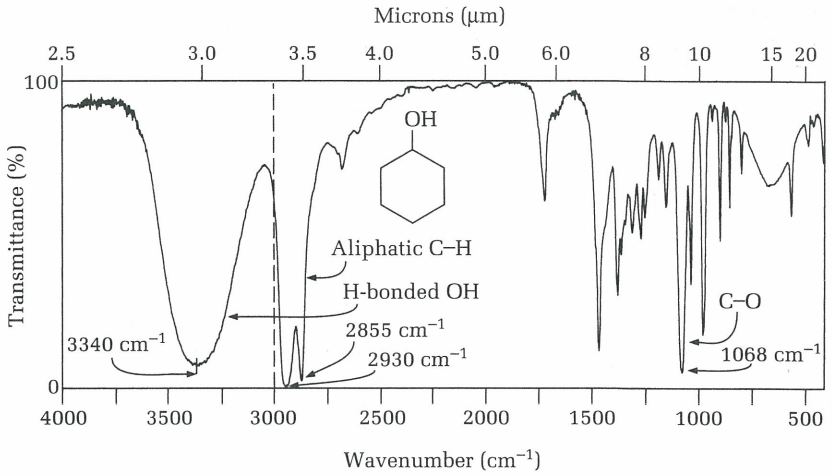
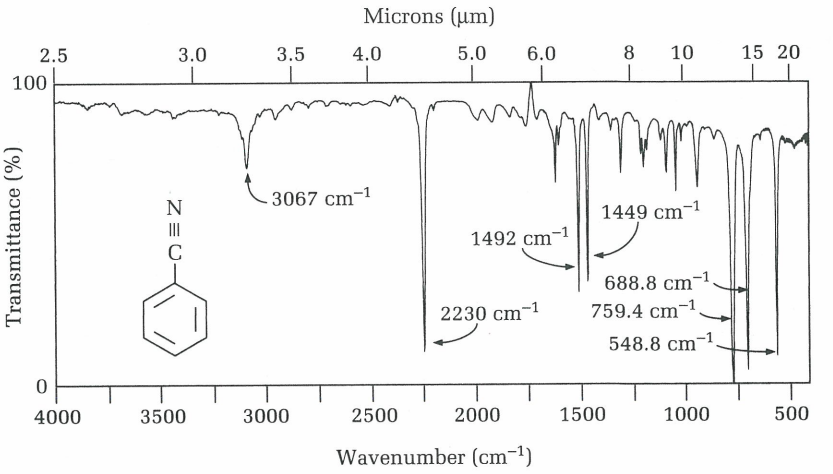


FIG. 11.5
The IR spectrum of benzonitrile (thin film).



2. If the spectrum lacks a carbonyl peak in the range 1820 cm^{-1} to 1625 cm^{-1}, does it have a broad band in the region 3650 cm^{-1} to 3200 cm^{-1}? If so, does it also have a peak at about 1200 cm^{-1}, a C—H stretching peak to the left of 3000 cm^{-1}, and a peak in the region 1600 cm^{-1} to 1470 cm^{-1}? If so, the compound is a phenol. If the spectrum does not meet these latter three criteria, the compound is an alcohol (Fig. 11.4, cyclohexanol). However, if there is no broad band in the region 3650 cm^{-1} to 3200 cm^{-1}, then . . .

(a) Is there a broad band in the region 3500 cm^{-1} to 3300 cm^{-1}, does the compound smell like an amine, or does it contain nitrogen? If so, are there two peaks in this region? If so, the compound is a primary amine; if not, it is a secondary amine. However, if there is no broad band in the region 3500 cm^{-1} to 3300 cm^{-1}, then . . .

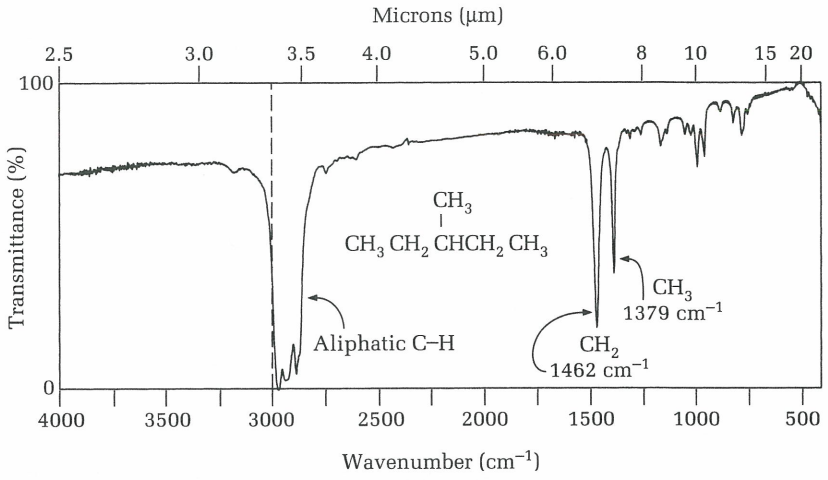


FIG. 11.6
The IR spectrum of 3-methylpentane (thin film).

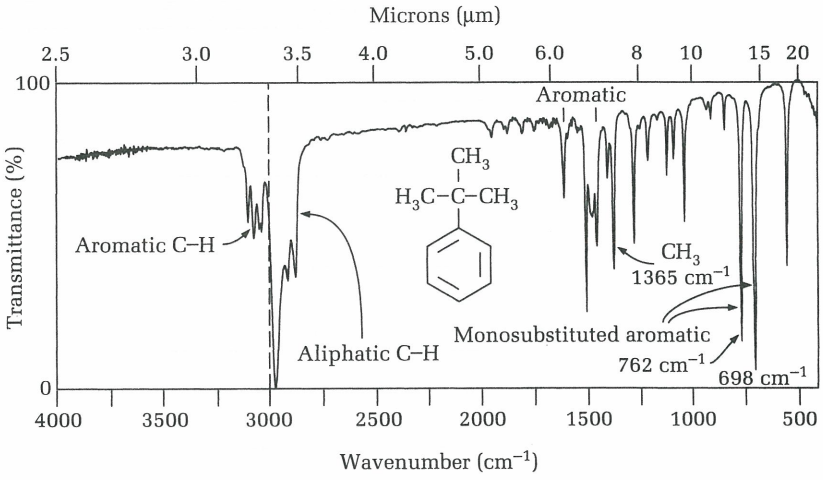


FIG. 11.7
The IR spectrum of *t*-butylbenzene (thin film).

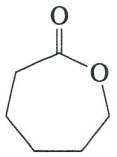
(b) Is there a sharp peak of medium-to-weak intensity at 2260 cm^{-1} to 2100 cm^{-1}? If so, is there also a peak at 3320 cm^{-1} to 3310 cm^{-1}? If so, then the compound is a terminal acetylene. If not, the compound is most likely a nitrile (Fig. 11.5, benzonitrile), although it might be an asymmetrically substituted acetylene. If there is no sharp peak of medium-to-weak intensity at 2260 cm^{-1} to 2100 cm^{-1}, then . . .

(c) Are there strong peaks in the region 1600 cm^{-1} to 1540 cm^{-1} and 1380 cm^{-1} to 1300 cm^{-1}? If so, the molecule contains a nitro group. If not . . .

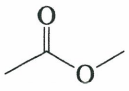
(d) Is there a strong peak in the region 1270 cm^{-1} to 1060 cm^{-1}? If so, the compound is an ether. If not . . .

(e) The compound is either a tertiary amine (odor?), a halogenated hydrocarbon (Beilstein test?), or just an ordinary hydrocarbon (Fig. 11.6, 3-methylpentane, and Fig. 11.7, *t*-butylbenzene).

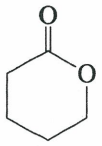
The effect of ring size on the carbonyl frequencies of lactones and esters:



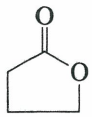
1727 cm^{-1}



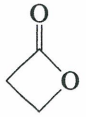
1745 cm^{-1}



1740 cm^{-1}



1775 cm^{-1}



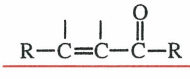
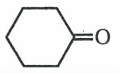
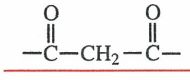
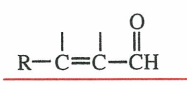
1832 cm^{-1}

Many comments can be added to this bare outline. For example, dilute solutions of alcohols will show a sharp peak at about 3600 cm^{-1} for a nonhydrogen-bonded O—H in addition to the usual broad hydrogen-bonded O—H peak.

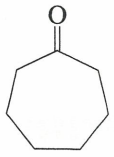
Aromatic hydrogens give peaks just to the left of 3000 cm^{-1}, whereas aliphatic hydrogens appear just to the right of 3000 cm^{-1}. However, NMR spectroscopy is the best method for identifying aromatic hydrogens.

The carbonyl frequencies listed earlier refer to an open chain or an unstrained functional group in a nonconjugated system. If the carbonyl group is conjugated with a double bond or an aromatic ring, the peak will be displaced to the right by 30 cm^{-1}. When the carbonyl group is in a ring smaller than six members or if there is oxygen substitution on the carbon adjacent to an aldehyde or ketone carbonyl, the peak will be moved to the left (refer to the margin notes about the effect of ring size and Table 11.2).

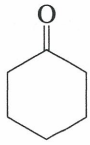
TABLE 11.2 • Characteristic IR Carbonyl Stretching Peaks (Chloroform Solutions)

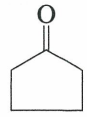
	Carbonyl-Containing Compounds	Wavenumber (cm^{-1})
	Aliphatic ketones	1725–1705
	Acid chlorides	1815–1785
	α,β-Unsaturated ketones	1685–1666
	Aryl ketones	1700–1680
	Cyclohexanones	1725–1705
	β-Diketones	1640–1540
	Aliphatic aldehydes	1740–1720
	α,β-Unsaturated aldehydes	1705–1685
	Aryl aldehydes	1715–1695

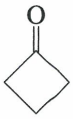
The effect of ring size on carbonyl frequency of ketones:


1705 cm^{-1}


1715 cm^{-1}

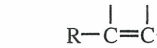
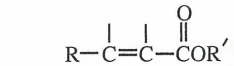
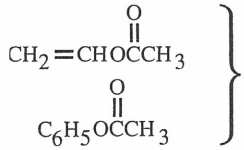
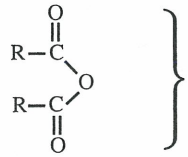

1715 cm^{-1}


1745 cm^{-1}


1780 cm^{-1}


1815 cm^{-1}

TABLE 11.2 • (Continued)

	Carbonyl-Containing Compounds	Wavenumber (cm^{-1})
RCOOH	Aliphatic acids	1725–1700
	α,β-Unsaturated acids	1700–1680
ArCOOH	Aryl acids	1700–1680
	Aliphatic esters	1740
	α,β-Unsaturated esters	1730–1715
	Aryl esters	1730–1715
	Formate esters	1730–1715
	Vinyl and phenyl acetate	1776
	Acyclic anhydrides (two peaks)	1840–1800 1780–1740
	Primary amides	1694–1650
	Secondary amides	1700–1670
	Tertiary amides	1670–1630

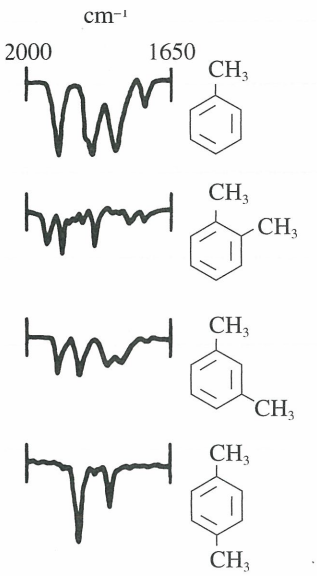
Methyl groups often give a peak near 1375 cm^{-1}, but NMR is a better method for detecting this group.

The pattern of substitution on an aromatic ring (mono-, *ortho*-, *meta*-, and *para*, di-, tri-, tetra-, and penta-) can be determined from C—H out-of-plane bending

vibrations in the region 670–900 cm^{-1}. Much weaker peaks between 1650 cm^{-1} and 2000 cm^{-1} are illustrated in Figure 11.8.

Extensive correlation tables and discussions of characteristic group frequencies can be found in the specialized references listed at the end of this chapter.

FIG. 11.8
The band patterns of toluene and *o*-, *m*-, and *p*-xylene. These peaks are *very weak*. They are characteristic of aromatic substitution patterns in general, not just for these four molecules. Try to find these patterns in other spectra throughout this text.



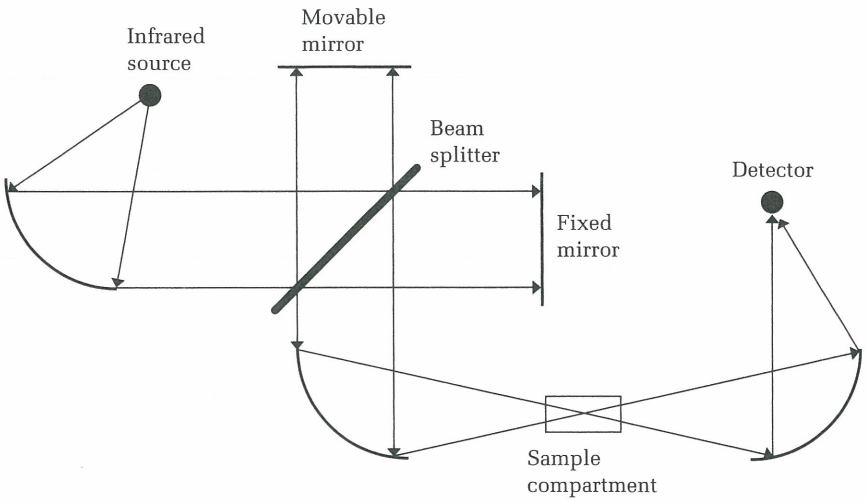
The Fourier Transform Infrared (FTIR) Spectrometer

Like their NMR counterparts, Fourier transform IR instruments are computer based, can sum a number of scans to increase the signal-to-noise ratio, and allow enormous flexibility in the ways spectra can be analyzed and displayed because they are digitally oriented. In addition, they are faster and more accurate than double-beam spectrometers.

A schematic diagram of a single-beam FTIR spectrometer is given in Figure 11.9. IR radiation goes to a Michelson interferometer in which half the light beam passes through a partially coated mirror to a fixed mirror and half goes to a moving mirror. The combined beams pass through the sample and are then focused on the detector. The motion of the mirror gives a signal that varies sinusoidally. Depending on the mirror position, the different frequencies of light either reinforce or cancel each other, resulting in an interferogram. The mirror, the only moving part of the spectrometer, thus affects the light frequencies that encode the very high optical frequencies, transforming them to low-frequency signals that change as the mirror moves back and forth. The Fourier transform convert the digitized signal into a signal that is a function of frequency—creating a spectrum.

Like Fourier transform NMR spectroscopy, all IR frequencies are sampled simultaneously instead of being scanned successively, so a spectrum is obtained in seconds. Because there is no slit to sort out the wavelengths, high resolution is possible without losing signal strength. Extremely small samples or very dilute solutions can

FIG. 11.9
The optical path diagram of an FTIR spectrometer.



be examined because it is easy to sum hundreds of scans in the computer. It is even possible to take a spectrum of an object seen under a microscope. The spectrum of one compound can be subtracted from, say, a binary mixture spectrum to reveal the nature of the other component. Data can be smoothed, added, resized, and so on because of the digital nature of the output from the spectrometer.

Experimental Considerations

Glass, quartz, and plastics are opaque to IR radiation and absorb it. Therefore, sample holders must be made of other transparent materials. Metal halide salts such as sodium or silver chloride, calcium or barium fluoride, and potassium bromide are transparent to IR radiation; these are prepared as large polished crystals for use in cell holders, with NaCl and KBr being the most common. They are fragile and are easily attacked by moisture, so they must be handled gently by the edges and kept away from aqueous solutions. IR spectra can be determined on neat (undiluted) liquids, on solutions with an appropriate solvent, and on solids using mulls and KBr pellets, and by diffuse reflectance of the solid mixed with KBr. All IR cells or KBr powder must be stored in a desiccator when not in use.

The sample, solvents, and equipment must be dry.

The Spectra of Neat Liquids

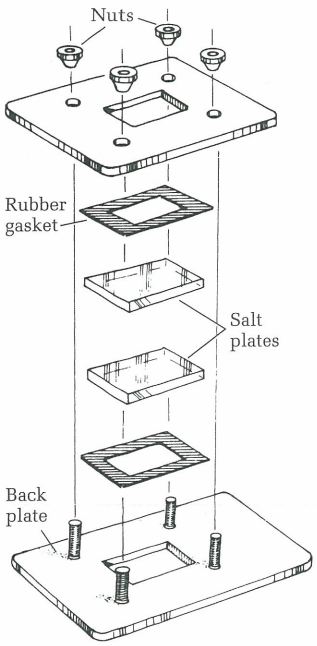
To run a spectrum of a neat (free of water!) liquid, remove a demountable cell (Fig. 11.10) from the desiccator, place a drop of the liquid between the salt plates, press the plates together gently to remove any air bubbles, and add the top rubber gasket and metal top plate. Next, put on all four of the nuts and *gently* tighten them to apply an even pressure to the top plate. Place the cell in the sample compartment (nearest the front of the spectrometer) and run the spectrum.

Although running a spectrum on a neat liquid is convenient and results in no extraneous bands to interpret, it is not possible to control the path length of the light through the liquid in a demountable cell. A low-viscosity liquid when squeezed between the salt plates may be so thin that the short path length gives peaks that are too weak. A viscous liquid, on the other hand, may give peaks that are too intense. A properly run spectrum will have the most intense peak with a transmittance of about 10%.

A fast, simple alternative: Place a drop of the compound on a round salt plate, add a top plate, and mount the two on the holder pictured in Figure 11.11.

Another demountable cell is pictured in Figure 11.11. The plates are thin wafers of silver chloride, which is transparent to IR radiation. This cell has advantages over the salt cell in that the silver chloride disks are more resistant to breakage than NaCl plates, less expensive, and not affected by water. Because silver chloride is photosensitive, the wafers must be stored in a dark place to prevent them from turning black. Because one side of each wafer is recessed, the thickness of the sample can be varied according to the manner in which the cell is assembled. In general, the spectra of pure liquids are run as the thinnest possible films. Most of the spectra in this chapter have been obtained in this way. The disks are cleaned by rinsing them with an organic solvent such as acetone or ethanol and wiping dry with an absorbent paper towel.

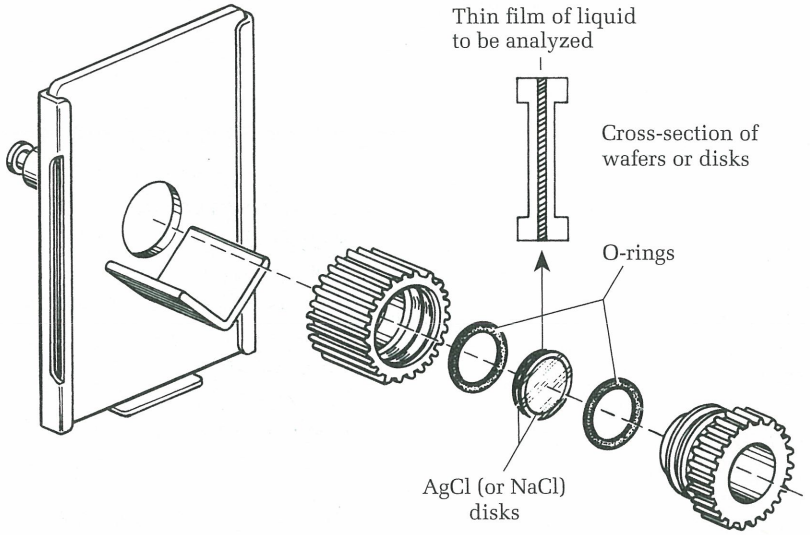
FIG. 11.10
An exploded view of a demountable salt cell for analyzing the IR spectra of neat liquids. The salt plates are fragile and expensive. Do not touch the surfaces. Use only dry solvents and samples.



Solvents: $CHCl_3$, CS_2, CCl_4

CAUTION: Chloroform, carbon tetrachloride, and carbon disulfide are toxic. The first two are carcinogens. Use a laboratory hood to minimize exposure to vapors.

FIG. 11.11
A demountable silver chloride or sodium chloride cell.



A very simple cell consists of two circular NaCl disks (1-in. diameter × 3/16-in. thick, 25 mm × 4 mm). The sample, 1 drop of a pure liquid or solution, is applied to the center of a disk with a polyethylene pipette (to avoid scratching the NaCl disk). The other disk is added, the sample is squeezed to a thin film, and the two disks are placed on the V-shaped holder shown in Figure 11.11.

The Spectra of Solutions

The most widely applicable method of running the spectra of solutions involves dissolving an amount of the liquid or solid sample in an appropriate solvent to give a 10% solution. Just as in NMR spectroscopy, the best solvents to use are carbon disulfide and carbon tetrachloride; because these compounds are not polar enough to dissolve many substances, chloroform is used as a compromise. Unlike NMR solvents, no solvent suitable in IR spectroscopy is entirely free of absorption bands in the frequency range of interest (Figs. 11.12, 11.13, and 11.14). In chloroform, for instance, no light passes through the cell between 650 cm^{-1} and 800 cm^{-1}. As can be seen from the figures, spectra obtained using carbon disulfide and chloroform cover the entire IR frequency range. Carbon tetrachloride would appear to be a good choice because it has few interfering peaks, but it is a poor solvent for polar compounds. In practice, a background spectrum is run with the same solvent in the same cell used to run the sample solution, and the data system subtracts the solvent peaks in background spectrum from the solution spectrum to yield an IR spectrum of the sample only.

FIG. 11.12
The IR spectrum of chloroform (thin film).

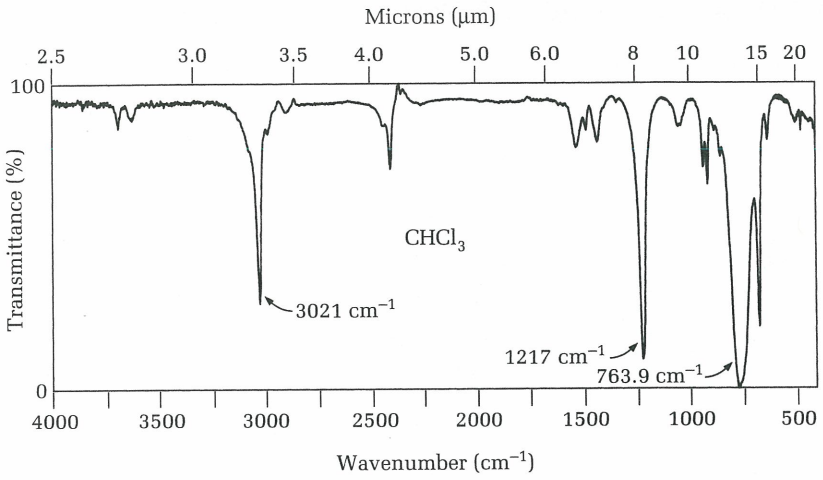


FIG. 11.13
The IR spectrum of carbon disulfide (thin film).

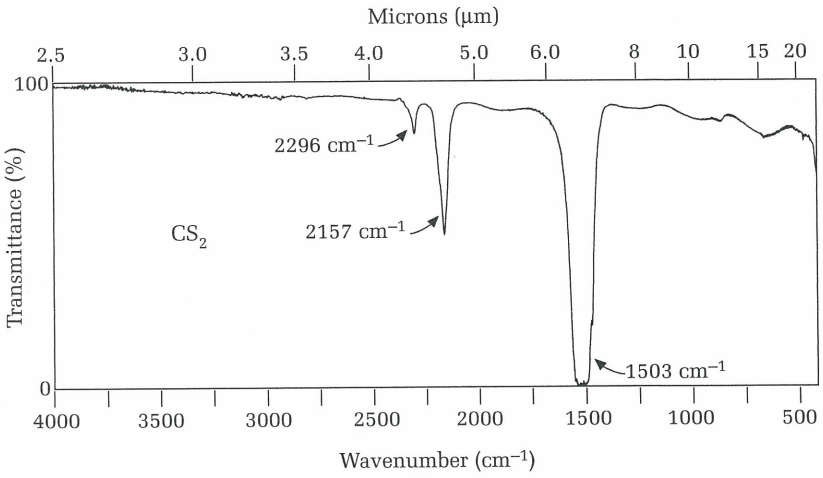


FIG. 11.14
The IR spectrum of carbon tetrachloride (thin film).

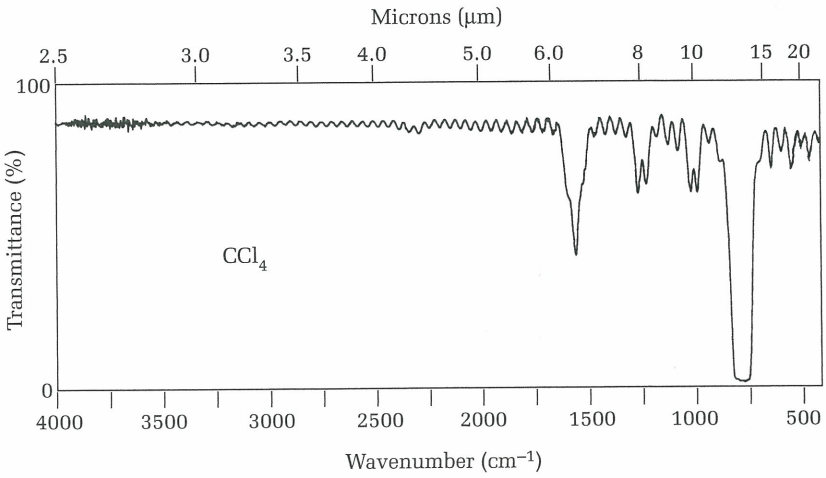


FIG. 11.15
A sealed IR sample cell.

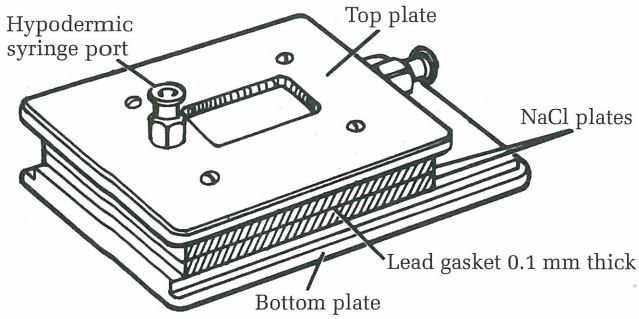


FIG. 11.16
Flushing an IR sample cell. The solvent used to dissolve the sample is used in this process.



Three drops are needed to fill the cell.

Three large drops of solution will fill the usual sealed IR cell (Fig. 11.15). A 10% solution of a liquid sample can be approximated by diluting 1 drop of the liquid sample with 9 drops of the solvent. Because weights are more difficult to estimate, solid samples should be weighed to obtain a 10% solution.

The solvent and the sample must be dry. Do not touch or breathe on NaCl plates. Cells are very expensive.

First, obtain a background spectrum of the solvent. The IR cell is filled by inclining it slightly and placing about 3 drops of the solvent in the lower hypodermic port with a capillary dropper. The cell must be completely dry because the new sample will not enter if the cell contains solvent. The liquid can be seen rising between the salt plates by looking into the window. In the most common sealed cell, the salt plates are spaced 0.1 mm apart. Be sure that the cell is filled past the window and that no air bubbles are present. Then place a Teflon stopper lightly but firmly in the hypodermic port. Be particularly careful not to spill any of the sample on the outside of the cell windows. Place the cell in the instrument cell holder and acquire a background spectrum. Blow dry nitrogen or draw dry air through the cell to remove the solvent and dry the cell, fill with the sample solution prepared above, and acquire the spectrum.

After running the sample, force clean solvent through the cell using a syringe attached to the top port of the cell (Fig. 11.16). Dry using dry nitrogen or air and store in a desiccator.

Dispose of waste solvents in the container provided.

Cleaning Up. Discard halogenated liquids in the halogenated organic waste container. Other solutions should be placed in the organic solvents container.

Mulls

The sample must be finely ground.

Solids insoluble in the usual solvents can be run as mulls. In preparing a mull, the sample is ground to a particle size less than that of the wavelength of light going through the sample (2.5 μm) to avoid scattering light. About 15–20 mg of the

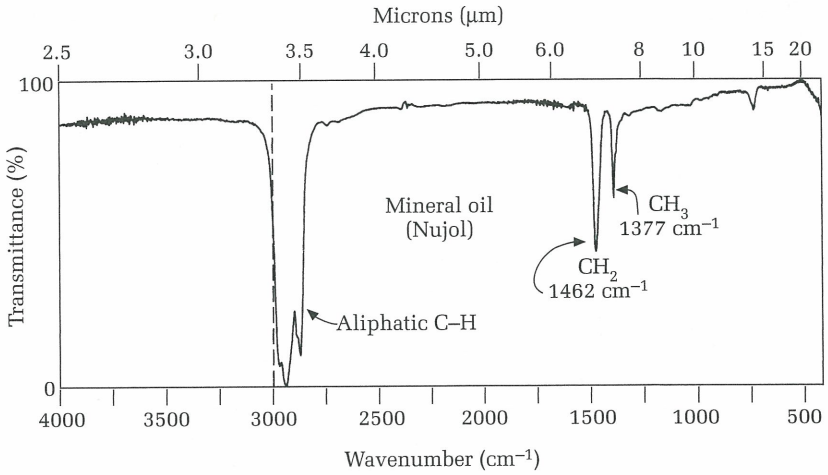


FIG. 11.17
The IR spectrum of Nujol (paraffin oil).

sample is ground for 3–10 min in an agate mortar until it is spread over the entire inner surface of the mortar and has a caked and glassy appearance. Then to make a mull, add 1 or 2 drops of paraffin oil (Nujol; Fig. 11.17) and grind the sample for 2–5 more minutes. The mull, which should have the consistency of thin margarine, is transferred to the bottom salt plate of a demountable cell (*see* Fig. 11.10 on page 242) using a rubber policeman, the top plate is added and rotated back and forth to distribute the sample evenly to eliminate all air pockets, and the spectrum is run. Because the bands from Nujol obscure certain frequency regions, running another mull using Fluorolube as the mulling agent will allow the entire IR spectral region to be covered. If the sample has not been ground sufficiently fine, there will be marked loss of transmittance at the short-wavelength end of the spectrum. After running the spectrum, the salt plates are wiped clean with a cloth saturated with an appropriate solvent.

A fast, simple alternative: Grind a few milligrams of the solid with 1 drop of tetrachloroethylene between two round salt plates. Mount on the holder as shown in Figure 11.11 on page 242.

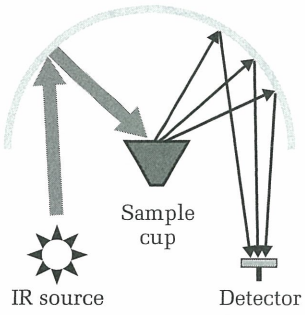
Potassium Bromide Disk

The spectrum of a solid sample can also be run by incorporating the sample in a potassium bromide (KBr) disk. This procedure needs only one disk to cover the entire spectral range because KBr is completely transparent to IR radiation. Although very little sample is required, making the disk calls for special equipment and time to prepare it. Because KBr is hygroscopic, water is a problem.

Into a stainless steel capsule containing a ball bearing are weighed 1.5–2 mg of the compound and 200 mg of spectroscopic-grade KBr (previously dried and stored in a desiccator). The capsule is shaken for 2 min on a Wig-L-Bug (the device used by dentists to mix silver amalgam). The sample is evenly distributed over the face of a 13-mm die and subjected to a pressure of 14,000–16,000 psi for 3–6 min while under vacuum in a hydraulic press. A transparent disk is produced, which is removed from the die with tweezers and placed in a holder like that shown in Figure 11.11 on page 242 prior to running the spectrum.

Diffuse Reflectance

FIG. 11.18
A simplified diagram of a diffuse reflectance system.



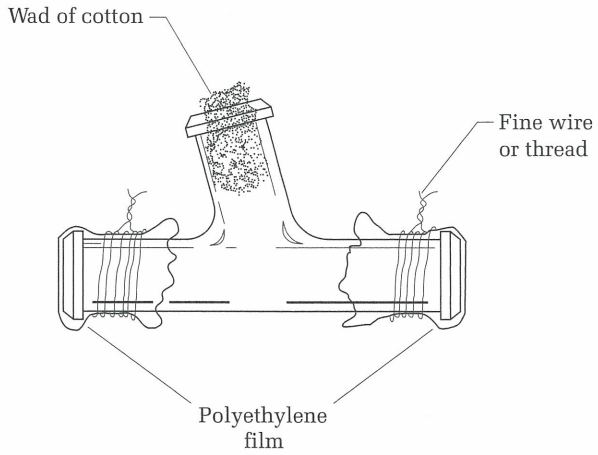
Reasonable IR spectra of solids can be obtained without pressing a KBr pellet if the IR instrument is equipped with diffuse reflectance optics. A mixture of the sample and KBr is put in a small sample cup, and this is placed in the diffuse reflectance optics system (Fig. 11.18). When the IR beam enters the sample, it can either be reflected off the surface of a particle or be transmitted through a particle. The IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle. This transmission-reflectance event can occur many times in the sample, which increases the path length. Finally, any scattered IR energy that is not absorbed by the sample is collected by a spherical mirror that is focused onto a detector. A background spectrum of only pure KBr should be run before the sample to subtract out any absorbance that is not from the sample.

Weigh out 0.160–0.170 g of KBr quickly (this compound readily absorbs atmospheric humidity) and place it in a vial. Weigh out between 4 mg and 7 mg of your solid and add this to the vial. Mix and dump into a small, dry mortar and pestle. Grind for 1–2 min until a fine powder is obtained. Transfer to weighing paper and then to the cup of the diffuse reflectance sample holder. Place the holder in the reflectance attachment and acquire the spectrum.

Gas Phase IR Spectroscopy: The Williamson Gas Phase IR Cell

In the past it was difficult to obtain the IR spectra of gases. A commercial gas cell costs hundreds of dollars; the cell must be evacuated, and the dry gas carefully introduced—not a routine process. But we have found that a uniquely simple gas phase IR cell can be assembled at virtually no cost from a 105° microscale connecting adapter.[2]

FIG. 11.19
The Williamson Gas Phase IR Cell utilizing the 105° connecting adapter from the microscale kit that accompanies this text.



2. The microscale connecting adapter is a available from Kimble Kontes (catalog no. 748001-1000).

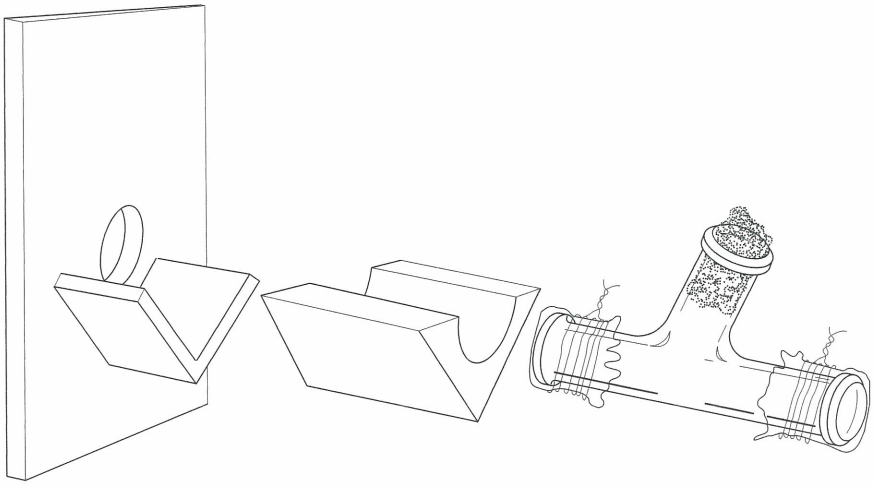


FIG. 11.20
The Williamson Gas Phase IR Cell mounted in a cell holder.

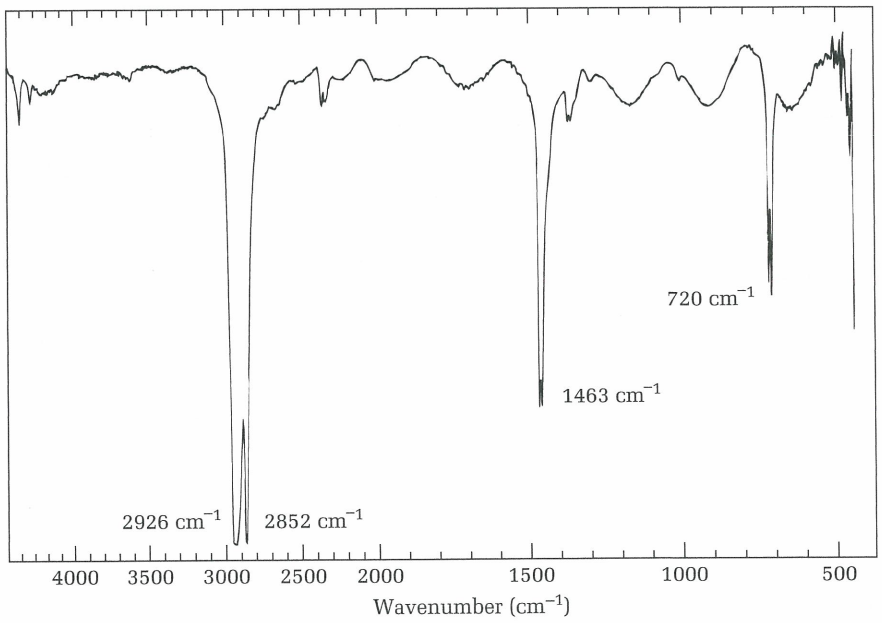


FIG. 11.21
The IR spectrum of polyethylene film.

To make the Williamson gas phase IR cell, attach a thin piece of polyethyene film from, for example, a sandwich bag to each end of the adapter with a small rubber band, fine wire, or thread. Place a loose wad of cotton in the side arm and mount the IR cell in the beam of the spectrometer (Fig. 11.19 and Fig. 11.20).

The adapter can be supported on a V-block as shown in Figure 11.20 or, temporarily, on a block of modeling clay. Be sure the beam, usually indicated by a red laser, strikes both ends of the cell. Run a background spectrum on the cell. The spectrum of polyethylene (Fig. 11.21) is very simple, so interfering bands will be few. This spectrum is automatically subtracted when you put a sample in the cell and run a spectrum.

A more permanent cell can be constructed by attaching two thin plates of silver chloride to the ends of the adapter with epoxy glue. These silver chloride plates can be made in the press used for making KBr discs, or they can be purchased.[3]

Obtaining a Spectrum

To run a gas phase spectrum, remove the cell from the spectrometer and spray a very short burst of a gas from an aerosol can onto the cotton. The nonvolatile components of the spray will stick to the cotton, and the propellant gas will diffuse into the cell. Run the spectrum in the usual way. The concentration of the gas is about the same as a thin film of liquid run between salt plates. If the concentration of the gas is too high, remove the cell from the spectrometer, remove the cotton, and "pour out" half the invisible gas by holding the cell in a vertical position.

You may be fortunate in having in your school's library a copy of Volume 3 of *The Aldrich Library of FT-IR Spectra: Vapor Phase* or an online database of IR spectra on your IR instrument data system. Either resource contains hundreds of reference spectra that will help you analyze the IR spectra of propellants in aerosol cans and any other gases you may encounter. Otherwise you may want to compare your spectra to the few in this text and available on the website for this text and assemble your own library of gas phase spectra. It is possible to make approximate calculations of IR vibrational frequencies using a semi-empirical calculation at the AM1 level (*see* Chapter 15).

Throughout the remainder of this book, representative IR spectra of starting materials and products are presented, and the important bands in each spectrum are identified.

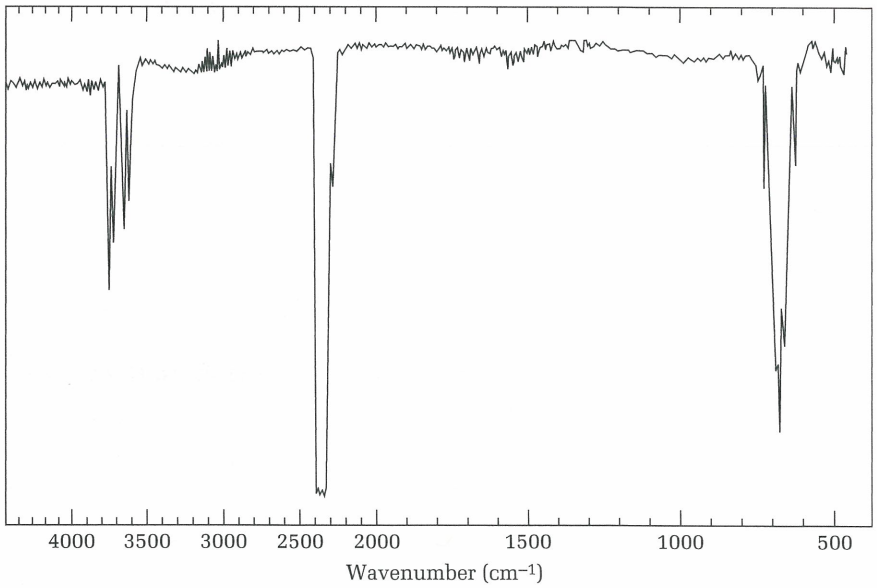


FIG. 11.22
The IR spectrum of carbon dioxide (gas phase).

3. The silver chloride disks can be purchased from Fisher Scientific (catalog no. 14-385-860).

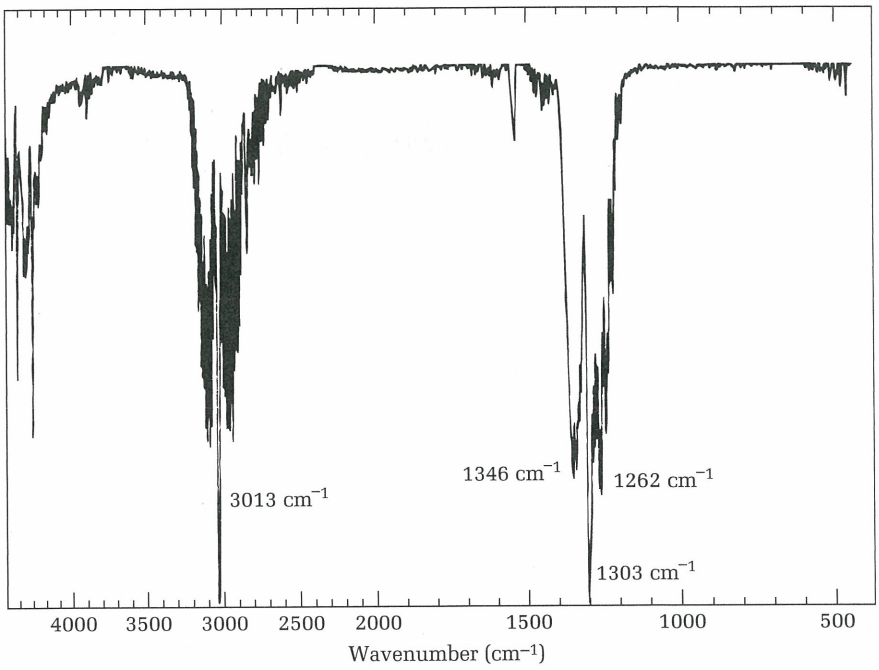


FIG. 11.23
The IR spectrum of methane (gas phase).

For Further Investigation

The Gas Phase IR Spectra of Aerosol Propellants

Acquire gas phase spectra from a number of substances from aerosol cans. Some cans will be labeled with the name of the propellant gas; others will not. Analyze the spectra, bearing in mind that the gas will be a small molecule such as carbon dioxide (Fig. 11.22), methane (Fig. 11.23), nitrous oxide (Fig. 11.24), propane, butane, isobutane, or a fluorocarbon such as 1,1,1,2-tetrafluoroethane. A very old aerosol can may contain an illegal chlorofluorocarbon, now outlawed because these substances destroy the ozone layer. Some examples of aerosol cans include hairsprays, lubricants (WD-40, Teflon), Freeze-It, inhalants for asthma, cigarette lighters, butane torches, and natural gas from the lab.

Other Gas Phase Spectral Research

You can deliberately generate hydrogen chloride (or deuterium chloride) and sulfur dioxide and then analyze the gas that is evolved from a thionyl chloride reaction. Can you detect carbon monoxide in automobile exhaust? How about marsh gas that you see bubbling out of ponds? With perhaps dozens of scans, can you record the spectra of vanillin over vanilla beans, eugenol vapor over cloves, anisaldehyde over anise seeds? What is the nature of the volatile components of chili peppers, orange peel, nail polish, and nail polish remover? Could you use this method to determine if someone has been drinking alcohol?

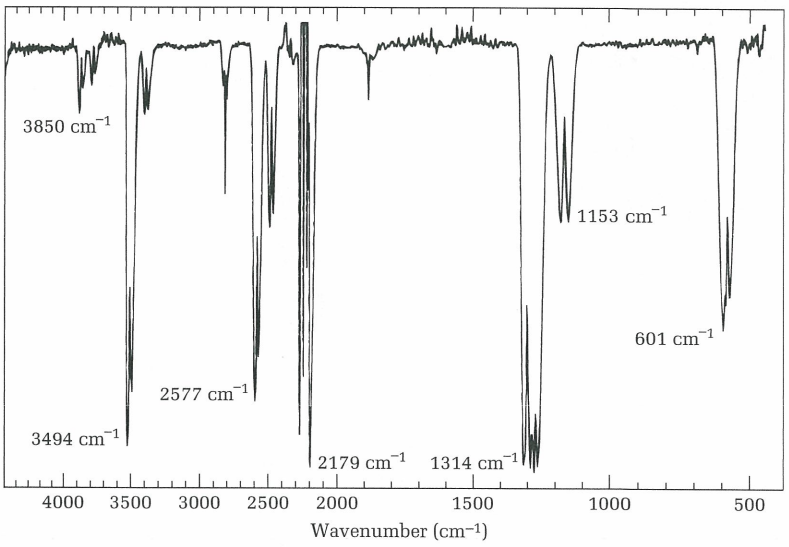


FIG. 11.24
The IR spectrum of nitrous oxide (gas phase).

EXPERIMENT

Unknown Carbonyl Compound

The sample, solvents, and apparatus must be dry.

Run the IR spectrum of an unknown carbonyl compound obtained from your laboratory instructor. Be particularly careful that all apparatus and solvents are completely free of water, which will damage the NaCl plates. Determine the frequency of the carbonyl peak in the unknown *and* list the possible types of compounds that could correspond to this frequency (Table 11.2).

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4. Pouchert, Charles J. *The Aldrich Library of FT-IR Spectra*, 2nd ed. Milwaukee: Aldrich Chemical Co., 1997.
5. Roeges, Noel P. G., *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*. New York: John Wiley, 1994.
6. Silverstein, Robert M., Francis X. Webster, and David Kiemle, *Spectrometric Identification of Organic Compounds*, 7th ed.[4] New York: Wiley, 2005.

4. This book includes IR, UV, and NMR spectra.