

An Introduction to Infrared Spectrometry

The infrared (IR) 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 . Because of similar applications and instrumentation, the IR spectrum is usually subdivided into three regions, the near-IR, the mid-IR, and the far-IR. The techniques and the applications of methods based on the three IR spectral regions differ considerably as discussed in this chapter.



Throughout this chapter, this logo indicates an opportunity for online self-study at www.tinyurl.com/skoogpia7, linking you to interactive tutorials, simulations, and exercises.

Table 16-1 gives the rough limits of each of the three IR regions. Measurements in the near-IR region are often made with photometers and spectrophotometers similar in design and components to the instruments described in earlier chapters for ultraviolet (UV)-visible spectrometry. The most important applications of this spectral region have been to the quantitative analysis of industrial and agricultural materials and for process control. Applications of near-IR spectrometry are discussed in Section 17D.

Until the early 1980s, instruments for the mid-IR region were largely of the dispersive type and used diffraction gratings. Since that time, however, mid-IR instrumentation has dramatically changed so that now almost all new instruments are of the Fourier transform (FT) type. Photometers based on interference filters also find use for measuring the composition of gases and atmospheric contaminants.

The appearance of relatively inexpensive FT spectrometers in the last decade has markedly increased the number and type of applications of mid-IR radiation. This increase has come about because interferometric instruments can produce improvements of an order of magnitude, or more, in signal-to-noise ratios and detection limits over dispersive instruments. Before the appearance of these instruments, the mid-IR spectral region was used largely for qualitative organic analysis and structure determinations based on absorption spectra. Now, in contrast, mid-IR spectrometry is beginning to be used in addition for quantitative analysis of complex samples by both absorption and emission spectrometry. Applications of this spectral region are also beginning to appear for microscopic studies of surfaces, analysis of solids by attenuated total reflectance and diffuse reflectance, photoacoustic measurements, and other uses. Several of these applications are described in Chapter 17.

In the past the far-IR region of the spectrum, although potentially quite valuable, had limited use because of experimental difficulties. The few sources of this type of radiation are notoriously weak and are further attenuated by the need for order-sorting filters that prevent radiation of higher grating orders from reaching the detector. FT spectrometers, with their much higher throughput, largely alleviate this problem and make the far-IR spectral region much more accessible to scientists. Several applications of far-IR spectroscopy are described in Section 17E.

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}

In this chapter, we first deal with the mechanisms of the absorption, emission, and reflection of IR radiation using absorption spectroscopy as the basis for this discussion. We follow this discussion with a description of the components of IR instruments and how these are arranged in dispersive and non-dispersive instruments as well as in FT spectrometers.¹

16A THEORY OF IR ABSORPTION SPECTROMETRY

IR absorption, emission, and reflection spectra for molecular species can be rationalized by assuming that all arise from various changes in energy brought about by transitions of molecules from one vibrational or rotational energy state to another. In this section we use molecular absorption to illustrate the nature of these transitions.

16A-1 Introduction

Figure 16-1 shows a typical output from a commercial IR spectrophotometer. Although the y -axis is shown as linear in transmittance, modern computer-based spectrophotometers can also produce spectra that are linear in absorbance. The abscissa in this spectrum is linear in wavenumbers with units of reciprocal centimeters. A wavelength scale is also shown at the top of the plot. Computer-based spectrophotometers can produce a variety of other spectral formats such as linear in wavelength, baseline corrected, and derivative and smoothed spectra.

A linear wavenumber scale is usually preferred in IR spectroscopy because of the direct proportionality between this quantity and both energy and frequency. The frequency of the absorbed radiation is, in turn, the molecular vibrational frequency actually responsible for the absorption process. Frequency, however, is seldom if ever used

as the abscissa because of the inconvenient size of the unit; that is, a frequency scale of the plot in Figure 16-1 would extend from 1.2×10^{14} to 2.0×10^{13} Hz. Although the axis in terms of wavenumbers is often referred to as a frequency axis, keep in mind that this terminology is not strictly correct because the wavenumber $\bar{\nu}$ is only proportional to frequency ν . The relationships are given in Equation 16-1.

$$\bar{\nu} (\text{cm}^{-1}) = \frac{1}{\lambda (\mu\text{m})} \times 10^4 (\mu\text{m}/\text{cm}) = \frac{\nu (\text{Hz})}{c (\text{cm/s})} \quad (16-1)$$

Finally, note that the horizontal scale of Figure 16-1 changes at 2000 cm^{-1} , with the units at higher wavenumbers being represented by half the linear distance of those at lower wavenumbers. The expanded scale in the region from 2000 to 650 cm^{-1} permits easier identification of the numerous IR bands that appear in this region.

Dipole Moment Changes during Vibrations and Rotations

IR radiation is not energetic enough to bring about the kinds of electronic transitions that we have encountered in our discussions of UV and visible radiation. Absorption of IR radiation is thus confined largely to molecular species that have small energy differences between various vibrational and rotational states.

To absorb IR radiation, a molecule must undergo a net change in dipole moment as it vibrates or rotates. Only under these circumstances can the alternating electric field of the radiation interact with the molecule and cause changes in the amplitude of one of its motions. For example, the charge distribution around a molecule such as hydrogen chloride is not symmetric because the chlorine has a higher electron density than the hydrogen. Thus, hydrogen chloride has a significant dipole moment and is said to be polar. The dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge. As a hydrogen chloride molecule vibrates, a regular fluctuation in its dipole moment occurs, and a field is established that can interact with the electric field associated with radiation. If the frequency of the radiation exactly matches a natural vibrational frequency of the molecule, absorption of the radiation takes place that produces a change in the amplitude of the molecular vibration. Similarly, the rotation of asymmetric molecules around their centers of mass results in periodic dipole moment fluctuations that allow interaction with the radiation field.

¹For detailed treatments of IR spectrometry, see *Introduction to Experimental Infrared Spectroscopy: Fundamentals and Practical Methods*, M. Tasumi, ed., Chichester, UK: Wiley, 2015; P. Larkin, *Infrared and Raman Spectroscopy: Principles and Spectral Interpretation*, Waltham, MA: Elsevier, 2011; N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., San Diego: Academic Press, 1990; C.-P. S. Hsu, in *Handbook of Instrumental Techniques for Analytical Chemistry*, F. Settle, ed., Upper Saddle River, NJ: Prentice Hall, 1997, Chap. 15.

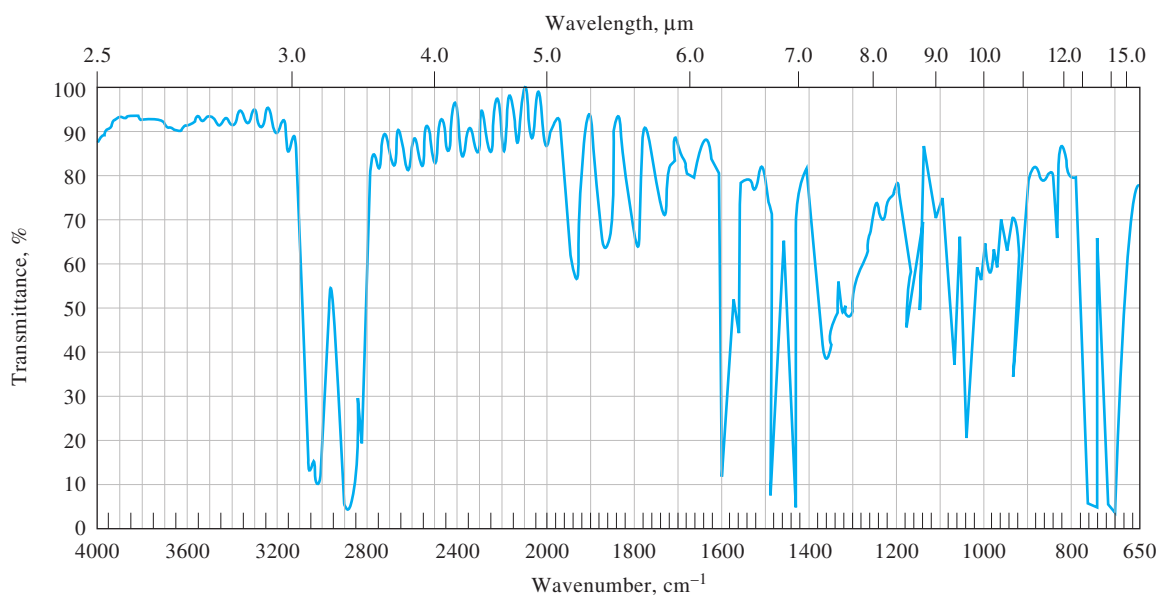


FIGURE 16-1 IR absorption spectrum of a thin polystyrene film. Note the scale change on the x-axis at 2000 cm^{-1} .

No net change in dipole moment occurs during the vibration or rotation of homonuclear species such as O_2 , N_2 , or Cl_2 . As a result, such compounds cannot absorb IR radiation. With the exception of a few compounds of this type, all other molecular species absorb IR radiation.

Rotational Transitions

The energy required to cause a change in rotational level is quite small and corresponds to radiation of $\bar{\nu} \leq 100\text{ cm}^{-1}$ ($\lambda > 100\text{ }\mu\text{m}$). Because rotational levels are quantized, absorption by gases in this far-IR region is characterized by discrete, well-defined lines. In liquids or solids, intramolecular collisions and interactions cause broadening of the lines into a continuum.

Vibrational-Rotational Transitions

Vibrational energy levels are also quantized, and for most molecules the energy differences between quantum states correspond to the mid-IR region. The IR spectrum of a gas usually consists of a series of closely spaced lines, because there are several rotational energy levels for each vibrational level. On the other hand, rotation is highly restricted in liquids and solids; in such samples, discrete vibrational-rotational lines disappear, leaving only somewhat broadened vibrational bands.

Types of Molecular Vibrations

The relative positions of atoms in a molecule are not fixed but instead fluctuate continuously because of a multitude of different types of vibrations and rotations about the bonds in the molecule. For a simple diatomic or triatomic molecule, it is easy to

define the number and nature of such vibrations and relate these to energies of absorption. An analysis of this kind becomes difficult if not impossible for molecules made up of many atoms. Not only do large molecules have a large number of vibrating centers, but also interactions among several centers can occur and must be taken into account for a complete analysis.

Vibrations fall into the basic categories of stretching and bending. A stretching vibration involves a continuous change in the interatomic distance along the axis of the bond between two atoms. Bending vibrations are characterized by a change in the angle between two bonds and are of four types: scissoring, rocking, wagging, and twisting. These are shown schematically in Figure 16-2.

All of the vibration types shown in Figure 16-2 may be possible in a molecule containing more than two atoms. In addition, interaction or coupling of vibrations can occur if the vibrations involve bonds to a single central atom. The result of coupling is a change in the characteristics of the vibrations involved.

In the treatment that follows, we first consider isolated vibrations represented by a simple harmonic oscillator model. Modifications to the theory of the harmonic oscillator, which are needed to describe a molecular system, are taken up next. Finally, the effects of vibrational interactions in molecular systems are discussed.

16A-2 Mechanical Model of a Stretching Vibration in a Diatomic Molecule

The characteristics of an atomic stretching vibration can be approximated by a mechanical model consisting of two masses connected by a spring. A disturbance of one of these masses



Tutorial: Learn more about **IR absorption** at www.tinyurl.com/skoogpia7

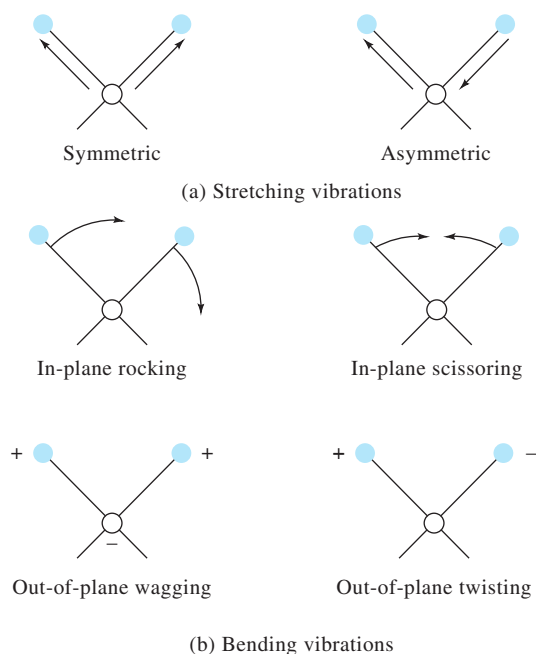


FIGURE 16-2 Types of molecular vibrations. Note that + indicates motion from the page toward the reader and – indicates motion away from the reader.

along the axis of the spring results in a vibration called a *simple harmonic motion*.

Let us first consider the vibration of a single mass attached to a spring that is hung from an immovable object (see Figure 16-3a). If the mass is displaced a distance y from its equilibrium position by application of a force along the axis of the spring, the

restoring force F is proportional to the displacement (Hooke's law). That is,

$$F = -ky \quad (16-2)$$

where k is the force constant, which depends on the stiffness of the spring. The negative sign indicates that F is a restoring force. This means that the direction of the force is opposite the direction of the displacement. Thus, the force tends to restore the mass to its original position.

Potential Energy of a Harmonic Oscillator

The potential energy E of the mass and spring can be arbitrarily assigned a value of zero when the mass is in its rest, or equilibrium, position. As the spring is compressed or stretched, however, the potential energy of this system increases by an amount equal to the work required to displace the mass. If, for example, the mass is moved from some position y to $y + dy$, the work and hence the change in potential energy dE is equal to the force F times the distance dy . Thus,

$$dE = -F dy \quad (16-3)$$

Combining Equations 16-3 and 16-2 yields

$$dE = ky dy$$

Integrating between the equilibrium position $y = 0$ and y gives

$$\int_0^E dE = \int_0^y ky dy$$

$$E = \frac{1}{2}ky^2 \quad (16-4)$$

The potential-energy curve for a simple harmonic oscillation, derived from Equation 16-4, is a parabola, as depicted in

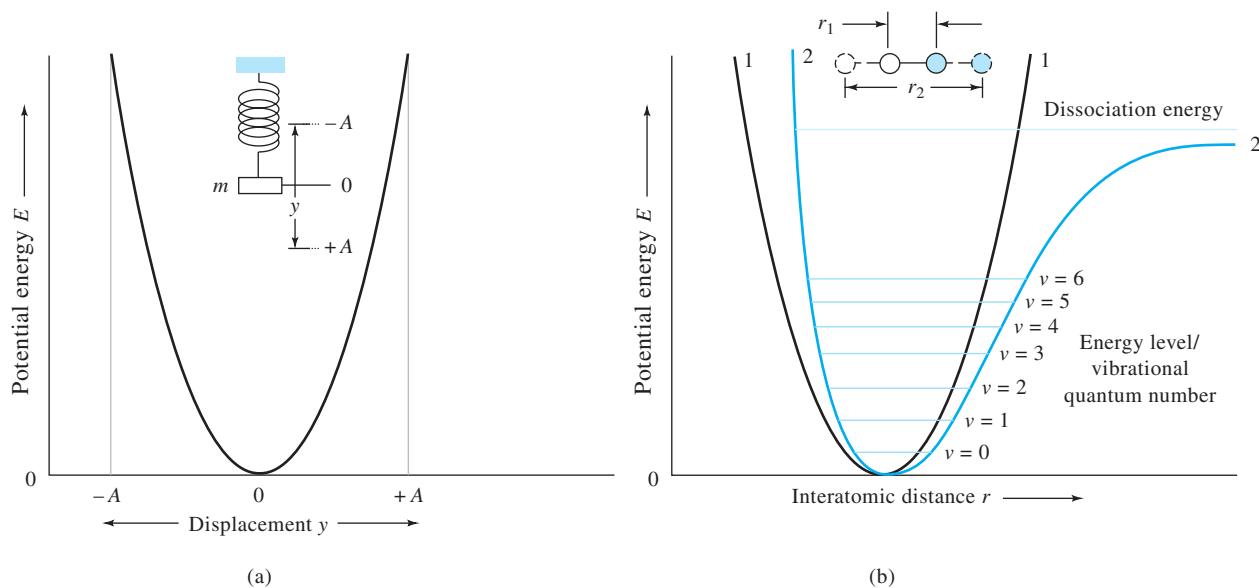


FIGURE 16-3 Potential-energy diagrams. (a) Harmonic oscillator. (b) Curve 1, harmonic oscillator; curve 2, anharmonic motion.

Figure 16-3a. Notice that the potential energy is a maximum when the spring is stretched or compressed to its maximum amplitude A , and it decreases to zero at the equilibrium position.

Vibrational Frequency

The motion of the mass as a function of time t can be deduced from classical mechanics as follows. Newton's second law states that

$$F = ma$$

where m is the mass and a is its acceleration. But acceleration is the second derivative of distance with respect to time. Thus,

$$a = \frac{d^2y}{dt^2}$$

Substituting these expressions into Equation 16-2 gives

$$m \frac{d^2y}{dt^2} = -ky \quad (16-5)$$

A solution to this equation must be a periodic function such that its second derivative is equal to the original function times $-k/m$. A suitable cosine relationship meets this requirement. Thus, the instantaneous displacement of the mass at time t can be written as

$$y = A \cos 2\pi\nu_m t \quad (16-6)$$

where ν_m is the natural vibrational frequency and A is the maximum amplitude of the motion. The second derivative of Equation 16-6 with respect to time is

$$\frac{d^2y}{dt^2} = -4\pi^2\nu_m^2 A \cos 2\pi\nu_m t \quad (16-7)$$

Substitution of Equations 16-6 and 16-7 into Equation 16-5 gives

$$A \cos 2\pi\nu_m t = \frac{4\pi^2\nu_m^2 m}{k} A \cos 2\pi\nu_m t$$

The natural frequency of the oscillation is then

$$\nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (16-8)$$

where ν_m is the natural frequency of the mechanical oscillator. Although it depends on the force constant of the spring and the mass of the attached body, the natural frequency is independent of the energy imparted to the system; changes in energy merely result in a change in the amplitude A of the vibration.

The equation just developed may be modified to describe the behavior of a system consisting of two masses m_1 and m_2 connected by a spring. This is accomplished by substituting the reduced mass μ for the single mass m where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (16-9)$$

Thus, the vibrational frequency for such a system is given by

$$\nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}} \quad (16-10)$$

Molecular Vibrations

The approximation is ordinarily made that the behavior of a molecular vibration is analogous to the mechanical model just described. Thus, the frequency of the molecular vibration is calculated from Equation 16-10 after substituting the masses of the two atoms for m_1 and m_2 . The quantity k is the force constant of the chemical bond, which is a measure of its stiffness.

16A-3 Quantum Treatment of Vibrations

The equations of ordinary mechanics that we have used thus far do not completely describe the behavior of particles of atomic dimensions. For example, the quantized nature of molecular vibrational energies, and of other atomic and molecular energies as well, does not appear in these equations. We may, however, invoke the concept of the simple harmonic oscillator to develop the wave equations of quantum mechanics. Solutions of these equations for potential energies have the form

$$E = \left(\nu + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad (16-11)$$

where h is Planck's constant, and ν is the *vibrational quantum number*, which can take only positive integer values (including zero). Thus, in contrast to ordinary mechanics where vibrators can assume any potential energy, quantum mechanical vibrators can take on only certain discrete energies.

It is interesting to note that the factor $\sqrt{k/\mu}/2\pi$ appears in both the classical and the quantum equations; by substituting Equation 16-10 into 16-11, we find

$$E = \left(\nu + \frac{1}{2} \right) h\nu_m \quad (16-12)$$

where ν_m is the vibrational frequency of the classical model.²

We now assume that transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation exactly matches the difference in energy levels ΔE between the vibrational quantum states and provided also the vibration causes a change in dipole moment. This difference is identical between any pair of adjacent levels, because ν in Equations 16-11 and 16-12 can assume only whole numbers; that is,

$$\Delta E = h\nu_m = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad (16-13)$$

²Unfortunately, the generally accepted symbol for the vibrational quantum number ν is similar in appearance to the Greek nu, ν , which symbolizes frequency. Thus, constant care must be exercised to avoid confusing the two in equations such as Equation 16-12.

At room temperature, the majority of molecules are in the ground state $\nu = 0$; thus, from Equation 16-12,

$$E_0 = \frac{1}{2}h\nu_m$$

Promotion to the first excited state $\nu = 1$ with energy

$$E_1 = \frac{3}{2}h\nu_m$$

requires radiation of energy

$$\left(\frac{3}{2}h\nu_m - \frac{1}{2}h\nu_m\right) = h\nu_m$$

The frequency of radiation ν that will bring about this change is identical to the classical vibrational frequency of the bond ν_m . That is,

$$E_{\text{radiation}} = h\nu = \Delta E = h\nu_m = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

or

$$\nu = \nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (16-14)$$

If we wish to express the radiation in wavenumbers, we substitute Equation 6-3 and rearrange:

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}} \quad (16-15)$$

where $\bar{\nu}$ is the wavenumber of an absorption maximum (cm^{-1}), k is the force constant for the bond in newtons per meter (N/m), c is the velocity of light (cm s^{-1}), and μ is the reduced mass (kg) defined by Equation 16-9.³

IR measurements in conjunction with Equation 16-14 or 16-15 permit the evaluation of the force constants for various types of chemical bonds. Generally, k has been found to lie in the range between 3×10^2 and 8×10^2 N/m for most single bonds, with 5×10^2 serving as a reasonable average value. Double and triple bonds are found by this same means to have force constants of about two and three times this value (1×10^3 and 1.5×10^3 N/m, respectively). With these average experimental values, Equation 16-15 can be used to estimate the wavenumber of the fundamental absorption band, or the absorption due to the transition from the ground state to the first excited state, for a variety of bond types. The following example demonstrates such a calculation.

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

$$\begin{aligned} m_1 &= \frac{12 \times 10^{-3} \text{ kg/mol}}{6.0 \times 10^{23} \text{ atom/mol}} \times 1 \text{ atom} \\ &= 2.0 \times 10^{-26} \text{ kg} \end{aligned}$$

Similarly, for oxygen,

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

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

$$\begin{aligned} \mu &= \frac{2.0 \times 10^{-26} \text{ kg} \times 2.7 \times 10^{-26} \text{ kg}}{(2.0 + 2.7) \times 10^{-26} \text{ kg}} \\ &= 1.1 \times 10^{-26} \text{ kg} \end{aligned}$$

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

$$\begin{aligned} \bar{\nu} &= 5.3 \times 10^{-12} \text{ s/cm} \sqrt{\frac{1 \times 10^3 \text{ N/m}}{1.1 \times 10^{-26} \text{ kg}}} \\ &= 1.6 \times 10^3 \text{ cm}^{-1} \end{aligned}$$

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

Selection Rules

As given by Equations 16-12 and 16-13, the energy for a transition from energy level 1 to 2 or from level 2 to 3 should be identical to that for the 0 to 1 transition. Furthermore, quantum theory indicates that the only transitions that can take place are those in which the vibrational quantum number changes by unity; that is, the *selection rule* states that $\Delta\nu = \pm 1$. Because the vibrational levels are equally spaced for a harmonic oscillator, only a single absorption peak should be observed for a given molecular vibration. In addition to the $\Delta\nu = \pm 1$ selection rule, there must be a change in dipole moment during the vibration.

Anharmonic Oscillator

Thus far, we have considered the classical and quantum mechanical treatments of the harmonic oscillator. The potential energy of such a vibrator changes periodically as the distance between the masses fluctuates (Figure 16-3a). From qualitative considerations, however, this description of a molecular vibration appears imperfect. For example, as the two atoms approach one

³By definition, the newton has the units of $\text{N} = \text{kg m/s}^2$. Thus, $\sqrt{k/\mu}$ has units of s^{-1} .

another, coulombic repulsion between the two nuclei produces a force that acts in the same direction as the restoring force of the bond. For this reason, the potential energy can be expected to rise more rapidly than the harmonic approximation predicts. At the other extreme of oscillation, a decrease in the restoring force, and thus the potential energy, occurs as the interatomic distance approaches that at which dissociation of the atoms takes place.

In theory, the wave equations of quantum mechanics permit the derivation of more nearly correct potential-energy curves for molecular vibrations. Unfortunately, however, the mathematical complexity of these equations prevents their quantitative application to all but simple diatomic systems. Qualitatively, the curves take the anharmonic form shown as curve 2 in Figure 16-3b. Such curves depart from harmonic behavior by varying degrees, depending on the nature of the bond and the atoms involved. Note, however, that the harmonic and anharmonic curves are nearly alike at low potential energies.

Anharmonicity leads to deviations of two kinds. At higher quantum numbers, ΔE becomes smaller (see curve 2 in Figure 16-3b), and the selection rule is not rigorously followed. As a result, weaker transitions called *overtone*s are sometimes observed. These transitions correspond to $\Delta v = \pm 2$ or ± 3 . The frequencies of such overtone transitions are approximately two or three times that of the fundamental frequency, and the intensities are lower than that of the fundamental.

Vibrational spectra are further complicated by two different vibrations in a molecule interacting to give absorptions at frequencies that are approximately the sums or differences of their fundamental frequencies. Again, the intensities of these sum and difference bands are generally low.

16A-4 Vibrational Modes

It is ordinarily possible to deduce the number and kinds of vibrations in simple diatomic and triatomic molecules and whether these vibrations will lead to absorption. Complex molecules may contain several types of atoms as well as bonds. For these molecules, the many types of possible vibrations give rise to IR spectra that are much more difficult to analyze or predict.

The number of possible vibrations in a polyatomic molecule can be calculated as follows. Three coordinates are needed to locate a point in space. To fix N points requires a set of three coordinates for each point, for a total of $3N$. Each coordinate corresponds to one degree of freedom for one of the atoms in a polyatomic molecule. For this reason, a molecule containing N atoms is said to have $3N$ degrees of freedom.

In defining the motion of a molecule, we need to consider (1) the motion of the entire molecule through space (that is, the translational motion of its center of gravity); (2) the rotational motion of the entire molecule around its center of gravity; and (3) the motion of each of its atoms relative to the other atoms, or in other words, its individual vibrations. Because all atoms in the molecule move in concert through space, definition of

translational motion requires three coordinates and thus this common motion requires three of the $3N$ degrees of freedom. Another three degrees of freedom are needed to describe the rotation of the molecule as a whole. The remaining $3N - 6$ degrees of freedom involve interatomic motion and hence represent the number of possible vibrations within the molecule. A linear molecule is a special case because, by definition, all of the atoms lie on a single, straight line. Rotation about the bond axis is not possible, and two degrees of freedom suffice to describe rotational motion. Thus, the number of vibrations for a linear molecule is given by $3N - 5$. Each of the $3N - 6$ or $3N - 5$ vibrations is called a *normal mode*.

For each normal mode of vibration, there is a potential-energy relationship such as that shown by the solid lines in Figure 16-3b. The same selection rules discussed earlier apply for each of these relationships. In addition, to the extent that a vibration approximates harmonic behavior, the differences between the energy levels of a given vibration are the same; that is, a single absorption peak appears for each vibration having a change in dipole moment.

Four factors tend to produce fewer experimental bands than would be expected from the theoretical number of normal modes. Fewer absorption bands are found when (1) the symmetry of the molecules is such that no change in dipole moment results from a particular vibration; (2) the energies of two or more vibrations are identical or nearly identical; (3) the absorption intensity is so low as to be undetectable by ordinary means; or (4) the vibrational energy is in a wavelength region beyond the range of the instrument used to measure absorption.

Occasionally, more absorption bands are found than are expected based on the number of normal modes. We have already mentioned the overtone bands that occur at two or three times the frequency of the fundamental. In addition, *combination bands* are sometimes encountered when a photon excites two vibrational modes simultaneously. The frequency of the combination band is approximately the sum or difference of the two fundamental frequencies. This phenomenon occurs when a quantum of energy is absorbed by two bonds rather than one.

16A-5 Vibrational Coupling

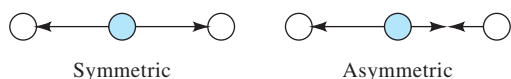
The energy of a vibration, and thus the wavelength of the corresponding absorption maximum, may be influenced by (or coupled with) other vibrators in the molecule. A number of factors influence the extent of such coupling.

1. Strong coupling between stretching vibrations occurs only when there is an atom common to the two vibrations.
2. Interaction between bending vibrations requires a common bond between the vibrating groups.
3. Coupling between a stretching and a bending vibration can occur if the stretching bond forms one side of the angle that varies in the bending vibration.

- Interaction is greatest when the coupled groups have individual energies that are nearly equal.
- Little or no interaction is observed between groups separated by two or more bonds.
- Coupling requires that the vibrations be of the same symmetry species.⁴

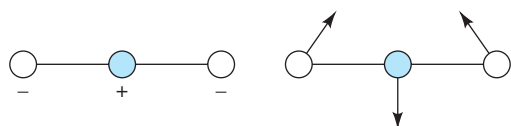
As an example of coupling effects, let us consider the IR spectrum of carbon dioxide. If no coupling occurred between the two C=O bonds, an absorption band would be expected at the same wavenumber as that for the C=O stretching vibration in an aliphatic ketone (about 1700 cm^{-1} , or $6\text{ }\mu\text{m}$; see Example 16-1). Experimentally, carbon dioxide exhibits two absorption maxima, one at 2350 cm^{-1} ($4.3\text{ }\mu\text{m}$) and the other at 667 cm^{-1} ($15\text{ }\mu\text{m}$).

Carbon dioxide is a linear molecule and thus has $(3 \times 3) - 5 = 4$ normal modes. Two stretching vibrations are possible; furthermore, interaction between the two can occur because the bonds involved are associated with a common carbon atom. As can be seen, one of the coupled vibrations is symmetric and the other is asymmetric.



The symmetric vibration causes no change in dipole moment, because the two oxygen atoms simultaneously move away from or toward the central carbon atom. Thus, the symmetric vibration is IR inactive. In the asymmetric vibration, one oxygen moves away from the carbon atom as the carbon atom moves toward the other oxygen. As a consequence, a net change in charge distribution occurs periodically, producing a change in dipole moment, so absorption at 2350 cm^{-1} results.

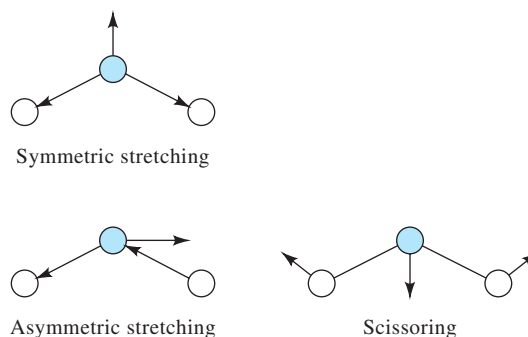
The remaining two vibrational modes of carbon dioxide involve scissoring, as shown here.



These two bending vibrations are the resolved components at 90° to one another of the bending motion in all possible planes around the bond axis. The two vibrations are identical in energy and thus produce a single absorption band at 667 cm^{-1} . Quantum states that are identical, as these are, are said to be *degenerate*.

It is of interest to compare the spectrum of carbon dioxide with that of a nonlinear, triatomic molecule such as water, sulfur dioxide, or nitrogen dioxide. These molecules have

$(3 \times 3) - 6 = 3$ vibrational modes that take the following forms:



Because the central atom is not in line with the other two, the symmetric stretching vibration produces a change in dipole moment and is thus IR active. For example, stretching peaks at 3657 and 3766 cm^{-1} (2.74 and $2.66\text{ }\mu\text{m}$) appear in the IR spectrum for the symmetric and asymmetric stretching vibrations of the water molecule. There is only one component to the scissoring vibration for this nonlinear molecule because motion in the plane of the molecule constitutes a rotational degree of freedom. For water, the bending vibration causes absorption at 1595 cm^{-1} ($6.27\text{ }\mu\text{m}$). The difference in behavior of linear and nonlinear triatomic molecules with two and three absorption bands, respectively, illustrates how IR absorption spectroscopy can sometimes be used to deduce molecular shapes.

Coupling of vibrations is a common phenomenon. As a result, the position of an absorption band corresponding to a given organic functional group cannot be specified exactly. For example, the C—O stretching frequency in methanol is 1034 cm^{-1} ($9.67\text{ }\mu\text{m}$), in ethanol it is 1053 cm^{-1} ($9.50\text{ }\mu\text{m}$), and in 2-butanol it is 1105 cm^{-1} ($9.05\text{ }\mu\text{m}$). These variations result from a coupling of the C—O stretching with adjacent C—C stretching or C—H vibrations.

Although interaction effects may lead to uncertainties in the identification of functional groups contained in a compound, it is this very effect that provides the unique features of an IR absorption spectrum that are so important for the positive identification of a specific compound.

16B IR INSTRUMENTATION

Three types of instruments for IR absorption measurements are commonly available: (1) dispersive spectrophotometers with a grating monochromator, (2) FT spectrometers employing an interferometer (Section 71), and (3) nondispersive photometers using a filter or an absorbing gas that are used for analysis of atmospheric gases at specific wavelengths.

Until the 1980s, the most widely used instruments for IR measurements were dispersive spectrophotometers. Now, however, this type of instrument has been largely displaced for

⁴For a discussion of symmetry operations and symmetry species, see F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., New York: Wiley 1990; R. S. Drago, *Physical Methods for Chemists*, 2nd ed., Philadelphia: Saunders, 1992; A. Vincent, *Molecular Symmetry and Group Theory*, Chichester: Wiley, 2001.

mid- and far-IR measurements by FT spectrometers because of their speed, reliability, signal-to-noise advantage, and convenience. Dispersive spectrometers are still used in the near-IR where they are often extensions of UV-visible instruments, but many dedicated near-IR instruments are of the Fourier transform-IR (FTIR) type.

16B-1 FT Spectrometers

The theoretical basis and the inherent advantages of FT and other multiplex instruments were discussed in some detail in Section 7I, and the reader may find it worthwhile to review that section before proceeding further. Two types of multiplex instruments have been described for the IR region. In the FT spectrometer, coding is accomplished by splitting the source into two beams whose path lengths can be varied periodically to give interference patterns. The FT is then used for data processing.⁵ The second is the Hadamard transform spectrometer, which is a dispersive instrument that uses a moving mask at the focal plane of a monochromator for encoding the spectral data. Hadamard transform IR instruments have not been widely adopted and will, therefore, not be discussed further in this book.⁶

When FTIR spectrometers first appeared in the marketplace, they were bulky, expensive (>\$100,000), and required frequent mechanical adjustments. For these reasons, their use was limited to special applications where their unique characteristics (speed, high resolution, sensitivity, and unparalleled wavelength precision and accuracy) were essential. FT instruments have now been reduced to benchtop size and have become reliable and easy to maintain. Furthermore, the price of simpler models has been reduced to the point where they are competitive with all but the simplest dispersive instruments (~\$15,000 and more). For these reasons, FT instruments have largely displaced dispersive instruments in the laboratory.⁷

Components of FT Instruments

The majority of commercially available FTIR instruments are based on the Michelson interferometer, although other types of optical systems are also encountered. We shall consider the Michelson design only, which is illustrated in Figure 7-43.⁸

⁵For detailed discussions of FTIR spectroscopy, see B. C. Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy*, 2nd ed., Boca Raton, FL: CRC Press, 2011; P. R. Griffiths and J. A. deHaseth, *Fourier Transform Infrared Spectroscopy*, 2nd ed., New York: Wiley, 2007.

⁶For a description of the Hadamard transform and Hadamard transform spectroscopy, see D. K. Graff, *J. Chem. Educ.*, **1995**, *72*, 304, DOI: 10.1021/ed072p304; *Fourier, Hadamard, and Hilbert Transforms in Chemistry*, A. G. Marshall, ed., New York: Plenum Press, 1982.

⁷For reviews of commercial FTIR spectrometers, see J. P. Smith and V. Hinson-Smith, *Anal. Chem.*, **2003**, *75*, 37A, DOI: 10.1021/ac031224d; R. Mukhopadhyay, *Anal. Chem.*, **2004**, *76*, 369A, DOI: 10.1021/ac041652z.

⁸The Michelson interferometer was designed and built in 1891 by A. A. Michelson. He was awarded the 1907 Nobel Prize in physics for the invention of interferometry.

Drive Mechanism. Requirements for satisfactory interferograms (and thus satisfactory spectra) are that the moving mirror have constant velocity and that its position be precisely known at many points along its travel. The planarity of the mirror must also remain constant during its entire sweep of 10 cm or more.

In the far-IR region, where wavelengths range from 50 to 1000 μm (200 to 10 cm^{-1}), displacement of the mirror by a fraction of a wavelength, and accurate measurement of its position, can be accomplished by means of a motor-driven micrometer screw. A more precise and sophisticated mechanism is required for the mid- and near-IR regions, however. Here, the mirror mount is generally floated on an air bearing held within close-fitting stainless steel sleeves (see Figure 16-4). The mount is driven by a linear drive motor and an electromagnetic coil similar to the voice coil in a loudspeaker; an increasing current in the coil drives the mirror at constant velocity. After reaching its terminus, the mirror is returned rapidly to the starting point for the next sweep by a rapid reversal of the current. The length of travel varies from 1 to about 20 cm; the scan rates range from 0.01 to 10 cm/s.

Two additional features of the mirror system are necessary for successful operation. The first is a means of sampling the interferogram at precisely spaced retardation intervals. The second is a method for determining exactly the zero retardation point to permit signal averaging. If this point is not known precisely, the signals from repetitive sweeps would not be in phase, and averaging would then tend to degrade rather than improve the signal.

The problem of precise signal sampling and signal averaging can be accomplished by using two or three interferometers rather than one, with a single mirror mount holding the movable mirrors. Figure 16-4 is a schematic showing such an arrangement. The components and radiation paths for each of the three interferometer systems are indicated by the subscripts 1, 2, and 3, respectively. System 1 is the IR system that ultimately provides an interferogram similar to that shown as curve A in Figure 16-5. System 2 is a so-called laser-fringe reference system, which provides sampling-interval information. It consists of a He-Ne laser S_2 , an interferometric system including mirrors MM_2 and M_2 , a beamsplitter B_2 , and a transducer T_2 . The output from this system is a cosine wave, as shown in C of Figure 16-5. This signal is converted electronically to the square-wave form shown in D; sampling begins or terminates at each successive zero crossing. The laser-fringe reference system gives a highly reproducible and regularly spaced sampling interval. In most instruments, the laser signal is also used to control the speed of the mirror-drive system at a constant level.

The third interferometer system, sometimes called the white-light system, uses a tungsten source S_3 and transducer T_3 sensitive to visible radiation. Its mirror system is fixed to give a zero retardation displaced to the left from that for the analytical signal (see interferogram B, Figure 16-5). Because the source is polychromatic, its power at zero retardation is much larger than

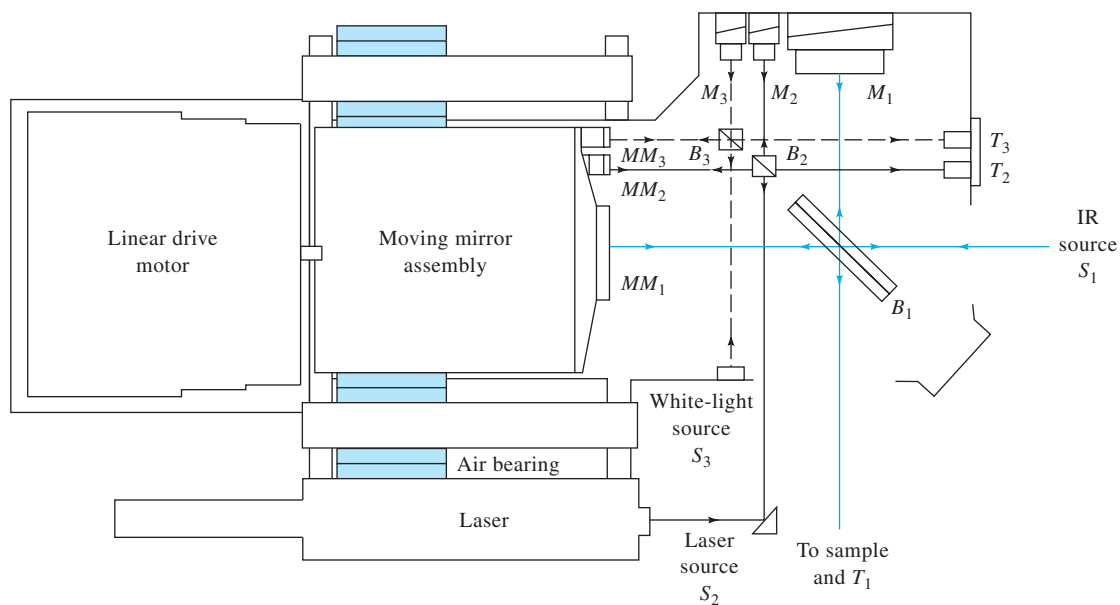


FIGURE 16-4 Interferometers in an FTIR spectrometer. Subscript 1 defines the radiation path in the IR interferometer. Subscripts 2 and 3 refer to the laser and white-light interferometers, respectively. (Courtesy of Thermo Fisher Scientific Inc., Waltham, MA.)

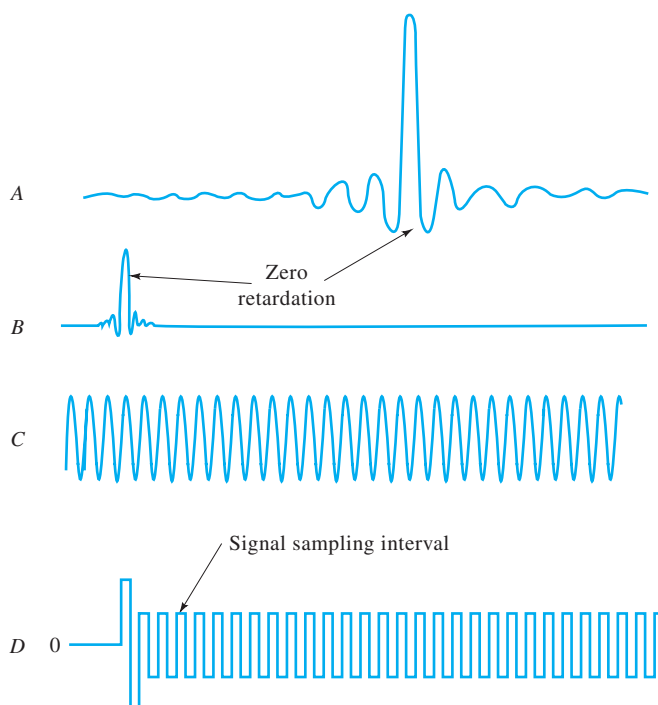


FIGURE 16-5 Time-domain signals for the three interferometers contained in many FTIR instruments. Curve A, IR signal; curve B, white-light signal; curve C, laser-fringe reference signal; curve D, square-wave electrical signal formed from the laser signal. (Adapted from P. R. Griffiths, *Anal. Chem.*, **1974**, *46*, 645A, DOI: 10.1021/ac60343a756. Copyright 1974 American Chemical Society.)



FIGURE 16-6 Photo of a basic, benchtop FTIR spectrometer suitable for student use. Spectra are recorded in a few seconds and displayed on a laptop computer. Software is available for controlling the instrument, collecting and processing data, and analyzing the results. An IR database is included for analysis and spectral interpretation. (Courtesy of Thermo Electron Corp., Madison, WI.)

any signal before and after that point. Thus, this maximum is used to trigger the start of data sampling for each sweep at a highly reproducible point.

The triple interferometer system just described leads to remarkable precision in determining spectral frequencies, which significantly exceeds that realizable with conventional grating instruments. This high reproducibility is particularly important when many scans are to be averaged. Contemporary instruments, such as the benchtop unit pictured in Figure 16-6, are able to achieve excellent frequency precision with one or two interferometers. In the instrument diagrammed in Figure 16-7, the interferometer is actually two parallel interferometers, one to modulate the IR radiation from the source before it passes through the sample and the second to modulate the red light from the He-Ne laser to provide the reference signal for acquiring data from the IR detector. No white-light source is used, and the IR interferogram is used to establish zero retardation. The maximum in the IR interferogram is an excellent reference because this is the only point at which all wavelengths interfere constructively.

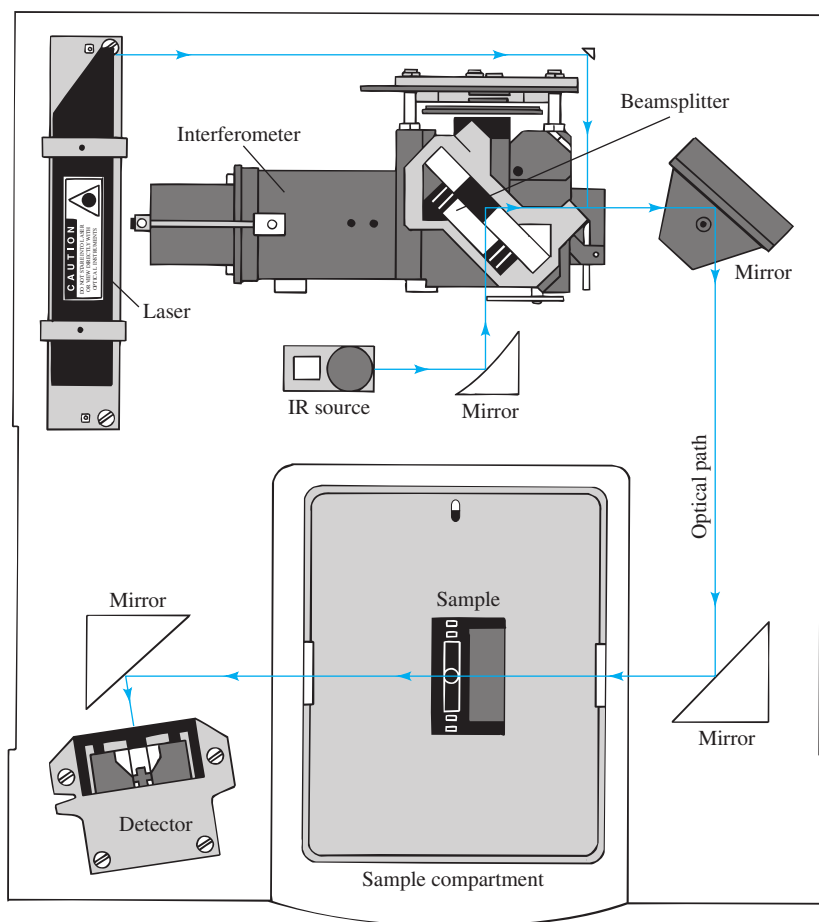


FIGURE 16-7 Diagram of a basic FTIR spectrometer. Radiation of all frequencies from the IR source is reflected into the interferometer where it is modulated by the moving mirror on the left. The modulated radiation is then reflected from the two mirrors on the right through the sample in the compartment at the bottom. After passing through the sample, the radiation falls on the transducer. A data-acquisition system attached to the transducer records the signal and stores it in the memory of a computer as an interferogram. (Courtesy of Thermo Fisher Scientific, Waltham, MA.)

The benchtop system shown in Figure 16-6 is capable of providing spectra with a resolution of better than 1 cm^{-1} . An educational kit is available to aid in using the instrument in an academic environment. The kit includes information on IR theory, FTIR instrumentation, and several experiments.

Instrument Designs

FTIR spectrometers can be single-beam or double-beam instruments. Figure 16-8 shows the optics of a basic single-beam spectrometer, which sells in the range of \$15,000 to \$25,000. A typical procedure for determining transmittance or absorbance with this type of instrument is to first obtain a reference interferogram by scanning a reference (usually air) twenty or thirty times, coadding the data, and storing the results in the memory of the instrument computer (usually after transforming it to the spectrum). A sample is then inserted in the radiation path and the process repeated. The ratio of sample and reference spectral data is then computed to give the transmittance at various frequencies. From this ratio the absorbance is calculated as a function of wavenumber. Ordinarily, modern IR sources and detectors are sufficiently stable so that reference spectra need to be obtained only occasionally.

A double-beam spectrometer is illustrated in Figure 16-9. The mirrors directing the interferometer beam through the sample and reference cells are oscillated rapidly compared to the movement of the interferometer mirror so that sample and reference information can be obtained at each mirror position. The double-beam design compensates for source and detector drifts.

Performance Characteristics of Commercial Instruments

A number of instrument manufacturers offer several models of FTIR instruments. The least expensive has a range of 7800 to 350 cm^{-1} (1.3 to $29\text{ }\mu\text{m}$) with a resolution of a few wavenumbers. This performance can be obtained with a scan time as brief as 1 second. More expensive instruments with interchangeable beamsplitters, sources, and transducers offer expanded frequency ranges and higher resolutions. For example, one instrument is reported to produce spectra from the far-IR (10 cm^{-1} or $1000\text{ }\mu\text{m}$) through the visible region to $50,000\text{ cm}^{-1}$, or 200 nm .



Simulation: Learn more about **IR instrumentation** at www.tinyurl.com/skoogpia7

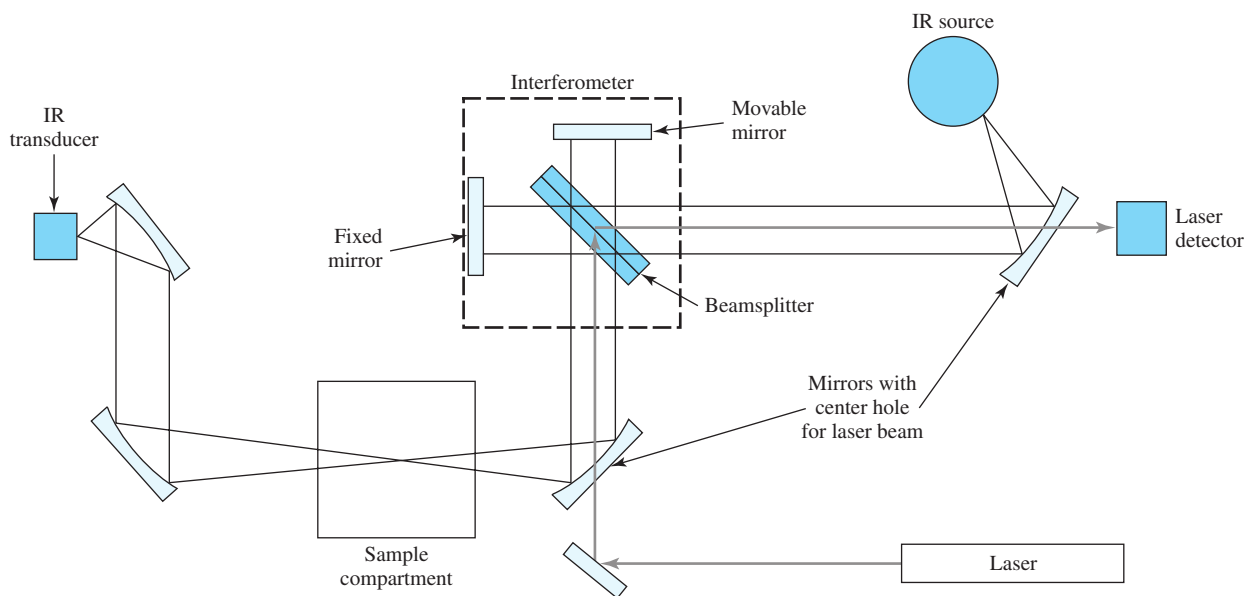


FIGURE 16-8 Single-beam FTIR spectrometer. In one arm of the interferometer, the IR source radiation travels through the beamsplitter to the fixed mirror, back to the beamsplitter, and through the sample to the IR transducer. In the other arm, the IR source radiation travels to the beamsplitter, is reflected to the movable mirror, and travels back through the beamsplitter to the sample and to the transducer. When the two beams meet again at the beamsplitter, they can interfere with each other if the phase difference (path difference) is appropriate. A plot of the signal versus mirror displacement is the interferogram. The interferogram contains information about all the frequencies present. The spectrum, intensity versus wavenumber, is the FT of the interferogram. It can be calculated with a computer from the signal versus mirror displacement. An empty sample compartment allows the reference spectrum to be calculated. Next, the sample is placed in the sample compartment and the sample spectrum is obtained. The absorbance is then calculated at each wavenumber from the ratio of the sample intensity to the reference intensity.

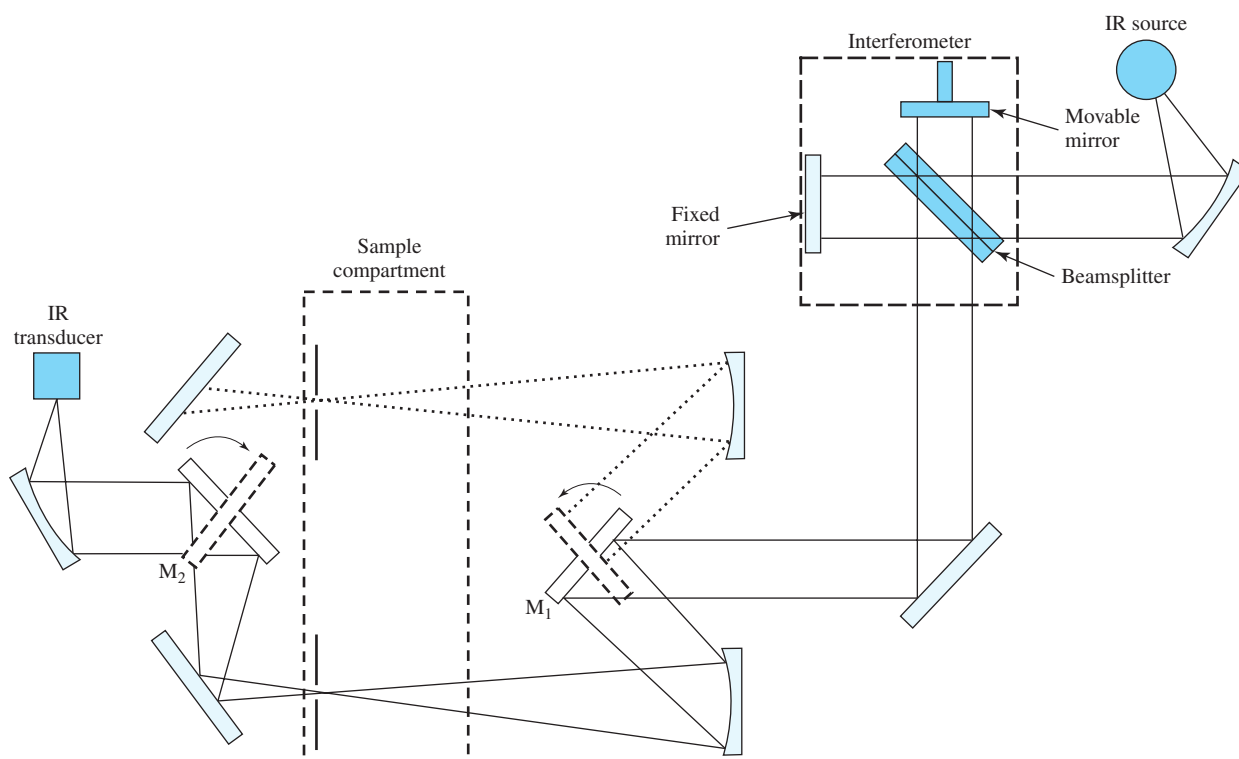


FIGURE 16-9 Double-beam FTIR spectrometer. The beam emerging from the interferometer strikes mirror M_1 , which in one position directs the beam through the reference cell and in the other position directs it through the sample cell. Mirror M_2 , which is synchronized to M_1 , alternately directs the reference beam and the sample beam to the transducer.

Resolutions for commercial instruments vary from 8 to less than 0.01 cm^{-1} . Several minutes are required to obtain a complete spectrum at the highest resolution.

Advantages of FT Spectrometers

Over most of the mid-IR spectral range, FT instruments have signal-to-noise ratios that are better than those of a good-quality dispersive instrument, usually by more than an order of magnitude. The enhanced signal-to-noise ratio can, of course, be traded for rapid scanning, with good spectra being attainable in a few seconds in most cases. Interferometric instruments are also characterized by high resolutions ($<0.1\text{ cm}^{-1}$) and highly accurate and reproducible frequency determinations. The latter property is particularly helpful when spectra are to be subtracted for background correction.

Another advantage of FT instruments is that their optics provide a much larger energy throughput (one to two orders of magnitude) than do dispersive instruments, which are limited in throughput by the need for narrow slit widths. The potential gain in throughput, however, may be partially offset by the lower sensitivity of the fast-response detector required for the interferometric measurements. Finally, it should be noted that the interferometer is free from the problem of stray radiation because each IR frequency is, in effect, chopped at a different frequency.

FTIR instruments have advantages over dispersive instruments in all areas of chemistry, particularly for (1) very high-resolution work that is encountered with gaseous mixtures having complex spectra resulting from the superposition of vibrational and rotational bands, (2) the study of samples with high absorbances, (3) the study of substances with weak absorption bands (for example, the study of compounds that are chemisorbed on catalyst surfaces), (4) investigations requiring fast scanning such as kinetic studies or detection of chromatographic effluents, (5) collecting IR data from very small samples, (6) obtaining reflection spectra, and (7) IR emission studies.

16B-2 Dispersive Instruments

Although nearly all instruments produced today are FT systems, many dispersive spectrophotometers are still found in laboratories. Dispersive IR spectrophotometers are generally double-beam, recording instruments, which use reflection gratings for dispersing radiation. As was pointed out in Section 13D-2, the double-beam design is less demanding with respect to 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).

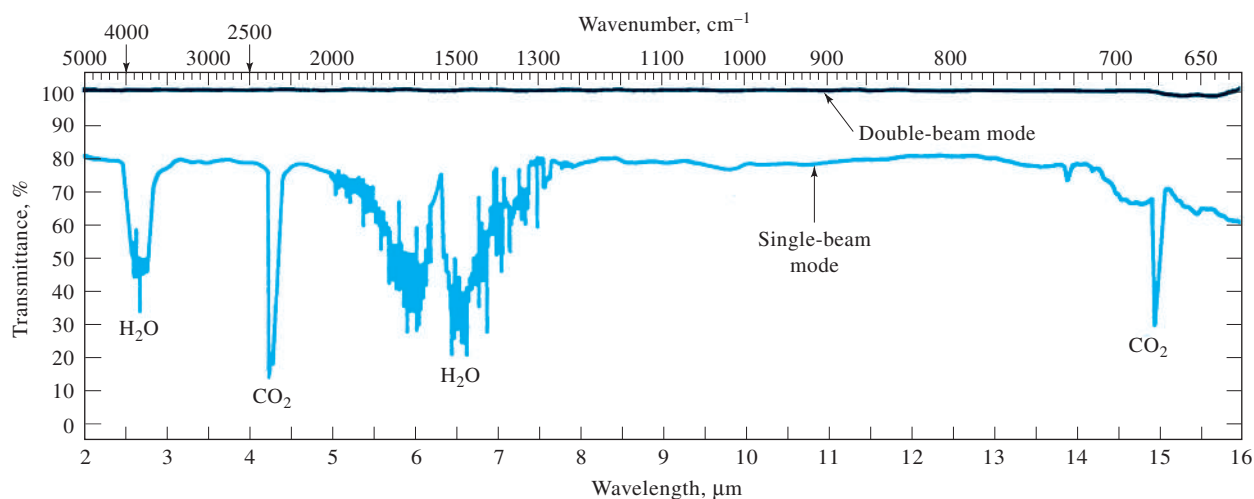


FIGURE 16-10 Single- and double-beam spectra of atmospheric water vapor and CO_2 . In the lower, single-beam trace, the absorption of atmospheric gases is apparent. The top, double-beam spectrum shows that the reference beam compensates very well for this absorption and allows for a stable 100% T baseline 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.)

An additional reason for the general use of double-beam instruments in the IR region is shown in Figure 16-10. The lower curve reveals that atmospheric water and carbon dioxide absorb radiation in some important spectral regions and can cause serious interference problems. The upper curve shows that the reference beam compensates nearly perfectly for absorption by both compounds. A stable 100% T baseline results.

Generally, dispersive IR spectrophotometers incorporate a low-frequency chopper (five to thirty cycles per second) that 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. Low chopping rates are demanded by the slow response times of the IR transducers used in most dispersive instruments. In general, the optical designs of dispersive instruments do not differ greatly from the double-beam UV-visible spectrophotometers discussed in the previous chapter except that the sample and reference compartments are always located between the source and the monochromator in IR instruments. This arrangement is possible because IR radiation, in contrast to UV-visible, is not sufficiently energetic to cause photochemical decomposition of the sample. Placing the sample and reference before the monochromator, however, has the advantage that most scattered radiation and IR emission, generated within the cell compartment, is effectively removed by the monochromator and thus does not reach the transducer.

Figure 16-11 shows schematically the arrangement of components in a typical IR spectrophotometer. Like many inexpensive dispersive IR instruments, it is an optical null type,

in which the radiant power of the reference beam is reduced, or attenuated, to match that of the beam passing through the sample. Attenuation is accomplished by imposing a device that removes a continuously variable fraction of the reference beam. The attenuator commonly takes the form of a comb, the teeth of which are tapered so that there is a linear relationship between the lateral movement of the comb and the decrease in power of the beam. Movement of the comb occurs when a difference in power of the two beams is sensed by the detection system. Most dispersive IR instruments are older instruments that use mechanical recorders instead of computers. For such instruments, the comb movement is synchronized with the recorder pen so that its position gives a measure of the relative power of the two beams and thus the transmittance of the sample.

Note that three types of systems link the components of the instrument in Figure 16-11: (1) a radiation linkage indicated by dashed lines, (2) a mechanical linkage shown by thick dark lines, and (3) an electrical connection shown by narrow solid lines.

Radiation from the source is split into two beams, half passing into the sample-cell compartment and the other half into the reference area. The reference beam then passes through the attenuator and on to a chopper. The chopper consists of a motor-driven disk that alternately reflects the reference or transmits the sample beam into the monochromator. After dispersion by a prism or grating, the alternating beams fall on the transducer and are converted to an electrical signal. The signal is amplified and passed to the synchronous rectifier, a device that is mechanically or electrically coupled to the chopper to cause

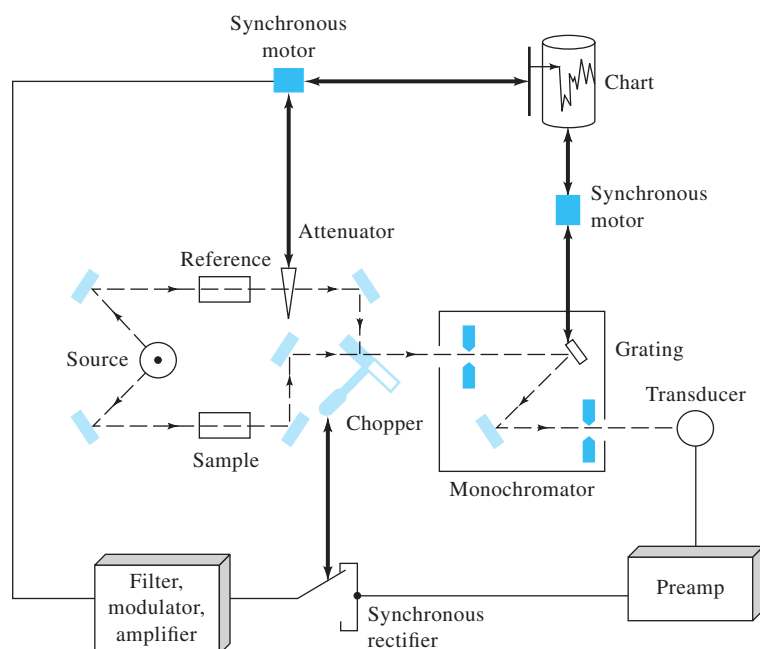


FIGURE 16-11 Schematic diagram of a double-beam, dispersive IR spectrophotometer. The heavy black lines indicate mechanical linkages, and the light lines indicate electrical connections. The radiation path is designated by dashed lines.

the rectifier switch and the beam leaving the chopper to change simultaneously. If the two beams are identical in power, the signal from the rectifier is constant direct current. If, on the other hand, the two beams differ in power, a fluctuating, or ac, current is produced, the phase of which is determined by which beam is the more intense. The current from the rectifier is filtered and further amplified to drive a synchronous motor in one direction or the other, depending on the phase of the input current. The synchronous motor is mechanically linked to both the attenuator and the pen drive of the recorder and causes both to move until a null balance is achieved. A second synchronous motor simultaneously drives the chart and varies the wavelength. Frequently, a mechanical linkage between the wavelength and slit drives varies the slit width to keep the radiant power reaching the detector approximately constant.

The reference-beam attenuator system, such as the one just described, creates three limitations to the performance of dispersive IR instruments. First, the response of the attenuator system always lags behind the transmittance changes, particularly in scanning regions where the signal is changing most rapidly. Second, the momentum associated with both the mechanical attenuator and the recorder system may result in the pen drive overshooting the true transmittance. Third, in regions where the transmittance approaches zero, almost no radiation reaches the transducer, and the exact null position cannot be established accurately. The result is sluggish transducer response and rounded peaks. Figure 16-12

illustrates transmittance overshoot and rounded peaks in regions of low transmittance (1700 and 3000 cm^{-1}).

16B-3 Nondispersive Instruments

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

Filter Photometers

Figure 16-13 shows a schematic diagram of a portable, IR filter photometer designed for quantitative analysis of various substances in the atmosphere.⁹ Different models are available that are factory calibrated for 1, 5, 30, or more than 100 gases. The instrument is computer controlled. For many compounds, fixed bandpass filters of 1.8, 3.3, 3.6, 4.0, 4.2, 4.5, 4.7, 8, 11, and 14 μm can be used. A continuously variable filter, which transmits in the range between about 7.7 and 14.1 μm

⁹See P. A. Wilks, *Amer. Lab.*, **1994** (12), 44; *Proc. Control Qual.*, **1992**, 3, 283.

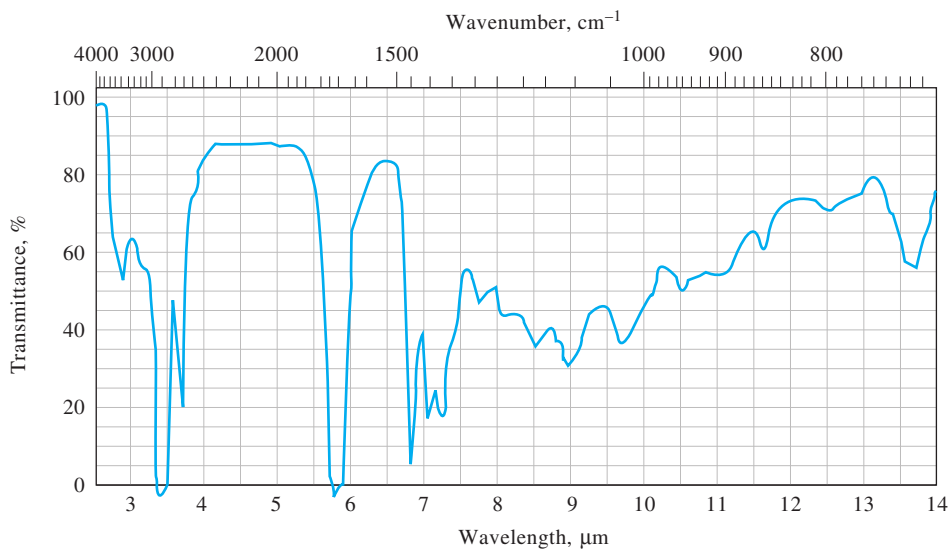


FIGURE 16-12 IR spectrum of *n*-hexanal illustrating overshoot at low %T.

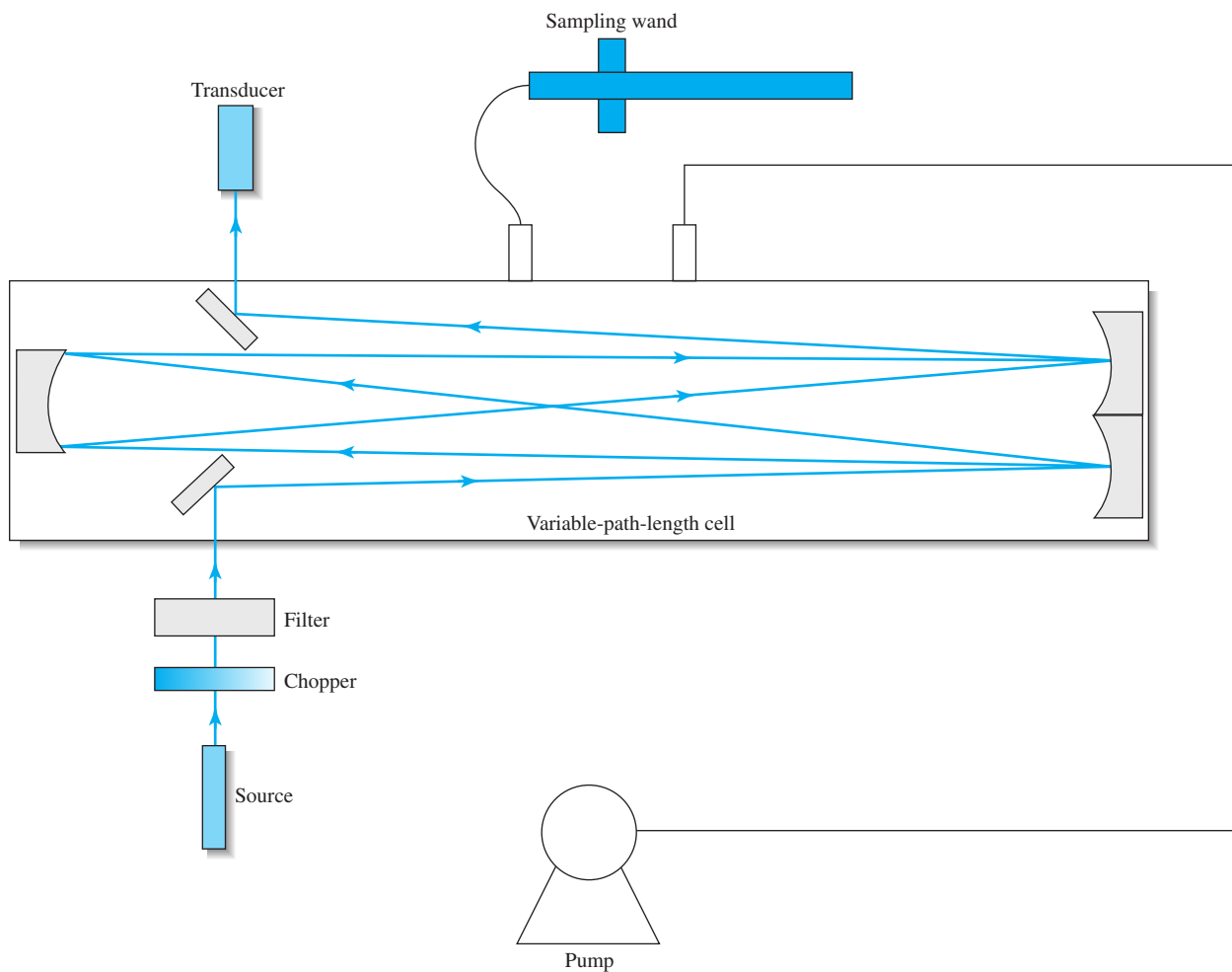


FIGURE 16-13 A portable IR photometer designed for gas analysis. The sample is introduced into the cell by means of a pump. The path length can be changed by altering the number of mirror reflections. (Courtesy of Thermo Fisher Scientific, Waltham, MA.)

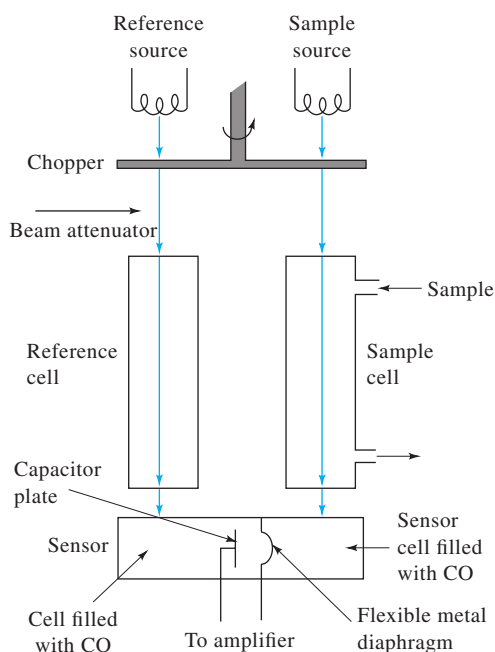


FIGURE 16-14 A nondispersive IR photometer for monitoring CO.

(1300 to 710 cm^{-1}), can also be used for selecting alternative wavelengths or for spectral scanning applications. The source is a nichrome-wire filament, and the transducer is a pyroelectric device (see Section 16C for descriptions of sources and transducers).

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.

A recently designed filter IR instrument has been reported for determination of CO_2 in industrial settings. The estimated limit of detection was 1 ppm.¹⁰

Photometers without Filters

Photometers, which have no wavelength-restricting device, are widely used to monitor gas streams for a single component.¹¹ Figure 16-14 shows a typical nondispersive instrument designed to determine carbon monoxide (CO) in a gaseous

mixture. The reference cell is a sealed container filled with a nonabsorbing gas; as shown in the figure, the sample flows through a second cell that is of similar length. The chopper blade is so arranged that the beams from identical sources are chopped simultaneously at the rate of about five times per second. 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 amplifier output drives a servomotor that moves the beam attenuator into the reference beam until the two compartments are again at the same temperature. The instrument thus operates as a null balance device. The chopper serves to provide an ac signal, which is less sensitive to drift and $1/f$ noise.

This type of instrument is highly selective because heating of the sensor gas occurs only from that narrow portion of the spectrum of radiation absorbed by the CO in the sample. The device can be adapted to the determination of any IR-absorbing gas (e.g., CO_2 , NO, or H_2S).¹²

Filter Correlation Analyzers

As shown in Figure 16-15, filter correlation analyzers use a rotating gas filter through which the IR beam passes. The filter has two compartments, one for the gas of interest and the other for a nonabsorbing gas such as nitrogen. When the gas of interest is in the beam, it selectively attenuates the IR source to produce a reference beam. The sample beam is produced by the transparent gas. Typically, the IR source is chopped at a fairly high frequency (360 Hz) whereas the filter rotates at a fairly low frequency (30 Hz). A modulated signal is produced that is related to the concentration of the analyte gas.

Filter correlation analyzers are available for such gases as CO_2 and CO. They can be set up to detect trace levels (<0.1 ppm) or higher amounts. The analyzers are calibrated by constructing a working curve by dilution of a gas standard.

¹⁰See J. Hodgkinson et al., *Sens. Actuators B*, **2013**, 186, 580, DOI: 10.1016/j.snb.2013.06.006.

¹¹For the determination of CO in cigarette smoke, see *Appl. Spectrosc.*, **2006**, 60, 272, DOI: 10.1366/000370206776342616.

¹²For CO_2 in seawater, see *Marine Chemistry*, **2006**, 100, 24, DOI: 10.1016/j.marchem.2005.10.009; for NO in cigarette smoke, see reference 11; for H_2S in acidic alkylamine gas streams, see *Hydrocarbon Processing*, **2009**, 88 (February, issue 2), 73.

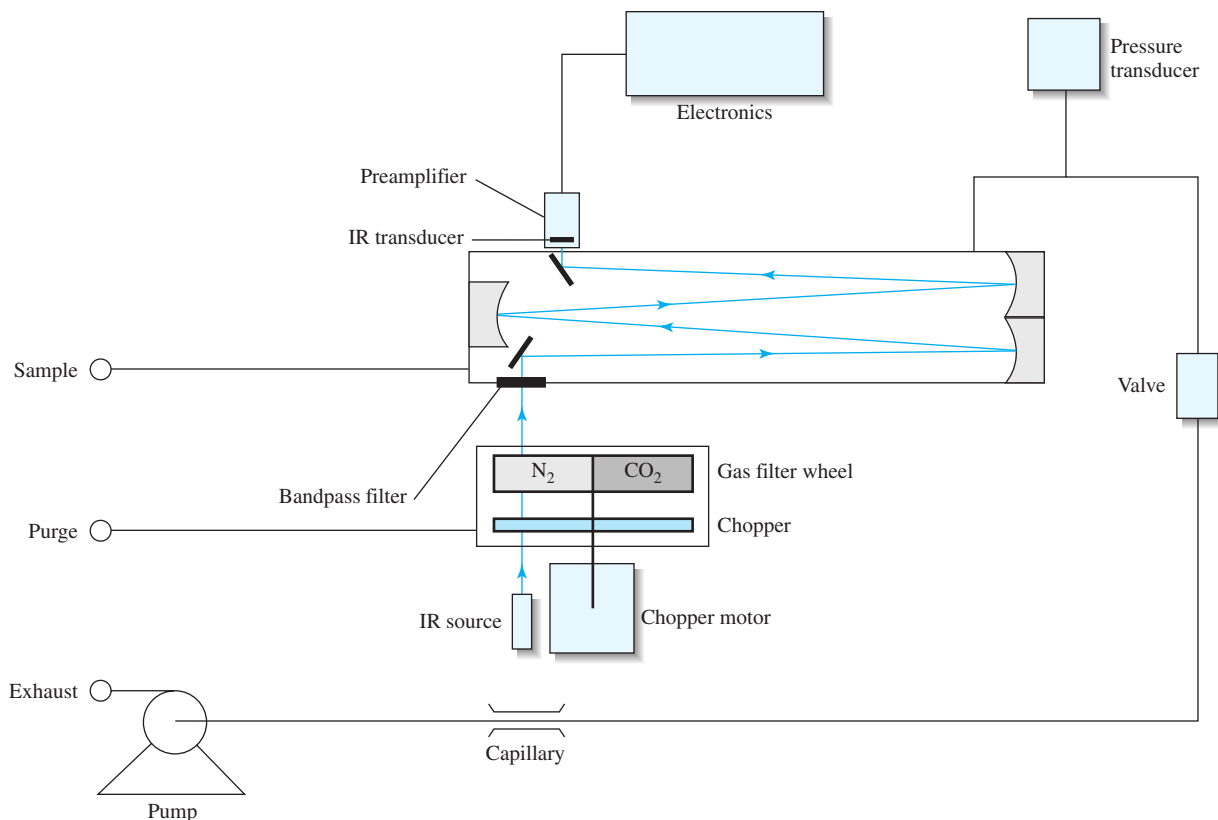


FIGURE 16-15 An IR filter correlation analyzer for determining CO_2 . The sample is drawn into the sample cell by a pump. The chopped IR source radiation (360 Hz) alternates between the N_2 and CO_2 sides of the filter wheel, which rotates at 30 Hz. The CO_2 side provides a reference beam that cannot be further attenuated by CO_2 in the sample cell. The N_2 side produces the sample beam by allowing the IR radiation to pass through to the cell where it can be attenuated by CO_2 in the sample. The modulated amplitude of the chopped detector signal is related to the CO_2 concentration in the sample. Other gases do not modulate the detector signal because they absorb the reference and sample beams equally. (Courtesy of Thermo Fisher Scientific Inc., Waltham, MA.)

16C IR SOURCES AND TRANSDUCERS

Instruments for measuring IR absorption all require a source of continuous IR radiation and an IR transducer. The desirable characteristics of these instrument components were listed in Sections 7B and 7E. In this section we describe sources and transducers that are found in modern IR instruments.

16C-1 Sources

IR sources consist of an inert solid that is heated electrically to a temperature between 1500 and 2200 K. These sources produce continuum radiation approximating that of a blackbody (see Figure 6-22). The maximum radiant intensity at these temperatures occurs between 5000 and 5900 cm^{-1} (2 and $1.7\text{ }\mu\text{m}$). At longer wavelengths, the intensity falls off smoothly until it is about 1% of the maximum at 670 cm^{-1} ($15\text{ }\mu\text{m}$). On the short wavelength side, the decrease is much more rapid, and a similar reduction in intensity is observed at about $10,000\text{ cm}^{-1}$ ($1\text{ }\mu\text{m}$).

The Nernst Glower

The Nernst glower is composed of rare earth oxides formed into a cylinder having a diameter of 1 to 3 mm and a length of 2 to 5 cm. Platinum leads are sealed to the ends of the cylinder to permit electrical connections to what amounts to a resistive heating element. As current passes through the device, its temperature increases to between 1200 K and 2200 K. The Nernst glower has a large negative temperature coefficient of electrical resistance, and it must be heated externally to a dull red heat before the current is large enough to maintain the desired temperature. Because the resistance decreases with increasing temperature, the source circuit must be designed to limit the current or the glower rapidly becomes so hot that it is destroyed.

Figure 16-16 shows the spectral output of a Nernst glower operated at approximately 2200 K. Note that the overall curve shape is similar to that of a blackbody. The small peaks and depressions are a function of the chemical composition of the device.

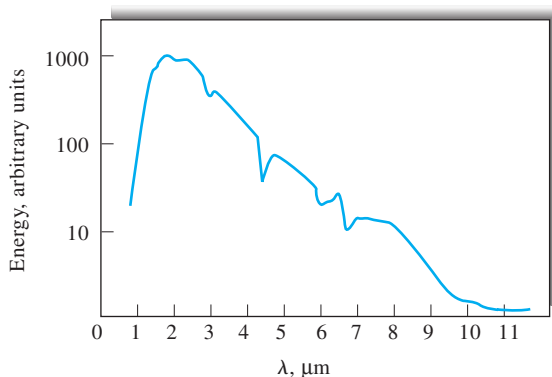


FIGURE 16-16 Spectral distribution of energy from a Nernst glower operated at approximately 2200 K.

The Global

A Global is a ceramic rod, usually silicon carbide or a composite material, electrically heated to more than 1000 K. Older dispersive instruments used Globals that were heated as high as 1500 K to provide sufficient intensity. The sensitivity of modern FTIR instruments has meant that lower source temperatures (1000 to 1300 K) can be used, resulting in longer source lifetimes.

Global sources for FTIR must be temperature controlled for high stability. Some simple sources in older instruments used a fan to provide air cooling, but water cooling is more effective. The Global has the advantage of a positive temperature coefficient of resistance that makes it possible to control temperature electronically. The most stable sources, therefore, use electronic temperature control, which eliminates the inconvenience and temperature fluctuations of circulating water. Electronic temperature control is also said to increase the source lifetime. Spectral energies of the Global and Nernst glower are similar, except in the region below 5 μm , where the Global is significantly more intense. Spectral energies of the Global and the Nernst glower are comparable except in the region below 5 μm , where the Global provides a significantly greater output.

Incandescent Wire Source

A source with somewhat lower intensity but with longer life than the Global or Nernst glower is a tightly wound spiral of nichrome wire heated to about 1100 K by an electrical current. A rhodium wire heater sealed in a ceramic cylinder has similar properties, although it is more expensive. Nichrome wire sources are less intense than many IR sources. However, the incandescent wire source requires no cooling and is nearly maintenance free. For this reason, the nichrome wire source is often used where reliability is paramount, such as in process analyzers.

The Mercury Arc

For the far-IR region of the spectrum ($\lambda > 50 \mu\text{m}$), none of the thermal sources just described provides sufficient radiant power for convenient detection. In this region, a high-pressure mercury arc is often used. This device consists of a quartz-jacketed tube containing mercury vapor at a pressure greater than

1 atmosphere. When an electric current passes through the vapor, an internal plasma is formed that provides continuum radiation in the far-IR region.

The Tungsten Filament Lamp

An ordinary tungsten filament lamp is a convenient source for the near-IR region of 4000 to 12,800 cm^{-1} (2.5 to 0.78 μm).

The Carbon Dioxide Laser Source

A tunable carbon dioxide laser is used as an IR source for monitoring the concentrations of certain atmospheric pollutants and for determining absorbing species in aqueous solutions.¹³ A carbon dioxide laser produces a band of radiation in the range of 900 to 1100 cm^{-1} (11 to 9 μm), which consists of about 100 closely spaced discrete lines. As described in Section 7B-3, any one of these lines can be chosen by tuning the laser. Although the range of wavelengths available is limited, the region from 900 to 1100 cm^{-1} is one particularly rich in absorption bands arising from the interactive stretching modes of CO_2 . Thus, this source is useful for quantitative determination of a number of important species such as ammonia, butadiene, benzene, ethanol, nitrogen dioxide, and trichloroethylene. An important property of the laser source is the radiant power available in each line, which is several orders of magnitude greater than that of blackbody sources.

Carbon dioxide lasers are widely used in remote-sensing applications such as light detection and ranging (lidar). The operating principle of lidar is similar to that of radar. The lidar system transmits radiation out to a target where it interacts with and is altered by the target. Some of the radiation is then reflected back to the lidar instrument where it is analyzed and used to obtain information about the target. By means of lidar, distance, speed, rotation, chemical composition, and concentration of remote targets can be obtained.

Semiconductor IR Laser Sources

Tunable semiconductor lasers have also been used as sources (see Section 7B-3 for a description of these devices) in the near- and mid-IR regions. As an example, the Sample Analysis at Mars (SAM) experiment on the Mars rover Curiosity's Science Laboratory uses a tunable diode laser spectrometer in the 2.78 μm region to detect carbon, hydrogen, and oxygen in the Martian environment and to determine their isotopic ratios. A quantum cascade tunable laser is used to detect methane by scanning across several of its rotational lines in the 3.3 μm region. Both lasers are used in Curiosity's two-channel tunable laser spectrometer (TLS) that can achieve a spectral resolution of 0.00002 cm^{-1} . Methane is determined by the difference in

¹³See A. A. Demidov, in *Introduction to Laser Spectroscopy*, 2nd ed., D. L. Andrews and A. A. Demidov, eds., New York: Kluwer Academic/Plenum Press, 2002; Z. Zelinger, M. Strizik, P. Kubat, and S. Civis, *Anal. Chim. Acta*, **2000**, 422, 179, DOI: 10.1016/S0003-2670(00)01069-2; P. L. Meyer, M. W. Sigrist, *Rev. Sci. Instrum.*, **1990**, 61, 1779, DOI: 10.1063/1.1141097.

the absorption signals obtained from a closed sample cell filled with the Mars atmosphere and the same cell evacuated by means of a turbo-molecular pump. How much of the methane detected arises from a chemical source in the Martian atmosphere and how much comes from the rover itself remains an open question.

16C-2 IR Transducers

IR transducers are of three general types: (1) pyroelectric transducers, (2) photoconducting transducers, and (3) thermal transducers. The first is found in photometers, many FTIR spectrometers, and dispersive spectrophotometers. Photoconducting transducers are also found in FTIR instruments. Thermal detectors are found in older dispersive instruments but are too slow to be used in FTIR spectrometers.

Pyroelectric Transducers

Pyroelectric transducers are constructed from single crystalline wafers of pyroelectric materials, which are insulators (dielectric materials) with very special thermal and electrical properties. Triglycine sulfate $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$ (usually deuterated, DTGS, and often with a fraction of the glycines replaced with alanine, DLaTGS), is the most important pyroelectric material used for IR detection systems.

When an electric field is applied across any dielectric material, polarization takes place, with the magnitude of the polarization being a function of the dielectric constant of the material. For most dielectrics, this induced polarization rapidly decays to zero when the external field is removed. Pyroelectric substances, in contrast, retain a strong temperature-dependent polarization after removal of the field. Thus, by sandwiching the pyroelectric crystal between two electrodes, one of which is IR transparent, a temperature-dependent capacitor is produced. Changing its temperature by irradiating it with IR radiation alters the charge distribution across the crystal, which can be detected as a current in an external electrical circuit connecting the two sides of the capacitor. The magnitude of this current is proportional to the surface area of the crystal and the rate of change of polarization with temperature. Pyroelectric crystals lose their residual polarization when they are heated to a temperature called the *Curie point*. For triglycine sulfate, the Curie point is 47°C.

Pyroelectric transducers exhibit response times that are fast enough to allow them to track the changes in the time-domain signal from an interferometer. For this reason, many FTIR spectrometers for the mid-IR region use this type of transducer.

Photoconducting Transducers

IR photoconducting transducers consist of a thin film of a semiconductor material, such as lead sulfide, mercury telluride–cadmium telluride (MCT), or indium antimonide, deposited on a nonconducting glass surface and sealed in an evacuated envelope

to protect the semiconductor from the atmosphere. Absorption of radiation by these materials promotes nonconducting valence electrons to a higher energy–conducting state, thus decreasing the electrical resistance of the semiconductor. Typically, a photoconductor is placed in series with a voltage source and load resistor, and the voltage drop across the load resistor serves as a measure of the power of the beam of radiation.

A lead sulfide photoconductor is the most widely used transducer for the near-IR region of the spectrum from 10,000 to 333 cm^{-1} (1 to 3 μm). It can be operated at room temperature. For mid- and far-IR radiation, MCT photoconductor transducers are used. They must be cooled with liquid nitrogen (77 K) to minimize thermal noise. The long-wavelength cutoff, and many of the other properties of these transducers, depend on the ratio of the mercury telluride to cadmium telluride, which can be varied continuously.

The MCT transducer is faster and more sensitive than the DTGS transducer discussed in the previous section. For this reason, the MCT transducer also finds widespread use in FTIR spectrometers, particularly those requiring fast response times, such as spectrometers interfaced to gas chromatographs and those intended for kinetic measurements.

Thermal Transducers

Thermal transducers, whose responses depend on the heating effect of radiation, are found in older dispersive spectrometers for detection of all but the shortest IR wavelengths. With these devices, the radiation is absorbed by a small blackbody and the resultant temperature rise is measured. The radiant power level from a spectrophotometer beam is minute (10^{-7} to 10^{-9} W), so that the heat capacity of the absorbing element must be as small as possible if a detectable temperature change is to be produced. Under the best of circumstances, temperature changes are confined to a few thousandths of a kelvin.

The problem of measuring IR radiation by thermal means is compounded by thermal noise from the surroundings. For this reason, thermal transducers are housed in a vacuum and carefully shielded from thermal radiation emitted by other nearby objects. To further minimize the effects of extraneous heat sources, the beam from the source is always chopped. In this way, the analyte signal, after transduction, has the frequency of the chopper and can be separated electronically from extraneous noise signals, which are ordinarily broad band or vary only slowly with time.

Thermocouples. In its simplest form, a thermocouple consists of a pair of junctions formed when two pieces of a metal such as bismuth are fused to each end of a dissimilar metal such as antimony. A potential difference between the two junctions varies with their difference in temperature.

The transducer junction for IR radiation is formed from very fine wires or alternatively by evaporating the metals onto a nonconducting support. In either case, the junction is usually

blackened (to improve its heat-absorbing capacity) and sealed in an evacuated chamber with a window that is transparent to IR radiation. The response time is typically about 30 ms.

The reference junction, which is usually housed in the same chamber as the active junction, is designed to have a relatively large heat capacity and is carefully shielded from the incident radiation. Because the analyte signal is chopped, only the difference in temperature between the two junctions is important; therefore, the reference junction does not need to be maintained at constant temperature. To enhance sensitivity, several thermocouples may be connected in series to produce a *thermopile*.

Bolometers. A bolometer is a type of resistance thermometer constructed of strips of metals, such as platinum or nickel, or from a semiconductor. This type of semiconductor device is sometimes called a *thermistor*. Semiconductor materials exhibit a relatively large change in resistance as a function of temperature. The responsive element in a bolometer is kept small and blackened to absorb the radiant heat. Bolometers are not so extensively used as other IR transducers for the mid-IR region. However, a germanium bolometer, operated at 1.5 K, is an excellent transducer for radiation in the range of 5 to 400 cm^{-1} (2000 to 25 μm). The response time is a few milliseconds.

QUESTIONS AND PROBLEMS

*Answers are provided at the end of the book for problems marked with an asterisk.

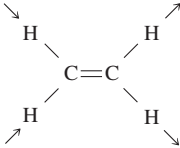
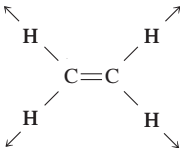
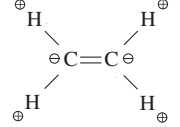
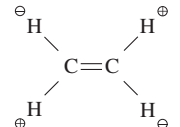


Problems with this icon are best solved using spreadsheets.

- * 16-1 The IR spectrum of CO shows a vibrational absorption band centered at 2170 cm^{-1} .
 - (a) What is the force constant for the CO bond?
 - (b) At what wavenumber would the corresponding peak for ^{14}CO occur?
- * 16-2 Gaseous HCl exhibits an IR absorption at 2890 cm^{-1} due to the hydrogen-chlorine stretching vibration.
 - (a) Calculate the force constant for the bond.
 - (b) Calculate the wavenumber of the absorption band for DCl assuming the force constant is the same as that calculated in part (a).
- 16-3 Calculate the absorption frequency corresponding to the —C—H stretching vibration treating the group as a simple diatomic C—H molecule with a force constant of $k = 5.0 \times 10^2 \text{ N/m}$. Compare the calculated value with the range found in correlation charts (such as the one shown in Figure 17-6). Repeat the calculation for the deuterated bond.
- 16-4 The force constant of the NO bond is approximately $1.53 \times 10^3 \text{ N/m}$. Treating the NO group as a simple diatomic molecule, calculate the absorption frequency in Hz and the wavelength and wavenumber of the fundamental absorption. How does this compare to the experimental value found for NO and NO dimers by Varetti, E. L.; Pimentel, G. C., *J. Chem. Phys.*, **1971**, *55*, 3813, DOI: 10.1063/1.1676666.
- * 16-5 The wavelength of the fundamental O—H stretching vibration is about 3.0 μm . What is the approximate wavenumber and wavelength of the first overtone band for the O—H stretch?
- * 16-6 The wavelength of the first overtone of the N—H stretching vibration is about 1.5 μm . What is the approximate wavenumber and wavelength of the fundamental band for the N—H stretch?
- * 16-7 Sulfur dioxide is a nonlinear molecule. How many vibrational modes will this compound have? How many IR absorption bands would sulfur dioxide be expected to have?

QUESTIONS AND PROBLEMS (continued)

* 16-8 Indicate whether the following vibrations are active or inactive in the IR spectrum.

Molecule	Motion
(a) CH ₃ —CH ₃	C—C stretching
(b) CH ₃ —CCl ₃	C—C stretching
(c) SO ₂	Symmetric stretching
(d) CH ₂ =CH ₂	C—H stretching:
	
(e) CH ₂ =CH ₂	C—H stretching:
	
(f) CH ₂ =CH ₂	CH ₂ wag:
	
(g) CH ₂ =CH ₂	CH ₂ twist:
	

16-9 What are the major advantages of an FTIR spectrometer compared with a dispersive instrument?



16-10 What length of mirror drive in an FTIR spectrometer would be required to provide a resolution of

(a) 0.010 cm⁻¹, (b) 0.50 cm⁻¹, and (c) 2.0 cm⁻¹?

* 16-11 It was stated that at room temperature (25°C) the majority of molecules are in the ground vibrational energy level ($\nu = 0$).

(a) Use the Boltzmann equation (Equation 8-1) to calculate the excited-state and ground-state population ratios for HCl: $N(\nu = 1)/N(\nu = 0)$. The fundamental vibrational frequency of HCl occurs at 2885 cm⁻¹.

(b) Use the results of part (a) to find $N(\nu = 2)/N(\nu = 0)$

16-12 Why are nondispersive IR instruments often used for the determination of gases rather than dispersive IR spectrometers?

16-13 The first FTIR instruments used three different interferometer systems. Briefly, describe how it has been possible to simplify the optical systems in more contemporary instruments.

* 16-14 In a particular trace analysis via FTIR, a set of sixteen interferograms were collected. The signal-to-noise ratio (S/N) associated with a particular spectral peak was approximately 4:1. How many interferograms would have to be collected and averaged if the goal is to obtain an $S/N = 20:1$?



- * **16-15** Radiation leaves a source at a natural frequency of (a) 9.10×10^{13} Hz. What is the wavenumber corresponding to this frequency? If a Michelson interferometer has a mirror velocity of 1.00 cm/s, what will the frequency be at the transducer. Find the wavenumber at the source and frequency at the transducer for source radiation of (b) 9.20×10^{13} Hz and (c) 9.30×10^{13} Hz.

Challenge Problem

- 16-16 (a)** The IR spectrum of gaseous N_2O shows three strong absorption bands at 2224 cm^{-1} , 1285 cm^{-1} , and 2089 cm^{-1} . In addition two quite weak bands are observed at 2563 cm^{-1} and 2798 cm^{-1} . It is known that N_2O is a linear molecule, but assume it is not known whether the structure is $\text{N}-\text{N}-\text{O}$ or $\text{N}-\text{O}-\text{N}$. Use the IR data to decide between the two structures. What vibrations can be assigned to the strong absorption bands? What are possible causes of the weak absorptions?
- (b)** The IR spectrum of HCN shows three strong absorption bands at 3312 cm^{-1} , 2089 cm^{-1} , and 712 cm^{-1} . From this information alone, can you deduce whether HCN is linear or nonlinear? Assuming that HCN is linear, assign vibrations to the three absorption bands.
- (c)** How many fundamental vibrational modes are expected for BF_3 ? Which of these are expected to be IR active? Why? Sketch the vibrations.
- (d)** How many fundamental vibrational modes would you predict for (1) methane, (2) benzene, (3) toluene, (4) ethylene, and (5) carbon tetrachloride?

Applications of Infrared Spectrometry

Infrared (IR) absorption spectrometry is a versatile tool that is applied to the qualitative and quantitative determination of molecular species of all types. In this chapter we first focus on the uses of mid-IR absorption and reflection spectrometry for structural investigations of molecular compounds, particularly organic compounds and species of interest in biochemistry. We then examine several of the other applications of IR spectroscopy, including photoacoustic IR, near- and far-IR spectroscopy, IR emission, and IR microscopy.

As shown in Table 17-1, the applications of IR spectrometry fall into three major categories based on the three IR spectral regions. The most widely used region is the mid-IR, which extends from about 670 to 4000 cm^{-1} (2.5 to $14.9\text{ }\mu\text{m}$). In this region, absorption, reflection, and emission spectra are used for both qualitative and quantitative analysis. The near-IR region, from 4000 to $14,000\text{ cm}^{-1}$ (0.75 to $2.5\text{ }\mu\text{m}$), also finds considerable use for the routine quantitative determination of certain species, such as water, carbon dioxide, sulfur, low-molecular-mass hydrocarbons, amine nitrogen, and other compounds of interest in agriculture and in industry. These determinations are often based on diffuse-reflectance measurements of untreated solid or liquid samples or absorption studies of gases. The primary use of the far-IR region (15 to $1000\text{ }\mu\text{m}$) has been for the determination of the structures of inorganic and metal-organic species based on absorption measurements.

17A MID-IR ABSORPTION 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

As we have seen in earlier chapters, ultraviolet (UV) and visible molecular spectra are obtained most conveniently from dilute solutions of the analyte. Absorbance measurements in the optimal range are obtained by suitably adjusting either the



Throughout this chapter, this logo indicates an opportunity for online self-study at www.tinyurl.com/skoogpia7, linking you to interactive tutorials, simulations, and exercises.

¹For further reading see R. M. Silverstein, F. X. Webster, D. Kiemle, and D. L. Bryce, *Spectrometric Identification of Organic Compounds*, 8th ed., Chap. 2, New York: Wiley, 2015; *Introduction to Experimental Infrared Spectroscopy: Fundamentals and Practical Methods*, M. Tasumi, ed., Chichester, UK: Wiley, 2015; P. Larkin, *Infrared and Raman Spectroscopy: Principles and Spectral Interpretation*, Waltham, MA: Elsevier, 2011; B. Schrader, *Infrared and Raman Spectroscopy*, New York: VCH, 1995; N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., San Diego: Academic Press, 1990.

TABLE 17-1 Major Applications of IR Spectrometry

Spectral Regions	Measurement Type	Kind of Analysis	Applicable Samples
Near-IR	Diffuse reflectance	Quantitative	Solid or liquid commercial materials
	Absorption	Quantitative	Gaseous mixtures
Mid-IR	Absorption	Qualitative	Pure solid, liquid, or gases
		Quantitative	Complex liquid, solid, or gaseous mixtures
		Chromatographic	Complex liquid, solid, or gaseous mixtures
Far-IR	Reflectance	Qualitative	Pure solids or liquids
	Emission	Quantitative	Atmospheric samples
	Absorption	Qualitative	Pure inorganic or organometallic species

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.² 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 (see Figure 16-13).

²See *Handbook of Spectroscopy*, G. Gauglitz and D. S. Moore, eds, Vol. 1, Section 1, Weinheim, Germany: Wiley-VCH, 2014; *Practical Sampling Techniques for Infrared Analysis*, P. B. Coleman, ed., Boca Raton, FL: CRC Press, 1993; T. J. Porro and S. C. Pattacini, *Spectroscopy*, **1993**, 8 (7), 40; *Ibid.*, 8 (8), 39; A. L. Smith, *Applied Infrared Spectroscopy*, New York: Wiley, 1979, Chap. 4.

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. Figure 17-1 lists several common solvents used for IR studies of organic compounds. This figure illustrates that no single solvent is transparent throughout the entire mid-IR region.

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. The spectrum of water is shown along with the spectrum of an aqueous solution of aspirin. The computer-calculated difference spectrum reveals the spectrum of the water-soluble aspirin. 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.

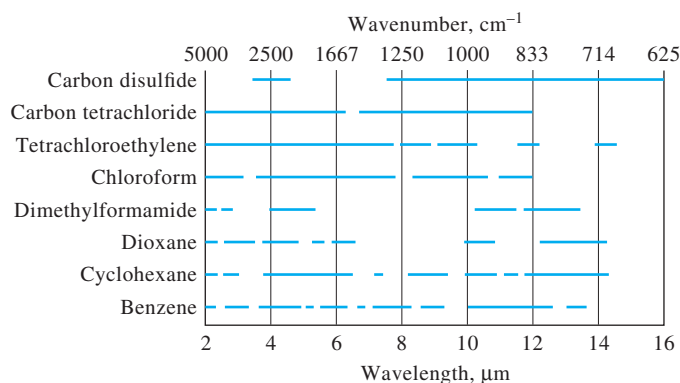


FIGURE 17-1 Solvents for IR spectroscopy. Horizontal lines indicate useful regions.