chapter**EIGHTEEN**

Raman Spectroscopy

When radiation passes through a transparent medium, the species present scatter a fraction of the beam in all directions (Section 6B-10). Raman scattering results from the same type of quantized vibrational changes associated with infrared (IR) absorption. Thus, the difference in wavelength between the incident and scattered visible radiation corresponds to wavelengths in the mid-IR region. Indeed, the Raman scattering spectrum and IR absorption spectrum for a given species often resemble one another quite closely. Although IR spectroscopy is still the more widely used vibrational spectroscopic tool, for several problems, **Raman spectroscopy** can provide more useful and selective information.

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.

In 1928 the Indian physicist C. V. Raman discovered that the visible wavelength of a small fraction of the radiation scattered by certain molecules differs from that of the incident beam and furthermore that the shifts in wavelength depend on the chemical structure of the molecules responsible for the scattering. Raman was awarded the 1931 Nobel Prize in physics for this discovery and for his systematic exploration of it.[1]

Although there can be striking similarities between Raman spectra and IR spectra, enough differences remain between the kinds of groups that are IR active and Raman active to make the techniques complementary rather than competitive. Water is quite useful as a solvent in Raman spectroscopy, which is a tremendous advantage of Raman over IR. In addition, because Raman scattering is usually measured in the visible or near-IR region, glass or quartz cells can be used, avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials. Despite these advantages, Raman spectroscopy was not widely used by chemists until laser sources in the 1960s made Raman spectra a good deal easier to obtain. In recent years, Raman spectroscopy has become a routine tool thanks to the laser, the array detector, and the availability of commercial instrumentation at moderate cost.

18A THEORY OF RAMAN SPECTROSCOPY

Raman spectra are acquired by irradiating a sample with a nearly monochromatic laser source in the visible or near-IR spectral region. During irradiation, the spectrum of the scattered radiation is measured at some angle (often 90°) with a suitable spectrometer. With the exception of Resonance Raman scattering, the excitation wavelength is usually well removed from an absorption band to minimize fluorescence. The Raman experiment was illustrated previously in Figure 6-18. At the very most, the intensities of Raman lines are 0.001% of the intensity of the

[1]For discussions of the theory and practice of Raman spectroscopy, see P. Vandenabeele, *Practical Raman Spectroscopy: An Introduction*, Chichester, UK: Wiley, 2013; E. Smith and G. Dent, *Modern Raman Spectroscopy: A Practical Approach*, Chichester, UK: Wiley, 2005; J. R. Ferraro, K. Nakamoto, and C. W. Brown, *Introductory Raman Spectroscopy*, 2nd ed., San Diego: Academic Press, 2003; R. L. McCreery, *Raman Spectroscopy for Chemical Analysis*, New York: Wiley, 2000.

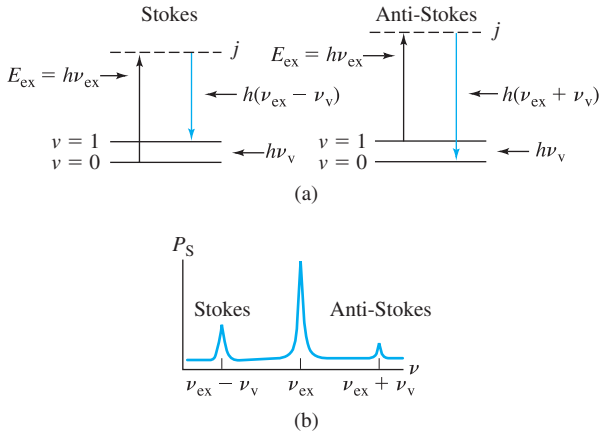

FIGURE 18-1 The origin of Raman spectra. In (a) radiation from a source that is incident on the sample produces scattering at all angles. The incident radiation causes excitation (a) to a virtual level *j* and subsequent reemission of a photon of lower (left) or higher (right) energy. The Raman spectrum (b) consists of lower-frequency emissions called Stokes scattering and higher-frequency emissions termed anti-Stokes scattering. Usually, the ground vibrational level ($v = 0$) is more highly populated than the excited vibration levels so that the Stokes lines are more intense than the anti-Stokes lines. Elastically scattered radiation is of the same frequency as the excitation beam and is called Rayleigh scattering.

source. Because of this, it might seem more difficult to detect and measure Raman bands than IR vibrational bands. However, the Raman scattered radiation is in the visible or near-IR regions for which more sensitive detectors are available. Hence, today, obtaining Raman spectra is nearly as easy as obtaining IR spectra.

18A-1 Excitation of Raman Spectra

In Figure 18-1, the sample is irradiated by a monochromatic beam of energy $h\nu_{ex}$. Because the excitation wavelength is usually well away from an absorption band, excitation can be considered to involve a *virtual state* of energy level *j*, indicated by the dashed line in Figure 18-1a.[2] A molecule in the ground vibrational level ($v = 0$) can absorb a photon of energy $h\nu_{ex}$ and reemit a photon of energy $h(\nu_{ex} - \nu_v)$, as shown on the left side of Figure 18-1a. When the scattered radiation is of a lower frequency than the excitation radiation, it is called *Stokes scattering*. Molecules in a vibrationally excited state ($v = 1$) can also scatter radiation inelastically and produce a Raman signal of energy $h(\nu_{ex} + \nu_v)$. Scattered radiation of a higher frequency than the source radiation is called *anti-Stokes scattering*. Elastic scattering can also occur with emission of a photon of the same energy as the excitation photon, $h\nu_{ex}$. Scattered radiation of the same frequency as the source is termed *Rayleigh scattering*. Note that the frequency shifts of the inelastically scattered radiation $(\nu_{ex} + \nu_v) - \nu_{ex} = \nu_v$ and $(\nu_{ex} - \nu_v) - \nu_{ex} = -\nu_v$ correspond to the vibrational frequency, ν_v. The simplified Raman spectrum corresponding to the transitions shown is given in Figure 18-1b.

Figure 18-2 depicts a portion of the Raman spectrum of carbon tetrachloride that was obtained by using an argon-ion laser having a wavelength of 488.0 nm as the source. As is usually the case for Raman spectra, the abscissa of Figure 18-2 is the wavenumber shift $\Delta\bar{\nu}$, which is defined as the difference in wavenumbers (cm^{-1}) between the observed radiation and that of the source. Note that three Raman lines are found on both sides of the Rayleigh lines and that the pattern of shifts on each side is identical. That is, Stokes lines are found at wavenumbers that are 218, 314, and 459 cm^{-1} smaller than the Rayleigh lines, and anti-Stokes lines occur at 218, 314, and 459 cm^{-1} greater than the wavenumber of the source. It should also be noted that additional lines can be found at ± 762 and ± 790 cm^{-1}. Because the anti-Stokes lines are appreciably less intense than the corresponding Stokes lines, only the Stokes part of a spectrum is generally used. Furthermore, the abscissa of the plot is often labeled simply "wavenumber $\bar{\nu}$, cm^{-1}" rather than "wavenumber or Raman shift $\Delta\bar{\nu}$." It is noteworthy that fluorescence may interfere seriously with the observation of Stokes shifts but not with anti-Stokes. With fluorescing samples, anti-Stokes signals may, therefore, be more useful despite their lower intensities.

It is important to appreciate that the magnitude of Raman shifts is *independent of the wavelength of excitation*. Thus, Raman shifts identical to those shown in Figure 18-2 are observed for carbon tetrachloride regardless of whether excitation was carried out with an argon-ion laser (488.0) or a helium-neon laser (632.8 nm).

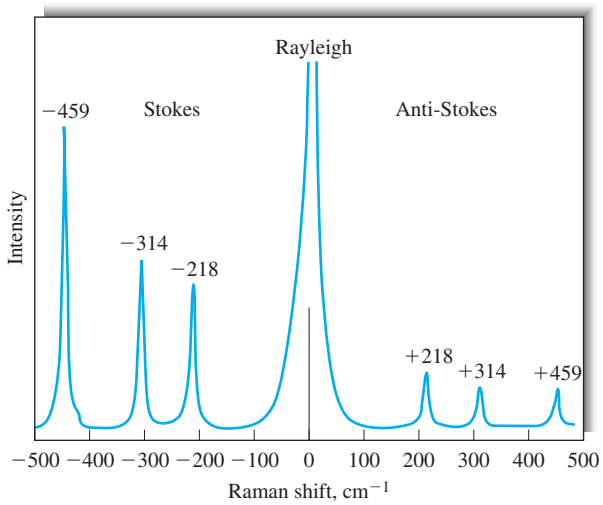

FIGURE 18-2 Raman spectrum of CCl_4, excited by laser radiation of $\lambda_{ex} = 488$ nm ($\bar{\nu}_{ex} = 20{,}492$ cm^{-1}). The number above the Raman lines is the Raman shift, $\Delta\nu = \nu_{ex} \pm \nu_v$, in cm^{-1}. Stokes-shifted lines are often given positive values rather than negative values as shown. (From J. R. Ferraro, K. Nakamoto, and C. W. Brown, *Introductory Raman Spectroscopy*, 2nd ed., San Diego: Academic Press, 2003. Reprinted with permission.)

[2]It should be noted that the virtual state is not a real state, but merely a mental construct to help in visualizing the scattering process.

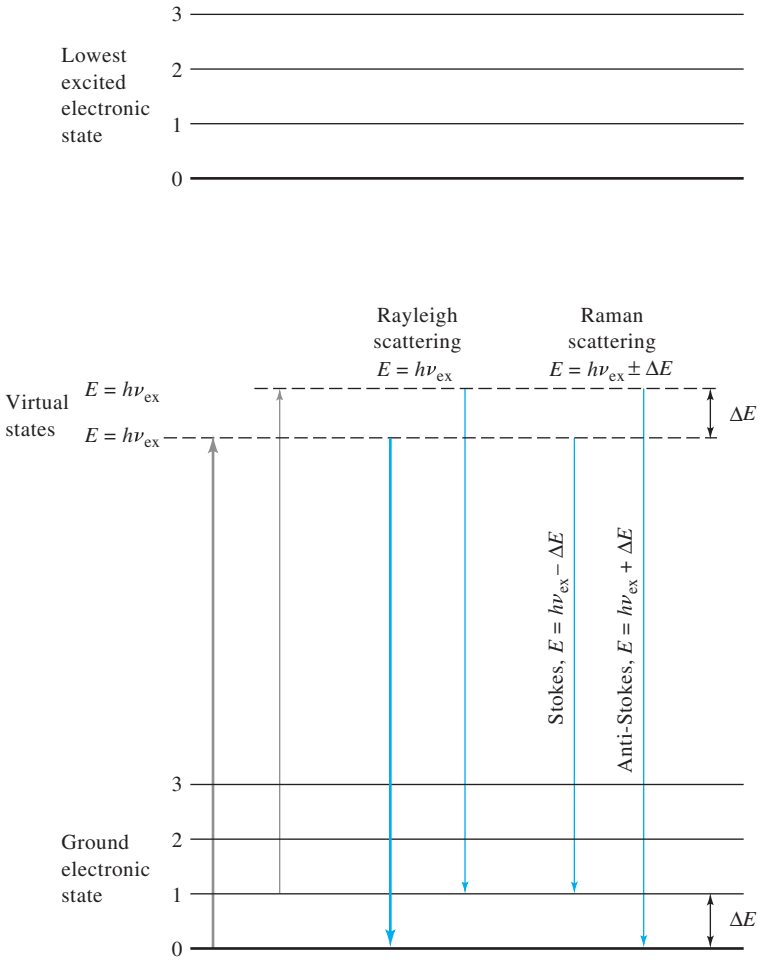

FIGURE 18-3 Origins of Rayleigh and Raman scattering.

Superficially, the Raman Stokes shifts to lower energies (longer wavelengths) are analogous to the Stokes shifts found in molecular fluorescence (see Section 6C-6). We note, however, that Raman and fluorescence spectra arise from fundamentally different processes.

18A-2 Mechanisms of Raman and Rayleigh Scattering

In normal Raman spectroscopy, spectral excitation is normally carried out by radiation having a wavelength that is well away from any absorption bands of the analyte. (Resonance Raman [see Section 18D-1] is an exception where excitation occurs near or within an absorption band.) The energy-level diagram of Figure 18-1a is expanded in Figure 18-3 and provides a qualitative picture of the sources of Raman and Rayleigh scattering. The heavy arrow on the far left depicts the energy change in the molecule when it interacts with a photon from the source. The increase in energy is equal to the energy of the photon $h\nu_{ex}$. It is important to appreciate that the process shown is *not quantized*; thus, depending on the frequency of the radiation from the source, the energy of the molecule can assume any of an infinite number of values, or *virtual states*, between the ground state and the lowest (first) electronic excited state shown in the upper part of the diagram. The second and lighter arrow on the left shows the type of change that would occur if the molecule encountered by the photon happened to be in the first vibrational level of the electronic ground state. At room temperature, the fraction of the molecules in this state is small. Thus, as indicated by the thickness of the arrows, the probability of this process occurring is much smaller.

The middle set of arrows depicts the changes that produce Rayleigh scattering. Again the more probable change is shown by the wider arrow. Note that no energy is lost in Rayleigh scattering, and because of this the collisions between the photon and the molecule are said to be *elastic*.

Finally, the energy changes that produce Stokes and anti-Stokes emission are depicted on the right. The two differ from the Rayleigh radiation by frequencies corresponding to $\pm\Delta E$, the energy of the first vibrational level of the ground state, $h\nu_v$. Note that if the bond were IR active, the energy of its absorption

would also be ΔE. Thus, the Raman *frequency shift* and the *IR absorption frequency* are identical.

Note also that the relative populations of the two upper energy states are such that Stokes emission is much favored over anti-Stokes. In addition, Rayleigh scattering has a considerably higher probability of occurring than Raman scattering because the most probable event is the energy transfer to molecules in the ground state and reemission by the return of these molecules to the ground state. Finally, it should be noted that the ratio of anti-Stokes to Stokes intensities increases with temperature because a larger fraction of the molecules is in the first vibrationally excited state under these circumstances.

18A-3 Wave Model of Raman and Rayleigh Scattering

Let us assume that a beam of radiation having a frequency ν_{ex} is incident on a solution of an analyte. The electric field E of this radiation can be described by the equation

$$E = E_0 \cos(2\pi\nu_{ex}t) \tag{18-1}$$

where E_0 is the amplitude of the wave. When the electric field of the radiation interacts with an electron cloud of an analyte bond, it induces a dipole moment m in the bond that is given by

$$m = \alpha E = \alpha E_0 \cos(2\pi\nu_{ex}t) \tag{18-2}$$

where α is a proportionality constant called the *polarizability* of the bond. This constant is a measure of the deformability of the bond in an electric field.

The polarizability α varies as a function of the distance between nuclei according to the equation

$$\alpha = \alpha_0 + (r - r_{eq})\left(\frac{\partial\alpha}{\partial r}\right) \tag{18-3}$$

where α_0 is the polarizability of the bond at the equilibrium internuclear distance r_{eq} and r is the internuclear separation at any instant. The change in internuclear separation varies with the frequency of the vibration ν_v as given by

$$r - r_{eq} = r_m \cos(2\pi\nu_v t) \tag{18-4}$$

where r_m is the maximum internuclear separation relative to the equilibrium position.

Substituting Equation 18-4 into 18-3 gives

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial r}\right) r_m \cos(2\pi\nu_v t) \tag{18-5}$$

We can then obtain an expression for the induced dipole moment m by substituting Equation 18-5 into Equation 18-2. Thus,

$$m = \alpha_0 E_0 \cos(2\pi\nu_{ex}t) + E_0 r_m\left(\frac{\partial\alpha}{\partial r}\right)\cos(2\pi\nu_v t)\cos(2\pi\nu_{ex}t) \tag{18-6}$$

If we use the trigonometric identity for the product of two cosines

$$\cos x \cos y = [\cos(x + y) + \cos(x - y)]/2$$

we obtain from Equation 18-6

$$m = \alpha_0 E_0 \cos(2\pi\nu_{ex}t) + \frac{E_0}{2} r_m\left(\frac{\partial\alpha}{\partial r}\right)\cos[2\pi(\nu_{ex} - \nu_v)t] + \frac{E_0}{2} r_m\left(\frac{\partial\alpha}{\partial r}\right)\cos[2\pi(\nu_{ex} + \nu_v)t] \tag{18-7}$$

The first term in this equation represents Rayleigh scattering, which occurs at the excitation frequency ν_{ex}. The second and third terms in Equation 18-7 correspond, respectively, to the Stokes and anti-Stokes frequencies of $\nu_{ex} - \nu_v$ and $\nu_{ex} + \nu_v$. In essence then, the excitation frequency is modulated by the vibrational frequency of the bond. It is important to note that the selection rules for Raman scattering require that there be a change in polarizability during the vibration—that is, $\partial\alpha/\partial r$ in Equation 18-7 must be greater than zero for Raman lines to appear. The selection rules also predict that Raman lines corresponding to fundamental modes of vibration occur with $\Delta\nu = \pm 1$. Just as with IR spectroscopy, much weaker overtone transitions appear at $\Delta\nu = \pm 2$.

We have noted that, for a given bond, the energy *shifts* observed in a Raman experiment should be identical to the *energies* of its IR absorption bands, provided the vibrational modes involved are both IR and Raman active. Figure 18-4 illustrates the similarity of the two types of spectra; it is seen that there are several bands with identical $\bar{\nu}$ and $\Delta\bar{\nu}$ values for the two compounds. We should also note, however, that the relative intensities of the corresponding bands are frequently quite different. Moreover, certain peaks that occur in one spectrum are absent in the other.

The differences between a Raman spectrum and an IR spectrum are not surprising when it is considered that the basic mechanisms, although dependent on the same vibrational modes, arise from processes that are mechanistically different. IR absorption requires that there be a change in dipole moment or charge distribution during the vibration. Only then can radiation of the same frequency interact with the molecule and promote it to an excited vibrational state. In contrast, scattering involves a momentary distortion of the electrons distributed around a bond in a molecule, followed by reemission of the radiation as the bond returns to its normal state. In its distorted form, the molecule is temporarily polarized; that is, it develops momentarily an induced dipole that disappears on relaxation and reemission. Because of this fundamental difference in mechanism, the Raman activity of a given vibrational mode may

Tutorial: Learn more about **Raman and IR spectra** at www.tinyurl.com/skoogpia7

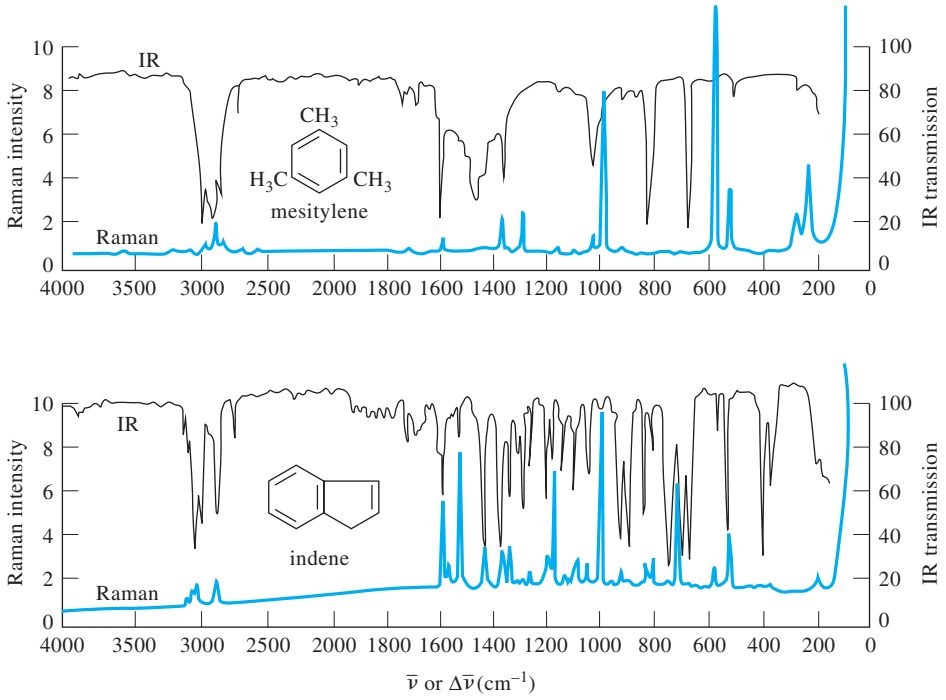

FIGURE 18-4 Comparison of Raman and IR spectra for mesitylene and indene. (Courtesy of Perkin-Elmer Corp., Norwalk, CT.)

differ markedly from its IR activity. For example, a homonuclear molecule such as nitrogen, chlorine, or hydrogen has no dipole moment either in its equilibrium position or when a stretching vibration causes a change in the distance between the two nuclei. Thus, absorption of radiation (IR) of the vibrational frequency cannot occur. On the other hand, the polarizability of the bond between the two atoms of such a molecule varies periodically in phase with the stretching vibrations, reaching a maximum at the greatest separation and a minimum at the closest approach. A Raman shift corresponding in frequency to that of the vibrational mode results.

It is of interest to compare the IR and the Raman activities of coupled vibrational modes such as those described earlier (page 396) for the carbon dioxide molecule. In the symmetric mode, no change in the dipole moment occurs as the two oxygen atoms move away from or toward the central carbon atom; thus, this mode is IR inactive. The polarizability, however, fluctuates in phase with the vibration because distortion of bonds becomes easier as they lengthen and more difficult as they shorten. Raman activity is associated with this mode.

In contrast, the dipole moment of carbon dioxide fluctuates in phase with the asymmetric vibrational mode. Thus, an IR absorption band arises from this mode. On the other hand, as the polarizability of one of the bonds increases as it lengthens, the polarizability of the other decreases, resulting in no net change in the molecular polarizability. Thus, the asymmetric stretching vibration is Raman inactive. For molecules with a center of symmetry, such as CO_2, no IR active transitions are in common with Raman active transitions. This is often called the *mutual exclusion principle*.

Often, as in the foregoing examples, parts of Raman and IR spectra are complementary, each being associated with a different set of vibrational modes within a molecule. For noncentrosymmetric molecules, many vibrational modes may be both Raman and IR active. For example, all of the vibrational modes of sulfur dioxide yield both Raman and IR bands. The intensities of the bands differ, however, because the probabilities for the transitions are different for the two mechanisms. Raman spectra are often simpler than IR spectra because the occurrence of overtone and combination bands is less common in Raman spectra.

18A-4 Intensity of Normal Raman Bands

The intensity or radiant power of a normal Raman band depends in a complex way on the polarizability of the molecule, the intensity of the source, and the concentration of the active group, as well as other factors. In the absence of absorption, the power of Raman emission increases with the fourth power of the frequency of the source. However, advantage can seldom be taken of this relationship because of the likelihood that ultraviolet (UV) irradiation will cause photodecomposition of the analyte or fluorescence of a sample constituent.

Raman intensities are usually directly proportional to the concentration of the active species. In this regard, Raman spectroscopy more closely resembles fluorescence than absorption with its logarithmic concentration-intensity relationship.

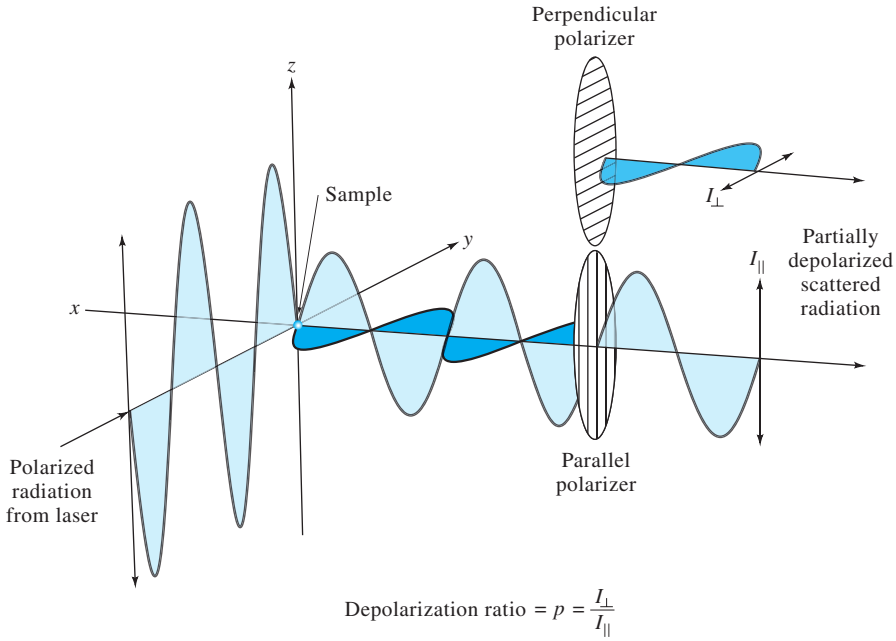

FIGURE 18-5 Depolarization resulting from Raman scattering.

18A-5 Raman Depolarization Ratios

In addition to intensity and frequency information, Raman measurements provide an additional variable that can be useful in determining the structure of molecules: the *depolarization ratio*.[3] In this discussion, it is important to distinguish carefully between the terms *polarizability* and *polarization*. The former term describes a *molecular* property having to do with the deformability of a bond. Polarization, in contrast, is a property of a beam of radiation and describes the plane in which the radiation vibrates.

When Raman spectra are excited by plane-polarized radiation, as they are when a laser source is used, the scattered radiation is found to be polarized to various degrees depending on the type of vibration responsible for the scattering. The nature of this effect is illustrated in Figure 18-5, where radiation from a laser source is shown as being polarized in the *yz* plane. Part of the resulting scattered radiation is shown as being polarized parallel to the original beam, that is, in the *xz* plane; the intensity of this radiation is symbolized by the subscript ∥. The remainder of the scattered beam is polarized in the *xy* plane, which is perpendicular to the polarization of the original beam; the intensity of this perpendicularly polarized radiation is shown by the subscript ⊥. The depolarization ratio p is defined as

$$p = \frac{I_\perp}{I_\parallel} \tag{18-8}$$

Experimentally, the depolarization ratio may be obtained by inserting a Polaroid sheet or other polarizer between the sample and the monochromator. Spectra are then obtained with the axis of the sheet oriented parallel with first the *xz* and then the *xy* plane shown in Figure 18-5.

The depolarization ratio depends on the symmetry of the vibrations responsible for the scattering. For example, the band for carbon tetrachloride at 459 cm^{-1} (Figure 18-2) arises from a totally symmetric "breathing" vibration involving the simultaneous movement of the four tetrahedrally arranged chlorine atoms toward and away from the central carbon atom. The depolarization ratio is 0.005, indicating minimal depolarization; the 459-cm^{-1} line is thus said to be polarized. In contrast, the carbon tetrachloride bands at 218 and 314 cm^{-1}, which arise from nonsymmetrical vibrations, have depolarization ratios of about 0.75. From scattering theory it is possible to demonstrate that the maximum depolarization for nonsymmetric vibrations is 6/7, and for symmetric vibrations the ratio is always less than this number. The depolarization ratio is thus useful in correlating Raman lines with modes of vibration.

18B INSTRUMENTATION

Instrumentation for modern Raman spectroscopy consists of a laser source, a sample illumination system, and a suitable spectrometer as illustrated in Figure 18-6.[4] The performance requirements for these components are more stringent than for the molecular spectrometers we have already described, however,

[3]D. P. Strommen, *J. Chem. Educ.*, **1992**, *69*, 803, **DOI**: 10.1021/ed069p803.

[4]For a description of Raman instrumentation, see P. Vandenabeele, *Practical Raman Spectroscopy: An Introduction*, Chichester, UK: Wiley, 2013, Chap. 4.

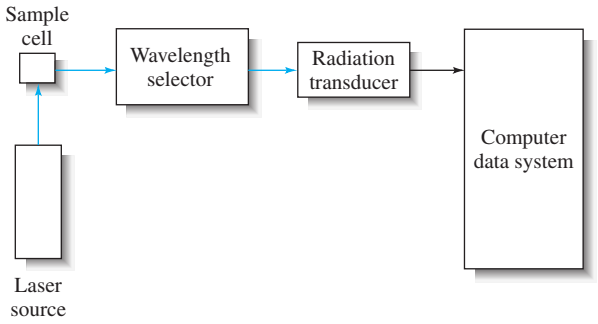

FIGURE 18-6 Block diagram of a Raman spectrometer. The laser radiation is directed into a sample cell. The Raman scattering is usually measured at right angles to avoid viewing the source radiation. A wavelength selector isolates the desired spectral region. The transducer converts the Raman signal into a proportional electrical signal that is processed by the computer data system.

because of the inherent weakness of the Raman scattering signal compared with the signal produced by the Rayleigh scattering.

18B-1 Sources

The sources used in modern Raman spectrometry are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal-to-noise ratio. Five of the most common lasers used for Raman spectroscopy are listed in Table 18-1. Because the intensity of Raman scattering varies as the fourth power of the frequency, argon and krypton ion sources that emit in the blue and green region of the spectrum have an advantage over the other sources shown in the table. For example, the argon ion line at 488 nm provides Raman lines that are nearly three times as intense as those excited by the He-Ne source, given the same input power. However, these short-wavelength sources can produce significant fluorescence and cause photodecomposition of the sample.

The last two sources in the table, which emit near-IR radiation, are finding more and more use as excitation sources. Near-IR sources have two major advantages over shorter-wavelength lasers. The first is that they can be operated at much higher power (up to 50 W) without causing photodecomposition of the sample. The second is that they are not energetic enough to populate a significant number of fluorescence-producing excited electronic energy states in most molecules. As a result, fluorescence is generally much less intense or nonexistent with these lasers. The Nd-YAG laser, used in Fourier transform Raman (FT-Raman) spectrometers is particularly effective in eliminating fluorescence. The two lines of the diode laser at 785 and 830 nm also markedly reduce fluorescence in most cases.

Figure 18-7 illustrates an example where the Nd-YAG source completely eliminates background fluorescence. The upper curve was obtained with conventional Raman equipment using the 514.5-nm line from an argon-ion laser for excitation. The sample was anthracene, and most of the recorded signal arises from the fluorescence of that compound. The lower curve in blue is for the same sample recorded with a Fourier transform spectrometer equipped with a Nd-YAG laser that emitted at 1064 nm. Note the total absence of fluorescence background signal.

The excitation wavelength in Raman spectrometry must be carefully chosen. Not only is photodecomposition and fluorescence a problem but colored samples and some solvents can absorb the incident radiation or the Raman-scattered radiation. Thus, there is a need for more than one source or for multiple wavelength sources.

TABLE 18-1 Some Common Laser Sources for Raman Spectroscopy

Laser Type	Wavelength, nm
Argon ion	488.0 or 514.5
Krypton ion	413.1, 530.9, 647.1
Helium-neon	632.8
Diode	660–880
Nd-YAG	1064

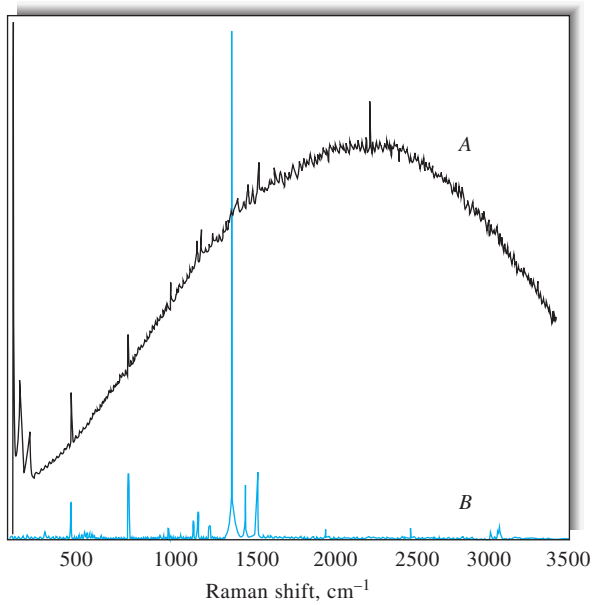

FIGURE 18-7 Spectra of anthracene taken with a conventional Raman instrument with an argon-ion laser source at 514.5 nm (*A*) and with an FT-Raman instrument with a Nd-YAG source at 1064 nm (*B*). (From B. Chase, *Anal. Chem.*, **1987**, *59*, 881A, **DOI**: 10.1021/ac00141a714. Copyright 1987 American Chemical Society.)

18B-2 Sample-Illumination System

Sample handling for Raman spectroscopic measurements is simpler than for IR spectroscopy because glass can be used for windows, lenses, and other optical components instead of the more fragile and atmospherically less stable crystalline halides. In addition, the laser source is easily focused on a small sample area and the emitted radiation efficiently transported to the slit or entrance aperture of a spectrometer. As a result, very small samples can be investigated. In fact, a common sample holder for nonabsorbing liquid samples is an ordinary glass-melting-point capillary.

Gas Samples

Gases are normally contained in glass tubes 1–2 cm in diameter and about 1 mm thick. Gases can also be sealed in small capillary tubes. For weak scatterers, an external multiple-pass setup with mirrors can be used as shown in Figure 18-8a. The resulting Raman scattering perpendicular to the sample tube and to the excitation laser beam is then focused on the entrance slit of the spectrometer by a large lens (L2 in the figure).

Liquid Samples

Liquids can be sealed in ampoules, glass tubes, or capillaries. Figure 18-8b and c show two of many systems for illuminating liquids. In Figure 18-8b a capillary cell is shown. Capillaries can be as small as 0.5–0.1 mm bore and 1 mm long. The spectra of nanoliter volumes of sample can be obtained with capillary cells. A large cylindrical cell, such as that illustrated in Figure 18-8c, can be used to reduce local heating, particularly for absorbing samples. The laser beam is focused to an area near the wall to minimize absorption of the incident beam. Further reduction of localized heating is often achieved by rotating the cell with an attached motor.

A major advantage of sample handling in Raman spectroscopy compared with IR arises because water is a weak Raman scatterer but a strong absorber of IR radiation. Thus, aqueous solutions can be studied by Raman spectroscopy but only with difficulty by IR. This advantage is particularly important for biological and inorganic systems and in studies dealing with water pollution.

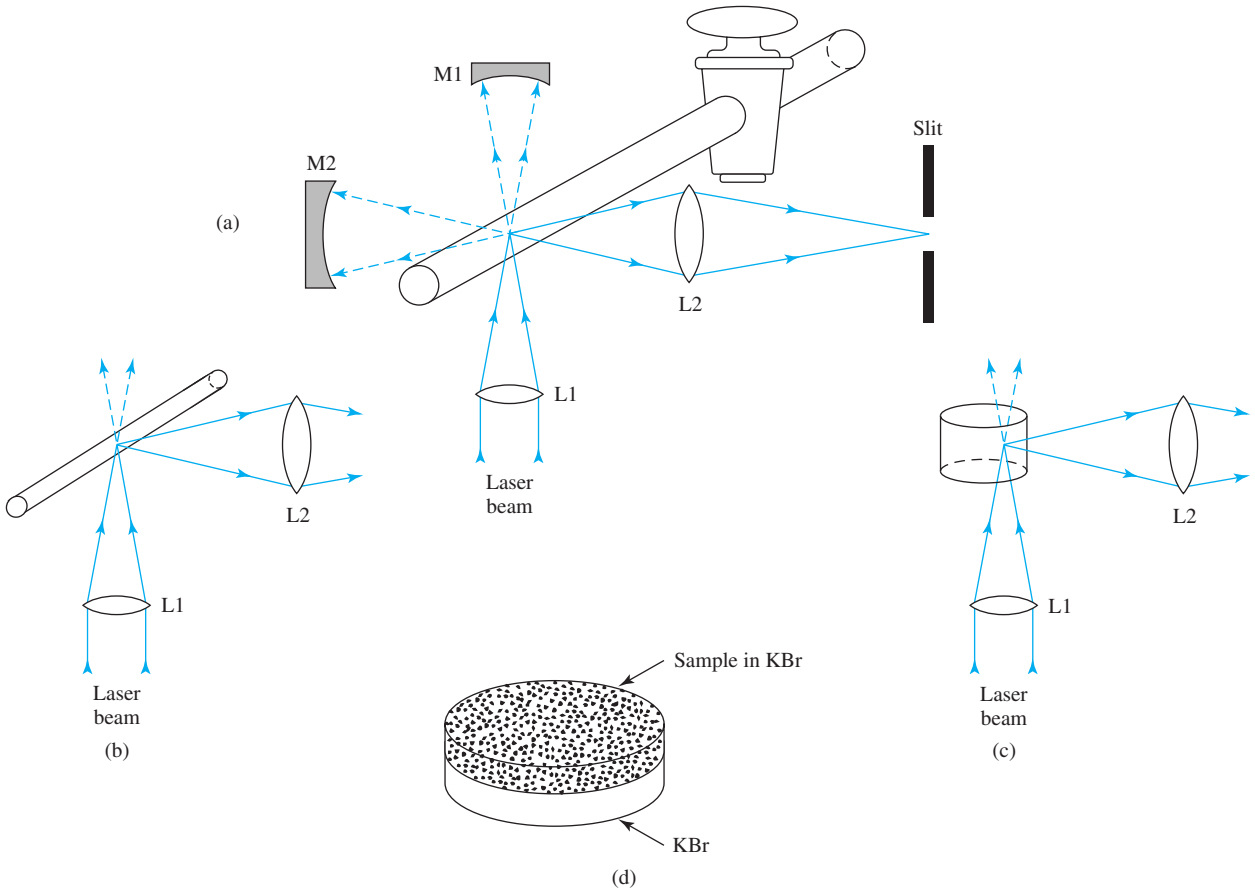

FIGURE 18-8 Sample illumination systems for Raman spectrometry. In (a), a gas cell is shown with external mirrors for passing the laser beam through the sample multiple times. Liquid cells can be capillaries (b) or cylindrical cells (c). Solids can be determined as powders packed in capillaries or as KBr pellets (d). (Adapted from J. R. Ferraro, K. Nakamoto, and C. W. Brown, *Introductory Raman Spectroscopy*, 2nd ed., San Diego: Academic Press, 2003. Reprinted with permission.)

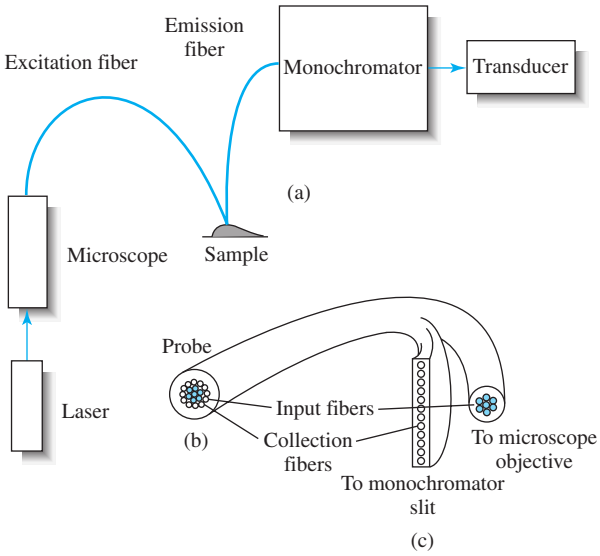

FIGURE 18-9 Raman spectrometer with fiber-optic probe. In (a) a microscope objective focuses the laser radiation onto excitation fibers that transport the beam to the sample. The Raman scattering is collected by emission fibers and carried to the entrance slit of a monochromator or to the entrance of an interferometer. A radiation transducer, such as a photomultiplier tube, converts the scattered light intensity to a proportional current or pulse rate, (b) end view of the probe, and (c) end view of collection fibers at entrance slit of monochromator. The colored circles represent the input fiber and the uncolored circles the collection fibers. (Adapted from R. L. McCreery, M. Fleischmann, and P. Hendra, *Anal. Chem.*, **1983**, *55*, 146, **DOI**: 10.1021/ac00252a039. Copyright 1983 American Chemical Society.)

Solid Samples

Raman spectra of solid samples are often acquired by filling a small cavity or capillary with the sample after it has been ground to a fine powder. Polymers can usually be examined directly with no sample pretreatment. In some cases, KBr pellets similar to those used in IR spectroscopy are used as shown in Figure 18-8d. Dilution with KBr can reduce decomposition of the sample produced by local heating.

Fiber-Optic Sampling

One of the significant advantages of Raman spectrometry is that it is based on visible or near-IR radiation that can be transmitted for a considerable distance (as much as 100 m or more) through optical fibers. Figure 18-9 shows the arrangement of a typical Raman instrument that uses a fiber-optic probe. In this experiment, a microscope objective lens is used to focus the laser excitation beam on one end of an excitation fiber of a fiber bundle. These fibers bring the excitation radiation to the sample. Fibers can be immersed in liquid samples or used to illuminate solids. A second fiber or fiber bundle collects the Raman scattering and transports it to the entrance slit of the spectrometer. Several commercial instruments are now available with such probes.

The Raman spectrum shown in Figure 18-10 illustrates how a fiber-optic probe can be used to monitor chemical processes. In this case a fiber-optic probe was used to monitor the hanging drop crystallization of aprotinin (a serine protease inhibitor) and $(NH_4)_2SO_4$ in aqueous solution. Raman bands were attributed to both the protein and the salt. By using chemometric techniques, changes in the spectrum during crystallization were correlated with depletion of both the protein and the salt. The authors were able to determine accurately supersaturation of aprotinin using this technique.

Fiber-optic probes are proving very useful for obtaining Raman spectra in locations remote from the sample site. Examples include hostile environments, such as hazardous reactors or molten salts; biological samples, such as tissues and arterial walls; and environmental samples, such as groundwater and seawater.

Raman Microprobe

A popular accessory for Raman spectrometers is the Raman microprobe. The first developments in Raman microscopy occurred in the 1970s. Today, several instrument companies make microprobe attachments. With these, the sample is placed on the stage of a microscope where it is illuminated by visible light. After selecting the area to be viewed and adjusting the focus, the illumination lamp is turned off and the exciting laser beam is directed to the sample. With modern optics, the Raman microprobe can obtain high-quality Raman spectra without sample preparation on picogram amounts of sample with 1-μm spatial resolution.

Raman Mapping and Imaging

Raman spectroscopy can be used for mapping and imaging applications similar to those described in Section 17-G for IR spectroscopy. In mapping, a full spectrum is acquired before the sample or fiber optic probe is repositioned for another spectrum. The process is repeated until the desired two-dimensional resolution is achieved. Acquiring a multi-position map in this

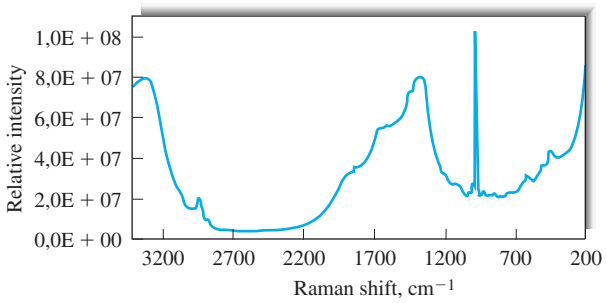

FIGURE 18-10 Raman spectrum of an aqueous solution containing aprotinin (100 mg/mL) and $(NH_4)_2SO_4$ (1.0 M) in 50 mM sodium acetate buffer at pH 4.5 and 24°C. A diode laser source at 785 nm was used with a CCD detector. (From R. E. Tamagawa, E. A. Miranda, and K. A. Berglund, *Cryst. Growth Des.*, **2002**, *2*, 511, **DOI**: 10.1021/cg025544m. Copyright 2002 American Chemical Society.)

manner with a spectrum at each position can be very time-consuming. Fast mapping techniques have been described to speed up the process.

In imaging applications, a larger area is illuminated with a partially defocused laser beam. By adjusting the wavelength selector (filters or monochromator), the user attempts to isolate a specific Raman band. The intensity of this band is then viewed as a function of position in the resulting image. In practice, the bandwidth isolated is usually larger than that of a single Raman band and hence a range of wavelengths is imaged.

Since the introduction of Raman mapping and imaging in the 1990s, many different applications have been described.[5] These include such diverse areas as the examination of meteorites in the search for extraterrestrial life, the identification of materials useful in forensic science, the examination of cancerous cells in human breast tissue, the identification of contaminants in pharmaceutical powders, and the characterization of such new materials as carbon nanotubes and graphene ribbons. One of the major advantages of Raman spectroscopy in biomedical applications is that molecular information can be acquired without the use of radioactive or fluorescent labels, which can introduce contaminants and perturb the sample. The valuable information provided by Raman spectroscopy ensures that we will very likely see an increasing number of these applications in the future.

18B-3 Raman Spectrometers

Until the early 1980s, Raman spectrometers were similar in design and used the same type of components as the classical ultraviolet-visible dispersing instruments described in Section 13D-3. Most spectrometers used double-grating systems to minimize the amount of stray and Rayleigh-scattered radiation reaching the transducer. Photomultipliers served as transducers. Now, however, most Raman spectrometers being marketed are either Fourier transform instruments equipped with cooled germanium transducers or multichannel instruments based on charge-coupled devices (CCDs).

Wavelength-Selection Devices and Transducers

A high-quality wavelength-selection device is required in Raman spectroscopy to separate the relatively weak Raman lines from the intense Rayleigh-scattered radiation. Traditional dispersive Raman spectrometers used double- or even triple-grating monochromators for this purpose. In recent years, holographic interference filters, called *notch filters*, and holographic gratings have improved to the extent that they have virtually eliminated the need for multiple-grating monochromators. In fact, the combination of a notch filter and a high-quality grating monochromator is now found in most commercial dispersive instruments.

Instruments with monochromators invariably use photomultiplier tubes as transducers because of the weak signals being measured. Many spectrometers also use photon-counting systems to measure the Raman intensity. Because photon counting is inherently a digital technique, such systems are readily interfaced to modern computer data systems.

Many newer Raman instruments have replaced the single-wavelength output monochromator with a spectrograph and an array detector. The photodiode array was the first array detector to be used. It allows the simultaneous collection of entire Raman spectra. Photodiode arrays are typically used in conjunction with an image intensifier to amplify the weak Raman signal.

More recently, charge-transfer devices, such as CCDs and charge-injection devices (CIDs), have been used in Raman spectrometers. Figure 18-11 shows a fiber-optic Raman spectrometer that uses a CCD as a multichannel detector. This instrument contains high-quality bandpass and band-rejection (notch) filters to provide good stray light rejection. The CCD array can be a two-dimensional array or in some cases a linear array.

Fourier Transform Raman Spectrometers

The Fourier transform Raman (FT-Raman) instrument uses a Michelson interferometer, similar to that used in FTIR spectrometers, and a continuous-wave (CW) Nd-YAG laser as shown in Figure 18-12. The use of a 1064-nm (1.064-μm) source virtually eliminates fluorescence and photodecomposition of samples. Hence, dyes and other fluorescing compounds can be investigated with FT-Raman instruments. The FT-Raman instrument also provides superior frequency precision relative to conventional instruments, which enable spectral subtractions and high-resolution measurements.

One disadvantage of the FT-Raman spectrometer is that water absorbs in the 1000-nm region, which can cancel the Raman advantage of being able to use aqueous solutions. Also, optical filtering, as shown in Figure 18-12, is a necessity. The stray light from the exciting laser must be eliminated because it can saturate many transducers. The Rayleigh-scattered line is often six orders of magnitude greater than the Stokes-shifted Raman lines, and the intensity of this line must be minimized before striking the transducer. Holographic notch filters and other filter types are used for this purpose. Because the Raman scattering from a Nd-YAG laser can occur at wavelengths as long as 1700 nm, photomultipliers and many array detectors are not used. Most FT-Raman instruments instead use InGaAs, Ge, and other photoconductive devices as transducers. These devices are usually operated at cryogenic temperatures.

Tutorial: Learn more about **Raman instrumentation** at www.tinyurl.com/skoogpia7

[5]See for example *Infrared and Raman Spectroscopic Imaging*, R. Salzer and H. W. Siesler, eds., 2nd ed., Weinheim, Germany: Wiley-VCH, 2014; *Infrared and Raman Spectroscopy in Forensic Science*, J. M. Chalmers, H. G. M. Edwards, and M. D. Hairgreaves, eds., Chichester, UK: Wiley, 2012.

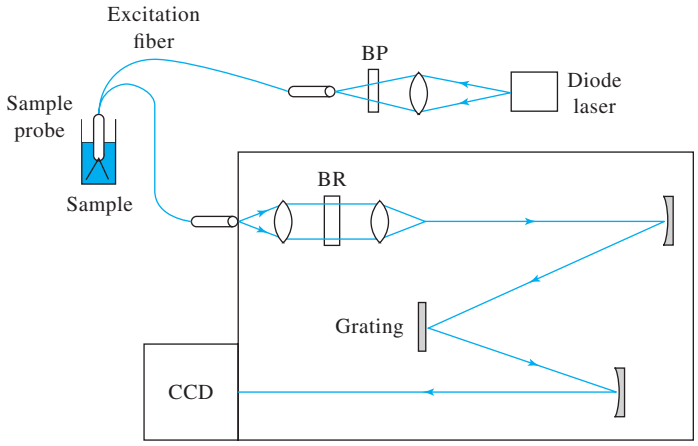

FIGURE 18-11 Fiber-optic Raman spectrometer with spectrograph and CCD detector. The bandpass filter (BP) is used to isolate a single laser line. The band-rejection filter (BR) minimizes the Rayleigh-scattered radiation.

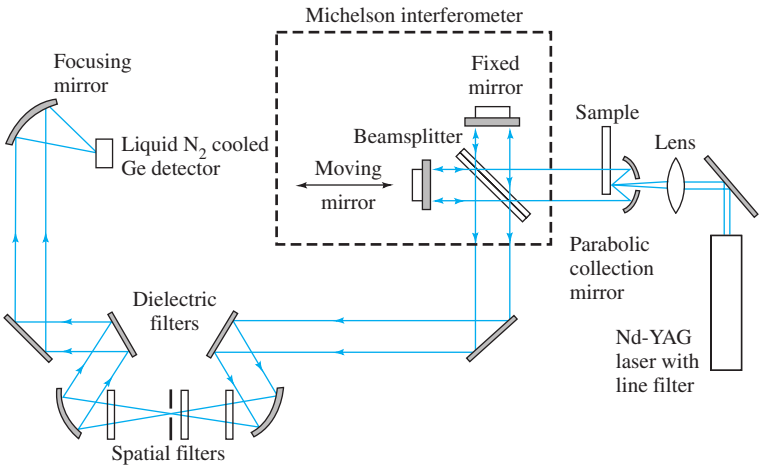

FIGURE 18-12 Optical diagram of an FT-Raman instrument. The laser radiation passes through the sample and then into the interferometer, consisting of the beamsplitter and the fixed and movable mirrors. The output of the interferometer is then extensively filtered to remove stray laser radiation and Rayleigh scattering. After passing through the filters, the radiation is focused onto a cooled Ge detector.

The FT-Raman spectrometer has a number of unique advantages for Raman spectrometry. However, the limitations previously noted mean that dispersive Raman instruments will still be used for some time.

Portable Raman Spectrometers

The availability of inexpensive diode lasers, narrow bandwidth filters, and CCD detectors has fostered the development of portable and handheld Raman instruments. Several instrument companies have introduced these devices. They are finding applications in identifying, verifying, and certifying materials for industry, homeland security, and forensics.

18C APPLICATIONS OF RAMAN SPECTROSCOPY

Raman spectroscopy has been applied to the qualitative and quantitative analysis of inorganic, organic, and biological systems.[6]

[6]See *Analytical Raman Spectroscopy*, J. G. Grasselli and B. J. Bulkin, eds., New York: Wiley, 1991.

18C-1 Raman Spectra of Inorganic Species

The Raman technique is often superior to IR spectroscopy for investigating inorganic systems because aqueous solutions can usually be used.[7] In addition, the vibrational energies of metal-ligand bonds are generally in the range of 100 to 700 cm^{-1}, a region of the IR that is experimentally difficult to study. These vibrations are frequently Raman active, however, and lines with $\Delta\bar{\nu}$ values in this range are readily observed. Raman studies are potentially useful sources of information concerning the composition, structure, and stability of coordination compounds. For example, numerous halogen and halogenoid complexes produce Raman spectra and thus are amenable to investigation by this means. Metal-oxygen bonds are also Raman active. Spectra for such species as VO_3^{4-}, $Al(OH)_4^-$, $Si(OH)_6^{2-}$, and $Sn(OH)_6^{2-}$ have been obtained. Raman studies have been useful in determining the probable structures of these and similar species. For example, in perchloric acid solutions, vanadium(IV) appears to be present as $VO^{2+}(aq)$ rather than as $V(OH)_2^{2+}(aq)$. Studies of boric acid solutions show that the anion formed by acid dissociation is the tetrahedral $B(OH)_4^-$ rather than $H_2BO_3^-$. Dissociation constants for strong acids such as H_2SO_4, HNO_3, H_2SeO_4, and H_5IO_6 have been calculated from Raman measurements. It seems probable that the future will see even wider use of Raman spectroscopy for theoretical verification and structural studies of inorganic systems.

18C-2 Raman Spectra of Organic Species

Raman spectra are similar to IR spectra in that they have regions useful for functional group detection and fingerprint regions that permit the identification of specific compounds. Daimay et al. have published a comprehensive treatment of Raman functional group frequencies.[8]

Raman spectra yield more information about certain types of organic compounds than do their IR counterparts. For example, the double-bond stretching vibration for olefins results in weak and sometimes undetected IR absorption. On the other hand, the Raman band (which like the IR band, occurs at about 1600 cm^{-1}) is intense, and its position is sensitive to the nature of substituents as well as to their geometry. Thus, Raman studies are likely to yield useful information about the olefinic functional group that may not be revealed by IR spectra. This statement applies to cycloparaffin derivatives as well; these compounds have a characteristic Raman band in the region of 700 to 1200 cm^{-1}. This band has been attributed to a breathing vibration in which the nuclei move in and out symmetrically with respect to the center of the ring. The position of the band decreases continuously from 1190 cm^{-1} for cyclopropane to 700 cm^{-1} for cyclooctane. Raman spectroscopy thus appears to be an excellent diagnostic tool for the estimation of ring size in paraffins. The IR band associated with this vibration is weak or nonexistent.

18C-3 Biological and Forensic Applications of Raman Spectroscopy

Raman spectroscopy has been applied widely for the study of biological systems.[9] The advantages of this technique include the small sample requirement, the minimal sensitivity to water, the spectral detail, and the conformational and environmental sensitivity.

Raman spectroscopy has become a useful tool in forensic science.[10] Raman methods, often implemented with portable or handheld instruments, have been used in the analysis of body fluids, gunshot residues, and trace evidence. In forensic applications, Raman spectroscopy is generally considered confirmatory to results obtained by other instrumental methods.

18C-4 Quantitative Applications

Raman spectra tend to be less cluttered with bands than IR spectra. Because of this, peak overlap in mixtures is less likely, and quantitative measurements are simpler. In addition, Raman sampling devices are not subject to attack by moisture, and small amounts of water in a sample do not interfere. Despite these advantages, Raman spectroscopy has only recently been exploited widely for quantitative analysis. The increasing use of Raman spectroscopy is due to the availability of inexpensive, routine Raman instrumentation.

There are, however, some drawbacks to the use of Raman spectroscopy for quantitative analysis. First, there are matrix effects that can occur in Raman measurements. Absorption of the Raman signal by concomitants in the sample can sometimes lead to errors. The method of standard additions is often used to compensate for matrix effects. There can also be effects from sample inhomogeneity. Another drawback occurs because of instrument instability. Fluctuations in laser intensity between samples and standards or samples and samples with added analyte can influence results. Changes can also occur in the position of Raman bands due to changes in temperature or instrument conditions. Also, sample positioning in the laser beam can change measurement results. Quantitative results attained with FT-Raman instruments are often superior to those

[7]See K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., New York: Wiley, 1996.

[8]L. Daimay, N. B. Colthup, W. G. Fately, and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, New York: Academic Press, 1991.

[9]See J. R. Ferraro, K. Nakamoto, and C. W. Brown, *Introductory Raman Spectroscopy*, 2nd ed., San Diego: Academic Press, 2003, Chap. 6; *Infrared and Raman Spectroscopy of Biological Materials*, H. U. Gremlich and B. Yan, eds., New York: Marcel Dekker, 2001; *Biological Applications of Raman Spectroscopy*, T. G. Spiro, ed., Vols. 1–3, New York: Wiley, 1987–88.

[10]For a review of Raman applications in forensic science, see K. C. Doty et al., *J. Raman Spectrosc.*, **2016**, *47*, 39, **DOI**: 10.1002/jrs.4826; see also *Infrared and Raman Spectroscopy in Forensic Science*, J. M. Chalmers, H. G. M. Edwards, and M. D. Hairgreaves, eds., Chichester, UK: Wiley, 2012.

with dispersive systems due to the higher stability of FT-Raman systems and the larger aperture of the spectrometer.

Because laser beams can be precisely focused, it becomes possible to perform quantitative analyses on very small samples. The Raman microprobe has been used to determine analytes in single bacterial cells, components in individual particles of smoke and fly ash, and species in microscopic inclusions in minerals. Surfaces have been examined by tuning the instrument to a given vibrational mode. This results in an image of regions on a surface where a particular bond or functional group is present as discussed previously.

The Raman microprobe has played a critical role in the authentication of some presumed ancient documents such as the Vinland map (see the Instrumental Analysis in Action feature at the end of Section 3). In the case of the map, the presence of TiO_2 in the ink was shown conclusively by Raman microscopy.

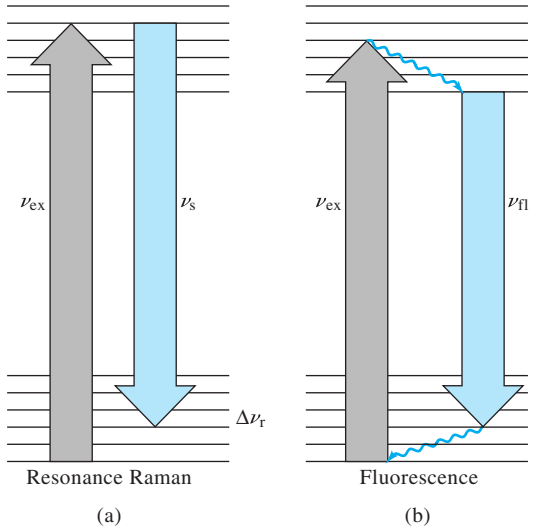

FIGURE 18-13 Energy diagram for (a) resonance Raman scattering and (b) fluorescence emission. Radiationless relaxation is shown as wavy arrows. In the resonance Raman case, the excited electron immediately relaxes into a vibrational level of the ground electronic state giving up a Stokes photon ν_s. In fluorescence, relaxation to the lowest vibrational level of the excited electronic state occurs prior to emission. Resonance Raman scattering is nearly instantaneous, and the spectral bands are very narrow. Fluorescence emission usually takes place on the nanosecond time scale. Fluorescence spectra are usually broad because of the many vibrational states.

18D OTHER TYPES OF RAMAN SPECTROSCOPY

Advancements in tunable lasers led to several new Raman spectroscopic methods in the early 1970s. A brief discussion of the applications of some of these techniques follows.

18D-1 Resonance Raman Spectroscopy

Resonance Raman scattering refers to a phenomenon in which Raman line intensities are greatly enhanced by excitation with wavelengths that closely approach that of an electronic absorption band of an analyte.[11] Under this circumstance, the magnitudes of Raman lines associated with the most symmetric vibrations are enhanced by a factor of 10^2 to 10^6. As a result, resonance Raman spectra have been obtained at analyte concentrations as low as 10^{-8} M. This level of sensitivity is in contrast to normal Raman studies, which are ordinarily limited to concentrations greater than 0.1%. Furthermore, because resonance enhancement is restricted to the Raman bands associated with the chromophore, resonance Raman spectra are usually quite selective.

Figure 18-13a illustrates the energy changes responsible for resonance Raman scattering. This figure differs from the energy diagram for normal Raman scattering (Figure 18-3) in that the electron is promoted into an excited electronic state followed by an immediate relaxation to a vibrational level of the electronic ground state. As shown in the figure, resonance Raman scattering differs from fluorescence (Figure 18-13b) in that relaxation to the ground state is not preceded by prior relaxation to the lowest vibrational level of the excited electronic state. The time scales for the two phenomena are also quite different, with Raman relaxation occurring in less than 10^{-14} s compared with the 10^{-6} to 10^{-10} s for fluorescence emission.

Line intensities in a resonance Raman experiment increase rapidly as the excitation wavelength approaches the wavelength of the electronic absorption band. Thus, to achieve the greatest signal enhancement for a broad range of absorption maxima, a tunable laser is required. With intense laser radiation, sample decomposition can become a major problem because electronic absorption bands often occur in the UV region. To circumvent this problem, it is common practice to circulate the sample past the focused beam of the laser. Circulation is normally accomplished in one of two ways: by pumping a solution or liquid through a capillary mounted in the sample position or by rotating a cylindrical cell containing the sample through the laser beam. Thus, only a small fraction of the sample is irradiated at any instant, and heating and sample decomposition are minimized.

Perhaps the most important application of resonance Raman spectroscopy has been to the study of biological molecules under physiologically significant conditions; that is, in the presence of water and at low to moderate concentration levels. As an example, the technique has been used to determine the oxidation state and spin of iron atoms in hemoglobin and cytochrome *c*. In these molecules, the resonance Raman bands are

[11]For brief reviews, see T. G. Spiro and R. S. Czernuszewicz in *Physical Methods in Bioinorganic Chemistry*, L. Que, ed., Sausalito, CA: University Science Books, 2000; S. A. Asher, *Anal. Chem.*, **1993**, *65*, 59A, **DOI**: 10.1021/ac00050a001.

due solely to vibrational modes of the tetrapyrrole chromophore. None of the other bands associated with the protein is enhanced, and at the concentrations normally used, these bands do not interfere.

Time-resolved resonance Raman spectrometry is a technique that allows collection of Raman spectra of excited state molecules. It has been used to study intermediates in enzyme reactions, the spectra of carotenoid excited states, ultrafast electron transfer steps, and a variety of other biological and bioinorganic processes.[12] Time-discrimination methods have been used to overcome a major limitation of resonance Raman spectroscopy, namely, fluorescence interference either by the analyte itself or by other species present in the sample.

18D-2 Surface-Enhanced Raman Spectroscopy

In surface-enhanced Raman spectroscopy (SERS),[13] Raman spectra are acquired in the usual way on samples that are adsorbed on the surface of colloidal metal particles (usually silver, gold, or copper) or on roughened surfaces of pieces of these metals. For reasons that are finally becoming understood, at least semiquantitatively, the Raman lines of the adsorbed molecule are often enhanced by a factor of 10^3 to 10^6.

Surface enhancement is thought to arise from two factors. First, there is an enhancement due to the electromagnetic field. This occurs because the incident electromagnetic wave interacts with the metal surface to excite localized surface plasmons, which amplifies the field near the surface. Because Raman scattering scales as the fourth power of the field, this effect can enhance signals by as much as a factor of 10,000. The second factor is a chemical enhancement that occurs because of the adsorbed molecule interacting with the surface. This effect can enhance the Raman signal by as much as 100 times. The net enhancement is the product of the two effects, which can be approximately 1 million.[14] When surface enhancement is combined with the resonance enhancement technique discussed in the previous section, the net increase in signal intensity is roughly the product of the intensity produced by each of the techniques. Consequently, detection limits in the range of 10^{-9} to 10^{-12} M have been observed.

Several sample-handling techniques are used for SERS. In one technique, colloidal silver or gold particles are suspended in a dilute solution (usually aqueous) of the sample. The solution is then held or flowed through a narrow glass tube while it is excited by a laser beam. In another method, a thin film of colloidal metal particles is deposited on a glass slide and a drop or two of the sample solution spotted on the film. The Raman spectrum is then obtained in the usual manner. Alternatively, the sample may be deposited electrolytically on a roughened metal electrode, which is then removed from the solution and exposed to the laser excitation source.

18D-3 Nonlinear Raman Spectroscopy

In Section 7B-3, we pointed out that many lasers are intense enough to produce significant amounts of nonlinear radiation. Throughout the 1970s and 1980s, many Raman techniques were developed that depend on polarization induced by second-order and higher field strengths. These techniques are termed *nonlinear Raman methods*.[15] Included in these methods are *stimulated Raman scattering*, *the hyper-Raman effect*, *stimulated Raman gain*, *inverse Raman spectroscopy*, *coherent anti-Stokes Raman spectroscopy*, and *coherent Stokes Raman spectroscopy*. The most widely used of these methods is coherent anti-Stokes Raman spectroscopy, or CARS.

Nonlinear techniques have been used to overcome some of the drawbacks of conventional Raman spectroscopy, particularly its low efficiency, its limitation to the visible and near-UV regions, and its susceptibility to interference from fluorescence. A major disadvantage of nonlinear methods is that they tend to be analyte specific and often require several different tunable lasers to be applicable to diverse species. To date, none of the nonlinear methods has found widespread application among nonspecialists. However, many of these methods have shown considerable promise. As less expensive and more routinely useful lasers become available, nonlinear Raman methods, particularly CARS, should become more widely used.

[12] J. R. Kincaid and K. Czarnecki, in *Comprehensive Coordination Chemistry II*, J. A. McCleverty and T. J. Meyer, eds., Oxford: Elsevier, 2004.

[13] See M. J. Weaver, S. Zou, and H. Y. Chan, *Anal. Chem.*, **2000**, *72*, 38A, **DOI**: 10.1021/ac0027136. American Chemical Society.

[14] See, P. L. Stiles, J. A. Dieringer, N. C. Shah, and R. P. Van Duyne, *Ann. Rev. Anal. Chem.*, **2008**, *1*, 601, **DOI**: 10.1146/annurev.anchem.1.031207.112814.

[15] See J. R. Ferraro, K. Nakamoto, and C. W. Brown, *Introductory Raman Spectroscopy*, 2nd ed., San Diego: Academic Press, 2003, pp. 194–202.

» 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.

18-1 What is a virtual state?

18-2 Why does the ratio of anti-Stokes to Stokes intensities increase with sample temperature?

***18-3** An antihistamine shows sharp peaks at Raman shifts of $\Delta\bar{\nu} = 488$, 725, 875, 925, and 1350 cm^{-1}. At what wavelengths in nanometers would the Stokes and anti-Stokes lines for the antihistamine appear if the source were

(a) a helium-neon laser (632.8 nm)?

(b) an argon-ion laser (488.0 nm)?

***18-4** Assume the excitation sources in Problem 18-3 have the same power. (a) Compare the relative intensities of the Raman lines of the antihistamine for each of the two excitation sources. (b) If the intensities were recorded with a typical monochromator-photomultiplier system, why would the measured intensity ratios differ from the ratio calculated in part (a)?

***18-5** For vibrational states, the Boltzmann equation can be written as

$$\frac{N_1}{N_0} = \exp(-\Delta E/kT)$$

where N_0 and N_1 are the populations of the lower and higher energy states, respectively, ΔE is the energy difference between the states, k is Boltzmann's constant, and T is the temperature in kelvins.

For temperatures of 20°C and 40°C, calculate the ratios of the intensities of the anti-Stokes and Stokes lines for CCl_4 at (a) 218 cm^{-1}, (b) 459 cm^{-1}, (c) 790 cm^{-1}.

For each temperature and Raman shift, calculate how much more intense the Stokes line is compared to the anti-Stokes line.

18-6 The following questions deal with laser sources in Raman spectroscopy.

(a) Under what circumstances would a helium-neon laser be preferable to an argon-ion laser?

(b) Under what circumstances would a diode laser be preferable to an argon-ion or helium-neon laser?

(c) Why are UV emitting sources avoided?

***18-7** The following Raman data were obtained for $CHCl_3$ with the polarizer of the spectrometer set (1) parallel to the plane of polarization of the laser and (2) at 90° to the plane of the source.

		Relative Intensities	
	$\Delta\bar{\nu}$, cm^{-1}	(1) $I_{\|\|}$	(2) $I_{\perp}$
(a)	760	0.60	0.46
(b)	660	8.4	0.1
(c)	357	7.9	0.6
(d)	258	4.2	3.2

Calculate the depolarization ratio and indicate which Raman lines are polarized.

18-8 Discuss the advantages and disadvantages of FT-Raman spectrometers compared to conventional dispersive Raman instruments.

QUESTIONS AND PROBLEMS (continued)

Challenge Problem

18-9 The following questions all deal with the similarities and differences between IR spectrometry and Raman spectrometry.

(a) What are the requirements for a vibrational mode in a molecule to show IR absorption? What are the requirements for a vibrational mode to be Raman active? Why do these requirements differ? Under what circumstances will vibrational modes be both Raman and IR active? Under what circumstances will vibrational modes be Raman active but not IR active and vice versa?

(b) Consider the molecule chloroacetonitrile ($ClCH_2CN$). How many vibrational modes should this molecule have? Why might one observe fewer Raman bands than expected?

(c) Chloroacetonitrile shows a strong Raman band at 2200 cm^{-1} due to the C—N stretching mode. The corresponding IR absorption is very weak or absent. By comparing spectra in the 2200 cm^{-1} region, what can you conclude about the C—N stretching mode in chloroacetonitrile?

(d) Compare and contrast IR and Raman spectrometry with respect to optics, cell materials, sample handling, solvent compatibility, and applicability to various sample types.

(e) Compare and contrast the sources and transducers used in Raman spectrometers to those used in FTIR instruments. Consider both FT-Raman and dispersive Raman spectrometers in your comparison.

(f) Compare and contrast IR and Raman spectrometry with respect to qualitative usefulness, detection limits, quantitative analysis, and instrumental complexity.