

Infrared, Near-Infrared, and Raman Spectroscopy

Infrared (IR) radiation was first discovered in 1800 by Sir William Herschel, who used a glass prism with blackened thermometers as detectors to measure the heating effect of sunlight within and beyond the boundaries of the visible spectrum. Coblentz laid the groundwork for IR spectroscopy with a systematic study of organic and inorganic absorption spectra. Experimental difficulties were immense. Since each point in the spectrum had to be measured separately, it could take 4 hours to record the full spectrum. But from this work came the realization that each compound had its own unique IR absorption pattern and that certain functional groups absorbed at about the same wavelength even in different molecules. The IR absorption spectrum provides a "fingerprint" of a molecule with covalent bonds. This can be used to identify the molecule. Qualitative identification of organic and inorganic compounds is a primary use of IR spectroscopy. In addition, the spectrum provides a quick way to check for the presence of a given functional group such as a carbonyl group in a molecule. IR spectroscopy and spectrometry as used by analytical and organic chemists is primarily *absorption* spectroscopy. IR absorption can also be used to provide quantitative measurements of compounds.

IR spectroscopy became widely used after the development of commercial spectrometers in the 1940s. Double-beam monochromator instruments were developed, better detectors were designed, and better dispersion elements, including gratings, were incorporated. These conventional spectrometer systems have been replaced by Fourier transform IR (FTIR) instrumentation. This chapter will focus on FTIR instrumentation and applications of IR spectroscopy. In addition, the related techniques of near-infrared (NIR) spectroscopy and Raman spectroscopy will be covered, as well as the use of IR and Raman microscopy.

The wavelengths of IR radiation of interest to chemists trying to identify or study organic molecules fall between 2 and 20 μm . These wavelengths are longer than those in the red end of the visible region, which is generally considered to end at about 0.75 μm . IR radiation therefore is of lower energy than visible radiation but of higher energy than radio waves. The entire IR region can be divided into the *NIR*, from 0.75 to 2.5 μm , the *mid-IR*, from about 2.5 to 20 μm , and the *far-IR*, from 20 to 200 μm . Visible radiation (red light) marks the upper energy end or minimum wavelength end of the IR region; the maximum wavelength end is defined somewhat arbitrarily; some texts consider the far-IR to extend to 1000 μm . The IR wavelength range tells us the IR frequency range from the equation (introduced in Chapter 2)

$$\nu = \frac{c}{\lambda} \quad (4.1)$$

where

- ν is the frequency
- c is the speed of light
- λ is the wavelength

We also know that $\Delta E = h\nu$. When the frequency is high, λ is short and the energy of the radiation is high.

It is common to use *wavenumber*, symbolized by either $\tilde{\nu}$ or $\bar{\nu}$, with units of cm^{-1} , in describing IR spectra. The first symbol is called "nu tilde"; the second symbol is called "nu bar"; both symbols are used in the literature. The unit cm^{-1} is called a *reciprocal centimeter*. The wavenumber is the reciprocal of the wavelength. Wavenumber is the number of waves of radiation per centimeter, $1/\lambda$; frequency is the number of waves per second, c/λ . Wavelength and wavenumber are related by

$$\text{Wavelength } (\mu\text{m}) \times \text{wavenumber } (\text{cm}^{-1}) = 10,000 = 1 \times 10^4 \quad (4.2)$$

Both wavenumbers and wavelengths will be used throughout the chapter, so it is important to be able to convert between these units. The older IR literature used the term *micron* and the symbol μ for wavelength in micrometers (μm).

4.1 ABSORPTION OF IR RADIATION BY MOLECULES

Molecules with covalent bonds may absorb IR radiation. This absorption is quantized, so only certain frequencies of IR radiation are absorbed. When radiation (i.e., energy) is absorbed, the molecule moves to a higher energy state. The energy associated with IR radiation is sufficient to cause molecules to rotate (if possible) and to vibrate. If the IR wavelengths are longer than $100 \mu\text{m}$, absorption will cause excitation to higher rotational states in the gas phase. If the wavelengths absorbed are between 1 and $100 \mu\text{m}$, the molecule will be excited to higher vibrational states. Because the energy required to cause a change in rotational level is small compared to the energy required to cause a vibrational level change, each vibrational change has multiple rotational changes associated with it. Gas phase IR spectra therefore consist of a series of discrete lines. Free rotation does not occur in condensed phases. Instead of a narrow line spectrum of individual vibrational absorption lines, the IR absorption spectrum for a liquid or solid is composed of broad vibrational absorption bands. A typical IR spectrum for a condensed phase (liquid or solid) is shown in Figure 4.1. This is the

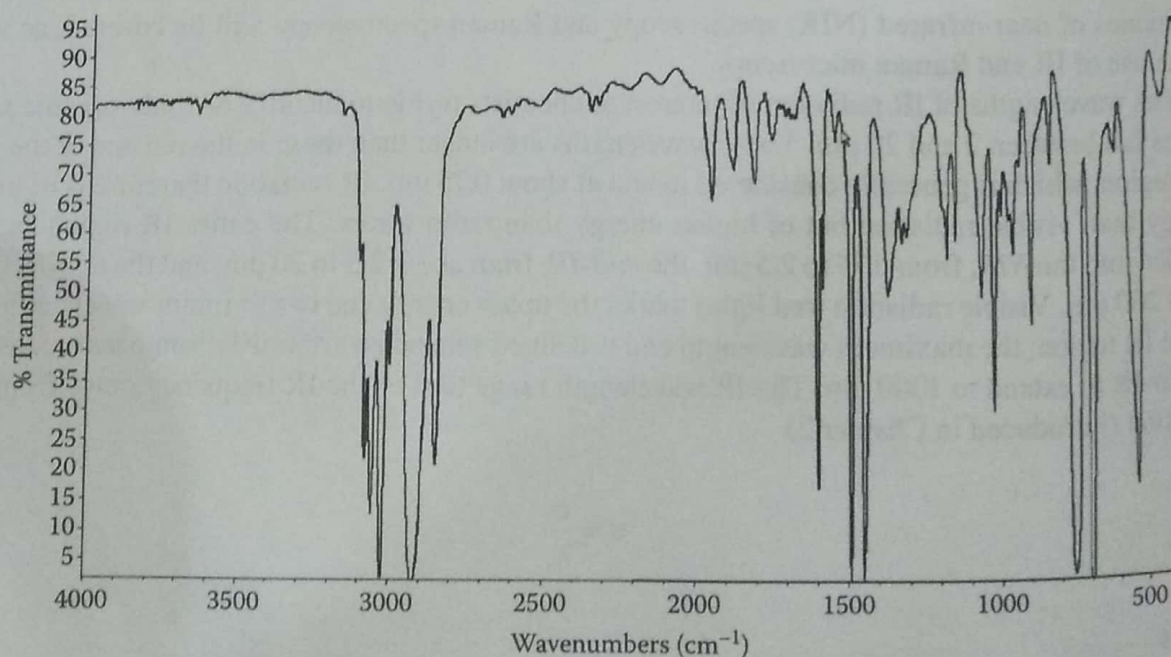


Figure 4.1 FTIR spectrum of a thin film of polystyrene. The y-axis unit is %T; the x-axis is in wavenumbers (cm^{-1}). Collected on a Thermo Scientific 6700 FTIR spectrometer with a deuterated triglycine sulfate (DTGS) detector. (© Thermo Fisher Scientific, www.thermofisher.com. Used with permission.)

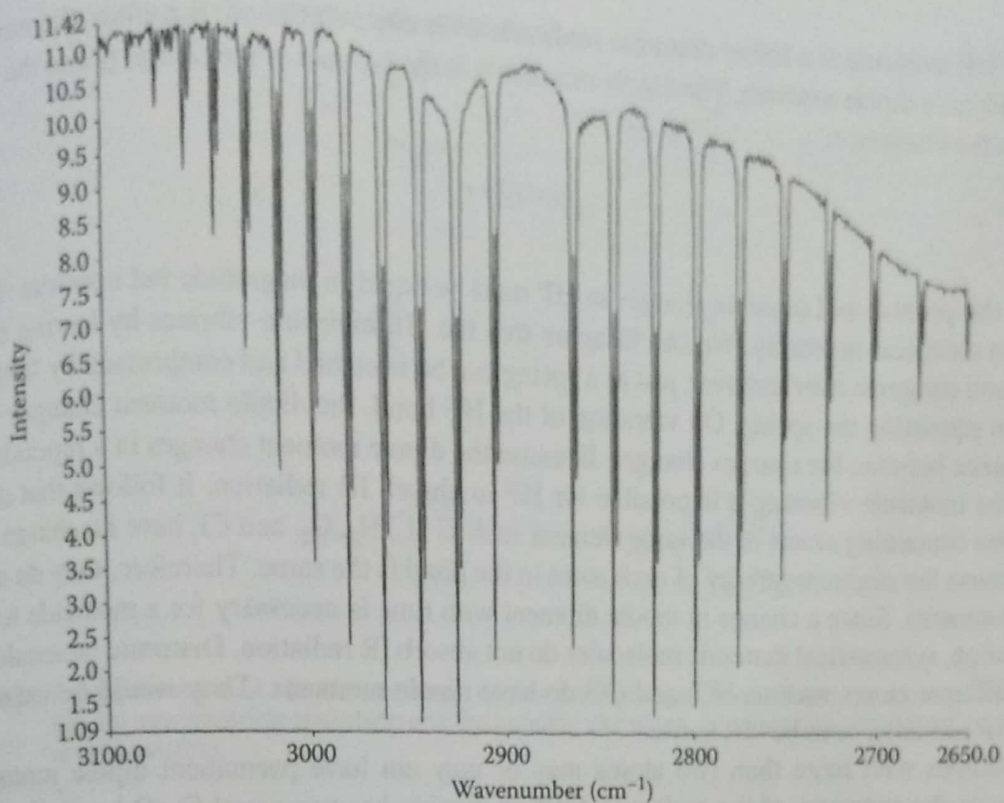


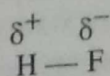
Figure 4.2 Vapor-phase FTIR spectrum of hydrogen chloride, HCl. Spectrum was collected in a 10 cm gas cell with NaCl windows on a Paragon 1000 FTIR spectrometer. [© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission. (www.perkinelmer.com).]

spectrum of a thin film of polystyrene; note that the absorption band at about 2950 cm^{-1} is more than 100 cm^{-1} wide at the top. The individual vibration–rotation lines can be seen in gas-phase IR spectra. These narrow lines are clearly seen in Figure 4.2, the gas-phase spectrum of hydrogen chloride, HCl.

Molecules absorb radiation when a bond in the molecule vibrates at the same frequency as the incident radiant energy. After absorbing radiation, the molecules have more energy and vibrate at increased amplitude. The frequency absorbed depends on the masses of the atoms in the bond, the geometry of the molecule, the strength of the bond, and several other factors. Not all molecules can absorb IR radiation. The molecule must have a change in **dipole moment** during vibration in order to absorb IR radiation.

4.1.1 Dipole Moments in Molecules

When two atoms with different electronegativities form a bond, the electron density in the bond is not equally distributed. For example, in the molecule hydrogen fluoride, HF, the electron density in the bond shifts away from the H atom toward the more electronegative fluorine atom. This results in a partial negative charge on F and a partial positive charge on H. The bond is said to be **polar** when such charge separation exists. The charge separation can be shown as



where δ indicates a partial charge. The dipole in the bond is indicated by a crossed arrow placed with the point on the more negative end of the bond as shown:

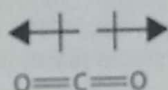


The HF molecule is a linear diatomic molecule with one polar bond; therefore, the molecule is polar and has a dipole moment. The dipole moment μ is the product of the charge Q and the distance between the charges, r :

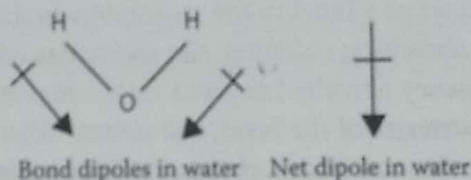
$$\mu = Q \times r \quad (4.3)$$

The partial positive and negative charges in HF must be equal in magnitude but opposite in sign to maintain electrical neutrality. We can imagine that the HF molecule vibrates by having the bond stretch and compress over and over, just as a spring can be stretched and compressed by first pulling and then squeezing the spring. On vibration of the HF bond, the dipole moment changes because the distance between the charges changes. Because the dipole moment changes in a repetitive manner as the molecule vibrates, it is possible for HF to absorb IR radiation. It follows that diatomic molecules containing atoms of the same element such as H_2 , N_2 , O_2 , and Cl_2 have no charge separation because the electronegativity of each atom in the bond is the same. Therefore, they do not have dipole moments. Since a change in dipole moment with time is necessary for a molecule to absorb IR radiation, symmetrical diatomic molecules do not absorb IR radiation. Diatomic molecules made up of different atoms such as HCl and CO do have dipole moments. They would be expected to absorb IR radiation or to be "IR active."

Molecules with more than two atoms may or may not have permanent dipole moments. It depends on the geometry of the molecule. Carbon dioxide has two equal C=O bond dipoles, but because the molecule is linear, the bond dipoles cancel and the molecule has no net dipole moment:



Water, H_2O , has two equal H-O bond dipoles. Water has a bent geometry and the vector sum of the bond dipoles does not cancel. The water molecule has a permanent net dipole moment:



Predicting the IR absorption behavior of molecules with more than two atoms is not as simple as looking at diatomic molecules. It is not the net dipole moment of the molecule that is important, but any change in the dipole moment on vibration. We need to understand how molecules vibrate. This is relatively simple for diatomic and triatomic molecules. Large molecules cannot be evaluated simply because of their large number of vibrations and interactions between vibrating atoms. It can be said that most molecules do absorb IR radiation, which is the reason this technique is so useful.

4.1.2 Types of Vibrations in Molecules

The common molecular vibrations that are excited by IR radiation are **stretching** vibrations and **bending** vibrations. These are called **modes** of vibration. Stretching involves a change in bond lengths resulting in a change in interatomic distance. Bending involves a change in bond angle or a change in the position of a group of atoms with respect to the rest of the molecule. For a group of three or more atoms, at least two of which are the same type of atom, there are two stretching modes: symmetrical stretching and asymmetrical stretching. These two modes of stretching are shown, respectively, in Figure 4.3 for a CH_2 group. In Figure 4.3a, the two H atoms both move

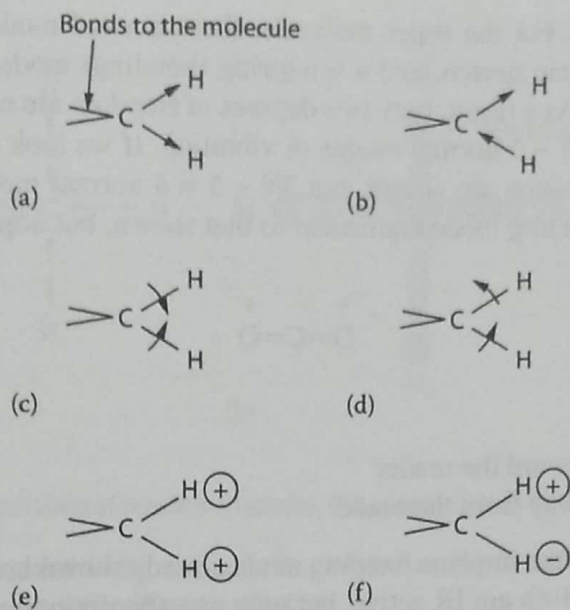
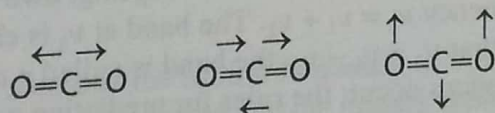


Figure 4.3 Principal modes of vibration between carbon and hydrogen in an alkane: (a) symmetrical stretching, (b) asymmetrical stretching and the bending vibrations, (c) scissoring, (d) rocking, (e) wagging, and (f) twisting.

away from the C atom—a symmetrical stretch. In Figure 4.3b, one H atom moves away from the C atom and one moves toward the C atom—an asymmetrical stretch. Bending modes are shown in Figure 4.3c–f. Scissoring and rocking are in-plane bending modes—the H atoms remain in the same plane as the C atom (i.e., in the plane of the page). Wagging and twisting are out-of-plane (oop) bending modes—the H atoms are moving out of the plane containing the C atom. The + sign in the circle indicates movement above the plane of the page toward the reader, while the – sign in the circle indicates movement below the plane of the page away from the reader. Bends are also called deformations and the term antisymmetric is used in place of asymmetric in various texts.

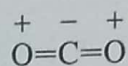
For the CO₂ molecule, we can draw a symmetric stretch, an asymmetric stretch, and a bending vibration, as shown:



The CO₂ molecule on the left is undergoing a symmetric stretch, the one in the middle an asymmetric stretch, and the one on the right an in-plane bend. The symmetric stretching vibration does not change the dipole moment of the molecule. This vibrational mode does not absorb IR radiation—it is said to be *IR inactive*. However, the other two modes of vibration do change the dipole moment—they are *IR active*. The asymmetric stretching frequency occurs at 2350 cm⁻¹ and the bending vibration occurs at 666 cm⁻¹.

For diatomic and triatomic molecules, it is possible to work out the number and kind of vibrations that occur. To locate a point in 3D space requires three coordinates. To locate a molecule containing *N* atoms in three dimensions, 3*N* coordinates are required. The molecule is said to have 3*N* degrees of freedom. To describe the motion of such a molecule, translational, rotational, and vibrational motions must be considered. Three coordinates or degrees of freedom are required to describe translational motion and three degrees of freedom are required to describe rotational motion about the molecule's center of gravity. This leaves 3*N* – 6 degrees of freedom to describe vibrational motion. There are 3*N* – 6 possible normal modes of vibration in a molecule of *N* atoms. For example, the water molecule contains 3 atoms, so it has 3 × 3 = 9 degrees of freedom and (3 × 3) – 6 = 3

normal modes of vibration. For the water molecule, these normal modes of vibration are a symmetric stretch, an asymmetric stretch, and a scissoring (bending) mode. Linear molecules cannot rotate about the bond axis. As a result, only two degrees of freedom are needed to describe rotation, so linear molecules have $3N - 5$ normal modes of vibration. If we look at the CO_2 molecule given earlier, three modes of vibration are shown, but $3N - 5 = 4$ normal modes of vibration, so one is missing. The fourth is a bending mode equivalent to that shown, but oop:



where

- + indicates movement toward the reader
- indicates movement away from the reader

The oop bending mode and the in-plane bending mode already shown both occur at 666 cm^{-1} . They are said to be *degenerate*. Both are IR active, but only one absorption band is seen since they both occur at the same frequency.

For simple molecules, this approach predicts the number of fundamental vibrations that exist. The use of the dipole moment rule indicates which vibrations are IR active, but the IR spectrum of a molecule rarely shows the number of absorption bands calculated. Fewer peaks than expected are seen due to IR-inactive vibrations, degenerate vibrations, and very weak vibrations. More often, additional peaks are seen in the spectrum due to overtones and other bands.

The excitation from the ground state V_0 to the first excited state V_1 is called the *fundamental transition*. It is the most likely transition to occur. Fundamental absorption bands are strong compared with other bands that may appear in the spectrum due to overtone, combination, and difference bands. *Overtone* bands result from excitation from the ground state to higher energy states V_2 , V_3 , and so on. These absorptions occur at approximately integral multiples of the frequency of the fundamental absorption. If the fundamental absorption occurs at frequency ν , the overtones will appear at about 2ν , 3ν , and so on. Overtones are weak bands and may not be observed under real experimental conditions. Vibrating atoms may interact with each other. The interaction between vibrational modes is called *coupling*. Two vibrational frequencies may couple to produce a new frequency $\nu_3 = \nu_1 + \nu_2$. The band at ν_3 is called a *combination* band. If two frequencies couple such that $\nu_3 = \nu_1 - \nu_2$, the band is called a *difference* band. Not all possible combinations and differences occur; the rules for predicting coupling are beyond the scope of this text.

The requirements for the absorption of IR radiation by molecules can be summarized as follows:

1. The natural frequency of vibration of the molecule must equal the frequency of the incident radiation.
2. The frequency of the radiation must satisfy $\Delta E = h\nu$, where ΔE is the energy difference between the vibrational states involved.
3. The vibration must cause a change in the dipole moment of the molecule.
4. The amount of radiation absorbed is proportional to the square of the rate of change of the dipole during the vibration.
5. The energy difference between the vibrational energy levels is modified by coupling to rotational energy levels and coupling between vibrations.

4.1.3 Vibrational Motion

A molecule is made up of two or more atoms joined by chemical bonds. Such atoms vibrate about each other. A simple model of vibration in a diatomic molecule can be made by considering the bond to be a spring with a weight on each end of the spring (Figure 4.4). The stretching of such a

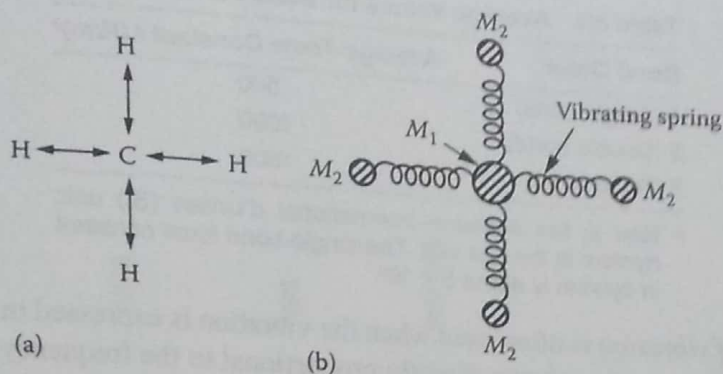


Figure 4.4 (a) The atoms and chemical bonds in methane, CH_4 , presented as (b) a system of masses and springs. spring along its axis in a regular fashion results in simple harmonic motion. Hooke's law states that two masses joined by a spring will vibrate such that

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}} \quad (4.4)$$

where

ν is the frequency of vibration

f is the force constant of the spring (a measure of the stiffness of the spring)

μ is the reduced mass

The reduced mass is calculated from the masses of the two weights joined by the spring:

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad (4.5)$$

where

M_1 is the mass of one vibrating body

M_2 is the mass of the other

From Equation 4.4, it can be seen that the natural frequency of vibration of the harmonic oscillator depends on the force constant of the spring and the masses attached to it but is independent of the amount of energy absorbed. Absorption of energy changes the amplitude of vibration, not the frequency. The frequency ν is given in hertz (Hz) or cps. If one divides ν in cps by c , the speed of light in cm/s, the result is the number of cycles per cm. This is $\bar{\nu}$, the wavenumber:

$$\bar{\nu} = \frac{\nu}{c} \quad (4.6)$$

Dividing both sides of Equation 4.4 by c , we get

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}} \quad (4.7)$$

where

$\bar{\nu}$ is the wavenumber of the absorption maximum in cm^{-1}

c is the speed of light in cm/s

f is the force constant of the bond in dyn/cm

μ is the reduced mass in g

Table 4.1 Average Values for Bond Force Constant

Bond Order	Average Force Constant f (N/m) ^a
1 (Single bond)	500
2 (Double bond)	1000
3 (Triple bond)	1500

^a N/m is the Systeme International d'Unites (SI) unit; dyn/cm is the cgs unit. The single-bond force constant in dyn/cm is about 5×10^9 .

The term *frequency of vibration* is often used when the vibration is expressed in wavenumbers, but it must be remembered that wavenumber is directly proportional to the frequency ν , not identical to it. Equation 4.7 tells us the frequency of vibration of two atoms joined by a chemical bond, where the force constant f is a measure of the *strength* of the chemical bond and μ is the reduced mass of the vibrating atoms. The term f varies with bond strength; a simple but useful approximation is that a triple bond between two atoms is three times as strong as a single bond between the same two atoms, so f would be three times as large for the triple bond. A double bond is twice as strong as a single bond. The force constant f is directly proportional to the bond order and depends on the electronegativity of the vibrating atoms and the mean distance between them. These are all physical constants and properties of the molecule. Since f and μ are constant for any given set of atoms and chemical bonds, the frequency of vibration ν is also constant. *The radiation absorbed by the system has the same frequency and is constant for a given set of atoms and chemical bonds*, that is, for a given molecule. The absorption spectrum is therefore a physical property of the molecule. Average values of the force constant for single, double, and triple bonds are given in Table 4.1. Using these values of f and the masses of given atoms, it is possible to estimate the wavenumber for fundamental stretching vibrations of given bonds as discussed. Table 4.2 presents frequencies for common vibrations.

From Equation 4.7, we can deduce that a C–C bond vibrates at a lower wavenumber than a C=C bond, because the force constant for the C–C bond is smaller than that for C=C. For example, C–C vibrates at 1200 cm^{-1} and C=C vibrates at 1650 cm^{-1} . In general, force constants for bending vibrations are lower than stretching vibrations. Resonance and hybridization in molecules also affect the force constant for a given bond.

4.2 IR INSTRUMENTATION

Until the early 1980s, most mid-IR spectrometer systems were double-beam dispersive grating spectrometers, similar in operation to the double-beam system for ultraviolet/visible (UV/VIS) spectroscopy described in Chapter 2. These instruments have been replaced almost entirely by FTIR spectrometers because of the advantages in speed, signal-to-noise ratio, and precision in determining spectral frequency that can be obtained from a modern multiplex instrument. There are NIR instruments that are part of double-beam dispersive UV/VIS/NIR systems, but many NIR instruments are stand-alone grating instruments.

The first requirement for material used in an IR spectrometer is that the material must be transparent to IR radiation. This requirement eliminates common materials such as glass and quartz for use in mid-IR instruments because glass and quartz are not transparent to IR radiation at wavelengths longer than $3.5 \mu\text{m}$. Second, the materials used must be strong enough to be shaped and polished for windows, sample cells, and the like. Common materials used are ionic salts, such as potassium bromide, calcium fluoride, sodium chloride (rock salt), and zinc selenide. The final choice among the compounds is determined by the wavelength range to be examined; for example, sodium chloride is transparent to radiation between 2.5 and $15 \mu\text{m}$. This wavelength range was therefore termed the *rock salt region* when an ionic salt prism was used as the wavelength dispersion device in

Table 4.3 Typical Materials Used in Mid-IR Optics

Material	Transmission Range (μm)	Solubility (g/100 g Water)	Refractive Index (RI)	Comments
Sodium chloride (NaCl)	0.25–16	36	1.49	Most widely used; reasonable range and low cost.
Potassium chloride (KCl)	0.30–20	35	1.46	Wider range than NaCl; used as a laser window.
Potassium bromide (KBr)	0.25–26	65	1.52	Extensively used; wide spectral range.
Barium fluoride (BaF_2)	0.2–11	0.1	1.39	Extremely brittle.
Cesium iodide (CsI)	0.3–60	160	1.74	Transmits to 60 μm .
Cesium bromide (CsBr)	0.3–45	125	1.66	
Thallium bromide/iodide eutectic (KRS-5)	0.6–40	<0.05	2.4	For internal reflection in the far when moisture is a problem.
Strontium fluoride (SrF_2)	0.13–11	1.7×10^{-3}		Resistant to thermal shock.
Silver chloride (AgCl)	0.4–25	1.5×10^{-4}	2.0	Darkens under UV light.
Silver bromide (AgBr)	0.5–35	1.2×10^{-5}	2.2	Darkens under UV light.
Germanium	2–11	Insoluble	4.00	
Fused silica	0.2–4.5	Insoluble	1.5 at 1 μm	Most useful for NIR.
Magnesium fluoride (MgF_2)	0.5–9	Insoluble	1.34 at 5 μm	This and the next five materials are known commercially at Irtran [®] 1 through 6.
Zinc sulfide (ZnS)	0.4–14.5	Insoluble	2.2	
Calcium fluoride (CaF_2)	0.4–11.5	Insoluble	1.3	
Zinc selenide (ZnSe)	0.5–22	Insoluble	2.4	
Magnesium oxide (MgO)	0.4–9.5	Insoluble	1.6 at 5 μm	
Cadmium telluride (CdTe)	0.9–31	Insoluble	2.7	

early instruments. Potassium bromide or cesium bromide can be used over the range of 2.1–2.6 μm , and calcium fluoride in the range of 2.4–7.7 μm . The wavelength ranges of some materials used for IR optics and sample holders are given in Table 4.3.

The major problem with the use of NaCl, KBr, and similar ionic salts is that they are very soluble in water. Any moisture, even atmospheric moisture, can dissolve the surface of a polished salt crystal, causing the material to become opaque and scatter light. Optics and sample containers made of salts must be kept desiccated. This limitation is one of the reasons salt prisms are no longer used in dispersive IR spectrometers.

4.2.1 Radiation Sources

A radiation source for IR spectroscopy should fulfill the requirements of an ideal radiation source, namely, that the intensity of radiation (1) be continuous over the wavelength range used, (2) cover a wide wavelength range, and (3) be constant over long periods of time. The most common sources of IR radiation for the mid-IR region are *Nernst glowers*, *Globars*, and *heated wires*. All of these heated sources emit continuous radiation, with a spectral output very similar to that of a blackbody radiation source. Spectral curves for blackbody radiators at several temperatures are shown in Figure 4.5. The normal operating temperatures for IR sources are between 1100 and 1500 K. The range of light put out by mid-IR sources extends into both the NIR and far-IR regions, but intensity is at a maximum in the mid-IR region from 4000 to 400 cm^{-1} .

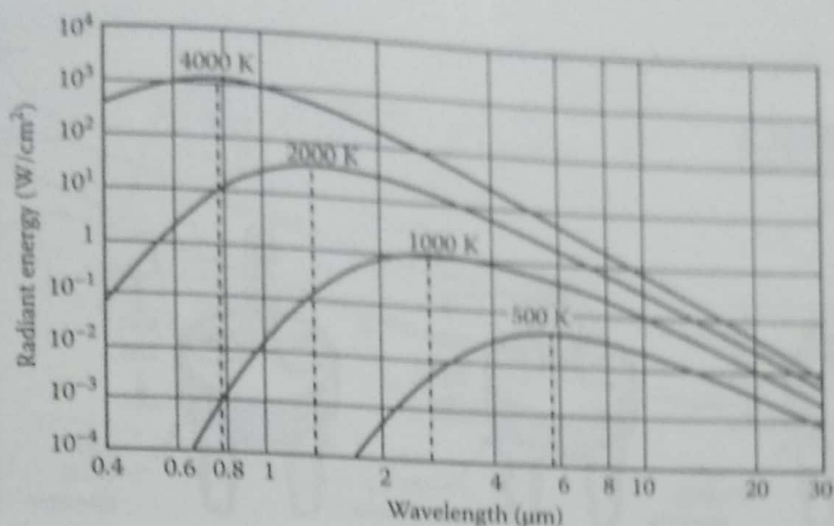


Figure 4.5 Radiant energy distribution curves for a blackbody source operated at various temperatures. (From Coates, J., *Vibrational spectroscopy*, in Ewing, G.W., ed., *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. With permission.)

4.2.1.1 Mid-IR Sources

The two main types of sources for mid-IR radiation are electrically heated rigid ceramic rods and coiled wires.

The Nernst glower is a cylindrical bar composed of zirconium oxide, cerium oxide, and thorium oxide that is heated electrically to a temperature between 1500 and 2000 K. The source is generally about 20 mm long and 2 mm in diameter. The rare-earth oxide ceramic is an electrical resistor; passing current through it causes it to heat and glow, giving off continuous IR radiation. The Nernst glower requires an external preheater because of the negative coefficient of electrical resistance; it only conducts at elevated temperature. In addition, the Nernst glower can easily overheat and burn out because its resistance decreases as the temperature increases. The circuitry must be designed to control the current accurately. A related source, the Opperman, consists of a bar of rare-earth ceramic material with a Pt or other wire running coaxially through the center of the ceramic. Electrical current through the wire heats the wire and that heats the ceramic, providing a source similar to the Nernst glower without the preheating requirement. The Globar is a bar of sintered silicon carbide, which is heated electrically to emit continuous IR radiation. The Globar is a more intense source than the Nernst glower. These rigid cylinders were designed so that their shape matched the shape of the slit on a classical dispersive spectrometer. Modern FTIRs do not have slits, so the geometry of the source can now be made more compact. Commercial ceramic IR sources are available in a variety of sizes and shapes, as seen in Figure 4.6. Typical spectral outputs from these commercial ceramic sources are compared with a blackbody radiator in Figure 4.7.

Electrically heated wire coils, similar in shape to incandescent light bulb filaments, have also been used successfully as a light source. Nichrome wire is commonly used, although other metals such as rhodium are used as well. These wires are heated electrically in air to a temperature of $\sim 1100^{\circ}\text{C}$. The main problem with these wire coils is "sagging" and embrittlement due to aging, resulting in fracture of the filament, exactly the way a light bulb filament "burns out." Some coiled wire sources are wound around a ceramic rod for support; this results in a more uniform light output over time than that from an unsupported coil.

Modern sources for the mid-IR region are variants of the incandescent wire source or the Globar, but generally in a compact geometry. Commercial furnace ignitors and diesel engine heaters such

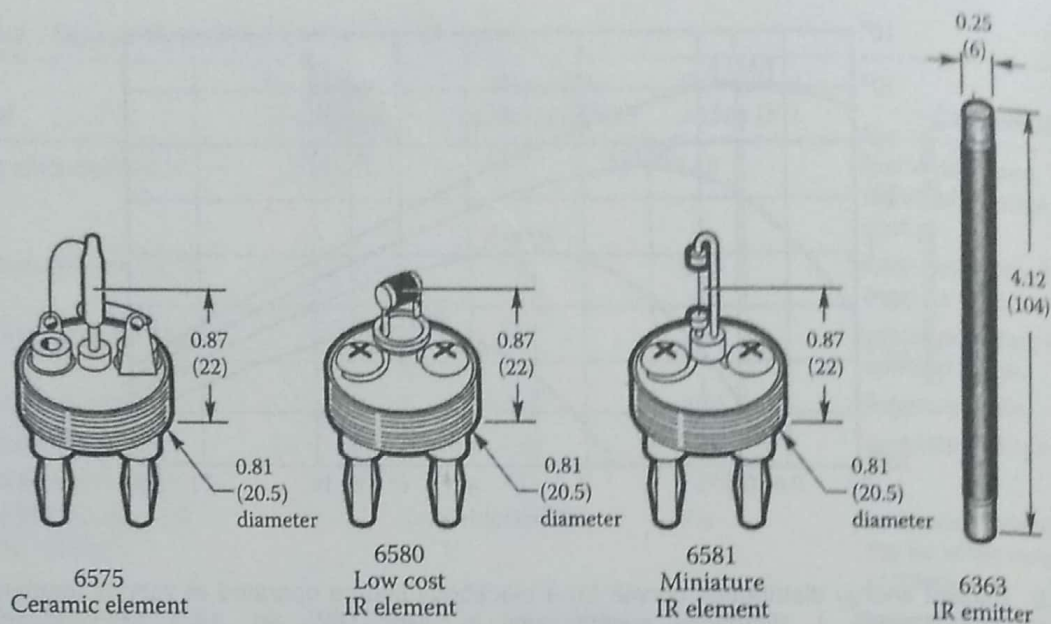


Figure 4.6 Commercial IR radiation sources. (Top) A variety of designs. Dimensions given are in inches and (mm). (Courtesy of Newport Corporation, Irvine, CA, www.newport.com.) (Bottom) FTIR source element used in the PerkinElmer Spectrum One instrument. It is made of a proprietary ceramic/metallic composite and is designed to minimize hot spots to the end of the element. Only the last 5 mm on the end lights up. [© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission. (www.perkinelmer.com.)]

as the silicon carbide tipped “glow plug” have been adapted for use as IR sources because of their robustness, low operating voltage, and low current requirements.

Sources are often surrounded by a thermally insulated enclosure to reduce noise caused by refractive index gradients between the hot air near the source and cooler air in the light path. Short-term fluctuations in spectral output are usually due to voltage fluctuations and can be overcome by use of a stabilized power supply. Long-term changes occur as result of changes in the source material due to oxidation or other high-temperature reactions. These types of changes may be seen as hot or cold “spots” in the source and usually require replacement of the source.

4.2.1.2 NIR Sources

As can be seen in Figure 4.5, operating a mid-IR source at higher temperatures (>2000 K) increases the intensity of NIR light from the source. Operation at very high temperatures is usually not practical due to the excessive heat generated in the instrument and premature burnout of the source. For work in the NIR region, a quartz-halogen lamp is used as the source. A quartz-halogen lamp contains a tungsten wire filament and iodine vapor sealed in a quartz envelope or bulb.