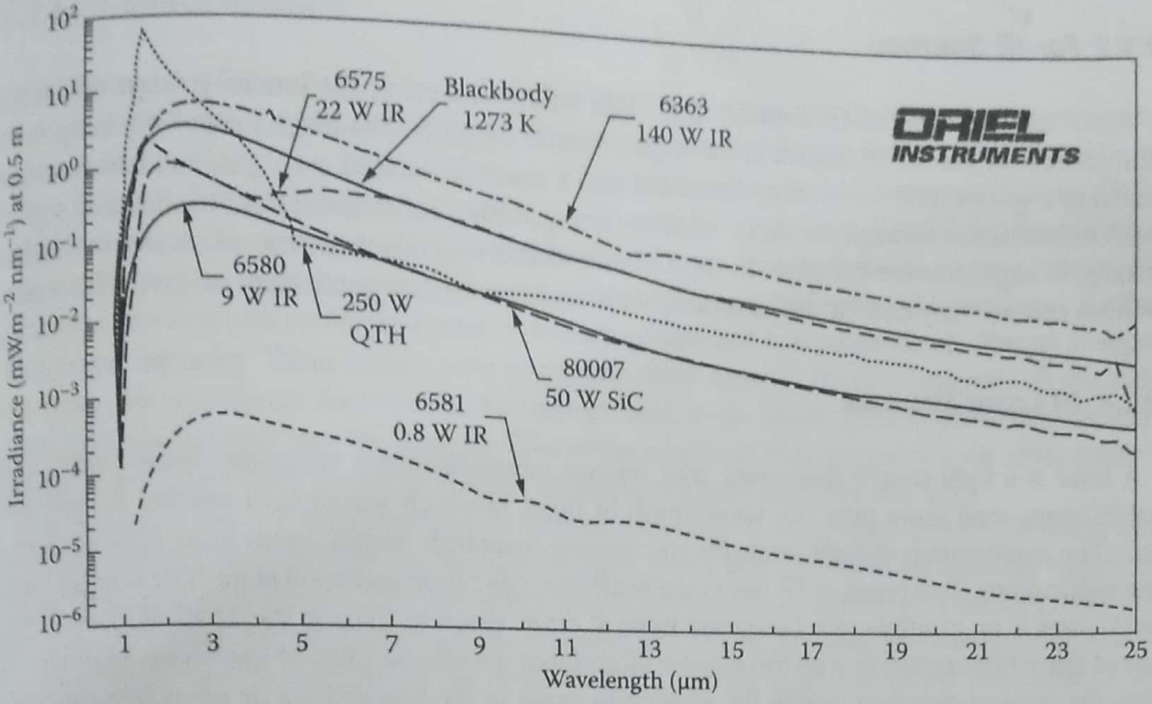
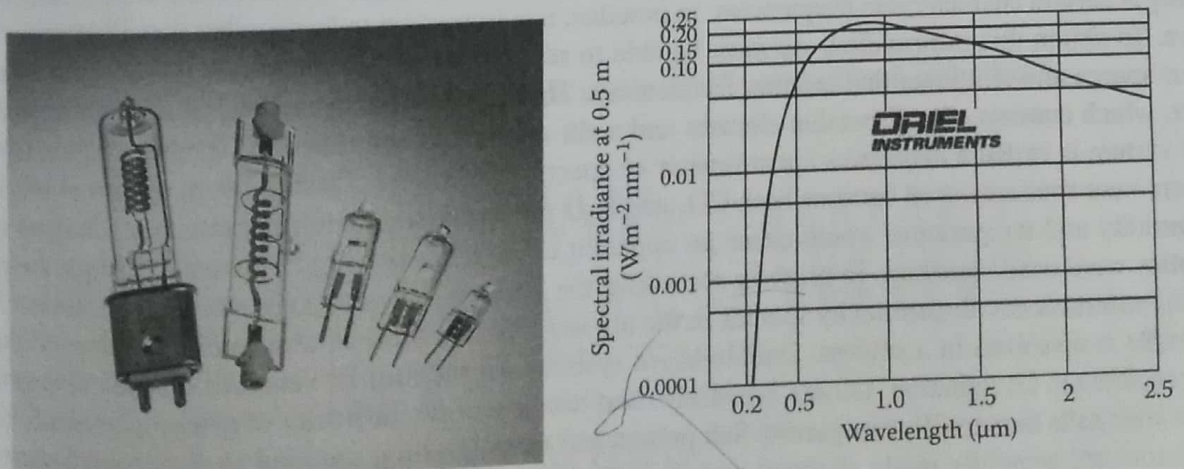


Figure 4.7 Spectral output of a variety of commercial IR radiation sources, including a silicon carbide source (dashed line marked SiC) and an NIR quartz tungsten-halogen lamp (the dotted line marked QTH). A blackbody curve at 1273 K is included for comparison. (Courtesy of Newport Corporation, Irvine, CA, www.newport.com.)

In a standard tungsten filament lamp, the tungsten evaporates from the filament and deposits on the lamp wall. This process reduces the light output as a result of the black deposit on the wall and the thinner filament. The halogen gas in a tungsten-halogen lamp removes the evaporated tungsten and redeposits it on the filament, increasing the light output and source stability. The intensity of this source is very high compared to a standard tungsten filament incandescent lamp. The range of light put out by this source is from 25,000 to 2,000 cm^{-1}. Figure 4.8 shows typical commercial quartz tungsten-halogen lamps and a plot of the spectral output of such a source.



(a)

(b)

Figure 4.8 (a) Commercial quartz tungsten-halogen lamps for use in the NIR region. The lamps are constructed of a doped tungsten coiled filament inside a quartz envelope. The envelope is filled with a rare gas and a small amount of halogen. (b) The spectral output of a model 6315 1000 W quartz tungsten-halogen lamp. The location and height of the peak depend on the model of lamp and the operating conditions. (Courtesy of Newport Corporation, Irvine, CA, www.newport.com.)

4.2.1.3 *Far-IR Sources*

While some of the mid-IR sources emit light below 400 cm^{-1}, the intensity drops off. A more useful source for the far-IR region is the high-pressure mercury discharge lamp. This lamp is constructed of a quartz bulb containing elemental Hg, a small amount of inert gas, and two electrodes. When current passes through the lamp, mercury is vaporized, excited, and ionized, forming a plasma discharge at high pressure (>1 atm). In the UV and visible regions, this lamp emits atomic Hg emission lines that are very narrow and discrete, but it emits an intense continuum in the far-IR region.

4.2.1.4 *IR Laser Sources*

A laser is a light source that emits very intense monochromatic radiation. Some lasers, called tunable lasers, emit more than one wavelength of light, but each wavelength emitted is monochromatic. The combination of high intensity and narrow linewidth makes lasers ideal light sources for some applications. Two types of IR lasers are available: gas phase and solid state. The tunable carbon dioxide laser is an example of a gas-phase laser. It emits discrete lines in the 1100–900 cm^{-1} range. Some of these lines coincide with the narrow vibrational–rotational lines of gas-phase analytes. This makes the laser an excellent source for measuring gases in the atmosphere or gases in a production process. Open path environmental measurements of atmospheric hydrogen sulfide, nitrogen dioxide, chlorinated hydrocarbons, and other pollutants can be made using a carbon dioxide laser.

Tunable gas-phase lasers are expensive. Less expensive solid-state diode lasers with wavelengths in the NIR are available. Commercial instruments using multiple diode lasers are available for NIR analyses of food and fuels. Because of the narrow emission lines from a laser system, laser sources are often used in dedicated applications for specific analytes. They can be ideal for process analysis and product quality control (QC), for example, but are not as flexible in their applications as a continuous source or a tunable laser.

4.2.2 Monochromators and Interferometers

The radiation emitted by the source covers a wide frequency range. However, the sample absorbs only at certain characteristic frequencies. In practice, it is important to know what these frequencies are. To obtain this information, we must be able to select radiation of any desired frequency from our source and eliminate that at other frequencies. This can be done by means of a monochromator, which consists of a dispersion element and a slit system, as discussed in Chapter 2. This type of system is called a *dispersive* spectrometer or spectrophotometer. Double-beam spectrophotometers were routinely used because both CO_2 and H_2O present in air absorb IR radiation. Changes in humidity and temperature would cause an apparent change in the source intensity if single-beam optics were used, resulting in error in recording the spectrum. A double-beam system automatically subtracts the absorption by species in the air and also can subtract absorption by solvent if the sample is dissolved in a solvent. Double-beam systems for the mid-IR required that the optics be transparent to IR radiation. Lenses are rarely used because of the difficulty of grinding lenses from the ionic salts that are IR transparent. Salt prisms and metal gratings are used as dispersion devices. Mirrors are generally made of metal and front surface polished. The IR spectrum is recorded by moving the prism or grating so that different frequencies of light pass through the exit slit to the detector. The spectrum is a plot of transmission intensity, usually as percent transmittance, versus frequency of light. A dispersive system is said to record a spectrum in the *frequency domain*. It was estimated (Coates, 1997) that no more than 5% of the IR spectrometers in use in 1997 were dispersive instruments and that figure has undoubtedly dropped today. Therefore, the discussion will focus on the FTIR based on a Michelson interferometer.

4.2.2.1 *FT Spectrometers*

If two beams of light of the same wavelength are brought together in phase, the beams reinforce each other and continue down the light path. However, if the two beams are out of phase, destructive interference takes place. This interference is at a maximum when the two beams of light are 180° out of phase (Figure 4.9). Advantage is taken of this fact in the FT instrument. The FT instrument is based on a Michelson interferometer; a schematic is shown in Figure 4.10. The system consists of four optical arms, usually at right angles to each other, with a *beam splitter* at their point of intersection. Radiation passes down the first arm and is separated by a beam splitter into two perpendicular beams of approximately equal intensity. These beams pass down into other arms of the spectrometer. At the ends of these arms, the two beams are reflected by mirrors back to the beam splitter, where they recombine and are reflected together onto the detector. One of the mirrors is fixed in position; the other mirror can move toward or away from the beam splitter, changing the path length of that arm.

It is easiest to discuss what happens in the interferometer if we assume that the source is monochromatic, emitting only a single wavelength of light. If the side arm paths are equal in length, there is no difference in path length. This position is shown in Figure 4.10 as the zero path difference (ZPD) point. For ZPD, when the two beams are recombined they will be in phase, reinforcing each other. The maximum signal will be obtained by the detector. If the moving mirror is moved from ZPD by 1/8 of a wavelength, the total path difference on recombination is $[2 \times (1/8)\lambda]$ or $(1/4)\lambda$ and partial interference will occur. If the moving mirror is moved from ZPD by 1/4 of a wavelength, then the beams will be one-half of a wavelength out of phase with each other; that is, they will destructively interfere with each other such that a minimum signal reaches the detector. Figure 4.11 shows the signal at the detector as a function of path length difference for monochromatic light. In practice, the mirror in one arm is kept stationary and that in the second arm is moved slowly. As the moving mirror moves, the net signal falling on the detector is a cosine wave with the usual maxima and minima when plotted against the travel of the mirror. The frequency of the cosine signal is equal to

$$f = \frac{2}{\lambda}(v) \tag{4.8}$$

where

f is the frequency
v is the velocity of the moving mirror
λ is the wavelength of radiation. (Note: v is an italic "v," not the Greek letter "nu.")

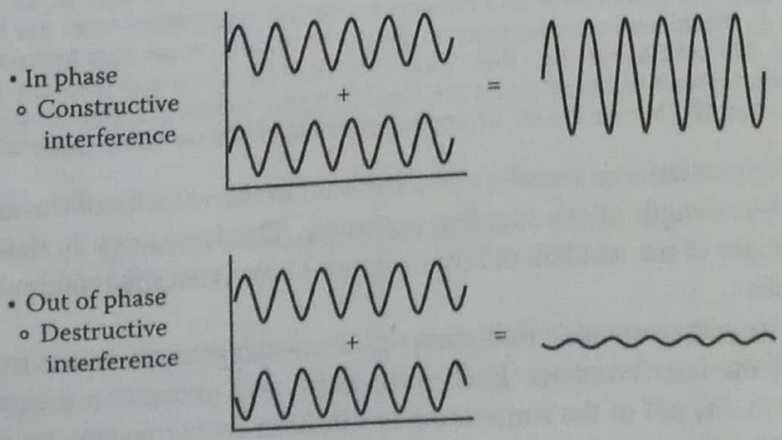


Figure 4.9 Wave interactions. (Top) Constructive interference occurs when both waves are in phase. (Bottom) Destructive interference occurs when both waves are out of phase. (© Thermo Fisher Scientific, www.thermofisher.com. Used with permission.)

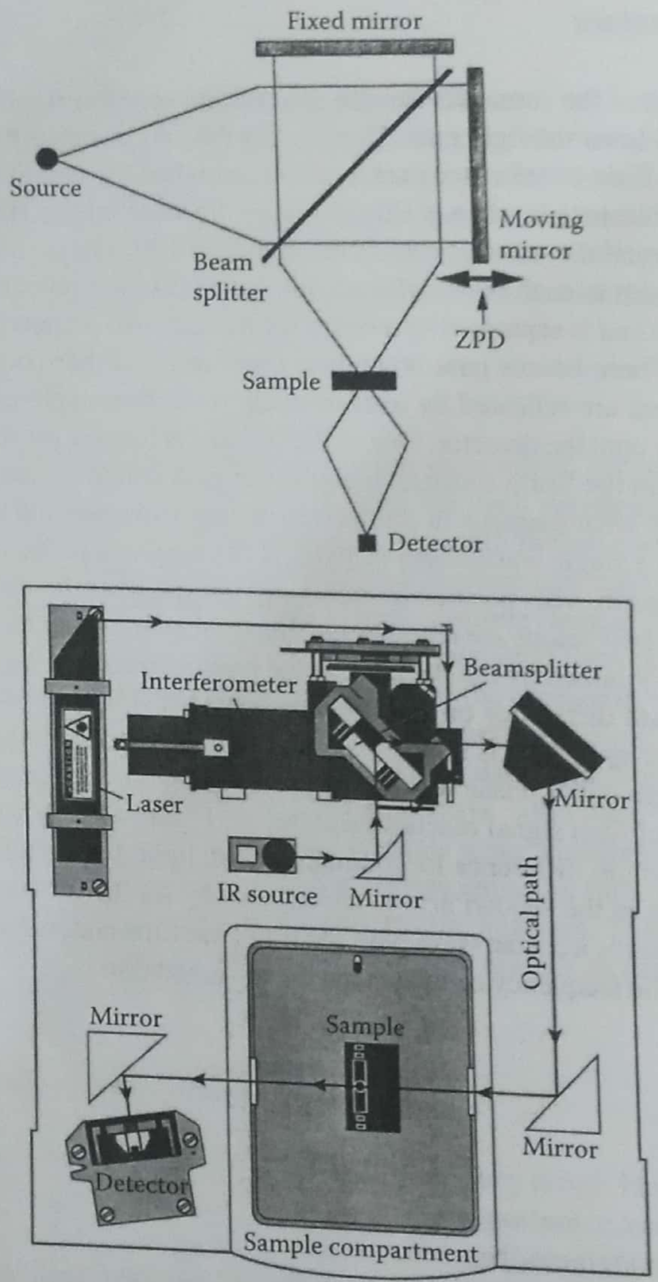


Figure 4.10 (Top) Schematic diagram of a Michelson interferometer. ZPD stands for zero path length difference (i.e., the fixed mirror and moving mirror are equidistant from the beam splitter). (From Coates, J., Vibrational spectroscopy, in Ewing, G.W., ed., *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. With permission.) (Bottom) A simple commercial FTIR spectrometer layout showing the He–Ne laser, optics, the source, interferometer, sample, and detector. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)

The frequency of modulation is therefore proportional to the velocity of the mirror and inversely proportional to the wavelength of the incident radiation. The frequency is therefore also proportional to the wavenumber of the incident radiation, as we know from the relationship between wavelength and wavenumber.

Real IR sources are polychromatic. Radiation of all wavelengths generated from the source travels down the arms of the interferometer. Each wavelength will generate a unique cosine wave; the signal at the detector is a result of the summation of all these cosine waves. An idealized interferogram from a polychromatic source is shown in Figure 4.12. The "centerburst" is located in the center of the interferogram because modern FTIR systems scan the moving mirror symmetrically around ZPD. The interferogram holds the spectral information from the source (or sample) in a *time domain*.