and also if a resonance or near-resonance condition applies at certain wavelengths (Section 4.8.4).

Less commonly, the molecule *decreases* in vibrational energy after interacting with a photon. This might occur if the molecule is in an excited vibrational state to begin with and relaxes to the ground vibrational state. In this case, the molecule has given energy to the scattered photon. The photon is shifted to a frequency higher than the incident radiation. These higher frequency lines, the Raman–anti-Stokes lines, are less important to analytical chemists than the Stokes lines because of their lower intensity. One exception to this is for samples that fluoresce strongly. Fluorescence interferes with the Stokes lines but to a much lesser extent with the anti-Stokes lines.

It is convenient to plot the Raman spectrum as intensity vs. shift in wavenumbers in cm^{-1}, because these can be related directly to IR spectra. The Raman shift in cm^{-1} is identical to the IR absorption peak in cm^{-1} for a given vibration, because both processes are exciting the same vibration. The Raman spectrum for benzene is shown in Fig. 4.62, along with the related IR transmission spectrum.

4.8.2. Raman Instrumentation

A Raman spectrometer requires a light source, a sample holder or cell, a wavelength selector (or interferometer), and a detector, along with the usual signal processing and display equipment. Since Raman spectroscopy measures scattered radiation, the light source and sample cell are usually placed at 90° to the wavelength selector, as shown schematically in Fig. 4.63. The radiation being measured in Raman spectroscopy is either visible or NIR; therefore spectrometer optics, windows, sample cells, and so on can be made of glass or quartz. It is critical in Raman spectroscopy to completely exclude fluorescent room lights from the spectrometer optics. Fluorescent lights give rise to numerous spurious signals.

(a)

(b)
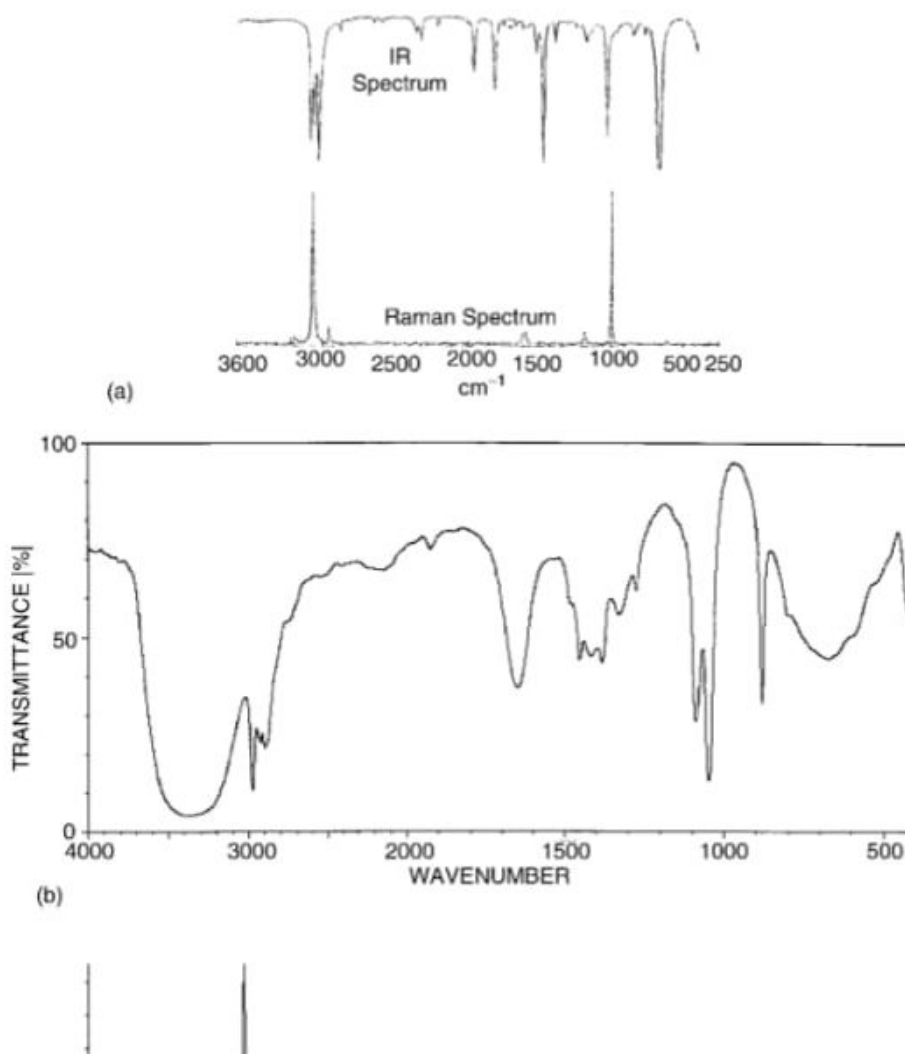
4.8.2.1. Light Sources

Monochromatic light sources are required for Raman spectroscopy. The light sources used originally were simple UV light sources, such as Hg arc lamps; however, these were weak sources and only weak Raman signals were observed. The Raman signal is directly
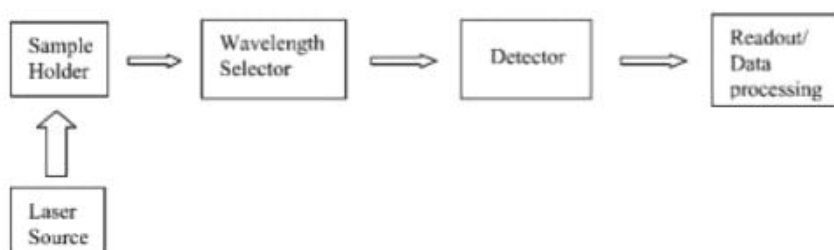
Figure 4.63 Idealized layout of a Raman spectrometer.

proportional to the power of the light source, which makes the laser, which is both monochromatic and very intense, a desirable light source. It was the development in the 1960s of lasers that made Raman spectroscopy a viable and useful analytical technique. Modern Raman instruments use a laser as the light source. The use of these intense light sources has greatly expanded the applications of Raman spectroscopy, because of the dramatically increased intensity of the signal and a simultaneous improvement of the signal-to-noise ratio. Lasers and excitation wavelengths commonly used for Raman instruments include visible wavelength helium/neon lasers and ion lasers such as the argon ion laser (488 nm) and the krypton ion laser (531 nm). The intensity of Raman scattering is proportional to the fourth power of the excitation frequency or to $1/\lambda^4$, so the shorter wavelength blue and green ion lasers have an advantage over the red helium/neon laser line at 633 nm. The disadvantage of the shorter wavelength lasers is that they can cause the sample to decompose on irradiation (photodecomposition) or fluoresce, an interference discussed subsequently. NIR lasers, such as neodymium/yttrium aluminum garnet, Nd/YAG, with an excitation line at 1064 nm, are used to advantage with some samples because they do not cause fluorescence or photodecomposition.

4.8.2.2. Dispersive Spectrometers Systems

Traditional Raman spectrometers used a monochromator with two or even three gratings to eliminate the intense Rayleigh scattering. The optical layout is similar to that for the UV/VIS single grating monochromators discussed in Chapters 2 and 5. Holographic interference filters, called *super notch filters*, have been developed that dramatically reduce the amount of Rayleigh scattering reaching the detector. These filters can eliminate the need for a multiple grating instrument unless spectra must be collected within 150 cm^{-1} of the source frequency. Dispersive systems generally use a visible laser as the source.

The traditional detector for these systems was a photomultiplier tube. Multichannel instruments with photodiode array (PDA), CID, or CCD detectors are commonly used today. All three detectors require cryogenic cooling. The PDA has the advantage of having the fastest response but requires more complicated optics than the other detectors. The CID has the advantage over both the PDA and CCD of not "blooming", that is, not having charge spill over onto adjacent pixels in the array, which would be read in error as a signal at a frequency where no signal exists. CCDs are the slowest of the three array detectors because they have to be read out by transferring the stored charge row by row, but they are also the least expensive of the detector arrays. Sensitivity is improved in newer CCD designs as well. A dispersive Raman spectrometer with a CCD detector is shown schematically in Fig. 4.64.

4.8.2.3. FT Raman Spectrometers

FT-Raman systems generally use an NIR laser source, such as the Nd/YAG laser, and a Michelson interferometer. A schematic FT-Raman spectrometer is shown in Fig. 4.65.

CCD detector is shown schematically in Fig. 4.64.

4.8.2.3. FT Raman Spectrometers

FT-Raman systems generally use an NIR laser source, such as the Nd/YAG laser, and a Michelson interferometer. A schematic FT-Raman spectrometer is shown in Fig. 4.65.
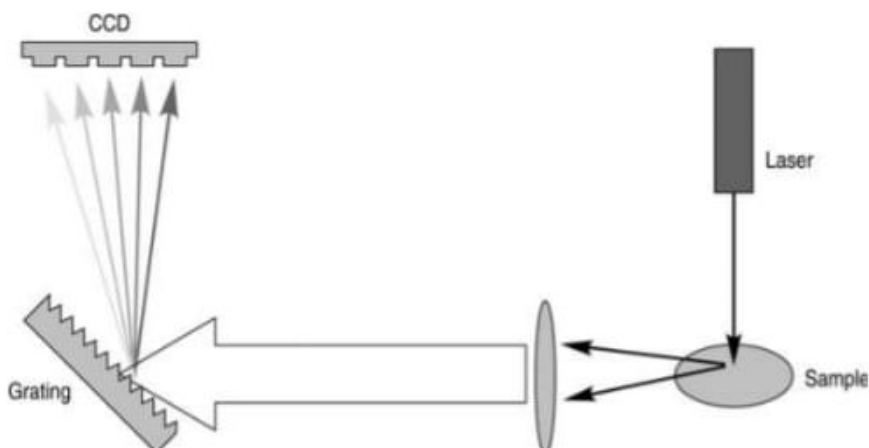
Figure 4.64 Schematic of a dispersive Raman spectrometer. (Reprinted from Weesner and Longmire, with permission from Advanstar Communications, Inc.)

The NIR laser source line is at 1064 nm, so the Raman–Stokes lines occur at longer wavelengths. This is beyond the detection range of the materials used in array detectors. The detector for an NIR FT-Raman system is a liquid nitrogen-cooled photoconductive detector such as Ge or InGaAs.

FT-Raman has many of the advantages of FTIR. There is high light throughput, simultaneous measurement of all wavelengths (the multiplex advantage), increased signal-to-noise ratio by signal averaging, and high precision in wavelength. A major advantage is in the use of the NIR laser, which dramatically reduces fluorescence in samples. Fluorescence occurs when the virtual states populated by excitation overlap excited electronic states in the molecule. Then, the molecule can undergo a radiationless transition to the lowest ground state of the excited electronic state before emitting a fluorescence photon on relaxation to the ground state. The fluorescence photon is of lower energy than the exciting radiation, and so fluorescence occurs at longer wavelengths, interfering with the Stokes scattering lines. The NIR laser is of low energy and does not populate virtual states that overlap the excited electronic states, as higher energy visible lasers
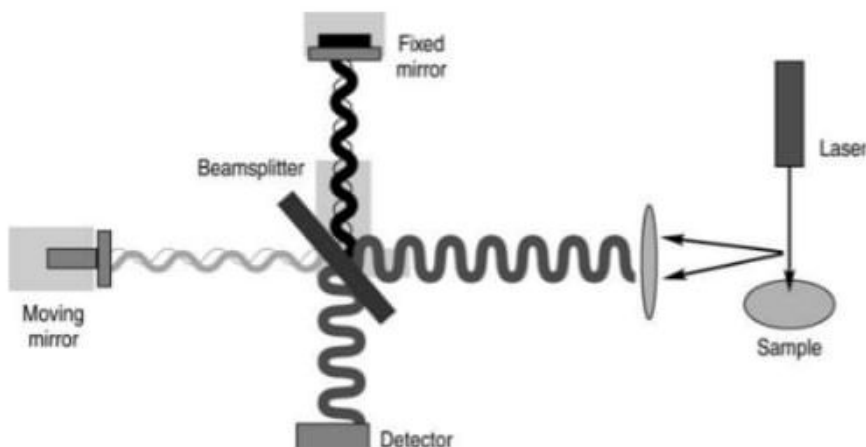

Figure 4.65 Schematic of an FT-Raman spectrometer. (Reprinted from Weesner and Longmire, with permission from Advanstar Communications, Inc.)