Spectroscopy Equipment

13

An important consideration for spectroscopic measurements is the availability and performance of light sources and detectors. Figure 13.1 shows the operating wavelength range for many common laser sources. This chapter is devoted to a discussion of laser light sources and detectors that operate between the UV and far-IR. While many of the sources and detectors find industrial uses, we concern ourselves here with the spectroscopic applications of these devices.

13.1 Sources

Laser light can be made at many wavelengths ranging from the UV to the far IR. Some lasers are quite large and expensive while others are small enough to fit in the palm of your hand and cost less than $100. Lasers can be pulsed or continuous wave (CW), with average powers ranging from microwatts to kilowatts or more. In this section we will discuss a few of the more popular sources and their uses.

13.1.1 The Helium–Neon Laser

The helium–neon (HeNe) laser is one of the simplest lasers and was one of the earliest lasers invented (the ruby laser was the first laser). The HeNe laser is so simple that there are books, web sites, and undergraduate classes that will teach motivated students to build their own [2]. The HeNe laser has a tube filled with a mixture of helium and neon (~0.1 Torr neon, 0.9 Torr helium) [3]. The helium is excited by an electrical discharge (which looks very much like a neon light). The excited helium atoms transfer energy to the neon atoms which produce the laser light. HeNe's are CW devices with typical powers ranging from 1 to 50 mW.

HeNe lasers are most commonly used to produce 632 nm light, but HeNe's are also available with output at 3.3903 μm, 1.15 μm, and several other visible

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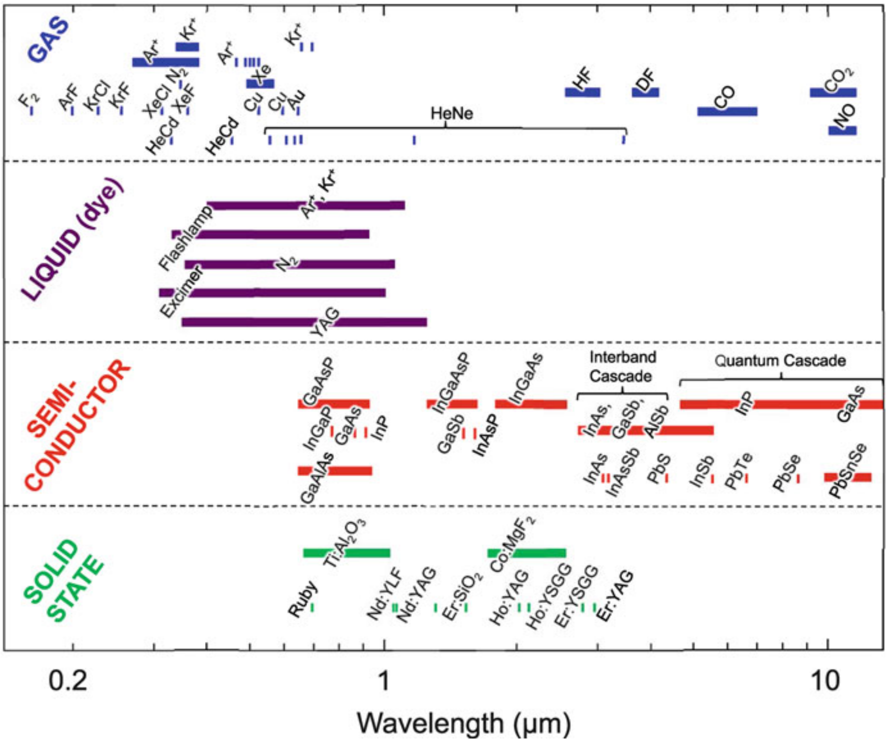

Fig. 13.1 Wavelengths of operation for many common lasers [1]

and IR wavelengths [4, 5]. Visible HeNe's are useful for optical alignment and optical scattering measurements. The 3.39 μm HeNe laser is useful in absorption spectroscopy for detection of hydrocarbons because the C–H stretch oscillates near 3.4 μm [6].

Argon-ion lasers are similar to HeNe lasers because they are gas lasers that are pumped by an electrical discharge. However, in an argon-ion laser, the argon is ionized in the plasma and ions act as the gain medium. Argon-ion lasers are typically CW devices, but can provide significantly more power than the HeNe laser. Argon-ion lasers can lase at many discrete wavelengths between 275 and 550 nm [7].

Argon-ion lasers can be used for direct absorption measurements at their fundamental wavelength [8] or at wavelengths of higher order harmonics [9]. They can also be used to pump dye lasers for absorption or fluorescence measurements [9].

13.1.2 The Nd:YAG Laser

The Nd:YAG laser (i.e., neodymium-doped yttrium aluminum garnet: $Nd:Y_3Al_5O_{12}$) is a common laser for high-power applications. The YAG crystal is doped with triply ionized neodymium, which replaces another element of roughly the same size, typically yttrium. To emit coherent radiation, the neodymium must first be pumped from the equilibrium state into a higher energy level. For these solid state lasers, this is often done using flashlamps, but diode lasers are also used. Nd:YAG lasers can be CW or pulsed. Higher peak powers are available when operated in pulsed mode, which is important for frequency conversion (i.e., frequency doubling, difference frequency generation, and sum frequency generation) and fluorescence.

Nd:YAG lasers are useful for their high power output. Nonlinear processes are often used to convert the IR light (usually at 1064 nm) to mid-IR light (2–4 μm) using an optical parametric oscillator (OPO) [10], or to visible and UV light (532, 355, 266 nm) through harmonic generation [11,12]. Nd:YAG lasers can also be used to pump dye lasers [13]. Because of the high achievable powers and wide range of wavelengths that can be accessed using the Nd:YAG laser, they are a common component in many fluorescence and absorption experiments, both in the UV [12] and IR [10].

13.1.3 The Excimer Laser

Excimer lasers (short for *Exci*ted Di*mer*) are pulsed UV lasers with a gain medium that is a short-lived molecule made up of one rare-gas atom and one halogen (e.g., ArF, KrCl, KrF, XeCl, XeF) [4]. Excimer lasers are used for LIF because they have high output powers in the UV [12]. A UV laser photolysis technique has also been demonstrated using the excimer laser as the photolyzing source [14].

13.1.4 The CO_2 Laser

In the CO_2 laser, the molecular vibrations are pumped by a plasma discharge. CO_2 lasers can be either pulsed or CW. CO_2 lasers can operate at discrete wavelengths between 9.3 and 11.4 μm, however the 10.6 μm transitions are popular choices [5]. High-power CO_2 lasers are useful in manufacturing for cutting, welding, and other processing technologies [3]. CO_2 lasers are also utilized in spectroscopy for fluorescence and absorption measurements [15].

13.1.5 Semiconductor Lasers

Semiconductor lasers (e.g., diode lasers, quantum cascade lasers, external cavity diode lasers, distributed feedback (DFB) lasers) have become increasingly important in spectroscopy and remote sensing. Semiconductor lasers are available in wavelengths from the near UV (375 nm) to the far-IR ($\sim$11 μm) and produce powers from $\sim$1 to 500 mW. Near-IR diode lasers are well developed and commercially available due to significant investment from the telecom industry. These lasers are compact and rugged and can often be purchased in a prepackaged, fiber-coupled unit. Many DFB lasers can be rapidly tuned over several wavenumbers by changing the injection current or laser temperature. Some external cavity diode lasers can be tuned more than $100\,\mathrm{cm}^{-1}$.

Due to their lower power outputs, tunable diode lasers are used primarily in absorption spectroscopy. Wavelength-tunability enables the user to interrogate an individual absorption feature of an atom (e.g., potassium or cesium) or small molecule (e.g., CO, CO_2, H_2O, or CH_4). Absorption measurements at multiple wavelengths have been used for simultaneous measurements of temperature and multiple species [16] or pressure, temperature, and velocity [17].

13.1.6 Dye Lasers

Dye lasers use an organic dye as the gain medium. Because the dye is a liquid, the absorption and fluorescence spectra are broadband, but the laser cavity is designed to emit "monochromatic" laser light somewhere within this emission band. Dye lasers are tunable over this emission band; each specific dye provides a range of wavelengths (10 to 70 nm), mostly in the visible and UV. Dye lasers are pumped by other UV lasers (such as an argon-ion laser) or by flashlamps.

Laser dyes can be found that emit between 300 and 1200 nm [18]. Harmonic generation of these tunable lasers facilitates spectroscopic work in the UV [9, 13].

13.1.7 Non-Laser Sources

While lasers act as valuable spectroscopic tools, and cover much of the electromagnetic spectrum from the UV to the far-IR, some wavelengths cannot be accessed using laser sources. Broadband lamps are useful tools for accessing wavelengths that cannot be easily obtained with lasers. Lamps offer the additional benefit of being simpler and less expensive than lasers, however, the lower spectral intensities reduce the SNR for spectrally resolved measurements.

13.2 Detectors

In an optical experiment, the detection system is an important consideration, second only to the optical source. Thus, we will devote some time to describing the different types of detectors and their characteristics. Before examining detectors in detail, some basic detector vocabulary is reviewed. Next, three common types of detectors are described. Finally, detector wavelength range, time response, and signal-to-noise ratio are compared for several common detectors. While this is only an introductory treatment, more information can be found in [19–21].

Shot noise refers to noise that is a result of random fluctuations in the time of arrival of the photons or electrons.

Dark current is the current produced by the detector with no signal from the source. Sources of dark current include background radiation from the environment and random thermal excitation of electrons within the detector itself.

Johnson noise is the noise generated by the equilibrium fluctuations of the electric current inside an electrical conductor, which happens without any applied voltage, due to the random thermal motion of the charge carriers (i.e., the electrons). In other words, Johnson noise is caused by random electron motion in the circuit.

Generation-recombination noise occurs in photoconductors because the photoexcited carrier has a characteristic lifetime, τ. The lifetime of each carrier is not exact, but described statistically. Thus, there is uncertainty in the precise time that the carrier recombines and this uncertainty results in random noise.

Background limited infrared performance (BLIP) occurs when the detector noise is limited by the background shot noise and not by intrinsic detector noise. Infrared detectors are often cryogenically cooled to approach this ideal condition.

Bandgap energy is the energy difference between the top of the valence band and the bottom of the conduction band in a semiconductor. Photons with energy that is lower than this bandgap energy are not detected by the semiconductor.

The detectors we will consider here are referred to as quantum detectors. Quantum detectors respond to individual photons and offer a fast response time. Thermal detectors are not discussed here, but more information can be found in [19]. It is sufficient to say that thermal detectors offer broad wavelength sensitivity, but at the cost of reduced time response.

13.2.1 The Photomultiplier

The photomultiplier is a popular optical detector used to measure radiation in the UV, visible, and near-IR wavelength regions. The photomultiplier consists of a photocathode, a series of electrodes, called dynodes, and an anode. When a photon strikes the photocathode, there is some probability that an electron will be emitted and accelerated towards the first dynode. Each dynode is held at a higher electrical potential than the previous so that it can attract the electrons. When an electron strikes the dynode, it sheds multiple electrons which accelerate to the next dynode. In this way, the signal is amplified at each dynode. Primary sources of noise in a photomultiplier are shot noise (generated by both the signal and the dark current) and Johnson noise.

13.2.2 Photoconductive Detectors

A photoconductive (PC) detector is a semiconductor-based detector with an electrical resistance that is sensitive to the light incident on it. A voltage placed across the detection element is used to measure the resistance. Photoconductive detectors are available in the near-IR to the far-IR (wavelengths from 1 to 50 μm).

Photoconductive detectors (and other semiconductor-based detectors) have a bandgap energy associated with them. Photons with energy that is smaller than this bandgap energy are not observed by the detector. For photons with energy that is greater than the bandgap energy, the current generated is proportional to the number of photons striking the active area. Thus, for fixed power, the detector sensitivity increases linearly with wavelength until the bandgap energy is reached, then the sensitivity drops off rapidly.

When a photon is absorbed by the material, an electron is excited from the valence band to an acceptor atom. There is a minimum photon energy required to excite the electron, placing a lower limit on the photon energy (or an upper limit on the detectable wavelength). The electron hole is acted on by the electric field (the applied voltage) and drifts along the field direction, resulting in a current. The contribution of a particular hole to the total current ends when an electron recombines with the hole. This process is referred to as electron-hole recombination. Photoconductive detectors are often cryogenically cooled so that thermal excitation of the carriers does not dominate over the photoexcitation process. There are two primary sources of noise in photoconductors. The first noise source is shot noise which can originate from the dark current or from the measured signal. The second source of noise is generation-recombination noise, which is a result of the finite lifetime of the photoexcited carrier.

13.2.3 Photodiode Detectors

A photodiode is a semiconductor that generates a voltage (or current) when light is incident on it and is often called a photovoltaic (PV) detector. Like photoconductors, photodiodes have a minimum photon energy associated with the energy bandgap of the semiconductor. Noise in a photodiode is dominated by the Johnson noise and therefore is not usually shot-noise limited.

A variation of the standard photodiode is an avalanche photodiode. In an avalanche photodiode, an electric voltage is placed across the diode. When a carrier is produced, it is accelerated by the electric field to energies great enough to knock new electrons out of the valence band. Thus, the signal is amplified resulting in more sensitive detection. The shot noise of the avalanche photodiode is also amplified in this system, but because a standard photodiode is Johnson noise limited, the SNR increases with increasing amplification until the shot noise dominates.

13.2.4 Selecting a Detector

There are many criteria that might be used to choose the correct detector for a specific application including wavelength, time response, noise characteristics, simplicity, and cost. Different types of detectors are sensitive to different wavelengths of light. Figure 13.2 shows the wavelength range for many common detectors.

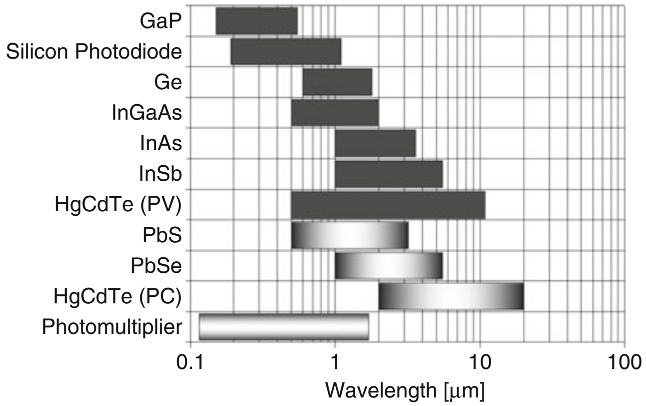

Fig. 13.2 Wavelength range for common detectors. *Black boxes* indicate photovoltaic detectors (photodiodes). *Gradient from left to right* indicates a photoconductor and *gradient from top to bottom* indicates a photomultiplier

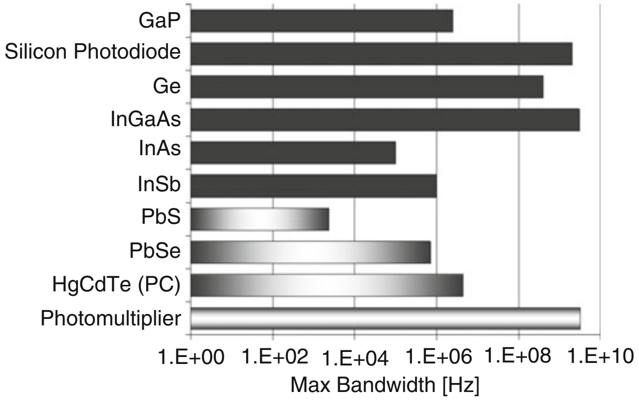

Fig. 13.3 Typical bandwidth for common detectors. *Black boxes* indicate photovoltaic detectors (photodiodes). *Gradient from left to right* indicates a photoconductor and *gradient from top to bottom* indicates a photomultiplier

By choosing a specific wavelength or set of wavelengths, the choice of detectors will be some subset of the detectors indicated in the figure.

As shown in Fig. 13.2, there are often several detectors available for a particular wavelength, so more selection criteria can be used to reduce this list. Detectors have a frequency bandwidth which is important for time-resolved measurements. Bandwidth can be dependent on the detector area and temperature as well as the preamplifier gain, and of course, the detector material. By increasing the detector area or the preamplifier gain, the frequency bandwidth will generally be reduced. Typical commercially available bandwidth for some common detector types is plotted in Fig. 13.3.

Detector noise can also be an important issue, especially when measuring weak signals (such as with fluorescence). Detector noise is characterized by the detectivity (D^*):

$$D^* = \frac{\sqrt{A_{\text{Detector}}\Delta f}}{\text{NEP}} \tag{13.1}$$

where A_{Detector} is the detector area, Δf is the bandwidth, and NEP, the noise equivalent power, is the amount of optical power required to equal the magnitude of the detector noise. The signal-to-noise ratio for a measurement dominated by detector noise can be calculated using this equation:

$$\text{SNR} = \frac{P_{\text{incident}}}{\text{NEP}} = \frac{P_{\text{incident}}D^*}{\sqrt{A_{\text{Detector}}\Delta f}} \tag{13.2}$$

where P_{incident} is the incident optical power. Thus a high D^* is required for sensitive optical measurements.

Cost and complexity should also be considered when choosing detectors. Most near-IR, visible, and UV photodiodes are available in compact packages at a relatively low price while photomultipliers typically are bulkier and more fragile and expensive. Many IR detectors are mounted in large dewars and require cryogenic cooling which can be inconvenient and makes the detector package more expensive and fragile. However, some IR detectors operate at room temperature or can be thermo-electrically cooled, making these detectors more compact, rugged, and portable.

Spatially uniform responsivity is an important factor that should not be ignored. IR detectors (particularly HgCdTe and room temperature and TE cooled PV detectors) can have a spatially nonuniform response across the active detector surface. This nonuniform response can manifest itself as noise in a poorly controlled experiment. Oftentimes smaller detectors are more uniform than large detectors and cooled detectors are more uniform than uncooled detectors. In the end, there is often a tradeoff between cost, sensitivity, bandwidth, noise, size, and complexity.

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