3.   Radiation Sources & Detectors

Radiation Sources

Until recently, most spectrochemical measurements were made using incoherent sources, i.e., incandescent lamps, such as tungsten wire sources or discharge lamps such as the deuterium lamp. These sources are still widely used in many applications, such as UV-VIS spectrometers that do not require the unique features of laser emission: high irradiance, low divergence, near monochromaticity, coherence. The earliest lasers, such as the ruby or noble gas laser, operated at a small number of resonant frequencies (wavelengths). The development of tunable lasers has made lasers useful in a broad range of spectrochemical measurements. Lasing occurs in a medium when the number of photons produced by stimulated emission exceeds the number lost to absorption and scattering. Stimulated emission occurs when a photon of the appropriate frequency ($\Delta E_{medium}=h\nu$) encounters excited species in the lasing medium, which will emit a second photon of the same energy and phase, traveling in the same direction when the medium is relaxed to the lower energy level by the first photon. When the medium is at thermal equilibrium, the number of lower energy states in the medium must outnumber the number of excited states. In order for the number of stimulated emission photons to exceed the number of absorbed photons, the number of excited states must exceed the number of lower energy states in the medium. This condition is called a population inversion; this is the first requirement for lasing. Only lasing media that have more than two energy levels near the lasing transition can support a population inversion. The population inversion is produced by "pumping" the lasing medium using an external energy source such as an electrical discharge, electrical current or photon irradiation. When the active lasing medium is placed in a Fabry-Perot cavity (a pair of mirrors at a
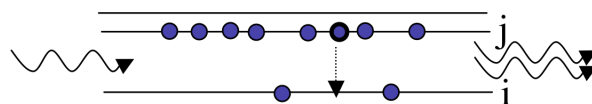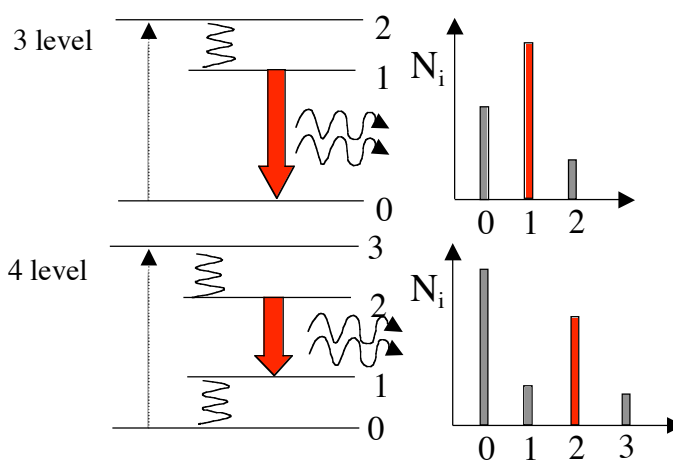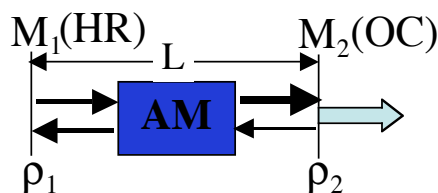

Figure 3.2: Stimulated Emission

Three and four energy level systems and the population levels they exhibit with continuous pumping.

Figure 3.3: Population Inversion

Figure 3.1: Beam Amplification in Resonant Cavity

distance that is determined by the laser wavelength), the amplifying medium becomes an oscillator. One of the mirrors, the output coupler (OC), is partially transmissive, so a fraction of the radiation in the cavity exits as a beam. The high reflector has a reflectivity as close to 1 as possible.

Lasing is sustained in the medium when amplification by stimulated emission (generated by multiple passes through the medium) exceeds absorption and reflection losses. The increase in radiant flux as the beam passes through the medium is analogous to the decrease we observe in absorption measurements. Using Beer's law as an analogy we can write the following expression to describe the amplification by stimulated emission that occurs as the beam makes a round trip in the cavity:

$$\mathcal{E} = (1-\ell)\rho_1\rho_2\mathcal{E}_o \exp\left(2\sigma_{SE}(v)\left(N_j - N_i\right)l\right),$$

where ℓ is the round trip cavity absorption and scattering loss, ρ_1 and ρ_2 are reflectivities of the resonant cavity mirrors, $\mathcal{E}_0$ is the incident irradiance, σ_{SE} is the stimulated emission coefficient, N_j and N_i are the number of excited and lower energy state species, respectively, and l is the medium length. Beam amplification is often called 'gain' to reflect the increase in irradiance. Unfortunately, there are at least two definitions of gain used by different communities of scientists. One, in m^{-1}, refers to the increase reflected in the argument of the exponential, γ, the other, unitless, refers to the irradiance ratio (before and after amplification), G.

$$\frac{\mathcal{E}}{\mathcal{E}_o} = (1-\ell)\rho_1\rho_2 \exp\left(2\sigma_{SE}(v)\left(N_j - N_i\right)l\right) > 1$$

$$\frac{\mathcal{E}}{(1-\ell)\rho_1\rho_2\mathcal{E}_o} = \exp\left(2\gamma(v)l\right) \geq \frac{1}{(1-\ell)\rho_1\rho_2}$$

$$\gamma(v)l \geq \frac{1}{2}\ln\left(\frac{1}{(1-\ell)\rho_1\rho_2}\right)$$

$$G(v) = e^{\gamma(v)l} = \sqrt{\frac{1}{(1-\ell)\rho_1\rho_2}}$$

The difference in the number of excited and lower energy species in the medium is a measure of the population inversion. Ignoring absorption and scattering losses, the threshold population inversion (the point where gain just matches losses) is

$$\Delta N_{thr} = \left(N_j - N_i\right)_{thr} = \frac{\ln\left(1/\rho_1\rho_2\right)}{2\sigma_{SE}(v)l}.$$

It may strike you as strange that the gain, γ, and stimulated emission coefficient, σ_{SE}, are frequency dependent if you are taking the simple energy level diagrams with discrete energy levels depicted in Figure 24 literally. Remember that even gas molecules are homogeneously and inhomogeneously broadened at temperatures above the cryogenic. Therefore the gain profile and stimulated emission coefficient have finite widths. One consequence of this broadened transition is that there are usually a number of longitudinal modes
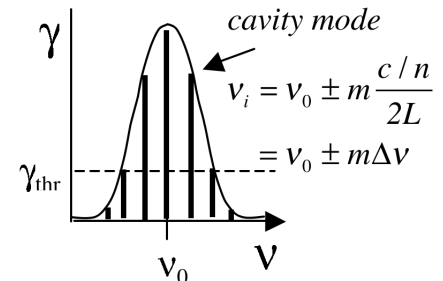

$$v_i = v_0 \pm m\frac{c/n}{2L}$$
$$= v_0 \pm m\Delta v$$

Figure 3.4: Gain Bandwidth and Threshold

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(standing light waves) along the length of the cavity that have frequencies within the gain bandwidth over the threshold. The frequencies of these modes are separated
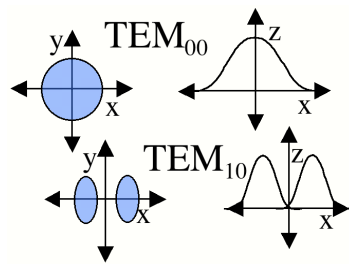

Figure 3.5: Transverse Electromagnetic Modes

by $\Delta v = \dfrac{c/n}{2L}$, where L is the cavity (as opposed to medium) length (as usual c and n are the speed of light and refractive index). We can use optics, such as etalons, if we really need to isolate a single frequency. Similarly, laser emission travels across the width of the resonant cavity in a number of transverse (electromagnetic) modes that are designated by the number of nodes in the amplitude in the x and y directions. The fundamental mode, TEM_{00}, has a nodeless gaussian profile in both the x and y directions as Figure 28 shows.

So far, this discussion could give the impression that once a population inversion is achieved and lasing is initiated, it continues as long as the pumping mechanism is not interrupted. This depends entirely on the system. Lasers that have a constant output with respect to time are called continuous wave (CW) lasers. He:Ne (helium:neon, λ~633 nm) and ion lasers (Ar^+, λ~488,5 514 nm; Kr^+ λ~568 nm) are typically operated in this mode. The output of pulsed lasers varies periodically with respect to time. Pulsed lasers are very useful for conducting kinetic measurements or using time-dependence as a selectivity enhancement or noise discriminator. Many 3-level laser systems operate in the pulsed mode because lasing depletes the population inversion faster than the pumping mechanism can replenish it. For many systems, the pulse duration is approximately twice the cavity lifetime, which is the ratio of the roundtrip time for a photon in the cavity and the power loss during that round trip. Ignoring absorption and scattering losses, the cavity lifetime is

$$\tau_{cavity} \approx \frac{2L/(c/n)}{\ln(1/\rho_1\rho_2)}.$$

There are a number of different operational modes for pulsed lasers. The peak power of Q-switched lasers is much larger than that of normal pulsed lasers because an electrooptic modulator (very fast shutter) temporarily blocks the high reflector so that the population inversion grows substantially above the threshold value. When the modulator opens and lasing is initiated, a very large pulse exits the cavity. Of course, the average power of a pulsed beam is much lower than the pulse power because the duty cycle (fraction of time laser is emitting) of most lasers is small. For example, when a Q-switched CO_2 (λ~10.6 μm) laser emits 1 mJ pulses in 1 msec, the peak power is 1W. If the pulse repetition rate (rate at which pulses exit the cavity) is 300 Hz, the average power is only 0.3W because the output is zero almost two-thirds of the time. Mode-locked lasers produce pulse trains of very narrow (< ps) pulses by forcing all the longitudinal cavity modes (standing light waves that set up in the cavity) to oscillate in phase. This is accomplished by putting a modulator that has its oscillation frequency set to the reciprocal of the time it takes a photon to make a round trip across the laser cavity. In this case the pulse duration is given by

$$t_p = 0.45 \left(\frac{\gamma l}{m_{AOM}} \right)^{1/4} \left(\frac{1}{\Delta\nu f_{AOM}} \right)^{1/2}$$

where γ is the gain threshold, l is the active medium length (rather than the cavity length L), $\Delta\nu$ is the laser linewidth (in Hz) and m_{AOM} and f_{AOM} are the modulation depth and frequency applied to the beam by the acousto-optic modulator. One important consequence of the narrowness of mode-locked pulses is the broadening of the frequency bandwidth. There is an uncertainty principle at work, so the product of the bandwidth and pulse duration is fixed. The value of the product depends on the shape of the laser pulse; for Gaussian pulses, $\Delta\nu\Delta t = 0.441$. Cavity-dumpers reduce the repetition rate of pulsed lasers by periodically deflecting the transmission of selected pulses. Many cavity dumpers are based on electro- or acousto-optical devices.

Until recently, the workhorse of laser spectroscopy has been the dye laser because the bandwidth of most organic dye spectra is around 50 - 100 nm, broad enough to provide limited tunability. Dye lasers have solutions of a fluorescent dye inside a resonant cavity that has the high reflector (non-transmissive mirror) replaced by a wavelength selection grating. The position of the high reflector grating determines which wavelength will exit the cavity. Flashlamps or single-wavelength pulsed lasers can be used to excite dye molecules into excited electronic and vibrational states. The molecules relax rapidly (in picoseconds) to the lowest vibrational level of the first excited state, which typically has a relatively long (1-10 ns) lifetime. Consequently, a population inversion can build up in the dye solution. More recently, vibronic lasers, especially the titanium:sapphire laser, have become important tunable laser sources for spectroscopic measurements. The energy levels of the titanium (III) ion doped into sapphire (Al_2O_3) crystals are such that excited electronic states of the ion can couple to the lattice vibrations of the crystal, forming a wide vibronic band in the ion ground state. The Ti:sapphire laser wavelength can be tuned from ~650 -1100 nm. Moreover, the Ti:sapphire laser can be modelocked to produce ultrashort (<100 fs) pulses.

Another source of optical tuning is frequency mixing. We have already discussed the fact that when two beams interact in non-linear materials frequency-doubled (wavelength-halved) radiation beams are generated because the polarization depends on the square of the electric field. This is a trivial example of this more general phenomenon. In frequency mixing, the two beams need not have the same frequency. When two laser beams of different frequencies, ν_1 and ν_2, are mixed in a non-linear crystal, such as β-phase barium borate (BBO), one of two new beams can be generated. The frequency of one beam is the sum ($\nu_3 = \nu_1 + \nu_2$) of the incident beams; the frequency of the other is the difference of the frequencies of the incident beam ($\nu_3 = \nu_1 - \nu_2$). Both of these phenomena require that the phases of the beams be matched ($\Delta k = k_3 - (k_1 + k_2) = 0$). Sum and difference frequency generation are used to extend the range of wavelengths available from tunable laser systems usually by mixing the tunable band, e.g. from a Ti:sapphire, with a beam from a monochromatic laser such as a Nd:YAG (λ~1064 nm). The frequency mixing principle is also used in optical parametric oscillators, coherent sources in which the optical gain comes from parametric amplification in non-linear materials rather than stimulated emission. In this case, the nonlinear crystal facilitates an exchange of energy from the pump beam to the signal and the idler beams (historical nomenclature). When the phase matching

condition is met, the amplitude of the pump beam is depleted as the amplitude of the signal and idler beams increase. These sources are very widely tunable, so they are used for spectroscopy (vibrational) and to generate difficult to access wavelengths.

Radiation Detectors

For our discussion, radiation detectors are devices that convert radiant energy to electrical signals. A broad range of detector types is commercially available from photomultiplier tubes, which are vacuum tube technology, to semiconductors. IR radiation is detected using thermal detectors. Detectors are classified by various figures of merit that specify the devices' performance. Among the most important classifiers are the responsivity, $R(\lambda)$, the ratio of the electrical output to the incident radiant power; the detectivity, D^*, a measure how well the device measures small signals; the time constant, τ, a measure of the detector's ability to respond to a sharply rising or falling optical signal; and the linear dynamic range, LDR, a measure of the extent to which the plot of output vs. incident power is linear. We will discuss noise and bandwidth in more detail after the discussion of Fourier transforms. For now, remember that any sequence of signals can be represented as a combination of pure component oscillations. The bandwidth of a detector is the range of signal frequencies to which the device responds. Therefore, the time constant is given by

$$\tau = \left(2\pi f_c\right)^{-1}$$

where f_c is a 'cut-off' frequency, the frequency at which responsivity falls to 0.707 times its maximum value. The rise time, the time it takes the detector response to reach 90% of its maximum value when a sharp input is applied, is proportional to the time constant.

The ability of a detector to respond to low radiant power depends on its dark current, which is the electrical output in the absence of light, as well as its sensitivity. The noise equivalent power, Φ_n, is the radiant power of an oscillating signal that produces an electrical signal with the same amplitude as the dark current in a 1 Hz bandwidth. The dectectivity is

$$D^* = \left(\frac{1}{\Phi_n}\right)\sqrt{A}\sqrt{\Delta f}$$

where A is the detector area and Δf is the detector bandwidth.

The photomultiplier tube (PMT) has been the workhorse detector of optical spectroscopy for many years. It responds to a wide spectral range, ~110 – 1000 nm, is
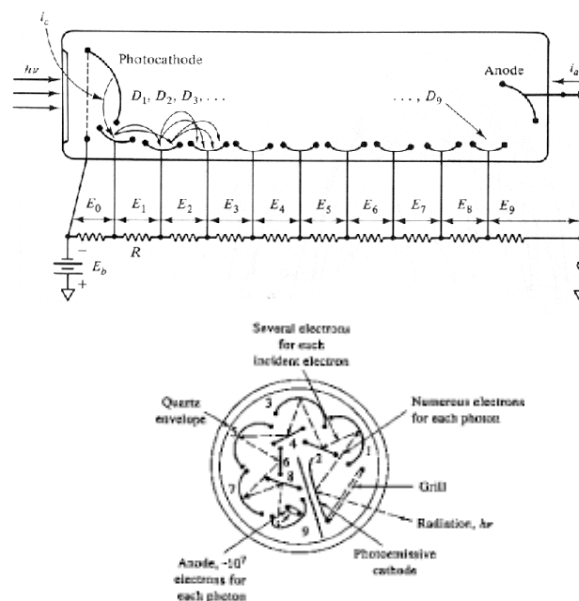
Side and top views of PMT. From Ingle & Crouch, Spectrochemical Analysis, 1988.

Figure 3.6: Photomultiplier Tube

very responsive, R>10^{12} WA^{-1}, has a wide linear dynamic range (6 decades) and a short, <10 ns, rise time. PMTs are electrodes sealed in an evacuated glass or silica envelope, i.e. a vacuum tube. Electrons are dislodged from the alkali metal oxide photocathode by incident photons and accelerated toward the photoanode by positive potential. On the way to the photoanode, the electrons are attracted to a series of intermediate electrodes, called dynodes, poised at successively more positive potentials. The dynodes are coated with secondary emissive materials, such as MgO, which release 3-5 electrons on single electron impact. The cascade of electrons that results from the a single photon on the photocathode, called the gain, m, (sometimes you'll see G for the gain) gives the PMT its responsivity. It is also responsible for the high detectivity of the PMT, which is even a little higher than that of the dark adapted human eye. The current generated by monochromatic radiation incident on a photomultiplier tube is

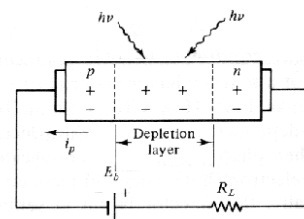$$i = \eta GR(\lambda)\Phi(\lambda)$$

where η is the collection efficiency of the photoanode, G is the gain, R is the responsivity and Φ is the incident radiant power.

Semiconductor detectors do not generally have the range of features that PMTs have. They do not respond as deeply into the UV and they are generally several orders of magnitude less responsive. (There is usually no cascade or gain mechanism; the exception are avalanche phodiodes.) However, they are rugged, linear, just as fast, have pretty good detectibility and are easily miniaturized. Consequently, they are used in many modern applications. A semiconductor detector is a diode, an electrical device with greater conductivity in one direction. Diodes are formed, for example, at the interface of silicon crystals doped with positive charge carriers (Ga) and negative charge carriers (As).

Photodiode. From Engle & Crouch, Spectrochemical Analysis, 1988.

Figure 3.7: Photodiode

When a negative potential is applied to the p-region and a positive potential to the n-region of the diode, a depletion layer forms at the pn junction. This is called reverse bias. Photons incident on the depletion region generate a electron/hole pair, and thus, a current that is proportional to the incident power. Avalanche photodiodes (APDs) are becoming important photon detectors in spectrochemical analysis. A large reverse-bias accelerates the electrons produced by photon irradiation so that they collide with the semiconductor lattice producing a cascade of electrons for each photon detector. Although the gain produced by this mechanism is smaller than that observed in the PMT (G~10^3), the quantum efficiency of these devices is close to 90%. Moreover, they exhibit less noise, larger linear dynamic ranges and better electrical efficiency (less resistive heating) than PMTs. When these features and the compactness and flexibility of their packaging are considered, APDs can be better detection sytems for many applications.

Multichannel detectors, which are used to measure images at several sample locations or spectra at several wavelengths simultaneously, are constructed from arrays of diodes or integrated circuits, such as semiconductor capacitors in charge transfer devices. Photodiode arrays are just what the name says: linear arrays of 25 um

photodiodes. What the name doesn't include are the small storage capacitors connecting each diode to a shift register. In a measurement, the diodes are simultaneously irradiated, generating radiant flux dependent charges in each diode that discharge the adjacent capacitor. The current required to recharge each capacitor and reestablish reverse bias in the adjacent diode is advanced to a preamplifier by a shift register and converted to voltage. Photodiode arrays are great for absorbance measurements because the sample and reference signals are typically both large. In this case, the large dark current (noise when detector is not illuminated) is less important.
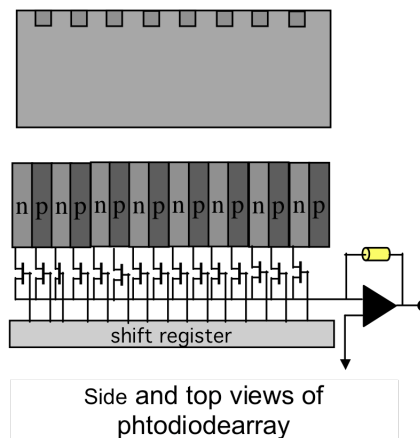

Side and top views of phtodiodearray

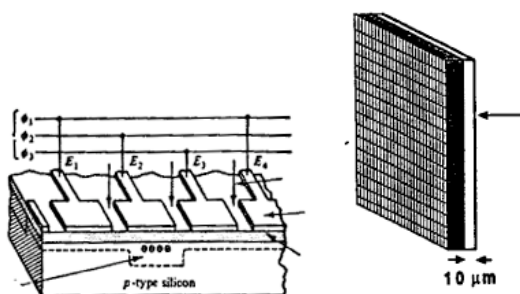**Figure 3.8: Photodiode Array**

Figure 3.9: Pixel Electronics & Backside Illuminated CCD

For other measurements, e.g. fluorescence or Raman, charge-coupled devices provide much better performance. CCDs are arrays of electrodes (metal oxide semiconductor capacitors) that store, then measure the charge created in the deplection layer by photon irradiation. A single pixel consists of three electrodes (called gates) poised at low (ends) and high (middle) potentials so that the electrons generated by photon irradiation will be trapped under the middle gate. The charge is pushed to a shift register on the side of the chip by cycling the potentials on the electrodes so that the charge advances across the chip. The most responsive CCDs are constructed on thinned substrate (~10 μm) and backside (relative to electrodes) illuminated, Quantum efficiencies >80% can be achieved for some wavelengths. Most importantly, the capacitor stores relatively large amounts of charge, so the LDR is wider and SNRs are larger than those of PDAs. One feature that PMTs have that CCDs lack is fast rise times. The fastest commercial chips acquire data at around 50 frames per second, which puts the rise time in the millisecond regime, compared nanosecond rise times in PMTs. Intensifiers, which act as fast shutters, are being added to CCDs to address this limitation.

Infrared photons are not energetic enough to produce current in PMTs or photodiodes. A number of IR detectors, including the Golay detector, thermocouple and bolometer have been described. The detector that often is used in FT-IR instruments is a pyroelectric detector that has a fast response time for detectors for this wavelength range, < 1 ms. The detector is made of triglycine sulfate (TGS), a material that develops a substantial surface charge when placed in an electric field. When IR radiation falls on the surface, the surface charge is disrupted and a current that is proportional to the derivative of the temperature change is produced. Hence, it is not useful for measuring constant radiation levels. Semiconductor detectors also are available for the IR region. Single- and multichannel detectors based on HgCdTe (also abbreviated MCT) are commercially available.