CHEMICAL KINETICS

1. Propose a mechanism:

\[ M^* \xrightarrow{k} M \]

2. Define the rate law for the proposed mechanism:

\[- \frac{\partial [M^*]}{\partial t} = \frac{\partial [M]}{\partial t} = k [M^*] \]

3. Solve the differential equations to yield the time dependence of the concentrations of reactants and products

\[ [M^*] = [M^*_0] e^{-kt} \]

\[ [M] = [M_f] + ([M]_0 - [M_f]) e^{-kt} \]

([M^*_0] is the concentration of \( M^* \) at time zero; \([M]_0 \) is the concentration of \( M \) at time zero; \([M_f] \) is total concentration of \( M \) plus \( M^* \))

The experimental problem is to find a way to measure the time-varying concentrations of \([M^*]\) and/or \([M]\). Spectroscopy is the standard method for determining the concentrations of reagents in solutions.
STEADY-STATE SPECTROSCOPY

Transmission ($T$):

\[ T = \frac{I}{I_0} \]

($I_0$ is the intensity of the incident, monochromatic light; $I$ is the intensity of the transmitted light)

Absorbance ($A$):

\[ A = -\log_{10}(T) \]

\[ A = -\log_{10}\left(\frac{I}{I_0}\right) \]

Beer’s Law:

\[ A(\lambda) = [M] \varepsilon(\lambda) \ell \]

($\lambda$ is the wavelength of light; $\varepsilon$ is the extinction coefficient; $\ell$ is the path length). Beer’s law holds for low light levels such that the concentration of excited chromophores is much less than the concentration of ground-state chromophores (i.e., $[M^*] \ll [M]$).
In a double beam spectrometer, the incident light beam ($I_0$) is split into two components by BS and two detectors are used - one records the intensity of the reference beam ($I_R$), the other records the intensity of light transmitted through the sample ($I_S$). A monochromator before the beamsplitter selects the wavelength and bandpass of $I_0$.

\[
A = - \log_{10} \left( \frac{I_S}{I_{S0}} \right)
\]

\[
I_R = \alpha_R I_0 \; ; \quad I_{S0} = \alpha_T I_0 = \left( \frac{\alpha_T}{\alpha_R} \right) I_R
\]

\[
A = - \log_{10} \left( \frac{I_S}{I_R} \right) + \log_{10} \left( \frac{\alpha_T}{\alpha_R} \right)
\]
The advantage of a double beam spectrometer is that fluctuations in probe-light intensity can be accounted for by recording the intensity of the reference beam. But, owing to the wavelength dependence of the beamsplitting ratio (i.e., $\partial \alpha_R/\partial \lambda \neq 0$; $\partial \alpha_T/\partial \lambda \neq 0$), a baseline calibration scan is necessary.

**Single-Beam Spectrometer**

With sufficiently stable probe sources, a single-beam spectrometer will provide $A$ values as accurately as a double-beam instrument. A blank scan is necessary and errors will result from changes in the probe light intensity and/or spectrum.

The advantage of the single-beam spectrometer is its lower cost. With single-channel detectors, a monochromator before the beamsplitter selects the wavelength and bandpass of $I_0$. With a multichannel array detector, a spectrograph after the sample provides a full spectrum ($A(\lambda)$) in a single measurement.

The HP diode array spectrometers are single-beam instruments. The *blank* spectrum provides a record of $I_0(\lambda)$. 
In time resolved spectroscopy, there is a triggering event (e.g., a laser pulse; a stopped-flow mixing cycle) that rapidly changes the concentrations of the reagents in sample cell.

For a given $\lambda$ (one-component case):

$$A(t<0) = [M]_0 \varepsilon_M \ell$$

$$A(t>0) = [M](t) \varepsilon_M \ell + [M^*](t) \varepsilon_{M^*} \ell$$

Define the change in absorbance as:

$$\Delta A(t) \equiv A(t>0) - A(t<0)$$

$$\Delta A(t) = [M](t) \varepsilon_M \ell + [M^*](t) \varepsilon_{M^*} \ell - [M]_0 \varepsilon_M \ell$$
For this one-component case:

\[
[M]_0 = [M](t) + [M^*](t)
\]

\[
\Delta A(t) = [M](t) \varepsilon_M \ell + [M^*](t) \varepsilon_{M^*} \ell - [M](t) \varepsilon_M \ell - [M^*](t) \varepsilon_{M^*} \ell
\]

The time dependent absorbance at a given wavelength will be:

\[
\Delta A(t) = [M^*](t) [\varepsilon_{M^*} - \varepsilon_M] \ell
\]

In general, for the one-component case:

\[
\Delta A(\lambda, t) = [M^*](t) \Delta \varepsilon(\lambda) \ell
\]

From the example on the first page:

\[
[M^*](t) = [M^*]_0 e^{-kt}
\]

\[
\Delta A(\lambda, t) = [M^*]_0 \Delta \varepsilon(\lambda) \ell e^{-kt}
\]

The objective in a time-resolved experiment is to measure time-varying reagent concentrations, but what one actually measures are time-varying light intensities (I(t)).

\[
\Delta A(t) \equiv A(t>0) - A(t<0)
\]
For a single-beam spectrometer:

\[ \Delta A(t) = -\log_{10}\left[ \frac{I(t>0)}{I_0}\right] - \left[ -\log_{10}\left( \frac{I(t<0)}{I_0}\right) \right] \]

\[ \Delta A(t) = -\log_{10}\left[ \left( \frac{I(t>0)}{I_0}\right) \left( \frac{I_0}{I(t<0)}\right) \right] \]

If the probe light intensity is time invariant \((i.e., \partial I_0/\partial t = 0)\) then absorbance changes can be determined directly from measurements of the transmitted light intensity before and after the triggering event:

\[ \Delta A(t) = -\log_{10}\left[ \frac{I(t>0)}{I(t<0)}\right] \]

If \(I_0\) is time-invariant, it is sufficient to know \(I(t < 0)\) in order to measure changes in absorbance. If \(I_0\) is not time-invariant, then you must determine \(I(t < 0)\) and \(I_0(t)\) in order to measure changes in absorbance.
It is important to note that since reagent concentrations are NOT proportional to light intensities, you will not find that $I$ is a simple function (e.g., exponential; sum of exponentials) of $t$.

That is:

<table>
<thead>
<tr>
<th>$\Delta A$</th>
<th>$I(t &gt; 0) / I(t &lt; 0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.10</td>
</tr>
<tr>
<td>0.10</td>
<td>0.79</td>
</tr>
<tr>
<td>0.01</td>
<td>0.98</td>
</tr>
<tr>
<td>0.001</td>
<td>0.998</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

**SPECTROMETER COMPONENTS**

**Detectors**

1. Photomultiplier Tubes (PMT)
The photomultiplier tube generally has a photocathode in either a side-on or a head-on configuration. In our nanosecond spectrometers we use a Hamamatsu model R928, side-on PMT (see Appendix 1 for specifications). Side-on PMTs receive incident light through the side of the glass bulb, while in the head-on type, it is received through the end of the glass bulb. Most side-on PMTs employ an opaque photocathode (reflection-mode photocathode) and a circular-cage structure electron multiplier which has good sensitivity and high amplification at a relatively low supply voltage.

The sensitivity of the photocathode is a function of the wavelength of light. The R928 has a multialkali photocathode giving it good spectral sensitivity from 180 to 900 nm (see Appendix 1 for spectral response curve). We also have a PMT that extends to 1100 nm (R406), but this PMT is less sensitive and has higher dark current than the R928.

Photoelectrons emitted from a photocathode are accelerated by an electric field so as to strike the first dynode and produce secondary electron emissions. These secondary electrons then impinge upon the next dynode to produce additional secondary electron emissions. Repeating this process over successive dynode stages, a high current amplification is achieved. A very small photoelectric current from the photocathode can be observed as a large output current from the anode of the photomultiplier tube.

Current amplification is simply the ratio of the anode output current to the photoelectric current from the photocathode. Ideally, the current amplification of a photomultiplier tube having \( n \) dynode stages and an average secondary emission ratio \( \delta \) per stage is \( \delta^n \). The secondary electron emission ratio \( \delta \) is given by
\[ \delta = \eta E^\alpha \]

where \( \eta \) is a constant, \( E \) is the interstage voltage, and \( \alpha \) is a coefficient determined by the dynode material and geometric structure. It usually has a value of 0.7 to 0.8. When a voltage \( V \) is applied between the cathode and the anode of a photomultiplier tube having \( n \) dynode stages, current amplification, \( \mu \), becomes

\[ \mu = \delta^n = (\eta E^\alpha)^n \]

\[ \mu = n \left( \frac{V}{n+1} \right)^\alpha^n \]

\[ \mu = \frac{\eta^n}{(n+1)^{\alpha^n}} V^{\alpha^n} = K V^{\alpha^n} \]

Since photomultiplier tubes generally have 9 to 12 dynode stages, the anode output varies directly with the 6th to 10th power of the applied voltage. (The R928 is a 9-stage PMT; in the nanosecond spectrometer, we short the last four dynodes together, making it effectively a 5-stage PMT.) The output signal of the photomultiplier tube is extremely susceptible to fluctuations in the power supply voltage, thus the power supply must be very stable and provide minimum ripple, drift, and temperature coefficient.

A small amount of current flows in a photomultiplier tube even when the tube is operated in a completely dark state. This output current, called the anode dark current, and the resulting noise are critical factors in determining the sensitivity of a photomultiplier
tube. The figures below show the current amplification as a function of cathode-anode voltage; and the dependence of dark current on the supply voltage.
More details on the construction and operating characteristics of PMTs are given in Appendix 2.

The key feature of a PMT is that the anode current \( i \) is a linear function of the light intensity, up to a maximum value.

\[ i = g(\lambda) I \]

The gain factor depends on the overall current amplification (\( \mu \)) and the photocathode sensitivity. For the R928 the maximum average anode current is 0.1 mA.

1. Photodiodes (PD)

Silicon photodiodes form the second major class of light detectors used in spectroscopy. When photons with energies greater than the band-gap energy \( (E_g) \) strike a photodiode, electrons are excited into the conduction band, leaving holes in the valence band. The concentration of electron-hole pairs is proportional to the light intensity. These electron-hole pairs occur throughout the P-layer, the depletion layer, and N-layer. In the depletion layer the electric field accelerates these electrons toward the N-layer and the holes toward the P-layer. This results in a positive charge in the P-layer and a negative charge in the...
N-layer. If an external circuit is connected between the P- and N-layers, electrons will flow away from the N-layer, and holes will flow away from the P-layer toward the opposite respective electrodes.

The short circuit current ($i_{sc}$) is extremely linear with respect to the incident light level; light intensities in the range of $10^{-12}$ to $10^{-2}$ W, produce linear output currents, depending on the type of photodiode and its operating circuit.

The radiant sensitivity of a silicon photodiode is lower than that of a PMT and, although better in the red, silicon has a poorer blue sensitivity than a multialkali PMT. In most cases, our probe light is not sufficiently intense for us to use photodiode detectors.

**Detector Circuits**

A PMT is an example of a current source (in contrast to a voltage source). Current is usually measured using some type of current-to-voltage converter; the simplest is a load resistor ($R_L$).

For the R928, the maximum anode current is 0.1 mA, which places a upper limit on the voltage drop ($V_L$) across the load.
resistor (i.e., Ohm’s Law, $V_L = R_L \times i_a$). A larger load resister will give a larger voltage drop, but at the cost of slower response time (i.e., lower bandwidth).

The following table shows the voltage changes that correspond to three different absorbance changes ($\Delta A$) with three different load resistances, if the anode current is at its maximum value (0.1 mA).

<table>
<thead>
<tr>
<th>speed</th>
<th>$R_L$, $\Omega$ (max)</th>
<th>$V_L$</th>
<th>$\Delta A = 10^{-2}$</th>
<th>$\Delta A = 10^{-3}$</th>
<th>$\Delta A = 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast</td>
<td>50</td>
<td>5 $\times$ 10$^{-3}$</td>
<td>1.1 $\times$ 10$^{-4}$</td>
<td>1.1 $\times$ 10$^{-5}$</td>
<td>1.2 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>↓</td>
<td>10$^3$</td>
<td>0.1</td>
<td>2.3 $\times$ 10$^{-3}$</td>
<td>2.3 $\times$ 10$^{-4}$</td>
<td>2.3 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>slow</td>
<td>10$^6$</td>
<td>100</td>
<td>2.3</td>
<td>0.23</td>
<td>2.3 $\times$ 10$^{-2}$</td>
</tr>
</tbody>
</table>

The 10$^6$ $\Omega$ load looks good, but it is not fast. And, the PMT does not perform well (linearly) if there is a large (compared to the interstage voltage) voltage drop across $R_L$.

With our 10-bit transient digitizer and most sensitive input range of −0.100 to +0.100 V, 1-bit corresponds to 2 $\times$ 10$^{-4}$ V. For high speed applications, a 50-$\Omega$ load resistor is required. But, if it is used as the current-to-voltage converter, only very large transient absorption signals will produce measurable voltage changes. More signal gain is necessary to measure small, short-lived absorbance changes, so we use a wide-bandwidth, high-gain, current-sensitive amplifier.
**PROBE LIGHT**

To maximize sensitivity in transient absorption measurements, we want to use as much probe light as possible to get the maximum current from the PMT.

**Compact Arc Lamps**

High pressure gas discharge lamps with arc lengths that are small compared with the size of the electrodes are called short arc or compact arc lamps. Depending on rated wattage and intended application, the arc length of these lamps may vary from about a third of a millimeter to about a centimeter. *These lamps have the highest luminance and radiance of any continuously operating light source and are the closest approach to a true "point" source.*

The envelope is made from optically clear quartz material of various grades and has a spherical or ellipsoidal shape. The grade of the quartz will determine the amount of ozone generated. The most widely used material for the electrodes is tungsten.

Most compact arc lamps are designed for DC operation. This results in better arc stability and substantially longer life. DC systems consist of an igniter and a regulated power supply. High voltage pulses (up to 50,000 volts) break down the gap between the electrodes, ionize the gas and heat the cathode tip to thermionic emitting temperatures.

*Note that higher wattage lamps do not necessarily yield more light intensity. When higher illumination intensity is needed, lamps must be selected with greater brightness, and this does not always increase with lamp wattage.*
Xenon Lamps

Xenon compact arc lamps are filled with several atmospheres of xenon gas. They reach 80% of final output within 10 minutes or less of starting. The arc color is very close to daylight (6000 deg. K). The spectrum is continuous in the visible range and extends far into the ultraviolet. A Xenon lamp exhibits strong lines in the near infrared between 800 and 1000 nm and some weak lines in the blue portion of the spectrum.

Xenon compact arc lamps are made with rated powers from 75 to 30,000 watts and are available for operation in either a vertical or horizontal position. The breakdown voltage between the electrodes will run from 10kv for a small lamp up to 60kv or more for lamps rated 30kw.
Mercury-Xenon Lamps

A Mercury-Xenon lamp contains a specific amount of mercury and a small amount of xenon added at a pressure exceeding one atmosphere. The xenon is necessary to facilitate starting and to sustain the arc until the mercury is fully vaporized; it also reduces the warm-up period. Normal warm-up time is 10-15 minutes. Mercury lamps are sensitive to cooling because the bulb temperature determines the Hg vapor pressure. The lamp can be over-cooled to the point that full output in the mercury spectrum is never achieved.

Typical steady state voltage of a Mercury-Xenon lamp is higher than that of a xenon lamp. The output in the visible range consists mainly of four mercury lines and some continuum, due to the high operating pressure. A properly warmed lamp will show no significant trace of the xenon gas spectrum.
Tungsten Lamps

Tungsten lamps consist of a coiled tungsten filament mounted in a precision glass envelope. The envelope may have a vacuum or, more commonly, be filled with an inert gas such as argon or krypton. Typical lamp operating parameters are 2.5 to 12 volts and .02 to 1 amp. Color temperature ranges from 2,200 to 3,000 degrees Kelvin.

Tungsten-Halogen lamps feature a tungsten coil filament mounted in a quartz glass envelope that has been filled with an inert gas plus a trace of halogen (normally bromine). This gas creates the “halogen cycle” that prolongs the life of the filament considerably, and also eliminates blackening of the bulb by preventing the evaporated tungsten from condensing on the envelope. The Halogen lamp color temperature runs from 2900 to 3400 deg. Kelvin and are available in wattages from 10 to 250 at operating voltages from 6 to 24. Tungsten-Halogen lamps must be operated at voltages that maintain an envelope temperature between 250 and 350 °C. Cooler temperatures will not allow the halogen cycle to take place.
Arc Lamp Handling

WARNING: Compact arc lamps contain highly pressurized gas, and present an explosion hazard even when cold. Wear eye/face protection whenever handling arc lamps.

Safety goggles should be worn when removing and installing lamps. Never touch the quartz envelope with bare hands; such handling may lead to deterioration and premature failure. If a lamp is accidentally touched, clean the lamp surface with an alcohol swab to remove any residue.

WARNING: Never look directly at an operating arc lamp; severe eye injury can result. Wear U.V. protective lenses, such as a welder's goggles, when aligning operating arc lamps.

Electrode Polarization

Some lamps can only be mounted one way in the arc lamp housing since the anode (+) and cathode (-) have different diameters. However, some lamps have the same diameter anode and cathode, allowing room for error. Refer to the lamp manufacturer's data sheet for proper identification of the anode and cathode.

Note that reversed polarization will result in immediate and permanent damage to the lamp electrodes. A lamp that has been fired with reversed polarization will have obvious physical damage to the electrodes. A damaged lamp will fire, but it will exhibit unstable performance and a severely shortened operating life.
**Lamp Stability**

Short term stability is measured over seconds, while long term stability is measured over minutes, hours, or even days.

Short term stability is affected by arc "wander," "flare" and "flutter." Arc wander is the movement of the attachment point of the arc on the cathode surface. Typically the arc moves around the conical cathode tip in a circular fashion, taking several seconds to move a full circle. Arc flare refers to the momentary change in brightness as the arc moves to an area on the cathode having a preferential emissive quality over the previous attachment point. Arc flutter is the rapid side-to-side displacement of the arc column as it is buffeted by convection currents in the xenon gas which are caused as the gas is heated by the arc and cooled by the envelope walls.

Lamp stability usually improves once the lamp becomes thermally equilibrated (10-15 min).

**Lamp Life**

The useful life of compact arc lamps is determined primarily by the decrease of luminous flux caused by the deposit of evaporated electrode material on the inner wall of the envelope. Frequent ignition accelerates electrode wear and hastens the blackening of the envelope. As the lamp ages, the operating voltage will increase. Lamp current should be decreased to maintain output until the minimum operating current is reached. At this time the lamp should be replaced. Current pulsing shortens arc lamp life in the nanosecond transient absorption system. Old lamps have severely worn electrodes and poor arc stability.

**75-W Xe Arc Lamp: 14–15 V; 5–5.4 A.**
Arc Lamp Housing

A high power lamp does not necessarily result in higher optical output collected from a light source. Since light is emitted by the lamp in all directions, the important thing is not the amount of light emitted, but the amount of light collected.

The PTI A-1000 lamp housing collects and focuses emitted light with a single optical element: an ellipsoidal reflector. Because the ellipsoid encloses a large portion of the solid angle about the arc lamp, over 65% of the lamp's emission is collected and focused at the output. A traditional lamp housing with a spherical reflector and lens will collect roughly 10% of the emitted light.
The A1000 lamp housing that we use on the NS-1 system has a custom f/15 ellipsoidal reflector.

Approximate dimensions for the A1000 housing with the f/15 reflector are given below.

\[
\begin{align*}
D &= 65 \text{ mm} \\
F &= 1065 \text{ mm} \\
X &= 975 \text{ mm}
\end{align*}
\]
When irradiating a small aperture (e.g., a 1-mm diameter pinhole), brightness is the key factor, not total flux. Arc lamps are 5-50 times brighter than quartz-halogen lamps. Furthermore, a 75-W Xe arc lamp is as bright as a 1000 W Xe arc lamp. The 1 kW lamp has a much larger arc and greater total flux, but is not brighter than a 75-W lamp. We could get no more light through the 1-mm aperture with a 1 kW lamp than we can with the 75-W lamp.

We can increase the brightness of the 75-W Xe arc lamp for short time periods by delivering a short current pulse to a simmering lamp. We use an Analog Modules 778P laser diode driver in parallel with the arc lamp power supply to deliver a 1-ms, ~50-A pulse that increases the lamp brightness by about a factor of 10.
The PULSED ARC LAMP mode is only useful for time scales less than 1-ms. As a practical matter the lamp pulse is flat enough for transient absorption measurements on the 250 μs time window. The signal shown above was recorded with the 5-stage base on the R928 PMT. Note the high-frequency noise on the probe light signal.

Under some conditions, 100 μA of PMT current can be obtained running the lamp CW, using the 5-stage PMT, and the FAST AMP. In this case pulsing the lamp would offer no signal-to-noise advantage. But, it can help in increasing the ratio of probe-to-scattered light (laser or luminescence). If scattered light is a problem, it can be advantageous to pulse the lamp, then use a neutral density filter before the monochromator to limit the PMT current to ≤100 μA.

On time scales less than 100 μs, the lamp output is reasonably flat, and pulsing the arc lamp is an effective means of improving signal to noise. On longer time scales, the lamp must be run CW, but a high-gain, lower bandwidth amplifier (SLOW AMP) can improve signal to noise.

Using the pulsed lamp and 5-stage PMT, we can obtain 100 μA currents but, terminated across 50 Ω, this will give only a 5 mV signal and the minimum detectable OD change will be 0.02 (Table, p. 14). The solution to this problem is to use a high-gain, wide-bandwidth, current sensitive amplifier. Amplifiers will not improve signal to noise because they amplify the noise along with the signal and add more noise of their own. The reason we amplify is to increase the magnitude of I₀ (or V₀) so that the magnitude of ΔI (or ΔV) is larger. This is necessary because of the finite resolution of our A-to-D converters.
FAST AMP

We use a custom designed, 200 MHz bandwidth, current-sensitive “FAST AMP” with a gain of \( \sim 7 \text{ mV}/\mu\text{A} \). With a 100 \( \mu\text{A} \) PMT current, this amplifier will generate a 700 mV output. But, the FAST AMP can only drive 50-\( \Omega \) loads linearly to 500 mV. So, the amplifier will go nonlinear before the PMT does. The software and hardware of the NS-1 system are configured so that, when used properly, the amplifier does not deliver more than 500 mV.

Running the FAST AMP in single-ended mode gives the following output with the pulsed arc lamp.
The transient digitizer has a 10-bit AD converter. The minimum detectable OD changes with this ~400-mV signal from the fast amp are shown in the Table below.

<table>
<thead>
<tr>
<th>Digitizer Input Range</th>
<th>1-bit</th>
<th>( \Delta A_{\text{min}} (I_0 = 400 \text{ mV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pm 100 \text{ mV} )</td>
<td>0.20 mV</td>
<td>( 2.2 \times 10^{-4} )</td>
</tr>
<tr>
<td>( \pm 200 \text{ mV} )</td>
<td>0.39 mV</td>
<td>( 4.2 \times 10^{-4} )</td>
</tr>
<tr>
<td>( \pm 500 \text{ mV} )</td>
<td>0.98 mV</td>
<td>( 1.1 \times 10^{-3} )</td>
</tr>
<tr>
<td>( \pm 620 \text{ mV} )</td>
<td>1.21 mV</td>
<td>( 1.3 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

On the most sensitive digitizer input range, the minimum detectable signals are about 0.2 mOD. The problem is that the ~400-mV signal from the FAST AMP is outside of the digitizer input range. For a signal of ~400 mV, it is necessary (when not using input offset correction) to use the \( \pm 500 \text{ mV} \) (or greater) input range. In this case, the minimum detectable signal is \( \sim 1 \text{ mOD} \).

To take advantage of the full pulsed-lamp output signal and use the most sensitive input range of the digitizer, we run the FAST AMP in a “quasi-differential” mode.

A functional block diagram of the FAST AMP is shown on the next page. NOTE: this is not the actual schematic diagram for the FAST AMP; it is intended only to illustrate how the amplifier works.
A  Current-to-voltage converter: gain = 7 mV/µA.

B  Unity-Gain Differential Amplifier: \( V_{\text{OUT}} = V_1 - V_2 \)

C  Sample & Hold Amplifier: two-state unity gain amplifier

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State 1:

\[ V_H = 0 \text{ V (low)} \]

\[ V_{\text{OUT}} = V_1 \]

State 2:

\[ V_H = 5 \text{ V (high)} \]

\[ V_{\text{OUT}} = \text{fixed at value of } V_1 \text{ at the time of the low→high transition on } V_H \]

The signal from the current-to-voltage converter is monitored by the S/H amplifier and is fed to the non-inverting input of the differential amplifier. The S/H output is fed to the inverting input of the differential amplifier. When \( V_H \) is low, the S/H amplifier tracks the signal from the current-to-voltage converter, resulting in 0-V output at Amp OUT. When \( V_H \) goes high, the S/H amplifier stops tracking changes from the current-to-voltage converter, and holds the output at its value at the time of the low-to-high transition on \( V_H \). After \( V_H \) goes high, the laser fires and any changes in PMT current are now reflected at Amp OUT.

\[ \text{D Inverting Amplifier: voltage gain } = -10 \times ; V_{\text{OUT}} = -10 \times V_1 \]
The signal from Amp OUT goes to the Channel-1 input on the transient digitizer. The digitizer input is internally terminated at 1 MΩ. *For maximum bandwidth, the Amp OUT signal should be externally terminated with a 50 Ω load resistor.*

The Base Out signal is fed to the Camac A/D converter so that we determine the magnitude of the voltage offset. This is necessary accurate ∆A calculations (p. 7).
The upper trace on the previous page shows Amp OUT signal with the pulsed arc lamp and the amplifier in the quasi-differential mode. The lamp pulse begins to drive the signal negative, but the differentiating circuit drives it back to zero. The response time for the differentiator is somewhat slower than the rise time of the amplifier. Once the Amp OUT signal is driven back to zero, the amplifier HOLD pulse is applied ($V_{IH}$ low-to-high transition). After this point the S/H amplifier ignores changes on its non-inverting input and holds its output fixed. About 150 μs after the HOLD pulse, the laser fires and changes in PMT current will appear at Amp OUT. The Amp out signal is flat only for about 500 μs; this is the time-range limit for current pulsing with the arc lamp. The HOLD pulse is only $\sim$2-ms long, so this creates an upper limit for the time range when using the FAST AMP.

The advantage of lamp pulsing with the fast amp is that voltage changes due to transient absorption occur about a 0-V output level so that the most sensitive digitizer input range can be used.
SLOW AMPLIFIER

On time scales longer than ~0.5 ms, we cannot use the pulsed arc lamp. The FAST AMP will work as long as the HOLD pulse is held high (~2 ms). We could extend this further for longer time bases, but there is no need to have 200 MHz bandwidth for millisecond time-scale measurements. Instead, we sacrifice some bandwidth, reduce the noise level on the probe light signal with analog filtering, and increase the amplification of the PMT signal. The SLOW AMP accomplishes these tasks.

SLOW AMP

DSP 1402E Programmable Amplifier (CAMAC module)
Gain (V/V): $1 - 5 \times 10^3$ (inverting)
Maximum Bandwidth: $10^5$ Hz
Programmable Cutoff Filters: $10^2 - 10^5$ Hz
Maximum Output Voltage: ±10 V @ 15 mA

The final specification is important. The maximum current output from the amplifier is 15 mA. If the SLOW AMP output is terminated across a 50-Ω load

$$ (0.015 \text{ A}) \times (50 \text{ Ω}) = 0.75 \text{ V} $$

The point is, the SLOW AMP cannot drive a 50-Ω load to the full 10-V output voltage. The SLOW AMP cannot be terminated with 50 Ω at the digitizer input; it must be fed directly into the $10^6$ Ω load of the digitizer.
The SLOW AMP is a voltage amplifier and the PMT is a current source, so we need to use a current-to-voltage converter. We use a $10^3 \, \Omega$ resistee for this job (A). At the maximum PMT anode current of $-100 \, \mu$A, the SLOW AMP input voltage will be $-0.1 \, V$ (i.e., $-10^{-4} \, A \times 10^3 \, \Omega = -0.1 \, V$).

The SLOW AMP has two stages: Pre-Amp (B) and Post-Amp (C) with variable gain factors of $1-100$ and $1-50$, respectively. In our “standard configuration” we use a Pre-Amp gain of 100 and a Post-Amp gain of 1. At the maximum PMT anode current with a $10^3 \, \Omega$ terminator, $V_{IN} = -0.1 \, V$ and $V_{OUT} = 10 \, V$.

For small light intensities, we can use some additional POST-AMP Gain, but there are minor problems with Amplification of offset errors from the Pre-Amp stage.

As with the FAST AMP, we want to offset $V_{OUT}$ to 0 V before the laser fire so that we can take advantage of the higher sensitivity digitizer input ranges. The signal offset is performed with software on the SLOW AMP.
The SLOW AMP output voltage is:

\[ V_{OUT} = [(V_{IN} \times G_1) + V_P] \times G_2 \]

The offset voltage \( V_P \) is provided by a D-to-A converter on a National Instruments multifunction IO card in the PC. Since the laser is firing at \( \leq 10 \) Hz, we have \( \geq 100 \) ms to calculate the proper offset voltage and apply it to the SLOW AMP.

The sequence of events is:

1. Read the NI AD converter to measure \( V_{OUT} \)
2. Apply proper offset voltage to \( V_P \) using the NI DA converter.
3. Read the NI AD converter to check that \( V_{OUT} \) is \( \sim 0 \) V. If not, print an error message.
4. Wait for the Laser Fire
5. Check to determine if it was a "good" laser shot. If not, go back to (1). If yes, save offset voltage (\( V_P \)) then go back to (1) if there are more shots in the cycle, or end the data collection cycle.

This sequence of events is repeated for each laser shot. If the sample absorbance changes or the probe light intensity varies, this loop will ensure that the pre-flash signal stays inside the digitizer input window.
It is important that the digitizer input window be wide enough to accept the voltage change corresponding to the transient absorption signal. This depends on the probe light intensity and the magnitude of the absorbance change.

For both the FAST AMP and SLOW AMP, the EXCITATION and BLANK OFFSETs (reported on screen at the end of each data collection cycle) reflect probe light intensity. The value written to the screen corresponds to the output from a 12-bit AD converter on the NI interface card.

FAST AMP: 0–4095 \implies 0–0.5 V Amp output  
SLOW AMP: 0–4095 \implies 0–10 V Amp output

In both cases, 4095 counts corresponds to the maximum amplifier output. For the FAST AMP, $|\Delta V|$ will be $\leq 0.1$ V for all but the largest $\Delta$Abs values. A $\pm 0.2$ V window will capture virtually all transient absorption changes measured with the FAST AMP.
With the SLOW AMP, greater care must be exercised to ensure that $\Delta V$ changes fit inside the digitizer input window. Keep in mind there will be pulse-to-pulse fluctuations in $\Delta V$, so you want to leave room in the input window to accommodate these fluctuations. Signals that go out of range on some laser shots are very difficult to discern by visual inspection of the decay trace, but they can lead to distorted kinetics profiles.
EVENT TIMING

Event timing for data acquisition is controlled by the: (1) NI DIO/ADC board; (2) a custom digital pulse sequencer; and (3) the EG&G gate and delay generator. The key feature is that we need some events to occur PRIOR to arrival of the laser pulse at the sample (e.g., digitizer arm, lamp pulse, amp hold pulse, slow amp ADC read). To accomplish this, we use a square (almost) wave timing pulse sequence.

When using the excimer-pumped dye laser for excitation, the NI DIO and pulse sequencer generate the square-wave pulse train. The laser is triggered externally by pulses from these components. It is straightforward to produce sync pulses in advance of the laser pulse.

With the YAG-pumped OPO, the NI DIO and pulse sequencer cannot drive the laser. In this case, the laser is the master oscillator and the control electronics synchronize the square-wave train to the laser. This configuration makes it more difficult to get advance-timing pulses. In addition, the YAG oscillator must run at 10 Hz. To get lower sample excitation rates, we select individual pulses from the 10 Hz train using a pneumatically driven shutter that will open and close within 50 ms.

\[ \tau = (\text{rate})^{-1} \]

† Falling Edges: ARM digitizer

† Rising Edges: Trigger EG&G SLOW AMP ADC
The pulse sequencer generates the Digitizer ARM pulse on the falling edge of the square wave. The digitizer must receive the ARM pulse one full data-record time period BEFORE the trigger pulse from the laser. This trigger pulse arrives after the square-wave rising edge. For time bases longer than 50 ms, the repetition rate must be slow enough to allow enough time between the DIG ARM pulse and the DIG trigger.

The pulse sequencer triggers the EG&G delay generator on the rising edge of the square wave. This delay generator produces timing pulses for the rest of the experiment.

\[ V_{\text{OUT}} : \text{NIM (-0.8 V); +5 V; +10V} \]
Key points about the EG&G delay generator:

- the delay generator should be set for external trigger, 1 MΩ trigger termination; and TTL trigger level

- all voltage outputs should be set to TTL (i.e., +5 V) levels

- pulse width are adjusted by trim pots and are not likely to need changing; the most critical is output C which controls the FAST AMP HOLD and should always be set to maximum width (~2 ms)

- the delay times for all channels are set by software, and are reset at the beginning of every new data collection cycle.

- the delay generator communicates with computer via the GPIB interface; when communication is established with the computer, “REMOTE” will appear on the front panel display; the GPIB address for this device is 5

One common event-timing problem occurs when the laser fire does not trigger the digitizer while the FAST AMP HOLD pulse is high. A clear indicator of this problem is a luminescence decay trace that looks like this:
TRANSIENT DIGITIZER

Data Records
The transient digitizer records waveforms from the FAST and SLOW AMPs. Data are stored in RECORDS; we use a record length of 1024 words (2-byte integers). The KINFIT program refers to EXTENDED and REGULAR data sets. In the EXTENDED data set, all 1024 words are used in the fitting routine; in the REGULAR data set, words are averaged to give 256 words for fitting.

The DIG ARM pulse initiates data writing to the memory record. Data are written in a continuous loop. In order to get pretrigger information, the digitizer software inhibits triggers until one full data record has been written in memory. The digitizer will then accept triggers at any time after that point. Because of this delay between arming and triggering, we generate ARM pulses 180° out of phase with the laser-fire or shutter-open pulses.

Clearly, if you are working on a time base longer than 50 ms, you must run the laser at a repetition rate less than 10 Hz. There is some software protection here, but it is possible to choose a repetition rate that does not leave enough time for a full data record to be written to memory before the digitizer trigger arrives. If this is the case, there will always be two laser shots after the DIG ARM light turns on (digitizer front panel); the first laser shot is ignored, the second one triggers the digitizer. This can be a problem if you’re looking at a sample that undergoes a net photochemical change.

Once the digitizer triggers, it writes the remaining words (RECORD LENGTH – PRE-TRIGGER) to the digitizer memory. The software is calibrated to provide ~10% of full scale in PRE-TRIGGER data. The full 1024-word data record is transferred to the PC after each laser shot. This process limits data acquisition rates to ~10 Hz.
Digitizer Input

The FAST AMP and SLOW AMP output signals are fed into the CH-1 input to the digitizer. This input is internally terminated at 1 MΩ. With the FAST AMP, we use an external 50 Ω terminator. Be sure that you do not use the terminator with the SLOW AMP because it cannot drive 50-Ω loads.

Digitizer Trigger

From p. 6 we have the relationship:

\[ \Delta A(\lambda, t) = [M^*]_0 \Delta \varepsilon(\lambda) \ell e^{-kt} \]

To compare \( \Delta A \) values measured at different wavelengths (i.e., a transient spectrum), it is necessary for \([M^*]_0\) to be roughly constant for each laser shot. This requires that pulse-to-pulse fluctuations in laser intensity be minimized. The first thing you should do is make sure that the laser is tuned well. Then, we use a fast discriminator to reject shots that are much weaker or stronger than the mean value.

The discriminator is used to measure relative laser intensities; not absolute pulse energies. A glass plate picks off a small amount of light from the excitation beam (Fresnel reflection). This light is directed onto a fast photodiode. The discriminator requires a negative input voltage. Therefore, the photodiode must give a negative voltage output when irradiated. This depends on how the photodiode circuit is wired.
If you are unsure about the polarity of the diode, connect it to a voltmeter and allow room light to strike its active surface. If the voltmeter does not read a negative value, then you don’t have the correct diode. If you don’t read much voltage when you shine a flashlight on the diode, then the batteries may be low (if it is a battery operated diode); there is something wrong with the photodiode power supply; or the photodiode itself is damaged.

If the diode operates properly with voltmeter, then the only task required is adjust the intensity of the laser light striking the diode so that the discriminator will generate an output pulse. The discriminator has two voltage levels that are set by trim-pots: LLD is the lower voltage level; ULD is the upper level. The relationship between these voltages and the input pulse from the photodiode is shown below:

![Diagram showing the relationship between voltages and input pulse from photodiode]
The discriminator has three operating modes selected by a toggle switch on the input panel. We only use two of these modes: LED and ΔE.

**LED Mode:** trigger is generated if the peak of the pulse is greater than LLD

**ΔE Mode:** a trigger is generated if the peak of the pulse is greater than LLD AND below ULD

In the ΔE mode, the digitizer will trigger only on “good” laser shots.

To set up the discriminator, it is necessary to adjust the intensity of the light striking the surface of the photodiode. The easiest way to do this is to raise or lower the diode.

A reliable procedure for setting the laser intensity on the photodiode is first to set the discriminator to LED mode, then adjust the intensity until the discriminator triggers (LED on the front panel will flash). Next switch to ΔE mode; if the triggers stop, the laser intensity is too high. If you get partial triggering, fine tune the laser intensity to get the maximum triggering frequency. With the excimer-pumped dye laser, the pulse energy will depend on the laser repetition rate. This will not be the case for the YAG-pumped OPO.
Paraxial Formulas

SIGN CONVENTIONS

The validity of the paraxial lens formulas is dependent on adherence to the sign conventions shown here:

**For lenses:** (refer to Figure A1.1)

- \( s \) is + for object to left of \( H \) (the first principal point)
- \( s \) is − for object to right of \( H \)
- \( s' \) is + for image to right of \( H' \) (the second principal point)
- \( s' \) is − for image to left of \( H' \)
- \( m \) is + for an inverted image
- \( m \) is − for an upright image

**For mirrors:**

- \( f \) is + for convex (diverging) mirrors
- \( f \) is − for concave (converging) mirrors
- \( s \) is + for object to left of \( H \)
- \( s \) is − for object to right of \( H \)
- \( s' \) is − for image to right of \( H' \)
- \( s' \) is + for image to left of \( H' \)
- \( m \) is + for an inverted image
- \( m \) is − for an upright image

When using the thin lens approximation, we can just refer to the left and right of the lens.

---

![Diagram of paraxial optical system showing front and rear focal points, principal points, object, image, lens, etc.](image)

*Note location of object and image relative to front and rear focal points.*

**Formulas:**

- \( \phi \) = Lens diameter
- \( m = \frac{s'}{s} = \frac{h'}{h} = \text{magnification or conjugate ratio, said to be infinite if either } s' \text{ or } s \text{ is infinite} \)
- \( \theta = \arcsin \left( \frac{f}{2s} \right) \)
- \( h = \text{object height} \)
- \( h' = \text{image height} \)
- \( s = \text{Object distance, positive for object (whether real or virtual) to the left of principal point } H \)
- \( s' = \text{Image distance } (s \text{ and } s' \text{ are collectively called conjugate distances, with object and image in conjugate planes, positive for image (whether real or virtual) to the right of the principal point } H') \)
- \( f = \text{Effective focal length (EFL), may be positive (as shown) or negative. } f \text{ represents both } FH \text{ and } H'F', \text{ assuming lens to be surrounded by medium of index 1.0} \)

---

Figure A1.1  Sign conventions
Typically, the first step in optical problem solving is to select system focal length based on constraints such as magnification or conjugate distances (object and image distance). The relationship between focal length, object position, and image position is given by:

\[
\frac{1}{f} = \frac{1}{s} + \frac{1}{s''}
\]

This formula is referenced to figure A1.1 and the sign convention on page A1.3.

By definition, magnification is the ratio of image size to object size or

\[
m = \frac{s''}{s} = \frac{h''}{h}
\]

Using this relationship, we can recast the first formula into the following forms:

\[
f = \frac{m}{m + 1} \left( s + s'' \right)
\]

where \( (s + s'') \) is the approximate object-to-image distance.

\[
f = \frac{sm}{m + 1}
\]

\[
\frac{1}{f} = \frac{1}{s} + \frac{1}{m}
\]

\[
s \ (m + 1) = s + s''
\]

Notice that a real lens of finite thickness, image distance, object distance, and focal length are all referenced to the principal points, not the physical center of the lens. By neglecting the distance between the lens’ principal points, known as the hiatus, \( s + s'' \) becomes the object to image distance. This simplification, called the thin lens approximation, can speed calculation when dealing with simple optical systems.

**Example 1 (refer to figure A1.2):**

A 1 mm high object is placed on the optical axis, 200 mm left of the left principal point of a 01 LDX 103 (50 mm fl). Where is the image formed, and what is the magnification?

\[
\frac{1}{s''} = \frac{1}{f} - \frac{1}{s}
\]

\[
\frac{1}{s''} = \frac{1}{50} - \frac{1}{200}
\]

\[
s'' = 66.7 \text{ mm}
\]

\[
m = \frac{s''}{s} = \frac{66.7}{200} = 0.33
\]

(or real image is 0.33 mm high and inverted)

**Example 2 (refer to figure A1.3):**

The same object is placed 30 mm left of the left principal point of the same lens. Where is the image formed, and what is the magnification?

\[
\frac{1}{s''} = \frac{1}{f} - \frac{1}{s}
\]

\[
\frac{1}{s''} = \frac{1}{50} - \frac{1}{30}
\]

\[
s'' = -75 \text{ mm}
\]

\[
m = \frac{s''}{s} = \frac{-75}{30} = -2.5
\]

(or virtual image is 2.5 mm high and upright)

In this case, the lens is being used as a magnifier, and the image could only be viewed back through the lens.

**Example 3 (refer to figure A1.4):**

A 1 mm high object is placed on the optical axis, 50 mm left of the first principal point of an 01 LDK 019 (50 mm fl). Where is the image formed, and what is the magnification?

\[
\frac{1}{s''} = \frac{1}{f} - \frac{1}{s}
\]

\[
\frac{1}{s''} = \frac{1}{-50} - \frac{1}{50}
\]

\[
s'' = -25 \text{ mm}
\]

\[
m = \frac{s''}{s} = \frac{-25}{50} = -0.5
\]

(or virtual image is 0.5 mm high and upright)
The gathering power of an optical system is critical, such as when focusing light into a monochromator or in high power projection optics. The other commonly used term to define this cone angle is numerical aperture (N.A.). Numerical aperture is the sine of the angle the marginal ray makes with the optical axis. Referring to figure A1.5 and using simple trigonometry, it can be seen that

\[ \text{N.A.} = \sin \theta = \frac{\phi}{2f} \]

or

\[ \text{N.A.} = \frac{1}{2f(\text{f-number})} \]

Ray f-numbers can also be defined for any arbitrary ray, knowing its conjugate distance, and the diameter at which it intersects the principal surface of the optical system.

NOTE

The sign convention given previously is not used universally in all optics texts, hence, the reader may notice differences in the paraxial formulas. However, results will be correct as long as a consistent set of formulas and sign conventions are used.
Spherical Concave Mirrors

Spherical concave mirrors are suitable for a variety of applications, including laser beam manipulation and imaging systems.

- These mirrors are polished to a high accuracy of $\lambda/10$ over 90% of the diameter.
- Protected aluminum is standard on these mirrors to ensure high reflectivity over a broad spectral range. Other coatings are available upon request.
- Paraxial conjugate distances can be calculated from the following formula:

$$\frac{1}{s} + \frac{1}{s'} = -\frac{2}{r}$$

**SPECIFICATIONS: SPHERICAL CONCAVE MIRRORS**

**Surface Accuracy:**

$\lambda/10$ at 546 nm over central 90% of diameter

**Diameter** ($\phi$): ± 0.5 mm

**Material:** LEBG

**Surface Quality:** 60–40 scratch and dig

**Coating:** Protected aluminum (001)

$R_{\text{avg}} \geq 87\%$ from 400–800 nm

---

### Spherical Concave Mirrors

<table>
<thead>
<tr>
<th>$r$ (m)</th>
<th>$\phi$ (mm)</th>
<th>$f=r/2$ (mm)</th>
<th>$t_s$ (mm)</th>
<th>$f/#$</th>
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**PRICE**

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<tr>
<td>183</td>
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<td>290</td>
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</table>

Supplied with a protected aluminum coating unless otherwise specified. To request a different coating, simply append the appropriate coating suffix (refer to chapter 1 for alternative options).

Note: We neglect the radius sign convention and publish absolute radius values.

---

### MIRROR COATINGS ON OTHER OPTICAL COMPONENTS

Most Melles Griot mirror coatings can be applied to standard optical components. Common examples include using plano-convex lenses to make secondary mirrors for Cassegrain beam expanders or telescopes. Coating cylindrical lenses for use as mirrors is a popular way of focusing energy through a slit aperture, or to spread the beam out in one axis. Windows are often coated to make second surface mirrors.
The Reflection of Light

REFLECTIONS AT UNCOATED SURFACES

Whenever light is incident on the boundary between two media, some light is reflected and some is transmitted (undergoing refraction) into the second medium. There are several physical laws which govern the direction, phase, and relative amplitude of the reflected light. For our purposes it is only necessary to consider polished optical surfaces. Diffuse reflections from rough surfaces are not considered.

The law of reflection states that the angle of incidence equals the angle of reflection. This is illustrated in figure A5.1 which shows reflection of a light ray at a simple air/glass interface. The incident and reflected rays make an equal angle with the axis perpendicular to the interface between the two media.

INTENSITY

At a simple interface between two dielectric materials, the amplitude of reflected light is a function of the ratio of refractive index of the two materials, polarization of the incident light, and angle of incidence.

When a beam of light is incident on a plane surface at normal incidence, the relative amplitude of the reflected light, as a proportion of the incident light, is given by

\[
\frac{(1 - p)}{(1 + p)}
\]

where \( p \) is the ratio of the refractive indices of the two materials \((n_1/n_2)\). Intensity is the square of this expression.

The amount of reflected light is therefore larger when the disparity between the two refractive indices is greater. For an air/glass interface with the glass having a refractive index of 1.5, the intensity of the reflected light will be 4% of the incident light. For an optical system containing 10 such surfaces, this shows that the transmitted beam will be attenuated to 66% of the incident beam from reflection losses alone.

INCIDENT ANGLE

The intensity of reflected and transmitted beams is also a function of the angle of incidence. Because of refraction effects, it is necessary to consider internal and external reflection separately at this point. External reflection is defined as reflection at an interface where the incident beam originates in the material of lower refractive index, i.e., air in the case of an air/glass or air/water interface. Internal reflection refers to the opposite case.

EXTERNAL REFLECTION AT A DIELECTRIC BOUNDARY

Fresnel’s laws of reflection precisely describe amplitude and phase relationships between reflected and incident light at a boundary between two dielectric media. It is convenient to think of incident radiation as the superposition of two plane-polarized beams, one with its electric field parallel to the plane of incidence (p-polarized) and the other with its electric field perpendicular to the plane of incidence (s-polarized). Fresnel’s laws can be...
summarized in the following two equations giving the reflectance of the s- and p-polarized components:

\[
\begin{align*}
    r_s &= \left( \frac{\sin(\theta_2 - \theta_1)}{\sin(\theta_2 + \theta_1)} \right)^2 \\
    r_p &= \left( \frac{\tan(\theta_2 - \theta_1)}{\tan(\theta_2 + \theta_1)} \right)^2
\end{align*}
\]

In the limit of normal incidence in air, Fresnel’s laws reduce to the following simple equation:

\[
r = \left( \frac{n - 1}{n + 1} \right)^2
\]

It can easily be seen that, for a refractive index of 1.52 (crown glass) this gives a reflectance of 4%. This important result shows that about 4% of all illumination incident normally on an air-glass surface will be reflected. In multi-element lens systems, reflection losses would be very high if antireflection coatings were not used.

The variation of reflectance with angle of incidence for both the s- and p-polarized components can be seen in figure A5.2. It can be seen that the reflectance remains close to 4% over about 30° incidence, and that it rises rapidly to 100% at grazing incidence. In addition, note that the p-component vanishes at 56°39’. This angle is called Brewster’s angle. It is the angle at which the reflected light is completely polarized as in figure A5.3. This situation occurs when the reflected and refracted rays are perpendicular to each other (§1 + §2 = 90°). This leads to the expression that Brewster’s angle, §1 = \arctan (n2/n1). Under these conditions electric dipole oscillations of the p-component would be along the direction of propagation, and could therefore not contribute to, the reflected ray. At the polarizing angle, reflectance of the s-component is about 15%.

FOR LIGHT INCIDENT FROM HIGHER TO LOWER REFRACTIVE INDEX MEDIUM we can apply the results of Fresnel’s laws in exactly the same way. The angle in the high index material at which polarization occurs is smaller by the ratio of the refractive indices in accordance with Snell’s law. The internal polarizing angle is 33°21’, for a refractive index of 1.52, corresponding to the Brewster angle (56°39’) in the external medium as in figure A5.4. The angle at which the emerging ray is at grazing incidence is called the critical angle as shown in figure A5.5. For an external medium of air or vacuum (n = 1), the critical angle is given by

\[
\theta_c(\lambda) = \arcsin \left( \frac{1}{n(\lambda)} \right)
\]

and depends on the refractive index n(λ), which is a function of wavelength. For all angles of incidence higher than the critical angle, total internal reflection occurs.

**INTERNAL REFLECTION AT A DIELECTRIC BOUNDARY**

For light incident from higher to lower refractive index medium we can apply the results of Fresnel’s laws in exactly the same way. The angle in the high index material at which polarization occurs is smaller by the ratio of the refractive indices in accordance with Snell’s law. The internal polarizing angle is 33°21’, for a refractive index of 1.52, corresponding to the Brewster angle (56°39’) in the external medium as in figure A5.4.

The angle at which the emerging refracted ray is at grazing incidence is called the critical angle as shown in figure A5.5. For an external medium of air or vacuum (n = 1), the critical angle is given by

\[
\theta_c(\lambda) = \arcsin \left( \frac{1}{n(\lambda)} \right)
\]

and depends on the refractive index n(λ), which is a function of wavelength. For all angles of incidence higher than the critical angle, total internal reflection occurs.
Right-angle prisms can be used to direct a beam of light at 90 degrees from the incident or retroreflect beam. A right-angle prism may also be used as a front surface mirror.

- High transmission can be achieved using the hypotenuse face in total internal reflection (TIR), with an antirefection coating on the entrance and exit faces.

- The prism can be used as an internal or external mirror by specifying a metallic coating on the hypotenuse.

Most coatings described in Chapter 1, Optical Coatings, may be applied to prism surfaces. The commonly specified antireflection coatings and high reflection coatings are listed here for your convenience. Please be sure to specify which surfaces to coat.

### Coatings for Right-Angle Prisms

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<th>Type</th>
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<tr>
<td>Internal Silver</td>
<td>/036</td>
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Please refer to Chapter 1, Optical Coatings, for additional coating options.

### APPLICATION NOTE

**Right Angle Prism as a Mirror**

Aluminized hypotenuse is coated with /011 protected aluminum and an overcoat of black paint which is acetone soluble for easy removal.

**APPLICATION NOTE**

**Right-Angle Prism as a Retroreflector**

An antireflection coating on the hypotenuse improves the efficiency of the prism as a retroreflector as long as acceptance angle limitations for TIR on the roof faces are not exceeded.
OPTICAL CONFIGURATION

The full NS-1 optical configuration is shown below. On the following pages is an alignment algorithm. It is not the only way to align the optics, but it does work.

When placing optical mounts on the table, always use TWO bolts to hold them in place securely.
The centers of all optics should be 20.7 cm above the table top.

Place the aperture on the table first. It should be 20.7 cm above the table top. Its position on the table is not crucial but make sure that there is room on the left for steering in the excitation beam.
Put the Arc Lamp and steering mirrors (M1, M2) in place.

The centers of all optics should be 20.7 cm above the table top.

M2 mirror should be about 15 cm from the aperture.

Adjust mirrors M1 and M2 so that the beam passing through the aperture is level (20.7 cm center height) with a propagation direction normal to the plane of the aperture.

Once M1 and M2 are aligned, focus the arc lamp to give the smallest and brightest image at the aperture (view the image using welder’s goggles).

Re-optimize M1 and M2.

Optical path length from arc lamp window to aperture should be 70-75 cm. Too long and the beam will underfill downstream optics; too short and the beam will overfill downstream optics.

M1 mirror should be far enough from lamp to ensure that beam does not overfill the optic (~40 cm). Keep the LAMP-M1-M2 angle as small as possible.
Put shutter and turning mirror M3 in place.

The centers of all optics should be 20.7 cm above the table top.

Place the probe shutter immediately after the 1-mm aperture. Next put M3 in place.

Distance from aperture to 25-mm φ mirror is about 15 cm. Beam should nearly fill the optic.
Put spherical concave mirror M4 in place.

The centers of all optics should be 20.7 cm above the table top.

Angle between incident and reflected beam should be as small as possible (≤ 5°). Reflected beam will just clear the 25-mm mirror mount.

Optical path length from the 1-mm aperture to the 50-cm ROC spherical concave mirror should be 50 cm. If this distance is correct, then the reflected image will appear 50 cm from the mirror and will be 1-mm Φ. If the distance from the mirror to the image is <50 cm, then the distance to the aperture is >50 cm. If the probe light drastically underfills the mirror, the distance from the lamp to the aperture is too long; if it overfills, the lamp to aperture distance is too short.
Put spherical concave mirror M5 in place.

The centers of all optics should be 20.7 cm above the table top.

M5 should be exactly 100 cm from M4 at a height of 20.7 cm. Center the beam on M5 by adjusting M4, then adjust M5 so that the reflected beam makes a small angle (≤ 5°) with the incident beam.
Put steering mirror M6 in place.

The centers of all optics should be 20.7 cm above the table top.

M6 should be about 30 cm away from M5. The beam should not overfill the optic. The beam from M4 to M5 should just miss the mount for M6 (minimize the M4-M5-M6 angle). Steer the reflected beam from M6 back and to the left at about a 45° angle to the M4-M5 line. A 1-mm round image should form about 20 cm from M6. The optical pathlength from M5 to this image should be 50 cm. If it is >50 cm, then the spot size will be >1 mm, suggesting that the M4-M5 distance is too short. If the M5-image distance is <50 cm, then the image will be <1 mm suggesting that the M4-M5 distance is too long; M5 might be overfilled.
Put the double monochromator in place.

The centers of all optics should be 20.7 cm above the table top.

Position the 1-mm entrance slit of the double 0.1-m monochromator at the 1-mm image formed by M6. Remove the top from the monochromator and adjust the angle of the DMC so that the image is centered on the first grating. **DO NOT EVER TOUCH A DIFFRACTION GRATING (they can only be ruined, never cleaned)!** If all of the optics have been kept at 20.7 cm height, then the image on the grating will be centered vertically when M6 is adjusted to steer the beam through the vertical center of the DMC entrance slit. Lock the DMC in place with table clamps. Fine tune the M5-DMC distance by adjusting the position of M6.
Put PMT and filters in place.

The centers of all optics should be 20.7 cm above the table top.

Mount the PMT housing onto the output port of the DMC. Clamp the PMT to the table. Wrap black electrical tape around the PMT housing flange to seal any light leaks.

Put the Short-Pass/Long-Pass filter wheels immediately in front of the DMC entrance slit. Adjust the angle so that the filters are perpendicular to the beam from M6. Place the Neutral Density filter wheel as close as possible to the SPF/LPF wheels. The NDF should be perpendicular to the incident beam.

SPF - short pass filter wheel
LPF - long pass filter wheel
NDF - neutral density filter wheel
Put excitation-beam irises, and beam dump in place.

The centers of all optics should be 20.7 cm above the table top.

Mount a HeNe laser on the table so that its path approximates the path of the excitation laser. Use a right-angle prism to steer the HeNe beam through the centers of the holes in M4 and M5. Place irises in front of M4 and M5 (as close as possible to the mirror mounts) and adjust their positions so that the beam passes through the center of each iris. The HeNe beam should overlap the probe beam at the image midway between M4 and M5.

Place a beam dump behind M4.

50-cm ROC Al mirror

SPF - short pass filter wheel
LPF - long pass filter wheel
NDF - neutral density filter wheel
Put excitation lens in place.

The centers of all optics should be 20.7 cm above the table top.

With the HeNe laser still in place, put a 75-cm focal length, plano-convex, fused silica lens about 10 cm to the left of M5. Adjust its height and lateral position so that the HeNe remains overlapped with the probe beam at the image midway between M4 and M5. The incident HeNe beam should strike the convex face of the lens; check for one collimated and one divergent back-reflection from this lens.

SPF - short pass filter wheel
LPF - long pass filter wheel
NDF - neutral density filter wheel
Put PD, pick-off, and shutter in place

The centers of all optics should be 20.7 cm above the table top.

With the HeNe laser still in place, put a shutter before the focusing lens. Place a fused-silica 5-cm square plate in the HeNe path and steer the reflected beam onto the face of the triggering diode. Lock the diode mount into place, then raise the diode so that the reflected HeNe strikes the diode housing below the diode.

SPF - short pass filter wheel
LPF - long pass filter wheel
NDF - neutral density filter wheel
Put shutter in place and steer in the pulsed excitation beam.

Remove the HeNe laser and lower the focusing lens, but do not remove its mount. Close both iris wheels. With the excitation laser power minimized, put a shutter in place at the edge of the table before the turning prism. Make sure that the shutter blocks the beam when closed and clears the beam when opened. Position the right-angle prism so that the excitation beam strikes the center of the input face. Block the back reflection from this prism with a beam dump on the excimer table. Adjust the position and angle of this prism so that the excitation beam goes through the holes in the centers of M4 and M5 (and their iris wheels).

SPF - short pass filter wheel
LPF - long pass filter wheel
NDF - neutral density filter wheel

The centers of all optics should be 20.7 cm above the table top.
Put sample and focusing lens in place.

Close the excitation shutter, open the iris in front of M4 and center the sample holder at the position of the image midway between M4 and M5; the center of the cuvette should be 50 cm from M4 AND 50 cm from M5. Close the iris in front of M4. Open the iris in front of M5 to 1-cm diameter. Open the excitation shutter and adjust the right-angle prism so that the excitation beam overlaps with the probe beam in the center of the cuvette holder. The beam should still be centered on the iris in front of M4. Put the focusing lens in place and adjust its height and lateral position to optimize pump-probe overlap in the center of the cuvette. The excitation beam should still be centered on the iris in front of M4.

Put a filled cuvette in the holder. Adjust the angle of the holder so that the back reflection from the cuvette face strikes the M5 or M6 mirror mount (not the mirror). The excitation beam should still be centered on the iris in front of M4. Close all shutters and open the irises.

The centers of all optics should be 20.7 cm above the table top.