

Appendix D

from

Silicon Microwire Photovoltaics

Thesis by
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Note

This appendix discusses the theory and operation of the integrating sphere spectrophotometer that was developed during the course of the author's PhD thesis work. It is intended to assist future users of the instrument or those developing similar instruments elsewhere. The author's own use of the spectrophotometer and discussions of the results are presented within the main chapters of the thesis.

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Spectrophotometer instrument

In this thesis work, the optical absorption of Si microwire arrays was characterized using a custom-built spectrophotometer instrument (see Chapter 3). Hemispherical reflection and transmission measurements were performed using an integrating sphere, and external quantum efficiency measurements were performed using a photoelectrochemical cell. This appendix provides details on the design and operation of the spectrophotometer instrumentation.

The spectrophotometer system consists of four basic components: A tunable light source, a motorized specimen stage, computer control software, and a light-detection system. All experiments share largely similar configurations for the light source, stage, and computer software; however, by changing the type or configuration of the light detection system, a variety of measurements are possible. The most commonly used light detection system consists of an integrating sphere with a photodiode, which can be configured for either *transmission mode* or *reflection mode* measurements. Alternatively, photovoltaic or photoconductive devices may themselves serve as the light detector—for example, using a photoelectrochemical cell to measure the external quantum efficiency (E.Q.E.) of a Si wire-array photocathode, thereby determining its optical absorption and charge-collection properties. For each measurement type, the computer software permits a variety of one- or two-dimensional parametric sweeps, including wavelength, incidence angle, and illumination position. The data acquisition software is written in LabVIEW (v.7, National Instruments), and can be easily extended to perform unforeseen types of measurements or parameter sweeps by those familiar with the programming environment.

Figure D.1 shows a simplified schematic of the spectrophotometer system configured for transmission-mode integrating sphere measurements. The diagram has not been drawn to scale, but does show the approximate position and size of the optical system components as viewed from above, and also shows the configuration of the electronic instrumentation located beneath the optics bench. The following sections discuss the components of the spectrophotometer system as they relate to each type of measurement. Step-by-step operating procedures are presented in section D.7.

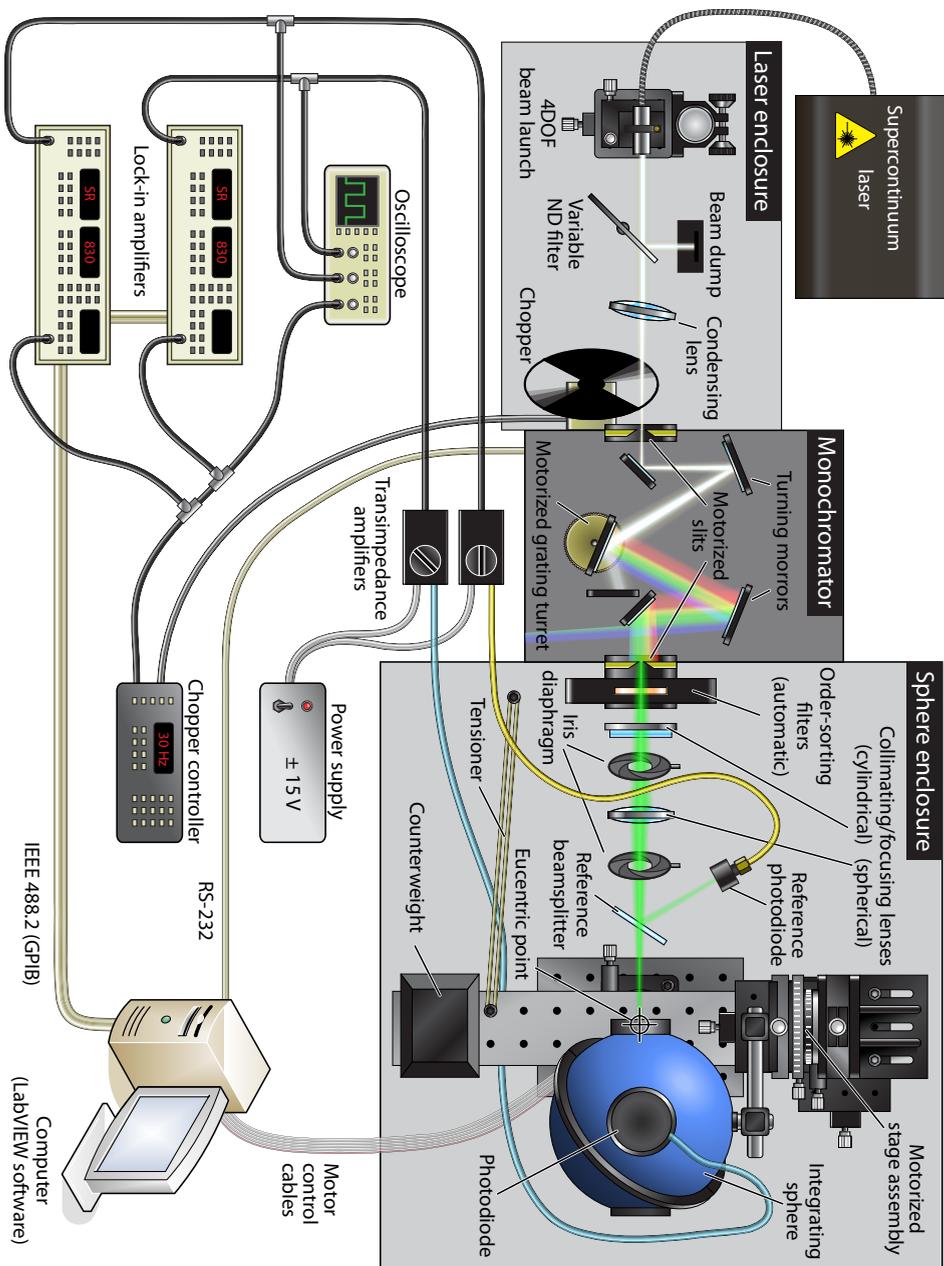


Figure D.1. Schematic illustration of spectrophotometer instrumentation.

D.1 Illumination source and optical path

Supercontinuum laser. A supercontinuum laser provides broadband (white) illumination in a highly collimated beam. For spectrophotometry, this enables a substantially greater combination of spectral, spatial, and angular resolution than possible using diffuse light sources (incandescent or arc lamps) of comparable power levels. Most measurements for this thesis were performed using a 2 W* “blue-enhanced” supercontinuum laser (Fianium SC400-2). This laser is rated to produce $>1 \text{ mW}\cdot\text{nm}^{-1}$ of spectral power density from $\lambda < 420 \text{ nm}$ to $\lambda > 2 \text{ }\mu\text{m}$, and in our system, can be used for measurements from $\lambda \sim 400 \text{ nm}$ to $\lambda \sim 1800 \text{ }\mu\text{m}$ (limited by detector sensitivity at longer wavelengths). A 4 W, “standard” spectrum laser (Fianium SC450-4) is also available for use, which provides slightly higher illumination power at most wavelengths, but whose useful spectral range does not extend below $\lambda \sim 450 \text{ nm}$. The increased power level might be useful for performing measurements with extreme spectral resolution; however in typical operation modes, the accuracy of measurements is not limited by a lack of source intensity. Either supercontinuum laser must be operated at full power to achieve the rated spectral range. The supercontinuum lasers can be connected to the computer via a serial port (over USB) for diagnostic purposes, but are generally operated manually.

Note: The supercontinuum lasers are damaged if light is allowed to reflected back into the source. For this reason, all optics in the source beam path are intentionally tilted slightly off-axis to prevent the specular beam reflection from re-entering the laser.

Laser enclosure. The high-power beam path is fully enclosed to prevent accidental exposure to (or disruption of) the supercontinuum laser source. The enclosure is only opened for initial beam alignment, or to attenuate the source brightness using a variable neutral-density (ND) filter wheel. The chopper wheel assembly is bolted to the input flange of the monochromator within the laser enclosure.

Monochromator. The supercontinuum laser source is coupled into a 1/4 m grating monochromator (Oriel MS257). The monochromator features motorized input/output slits, a 4-position motorized grating turret, and an automatic order-sorting filter assembly. The operation of this monochromator is controlled from the computer via RS-232 (serial port) communication. During measurements, the monochromator controller will automatically select the appropriate order-sorting filter for each wavelength. However, our spectrophotometry software does not explicitly instruct the monochromator to alter the grating or exit slit width settings. Users may manually select the appropriate grating and

*The power ratings reflect the continuous optical output power. Although we consider the illumination to be continuous here, the output from the supercontinuum lasers is in fact pulsed (20 MHz for the 2 W unit, 40 MHz for the 4 W unit).

Table D.1. Monochromator gratings.

Position	Line density (per mm)	Blaze wavelength (nm)	Max wavelength (nm)
1	150	800	11,200
2 ^a	1200	350	1400
3	1200	750	1400
4	600	1000	2800

^a Used in this work.

Table D.2. Monochromator passband values for symmetric entrance/exit slits.^a

Slit width (μm)	Passband ^b (nm)	
	1200-line grating	600-line grating
2000	6.5	12.9
1000	3.2	6.5
500	1.6	3.2
320	1.0 ^c	2.1
100 ^d	0.32	0.65
50 ^d	0.16	0.32

^a This assumes that the illumination source fills the entrance slit. In our system, the effective input slit width is actually the minimum of either the mechanical slit width or the width of the focused laser beam. The reported passband values are thus upper limits.

^b The passband varies slightly with wavelength. Peak values are shown.

^c Typical operating conditions.

^d With the present condenser lens, the beam cannot be focused to pass through such narrow entrance slit widths. Reflections from the beam striking either side of the slits could damage the laser source.

slit width before beginning measurements, or instruct the monochromator controller to automatically select the grating based on user-programmable crossover points. The monochromator can also be operated in “constant passband” mode, in which the controller modulates the slit width depending on wavelength. Our measurements typically use a fixed exit slit width of 320 μm and a 1200 line/mm grating, which provide a ~ 1 nm passband and excitation to $\lambda = 1400$ nm. The available gratings are listed in Table D.1, and typical system passband values are listed in Table D.2.

A lens focuses the laser source beam between the entrance slits of the monochromator, at an estimated focal ratio of F/30. This under-fills the monochromator’s

grating optics (F/3.9) but produces a less divergent beam at output. From a bandpass perspective, the size of the focused laser spot at the entrance port (estimated $< 300 \mu\text{m}$) serves as the effective entrance slit width. The physical input slits are kept slightly wider than the beam (typically fixed at $320 \mu\text{m}$) so that the laser beam can be easily focused without striking either side of the slit. This prevents reflection of light from the slit assembly, which could be destructive to the laser source or the eyes of an observer. Because of this potential hazard, the input slit motors are normally disabled (unplugged) to prevent inadvertent closure of the slits during alignment (or, for example, during system power-up routines).

Sphere enclosure. The illumination beam path and the motorized stage assembly are fully enclosed to prevent stray light from entering the light detection system. This was originally necessitated because measurements were performed at D.C. Measurements are now performed using chopped illumination with phase-sensitive detection, which rejects most stray light. However the system's light detectors are extremely sensitive, and typically saturate due to stray illumination at levels well below that of ambient room lighting.

Collimating/focusing optics. A series of lenses and apertures collimate and focus the monochromatic light beam to produce the desired spot size striking the specimen. The adjustable aperture diaphragms are mounted on micrometer-driven bases for precise positioning. With the diaphragms fully contracted, the two-lens configuration shown in Figure D.1 can produce a beam spot size of $\sim 1 \text{ mm}$, although other lens configurations can produce much smaller beam sizes at shorter working distance. For example, Figure D.2 shows a two-dimensional spatial transmission map performed using a $10\times$ microscope objective to focus the illumination to a $< 200 \mu\text{m}$ beam spot size at the entrance of the integrating sphere. Several polarizing filters are also available for insertion in the beam path near the exit of the monochromator. Explicit control of the polarization state is generally required for varied angle-of-incidence measurements (particularly for planar structures).

Reference detector. A reference photodiode continuously monitors the relative illumination intensity during measurements.* By normalizing the specimen response to the relative incidence intensity (see, e.g., equation D.1), the effects of virtually all fluctuations in source intensity can be eliminated. This greatly improves the accuracy of the spectrophotometer system, as the output spectrum of the supercontinuum source can potentially drift during the course of measurements (some of which can last several (>12) hours).

The reference detector assembly includes the beam splitter (microscope slide cover slip), the photodiode, and a baffle to prevent light reflected from the

*The *reference detector* should not be confused with *reference-position measurements*. The reference detector is used at all times—for both reference- and specimen-position measurements.

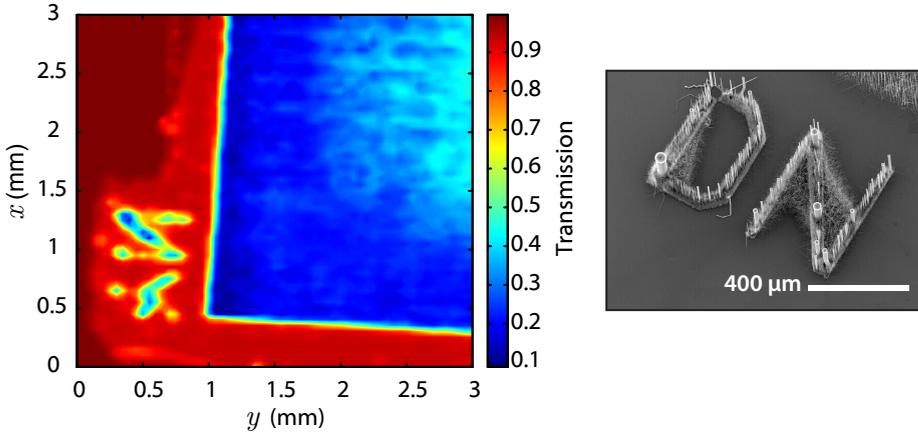


Figure D.2. Spatial transmission map of the edge of a Si wire-array film obtained using a $10\times$ microscope objective to focus $\lambda = 550$ nm illumination to a spot size of < 200 μm at the entrance of the integrating sphere. The wire array’s fiducial markings (“YN”) can be seen. Right: SEM image (45 tilt) showing the structure of similar fiducial markings on a *different* wire array (“DN”). (The actual fiducial markings on the “YN” array were not imaged by SEM.)

specimen from striking the detector. In order to minimize interference with the rotation of the specimen stage, the beam splitter and baffle are mounted on an adjustable arm protruding from the diode. Two interchangeable reference diodes are available: a 3.6×3.6 mm Si photodiode (Thorlabs SM05PD1A) for $\lambda = 400$ nm to 1150 nm, and a $\phi 3.0$ mm Ge photodiode (Thorlabs SM05PD6A) for $\lambda = 800$ nm to 1800 nm.

In this thesis work, reference-detector normalization eliminated all measurement artifacts due to varying source intensity except for a region of anomalous behavior near $\lambda = 1064$ nm, the wavelength of the supercontinuum lasers’ master source. Our approach was to “deglitch” the measured data by discarding measurements near $\lambda = 1064$ nm and interpolating the values from either edge of the anomalous behavior (typically ± 5 nm to ± 20 nm). The master source of the SC400-2 laser has recently been replaced, and preliminary measurements seem to indicate that the source of the artifact has been largely reduced.

The above components provide a referenced, monochromatic illumination beam for spectrophotometry measurements with a high degree of specular and spatial resolution. Figure D.3 plots the normalized reference photodiode signal observed during typical measurements performed in the course of this thesis. Our experience indicates that accurate measurements can be obtained when the signal levels are within ~ 60 dB of the peak value. The dynamic range of the system is presently limited by stray (broadband) light transmission through the monochromator (rather than the detection instrumentation).

For example, measurements performed at $\lambda < 400$ nm can produce seemingly stable readings from the photodiodes despite a lack of excitation energy at these wavelengths. This does not indicate that valid measurements can be obtained for these wavelengths—the system is simply measuring the stray light passing through the monochromator. Care must be taken not to attempt measurements beyond the spectral range of the source or detectors. Cleaning the monochromator optics by prove useful in extending the dynamic range of the system.

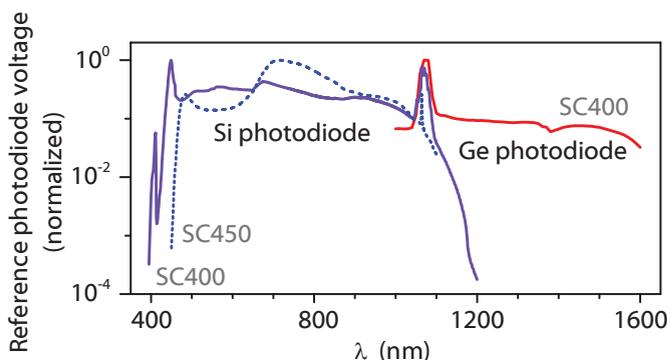


Figure D.3. Illumination spectra for spectrophotometry measurements. Spectra are plotted for both supercontinuum lasers and both reference photodiodes.

D.2 Specimen stage

The stage assembly enables specimen to be translated and tilted in two dimensions within the beam path. This requires four axes of kinematic articulation: a pair of rotation axes (Azimuth, Elevation) for specimen tilt, and a pair of linear translation axes (A_y , E_y) for specimen translation. Four additional axes of kinematic articulation are provided to align the system in a feasible manner. A pair of linear translation axes (A_d , E_h) permit each rotation axis to be aligned to the incident beam, and another pair of linear translation axes (A_x , E_x) permit the specimen to be aligned to the system eucentric plane. Table D.3 summarizes the type and purpose of each axes of the specimen stage. The specimen stage axes are illustrated in Figure D.4, as well as in the sections describing integrating sphere measurements (Figs. D.6 and D.7) and photoelectrochemical measurements (Fig. D.9).

Eucentric alignment is a key requirement for angle-resolved spectrophotometry measurements on small or nonhomogeneous specimen. Once eucentric alignment is reached, the specimen can be independently tilted and translated without affecting the beam focal length: tilting does not change the point of beam incidence on the specimen, while translation does not affect the beam incidence angle. In theory, the eight-axis stage configuration should be able to produce

Table D.3. Specimen stage axes.

Axis	Type	Operation (typ.)	Purpose
A_d	Linear	Manual ^a	Beam alignment ^b
E_h	Linear, 1''	Motorized	
A_x	Linear, 1''	Manual	Eucentric alignment
E_x ^c	Linear, 1/2''		
A_y (y) ^d	Linear, 1''	Motorized	Specimen translation
E_y (x) ^{c,d}	Linear, 1/2''	Manual ^e	
Azimuth (θ_y) ^d	Rotation	Motorized	Specimen tilt
Elevation (θ_x) ^d			

^a A_d is adjusted by sliding the entire stage assembly within guides at its base.

^b E_h is typically used instead of E_x for normal-incidence specimen translation due to the greater range and speed of the 1'' stage.

^c Not used for reflection mode.

^d Over the years, our convention of (θ_x, θ_y) and (x, y) has varied with respect to elevation and azimuth.

^e E_y is nominally motorized, but has been disconnected due to a lack of a functioning controller channel.

perfect eucentric alignment. In practice, system lash (free play) and misalignment will limit the degree to which true eucentric alignment can be reached. The primary mechanical culprit limiting tilt eucentricity is the shaft runout of the rotation axes. To reduce shaft runout, the azimuth axis is counterweighted to minimize the load imbalance over the rotation stage. Similarly, when the elevation rotation stage bears a heavier load (e.g., the integrating sphere assembly for transmission-mode measurements), a tensioning spring can be affixed to the sphere pivot point to alleviate the some or all of its weight. When maximal eucentric alignment is required (i.e., for the smallest specimen), some of the linear translation stages (E_x , E_y) can be removed, as each stage inevitably introduces mild hysteretic free play into the system. (Note, however, that alignment will be more difficult without these micrometer-driven translation stages.) With careful counterbalancing and specimen alignment, we have achieved two-dimensional eucentric positioning yielding < 2 mm of beam spot variation at the specimen, over the rotational limits of both tilt stages. Achieving one-dimensional eucentric alignment is generally much easier.

The resolution of the specimen stage is also limited by mechanical free play and hysteresis. Individually, each stage has relatively tight mechanical tolerance, but combined, the seven kinematic stages can lead to significant free play at the specimen. To mitigate lash, each rotational stage is tensioned with a rubber band during measurements. This yields $< 0.1^\circ$ of bi-directional repeatability in angular positioning. The linear translation stages are preloaded with internal

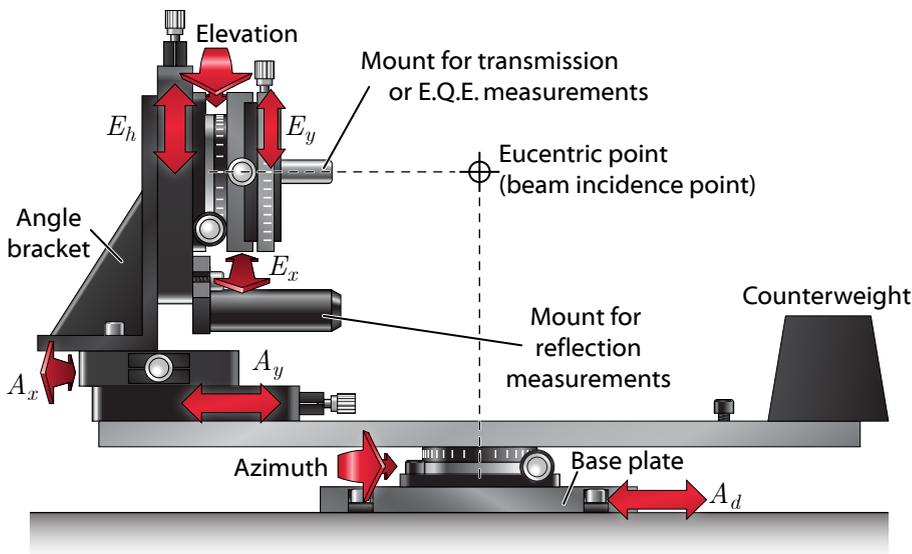


Figure D.4. Specimen stage (front view).

springs, and the more problematic axes have been outfitted with rubber-band tensioners to reduce out-of-plane lash. Hysteresis is largely mitigated by performing standard monotonic (vs. serpentine) rasters for two-dimensional scans. As shown in Figure D.2, we have achieved x - y positioning with apparent resolution of $<200\mu\text{m}$. In general, the lateral resolution of the system is limited by the size of the beam spot rather than the positioning accuracy of the specimen stage.

All rotation and linear translation stages are capable of motorized operation, depending on experimental requirements. The motorized axes are operated from the computer using an 8-channel PCI motor control card (DCX-PCI 100 Series Motion Controller, PMC). The rotation and $1/2''$ linear translation stages share interchangeable motors, as do all $1''$ linear translation stages. It appears that only four channels of the motor control card are operational following a recent failure of the computer's power supply. Manual micrometers can be installed in place of the motor-driven units on any of the $1''$ linear stages, and the worm-gear mechanisms of the rotation and $1/2''$ stages can be turned by hand using an appropriate hex key at the end of the shaft opposite the planetary gears.

D.3 Detection instrumentation

The following instrumentation is employed to perform spectrophotometry measurements. An overview of the equipment configuration is shown in Figure D.1.

Optical chopper. The optical chopper wheel is attached to the monochromator input slit assembly using a standard 1.5" flanged connection. The front panel of the chopper controller (Newport 75150) provides controls to adjust the chop speed. The "stop open" and "stop closed" buttons are particularly useful for alignment procedures, and can be used to temporarily block the beam without turning off the laser or opening the source enclosure. Measurements are typically performed at a chop frequency of $f = 30$ Hz. A two-aperture chopper wheel is used to minimize cyclic phase jitter.

Transimpedance amplifiers. A pair of transimpedance amplifiers (TIAs; DL Instruments Model 654) provide adjustable biasing (0 to -10 V) and gain (10^4 to 10^{10} Ω) for the reference and specimen photodetectors.* The amplifiers are powered by an external ± 15 V D.C. power supply.

The TIA gain is set using switches on the amplifier housing. Generally, measurements benefit from using the highest gain settings that provide adequate time response and avoid saturation of the lock-in amplifiers at the peak signal value.† In practice, the gain almost never needs to be adjusted, due to the fixed operating range of the instrument and high dynamic range of the lock-in amplifiers. Typical hemispherical reflection and transmission measurements (using Si photodiodes) are performed with gain settings of 10^5 Ω for the reference photodiode and 10^7 Ω for the integrating sphere photodiode. The gain might need to be adjusted if switching photodetectors (Ge vs. Si), substantially increasing or decreasing the illumination intensity, or if changing the detection configuration (e.g., for solid-state E.Q.E. measurements, in which the specimen-channel TIA can be connected to a photovoltaic or photoconductive device rather than the integrating-sphere photodiode).

Note: *The system is unaware of the TIA gain settings and does not correct for them. If the gain settings are changed between the specimen-position and reference-position measurements, the data will need to be manually corrected.*

The photodiode bias can be adjusted by turning a small potentiometer accessible through the side of the TIA housing. Reverse-biasing the photodiodes can improve their linearity, sensitivity, and speed; but also increases their dark noise. A bias is also required to measure the response of photoconductive devices. We generally obtain better system performance *without* reverse-biasing the photodiodes; thus, the bias is normally set to 0 V for both TIAs. However, users should check the bias before connecting the amplifiers to sensitive devices.

The bias voltage is applied to the *outer* conductor of the amplifiers' "current input" BNC connectors. For this reason, it is most convenient to measure the bias with a handheld multimeter, as most benchtop equipment measures the

*A potentiostat is used in place of the specimen-channel TIA for photoelectrochemical measurements.

†The input stage of the lock-in amplifiers will overload before the TIA amplifiers saturate.

voltage of the *inner* conductor while grounding the outer.* It is also important that the photodiodes do not form a chassis ground loop through the outer BNC conductor (common for laboratory equipment). Because the TIAs can only supply negative bias voltages, it is necessary to select the correct photodiode polarity to enable reverse-biasing. A small “coaxial polarity reverser” can be attached to the TIA input connector to reverse-bias some of the photodiodes.

Oscilloscope. An oscilloscope monitors the signals from the transimpedance amplifiers (or from the potentiostat for photoelectrochemical measurements). Observing the signal waveforms is generally only required for alignment or diagnostic purposes. Both detector channels should appear as nondistorted square waves on the oscilloscope display. Averaging is helpful to resolve weaker signals.

Lock-in amplifiers. A pair of digital lock-in amplifiers (LIAs; Stanford Research Systems SR830) measure the signals from the reference and specimen photodetectors. The operation of these instruments is similar to that described for SPCM measurements in Section C.2. Unlike the SPCM system, however, the spectrophotometer system interacts with the LIAs digitally, using the IEEE 488.2 bus (GPIB). This enables our spectrophotometry software to employ an adaptive algorithm (described below) to dynamically adjust the integration time and sensitivity range during measurements. This results in greater dynamic range and also alleviates the need to select a fixed sensitivity range for the LIA. For most measurements, the user need only select the desired time constant prior to beginning measurements—the other settings will be adjusted by the computer.† In this thesis work, most spectrophotometry measurements used second-order filtering with a time constant of 30 or 100 ms (in addition to synchronous filtering) on both LIAs.

LIA measurement algorithm. Although the computer communicates with the lock-in amplifiers digitally, the measurement resolution can still be limited by the sensitivity range of the LIAs. For example, using the 1 V sensitivity range, the LIAs do not report measurements with enough digits to resolve μV signal levels. Because the detector signals can vary over several orders of magnitude during wavelength sweeps, it is difficult to select a fixed sensitivity range for spectrophotometry measurements: choosing too low a sensitivity range will cause the LIAs to overload at “bright” wavelengths, while choosing too high a sensitivity range will produce inaccurate or noisy measurements for “dim” wavelengths. Thus, it is useful to dynamically alter the range of each LIA during measurement sequences.

Another dilemma facing lock-in measurements is the relatively long integrating time required to filter the D.C. output from the phase sensitive detector.

*If the impedance of the multimeter is not high enough, the TIA will saturate when it is connected to the input terminal. If so, the TIA gain should be temporarily reduced to prevent saturation when adjust the bias.

†The LIA’s input configuration and filters must also be set manually; however, these settings are not normally changed.

As a rule of thumb, a LIA require 5 time constants (per filter stage*) for the reading to settle to within 1% of its final value (from its *initial* value). However during spectrophotometric scans, there are many wavelength ranges where the signal values change only slightly between consecutive wavelengths. As an example, consider a transmission measurement where the signal values change by 2% between consecutive wavelengths. If 1% *absolute* accuracy is desired, the LIA reading need only settle to within 50% of its final value—which occurs in less than 1 time constant. Thus, by carefully monitoring the stability of the LIA output, it is possible to eliminate most of the integration (delay) time in “smooth” spectral regions, while still providing sufficient settling time in spectral regions where the signals vary greatly between consecutive data points.†

The above observations motivated our development of an adaptive measurement subroutine for the SR830 lock-in amplifiers. The algorithm is implemented in LabVIEW and is used by most of the spectrophotometer data acquisition programs, as well as in other instruments developed by this author. The subroutine begins by determining the LIA time constant setting, τ . When a measurement is requested, the LIA is polled every τ seconds until a minimum number of consecutive measurements (by default, 3) agree within a certain *settling threshold* (by default, 0.2%), in which case the average of the three values is returned. Measurements are repeated until suitable agreement is obtained, or by default, for up to 10 time constants per filter stage, after which the latter half of the readings are averaged to produce the result. The extended averaging time improves the accuracy of measurements for very weak signals, without slowing down the response speed for stronger signals.

During the measurement sequence, the program also adjusts the LIA sensitivity so that at least 10% (by default) of the full scale is utilized, ranging as low as 10 μV by default. The range is immediately increased whenever an overload condition occurs, discarding several subsequent readings before resuming the measurement procedure. If a continuous overload is registered on the maximum sensitivity range (1 V), a system error is issued (by default, halting the top-level program). To prevent range hunting, an overload-induced range-up operation will disable any subsequent range-down operations.‡ The subroutines are written to permit asynchronous (simultaneous) reading of both lock-in amplifiers. Using this algorithm, the typical duration of spectrophotometry measurements was halved with no noticeable loss of accuracy for several control specimen. In fact, the extended averaging helps reduce the noise in regions of weak signal intensity.

*Each low-pass filter stage provides 6 dB/oct roll off. Thus, selecting 12 dB/oct filtering utilizes 2 filter stages, and requires ~ 10 time constants to settle by this rule of thumb.

†A long integration time is also required in “smooth” regions if the signal is temporarily interrupted, e.g., when the order-sorting filter wheel is rotated between certain wavelengths, or following a LIA overload/uprange sequence.

‡If the overload-induced range-up operations place the instrument in a sensitivity range where the algorithm would normally range-down, a warning is issued, suggesting that the user either increase the dynamic reserve setting on the LIA, or increase the minimum permissible range for the auto-ranging algorithm. This condition does not affect the validity of measurements.

The LIA measurement settings typically require no user attention, as the default settings have thus far proven effective for all measurement types. This usually enables “hands-free” configuration of the detection instrumentation. However, users should be aware of the following:

- During measurements, it is normal for the LIAs to momentarily overload in the course of auto-ranging. This will not affect measurement accuracy.
- Selecting too short a time constant on the LIAs can actually *increase* the duration of measurements with this technique. The time constant must be chosen to yield a continuous output stability well within the settling threshold for the adaptive algorithm. If faster, less-accurate measurements are desired, the settling threshold should be increased appropriately. Optimal performance is obtained when the majority of measurements are resolved by quickly satisfying the settling criteria, rather than by extended averaging.
- Many of the spectrophotometry programs include a *delay time* setting (typically 100 ms). This is to ensure that the monochromator/stage motors have stopped moving prior to beginning the measurement subroutine. Users do not need to add lock-in settling delays to this value.

If needed, non-default settings for the adaptive algorithm can be specified within the LabVIEW data acquisition programs.

D.C. measurements. Measurements can also be performed under continuous (nonchopped) illumination by using a pair of D.C. current meters to monitor the photodetector signals. A version of the data acquisition software has been written to monitor the reference and specimen detectors with Keithley model 6430 and 487 current meters. D.C. measurements typically require longer integration times than those performed with chopped illumination and phase-sensitive detection.

D.4 Integrating sphere

Hemispherical transmission and reflection measurements are performed using a 4" integrating sphere that is affixed to the specimen stage to enable motorized tilt and translation. Figure D.5 depicts the internal sphere configuration for either type of measurement.

Sphere. The 4" integrating sphere has four ports: three 1" and one 1/2". All internal sphere components are coated to achieve near-ideal Lambertian reflectance. The sphere itself has been professionally recoated (Labsphere Spectrafect, 12/2009). The other (custom) parts have been sandblasted, cleaned, and coated with a BaSO₄ paint in our labs (Labsphere 6080 White Reflectance Coating).

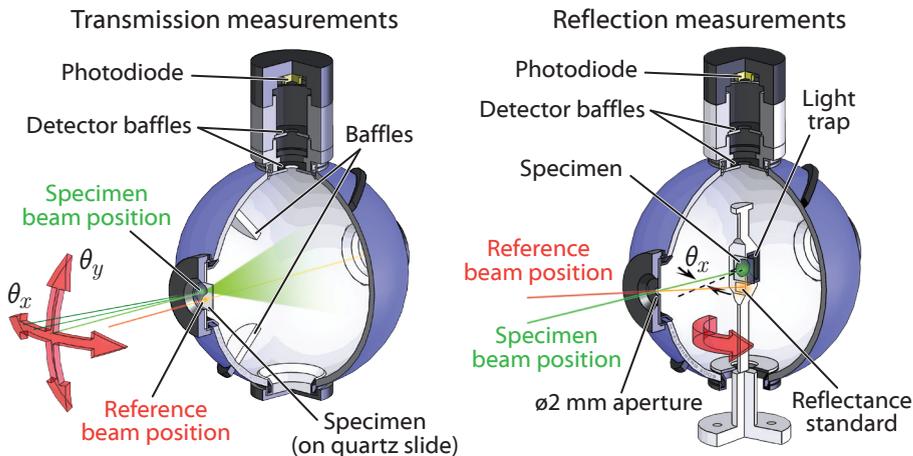


Figure D.5. Internal configuration of integrating sphere. Left: transmission measurements. Right: reflection measurements.

Baffles. The sphere originally included a single baffle that is attached with a screw through the side of the sphere. The second (lower) baffle for transmission measurements consists of a piece of sheet metal that is sandwiched between the sphere halves. Due to the frequent need to open the sphere when changing between transmission and reflection modes, we usually fasten the two halves together using binder clips rather than screws.

Photodiode assembly. The photodiode assembly consists of a photodiode and a series of adapters and baffles required to achieve the desired acceptance angle of light from within the sphere. Some of the custom-machined parts are depicted in section D.8.2. Two photodiodes are available for use with the integrating sphere: a 1 cm^2 Si diode (Newport 818-UV) for wavelengths up to $\sim 1170 \text{ nm}$, and a 0.071 cm^2 ($\phi 3.0 \text{ cm}$) Ge diode (Newport 818-IR) for wavelengths ranging from $\sim 800 \text{ nm}$ to $\sim 1800 \text{ nm}$. Both photodiodes mount to the photodiode assembly via $1''\text{-}40$ threads.

Note: The polarity of the 818-series integrating sphere photodiodes has been reversed to avoid a ground loop condition when biased using the transimpedance amplifier.

D.4.1 Transmission measurements

Figure D.6 depicts the configuration of the integrating sphere and specimen stage used to perform hemispherical transmission measurements. The sphere is attached to the E_y axis stage using a preassembled $1/2''$ post assembly identified as the “transmission mount.” Both baffles are installed for transmission measurements, and the photodiode is attached to the $1/2''$ port using the custom

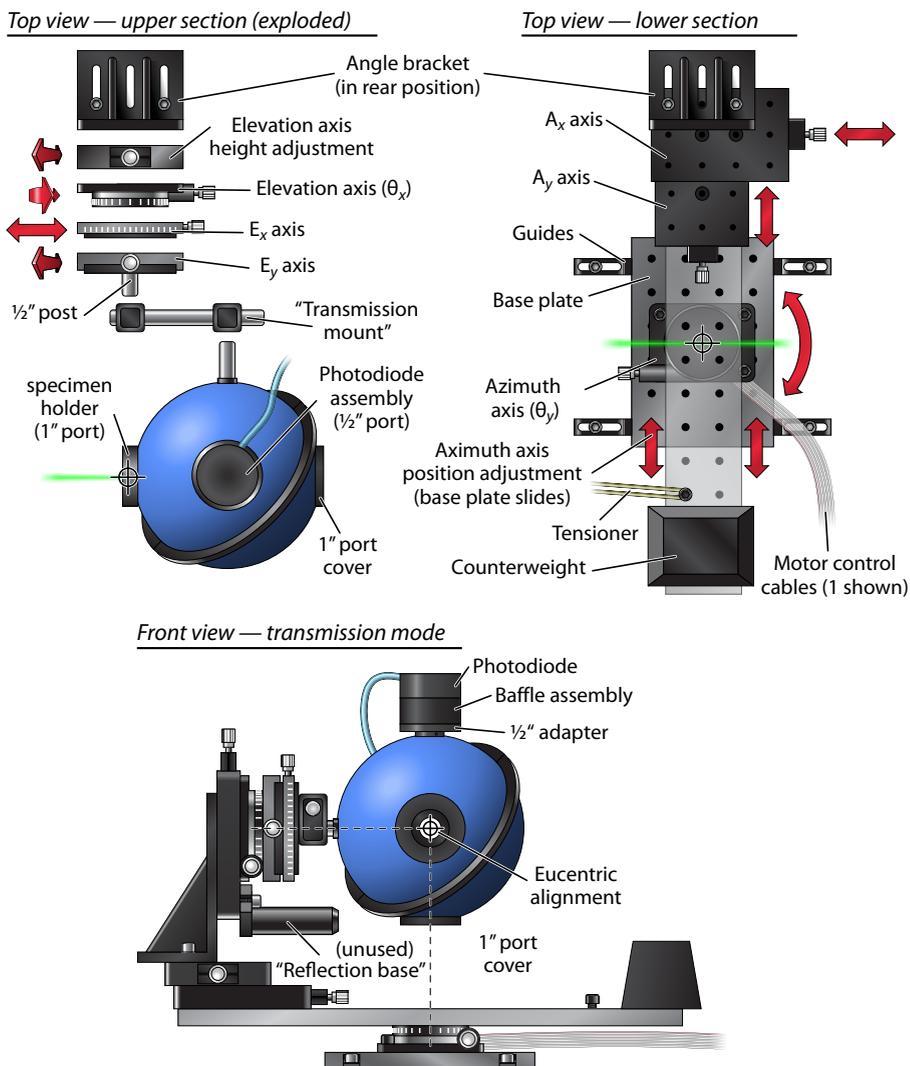


Figure D.6. Transmission-mode integrating sphere configuration.

“photodiode spacer” and “photodiode adapter” parts and the appropriate baffle inserts. The photodiode baffles restrict the acceptance of light to that from the sphere surface directly opposite the photodiode. The specimen is placed in a custom “specimen holder” at the 1” entrance port, and the remaining ports are covered.

During measurements, light that is transmitted into the integrating sphere produces a photocurrent from the sphere photodiode, I_{sph} . To determine the absolute transmission of a specimen, its I_{sph} signal is compared to that of a reference specimen of known transmittance, such as a quartz slide ($T_{\text{ref}} \approx 0.92$) or air ($T_{\text{ref}} = 1$). Both the specimen and reference readings are normalized to

the instantaneous reference photodiode current, I_{inc} . The absolute transmission can be calculated as:

$$T = \left(\frac{I_{\text{sph}}}{I_{\text{inc}}} \right)_{\text{Specimen position}} \cdot \left(\frac{I_{\text{inc}}}{I_{\text{sph}}} \right)_{\text{Reference position}} \cdot T_{\text{ref}} \quad (\text{D.1})$$

For multi-angle transmission scans, the reference position reading is typically only taken at normal incidence.

Because the sensitivity of the integrating sphere is affected by the presence and position of the specimen, the “tightness” of the hemispheres’ assembly, and other physical factors, it is imperative that the sphere configuration not be altered between the specimen and reference readings for accurate transmission measurements. For this reason, the specimen and reference measurements are usually performed under computer automation, using the motorized axes A_y and E_h to translate the sphere between the two positions without user interaction. The two measurement sequences are referred to as *specimen-position* and *reference-position* measurements. The spatial offsets between the specimen and reference beam positions are specified within the software prior to beginning the measurement sequence.

D.4.2 Reflection measurements

Figure D.7 depicts the configuration of the integrating sphere and specimen stage used to perform hemispherical reflection measurements. Unlike transmission measurements, the specimen can only be tilted in one direction (θ_x) during most reflection measurements. The E_x and E_y translation stages are removed, and the angle bracket is moved to the forward position. The sphere is mounted to the “reflection base” (protruding from the E_h axis stage) using a preassembled 1/2” post assembly identified as the “reflection mount.” Neither of the transmission-mode baffles are installed for reflection measurements. The photodiode is attached to a 1” port using the custom “photodiode spacer” (with appropriate baffle inserts) and a 1” adapter ring (Newport 819-DA). The photodiode baffles restrict the acceptance of light to that reflecting from the top surface of the reflection stage (which serves as the only baffle internal to the sphere).

A custom specimen stage holds the specimen at the eucentric point at the center of the sphere for reflection measurements. The reflection specimen stage is mounted directly to the elevation rotation stage, and enters the sphere through the 1/2” port. The specimen is placed over a light trap on the reflection stage: a hollow cavity coated with a diffuse nonreflective paint (Avian Technologies Black-S) that absorbs all transmitted light.* The specimen is typically affixed to the

*The light trap reduces the background reflection reading (i.e., the reading with no specimen loaded) from ~1%–2% to 0.2%–0.5%.

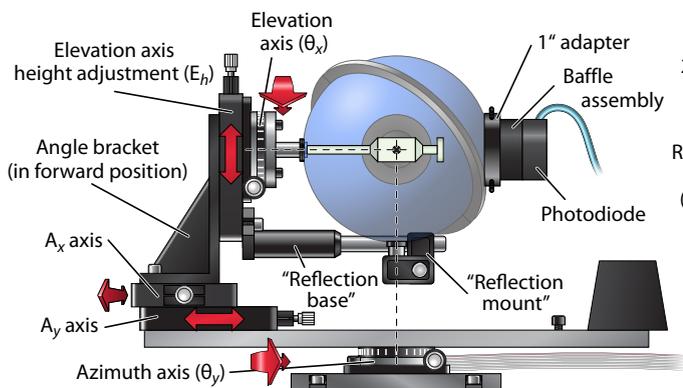
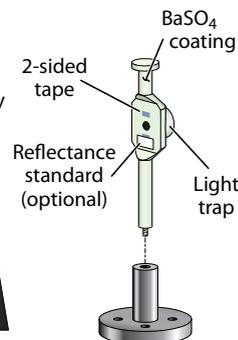
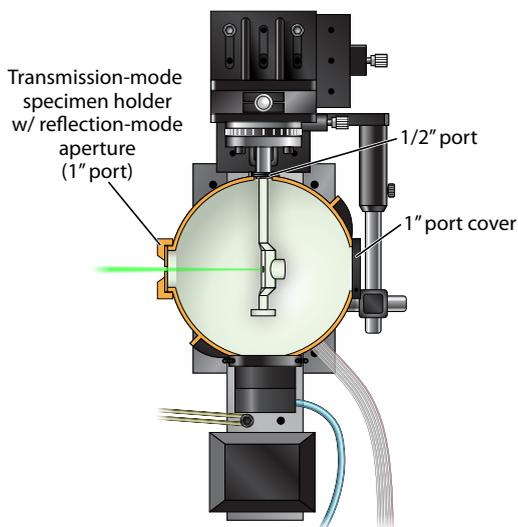
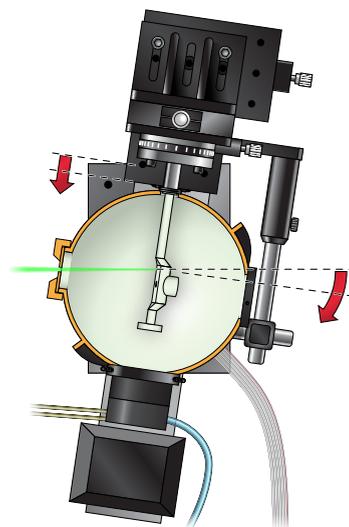
Front view — reflection modeSpecimen stageTop view (cut-away) — specimen positionTop view (cut-away) — reference position

Figure D.7. Reflection-mode integrating sphere configuration.

specimen stage using two-sided tape. Light is incident into the sphere through a $\varnothing 2$ mm aperture placed within the transmission-mode specimen holder. The use of a small-diameter incidence aperture ensures that nearly all reflected light is collected by the sphere. Typically, “normal-incidence” reflection measurements are performed at a slightly off-normal incidence angle ($\theta_y \geq 0.5^\circ$) so that the specular reflection does not exit the sphere through the illumination aperture. The remaining 1” sphere port is covered.

Reflection measurements are performed in a similar fashion to transmission measurements. The signal produced by illuminating the specimen is compared to that produced by illuminating a reference surface of known reflectance, R_{ref} . A small reflection standard (Labsphere) can be affixed to the stage adjacent to the specimen to provide a calibrated reference reading. In most cases, however, the exposed areas of the BaSO_4 -coated reflection stage can provide a reasonably accurate reflectance standard ($R_{\text{ref}} \sim 98\%$). Absolute reflection is calculated as:

$$R = \left(\frac{I_{\text{sph}}}{I_{\text{inc}}} \right)_{\text{Specimen position}} \cdot \left(\frac{I_{\text{inc}}}{I_{\text{sph}}} \right)_{\text{Reference position}} \cdot R_{\text{ref}} \quad (\text{D.2})$$

For multi-angle reflection scans, the reference-position reading is typically only taken at normal incidence. As with transmission measurements, the sequence of specimen- and reference-position reflection readings is performed under computer automation. The motorized azimuth and A_y axes pivot and translate the sphere to illuminate the reference area of the stage, as depicted in Figure D.7. The software must be configured with the correct values of rotation and translation to reach the reference position prior to beginning the measurement sequence. For ease of loading/unloading, the software will return the specimen stage to $\theta_x = 90^\circ$ (horizontal) following measurements.

Although we have not yet needed to perform two-dimensional (x - y) reflection maps, such measurements could be performed using the motorized E_h and A_y axes. The entrance aperture would need to be large enough to accommodate the scan area, requiring that the measurements be performed further from normal incidence in order to collect the specular reflection. A variety of entrance apertures (e.g., slits or dual holes) have been fabricated for different types of reflection-mode parameter sweeps.

D.4.3 Absorption measurements

Calculating absorption from reflection and transmission measurements, although conceptually simple, requires that the measurements be performed in a self-consistent manner in order to produce valid results. This requires that the same specimen area be illuminated in an identical fashion for both reflection and transmission measurements, and that together, the two measurements deterministically account for all non-absorbed light.

Spatial position and incidence angle. The beam should be aligned to strike the same specimen area for both reflection and transmission measurements. The specular reflection from the specimen or an underlying substrate can provide an easy reference point for aligning to normal incidence.

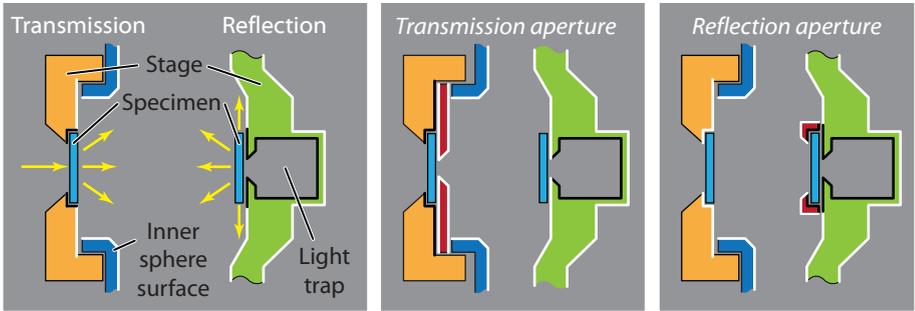


Figure D.8. Integrating sphere absorption measurement configurations. The heavy white and black lines indicate areas of reflective and nonreflective surface coatings, respectively.

Polarization state. For planar structures (particularly those with specular behavior) it is important that the specimen be tilted the same direction with respect to the polarization state of the illumination source. This requires either that the specimen be tilted using the same rotational axis (i.e., elevation) for both reflection and transmission measurements,^{*} or that the polarization state be explicitly controlled using a polarizer filter in the incident beam path. Rigorous absorption studies should independently characterize the specimen response under orthogonal polarization states. However, our experience indicated that Si wire arrays can be suitably characterized without controlling the beam polarization, by ensuring consistent array orientation and using the same tilt axis for both reflection and transmission measurements.

Specimen orientation. For structures with angularly anisotropic optical properties (such as ordered Si microwire arrays), it is also important that each specimen be tilted in a consistent direction with respect to its axis of angular anisotropy. Care should be taken to load each sample in the same orientation for all measurements. In this thesis work, specimen fiducial markings and reflected/transmitted diffraction patterns were used to align the lattice of each wire array to horizontal prior to measurements.

Collection geometry. For specimen with diffuse behavior, particular attention must be paid to the collection geometry. The reflection and transmission measurements must be designed with nominally identical specimen configurations such that combined, they account for all 4π sr of possible light emission directions. In other words, the surfaces surrounding the specimen should be virtually identical for transmission or reflection measurements, and each possible

^{*}The monochromator produces light whose polarization state varies greatly with wavelength (depending on the selected grating). However it can be assumed that, at each wavelength, the polarization state does not vary significantly between each sweep.

direction or light leaving the specimen should be counted as either reflection or transmission (but not both). Figure D.8 depicts three possible sets of collection geometries for diffuse specimen. The configuration on the left is required for highly scattering, nonabsorbing (i.e., ergodic) materials.* The Si microwire arrays of this thesis were only mildly diffuse over large areas, and were measured in a “transmission aperture” configuration. However, the aperture was larger than the specimen area, and served only to hold the quartz slide supporting the specimen in place without tape.

D.5 Photoelectrochemical cell

Photoelectrochemical measurements can be performed using the same illumination source and specimen articulation stage as integrating sphere measurements. The configuration of the system for photoelectrochemical measurements is shown in Figure D.9.

Cell. A ~100 mL rectangular cell was used for the measurements presented in this thesis. The cell was fabricated by Emily Warren, and featured a quartz sidewall and a loose-fitting lid with openings for three electrodes and a purge line. Other cells have also been used with the spectrophotometry equipment. Because of the tendency for the cells’ contents to leak or be spilled, they should be placed in a larger dish when filled with electrolyte.

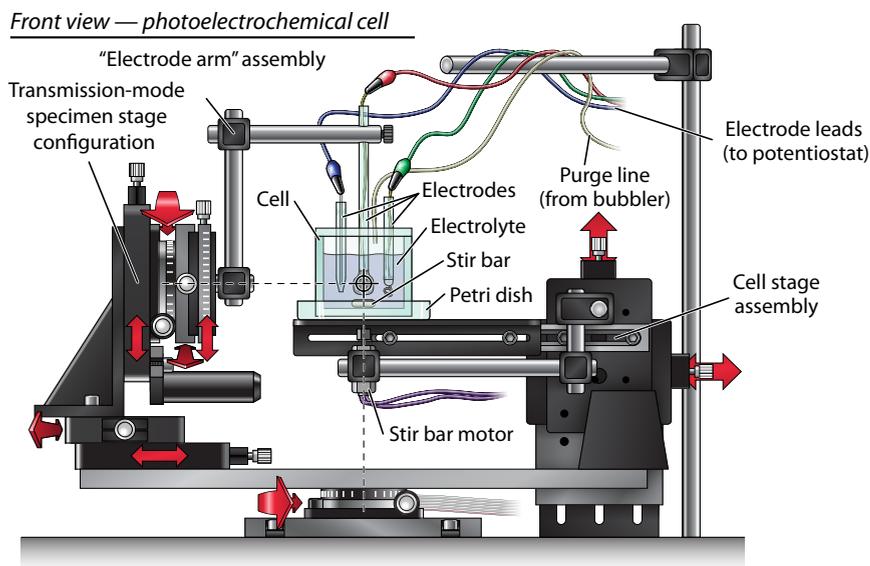


Figure D.9. Photoelectrochemical cell configuration: front view.

*For specimen whose size exceeds that of the light trap opening, this reflection geometry can be achieved by mounting the specimen on a piece of coated (black) sheet metal and placing it on the reflection stage (covering the light trap).

Cell stage. A platform can be pivoted into place above the motorized stage assembly to hold the cell at the correct location for eucentric articulation of the working electrode. Micrometer actuators are provided for adjusting the cell position and height.

Stirring. The cell is continuously stirred using a magnetic stir bar. A small D.C. motor with a magnet attached to its spindle is positioned beneath the cell platform. The motor is powered by a model railroad transformer.

Purging. To prevent oxygen from permeating the electrolyte solution, the cell can be continuously purged with house nitrogen or a bottled gas source (e.g., Ar). The nitrogen line has been plumbed to a regulator next to the sphere enclosure. The purge gas is passed through a bubbler (filled with H₂O for the methyl viologen cell) to prevent evaporation of the electrolyte solution.

Potentiostat. A potentiostat (Gamry Reference 600) is used to bias the cell and amplify the electrode photocurrent signal. The potentiostat is operated from the computer (via a USB connection) using manufacturer-supplied software, which permits a variety of sweep and biasing options. For spectrophotometry measurements, the potentiostat is operated in a continuous (D.C.) bias mode. Its analog output channel (± 3 V full scale) is connected to the input channel of the specimen lock-in amplifier (in place of the TIA). The potentiostat should be operated at the lowest fixed current range that does not cause it to overload (or saturate the LIA) at the peak signal value. The spectrophotometry software is unaware of the bias configuration or the current range of the potentiometer; thus, identical current ranges should be used for specimen (electrode) and reference (photodiode) measurements (or, the measurements must be manually corrected to account for different range settings).

Calibrated photodiode. In order to determine the E.Q.E. of the electrode, a photodetector of known E.Q.E. ($E.Q.E._{ref}$) is positioned in its place within the cell, and its response is measured to calibrate the amount of light striking the electrode at each wavelength.* For this thesis work, Emily Warren prepared an encapsulated, calibrated 3.6×3.6 mm Si photodiode (Thorlabs FDS100-CAL) matching the form factor of our wire-array electrodes, enabling it to be mounted and positioned within the cell using the same electrode holder. We typically used the potentiostat in a two-probe configuration to bias and amplify the response of the calibrated photodiode, although the specimen-channel TIA could also be used for this purpose.

*Note that the *calibrated* photodiode (used as the reference for absolute E.Q.E. measurements) should not be confused with the *reference* photodiode (used to monitor the relative source intensity for all measurements).

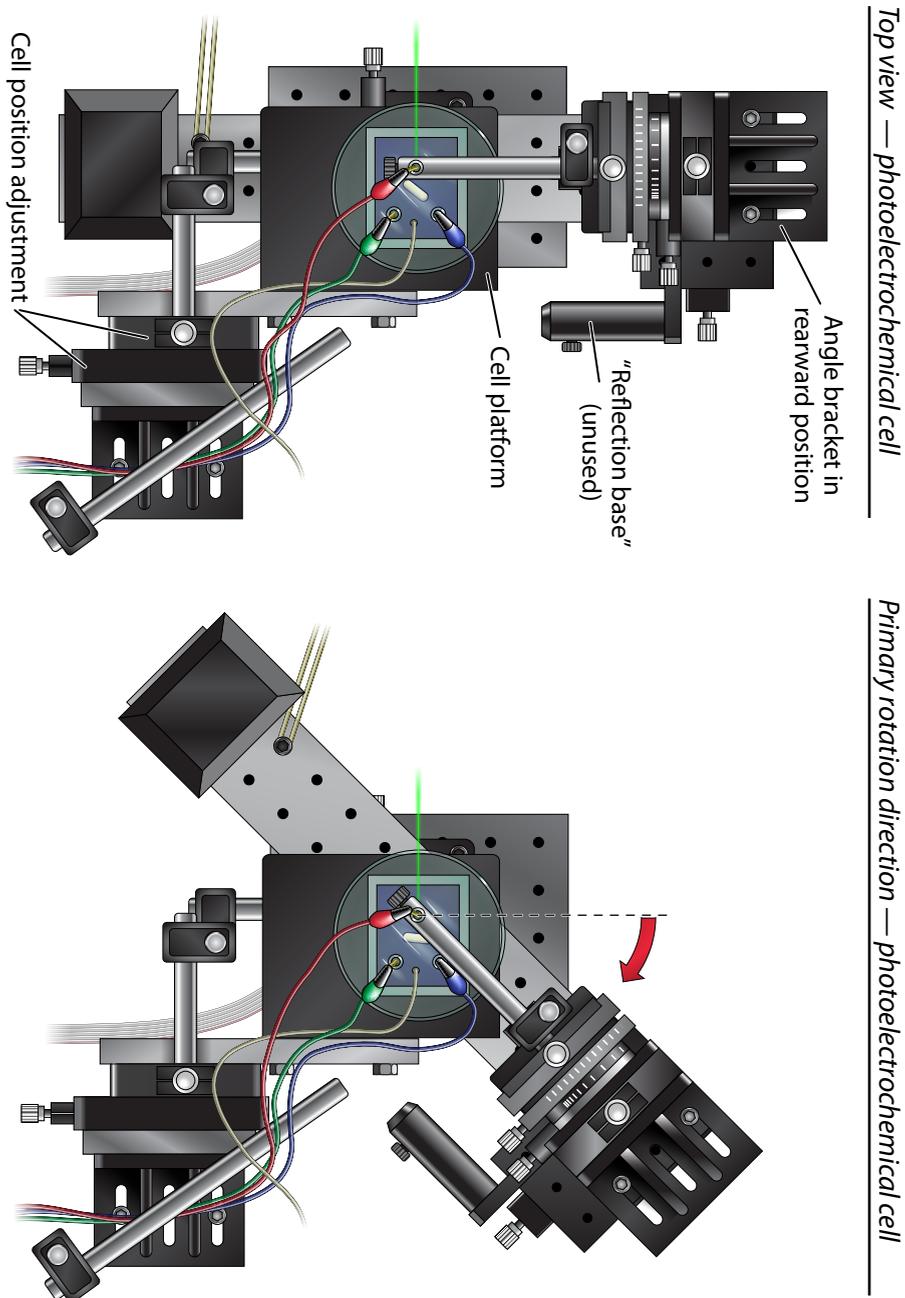


Figure D.10. Photoelectrochemical cell configuration: top view.

D.5.1 E.Q.E. measurements

Using the calibrated photodiode, the E.Q.E. of an electrode can be determined in a similar fashion as reflection and transmission measurements:

$$E.Q.E.(\lambda) = \left(\frac{i_{\text{spec}}}{I_{\text{inc}}} \right)_{\text{Unknown electrode}} \cdot \left(\frac{I_{\text{inc}}}{i_{\text{spec}}} \right)_{\text{Calibrated photodiode}} \cdot E.Q.E._{\text{ref}}(\lambda) \quad (\text{D.3})$$

In the above equation, the wavelength dependence of $E.Q.E._{\text{ref}}$ has been emphasized. Whereas we typically assume constant values for transmission and reflection references, E.Q.E. measurements must usually be normalized on a wavelength-by-wavelength basis using the photodiode calibration data.

D.5.2 Calibration issues

For photoelectrochemical E.Q.E. measurements, most electrolyte solutions are partially absorbing at some wavelengths. Thus, it is critical that the reference photodiode be placed at the exact same position within the cell as the electrode is measured (i.e., the eucentric point). Any positioning errors will alter the path length of the beam in the electrolyte, resulting in a disproportionate attenuation of the light reaching the calibrated photodiode vs. the specimen electrode, and will thus produce erroneous E.Q.E. measurements. Conveniently, the eucentric alignment procedure used to position the electrode prior to measurements can also be used to align the photodiode (in our experience, to within ~ 1 mm of the electrode position). However, E.Q.E. measurements will become increasingly difficult (if not impossible) if the electrolyte absorption is too high—e.g., having an absorption length of a few millimeters or less. Not only does this require positioning repeatability beyond the present alignment capabilities, but ultimately, if too little light reaches the specimen, the measurements will be dominated by noise or stray light at nonattenuated wavelengths. Furthermore, for structures like Si wire arrays, strong parasitic electrolyte absorption will actually change the optical properties of the device: light that would normally be scattered from one wire to another before being absorbed therein might instead be absorbed in the electrolyte between the wires.

For the above reasons, one should generally characterize the absorption of the electrolyte solution to confirm the feasibility of accurate E.Q.E. measurements. This is easily accomplished by measuring the response of the calibrated photodiode positioned within the cell, then removing the cell (or at least emptying it) and remeasuring the response.* The difference between these measurements reveals how much of the light incident on the cell actually reaches the electrode. The result of characterizing our methyl viologen cell in this fashion is shown in

*Logistically, it is easier to perform the latter measurement first, i.e., before the cell is installed or initially filled with electrolyte.

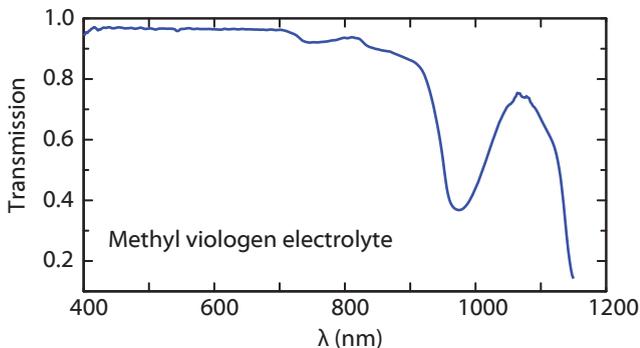


Figure D.11. Opacity of photoelectrochemical cell with methyl viologen electrolyte. Transmission was determined by comparing the light striking a photodiode immersed in the cell to that striking the same photodiode after the cell was removed from the beam path. The $\sim 96\%$ transmission plateau indicates the insertion loss (i.e., front-surface reflectance) of the cell, while the regions of lower transmission indicate absorption by the electrolyte solution. The illumination beam traversed ~ 1 cm of solution before striking the photodiode.

Figure D.11. Although as little as $\sim 40\%$ of the incident beam reached the electrode at some wavelengths (traveling through ~ 1 cm of electrolyte), the ~ 1 mm positioning reproducibility still enabled reasonably accurate E.Q.E. measurements.

Ultimately, one should be able to measure the response of the photodiode positioned in the cell, remove it for electrode measurements, then reinstall/reposition it and obtain the original response spectra within reasonable experimental error. Any deviation will indicate that the electrolyte is too opaque for accurate E.Q.E. measurements, in which case it may be necessary to dilute the electrolyte or otherwise alter the cell configuration.

The shape, encapsulation, and calibration conditions of the photodiode must be considered when using it to normalize photoelectrochemical E.Q.E. measurements. For example, the calibrated photodiode used in this thesis work was furnished in a metal can package (TO-39 type), in which the Si diode is recessed ~ 1.5 mm beneath a transparent front window. It is tempting to position the surface of the Si diode at the system eucentric point for calibration. However, this positioning would reduce the beam path in the electrolyte by 1.5 mm compared to that for electrode measurements, and would thus lead to erroneous E.Q.E. measurements at wavelengths of electrolyte opacity. Furthermore, our visual alignment procedure would prove inaccurate for bringing the Si diode surface to the system eucentric point, due to the refraction of the beam at its front window. Thus, the photodiode should be positioned with the *front window* of the package, rather than the diode surface, aligned to the system eucentric point.

An additional subtlety arises because most photodetectors are calibrated for operation in free space (air), whereas our photodiode is immersed in the



Figure D.12. Photoelectrochemical cell configuration, set up by Elizabeth Santori for characterizing n-type Si wire-array electrodes.

electrolyte solution to provide E.Q.E. reference measurements. Immersion in a liquid will generally change a detector's E.Q.E. For example, the reflectivity of bare Si is reduced by several percent when immersed in water (see Figure 3.2). Thus, the photodiode used for E.Q.E. reference measurements must be either calibrated for immersion in the electrolyte solution, or its free-space calibration data must be corrected to account for the effects of immersion. The correction factor can be measured, or calculated based on knowledge of the diode structure: for example, a diode packaged behind a glass window will exhibit $\sim 3.7\%$ higher E.Q.E. (relative to light striking the window) when immersed in H_2O , due to the decreased front-surface reflectance of the window.

D.5.3 Mass transport issues

Photoelectrochemical measurements can produce erroneous E.Q.E. values if the cell suffers from mass transport issues or other problems related to the electrolyte chemistry. When operating properly, the E.Q.E. readings for typical electrodes should exhibit no dependence on illumination intensity,* chop rate, or stir rate. This behavior should be confirmed prior to beginning measurements. If mass transport issues are identified, they can potentially be resolved by operating at reduced light levels, defocussing the beam, or by changing the cell configuration.

*The neutral density filter wheel in the source enclosure is the preferred means of attenuating the light intensity. Adjusting the supercontinuum laser power setting will reduce the usable wavelengths, while changing the monochromator slits or aperture diaphragms will change the bandwidth and spot size of the beam.

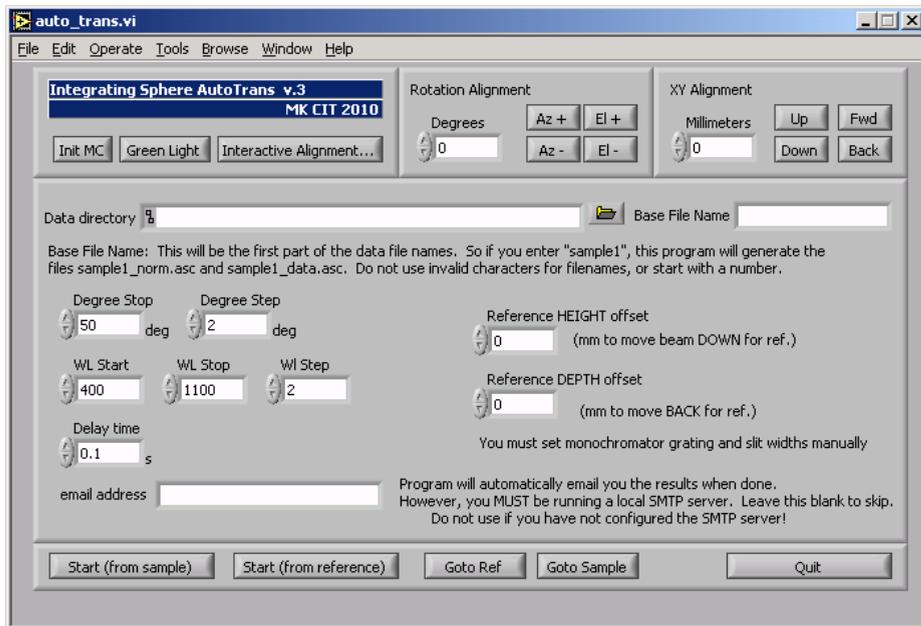


Figure D.13. Screenshot of transmission-mode software.

D.6 Computer software

D.6.1 Data acquisition software

The computer software for performing spectrophotometry measurements is written in LabVIEW (version 7). Each software module or subroutine is known as a *virtual instrument* (VI). Many of the original low-level instrument driver VIs were written by Robb Walters, and some of the spectrophotometry software was written by Jan Petykiewicz.

A screenshot of one of the program modules, `auto_trans` is shown in Figure D.13. This and similar top-level event-driven programs are used to perform most spectrophotometry measurements. They feature controls to align the instrument and configure parameter scans, and will automatically sequence the specimen and reference readings without user interaction (if possible). Each program can also email the results to a user upon completing the experiment (note that this requires a local SMTP server). The following top-level programs are available for measurements:

- `auto_trans` (transmission-mode λ - θ sweeps)
Example: Figure 3.8.
- `auto_refl` (reflection-mode λ - θ sweeps)
Example: Figure 3.8.

- `auto_pecsr` (photoelectrochemical cell λ - θ sweeps)
Example: Figure 3.31.
- `auto_angle` (transmission-mode or PEC θ_x - θ_y sweeps)
Example: Figure 3.32, Figure 3.18.
- `auto_xy` (transmission-mode or PEC x - y sweeps)
Example: Figure 3.30, Figure D.2.

All top-level program modules rely on the same set of subroutines wherever possible. Thus, each generally differs only in which axes are driven and how reference-position measurements are taken.

D.6.2 Alignment utilities

Several alignment tools are available both within and outside of the spectrophotometry software. Within the software, the *green light* button will bring the monochromator back to a visible wavelength for alignment ($\lambda = 550$ nm). The *interactive alignment* button opens a modal dialog window that monitors keystrokes, enabling the motors to be adjusted using the computer's keyboard. There are also several absolute translation/rotation motor controls, which are used to determine the exact distance the integrating sphere should travel between reference and specimen positions.

Outside of the spectrophotometry software modules, a number of VIs are available to control the monochromator, including a serial-port communication terminal (`mono_term`) for manually issuing monochromator commands. To avoid resource conflicts, it is important that operators use this program (as opposed to non-LabVIEW programs such as HyperTerminal) to communicate with the monochromator, especially if other experiments (e.g., photoluminescence) are running concurrently. Another useful monochromator control program is `mono_back_and_forth`, which simply scans the monochromator output across the visible spectrum in an oscillatory manner (from $\lambda = 460$ nm to 650 nm to avoid filter changes). Not only is this useful for beam alignment procedures, but more importantly, it makes for more interesting equipment demonstrations for lab visitors.

D.6.3 Data processing software

The LabVIEW data acquisition programs generate simple text-based output files containing raw experimental data, but do not contain functionality to process or plot this data. Included with this thesis is a simple MATLAB script for loading, normalizing, and plotting most types of measurements. It was written to provide a useful data plotting environment for those unfamiliar with MATLAB, and can be used for most spectrophotometry measurements without modification of the script. The source code is listed at the end of this appendix (section D.8.1), and can be easily copied from the electronic version of this thesis.

Measurement sequences are stored in four-column, tab-delimited text files containing raw measurement data. The first data column records the outer sweep variable (typically θ_x), and the second column records the inner sweep variable (typically λ). The third and fourth columns store the measured signal values for the specimen and source detectors, respectively.*

The files are given a name consisting of a *base file name* (a descriptor specified by the user within the data acquisition program), a measurement identifier (appended automatically by the software), and the extension `.asc` (chosen for ease of associating the files with, e.g., Excel or MATLAB). The MATLAB script parses the file names (and measurement range) to determine how to normalize and plot the data, as well as what to name the imported data within the MATLAB workspace. As an example, the file `wa45_ref1_norm.asc` contains the normalization data for a reflection measurement performed on a sample named `wa45`.

Each measurement sequence generates two files: a specimen data file and a normalization data file, recorded with the instrument in specimen and reference positions, respectively. From this, R , T , or E.Q.E. can be calculated from equations (D.1), (D.2), or (D.3), respectively. Most spectrophotometry measurements produce both files in the course of a single automated sequence, whereas the data files for most E.Q.E. measurements must be recorded in two separate sequences (as the calibrated photodiode must be manually positioned in place of the specimen to obtain the normalization data). Thus, in the `auto_pecsr` or other E.Q.E. acquisition programs, the user must manually specify the measurement identifier (`_data` or `_norm`) in the file name.

The data processing script includes options to normalize, crop, smooth, and “deglitch” measurement data using a quasi-GUI interface, as illustrated in Figures D.14 and D.15. The operating procedures are as follows:

1. Execute the script in MATLAB.
2. Select both files (specimen and normalization data) in the file selection dialog. The normalization data file should include the phrase “**norm**” in its file name to be recognized by the script. The script will parse the files and file names to guess the initial plot/import parameters.

Note: Both files are selected at the same time by holding the  key in the file selection dialog box.

3. Change the plot/import parameters as desired.

An important program option is the *normalization type* keyword. This determines the reference value to use in normalizing the data (e.g., T_{ref} in equation D.1). The normalization keywords (as-supplied) are listed in Table D.4. The default normalization options are wavelength-independent, which is reasonable for the listed types of measurement normalizations. In order to normalize E.Q.E. to

*The software records the raw readings (CH1 R) from the lock-in amplifiers. The values are not corrected for detector sensitivity, amplifier gain, etc. . .

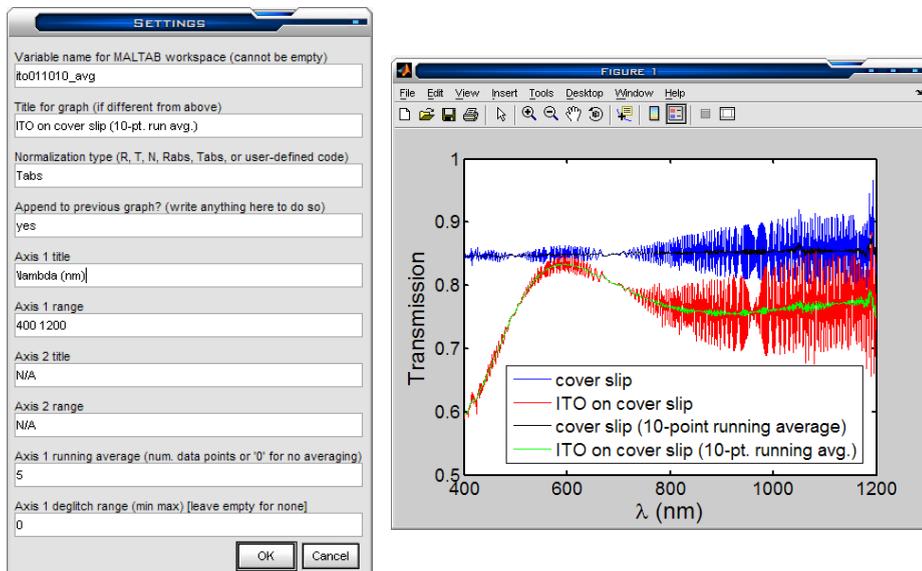


Figure D.14. Use of data processing software utility for one-dimensional sweeps. The plot shown on the right was produced by running the script four times (once per data set). The screenshot (left) depicts the settings used to append the fourth data set to the plot. A 10-point running average was used to suppress the interference fringes observed in the transmission of a microscope cover slip.

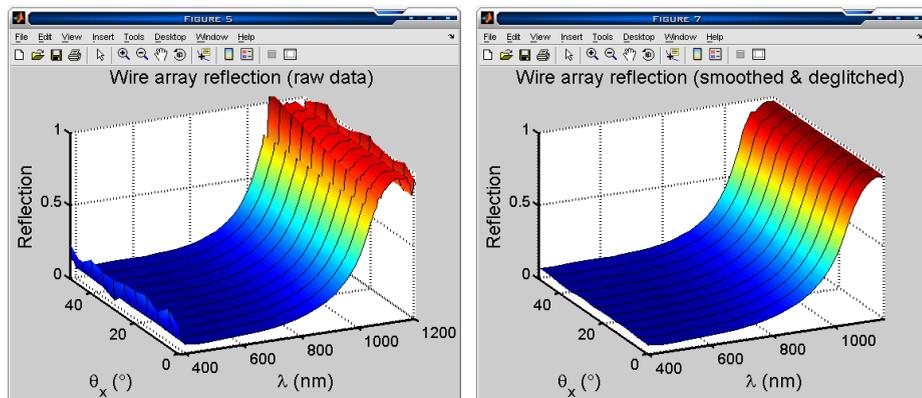


Figure D.15. Use of data processing software utility for two-dimensional sweeps. The plot on the left (raw data) exhibits artifacts due to the $\lambda = 1064$ nm excitation peak as well as measurements taken beyond the usable spectral range of the excitation and detection instrumentation ($\lambda = 380$ – 1200 nm). The plot on the right was obtained by truncating (*Axis 1 range*: 400 1160), deglitching (*Axis 1 deglitch range*: 1055 1080), and smoothing (*Axis 1 running average*: 1) the data using the data processing script.

Table D.4. Default normalization modes of data processing script.

Keyword	Reference value	Graph labeling
T	0.92 (glass slide)	Transmission
Tabs	1.0 (air)	Transmission
R	0.98 (BaSO ₄)	Reflection
Rabs	1.0 (ideal reflector)	Reflection
N	<i>varies</i> ^a	Normalized (A.U.)
EQE	<i>user-defined</i> ^b	E.Q.E.

^a Normalizes result to peak value of 1.0.

^b User must specify $E.Q.E._{ref}(\lambda)$ values within the script.

that of a calibrated photodiode, however, one must modify the script to calculate the value of $E.Q.E._{ref}$ at each wavelength (see comments in source code).

Once the data processing script has been used to plot and import the data into the MATLAB environment, further processing becomes straightforward. For example, after processing the reflection and transmission data for the data set *wa45*, one will find the following variables in the MATLAB workspace:

```
wa45_WL      wa45_Theta      wa45_R      wa45_T
```

One can then calculate and plot absorption as:

```
wa45_A = 1 - wa45_R - wa45_T;
mesh(wa45_Theta, wa45_WL, wa45_A);
```

D.7 Operating procedures

The following procedures are used to align the system and perform basic spectrophotometry measurements.

D.7.1 Laser operation guidelines

The Fianium supercontinuum lasers provide a useful illumination source for spectrophotometry measurements, but have proven to be extraordinarily fragile in operation in our labs. To prevent unnecessary damage to these lasers, and to avoid the downtime and high cost associated with their repair, users should abide by the following guidelines (in addition to standard laser safety protocol):

General handling

- Treat the laser carefully and avoid excessive shock when transporting.
- Always cover the end of the fiber to protect the collimating optics from dust or scratches.
- Do not discard the laser packing materials. They are required to return the unit for repair.

Power-on

1. Before plugging in the laser, verify that the master source and gain stage are switched off.
2. After connecting the power, allow the laser at least 10 minutes to stabilize before energizing the master source.
Note: On our earlier Fianium lasers, the fan operated whenever the unit was plugged in. However, the fan on our most recently refurbished unit appears to be controlled by a thermostat or logic within the laser, and does not always operate during warm-up or idle periods.
3. Attach a high-speed oscilloscope to the SMA connector on the laser. This provides a signal from a photodiode that monitors the output of the laser's master source.
4. Turn on the master source (oscillator).
5. The oscillator button should illuminate green to indicate that the source is operational. Verify that the pulse train is visible on the oscilloscope. Do not proceed if the source is not mode-locked (see Figure [D.16](#)).
6. Allow the master source at least 10 minutes to stabilize.
7. Before energizing the gain stage, verify that the power knob is at its lowest setting (fully counterclockwise).
8. Turn on the gain stage (keyed switch) and increase power to a moderate level (1–4 turns).
9. Operate the laser for an additional ~10 minutes before approaching full power.
10. Operate the laser at full power (10 turns) for measurements.

Standby/shut-down

1. Decrease the power knob fully (10 turns counterclockwise).
2. Turn off the amplifier stage (keyed switch).
3. If the laser will be unused for several hours, turn off the master source.
4. If the laser will be unused for several days, disconnect the power plug.

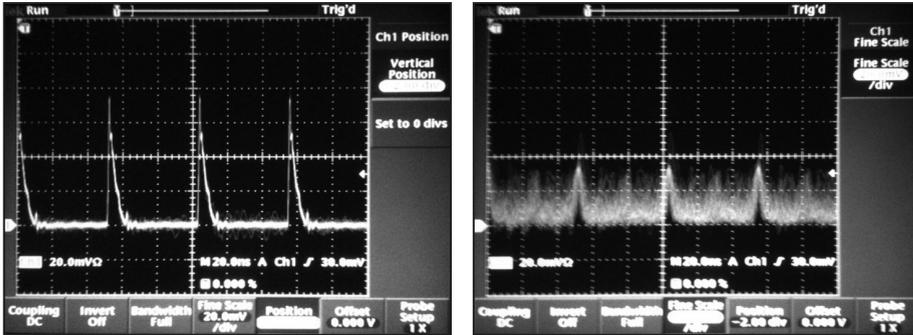


Figure D.16. Fianium laser master source waveforms as viewed on a high-speed oscilloscope. **Left:** normal (modelocked) operation. **Right:** abnormal (q-switching) operation. The laser should not be operated in this state.

Troubleshooting: We have encountered two failure modes for the supercontinuum lasers in our labs: master source failure and damaged splices (i.e., excessive internal back reflections). Diagnosing these conditions requires a high-speed oscilloscope to monitor the SMA connector on the front of the laser, an infrared indicator card, and the USB serial communication port on the laser. Users should consult the laser instruction manual and Fianium technical support at the first signs of trouble.

Master source failure. A master source failure results in rapid and complete loss of laser output. The oscillator button (green light) will usually remain dark even after attempts to reset it. Regardless of the indicator state, the sharp pulse train will not be visible on the oscilloscope (see Fig. D.16), and there will be negligible light output from the fiber (viewed with an infrared indicator card). Do not attempt to operate the amplifier stage if the master source is not working. The laser must be returned to the factory for repair.

Excessive back-reflections. If the laser’s internal detector indicates excessive back-reflections, it will automatically shut down the source and gain stages in an attempt to protect components from further damage. This will be recorded as a back-reflection alarm, which can be read by polling the laser over its USB serial communication port. The cause of the back reflections should be eliminated (e.g., by cleaning and realigning the optics) before returning to full-power operation. The laser can be restarted by turning down the power knob and turning off both switches, then resuming the power-up procedure.

Damaged splices. Over time, some lasers have suffered from reflections at internal splices that trigger the back-reflection alarm even when there are no external reflection sources (e.g., when the beam is sent into a broadband absorber). This causes the laser to shut off whenever the power knob is

turned above a certain threshold (which generally decreases with time), and full-power operation is not possible. One can continue operating the laser at decreased power levels, but the situation will eventually require that the laser be returned to the factory for repair. The USB serial communication port can be used to monitor the back-reflection photodiode value, and with the assistance of Fianium technical support, alter the shutoff threshold to delay the need for repair.

D.7.2 Source alignment

Safety warning: *The spectrophotometer employs a high-power supercontinuum laser source that must be operated at full power (2 or 4 W continuous) to achieve full spectral range. This is a pulsed, broadband laser that produces dangerous levels of visible and infrared radiation, and is capable of causing immediate and permanent blindness. No non-opaque goggles can protect against direct exposure to this laser. Users should be trained in laser safety procedures and comfortable working with high-power sources. Not all safety hazards are identified in these instructions.*

Source alignment is required if the supercontinuum laser has been exchanged or removed from the system, or if the optics have been disturbed. If the system has not been disturbed since the previous measurement session, users need only verify that the beam is properly focused between the monochromator slits prior to bringing the laser to full power. After turning the laser up to a low (but visible) power level, look at the monochromator input slit assembly. Confirm that the symmetric halo of a properly focused beam is visible at the edge of the slits (see Fig. D.17). The source enclosure can then be closed and the laser can be brought to full power for measurements. If, however, the halo appears highly asymmetric (or the beam falls somewhere other than between the slits) the source should be aligned by the following procedure.

1. Open the source and sphere enclosures. Mount the end of the laser fiber securely in the beam launch assembly. Unless the system has been disassembled, the beam launcher should already be near the correct alignment position.
2. Within the source enclosure, move the condenser lens out of the beam path and rotate the neutral density filter (NDF) to its minimum attenuation setting. The chopper should be set to “stop open” so that the monochromator input slits can be seen.

The condenser lens is supported by a magnetic base assembly that provides sufficient mass to hold the lens in place without fasteners. Note that the magnet itself is largely ineffective within the source enclosure as it rests on an aluminum breadboard.

3. Within the sphere enclosure, pivot the focusing lens out of the beam path and open all aperture diaphragms. Remove the integrating sphere (if installed) and set it aside.

4. Following the laser operation guidelines, turn on the laser and increase the power until a faint red beam is visible exiting the laser (1–4 turns).

Although the beam does not appear bright at this point, the laser is emitting dangerous levels of infrared light. For each of the remaining steps, always use as low a power level as possible for alignment.

5. Verify that the beam stop is properly placed to absorb light deflected by the neutral density filter. Recheck this whenever the source alignment is altered.
6. Use the pitch and yaw knobs on the beam launch assembly to direct the laser onto the input slits of the monochromator. The beam should be centered vertically within the slit opening, and should symmetrically straddle the slits.

The monochromator input slits are typically set to 320 μm , which with a 1200 line grating yields a ~ 1 nm passband. The input slit motors are sometimes disabled (unplugged) to prevent inadvertent closure or adjustment of the slits, which could damage the laser source. If unplugged, commands to read or change the slit width will return an E0200 error.

7. Set the monochromator to a red wavelength.

Monochromator commands can be issued using the *Mono_terminal* LabVIEW program. The command to change the wavelength to $\lambda = 650$ nm is:

```
!gw 650 
```

8. Temporarily increase the monochromator entrance slit width to 2 mm. (This is to prevent back-reflection into the laser source when the power is increased without the condenser lens in place.)

The command to set the entrance slit width to 2000 μm is:

```
!slita 2000 .
```

9. Decrease the room lights, increase the laser power, or increase the exit slit width until a beam spot is visible at the output side of the monochromator.

The exit slit width is set with the `!slitb` command. The value may be as large as 2000 μm . We generally use an exit slit width of 320 μm for measurements.

10. Using a ruler to measure the beam height, determine whether or not the beam is level within the sphere enclosure. The beam should deviate in height by no more than 1 cm from the front to the back of the enclosure.
11. If the beam is not level, slightly increase (or decrease) the height of the beam launch assembly using the cog wheel on the 1.5" post. Decrease (or increase) the pitch knob to recenter the beam (vertically) within the input slits. Recheck the output beam slope and iterate as necessary.

Remember to keep laser power to a minimum at each alignment step.

12. Follow a similar iterative procedure of horizontal translation/yaw adjustment of the beam launcher to align the beam horizontally. The aperture diaphragms in the sphere enclosure (which can be contracted as needed for alignment) should provide a target for the horizontal placement of the beam as it exits the monochromator.

If the established path in the sphere enclosure has been disturbed, and prior reference points such as the aperture diaphragms are not available, the monochromator user's manual should be consulted to determine the correct beam incidence and exit angles. A simple horizontal alignment check can be performed by opening the input slits fully (to prevent back-reflections), increasing the laser power to obtain broadband emission, and then running the *monochromator back and forth* alignment program, which continuously sweeps the beam wavelength across the visible spectrum. If the source is substantially misaligned, we have observed that the output spot will move back and forth with wavelength. The position and yaw of the beam launcher should be adjusted to eliminate any observed wobble in beam position as the wavelength is varied.

The laser power should always be reduced before manipulating the beam adjustment knobs.

13. Reduce the laser power to the lowest setting that produces visible light, and set the monochromator input and output slit widths to the values desired for measurements. Insert the condensing lens in the beam path. Vary its position along the beam path to obtain optimal focus onto the monochromator slits. Then move it back or forth to center the focused laser spot so that it disappears between the monochromator slits. The spot can be easily focused between 320 μm slits, with room on either side.

Because the supercontinuum laser is damaged by back-reflected light, keep the condensing lens tilted slightly off-axis to prevent its specular reflection from re-entering the laser (see Fig. D.1). Never close the monochromator input slits while the laser is operating at high power levels.

14. Repeat the above vertical and horizontal alignment procedures, now adjusting the height and position of the condenser lens (rather than the beam launcher) to produce a beam that emerges from the monochromator along the same path as the original beam.

Never manipulate the condenser lens at high laser power levels. The focused beam spot becomes blindingly bright if cast onto either slit.

15. The source beam is now aligned; the laser can be brought to full power. As the power is increased, there should be no visible sources of reflection within the source enclosure. The beam should fall completely between the monochromator input slits, casting only a dim, symmetric halo onto either side of the slits (see Fig. D.17).
16. Close the source enclosure and start the chopper wheel.

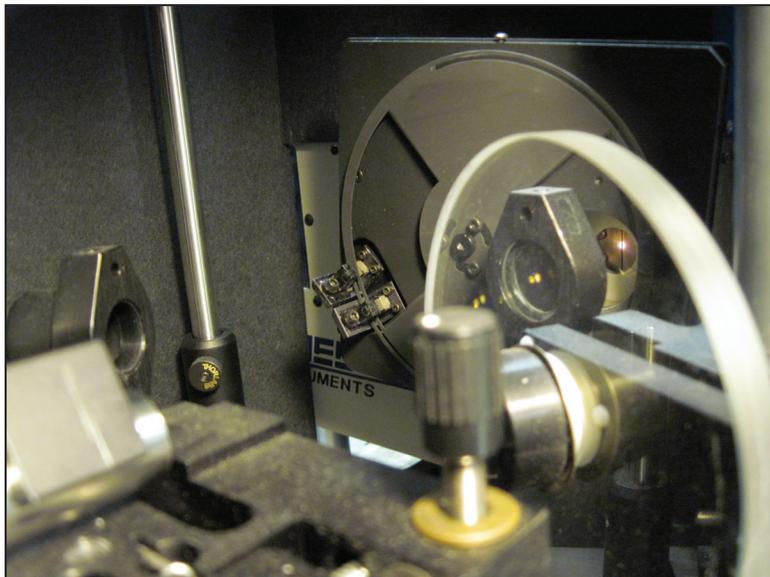


Figure D.17. Aligning the laser to the monochromator input slits. The beam halo can be seen straddling the monochromator input slit.

Following this procedure, the laser source can be run at full power without the need to open the source enclosure (with the possible exception of manipulating the neutral density filter to attenuate the illumination intensity).

D.7.3 Illumination beam alignment

Illumination beam alignment is most easily performed with the laser at full operating power* and the monochromator set to a visible wavelength (e.g., $\lambda = 550 \text{ nm}$). The monochromator grating and exit slit width should be set as desired for measurements.

1. Within the sphere enclosure, open the aperture diaphragms and pivot the focusing lens out of the beam path. (The cylindrical lens assembly, however, remains attached the monochromator output flange at all times.)
2. Center the first aperture diaphragm in the beam path and contract it slightly until a clipped beam halo is visible.
3. Contract the second aperture diaphragm and precisely center it in the beam path.

*The laser power can be attenuated using the NDF wheel in the source enclosure, but the source must be operated at full power to obtain full spectral bandwidth.

4. Open the second aperture diaphragm fully and pivot the focusing lens into position. Vary its position along the optical axis to produce optimal focus at the specimen plane. The reflection-mode specimen stage can provide a convenient target for focusing.
5. Contract the second aperture diaphragm fully. Move the focusing lens laterally to center the focused beam onto this aperture. Then open the aperture, but only as wide as necessary to fit the beam. This will block stray light and the beam halo from reaching the specimen.
6. Ensure that the beam passes through the reference beamsplitter, replacing the microscope slide cover slip if it has been broken. The posts holding the beam splitter and reference diode are snug but not tight so that they may be adjusted by hand. Pivot the beamsplitter holder to direct the reference beam into the center of the reference detector. Inspect the placement of the baffle to ensure that stray light will not reach the reference photodiode.

Make sure the correct reference photodiode (Si or Ge) is installed.

Following this procedure, a focused, referenced beam having the desired spatial and spectral resolution is striking the specimen plane. If the detection instrumentation is powered on, the reference photodiode signal should be visible on the oscilloscope and the reference-channel lock-in amplifier.

D.7.4 Specimen stage alignment

The specimen stage alignment procedure brings the specimen tilt axes (elevation and azimuth) into alignment with the beam. In order to achieve eucentric alignment, the axes of azimuthal and elevational rotation must precisely coincide with one another, and with the beam path, at a single point in space—the system eucentric point.

Before starting these procedures, the source and illumination beam paths should be aligned as described above. The azimuth axis should be oriented at its “normal incidence” position. During this alignment procedure, the position of the motorized axes can be adjusted from the computer keyboard using the *interactive alignment* LabVIEW program (accessed from the front panel of the reflection, transmission, or E.Q.E. data acquisition programs).

1. Remove the integrating sphere or photoelectrochemical cell stage if present.
2. Bolt a vertical post holder to the base rotational element, directly centered above the azimuth rotation stage. Insert a post that extends to the height of the beam. This will be called the *vertical alignment post*.
3. The beam should strike the vertical alignment post exactly at its center. If not, the entire stage must be translated within its guides (A_d axis). A handful of clamps must be loosened to enable A_d translation; these should be retightened following the alignment.

4. Retract the vertical alignment post into its post holder so that it does not extend to the height of the beam.
5. Remove the E_x and E_y stages (if installed) and move the angle bracket to the forward position (i.e., reflection mode, see Fig. D.7).

The E_x and E_y stages are removed as an assembly. Translate the E_x stage to the fully extended position (to the left) to reveal the two screws holding it to the elevation rotation stage.

To move the angle bracket to the forward position, loosen the two screws holding it to the A_x stage (3/16" hex socket), pull it forward to the end of its travel, and re-tighten the screws.

6. Bolt the reflection-mode specimen stage base to the elevation rotation stage, and attach an alignment post (or the rest of the specimen stage). This will be called the *horizontal alignment post*.

Use short screws to bolt the reflection-mode specimen stage in place. Longer screws will bind the elevation rotation stage.

7. Translate the E_h axis (`[Page ↑]` / `[Page ↓]` in the in the *interactive alignment* program) as necessary so that the horizontal alignment post is exactly centered within the illumination beam.

If the horizontal post is not long enough to reach the beam path, translate the A_y axis as necessary (`[Home]` / `[End]`).

8. Extend the vertical alignment post to reach the horizontal alignment post. The two axes should coincide at the beam position. If not, adjust A_x until the axes are coincident.
9. Remove the horizontal and vertical alignment posts. If performing reflection measurements, the reflection-mode specimen stage base can remain attached to the elevation stage.

Following this procedure, the A_d , E_h , and A_x axes are properly aligned for eucentric tilt. If two-dimensional eucentric tilt measurements are required, do not further alter the positioning of these three axes.

D.7.5 Reflection-mode configuration

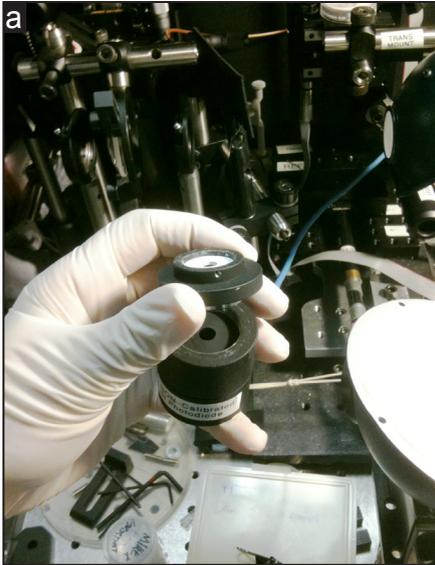
This procedure describe how the integrating sphere is configured and aligned for reflection measurements. The state of the system is assumed to be that following the above specimen stage alignment procedure, i.e., in eucentric alignment, with the angle bracket in the forward position, and with the E_x and E_y translation stages removed. Users may use the `auto_refl` program for alignment and data collection.

Note: *Wear clean gloves whenever handling internal sphere components. Efforts should be made to minimize physical contact with the $BaSO_4$ -coated components. These coatings are easily chipped away by mild physical abrasion, and*

their reflectivity is reduced by contact with dust or oils. Always store the unused components appropriately.

1. Install the reflection-mode specimen stage onto the elevation rotation stage, and rotate the elevation axis so that the specimen stage faces the incident beam ( /  in the *interactive alignment* program).
2. Translate the A_y axis until the incident beam falls directly into the center of the light trap within the specimen stage ( / ). The height of the elevation axis (E_h) should have been set correctly during the stage alignment procedure; however, this should be adjusted if necessary to center the beam in the light trap.
3. Unscrew the upper part of the reflection-mode specimen stage and set it aside.
4. Open the integrating sphere. Remove and store the interior baffles. The upper baffle is held in place by a screw, whereas the lower baffle is simply sandwiched between the hemispheres.
5. Prepare the *mounted* hemisphere (that is, the hemisphere attached to the 1/2" mounting post) by mounting the $\phi 2$ mm reflection aperture over the 1" port using one of the transmission-mode specimen holders. The BaSO₄-coated (white) surface of the aperture faces into the sphere (see Fig. D.18b).
6. Using the "reflection mount" (a 1/2" post assembly), affix the mounted hemisphere to the "reflection base" protruding from the E_h stage, as depicted in Figure D.7. The sphere should be aligned such that the reflection-mode specimen stage fits through the 1/2" port of the mounted hemisphere. Position the sphere at a depth such that its inner surface is approximately flush with the end of the reflection-mode specimen stage base. Lightly tighten the reflection mount and sphere assembly in place.
7. Rethread the reflection-mode specimen stage onto its base (see Fig. D.18c).
8. Adjust the azimuth axis ( / ) as necessary so that the incident beam passes through the center of the $\phi 2$ mm entrance aperture. The beam should now pass through both the entrance aperture and the light trap in the specimen stage. The iris diaphragms should be opened fully so that the beam halo can serve as a guide in centering the beam in the entrance aperture. In the event that the entrance aperture is at the wrong height for the beam, the reflection mount/base assembly can be loosened to permit the sphere to be more precisely aligned to the incident beam.

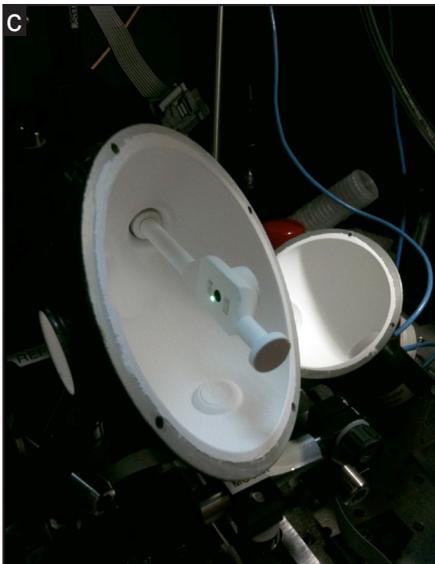
Note: *Aligning the sphere and reflection mount/base assembly from scratch requires a time consuming iterative adjustment approach. For this reason, the reflection mount and base components should not adjusted or disassembled when not in use. It should be generally be possible to archive proper alignment by loosening only the reflection base post-holder thumbscrew as well as the integrating sphere post holder.*



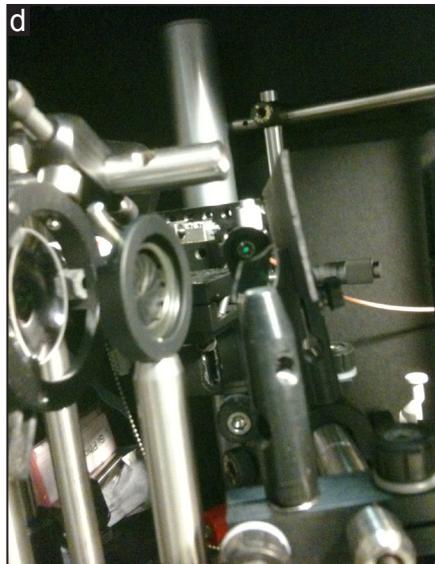
Photodiode assembly: removing the 1/2" adapter from the photodiode spacer



Reflection mode: installing the 2 mm-dia. entrance aperture on the 1" sphere port



Reflection mode: aligning the reflection stage (intentionally misaligned to show beam)



Illumination alignment: centering the reference beam on the reference photodiode

Figure D.18. Reflection-mode configuration.

9. The photodiode assembly is prepared as follows: the 818-series photodiode of choice (Si or Ge) is threaded onto the “photodiode spacer” with a nonreflecting (black) baffle installed between the two. A second baffle is mounted at the bottom of the photodiode spacer. Remove the 1/2” photodiode adapter from the photodiode spacer, if present (see Fig. D.18a).
10. Use the 1” photodiode adapter to affix the photodiode assembly to the 1” port of the other hemisphere (known as the *removable* hemisphere) that will be located opposite the 1/2” port when the sphere is assembled. A third baffle is sandwiched between the port opening and the photodiode spacer. This baffle has BaSO₄ (white) coating on the sphere-facing side, and nonreflective (black) coating on the diode-facing side.
11. Install a 1” port cover on the remaining port of the removable hemisphere.
12. The sphere can now be assembled for a test fit. Attach the removable hemisphere to the mounted hemisphere with 3 or more binder clips, using the original screw holes as guides to align the hemispheres. The four ports should lie in a perfectly horizontal plane, with the specimen stage exactly centered at the eucentric point within the sphere.
13. Check the alignment of the beamsplitter and reference photodiode. The reference beam should strike the center of the diode (see Fig. D.18d).

The integrating sphere is now aligned and prepared for hemispherical reflection measurements. The sphere mounting components should be tightened in place so that the alignment isn’t inadvertently disturbed while opening/closing the sphere, which is required for loading and unloading each sample.

D.7.6 Reflection measurements

Reflection measurements are typically performed as a function of wavelength (λ) and a single incidence angle (θ_x) using the LabVIEW program `auto_refl.vi`.

1. Open the integrating sphere and set the removable hemisphere (with attached photodiode) aside to facilitate loading/unloading the specimen. The specimen exchange is most easily performed with the stage facing upward.
2. Affix the specimen to the reflection stage within the sphere (usually, using two-sided tape). The area of interest should be centered over the light trap.

If desired, also affix a reflectance standard adjacent to the specimen. Most measurements do not require a reflectance standard, and are instead normalized to the reflectance of a clean area of the specimen stage.

3. Rotate the specimen stage ( / ) so that the specimen is illuminated at near-normal incidence. The specular reflection from the beam striking the specimen can be used as a guide.

The *Load* button in the software rotates the stage 90° toward the source, and is usually appropriate for bringing the specimen to normal incidence after loading.

4. Verify that the reference-position rotation and translation offsets within the program are valid. The *Goto Ref* or *Goto Sample* buttons should move the system between the reference and specimen positions as desired when actuated. The numerical adjustment controls may prove useful in fine-tuning the positioning offsets.

It is imperative that the incident beam does not strike the entrance aperture in either measurement position. The iris diaphragms should be opened for alignment so that the beam halo is visible on the entrance aperture (to facilitate centering the beam in the aperture). However for measurements, the diaphragms should be closed to produce a tightly focused beam that passes completely through the aperture.

Once the system is aligned with valid reference-position offsets, subsequent reflection measurements can be taken with relative ease as this alignment does not need to be independently established for each specimen.

5. Enter the scan parameters (wavelengths and angles) and specimen data (name and folder for data) in the software user interface.

To perform a measurement at a single angle only, set *Degree Stop* to 0.

6. To initiate the scan, press *Start (from sample)* or *Start (from reference)*, depending on the current system position.

The software will collect the reference-position spectra (at normal incidence only), then progress to the specimen-position scans. After the first scan, the software will provide an estimated time of completion. After the last scan, the specimen stage will be returned to the upright (90° elevation) position to facilitate unloading.

D.7.7 Transmission-mode configuration

This procedure describe how the integrating sphere is configured and aligned for transmission measurements. The initial state of the system is assumed to be that following reflection measurements.

Note: *Wear clean gloves whenever handling internal sphere components. Efforts should be made to minimize physical contact with the BaSO_4 -coated components. These coatings are easily chipped away by mild physical abrasion, and their reflectivity is reduced by contact with dust or oils. Always store the unused components appropriately.*

1. Open the sphere. Set the removable hemisphere aside.
2. Unscrew and remove the upper part of the reflection-mode specimen stage.
3. Loosen the “reflection base” thumbscrew and slide the sphere assembly forward. Remove the “reflection mount” from the sphere and stow it.

***Note:** Due to the difficulty of assembling and aligning these components, do not disassemble the reflection mount assembly, and leave the reflection base assembly attached to the stage. If the reflection base assembly interferes (collides) with the photoelectrochemical cell stage, the post holder can be removed while leaving its base bolted in place.*

4. Unbolt the reflection-mode specimen stage base from the elevation rotation stage. Reassemble and stow the reflection-mode specimen stage.
5. Move the angle bracket to the rearward position (i.e., the transmission-mode position, see Fig. D.6) as follows: loosen the two screws holding it to the A_x stage (3/16" hex socket), then push it rearward to the end of its travel and retighten the screws.
6. Install the E_x and E_y stages as an assembly. The E_x stage is bolted to the elevation rotation stage using the two rightmost screws. Translate both stages to be approximately centered in their travel. The post protruding from the E_y stage should be approximately concentric with the elevation rotation axis.

***Note:** Be certain to properly thread and tighten the screws holding the E_x stage to the rotation stage. If a screw becomes loose, it can become stuck beneath the stage, making it nearly impossible to translate or remove the stage.*

7. Install the “transmission mount” on the post protruding from the E_y stage (see Fig. D.6).
8. Install the upper baffle in the mounted hemisphere. It is screwed in place from above (see Fig. D.20b).
9. Mount the hemisphere to the transmission mount, with the 1/2" port facing up. The bubble level may be helpful in positioning the sphere. Tighten the thumbscrews with a hex driver to hold the sphere securely.
10. Remove the photodiode assembly from the removable hemisphere and stow the 1" port adapter and its baffle. Thread the 1/2" port adapter onto the photodiode spacer (see Fig. D.18a) and mount it to the top of the integrating sphere. Sandwich a 1/2" baffle between the photodiode adapter and the port opening, with the white (BaSO_4 -coated) side facing the sphere's interior.
11. Install a 1" port cover over the remaining port of the removable hemisphere.

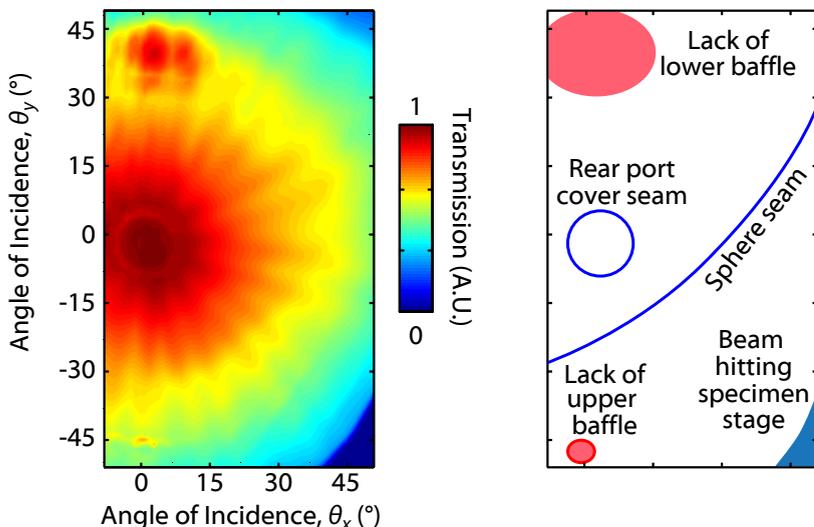
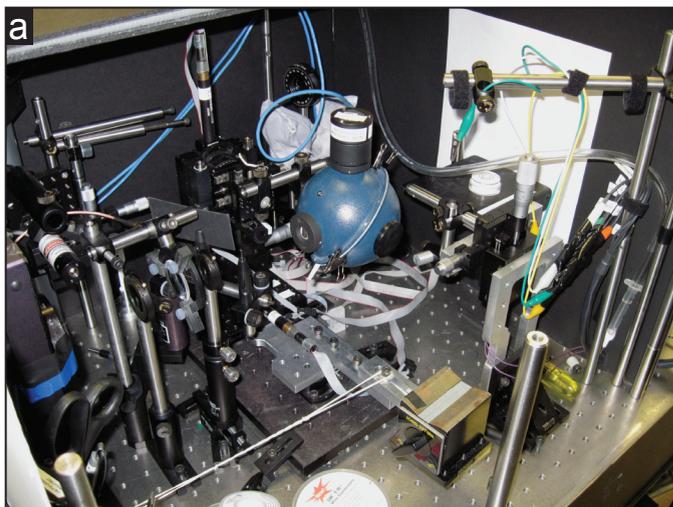


Figure D.19. Artifacts in two-angle transmission scans. **Left:** Two-angle (θ_x – θ_y) transmission measurements performed on a dodecagonally tiled Si wire array. **Right:** Diagram depicting the location and source of artifacts in the measured data. The array was intentionally measured without either baffle in place.

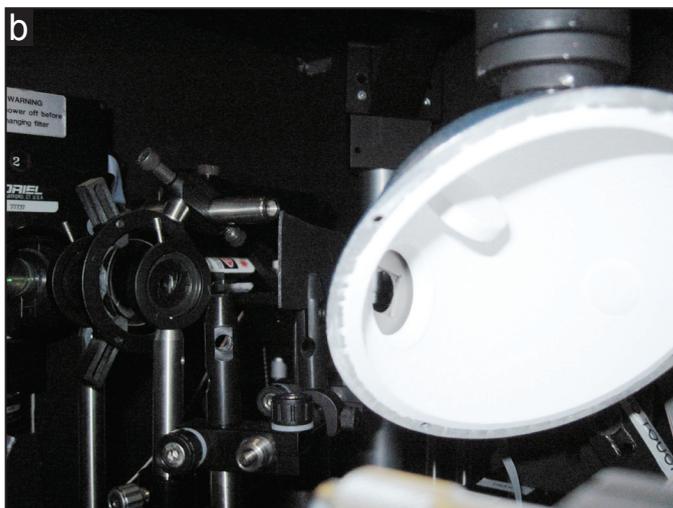
12. Assemble the hemispheres using binder clips. During assembly, position the lower baffle (the thin BaSO_4 -coated sheet metal cutout) so that it is sandwiched between the two hemispheres at the appropriate location.

Unlike the reflection-mode configuration, the hemispheres do not need to be aligned such that the ports oppose one another. In fact, for two-angle transmission measurements, it may be advantageous to rotate the removable hemisphere so that the ports are as far as possible from the back side of the sphere. This is true for specimen with non-ideally diffuse behavior such as wire arrays, which transmit a significant amount of the incident beam without scattering or absorbing it. When this beam is cast directly onto a port cover seam (or the sphere seam), some light escapes the sphere and the transmission appears artificially low. Thus, a port cover positioned directly opposite the specimen port can produce a circular artifact at the center of the data set (i.e., near normal incidence). Figure D.19 shows an example of such an artifact. The port seam artifact can be removed from the center of the scan by rotating the removable hemisphere so that the ports occupy other areas of the sphere. Careful inspection will reveal several seam artifacts in the data shown in Figure 3.18.

13. Check the alignment of the beamsplitter and reference photodiode. The reference beam should strike the center of the diode (see Fig. D.18d).



Transmission-mode integrating sphere configuration



Transmission-mode configuration—view inside sphere.

Figure D.20. Transmission-mode configuration.

14. Remove the specimen holder from the 1" port at the front of the sphere. Stow the $\phi 2$ mm reflection-mode entrance aperture. Load a sample or a blank slide in the specimen holder (using tape or a baffle to secure it) and reattach it to the sphere.
15. Move the A_y and E_y axes to illuminate an identifiable feature on the specimen (or mark the point of incidence with a marker). Rotate the azimuth to $\sim 45^\circ$ incidence angle. Adjust the E_x axis as necessary so that the beam strikes the identified specimen feature again. This translates the specimen plane to coincide with the system eucentric point, and ensures that the beam will strike the same spot on the specimen at all incidence angles.

D.7.8 Transmission measurements

Performing two-dimensional angular (θ_x - θ_y) transmission or E.Q.E. sweeps (e.g., Fig. 3.18) requires that the system be in precise eucentric alignment. Single-angle sweeps (i.e., θ_x - λ) can be performed more easily, and only require that one axis be aligned to the beam. Spatial (x - y) scans can be performed without either axis in eucentric alignment.

Two-angle transmission (or E.Q.E.) sweeps are performed using the `auto_angle.vi` program. To preserve eucentric alignment, users should not move the E_h (motorized) or the A_x (manual) axes during setup or measurements. Only the E_y (manual) and A_y (motorized) axes can be used to translate the specimen without disturbing eucentric alignment. Presently, however, the E_h axis is used for motorized translation between specimen- and reference-position measurements. This allows greater range of motion than the smaller E_y axis, but it also disturbs eucentric alignment. Thus, users should use the E_y and A_y stages to translate the specimen to the region of interest, reserving operation of the motorized E_h stage only for translating between this and the reference position. Because the software always returns the stage to the specimen position after measurements, the eucentric alignment of E_h will not be lost.

Single-angle transmission (or E.Q.E.) sweeps are performed using the `auto_trans.vi` (or `aut_pecsr.vi`) program. Only the azimuthal rotation axis needs to be in eucentric alignment for single-angle transmission sweeps. Conveniently, this is almost always the case, as the azimuthal rotation stage is bolted to the (stationary) base plate. Users may simplify the operating procedures for such measurements: the motorized E_h axis can be used to pan the specimen, and either the A_x or E_x stages can be used to bring the specimen plane to the eucentric point.

Spatial transmission (or E.Q.E.) sweeps are performed using the `auto_xy.vi`. The user need not check the eucentric alignment of either rotational axis before starting measurements.

The following procedures describe how to perform single-angle transmission sweeps:

1. Mount the specimen in one of the transmission-mode specimen holders, using two-sided tape or one of the apertures to hold it in place. Attach the specimen holder to the front port of the integrating sphere.

The specimen mounting configuration must allow for a reference reading to be taken (see Figure D.5). Thus, the specimen cannot occupy the entire open area of the specimen holder. Wire-array films, for example, can be mounted on a slide (leaving a portion of the slide uncovered to serve as the reference point), whereas brittle specimen can be cut to occupy only a portion of the specimen holder area.

Samples that are too large to fit the 1/2" form factor of the specimen holders can be taped directly to the entrance port of the sphere.

2. Adjust the E_y and A_y axes so that the desired area of the specimen is illuminated.
3. To verify that the specimen is aligned to the system eucentric point, rotate the azimuth axis by $\sim 45^\circ$. The beam incidence point should not move on the specimen. Adjust the E_x stage if necessary and return the stage to normal incidence.
4. Use the numerical motor controls at the top of the software window (*Up*, *Down*, *Fwd*, and *Back*) to translate the sphere to the reference alignment. Keep track of the total distance traveled in each direction, and set the reference-position translation offsets in the software accordingly. If these values are entered correctly, pressing *Goto Sample* should return the sphere exactly to the starting point (illuminating the specimen area of interest).
5. Enter the scan parameters (wavelengths and angles) and specimen data (name and folder for data) in the software user interface.

To perform a measurement at a single angle only, set *Degree Stop* to 0.

6. To initiate the scan, press *Start (from sample)* or *Start (from reference)*, depending on the current system position.

The software will collect the reference-position spectra (at normal incidence only), then progress to the specimen-position scans. After the first scan, the software will provide an estimated time of completion.

D.8 Supplementary information

D.8.1 Data processing program

The following MATLAB script can be used to process and plot the data taken by the spectrophotometer instrument. Use of the program is described in section D.6.3. The listing has been typeset to facilitate copying from this PDF file.

Listing D.1. Data plotting program for spectrophotometer system.

```
% Prompt user for file location
global mksearchpath
if (~isempty(mksearchpath))
    [FileName,PathName] = uigetfile({'*.asc;*.dat;*.txt;*.csv' '*'},...
    'Select norm and data file - norm file must include 'norm' in name.',...
    'MultiSelect','on',mksearchpath);
else
    [FileName,PathName] = uigetfile({'*.asc;*.dat;*.txt;*.csv' '*'},...
    'Select norm and data file - norm file must include 'norm' in name.',...
    'MultiSelect','on');
end

% Figure out which file is which, and determine sweep settings
if (~isempty(FileName))
    if( iscell(FileName))

        normfilename = [PathName FileName{1}];
        [pathstr, name, ext, versn] = fileparts(normfilename);
        one_data = dlmread( normfilename );

        samplefilename = [PathName FileName{2}];
        [pathstr, name, ext, versn] = fileparts(samplefilename);
        two_data = dlmread( samplefilename );

        if isempty( strfind( [name ext], 'norm' ) )
            norm_data = one_data; sample_data = two_data;
        else
            sample_data = one_data; norm_data = two_data;
        end

        probablename = name;
        nameend = strfind(name, '_');
        if (~isempty(nameend))
            probablename = name(1:nameend(1)-1);
        end

        probabletype = 'T';
        if (~isempty(strfind(name,'refl')) || ~isempty(strfind(name,'br')))
            probabletype = 'R';
        end

        sampleWL = sample_data(:,2);
        wl_range = [ min(sampleWL) (sampleWL(2)-sampleWL(1)) max(sampleWL)];
                                     % (min step max)
        numbersweep = length(wl_range(1):wl_range(2):wl_range(3));
        numsweeps = length(sampleWL)/numbersweep;
        sampleTheta = sample_data(:,1);

        normWL = norm_data(:,2);
        WL_max = min(max(normWL),wl_range(3)); % truncate data range to that
```

```

WL_min = max(min(normWL),wl_range(1)); % available in normalization file
alname = '\lambda (nm)';
if (WL_max < 400) alname = '\theta_y (\circ)'; end
if (WL_max < 10 ) alname = 'x (mm)'; end

if (numsweeps > 1)
    a2name = '\theta_x (\circ)';
    a2range = [num2str(min(sampleTheta)) ' ' num2str(max(sampleTheta))];
    dTheta = sampleTheta (numersweep+1)-sampleTheta(1);
    if (max(sampleTheta) < 10) a2name = 'y (mm)'; end
else
    a2name = 'N/A'; a2range = 'N/A'; dTheta = 0;
end

global mkrunavg mkdeglitch;
if (isempty(mkrunavg) || isempty(mkdeglitch))
    mkdeglitch = '1054 1074'; mkrunavg = '0';
end

%Now prompt user for user input
defAns = {probablename '' probabletype '' '\lambda (nm)' ...
    [num2str(WL_min) ' ' num2str(WL_max)] a2name a2range ...
    mkrunavg mkdeglitch };
sampleinfo = inputdlg({ ...
    'Variable name for MALTB workspace (cannot be empty)'...
    'Title for graph (if different from above)' ...
    'Normalization type (R, T, N, Rabs, Tabs, or user-defined code)'...
    'Append to previous graph? (write anything here to do so)' ...
    'Axis 1 title' 'Axis 1 range' 'Axis 2 title' 'Axis 2 range' ...
    'Axis 1 running average (num. data points or ''0'' for no averaging)'...
    'Axis 1 deglitch range (min max) [leave empty for none]', ...
    'Settings', 1, defAns);
end
mksearchpath = samplefilename; % remember folder for next time.
end

%Parse user input
if (isempty(sampleinfo{2})) titlename = sampleinfo{1}; %graph title name
else titlename = sampleinfo{2}; end
shouldhold = ~isempty(sampleinfo{4}); %whether to open new window
userwlrangle = str2num(sampleinfo{6});
userthetarange = str2num(sampleinfo{8});
WL_max = min(userwlrangle(2),WL_max); %truncate wavelength range?
WL_min = max(userwlrangle(1),WL_min);
if (numsweeps > 1) %truncate theta range?
    Theta_min = max(min(sampleTheta),userthetarange(1));
    Theta_max = min(max(sampleTheta),userthetarange(2));
end
deglitchrange = 0; %whether or not to deglitch the noisy peak at ~1064 nm
if ~isempty(sampleinfo{10})
    deglitchrange = str2num(sampleinfo{10});
    if (deglitchrange)
        deglitchrange = min(WL_max, deglitchrange);
        deglitchrange = max(WL_min, deglitchrange);
    end
end
runavg = floor(abs(str2num(sampleinfo{9}))); % running average
exptype = sampleinfo{3}; %What type of normalization (T, R, or other?)
samplename = sampleinfo{1}; %base name for workspace variable

%Save deglitch/avg settings for next time program is run
mkrunavg = num2str(runavg); mkdeglitch = mat2str(deglitchrange);

%Initialize arrays for normalized data
WL = WL_min:wl_range(2):WL_max;

```

```

nWL = length(WL);

if ( numsweeps > 1)
    Theta = Theta_min:dTheta:Theta_max;
    nT = length(Theta);
else
    Theta = 0; nT = 1; Theta_min = 0; Theta_max = 0;
end

normalizedData = zeros(nT,nWL);
sampleReading = sample_data(:,3)./sample_data(:,4);

%Re-sample the normalization data
normReadingOrig = norm_data(:,3)./norm_data(:,4);
normWLOrig = normWL;
normReading = interp1(normWLOrig, normReadingOrig, WL);

%Iterate through the file data to construct the 2D array of normalized data
ThetaIndex = 1;
WLIndex = 1;
recognizedNormalization = 1;
for n=1:length(sampleReading)
    thisWL = sampleWL(n);
    thisTheta = sampleTheta(n);

    if (thisTheta < Theta_min || thisTheta > Theta_max) continue
    elseif (thisWL < WL_min || thisWL > WL_max) continue
    end

    thisRelative = sampleReading(n)/normReading(WLIndex);

    %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
    % Normalization - this is where we determine what the "reference"
    % value is. We can add additional experiment types here, e.g. for a
    % reference photodiode (which must be interpolated by wavelength):
    %
    % if (strcmp(exptype,'EQE'))
    %     refValue = interp1(diodeWL,diodeEQE,thisWL);
    % end
    %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
    if (strcmp(exptype,'T'))
        refValue = 0.92; %approx transmission through quartz slide
    elseif (strcmp(exptype,'R'))
        refValue = 0.98; %approx reflectivity of BaSO4 coating on refl. stage
    elseif (strcmp(exptype,'N'))
        refValue = 1; % (Data is divided by max value later)
    elseif (strcmp(exptype,'Tabs') || strcmp(exptype,'Rabs'))
        refValue = 1; %Data is normalized to unity
    else
        refValue = 1; %default case
        recognizedNormalization = 0; %This will issue a warning after the loop
    end

    normalizedData(ThetaIndex, WLIndex) = thisRelative * refValue;

    WLIndex = WLIndex + 1;
    if (WLIndex > nWL)
        WLIndex = 1;
        ThetaIndex = ThetaIndex + 1;
        if (ThetaIndex > nT)
            break;
        end
    end
end
end
end

```

```

if (~recognizedNormalization)
    warndlg(['The experiment type '' exptype '' does not have an '...
            'associated normalization spectrum in this program. Data have '...
            'been normalized to unity.']);
end

%apply deglitching
if(deglitchrange)
    numdeglitches = size(deglitchrange); numdeglitches = numdeglitches(1);
    for nd = 1:numdeglitches
        temp_ND = normalizedData;
        deglitchFromIndex=max(floor((deglitchrange(nd,1)-WL_min)/wl_range(2)+1),1);
        deglitchToIndex=min(ceil((deglitchrange(nd,2)-WL_min)/wl_range(2)+1),nWL);
        for nTheta = 1:nT
            for nWavelen = deglitchFromIndex:deglitchToIndex;
                temp_ND(nTheta, nWavelen) = ...
                    interp1([deglitchFromIndex deglitchToIndex], ...
                        [normalizedData(nTheta,deglitchFromIndex) ...
                         normalizedData(nTheta,deglitchToIndex)], nWavelen);
            end
        end
        normalizedData = temp_ND;
    end
end

%apply running average
if (runavg)
    temp_ND = normalizedData;
    for nTheta = 1:nT
        for nWavelen = 1:length(WL)
            temp_ND(nTheta, nWavelen) = ...
                mean(normalizedData(nTheta, ...
                    (max(nWavelen-runavg,1):(min(nWavelen+runavg,nWL)))));
        end
    end
    normalizedData = temp_ND;
end

%Normalize data to unity for experiment type 'N':
if (strcmp(exptype,'N'))
    normalizedData = normalizedData./max(max(normalizedData));
end

%Prepare figure for plot
if(shouldhold)
   (gcf; hold on; legend(gca,'off')
    prettycolors = {'b' 'r' 'k' 'g' 'c' 'y' 'm'};
    linespec = prettycolors{mod(length(get(gca,'Children')),7)+1};
else
    figure; linespec = 'b'; %Note: linespec only affects 2D (line) plots.
end

%Determine human-readable experiment type for plots
if (exptype(1) == 'T')
    measuredQuantity = 'Transmission';
elseif (exptype(1) == 'R')
    measuredQuantity = 'Reflection';
elseif (strcmp(exptype,'EQE'))
    measuredQuantity = 'External Quantum Efficiency';
elseif (strcmp(exptype,'N'))
    measuredQuantity = '(Normalized)';
else
    measuredQuantity = [exptype ' (rel. to reference reading)'];
end

```

```

%Make 3-D plot for 2-dimensional data sets
if ( nT > 1 )
    hmesh = mesh(Theta, WL, normalizedData, 'DisplayName', titlename);
    xlabel(sampleinfo{7}, 'FontName', 'Helvetica', 'FontSize', 18)
    ylabel(sampleinfo{5}, 'FontName', 'Helvetica', 'FontSize', 18)
    zlabel(measuredQuantity, 'FontName', 'Helvetica', 'FontSize', 18)
    view(65, 30)
    set(hmesh, 'FaceColor', 'interp', 'EdgeColor', [0 0 0], 'MeshStyle', 'column')
    set(gca, 'FontSize', 14, 'FontName', 'Helvetica', 'LineWidth', 2)
    set(gca, 'YLim', [WL_min WL_max], 'XLim', [Theta_min Theta_max])
    title(titlename, 'FontName', 'Helvetica', 'FontSize', 18);
    if (exptype(1) == 'R')
        set(gca, 'XDir', 'reverse'); %This usually looks better
    end

%2D line plot for 1-dimensional data set
else
    plot(WL, normalizedData, linespec, 'DisplayName', titlename);
    xlabel(alname, 'FontName', 'Helvetica', 'FontSize', 18);
    title(titlename, 'FontName', 'Helvetica', 'FontSize', 18);
    ylabel(measuredQuantity, 'FontName', 'Helvetica', 'FontSize', 18);
    set(gca, 'LineWidth', 2, 'FontName', 'Helvetica', 'FontSize', 14);
end

hold on;
if (shouldhold) legend('show'); title(''); end

% Save data to workspace:
assignin('base', [samplename '_' exptype], normalizedData);
assignin('base', [samplename '_WL'], WL);
assignin('base', [samplename '_Theta'], Theta);

```

D.8.2 Diagrams of custom parts

This section provides the mechanical drawings of the two key custom parts that were machined for the integrating sphere by the Caltech instrument shop.

- Reflection-mode specimen stage

The reflection specimen stage bolts to the elevation rotation stage and suspends the specimen at the center of the sphere. It can be separated at the base to allow it to be threaded through the 1/2" sphere port. A cup-shaped light-trap seals the back of the cavity beneath the sample.
- Transmission-mode specimen holder

The transmission specimen holders affix to the 1" integrating sphere ports. Two have been built: one has a 1 cm diameter circular field while the second has a 1/2" diameter (slightly larger) field. They are designed to hold 1/2" square specimen. They can also hold a baffle or aperture over the sphere port (e.g., as used for reflection-mode measurements). A variety of aperture discs that fit within the transmission-mode specimen holders have been fabricated.

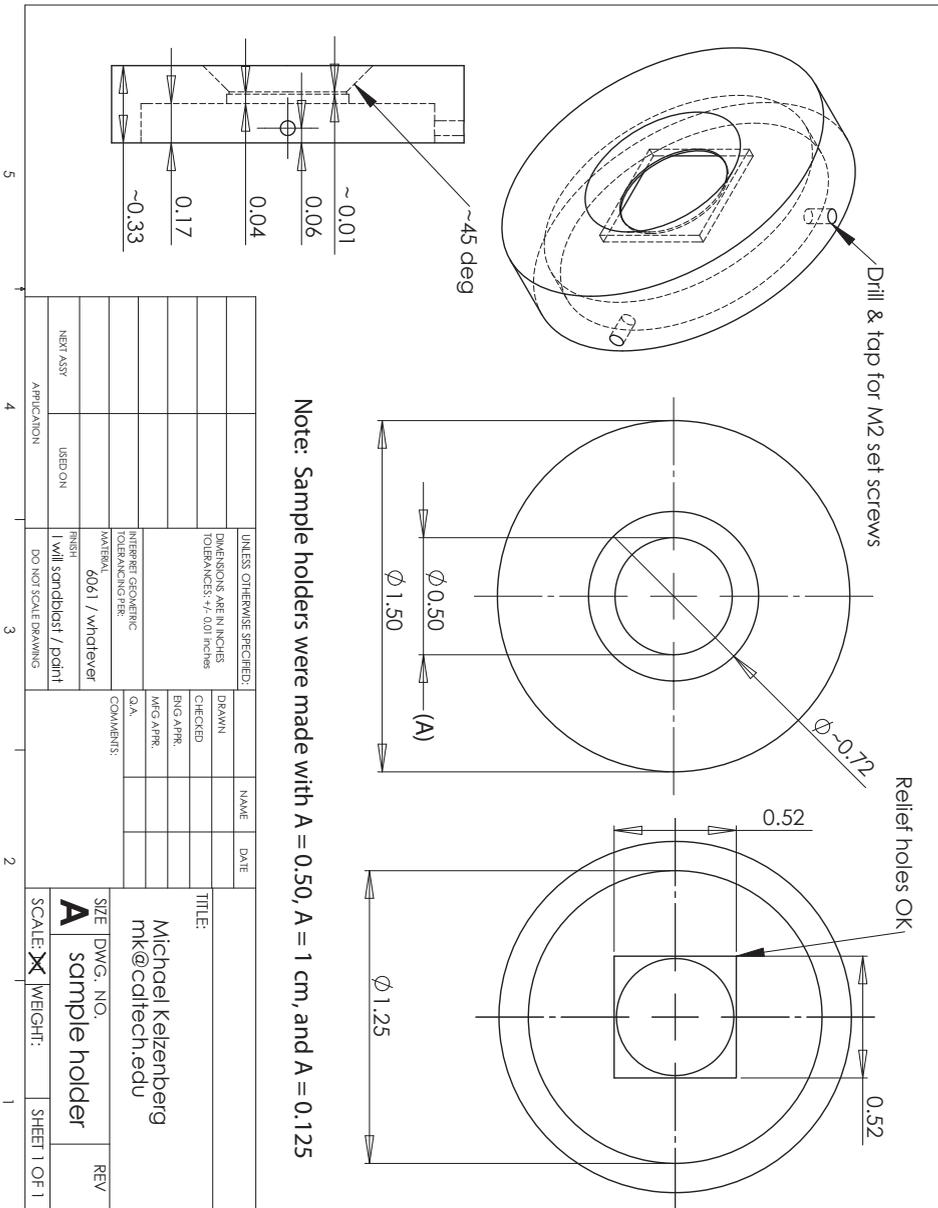


Figure D.22. Mechanical drawing: Transmission-mode specimen holder.