

Design and Implementation of Quasi-Steady-State Photoinduced Absorption Spectroscopy Setup

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by

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List of abbreviations

A	amplitude
A	absorbance
A	ampere
α	absorption coefficient
c	speed of light
c	concentration
d	groove spacing
ΔA	change of absorption
$\Delta \lambda$	smallest resolvable wavelength difference
ΔT	change in transmission
E	energy
e^-	electron
E_{HOMO}	energy level of the highest occupied molecular orbital
E_{LUMO}	energy level of the lowest unoccupied molecular orbital
e.g.	exempli gratia (for example)
EA	electron affinity
eV	electronvolt
ϵ	extinction coefficient
f	frequency
FIR	finite impulse response
fs	femtosecond
GSB	ground state bleach
H	fluence
h	Planck constant
h^+	hole
Hz	hertz

I	intensity of light
I_0	intensity of incident light
I_A	intensity of absorbed light
I_R	intensity of reflected light
I_S	intensity of scattered light
I_T	intensity of transmitted light
IC	internal conversion
IE	ionization energy
IR	infrared
ISC	intersystem crossing
IUPAC	International Union of Pure and Applied Chemistry
$k\Omega$	kiloohm
PM6	PBDB-T-2F, electron donor polymer
l	path length
λ	wavelength
MHz	megahertz
μm	micrometer
μs	microsecond
ms	millisecond
N	number of grooves illuminated
n	diffraction order
n	background noise
ns	nanosecond
ND-filter	neutral density filter
nm	nanometer
ω	circular frequency
PIA	photoinduced absorption

PIAS	photoinduced absorption spectroscopy
PL	photoluminescence
PSD	phase-sensitive detector
ϕ	phase shift
QTH-lamp	quartz tungsten halogen lamp
R	spectral resolution
R	amplitude of the signal
r	reference signal
RC	resistor-capacitor stages
s	second
s	signal
S_n	singlet energy state
SiN	silicon nitride (Si_3N_4)
SRS	Stanford Research Systems
$T_{n>0}$	triplet excited state
t	time
τ	time constant
θ	phase of signal
θ_d	angle of diffraction
θ_i	angle of incidence
TTL	transistor-transistor logic
UV-VIS	ultraviolet and visible
V	volt
W	watt
X	in-phase component of the signal
Y	out-of-phase component of the signal
Y6	BTP-4F, small electron acceptor molecule

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1 Introduction

The global shift toward sustainable energy has driven intensive research into novel materials for photovoltaic applications. To improve the efficiency and stability of next-generation solar cells, such as those based on organic semiconductors, perovskites, or other hybrid materials,^[1] it is essential to understand the underlying photophysical processes that govern their performance. These processes include the generation, separation, recombination, and transfer of charge carriers, as well as the formation of long-lived excited states, all of which occur on timescales ranging from nanoseconds (ns, 10^{-9} s) to milliseconds (ms, 10^{-3} s).^[2, 3]

Optical spectroscopy offers a powerful set of tools for probing such processes. By examining how a material interacts with light, whether through absorption, emission, or scattering, researchers can gain insight into its electronic structure, molecular dynamics, and energetic states. Classical spectroscopic methods provide valuable information about ground-state properties, but often fail to capture the full picture of photoexcited states.

Photoinduced absorption spectroscopy (PIAS) is a differential technique used to probe the presence and dynamics of excited states in a material. The core idea involves optically exciting the sample with a modulated pump beam while simultaneously probing it by scanning through the spectra of a continuous, spectrally broad light source. Upon excitation, new absorption features may arise due to the formation of transient species with a lifetime from microseconds to milliseconds, such as polarons or triplet states, which are not detectable by traditional steady state spectroscopy. These features appear as a small difference in transmission of the probe light by the sample. The signal, typically denoted as $\Delta T/T$ or ΔA , is proportional to the concentration of photo-generated species and their lifetime.

The modulation of the pump light allows for phase-sensitive detection using a lock-in amplifier. This technique enables the extraction of weak signals with high sensitivity, even in the presence of significant background noise. This makes it a powerful method for studying long-lived excited states, particularly in materials for optoelectronic applications and photoelectrochemical processes such as photovoltaics and photocatalysis.^[4, 5]

This thesis presents the design and construction of a quasi-steady-state PIAS setup, optimized for measurements in the visible and near-infrared spectral ranges. The goal is to construct a system that can be used to study long-lived species in a variety of materials. Additionally, custom LabVIEW software is developed to control the measurement sequence and data acquisition.

2 Theoretical Background

2.1 Fundamentals of Optical Spectroscopy

2.1.1 Light-Matter Interactions

The interaction of light with matter is the physical basis of optical spectroscopy. Light can be described both as an electromagnetic wave and as a stream of particles (photons). The wave character of the light is used to explain the interaction of light with electrons in atoms and molecules, applying the electromagnetic theory. The particle description can be used to explain the quantized amount of energy that can be transferred from photons to electrons by the laws of quantum optics. The Planck relation gives the energy (E) of a single photon:

$$E = \frac{hc}{\lambda} \quad (1)$$

using the speed of light in vacuum ($c \approx 2.998 \cdot 10^8 \frac{m}{s}$), the Planck constant ($h \approx 6.626 \cdot 10^{-34} Js$) and the wavelength (λ [m]) of the photon. This equation shows both aspects of light by combining the energy of a single photon with the corresponding wavelength of the electromagnetic wave.^[6, 7]

When light interacts with matter, it can be absorbed, transmitted, reflected, or scattered.

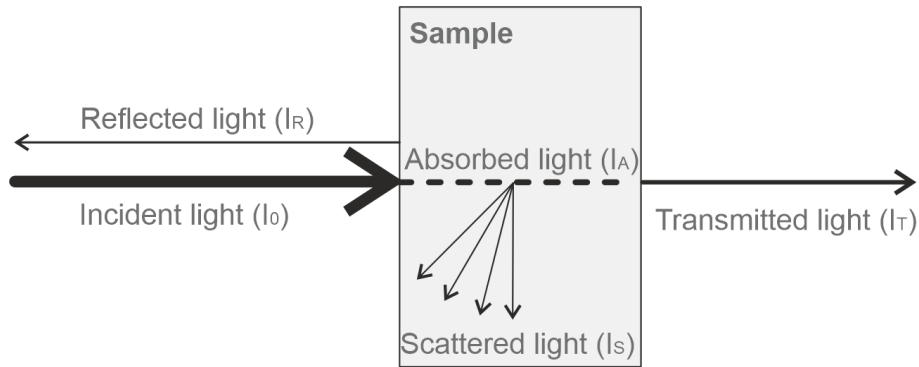


Figure 1: The different possible interactions of light with matter. Adapted from [8].

The energy balance of these processes can be described by the following equation:

$$I_0 = I_A + I_T + I_R + I_S \quad (2)$$

where I_0 is the incident light intensity, I_A is the intensity of absorbed light, I_T is the intensity of transmitted light, I_R is the intensity of reflected light, and I_S is the intensity of scattered light.

Transmitted, reflected, and scattered light can be measured directly by putting suitable detectors in the corresponding positions. However, the intensity of the absorbed light can only be determined by evaluating equation 2.^[8] Typically, only the transmitted light is measured. Therefore, it is important to reduce the scattered and reflected light to a minimum. Reflections can be minimized by shining the incident light perpendicularly onto a flat sample surface, e.g., on a film or the window of a cuvette. To reduce the scattered light, the sample should be homogeneous,

and the surface of the sample/cuvette should be cleaned and free of scratches or fingerprints.

Upon light absorption, the material's energetic state changes from a ground state to an excited state. When using electromagnetic radiation in the infrared (IR) spectral range ($\lambda = 700 \text{ nm} - 1 \text{ mm}$), rotations and vibrations are excited. With higher photon energy in the ultraviolet and visible (UV-VIS) range ($\lambda = 10 \text{ nm} - 700 \text{ nm}$), electronic and vibronic transitions can be observed. An excitation of electrons from the ground state is possible when the energy of an incoming photon is equal to or greater than the difference between the energy of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}):

$$E_{\text{photon}} \geq E_{LUMO} - E_{HOMO} \quad (3)$$

These transitions can be visualized in a Jablonsky diagram (Figure 2). Here, S_n marks the singlet energy states with $n = 0$ as the ground state and $n > 0$ as excited states. $T_{n>0}$ is used to mark excited triplet energy states. According to the International Union of Pure and Applied Chemistry (IUPAC), radiative transitions are indicated with straight arrows, and radiationless transitions are indicated using wavy arrows, e.g. via vibrational relaxation (heat, phonons), internal conversion, or intersystem crossing.^[9]

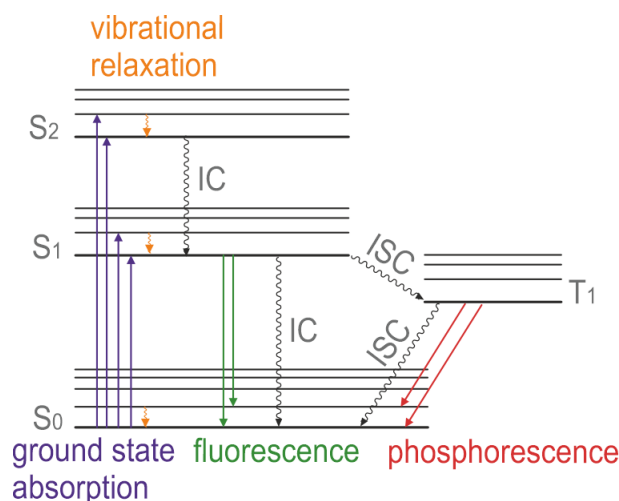


Figure 2: Jablonsky diagram depicting possible electronic states of a molecule and the transitions between them upon photoexcitation during optical spectroscopy. IC: internal conversion, ISC: intersystem crossing. Adapted from [10].

The intensity of the incident light is reduced with each transition it causes in the sample. This decrease in intensity of the transmitted light (assuming $I_R + I_S \approx 0$) can be described using the absorption coefficient (α) and the path length (l) of the light through the sample:

$$I = I_0 e^{-\alpha l} \quad (4)$$

By dividing the absorption coefficient by the concentration (c) of the optically active compound in the (liquid) sample, the extinction coefficient (ϵ) can be used to formulate the Beer-Lambert law:

$$I = I_0 e^{-\epsilon cl} \quad (5)$$

The logarithmic form of the Beer-Lambert law is used to define the absorbance (A):^[7]

$$A = \log \left(\frac{I_0}{I} \right) = \epsilon cl \quad (6)$$

The Beer-Lambert law is only valid for low concentrations of the absorbing species ($A \leq 1$). If the concentration is too high, the absorbance is no longer linear. It is important to note that the extinction coefficient is dependent on the wavelength of the incident light. To obtain a complete absorbance spectrum of the sample, the detected intensities must be scanned over a range of wavelengths.

It is important to differentiate between absorption, absorbance, and absorptance, as each term refers to a distinct concept of the interaction between light and matter. Absorption is the general process by which a material takes in light or electromagnetic radiation. Absorbance is a logarithmic measure of how much light is absorbed by a sample and is used in spectroscopy. It depends on the optical path length and concentration. Absorptance is the fraction of incident light that is absorbed by a material, expressed as a number between 0 and 1.

2.1.2 Basic principles of a monochromator

A monochromator is an optical device used to isolate a narrow band of wavelengths from a broader spectrum of light. It typically consists of an entrance slit, collimating optics, a dispersive element, and an exit slit. Light entering through the entrance slit is collimated into a parallel beam and directed onto the dispersive element. The dispersed light is then refocused towards the exit slit, which selects a specific wavelength range as the output.

In most modern monochromators, the dispersive element is a **reflective diffraction grating**. These gratings separate light based on wavelength by diffraction and interference, following the grating equation:

$$n\lambda = d(\sin(\theta_i) + \sin(\theta_d)) \quad (7)$$

where n is the diffraction order, λ is the wavelength, d is the groove spacing, θ_i is the angle of the incidence and θ_d is the angle of diffraction.

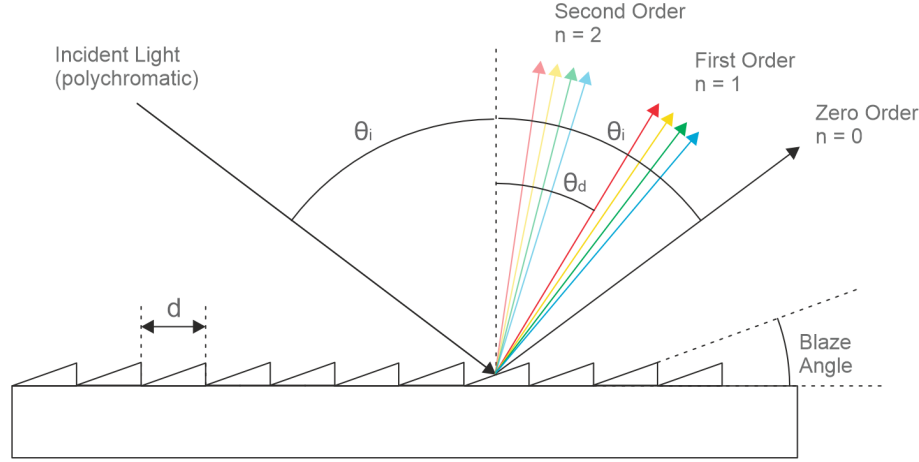


Figure 3: Schematic of a ruled reflective diffraction grating. Marked is the groove spacing (d), the blaze angle and diffractions of the 0th, 1st, and 2nd order.

To increase the efficiency for a specific wavelength and diffraction order, blazed gratings are used. These have grooves cut at a specific blaze angle, which concentrates diffracted light into the desired order. The blaze condition maximizes efficiency by directing the majority of the diffracted energy into a preferred direction. Although monochromators are often operated in the first diffraction order ($n = 1$), higher orders ($n > 1$) are also diffracted and can overlap with first-order wavelengths. Order-sorting filters are therefore commonly used to block unwanted higher-order diffractions.

The spectral resolution (R) of a monochromator describes its ability to distinguish between two closely spaced wavelengths. It depends on several factors, including the grating properties, slit widths, focal length, and optical aberrations. A higher groove density (more lines per mm), larger beam diameter (more illuminated grooves), and higher diffraction order all contribute to greater diffraction and therefore resolution:

$$R = \frac{\lambda}{\Delta\lambda} = nN \quad (8)$$

where $\Delta\lambda$ is the smallest resolvable wavelength difference and N is the number of grooves illuminated.

The actual resolution also depends on the slit width: narrower slits improve resolution but reduce the optical power reaching the detector or the sample, impacting signal-to-noise ratio.^[11]

2.2 Photoinduced Absorption Spectroscopy

PIAS is a powerful technique used to investigate long-lived excited species. It provides insight into photophysical processes that occur after optical excitation and is particularly sensitive to metastable states that persist beyond the initial excitation period.^[12] These processes can span timescales ranging from femtoseconds (fs, 10^{-15} s) to milliseconds (ms, 10^{-3} s). While ultrafast spectroscopy techniques are well-suited to probe rapid processes on femtosecond to nanosecond timescales, slower dynamics occurring on the microsecond (μ s, 10^{-6} s) to millisecond range can be studied using quasi-steady-state methods.

In the quasi-steady-state regime, the sample is excited by a modulated or pulsed pump laser beam. The modulation frequency is chosen such that a dynamic equilibrium between excitation and relaxation is established, enabling the accumulation of long-lived transient species. Although the system is not strictly in a steady state, the periodic modulation allows sensitive detection via lock-in amplification. By tuning the modulation frequency, it is possible to gain a first insight into the lifetimes of the underlying photophysical processes over extended timescales.^[5] Quasi-steady-state PIAS thus bridges the gap between ultrafast transient absorption spectroscopy and purely static techniques, providing high sensitivity to slow or rare excited-state processes that are otherwise challenging to detect.

The spectral signatures observed in PIAS measurements indicate the presence of excited states that absorb probe light, or in other words, alter the transmission spectrum. They appear as distinct signals in the $\Delta T/T$ spectrum at specific wavelength ranges, which identifies the nature of the corresponding electronic transitions.

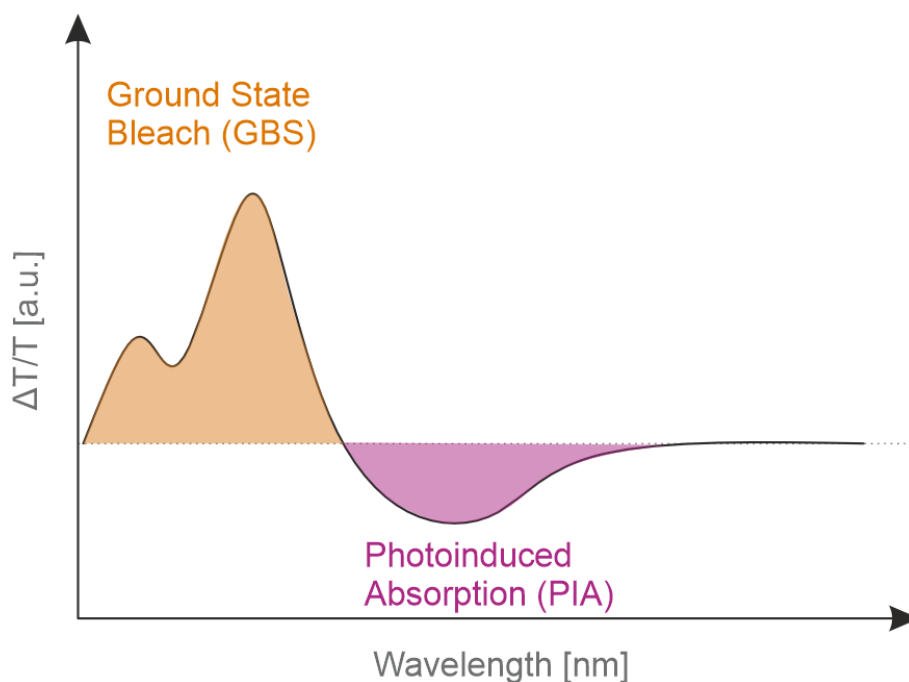


Figure 4: Spectral features of PIAS.

Figure 4 illustrates the characteristic spectral features that may be observed in PIAS, including:

- **Ground State Bleach (GSB):** A positive $\Delta T/T$ signal (orange curve). Upon excitation, a significant population of electrons is promoted from the ground state to an excited state, leading to a reduced absorption at wavelengths corresponding to ground-state transitions. As a result, the transmission of the probe beam increases in this spectral region, appearing as a positive feature in the $\Delta T/T$ spectrum.
- **Photoinduced Absorption (PIA):** A negative $\Delta T/T$ signal (purple curve). It arises from additional absorption pathways that are only accessible in the excited state, such as transitions from excited singlet or triplet states to higher-lying states. Since this leads to a decrease in probe transmission, the feature is negative. The signal amplitude is a convolution of the excited states lifetime and their concentration.

The following Jablonski diagram (Figure 5) provides an expanded view of the excitation and relaxation processes compared to Figure 2. In addition to the ground-state transitions, it includes excited-state processes such as excited-state absorptions, which are essential for understanding the spectral features observed in PIAS. Since these transitions can spectrally overlap, interpreting the resulting signals can be challenging.

Spontaneous photoluminescence (PL) contributes strongly to the detected signal. However, since PL is measured separately and subtracted during data analysis, it does not appear in the final PIA spectrum. Additionally, in PIA measurements, stimulated emission does not occur because the probe source is a lamp combined with a monochromator, which lacks the coherence required to induce stimulated processes. While population inversion can be achieved under excitation, both coherence and population inversion are necessary for stimulated emission to occur.

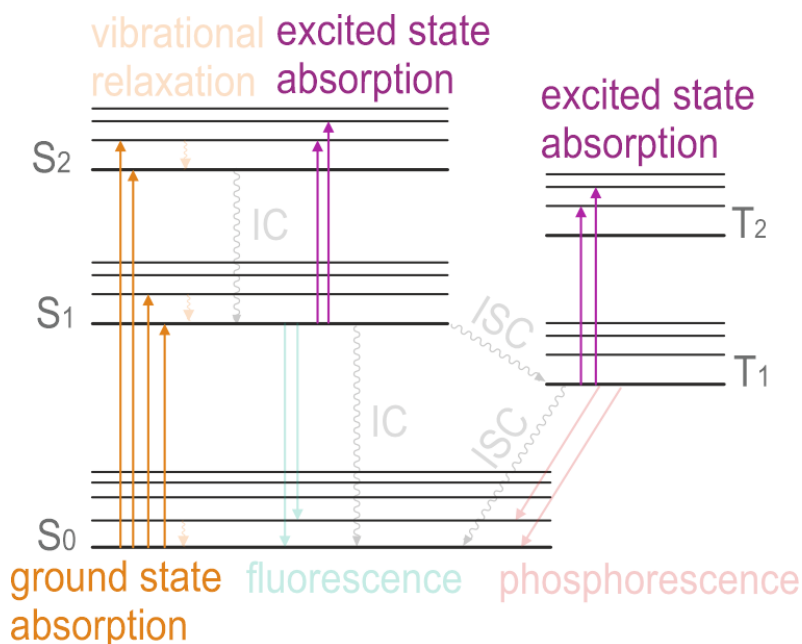


Figure 5: Expanded Jablonski diagram showing processes observed in PIAS. Adapted from [10].

Figure 6 shows the real spectra of a transient absorption measurement of a PM6:Y6 combination. PM6:Y6 can serve as an example of a real system which exhibit PIA signals. PM6 (PBDB-T-2F¹, Figure 7a) is an electron donor polymer and Y6 (BTP-4F², Figure 7b) is an electron acceptor small molecule. The PM6:Y6 bilayer (or so called bulk heterojunction film) is a common active layer in organic photovoltaic devices and is also used in this thesis as a test sample.

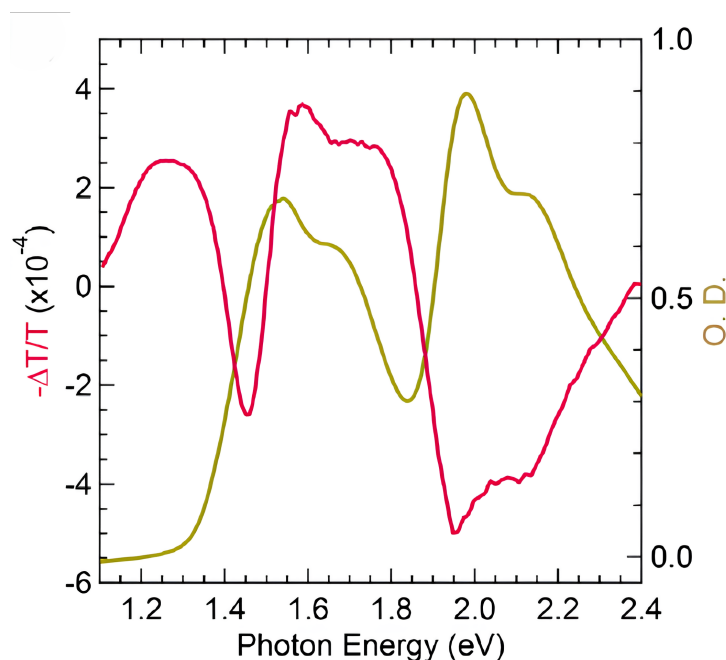


Figure 6: PIA spectra of PM6:Y6 film after 800 nm excitation, 1.5 sun probe light. [13].

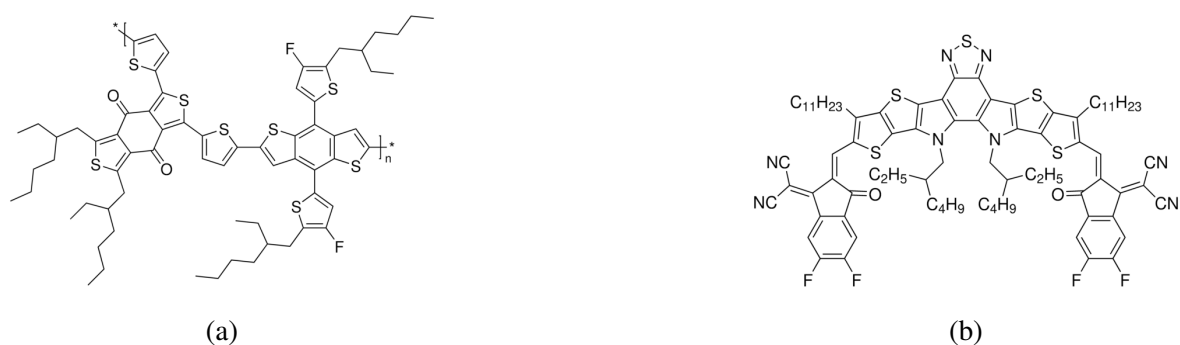


Figure 7: Chemical structures of PM6 (a) and Y6 (b).

The spectra show the negative $\Delta T/T$ signal against the photon energy in electronvolts.^[13] Similar signals were reported by [14], their corresponding wavelengths are put in brackets. The

¹Poly[[4,8-bis[5-(2-ethylhexyl)-4-fluoro-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-2,5-thiophenediyl[5,7-bis(2-ethylhexyl)-4,8-dioxo-4H,8H-benzo[1,2-c:4,5-c']dithiophene-1,3-diyl]-2,5-thiophenediyl]

²2,2'-(2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2,3'':4',5']thieno[2',3':4,5]))

range from 1.85-2.25 eV (580-650 nm) is dominated by GSB of the donor polymer PM6. The acceptor Y6 shows a GSB at 1.45 eV (830 nm). The positive signal is observed at 1.85-1.55 eV (670-790 nm) and at 1.25 eV (920 nm). It originates from the spectral overlap of PM6 hole (PM6^+) and Y6 electron (Y6^-) photoinduced absorption. The presence of PIA signals indicates that upon selective Y6 photoexcitation ($\lambda_{ex} = 800$ nm), charge/energy transfer happens between the two materials. (Figure 8)

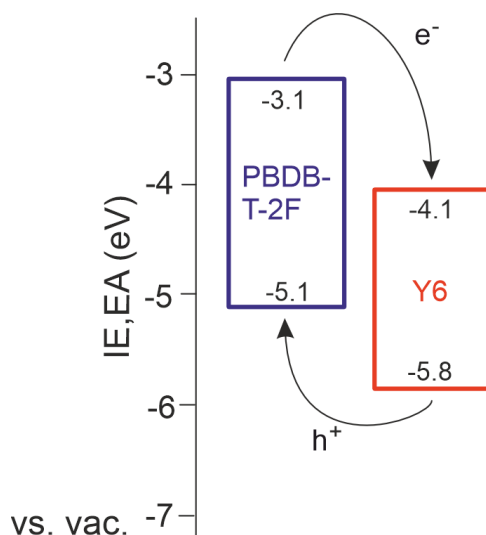


Figure 8: Energy levels (EA electron affinity, IE ionization energy) of the donor polymer (PM6, PBDB-T-2F) and the acceptor molecule (Y6). Electrons (e^-) are transferred from the donor to the acceptor. Holes (h^+) are transferred from the acceptor to the donor.^[15]

2.3 Principles of Lock-in Amplification

2.3.1 Modulation and Signal Extraction

A lock-in amplifier is a specialized electronic instrument used to extract weak signals from noisy backgrounds by using phase-sensitive detection. To use a lock-in amplifier, the signal of interest must be modulated at a known frequency. Since the signal is generated by the sample, it is not possible to modulate the signal directly. Instead, the modulation is applied to the excitation light source that induces the signal. This modulation can be achieved by using a mechanical chopper with a frequency reference signal (TTL) or by using an electronic oscillator, like a sine wave generator of the lock-in amplifier from Stanford Research Systems (SRS SR860). The reference signal (r) from the sine wave generator can be described as:

$$r = A \cdot \sin(\omega t) \quad (9)$$

where A is the amplitude, t is the time, and ω is the circular frequency defined using the frequency (f):

$$\omega = 2\pi f \quad (10)$$

During the experiment the signal (s) is generated, which contains a phase shift (ϕ) caused by the experimental setup and electronics:

$$s = a_1 \cdot \sin(\omega t + \phi) \quad (11)$$

The amplitude of the signal (a_1) in photoinduced absorption experiments is generally very small and is buried in background noise (n). As depicted in Figure 9, the superposition of signal and noise ($s+n$) and the reference signal (r) is used as inputs to the lock-in amplifier.

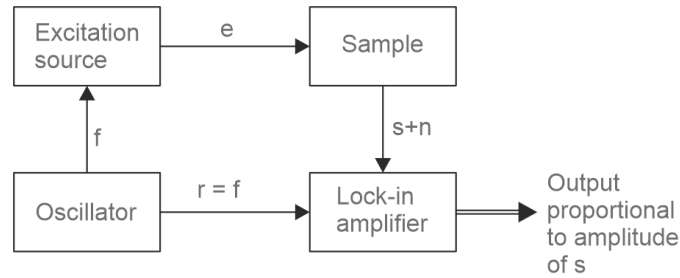


Figure 9: Basic concept of the lock-in technique with an excitation (e) modulated with the frequency (f). The signal (s) is extracted from the noise (n) using a lock-in amplifier locked at the frequency of the modulation. Adapted from [16].

The lock-in amplifier then uses a multiplication unit to generate the product $([s + n] \cdot r)$ of the two inputs (Figure 10). A low-pass filter is used to average the product:

$$u = \frac{1}{\tau} \int_0^{\tau} (s + n) \cdot r \, dt \quad (12)$$

where τ is the time constant of the low-pass filter.

Because of the random nature of the noise, it is filtered by the averaging process of the low-pass filter:

$$\frac{1}{\tau} \int_0^{\tau} n \cdot r \, dt = 0 \quad (13)$$

For effective filtering, the time constant needs to be much larger than the signal period. Typically, a time constant of 300 ms up to several seconds is chosen in the photoinduced absorption experiments.

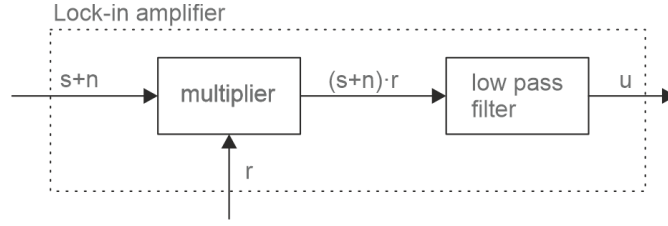


Figure 10: Extraction of the signal by multiplying the noisy signal with the reference signal and integrating using a low pass filter. Adapted from [16].

The filtered product can be expressed as:

$$s \cdot r = A \cdot a_1 \sin(\omega t + \phi) \sin(\omega t) \quad (14)$$

Using the following trigonometric relation:

$$\sin(x) \sin(y) = \frac{1}{2} [\cos(x - y) - \cos(x + y)] \quad (15)$$

Equation 14 can be simplified:

$$s \cdot r = \frac{a_1 A}{2} [\cos(-\phi) - \cos(2\omega t + \phi)] \quad (16)$$

Now the product can be integrated:

$$u = \frac{1}{\tau} \int_0^{\tau} s \cdot r \, dt = \frac{a_1 A}{2} \int_0^{\tau} \cos(-\phi) \, dt - \frac{a_1 A}{2} \int_0^{\tau} \cos(2\omega t + \phi) \, dt \quad (17)$$

With a sufficiently long time constant, the second integral will become zero, because the positive and negative contributions will cancel each other out.

$$u = \frac{a_1 A}{2\tau} \int_0^{\tau} \cos(\phi) \, dt = \frac{a_1 A}{2} \cos(\phi) \quad (18)$$

The output signal of the low-pass filter is a DC signal proportional to the signal amplitude and the cosine of the phase shift.^[16] This allows the extraction of weak signals in a noisy environment. The only noise that is not filtered occurs when the noise is also modulated at the same frequency as the signal.

2.3.2 Phase-Sensitive Detection and Noise Filtering

Since the output signal is proportional to the cosine of the phase shift (see Equation 18), the technique is referred to as phase-sensitive detection. For a sensitive detection, signal and reference need to be perfectly in-phase ($\phi = 0^\circ$), when the two signals are not in phase, the measured signal can be very weak. When the signal and the reference are completely out of phase ($\phi = 90^\circ$), the output can become zero, even when there is a signal. This problem can be solved by phase-sensitive detection. Using a second lock-in amplifier and a phase shifter to shift the phase of the reference signal by 90° , the out-of-phase component of the signal can be measured. By measuring both in-phase (X) and out-of-phase (Y) components of the signal, a vector computer can be used to calculate the amplitude (R) and phase (θ) of the signal:

$$R = \sqrt{X^2 + Y^2} \quad (19)$$

$$\theta = \arctan\left(\frac{Y}{X}\right) \quad (20)$$

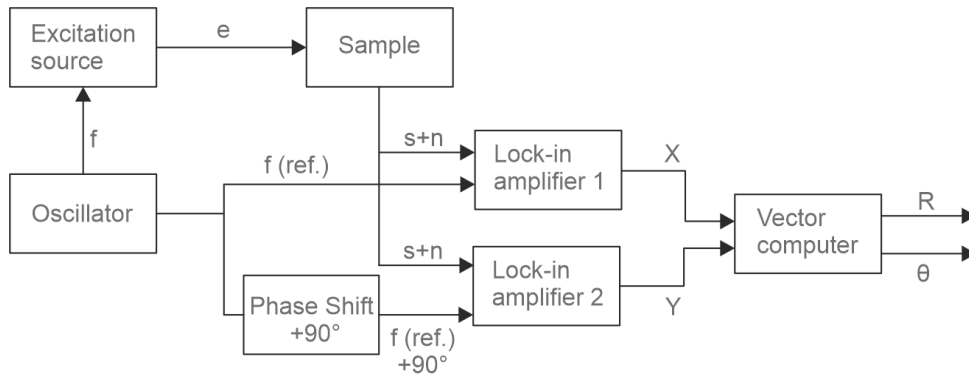


Figure 11: Phase sensitive detection enables to measure in-phase (X) and out-of-phase (Y) components of the signal. A vector computer is used to calculate the amplitude (R) and phase (θ) of the signal. Adapted from [16].

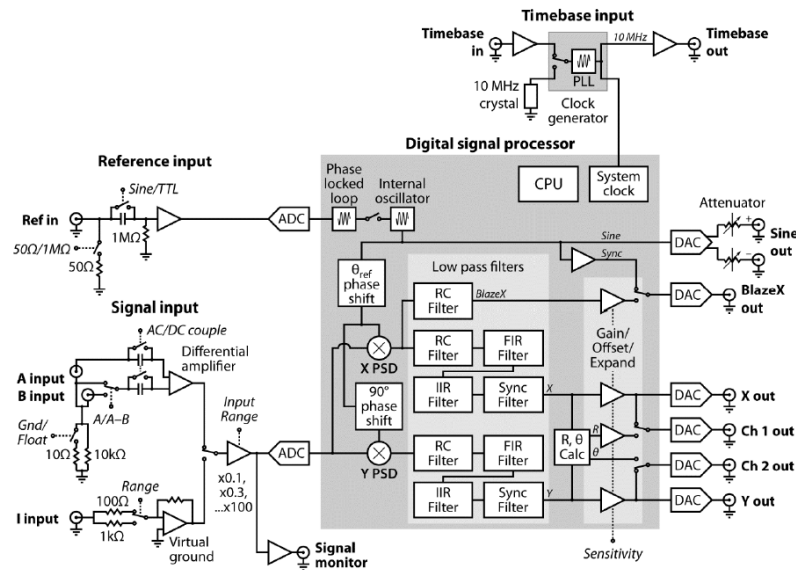


Figure 12: Simplified block diagram of the Stanford Research Systems lock-in amplifier SR860. [17]

Modern lock-in amplifiers, such as the SR860 from Stanford Research Systems, employ two phase-sensitive detectors (PSDs) and a variety of filters to extract the desired signal while effectively suppressing noise. While Equation 18 describes an idealized scenario in which the filter behaves like a perfect rectangular function in frequency space, real filters exhibit more complex roll-off characteristics (Figure 13, 14).

In practice, filters are often constructed from cascaded single-pole resistor-capacitor stages (RC). Increasing the number of such stages improves the sharpness of the cutoff, yielding better noise suppression. However, the non-ideal nature of these filters requires longer time constants to achieve sufficient noise reduction and accurate signal integration.

Lock-in amplifiers allow users to configure both the time constant and the low-pass filter slope, providing control over the trade-off between signal stability and response time. Additionally, modern instruments like the SR860 offer digital filtering options—such as advanced filtering algorithms and Gaussian FIR filters—which can significantly reduce settling times compared to traditional analog RC filters, while maintaining effective noise rejection (Table 1 and Figures 13, 14).

Table 1: Speed of the different filters to settle to within 1% of the final value. [17]

Time to settle to within 1% of final value (in time constants)			
Stages	RC	Gaussian	Linear Phase
1	4.6	2.3	4.6
2	6.6	4.0	4.4
3	8.4	5.6	4.8
4	10.0	7.1	5.4

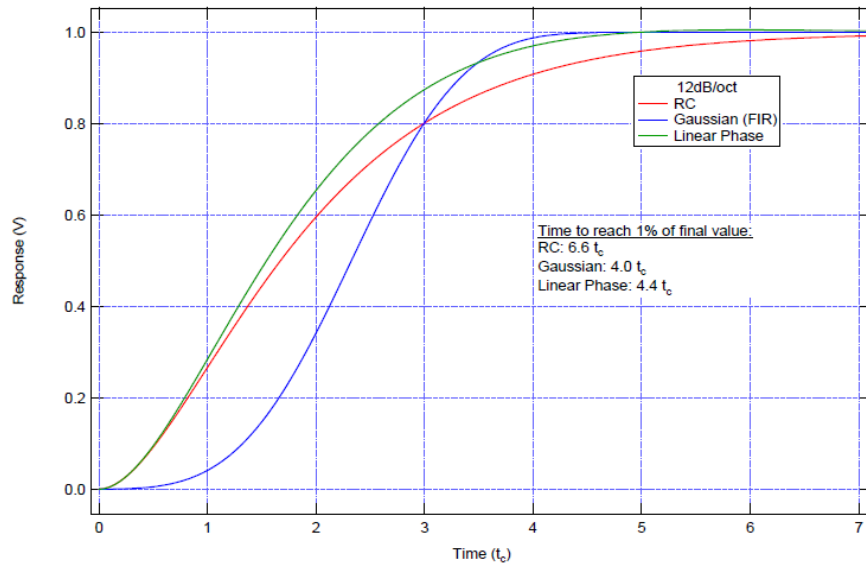


Figure 13: Step response graphs of the 12dB/oct filter slopes. Using time constants below 3 s the Gaussian (FIR) filter is used. [17]

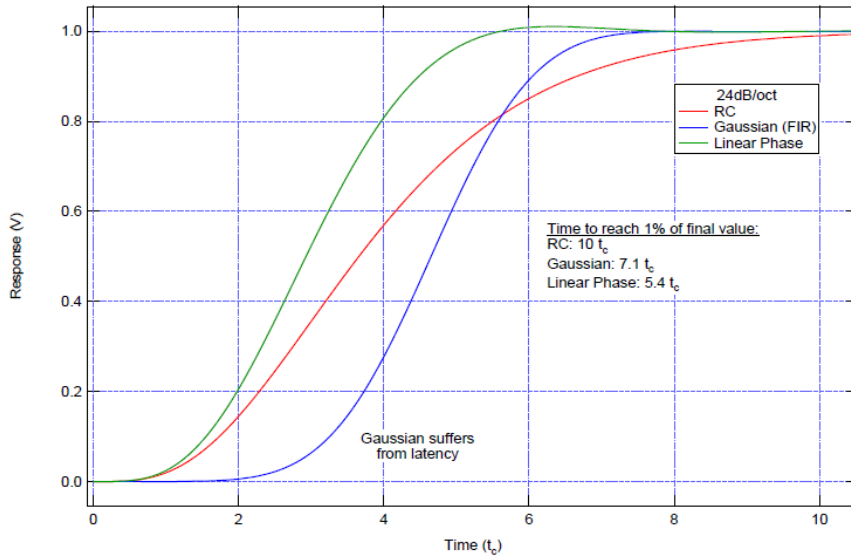


Figure 14: Step response graphs of the 24dB/oct filter slopes. Using time constants below 3 s the Gaussian (FIR) filter is used. [17]

3 Experimental Setup

3.1 Overview of the Experimental Setup

The optical components of the experimental setup can be divided into two separate beam paths: the probe beam (white light) and the pump beam (laser). The probe beam is used for transmission (T) and the photoinduced absorption + photoluminescence (PIA+PL) experiments, while the excitation beam is used for photoexcitation of the sample in the photoluminescence (PL) and PIA+PL experiments. The complete setup is shown in Figure 15.

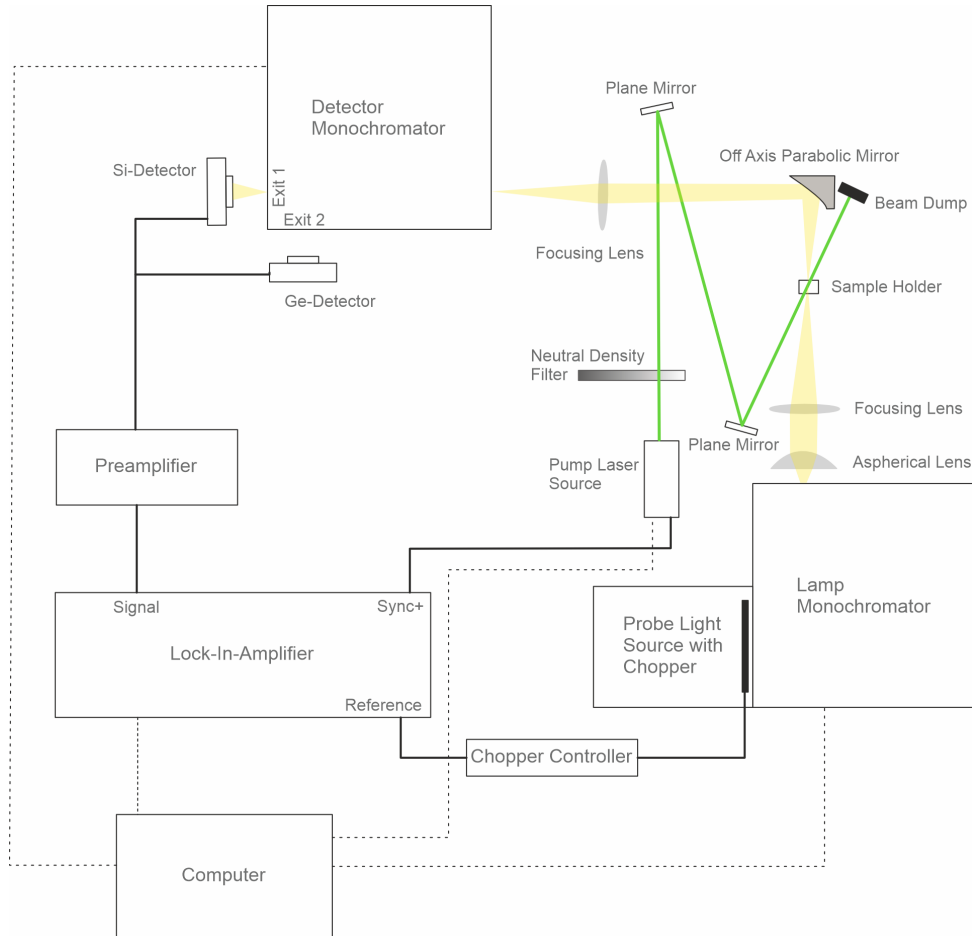


Figure 15: Scheme of the PIA setup including optical components and the detection system.

3.2 Optical Components

To fully understand the experimental setup, this section will describe all important parts of the optical setup. The optical components of the setup include a light source (probe), focusing optics, an excitation laser (pump), a mechanical chopper, two monochromators, a sample holder, and the detection system. All optical components of the experimental setup are fixed on an optical table (Smart Table Newport) to reduce mechanical vibrations and retain the alignment of the components. To prevent the laser beam from leaving the optical table, a black laser safety enclosure is placed around the setup.

3.2.1 Light Source (Probe)

The polychromatic light (probe) used in transmission and photoinduced absorption experiments is provided by an 'ILD-QH-IR-CH-Arrest' dual light source from Bentham Instruments. The schematic construction of the light source is shown in Figure 16.

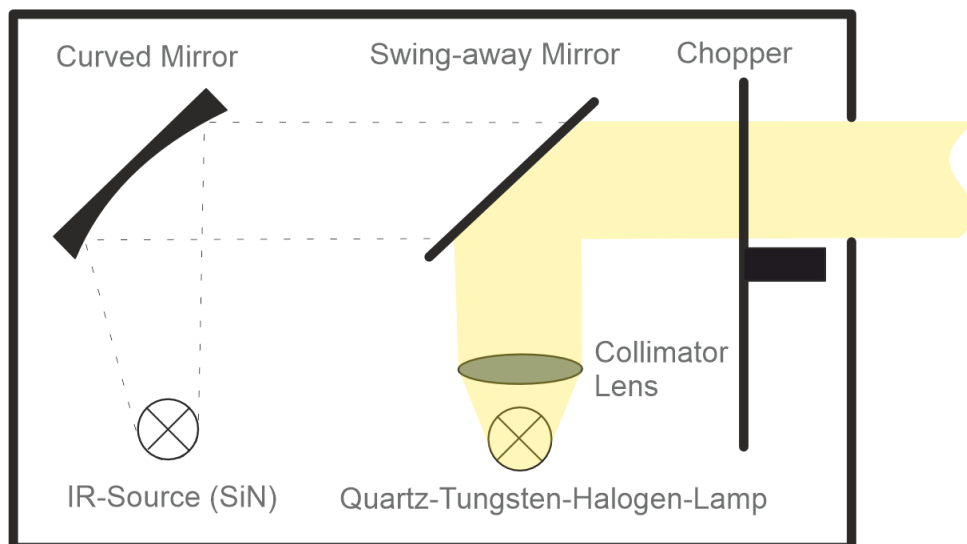


Figure 16: Scheme of the polychromatic probe light source with the swing away mirror in the position to select the quartz tungsten halogen lamp.

The light source consists of a quartz tungsten halogen lamp (QTH-lamp) and a SiN IR emitter. The output beam can be selected by a solenoid based swing away mirror which can be powered by 12 V provided from the directly connected monochromator. The powered state of the mirror is used to select the IR-emitter. The spectral output of both light sources is shown in Figure 17.

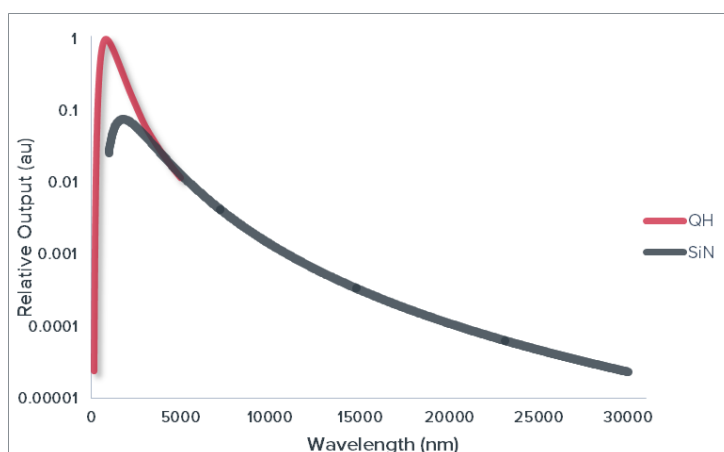
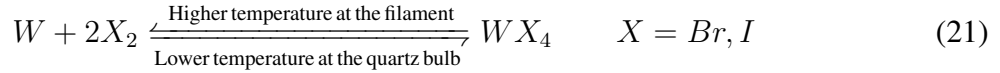


Figure 17: Spectral output of the QTH-lamp and IR light sources. [18]

The QTH-lamp lamp has a spectral range from 300 nm to 2500 nm and is powered by 8.5 A from a Bentham 610 power supply with a power input of 100 W. The lifetime of the lamp can be extended by turning it on for at least 20 minutes to start the tungsten halide cycle ^[19]. This

allows the lamp to heat up and deposit the evaporated tungsten back onto the filament using a small amount of halogen such as bromine or iodine (Equation 21):



To ensure a stable light output, the lamp should be turned on and allowed to warm up before a measurement is started.

A QTH-lamp is used, due to its smooth spectral output compared to Xe- and Hg-lamps. (Figure 18) Additionally, QTH-lamp provides a more stable output than arc-lamps.

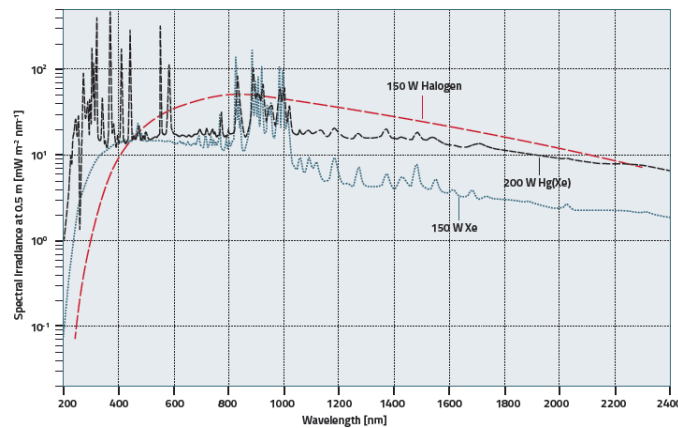


Figure 18: Spectral output of a halogen lamp in comparison with Xe and Hg lamps. [20]

The SiN IR emitter has a spectral range from 1 μm to 30 μm and can be powered by 3.3 A with a power input of 40 W. Both light sources can be approximated as black body radiators, because the light is generated by thermal radiation. The heat of the lamp is dissipated by a fan, which is powered by 12 V from the Bentham 610 power supply.

3.2.2 Mechanical Chopper

The mechanical chopper is used to modulate the probe beam for the transmission experiment. The chopper is built into the light source and consists of a rotating slotted disc. The magnetic disc contains five slots, and is arrested by an electromagnet in an open position, when the chopper head is powered and the modulation is turned off. The probe beam can be modulated with a frequency from 10 Hz to 500 Hz, by setting a potentiometer on the chopper head. The frequency of the chopper can be used as a reference signal for the lock-in amplifier in the detection system.

3.2.3 Excitation Laser (Pump)

The excitation laser used in the photoluminescence (PL) and photoinduced absorption + photoluminescence (PIA+PL) experiments is provided by a laser from Hübner Photonics (Cobolt 06-01 Series). The laser is a continuous wave laser with a fixed wavelength. Currently available wavelengths are 405 nm, 520 nm and 660 nm. To switch the wavelength of the excitation laser,

the laser head needs to be exchanged. The power output depends on the selected wavelength and can be reduced by a variable neutral density filter (ND-filter) directly after the laser source. The laser is mounted on a heat sink to prevent overheating. The laser is powered by a 12 V power supply and is modulated by a digital signal (Sync +) from the lock-in amplifier. To switch the mode of the laser from constant power to power modulation, the laser has to be connected to the computer via USB and the 'CoboltMonitor' software has to be used to set the laser mode. The laser can be modulated digitally with a frequency up to 10 MHz. The input signal is terminated in the laser with an impedance of 2 k Ω . The low input voltage ranges from 0 V to 0.8 V, while the high input voltage ranges from 2 V to 5 V. An analog power modulation is only possible up to 10 Hz. To avoid the detection of electrical noise from the power grid, the laser should not be operated at frequencies, which are multiples of 50 Hz. The laser has an internal shutter, which needs to be opened manually, when operating the laser.

3.2.4 Monochromators

The setup of two monochromators: one after the probe light source ('Lamp-Mono') and one after the sample holder ('Detector-Mono'). The monochromators are from Bentham Instruments (Model MSH-300). The monochromators are used to scan the wavelength of the detected light and to ensure that the wavelength of the probe light is not creating unwanted excitations in the sample. The monochromators are designed as optical Czerny-Turner monochromators with three grating positions. All slits of both monochromators are motorized and can be controlled by the LabVIEW program. The Lamp-Mono has a single exit and the Detector-Mono can be switched between two exit slits, using a swing away mirror. A schematic beam path of the detector monochromator is shown in Figure 19.

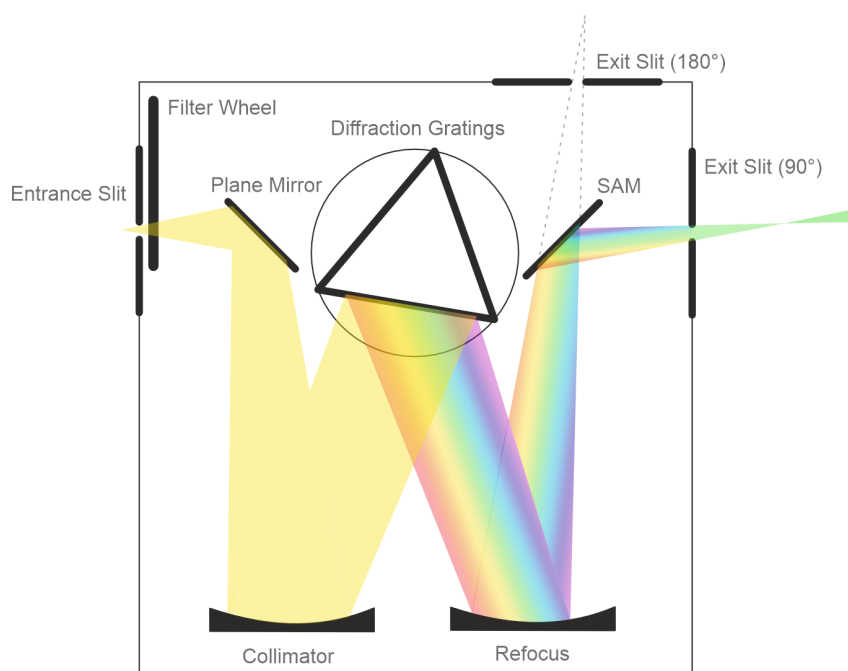


Figure 19: Schematic beam path of the detector monochromator with the swing away mirror in the 90° position.

Both monochromators have the same set of gratings mounted on their rotating turret. The installed gratings are listed in Table 2.

Table 2: Gratings used in both monochromators.

Turret Position	Grating	Type	Wavelength range	Lines per mm (mm ⁻¹)	Blaze wavelength (nm)	Theoretical resolution (nm) at 1 mm slit
1	MSG-T-1200-500	ruled	300 nm - 1.1 μ m	1200	500	2.5
2	MSG-T-600-1250	ruled	0.8 μ m - 2.4 μ m	600	1250	5
3	MSG-T-300-3000	ruled	1.7 μ m - 5.5 μ m	300	3000	10

Each grating has a different wavelength range and resolution, so it is important to select the correct grating. The grating efficiency is changing over the wavelength range, which is shown in Figure 20. The grating efficiency is defined as the ratio of the diffracted light intensity to the incident light intensity.

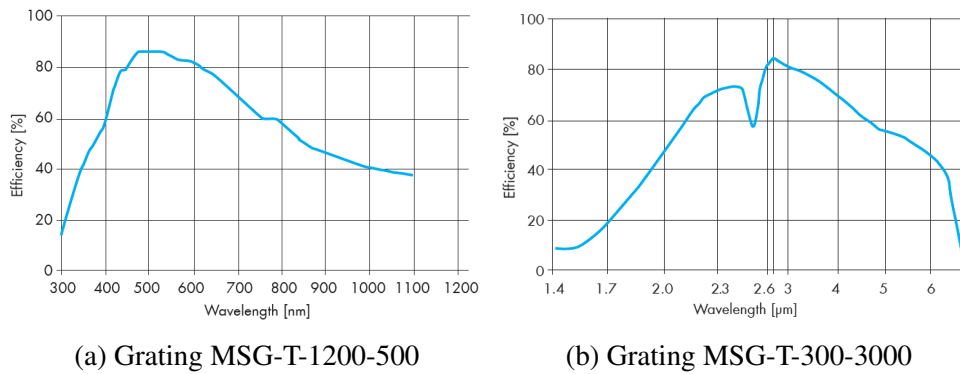


Figure 20: Grating efficiency of two of the gratings used in the monochromators.[21]

To remove second or higher order diffractions from the selected wavelength, a filter wheel with 5 different long pass order sorting filters is placed inside the monochromator. The first order diffraction of the selected wavelength is used as the output. The output of the monochromator can contain shorter wavelengths than required, because second or higher order diffractions of shorter wavelengths than the selected wavelength can appear at smaller angles than the first order diffraction of longer wavelengths. It is therefore useful to use long pass filters to remove these unwanted wavelengths. The installed filters on the filter wheel are shown in Table 3, positions 1 and 7 are open positions without a filter and position 8 is a shutter to block the light path.

Table 3: Positions of the built-in filter wheel with their installed order sorting filters.

Position	Filter	Wavelength used [nm]
1	OPEN	0
2	OS400	400
3	OS700	700
4	OS1250	1250
5	OS2000	2000
6	OS3600	3600
7	OPEN	-
8	SHUTTER	

3.2.5 Focusing Optics

The output beam of the monochromator is highly divergent, so it is necessary to collimate the beam before it is focused on the sample. The collimation is accomplished by a plano-convex aspheric lens directly after the monochromator. The collimated beam is then focused on the sample. Because the probe beam is an image of the slits of the monochromator it appears on the sample as a rectangular shape. An off-axis parabolic mirror is used to change the direction of the transmitted beam and to recollimate the beam after it has passed through the sample. A plano-convex lens is used to focus the transmitted light on the entrance slit of the detector monochromator.

3.2.6 Sample Holder and Cuvette

The sample holder is positioned to allow the sample to be aligned in the focal plane of the probe beam. The excitation laser is focused on the sample in a way that the excited volume of the sample is fully contained in the probe beam. Liquid samples can be measured in a quartz cuvette and films on a transparent substrate can be fixed in the sample holder position. To measure the full spectral range of the probe beam, it is necessary to use a quartz cuvette like the *Starna Cell* made of Spectrasil quartz (UV-VIS) or Infrasil quartz (IR) to avoid absorption by the cuvette material.

3.3 Detection System

The detection system is used to detect the intensity of the light transmitted through and emitted by the sample. The detection system consists of a Si-biased photodiode, a Ge-biased photodiode, a low noise current preamplifier and a lock-in amplifier. Due to the weak signal of the photoinduced absorption experiment a lock-in technique is used to filter the signal from the noise. The necessary modulation of the probe beam during a transmission measurement is provided by the mechanical chopper. To demodulate the transmission signal the reference signal of the mechanical chopper is used. The modulation of the excitation laser is provided by a direct digital modulation, using the lock-in amplifier as a digital signal generator. To demodulate the photoluminescence and photoinduced absorption signal, the internal frequency of the lock-in amplifier is used.

3.3.1 Si-biased Photodiode

To detect light in the range of 320 nm to 1100 nm, a Si-biased photodiode from Thorlabs (Model DET100A2) is used. Silicon can absorb photons with an energy greater than its bandgap, which is 1.1 eV at room temperature.^[22]

The responsivity of the photodiode is shown in Figure 21.

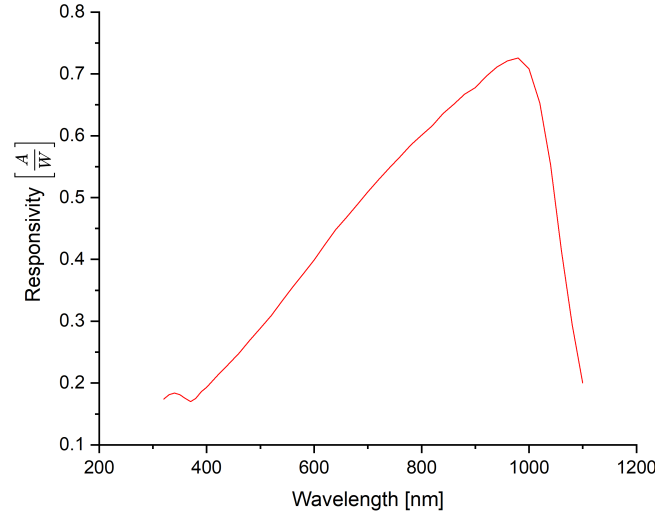


Figure 21: Responsivity of the Si-biased photodiode in dependence of the wavelength. [23]

The responsivity (R) of the photodiode is defined (Equation 22) as the ratio of the generated photocurrent (I_{PD}) to the incident optical power (P):

$$R(\lambda) = \frac{I_{PD}}{P} \quad (22)$$

The responsivity of the detector drops significantly with wavelengths higher than 1000 nm so it is recommended to use the Ge biased detector for higher wavelengths. It is important to operate the photodiode in the photoconductive mode, where an external reverse bias voltage is applied to the photodiode. This mode is selected by switching the power switch on the photodiode to the 'on' position. If the switch is in the 'off' position, the photodiode is operated in the photovoltaic mode, where no external bias voltage is applied. To measure consistently, it is important to operate the photodiode in the photoconductive mode, due to a higher and generally more linear response. The bias voltage of 10 V is provided by a 12 V battery regulated by internal electronic components. Using a power supply can lead to increased noise in the signal due to the electrical noise from the power grid. The signal of the photodiode needs to be terminated with an impedance of 50 Ω , this is achieved by connecting the photodiode with a coaxial cable to the 50 Ω BNC input connector of the preamplifier.^[23]

3.3.2 Ge-biased Photodiode

The Ge-biased photodiode from Thorlabs (Model DET50B2) is used to detect signals in the range of 800 nm to 1800 nm. The Ge-detector can detect photons with lower energy, because the band gap of germanium (0.66 eV) ^[24] is smaller than the band gap of silicon. The responsivity of the Ge-biased photodiode is shown in Figure 22. Here, the sensitivity drops significantly with wavelengths higher than 1600 nm. It is not recommended to use this detector for the detection of higher wavelengths. The Ge-biased photodiode is operated in the photoconductive mode, where a bias voltage of 5 V is applied to the photodiode.

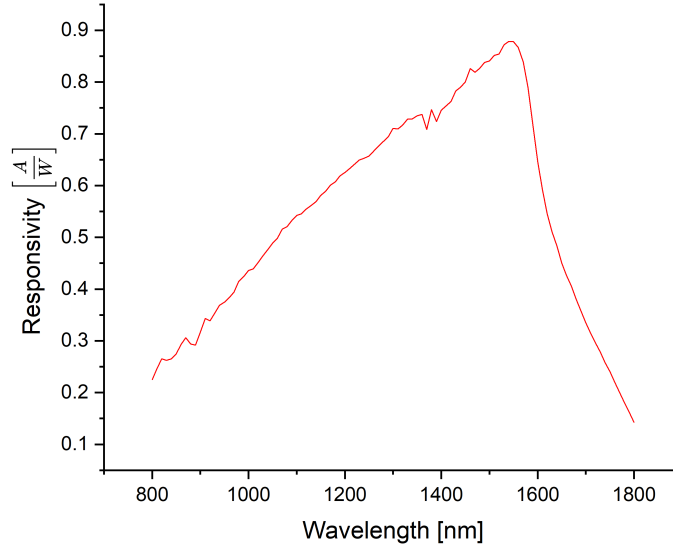


Figure 22: Responsivity of the Ge-biased photodiode in dependence of the wavelength. [23]

3.3.3 Preamplifier

To amplify the signal of the photodiodes, a low noise current preamplifier from Stanford Research Systems (Model SR570) is used. This preamplifier is used to generate a voltage output signal proportional to the input current of the photodiode. This voltage output signal is then used as the input signal for the lock-in amplifier. The sensitivity of the preamplifier can be adjusted in a range from 1 mA/V to 1 pA/V. The setting needs to be adjusted manually to prevent an overload of the preamplifier or the lock-in amplifier. The output impedance of the preamplifier is $50\ \Omega$. The input impedance of the lock-in amplifier is $10\ M\Omega$. The gain of the preamplifier is calibrated for high impedance loads.^[25]

3.3.4 Lock-in Amplifier

To demodulate and measure the preamplified signal from the photodiode, a lock-in amplifier from Stanford Research Systems (Model SR860) is used. The output of the preamplifier is connected to the A input on the front panel of the lock in amplifier. If a transmission experiment is conducted, the reference signal from the mechanical chopper is connected to the reference input. If a photoluminescence or photoinduced absorption experiment is conducted, the internal frequency of the lock-in amplifier is used as the reference signal, since in this case the internal frequency is used to digitally modulate the excitation laser. The laser is connected to the BlazeX output on the rear panel of the lock-in amplifier. The measured data of the phase sensitive detection is read by the computer via a USB connection. All important parameters and functions (e.g. time constant, filter slope, reference source, sync+ output, autophase, autorange, autoscale) of the lock-in amplifier can be set/called via the LabVIEW program (see section 5).

4 Measurement Procedure and Data Processing

4.1 Laser Safety

In order to use a laser, the person performing the measurement must have completed laser safety training. The 'Hübner Photonics Cobolt-06' lasers are classified as class 3B lasers.^[26] When the laser is turned on, the laser warning light needs to be turned on and suitable eye protection should be used. When the laser is not in use, the beam path of the laser should be blocked with a beam stop and the internal shutter of the laser should be closed manually. To prevent the laser beam from leaving the optical table, an enclosure is placed around the optical setup. If the laser needs to be realigned, the power of the laser should be reduced to minimal visible intensity/power using the 'CoboltMonitor' software.

4.2 Measurement Procedure

4.2.1 Initial Setup

To use the setup the following steps must be performed:

1. Turn on the Bentham 610 power supply. This will automatically power the cooling fans of the QTH-IR Lamp.
2. Check if the right current is selected on the front panel of the Bentham 610 Power Supply (QTH: 8.5 A; IR: 3.3 A) and turn on the light source by pressing the 'Output' button. The lamp needs to be turned on at least 20 min before a measurement is started.
3. Turn on the lock-in amplifier, current preamplifier, Si-biased detector, Ge-biased detector, both monochromators and the chopper head.
4. Start the computer and open the 'PIA_Launcher.vi' LabVIEW program. The program needs to be started by pressing the 'Run' arrow.
5. Select the VISA-resource name of the lock-in amplifier in the drop-down menu.
6. Press the 'Init' Button in the Initialisation frame (Figure 23) to initialize both monochromators and reset the lock-in amplifier.

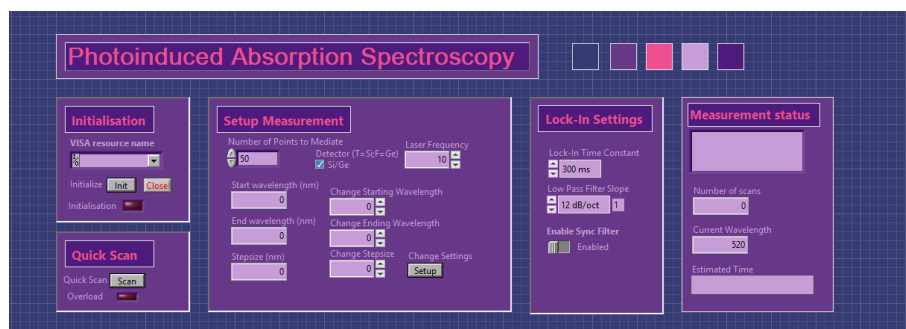


Figure 23: Front Panel (top part) of the PIA_Launcher.vi program.

The system is initialized, when the indicator light turns on. The settings of the lock-in amplifier can be changed in the 'Lock-In Settings' frame and the measurement parameters can be set in the 'Setup Measurement' frame (Figure 23). To apply the wavelength settings of the measurement, the 'Setup' button needs to be pressed. The change was successful if the 'Start-, End-wavelength and Stepsize' values are shown and the 'Number of scans' and 'Estimated Time' values in the 'Measurement status' frame are displayed.

4.2.2 Sample Alignment

To start a measurement, the sample must be placed correctly at the sample position. To measure liquid samples, the sample needs to be prepared inside a cuvette ($d = 1\text{ mm}$ or 10 mm). The cuvette is then fixed in the sample holder. To align the sample, the 'Monochromator Control' software from 'QuantumDesign' can be used to set the wavelength of the first monochromator to 0 nm . The reflective grating of the monochromator acts as a mirror in this position, and the white light can be used to align the sample, so the sample is positioned in the focused area of the beam. To align the laser, it needs to be turned on using the 'CoboltMonitor' software (1 mW constant power for alignment). The position of the laser beam can be varied by adjusting the pitch and yaw screws. It is important that the volume of the laser pumped sample is contained in the volume of the white light probe.

When films are measured, the substrate can be fixed in the sample holder position. The sample can be aligned using the probe beam and the same alignment procedure has to be repeated.

4.2.3 Starting a Measurement

To start a measurement, the setup needs to be modified depending on the type of measurement to be performed. The following sections describe the different types of measurements and their modifications. When the setup is initialized, the measurement parameters are set, the sample is aligned and the setup is modified accordingly, the measurement can be started by pressing the 'Measure' button below the title of the according experiment (Figure 24). After starting the measurement the user is prompted to choose a file name and location to save the measured data. It is recommended to choose a name, that contains all important settings of the measurement. Table 4 is providing an example of a good file name.

Table 4: Recommended template to name the measurement output file.

Example name	T_	IR140_DMSO_	800-1500nm_	10nm_	300ms_	12dBoc_	3N_	2uAV_	45Hz_	Ge
Description	Type of measurement	Sample name (+ Solvent)	Wavelength range	Stepsize of the scan	Lock-in time constant	Lock-in filter slope	Number of mediated points	Preamplifier sensitivity	Modulation frequency	Used detector

During the measurement, the mean values (X, Y, R, Theta) of each scanned wavelength is displayed and the mean X and Y values are plotted (Figure 24). The measurement can be stopped by pressing the 'Abort' button.

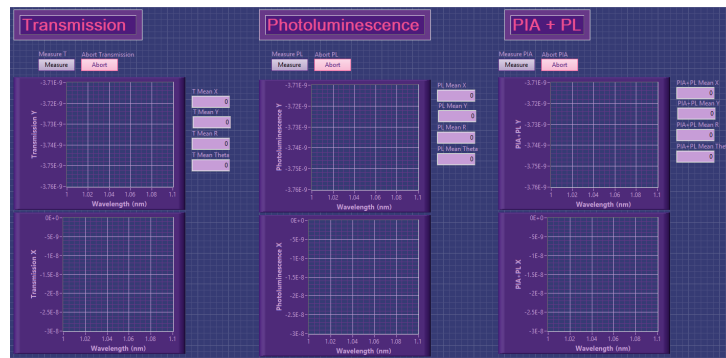


Figure 24: Front Panel (lower part) of the PIA_Launcher.vi program.

4.2.4 Transmission Measurement

To measure the probe beam transmission of the sample, the probe light needs to be modulated by the mechanical chopper. The modulation frequency needs to be set manually on the chopper head. The frequency can be varied but should not be a multiple of 50 Hz to avoid electrical noise from the power grid. A typical setting is 45 Hz. The frequency of the chopper is used as the external reference frequency of the lock-in amplifier. For the transmission experiment, the laser is turned off and the beam path of the laser is closed. The modifications of the setup are shown in Figure 25.

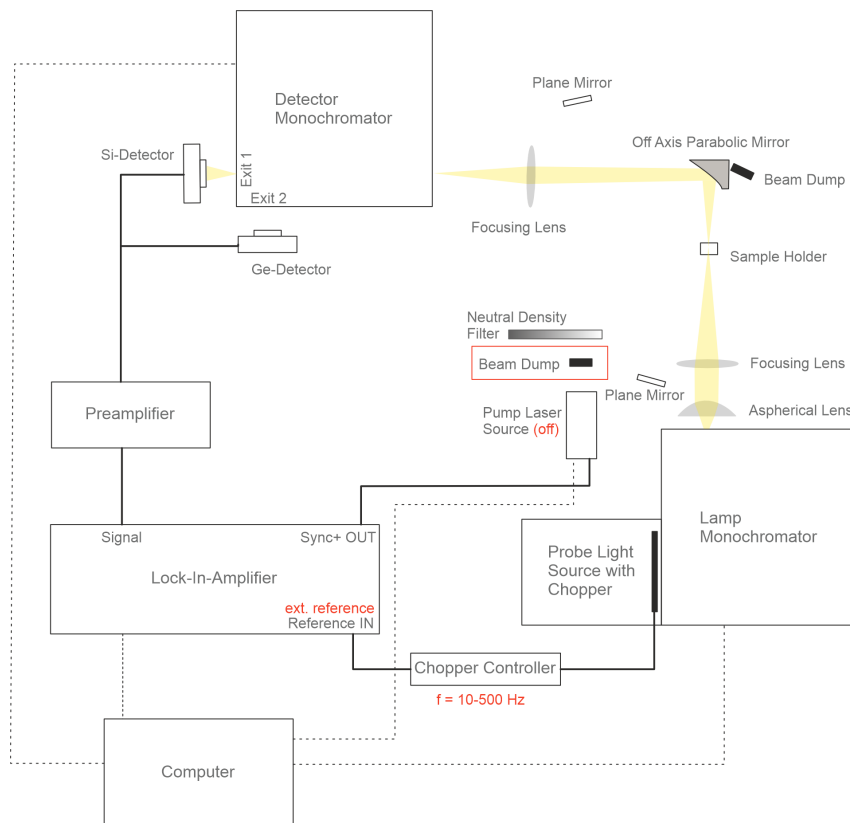


Figure 25: Schematic experimental setup to measure transmission. Important modifications of the setup are marked in red.

The setup can be used additionally to measure Absorption spectra. An additional transmission measurement with a cuvette containing only the used solvent or a blank transparent substrate is necessary to evaluate equation 6.

4.2.5 Photoluminescence Measurement

To measure the photoluminescence of the sample, only the pump beam is used to excite the sample. Using the 'CoboltMonitor' software, the laser needs to be turned on and changed to the power modulation mode using full power. The internal shutter of the laser needs to be opened and the key on the laser head needs to be turned to power the laser. The power reaching the sample can be varied by rotating the neutral density filter. The filter should be adjusted before the measurement is started and should not be rotated when the measurement is running. The laser is modulated digitally using the internal frequency of the lock-in amplifier. The probe beam needs to be blocked by a beam dump. The frequency is adjusted using the LabVIEW program. The modifications of the setup are shown in Figure 26.

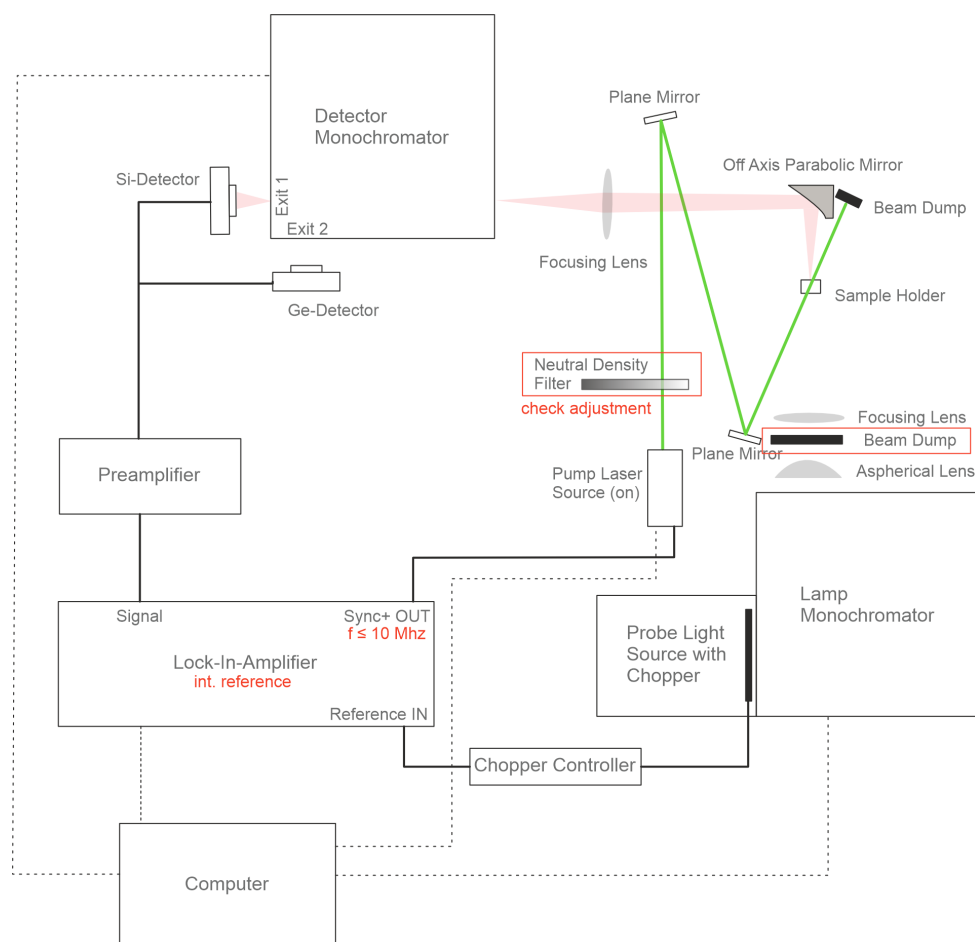


Figure 26: Schematic experimental setup to measure photoluminescence. Important modifications of the setup are marked in red.

4.2.6 Photoinduced Absorption and Photoluminescence Measurement

A modulated pump beam and a continuous probe beam are used to measure PIA+PL. The setup of the pump beam is identical to the photoluminescence experiment. The probe beam needs to be opened and the modulation of the mechanical chopper needs to be turned off. The modifications of the setup are shown in Figure 27.

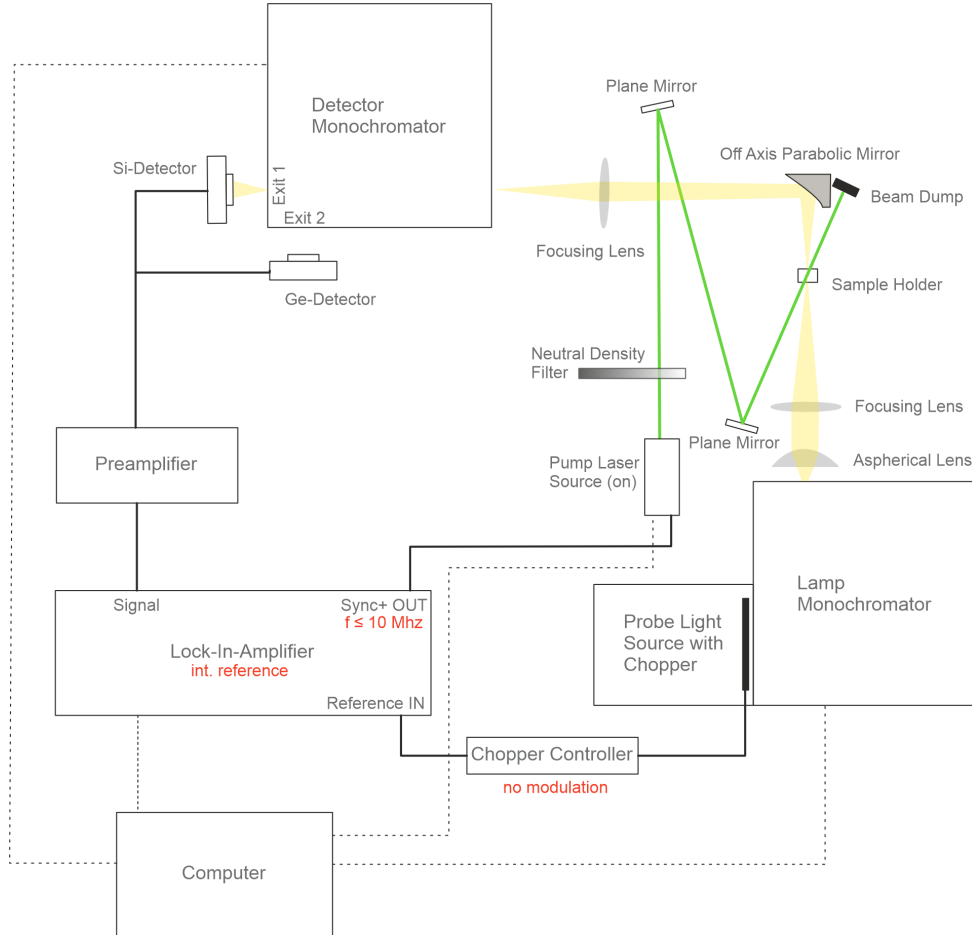


Figure 27: Schematic experimental setup to measure photoinduced absorption and photoluminescence. Important modifications of the setup are marked in red.

4.3 Data Processing

The measured data of each experiment is saved in a comma separated value (CSV) file. The first column contains the wavelength in nanometers, the next four columns contain the mean values of the lock-in amplifier (X, Y, Amplitude (R), Phase (Θ)) and the last column contains the temperature of the sample. The last column is not implemented in the program yet, but can be added when a temperature sensor is added to the setup. To extract the photoinduced absorption signal ($\frac{\Delta T}{T}(\lambda)$) from the measured data, the following equation is used:

$$\frac{\Delta T}{T}(\lambda) = \frac{(PIA + PL)(\lambda) - PL(\lambda)}{T(\lambda)} \quad (23)$$

where $T(\lambda)$ is the transmission of the sample without the pump beam (Transmission experiment), $(PIA + PL)(\lambda)$ is the amplitude of the sample measured in the photoinduced absorption and photoluminescence experiment and $PL(\lambda)$ is the amplitude of the sample measured in the photoluminescence experiment.

5 Implementation of the Measurement Control Software

The experimental setup is controlled by a LabVIEW program, which can operate the monochromators and the lock-in amplifier to perform the experiments and record the data. The laser mode is controlled by the 'CoboltMonitor' application version 6.1.3.2. Due to laser safety the laser needs to be switched on by manually turning the key on the laser head. The frequency of the mechanical chopper needs to be controlled manually.

5.1 Controlling the Monochromators

The monochromators can be controlled using the dynamic link library (DLL) provided by Bentham Instruments. To use the DLL, the monochromators need to be connected to the computer via a USB interface. To control the hardware of the monochromators, the program creates a system model of the monochromators which mirrors the hardware components. This system model is constructed using a configuration XML file, which contains the information about the hardware components and their initial configuration. To control both monochromators, the program has to use two DLLs to create two separate system models, one for each monochromator. Because both monochromators USB interfaces are configured to use the same product ID (pid) and vendor ID (vid) the USB_COMMS device of the configuration XML file needs a serial number attribute to distinguish between the two monochromators. (Code Example 1, line 7) The serial number of the detector monochromator is '43431/1' and the lamp monochromator has the serial number '43439/1'. The modified configuration XML files are attached in the appendix (Appendix A.1 and A.2).

Code Example 1: Configuration XML file including the serial attribute for the detector monochromators.

```

1 <Comms>
2   <id>imac</id>
3   <Type>USB_COMMS</Type>
4   <attributes>
5     <vid>1240</vid>
6     <pid>5893</pid>
7     <serial>43431/1</serial>
8   </attributes>
9 </Comms>

```

To control the monochromators via LabVIEW, a sub-VI (Mono_Initialize see B.1) is created, which calls the following functions of the DLL using the LabVIEW 'Call Library Function' node:

1. LOT_version - determines the version of the DLL (Appendix B.1, Figure 39).
2. LOT_build_system_model - builds the system model of the monochromators using a specified configuration file (Appendix B.1, Figure 40).
3. LOT_initialise - initializes the hardware components of the monochromators (Appendix B.1, Figure 41).

Each of the functions produces an integer error code. If this error code is equal to zero, the function was executed successfully. The error codes are defined by the DLL and can be found in the documentation of the DLL. If all error codes are zero, the monochromators are initialized and ready to use. This is indicated by a status LED (boolean) on the front panel of the application.

5.2 LabVIEW Program Structure and Functionality

The 'PIA-Launcher' program is build using LabVIEW version 20.0.1 (64-bit). LabVIEW programs are written in the visual programming language 'G', which uses nodes and frames as variables, functions and loops, connected by wires as logical links. LabVIEW is a parallel data flow programming language. When all inputs of a function are provided, the function will execute. The user interface is realized by elements positioned on the front panel, whereby the program is written on the back panel. The program is made interactive by using an infinite loop to continuously check the user inputs. When the program is started commonly used variables are initialized outside the main loop of the program to reduce the amount of wires used and improve readability of the program. The individual functions of the program are often implemented in sub-VIs (see Appendix B) to modularize the program and further increase readability.

5.3 Initialisation and Closing

The button 'Init' inside the Initialisation frame is used to initialize the monochromators and reset the lock-in amplifier settings. Here the Mono_Initialize subVI (see B.1) is called. Additionally the SR865 Initialize subVI from the SR865 LabVIEW driver package is called. The subVI's of the driver needs small modifications (changed ID query) to work with the SR860 lock-in amplifier. This subVI starts a VISA session to communicate with the lock-in amplifier. After the session is started, the lock-in amplifier gets the order to reset to its default instrument setup. After both subVI's were executed the indicator LED on the front panel turns on to signal to the user, that the system is ready to start measurements. The 'Close' button calls the mono_close subVI (see B.2) as well as the SR865 close subVI to destroy the system model of the Monochromators and to close the open VISA session. After the system is closed, the indicator LED is turned off.

5.3.1 Setup Measurement Parameters

To change the settings for the measurement the values in the setup measurement frame of the front panel needs to be set. The measurement parameters of the lock-in amplifier can be changed in the 'Lock-in settings' frame. It is important to check the detector box when the Si-biased detector is connected or uncheck it when the Ge-biased detector is connected. This checkbox will alter the position of the SAM in the detector monochromator accordingly passing the information to the 'Mono_Set_SAM' subVI (see B.4). The number of points to mediate (N) adjust the number of individual measurements the program will mediate over. When changing the scanning parameters ('Change Starting Wavelength', 'Change Ending Wavelength', and 'Change Stepsize') it is important to press the Setup button. Then the new settings are applied and the number of scans is calculated:

$$\text{Number of scans} = \lfloor (\lambda_{End} - \lambda_{Start}) : \text{Stepsize} \rfloor + 1 \quad (24)$$

After the number of scans is calculated an approximate measurement time in minutes is calculated assuming the detector needs 2.3 time constants to settle for each measurement:

$$\text{Measurement Time [min]} = \lfloor (N \cdot \text{Number of scans} \cdot 2.3 \cdot \text{Time constant}) : 60000 \rfloor \quad (25)$$

The number of scans and the estimated time are displayed in the 'Measurement status' frame.

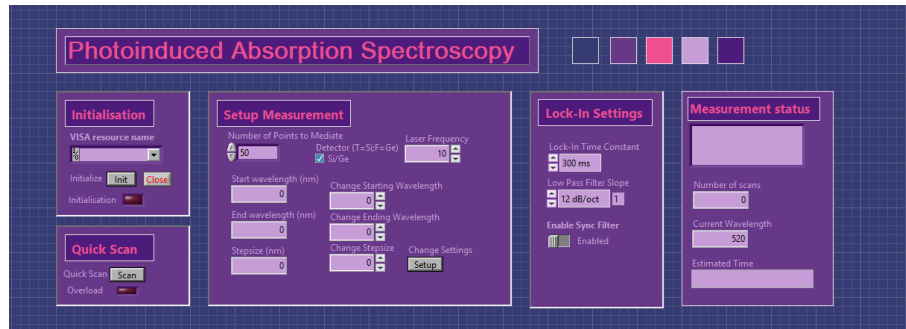


Figure 28: Front Panel (top part) of the PIA_Launcher.vi program.

5.3.2 Quick Scan

To set the sensitivity of the current preamplifier, it is important to check transmission at all measured wavelengths for unwanted overloads of the lock-in amplifier. Therefore, a quick scan is done before the measurement after completing sample alignment, initialisation of the system, and setting up the measurement parameters correctly. The quick scan is activated by pressing the 'scan' button.

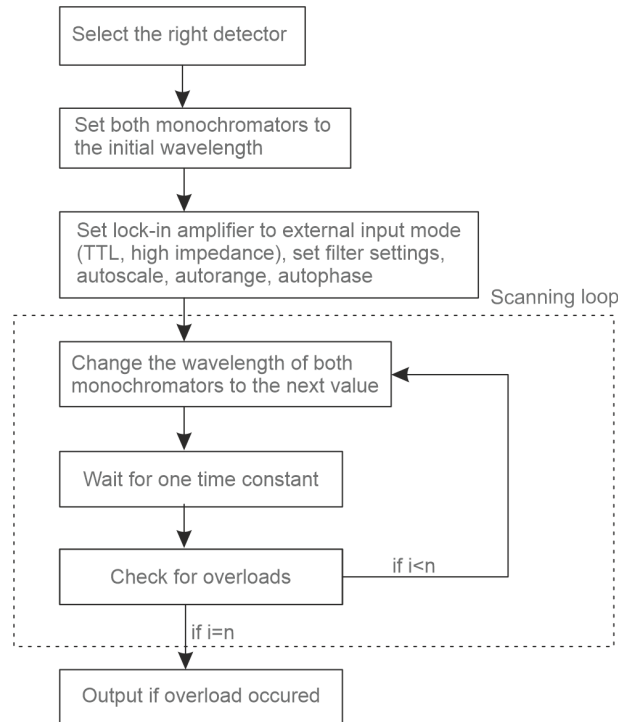


Figure 29: Block diagram of the LabVIEW program used for the quick scan.

5.3.3 Transmission Experiment

The T experiment subprogram is included in the main program loop. The LabVIEW program can be found in the Appendix (C). Figure 30 shows the block diagram of the implemented control logic. The measurement begins with the creation of an output file for data storage and the selection of the appropriate photodetector. Both monochromators are then set to the initial wavelength of the scan range. A waiting period of 2.3 time constants is introduced to ensure that the optical and electronic signals reach a steady state before data acquisition begins. Subsequently, the lock-in amplifier is configured to external input mode (TTL, high impedance) with the desired filter settings. The lock-in amplifier is also auto-scaled, auto-ranged, and auto-phased to optimize signal quality. Another waiting period of 2.3 time constants follows to ensure that the system has stabilized after these adjustments.

The scanning loop then commences. In each iteration, the mean value of the corrected signal from the lock-in amplifier is acquired and written to the output file. The correction is done by dividing the measured value by the corresponding interpolated responsivity value (see Appendix B.8). The wavelength of both monochromators is incremented to the next step, followed by another waiting time of 2.3 time constants to allow the system and the filters to stabilize. The lock-in amplifier is auto-scaled at each step to account for signal amplitude changes over the scan range. This process repeats until the loop variable i reaches the total number of scans n calculated beforehand. Once the final wavelength step is completed, the output file is closed, concluding the transmission measurement.

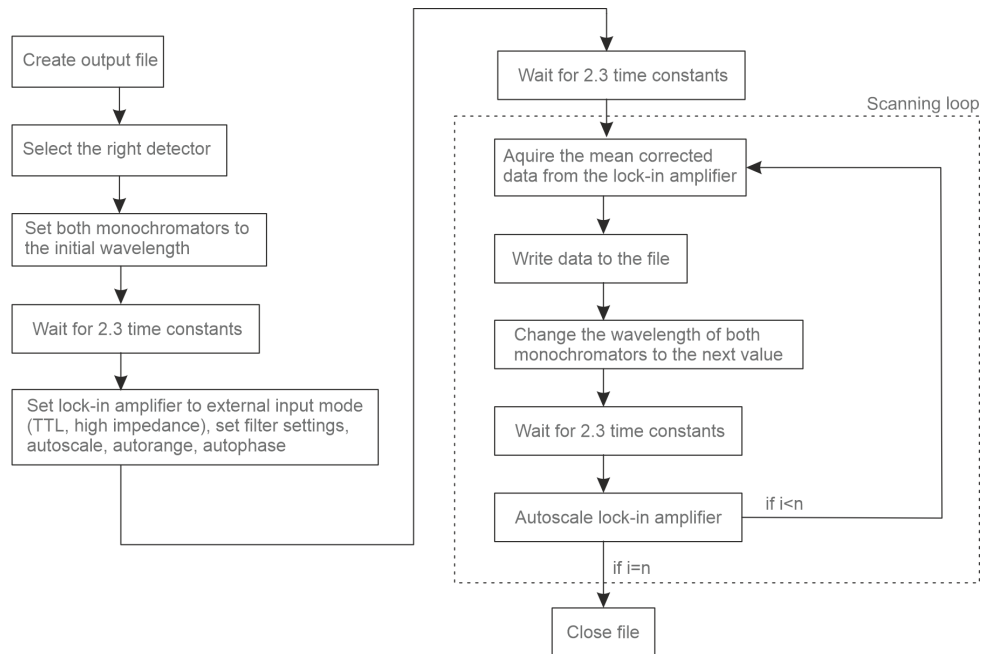


Figure 30: Block diagram of the LabVIEW program used for the transmission experiment.

5.3.4 Photoluminescence Experiment

The PL experiment subprogram is included in the main program loop. The LabVIEW program can be found in the Appendix (C). The corresponding block diagram of the measurement sequence is shown in Figure 31.

The procedure begins with the creation of an output file for storing the acquired data, followed by the selection of the appropriate detector. The exit slit of the lamp monochromator is closed to suppress the probe light during the measurement. A waiting time of 2.3 time constants is introduced to allow the system to settle. Next, the lock-in amplifier is configured for internal input mode with the desired filter settings, internal reference frequency, autoscale, and autorange functions. In this step, the lock-in amplifier is set to use the BlazeX output to modulate the laser. After this configuration step, the program again waits for 2.3 time constants to settle. The lock-in amplifier is then auto-phased to align the reference signal with the measured signal phase. The main scanning loop then starts. During the PL experiment, only the detector monochromator is scanning through the spectra.

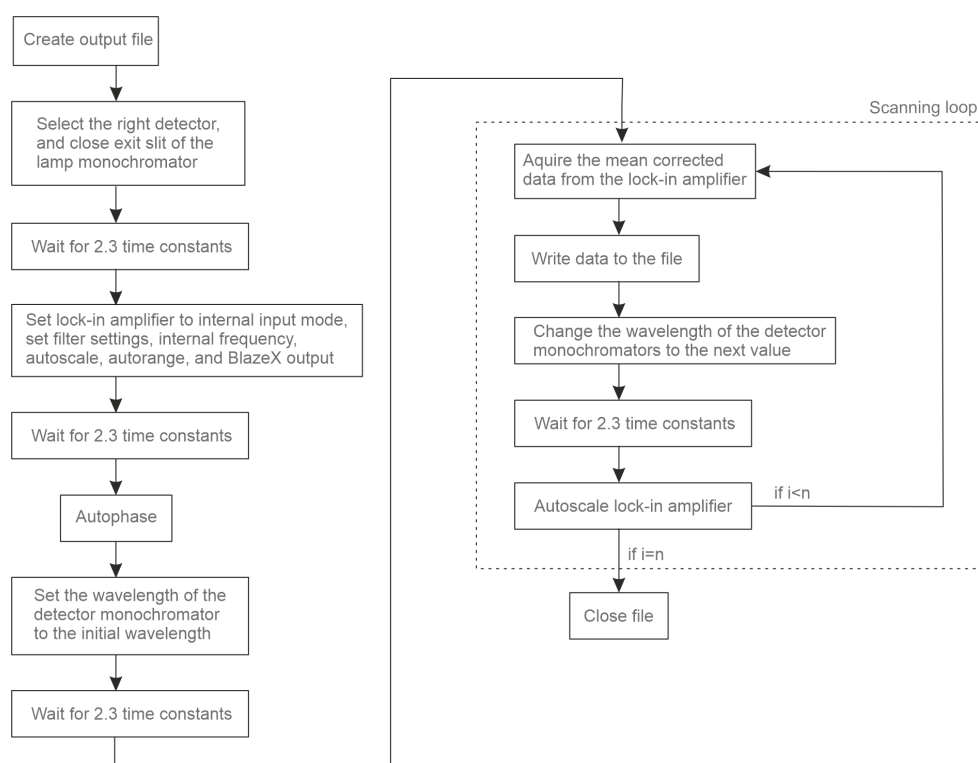


Figure 31: Block diagram of the LabVIEW program used for the photoluminescence experiment.

5.3.5 Photoinduced Absorption and Photoluminescence Experiment

The PIA+PL experiment subprogram is included in the main program loop. The LabVIEW program can be found in the Appendix (C). The corresponding block diagram of the measurement sequence is shown in Figure 32. The procedure begins with the creation of an output file and the selection of the appropriate detector. The lock-in amplifier is configured for internal input mode with specified filter settings, internal reference frequency, autoscale, autorange, and the BlazeX output enabled for laser modulation. After these adjustments, the system waits again for 2.3 time constants before auto-phasing the lock-in amplifier to align the phase reference with the measured signal. Next, the monochromators are set to the initial wavelength of the scan range, followed by another stabilization period of 2.3 time constants. At this point, the scanning loop begins.

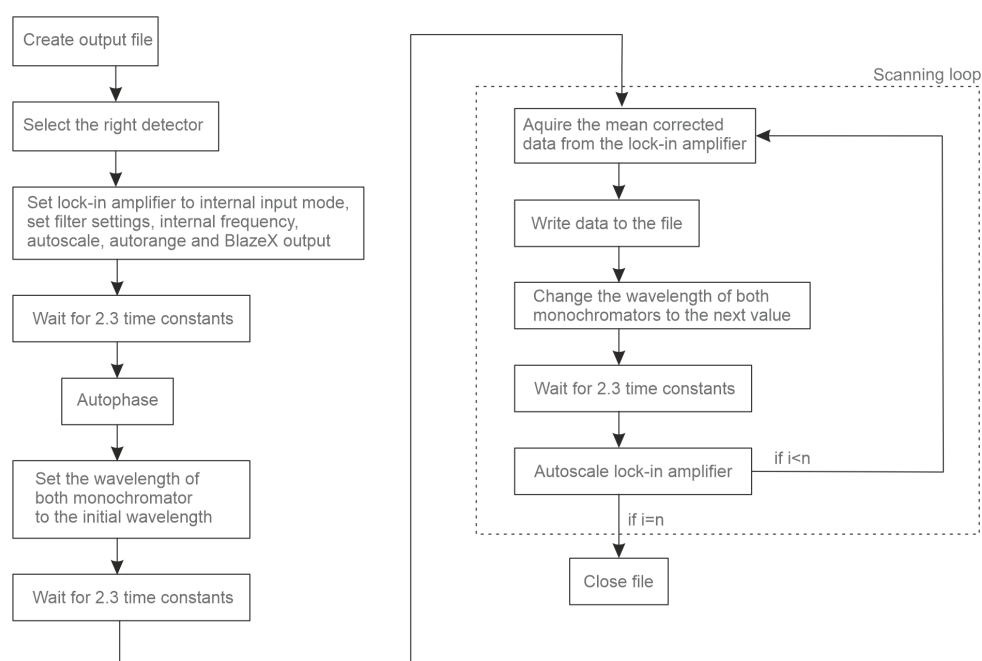


Figure 32: Block diagram of the LabVIEW program used for the PIA+PL experiment.

6 Results and Discussion

6.1 Characteristics of light sources

To evaluate the optical throughput of the PIAS setup, the beam power of the probe light was measured at two key positions, it was measured at the sample position, where the light passed through only the lamp monochromator. Second, the beam power at detector position was measured, where the light passed through the lamp and detector monochromators. To measure the power a Thorlabs PM100USB power meter equipped with a Si photodiode sensor was used. The monochromator slits were adjusted to yield a spectral bandwidth of 5 nm. Beam power was recorded manually by varying the wavelength of the monochromator via the monochromator control software. At the sample position, the first monochromator was scanned, while at the detector position, both monochromators were used in series. For the first monochromator, a grating change occurred at 900 nm, which caused artifacts in the measured power spectrum. Additionally, variations in grating efficiency and alignment may introduce small errors in the results. It should be noted that the powermeter used was not recently calibrated; therefore, the reported values should be considered as relative rather than absolute. The goal of the measurement was to compare the relative power levels at different wavelengths and between the two positions. The resulting beam power spectra for both positions are shown in Figure 33. The comparison clearly demonstrates the expected loss in optical power when two monochromators are used in series, as well as the characteristic wavelength dependence introduced by the grating efficiency.

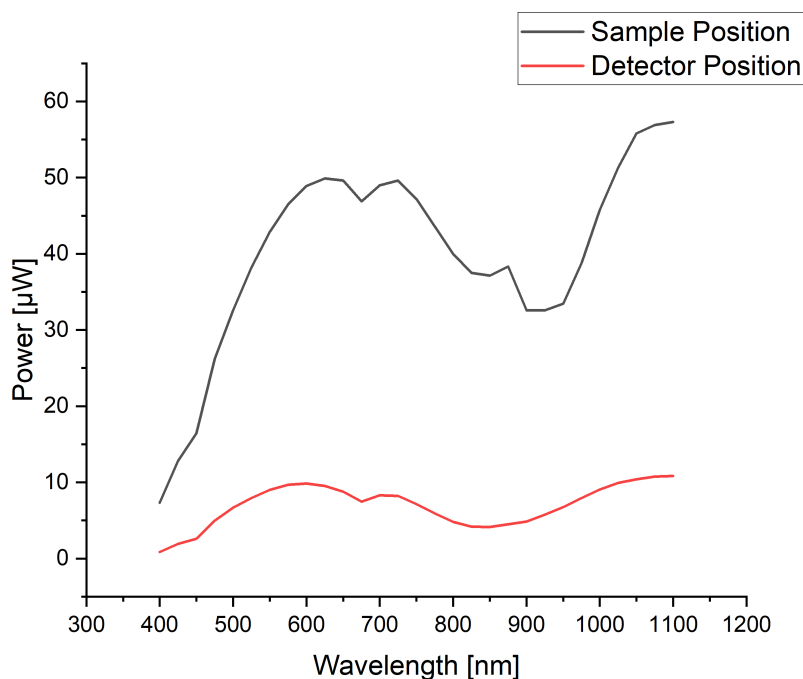


Figure 33: Power measurement of the probe light at sample and detector position.

The laser power was measured using the Thorlabs powermeter. The laser was used in the

constant power mode at 80 mW with the ND-filter in the right position for the measurement (marked on the ND-filter). The measured power was 5.86 W. The beam profile was measured using a beam profiler. The beam is elliptical with a length (a) of 3 mm and a width (b) of 2 mm. The area (A) of the ellipse can be calculated using:

$$A = \frac{a}{2} \cdot \frac{b}{2} \cdot \pi$$

$$A = \frac{3 \text{ mm}}{2} \cdot \frac{2 \text{ mm}}{2} \cdot \pi = 4.71 \text{ mm}^2 \quad (26)$$

The energy density (Fluence, H) can be calculated dividing the measured power (P) by the beam area and frequency of modulation:

$$H = \frac{P}{A \cdot f}$$

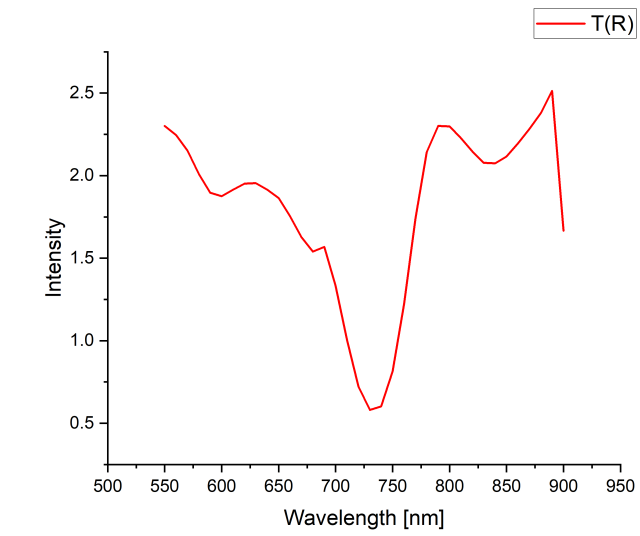
$$H = \frac{5.86 \text{ W}}{4.71 \cdot 10^{-2} \text{ cm}^2 \cdot 391 \text{ Hz}} = 3.18 \cdot 10^{-1} \frac{\text{mJ}}{\text{cm}^2} \quad (27)$$

6.2 Measurements of PM6:Y6 Test Samples

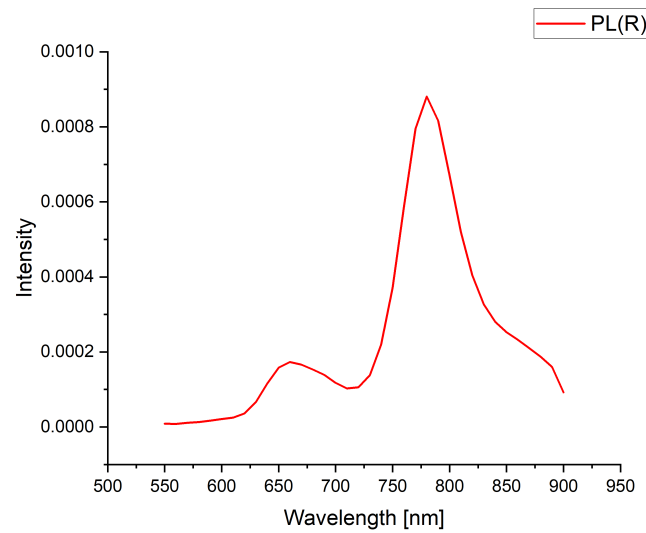
This section demonstrates whether the spectrometer can replicate PIA measurements on the model system PM6:Y6.

6.2.1 Measurements on Solutions

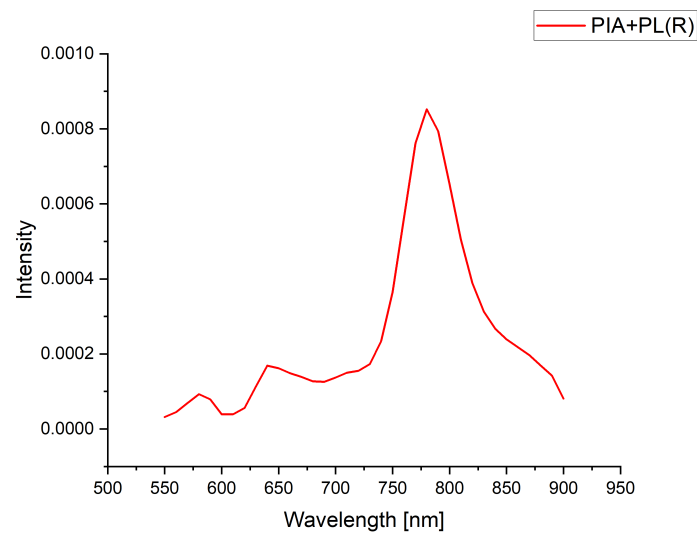
To evaluate the performance of the experimental setup, a chloroform solution containing PM6 and Y6 was prepared and characterized. The sample preparation was carried out in a glovebox to prevent degradation. The solutions of PM6 ($0.1 \frac{\text{mg}}{\text{ml}}$) and Y6 ($0.12 \frac{\text{mg}}{\text{ml}}$) were combined in a 1:1 ratio. The solution was placed in a Spectrosil cuvette with an optical path length of 1 mm. The measurements were performed over the range of 550-900 nm with a scan step size of 10 nm. At each wavelength, three measurements were recorded and averaged, with the current preamplifier sensitivity maintained at 1 $\mu\text{A/V}$ throughout. For the PL (Figure 34b) and PIA+PL (Figure 34c) measurements, excitation was provided by a 520 nm laser modulated at 391 Hz. In all measurements, the Si-biased detector was used. The PIA signal (Figure 35) was subsequently calculated according to Equation 23.



(a) Transmission.



(b) Photoluminescence.



(c) PIA+PL (Amplitude).

Figure 34: The individual measurements of a PM6:Y6 solution.

In the transmission experiment the artifact introduced by the grating change of the monochromator at 900 nm is clearly visible.

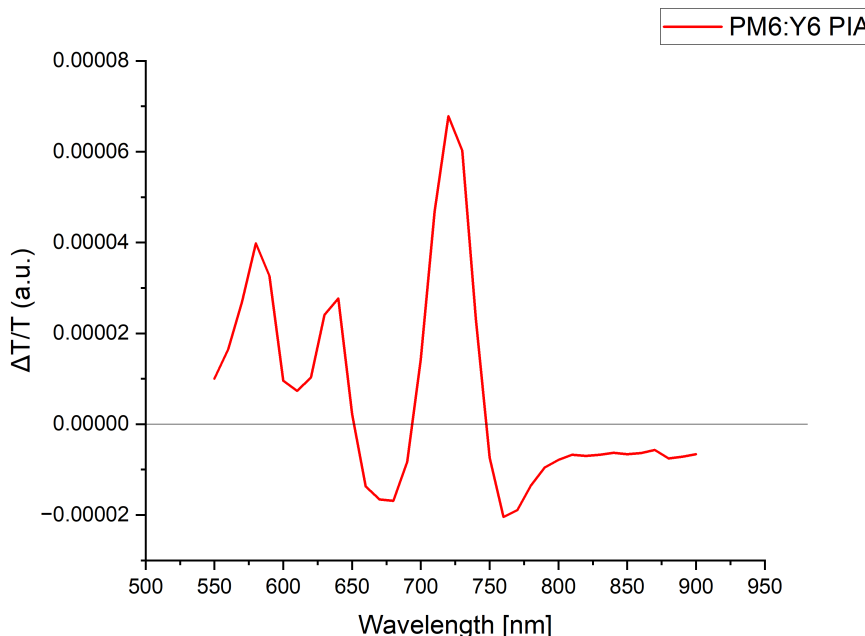


Figure 35: Calculated PIA signal of a PM6:Y6 solution upon 520nm excitation with laser irradiance of $61.12 \frac{mW}{cm^2}$.

The PIA spectrum of the PM6:Y6 solution shows distinct photoinduced absorption features across the measured wavelength range. Positive $\Delta T/T$ signal observed at 550–680 nm corresponds to PM6 GSB; while Y6 GSB appears at 720 nm. The spectrum shows distinct PIA features in the region of 650–690 nm and 750–910 nm, which was previously assigned to $PM6^+$ and $Y6^-$ [14]. The presence of these negative features confirms that excited-state absorption is a significant component of the transient optical response in this blend.

6.2.2 Measurements on Thin Films

A PM6:Y6 film sample was prepared by spin coating (1000 rpm), in which a PM6:Y6 solution (final total concentration = $15 \frac{mg}{ml}$) was deposited onto a rotating quartz substrate. Residual solvent was removed by heating the sample on a hot plate. The resulting film was then measured over the spectral range of 550–1000 nm, with a scan step size of 10 nm. At each wavelength, three measurements were recorded and averaged, while maintaining the current preamplifier sensitivity at $1 \frac{\mu A}{V}$. Transmission measurements were performed using a probe modulation frequency of 40 Hz. For the combined PIA+PL and PL measurements, excitation was provided by a 520 nm laser modulated at 391 Hz. In all cases, a Si-biased detector was employed.

When the PM6:Y6 mixture is prepared as a film, it is important to analyze the difference between the in-phase and out-of-phase signals obtained from the lock-in amplifier. By employing a quasi-steady-state technique, the excited species can persist for some time after the excitation

source is switched off, resulting in a measurable phase shift in the signal. In cases where the species have extremely long lifetimes, their concentration can accumulate over time, potentially leading to distorted signals that don't follow the modulation and thus cannot be measured. This behaviour is shown in Figure 36.^[12]

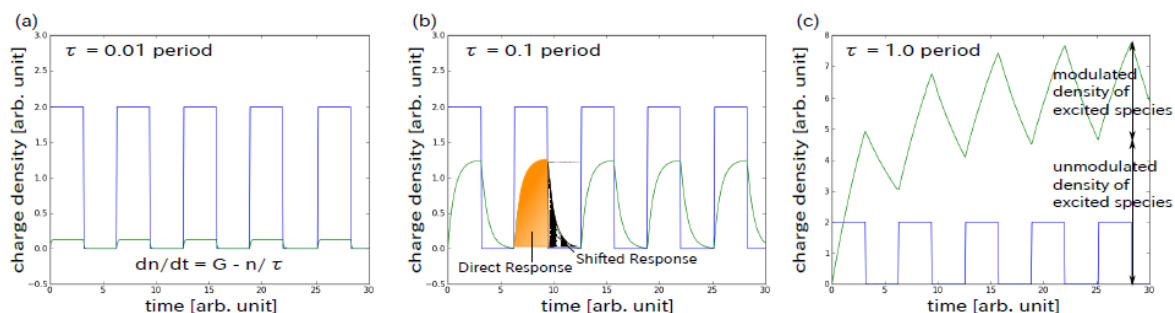


Figure 36: Response (green line) of the density (n) of an excited species with the lifetime (τ) to a modulated excitation (blue line). [12]

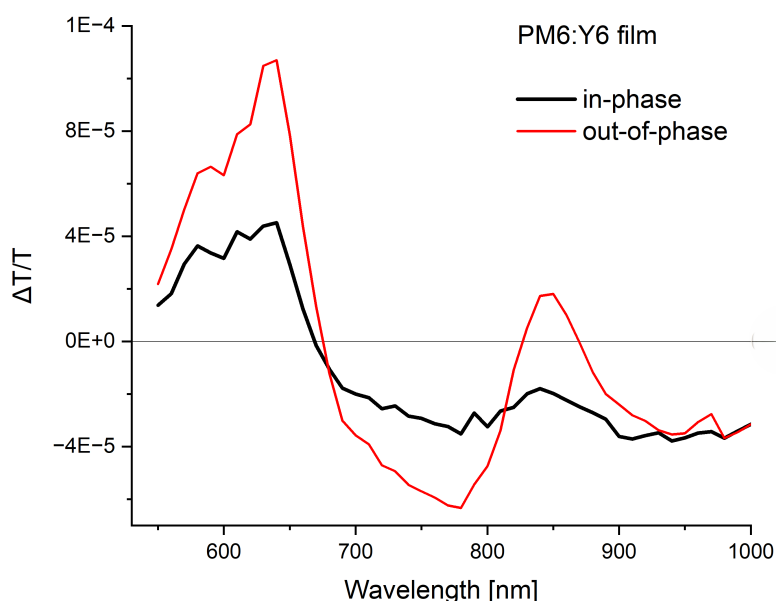


Figure 37: Comparison of the in-phase signal with the out-of-phase signal.

The PM6:Y6 film exhibits distinct spectral features in both the in-phase and out-of-phase components of the PIA measurement (Figure 37). A broad positive $\Delta T/T$ signal is observed between ~ 580 - 700 nm, which can be attributed to PM6 GSB. The positive signal observable at 840 nm in the out-of-phase signal can be attributed to Y6 GSB, while pronounced negative bands in the 770 - 820 nm range and beyond 900 nm are characteristic of photoinduced absorption from long-lived excited species. The out-of-phase signal shows significantly increased

amplitude, indicating that a substantial fraction of the excited species persists beyond the excitation period and introduces a measurable phase lag. This behavior suggests the coexistence of fast ($\ll 2.6$ ms), prompt photoresponses and slower, longer-lived states.

6.3 Limitations of the Current Implementation and Future Improvements

Planned and recommended optimizations for the PIAS setup include several software, hardware, and workflow improvements aimed at enhancing stability, accuracy, and usability. On the software side, the LabVIEW program will be modified to remove the crash associated with creating new output files, ensure the Abort button stops measurements promptly, and introduce comprehensive error handling with centralized logging and clear on-screen feedback.

- Hardware-related upgrades will focus on optimization of the Ge detector, including optimizing of the filter settings and preamplifier tuning, to enable accurate performance into the near-IR spectral range.
- Optical throughput and spectral coverage can be improved by replacing refractive lenses with reflective optics such as mirror based collimation optics.
- Workflow enhancements will include integrating direct laser control into the LabVIEW interface for automated power and modulation adjustments, as well as adding a dedicated “alignment mode” to streamline sample positioning.

Collectively, these optimizations will expand the system’s measurement capabilities, increase operational reliability, and improve overall ease of use.

7 Conclusion

In this thesis, a quasi-steady-state photoinduced absorption spectroscopy setup was successfully designed, constructed, and programmed. The optical layout was constructed on the laboratory's optical table and integrates two monochromators, enabling precise wavelength selection while minimizing secondary effects. A QTH lamp and a continuous-wave laser were implemented as excitation sources, while detection was achieved using biased silicon and germanium photodiodes to cover a broad spectral range from the visible to the near-infrared region. The control and data acquisition routines were implemented in LabVIEW. The program enables multiple measurement modes, including transmission, photoluminescence, and PIA+PL. Test measurements of liquid and film samples confirmed that the system operates as intended, demonstrating its capability to detect photoinduced absorption signals reliably. While minor software issues remain, such as the unreliable abort function and the accessible spectral range is currently limited to the near-infrared region, these aspects can be addressed in future developments. Overall, the setup provides a solid foundation for further experimental investigations and can be readily adapted to extended measurement requirements.

A Appendix: Monochromator Configuration Files

A.1 Lamp Monochromator Configuration File

Code Example 2: Configuration XML file for the lamp monochromator

```

1 <?xml version="1.0"?>
2 <Configuration>
3   <Comms>
4     <id>imac</id>
5     <Type>USB_COMMS</Type>
6     <attributes>
7       <vid>1240</vid>
8       <pid>5893</pid>
9       <serial>43439/1</serial>
10    </attributes>
11  </Comms>
12  <Monos>
13    <id>mono</id>
14    <Type>MSH-300</Type>
15    <SMDType>IMAC</SMDType>
16    <UseComms>imac</UseComms>
17    <Turret>
18      <Address>24</Address>
19      <attributes>
20        <grating index="1">1200</grating>
21        <grating_blaze index="1">500</grating_blaze>
22        <grating_switch_wavelength index="1">0</grating_switch_wavelength>
23        <sine_correction index="1">1</sine_correction>
24        <zord index="1" setup="1">41375</zord>
25        <alpha index="1" setup="1">1.0004</alpha>
26        <phase index="1" setup="1">13.345086</phase>
27        <amplitude index="1" setup="1">77.256018</amplitude>
28        <zord index="1" setup="2">41375</zord>
29        <alpha index="1" setup="2">1.0004</alpha>
30        <phase index="1" setup="2">13.345086</phase>
31        <amplitude index="1" setup="2">77.256018</amplitude>
32        <grating index="2">600</grating>
33        <grating_blaze index="2">1250</grating_blaze>
34        <grating_switch_wavelength index="2">900</grating_switch_wavelength>
35      </attributes>
36      <sine_correction index="2">1</sine_correction>
37      <zord index="2" setup="1">893965</zord>
38      <alpha index="2" setup="1">1.0027</alpha>
39      <phase index="2" setup="1">13.345086</phase>
40      <amplitude index="2" setup="1">77.256018</amplitude>
41      <zord index="2" setup="2">893965</zord>
42      <alpha index="2" setup="2">1.0027</alpha>
43      <phase index="2" setup="2">13.345086</phase>
44      <amplitude index="2" setup="2">77.256018</amplitude>
45      <grating index="3">300</grating>
46      <grating_blaze index="3">3000</grating_blaze>
      <grating_switch_wavelength index="3">2500</grating_switch_wavelength>

```

```

47     <sine_correction index="3">1</sine_correction>
48     <zord index="3" setup="1">1755758</zord>
49     <alpha index="3" setup="1">1.0016</alpha>
50     <phase index="3" setup="1">13.345086</phase>
51     <amplitude index="3" setup="1">77.256018</amplitude>
52     <zord index="3" setup="2">1755758</zord>
53     <alpha index="3" setup="2">1.0016</alpha>
54     <phase index="3" setup="2">13.345086</phase>
55     <amplitude index="3" setup="2">77.256018</amplitude>
56     <microstepping>128</microstepping>
57     <move_current>8</move_current>
58     <idle_current>8</idle_current>
59     </attributes>
60 </Turret>
61 <Use>fwheel</Use>
62 <Use>sam1</Use>
63 <Use>ent</Use>
64 <Use>exit</Use>
65 <attributes>
66     <cos_alpha>0.9727</cos_alpha>
67     <auto_select_wavelength>1</auto_select_wavelength>
68     <ZordSwitch_SAM_for_turret index="1">1</ZordSwitch_SAM_for_turret>
69 </attributes>
70 </Monos>
71 <SMDs>
72     <id>fwheel</id>
73     <Type>FW252</Type>
74     <Address>26</Address>
75     <SMDType>IMAC</SMDType>
76     <UseComms>imac</UseComms>
77     <attributes>
78         <number_of_positions>8</number_of_positions>
79         <filter index="1">0</filter>
80         <filter index="2">400</filter>
81         <filter index="3">700</filter>
82         <filter index="4">1250</filter>
83         <filter index="5">2000</filter>
84         <filter index="6">3600</filter>
85         <filter index="7">0</filter>
86         <filter index="8">0</filter>
87         <move_at_each_wavelength>1</move_at_each_wavelength>
88         <filter_park_offset>180</filter_park_offset>
89     </attributes>
90 </SMDs>
91 <SMDs>
92     <id>sam1</id>
93     <Type>SAM</Type>
94     <Address>24</Address>
95     <SMDType>IMAC</SMDType>
96     <UseComms>imac</UseComms>
97     <attributes>
98         <initial_state>0</initial_state>
99         <deflect>deflect</deflect>
100         <no_deflect>no deflect</no_deflect>
101         <move_at_each_wavelength>0</move_at_each_wavelength>

```

```

102     </attributes>
103 </SMDs>
104 <Comms>
105     <id>slit_drv</id>
106     <Type>USB_COMMS</Type>
107     <attributes>
108         <vid>1240</vid>
109         <pid>5893</pid>
110         <serial>43439/1</serial>
111     </attributes>
112 </Comms>
113 <SMDs>
114     <id>ent</id>
115     <Type>MVSS_MK2</Type>
116     <Address>28</Address>
117     <SMDType>IMAC</SMDType>
118     <UseComms>slit_drv</UseComms>
119     <attributes>
120         <Current_Slit_mode>1</Current_Slit_mode>
121         <Constant_bandwidth_nm>5</Constant_bandwidth_nm>
122         <Constant_width_mm>0</Constant_width_mm>
123         <Slit_Type>entrance</Slit_Type>
124         <Minimum_slit_width>0</Minimum_slit_width>
125         <Backlash_mm>1</Backlash_mm>
126         <Slit_offset_mm>0</Slit_offset_mm>
127         <Slit_park_offset_steps>1440</Slit_park_offset_steps>
128     </attributes>
129 </SMDs>
130 <SMDs>
131     <id>exit</id>
132     <Type>MVSS_MK2</Type>
133     <Address>30</Address>
134     <SMDType>IMAC</SMDType>
135     <UseComms>slit_drv</UseComms>
136     <attributes>
137         <Current_Slit_mode>1</Current_Slit_mode>
138         <Constant_bandwidth_nm>5</Constant_bandwidth_nm>
139         <Constant_width_mm>0</Constant_width_mm>
140         <Slit_Type>exit</Slit_Type>
141         <Minimum_slit_width>0</Minimum_slit_width>
142         <Backlash_mm>1</Backlash_mm>
143         <Slit_offset_mm>0</Slit_offset_mm>
144         <Slit_park_offset_steps>1740</Slit_park_offset_steps>
145     </attributes>
146 </SMDs>
147 <Groups>
148     <id>Group 1</id>
149     <Use>mono</Use>
150 </Groups>
151 </Configuration>

```

A.2 Detector Monochromator Configuration File

Code Example 3: Configuration XML file for the detector monochromator

```

1 <?xml version="1.0"?>
2 <Configuration>
3   <Comms>
4     <id>imac</id>
5     <Type>USB_COMMS</Type>
6     <attributes>
7       <vid>1240</vid>
8       <pid>5893</pid>
9       <serial>43431/1</serial>
10    </attributes>
11  </Comms>
12  <Monos>
13    <id>mono</id>
14    <Type>MSH-300</Type>
15    <SMDType>IMAC</SMDType>
16    <UseComms>imac</UseComms>
17    <Turret>
18      <Address>24</Address>
19      <attributes>
20        <grating index="1">1200</grating>
21        <grating_blaze index="1">500</grating_blaze>
22        <grating_switch_wavelength index="1">0</grating_switch_wavelength>
23        <sine_correction index="1">1</sine_correction>
24        <zord index="1" setup="1">17285</zord>
25        <alpha index="1" setup="1">1.001</alpha>
26        <phase index="1" setup="1">-25.845063</phase>
27        <amplitude index="1" setup="1">39.087569</amplitude>
28        <zord index="1" setup="2">17182</zord>
29        <alpha index="1" setup="2">1.001</alpha>
30        <phase index="1" setup="2">-25.845063</phase>
31        <amplitude index="1" setup="2">39.087569</amplitude>
32        <grating index="2">600</grating>
33        <grating_blaze index="2">1250</grating_blaze>
34        <grating_switch_wavelength index="2">900</grating_switch_wavelength>
35      </attributes>
36      <attributes>
37        <sine_correction index="2">1</sine_correction>
38        <zord index="2" setup="1">868050</zord>
39        <alpha index="2" setup="1">1.002</alpha>
40        <phase index="2" setup="1">-25.845063</phase>
41        <amplitude index="2" setup="1">39.087569</amplitude>
42        <zord index="2" setup="2">867956</zord>
43        <alpha index="2" setup="2">1.002</alpha>
44        <phase index="2" setup="2">-25.845063</phase>
45        <amplitude index="2" setup="2">39.087569</amplitude>
46        <grating index="3">300</grating>
47        <grating_blaze index="3">3000</grating_blaze>
48        <grating_switch_wavelength index="3">2300</grating_switch_wavelength>
49      </attributes>
50    </Turret>
51  </Monos>
52 </Configuration>

```

```

50     <phase index="3" setup="1">-25.845063</phase>
51     <amplitude index="3" setup="1">39.087569</amplitude>
52     <zord index="3" setup="2">1720175</zord>
53     <alpha index="3" setup="2">1.0015</alpha>
54     <phase index="3" setup="2">-25.845063</phase>
55     <amplitude index="3" setup="2">39.087569</amplitude>
56     <microstepping>128</microstepping>
57     <move_current>8</move_current>
58     <idle_current>8</idle_current>
59     </attributes>
60 </Turret>
61 <Use>fwheel</Use>
62 <Use>sam1</Use>
63 <Use>ent</Use>
64 <Use>exit1</Use>
65 <Use>exit2</Use>
66 <attributes>
67     <cos_alpha>0.9727</cos_alpha>
68     <auto_select_wavelength>1</auto_select_wavelength>
69     <ZordSwitch_SAM_for_turret index="1">1</ZordSwitch_SAM_for_turret>
70 </attributes>
71 </Monos>
72 <SMDs>
73     <id>fwheel</id>
74     <Type>FW252</Type>
75     <Address>26</Address>
76     <SMDType>IMAC</SMDType>
77     <UseComms>imac</UseComms>
78     <attributes>
79         <number_of_positions>8</number_of_positions>
80         <filter index="1">0</filter>
81         <filter index="2">400</filter>
82         <filter index="3">700</filter>
83         <filter index="4">1250</filter>
84         <filter index="5">2000</filter>
85         <filter index="6">3600</filter>
86         <filter index="7">0</filter><filter index="8">0</filter>
87         <move_at_each_wavelength>1</move_at_each_wavelength>
88         <filter_park_offset>180</filter_park_offset>
89     </attributes>
90 </SMDs>
91 <SMDs>
92     <id>sam1</id>
93     <Type>SAM</Type>
94     <Address>24</Address>
95     <SMDType>IMAC</SMDType>
96     <UseComms>imac</UseComms>
97     <attributes>
98         <initial_state>0</initial_state>
99         <switch_wavelength index="1">0</switch_wavelength>
100        <state index="1">0</state>
101        <switch_wavelength index="2">1000</switch_wavelength>
102        <state index="2">1</state>
103        <deflect>deflect</deflect>
104        <no_deflect>no deflect</no_deflect>

```

```

105     <move_at_each_wavelength>0</move_at_each_wavelength>
106   </attributes>
107 </SMDs>
108 <Comms>
109   <id>slit_drv</id>
110   <Type>USB_COMMS</Type>
111   <attributes>
112     <vid>1240</vid>
113     <pid>5893</pid>
114     <serial>43431/1</serial>
115   </attributes>
116 </Comms>
117 <SMDs>
118   <id>ent</id>
119   <Type>MVSS_MK2</Type>
120   <Address>28</Address>
121   <SMDType>IMAC</SMDType>
122   <UseComms>slit_drv</UseComms>
123   <attributes>
124     <Current_Slit_mode>1</Current_Slit_mode>
125     <Constant_bandwidth_nm>5</Constant_bandwidth_nm>
126     <Constant_width_mm>0</Constant_width_mm>
127     <Slit_Type>entrance</Slit_Type>
128     <Minimum_slit_width>0</Minimum_slit_width>
129     <Backlash_mm>1</Backlash_mm>
130     <Slit_offset_mm>0</Slit_offset_mm>
131     <Slit_park_offset_steps>1700</Slit_park_offset_steps>
132   </attributes>
133 </SMDs>
134 <SMDs>
135   <id>exit1</id>
136   <Type>MVSS_MK2</Type>
137   <Address>30</Address>
138   <SMDType>IMAC</SMDType>
139   <UseComms>slit_drv</UseComms>
140   <attributes>
141     <Current_Slit_mode>1</Current_Slit_mode>
142     <Constant_bandwidth_nm>5</Constant_bandwidth_nm>
143     <Constant_width_mm>0</Constant_width_mm>
144     <Slit_Type>exit</Slit_Type>
145     <Minimum_slit_width>0</Minimum_slit_width>
146     <Backlash_mm>1</Backlash_mm>
147     <Slit_offset_mm>0</Slit_offset_mm>
148     <Slit_park_offset_steps>1680</Slit_park_offset_steps>
149   </attributes>
150 </SMDs>
151 <SMDs>
152   <id>exit2</id>
153   <Type>MVSS_MK2</Type>
154   <Address>32</Address>
155   <SMDType>IMAC</SMDType>
156   <UseComms>slit_drv</UseComms>
157   <attributes>
158     <Current_Slit_mode>1</Current_Slit_mode>
159     <Constant_bandwidth_nm>5</Constant_bandwidth_nm>

```

```
160     <Constant_width_mm>0</Constant_width_mm>
161     <Slit_Type>exit</Slit_Type>
162     <Minimum_slit_width>0</Minimum_slit_width>
163     <Backlash_mm>1</Backlash_mm>
164     <Slit_offset_mm>0</Slit_offset_mm>
165     <Slit_park_offset_steps>1640</Slit_park_offset_steps>
166   </attributes>
167 </SMDs>
168 <Groups>
169   <id>Group 1</id>
170   <Use>mono</Use>
171 </Groups>
172 </Configuration>
```

B Appendix: LabVIEW Sub-VI's

B.1 Mono_Initialize

The Mono_Initialize VI is used to check if the DLL's for the Monochromators are available, to build the system model of the monochromators using the specified configuration XML files, and initialize the hardware components of the monochromators. To use the Mono_Initialize VI, the file paths to the DLL's and file paths to the configuration XML files for both monochromators are needed as inputs (relative paths as strings). The Mono_Initialize VI returns a boolean indicating if the initialization was successful.

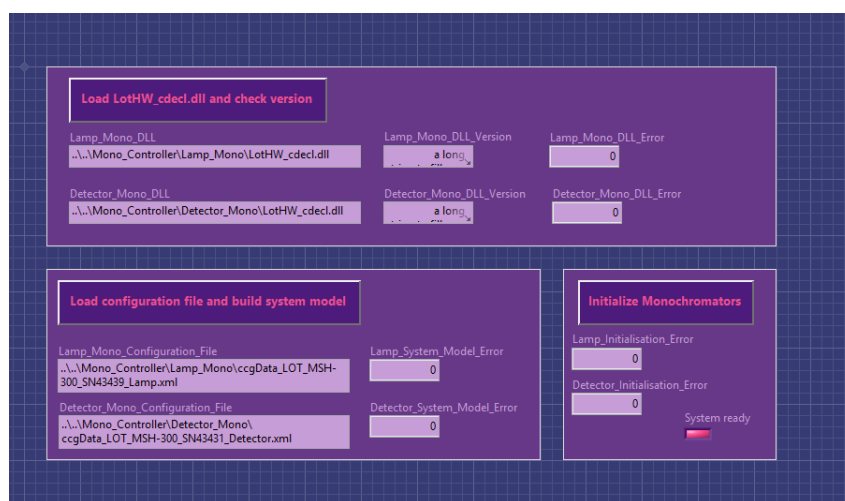


Figure 38: Front panel of the Mono_Initialize VI.

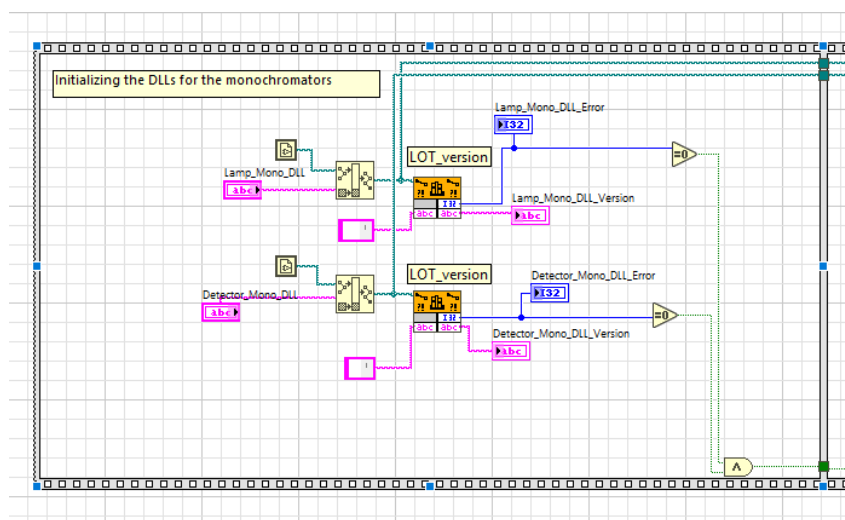


Figure 39: Calling the LOT_version function of the DLL to determine the version of the monochromators. (Frame 1 of the Mono_Initialize VI).

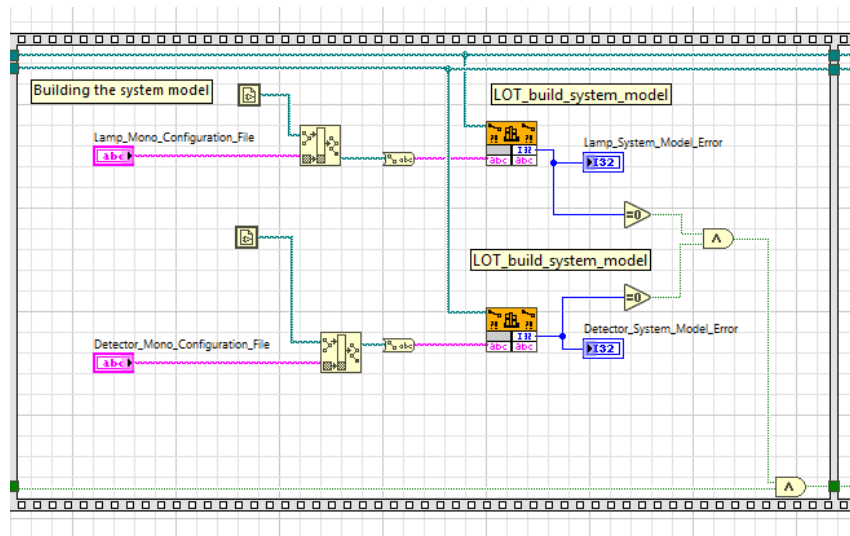


Figure 40: Calling the `LOT_build_system_model` function of the DLL to build the system model using the specified configuration file. (Frame 2 of the `Mono_Initialize VI`).

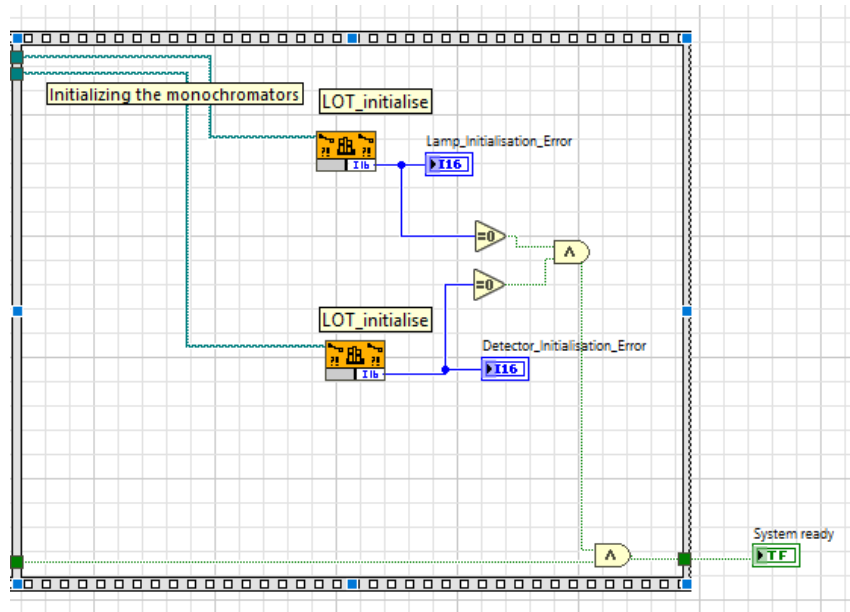


Figure 41: Calling the `LOT_initialise` function of the DLL to initialize the hardware components of the monochromator. (Frame 3 of the `Mono_Initialize VI`).

B.2 Mono_Close

The Mono_Close VI is used to instruct the DLL to destroy the system model of the monochromators. This function should be called before the LabVIEW application is closed to be sure the program is not using the same system model when it is started again.

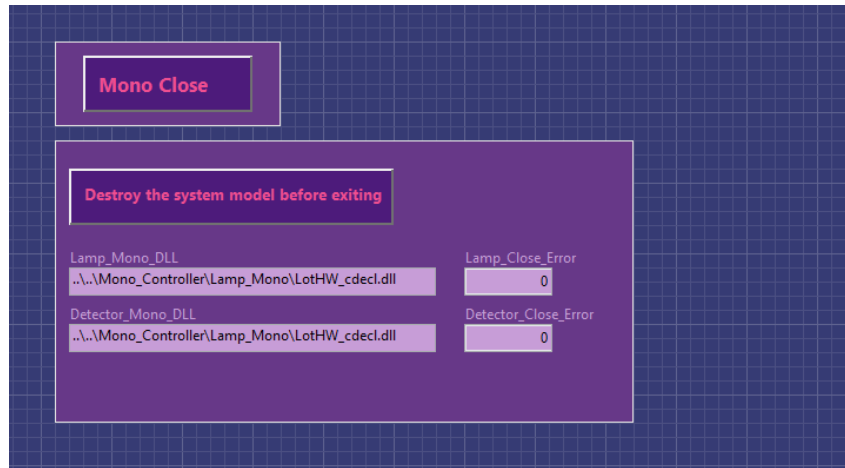


Figure 42: Front panel of the Mono_Close VI.

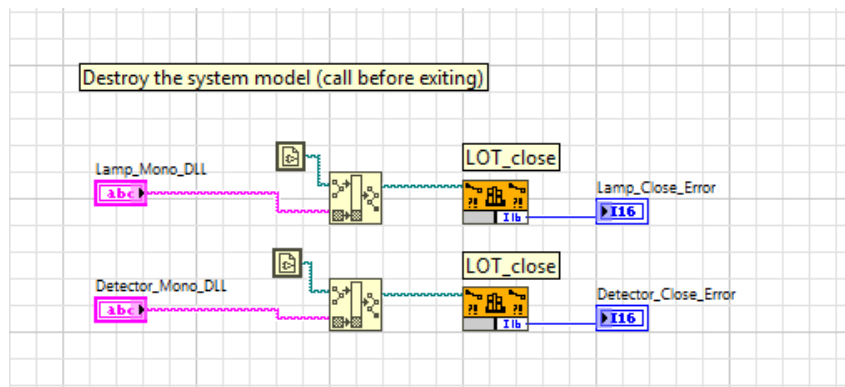


Figure 43: Calling the LOT_close function of the DLL to destroy the system model.

B.3 Mono_Change_Wavelength

The Mono_Change_Wavelength VI is used to change the wavelength and the as wavelength-dependent parameters of the monochromators. The VI takes the wavelength (DBL) and a boolean as inputs. The boolean indicates if both monochromators should change their wavelength (True) or only the detector monochromator (False). The VI returns the current wavelength (DBL) and a boolean after the successful execution of the LOT_select_wavelength function of the DLL. The boolean indicates if the wavelength change was successful.

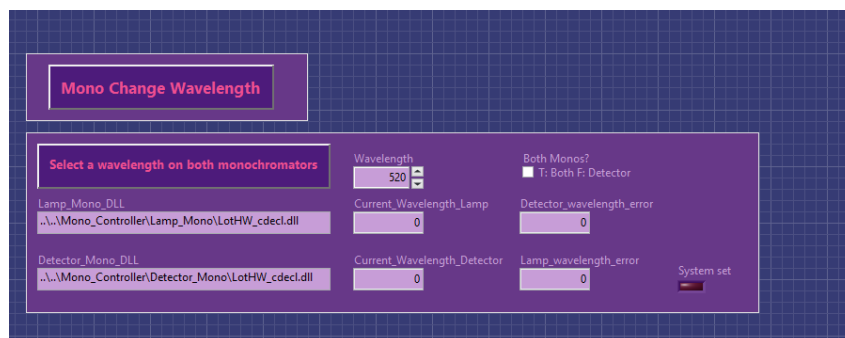


Figure 44: Front panel of the Mono_Change_Wavelength VI.

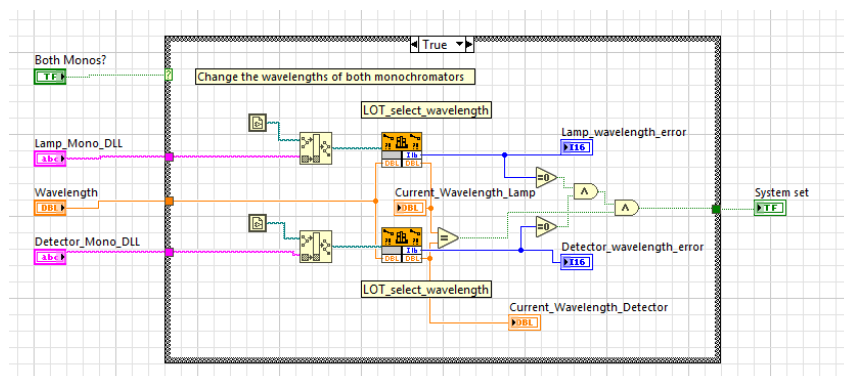


Figure 45: Calling the LOT_select_wavelength function of the DLL to change the wavelength of both monochromators. (Case 1 of the Mono_Change_Wavelength VI).

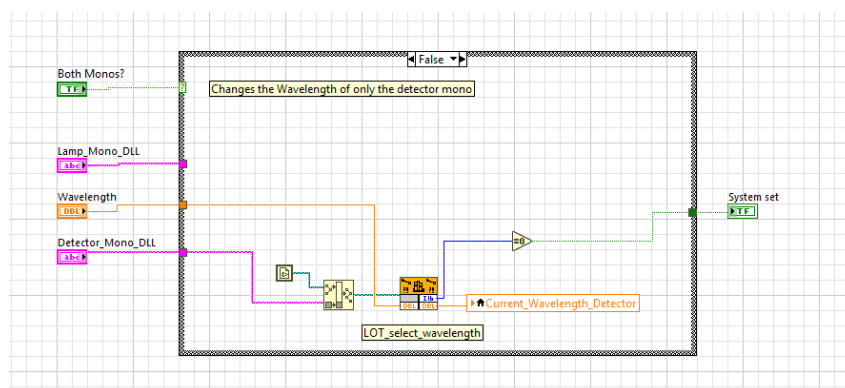


Figure 46: Calling the `LOT_select_wavelength` function of the DLL to change the wavelength of only the detector monochromators. (Case 2 of the `Mono_Change_Wavelength` VI).

B.4 Mono_Set_SAM

The `Mono_Set_SAM` VI is used to set the state of the SAM of the monochromators. The VI takes the relative file path of the monochromator DLL (STR), the ID of the SAM (STR), and a boolean as an input. The VI will change the state of the detector SAM according to the given boolean: True: Si-detector, False: Ge-detector.

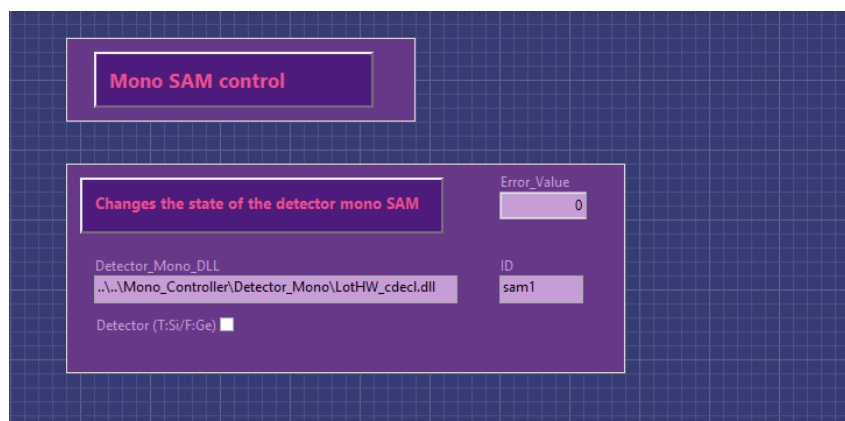


Figure 47: Front panel of the `Mono_Set_SAM` VI.

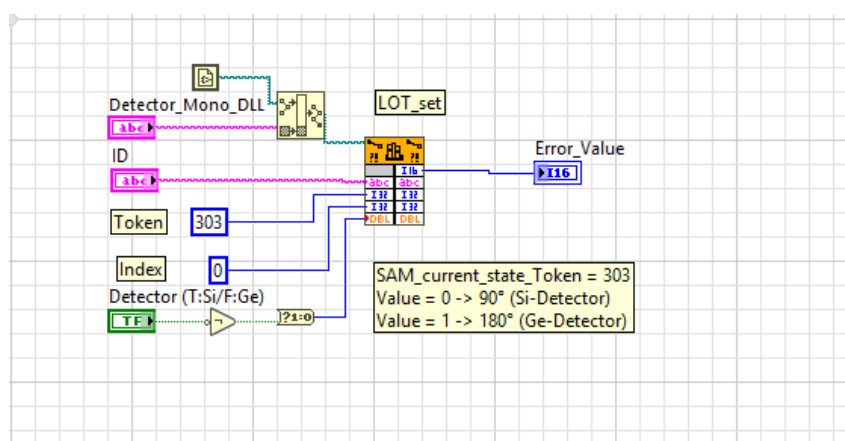


Figure 48: Calling the LOT_set function of the DLL to change the SAM state of the detector monochromator.

B.5 Mono_Set_Slit

The Mono_Set_Slit VI is used to set the slit width of the motorized slits of the lamp monochromator. The VI takes the relative file path of the monochromator DLL (STR), the ID of the slit (STR) and a value for the slit width (DBL).

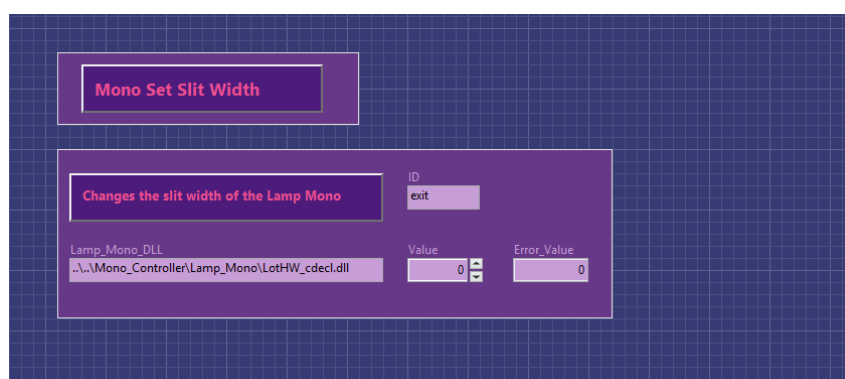


Figure 49: Front panel of the Mono_Set_Slit VI.

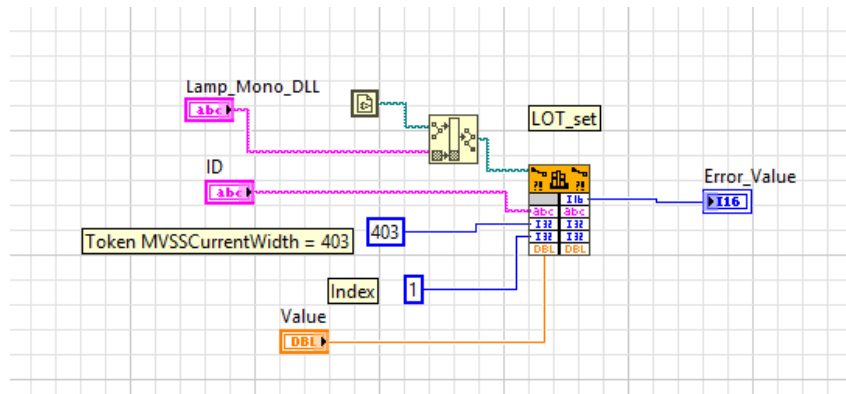


Figure 50: Calling the LOT_set function of the DLL to change the slit width of the lamp monochromator.

B.6 Autoscale

The Autoscale VI is used to autoscale and autophase the lock-in amplifier. The VI takes the VISA Refnum of the lock-in amplifier (VISA) and a boolean. The boolean decides if the autophase is executed (True: Autophase, False: No Autophase).

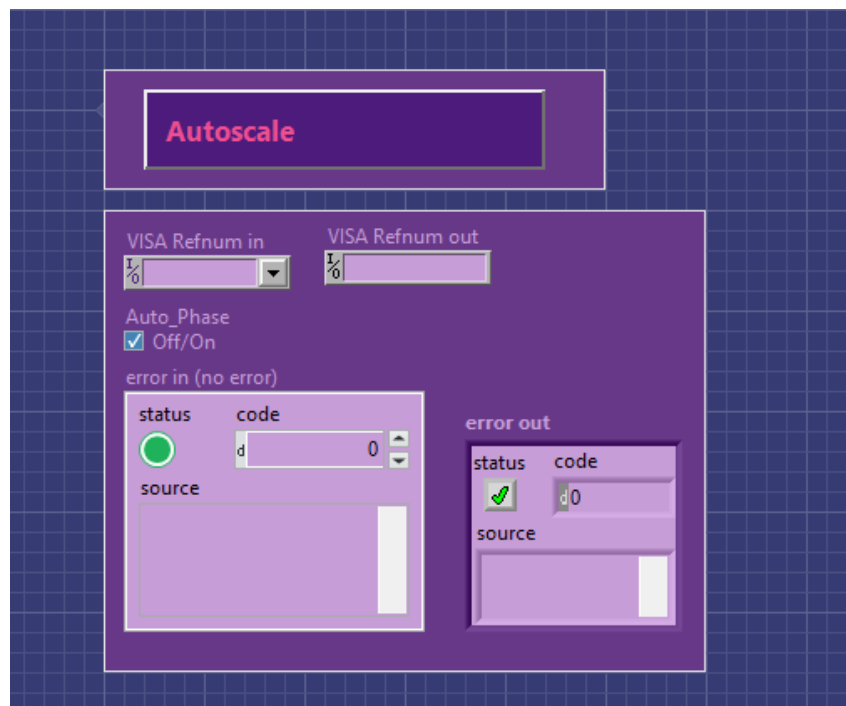


Figure 51: Front panel of the Autoscale VI.

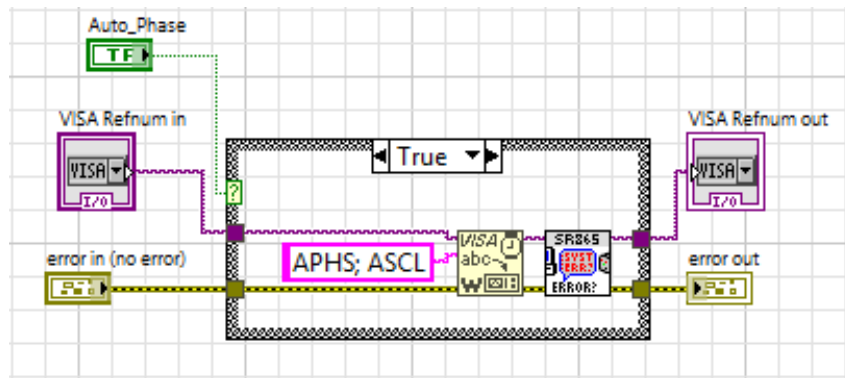


Figure 52: Calling the APLS and ASCL function of the lock-in amplifier to autoscale and autophase. With the False case, only ASCL is called.

B.7 Detector_correction

The Detector_correction VI is used to calculate the incident power on the detector, using the measured intensity and the corresponding interpolated responsivity of the detector. The VI takes the measured value (DBL), the wavelength (DBL) and a boolean to indicate which detector was used (True: Si-detector, False: Ge-detector).

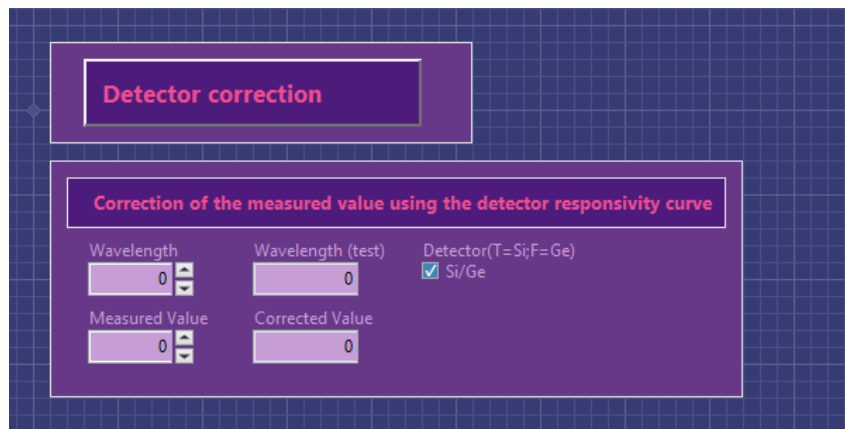


Figure 53: Front panel of the Detector_correction VI.

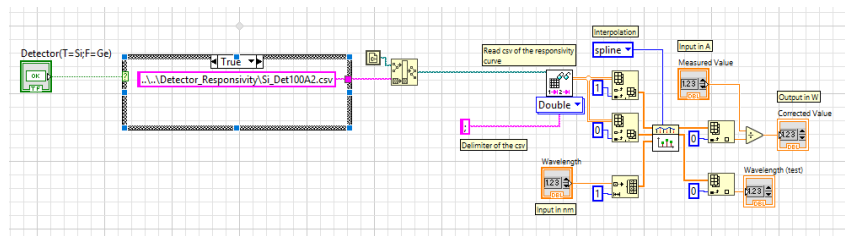


Figure 54: Interpolating the specified sensitivity curve to calculate the incident power. The responsivity values are provided by Thorlabs.

B.8 LIA_Aquire

The LIA_Aquire VI is used to take a mean value of a specified amount of corrected readings from the lock-in amplifier. The VI takes the VISA refnum of the lock-in amplifier (VISA), the number of points to mediate over (I32), the current wavelength (DBL)

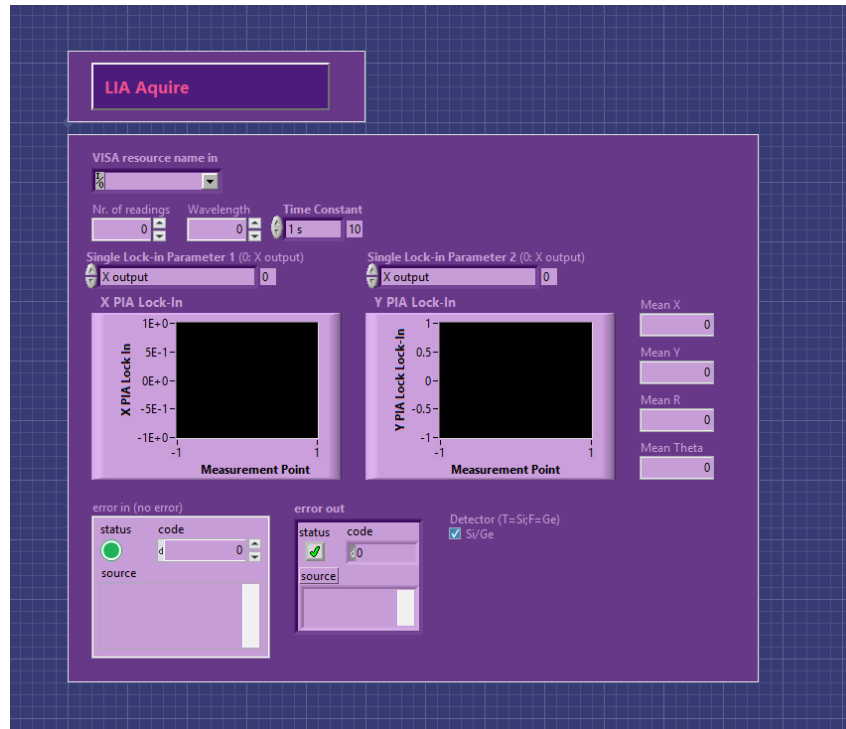


Figure 55: Front panel of the LIA_acquire VI.

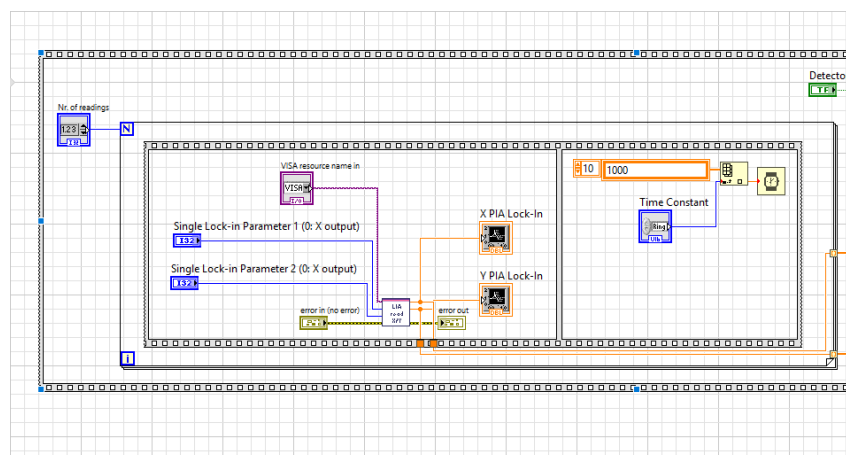


Figure 56: LIA_acquire1/2.

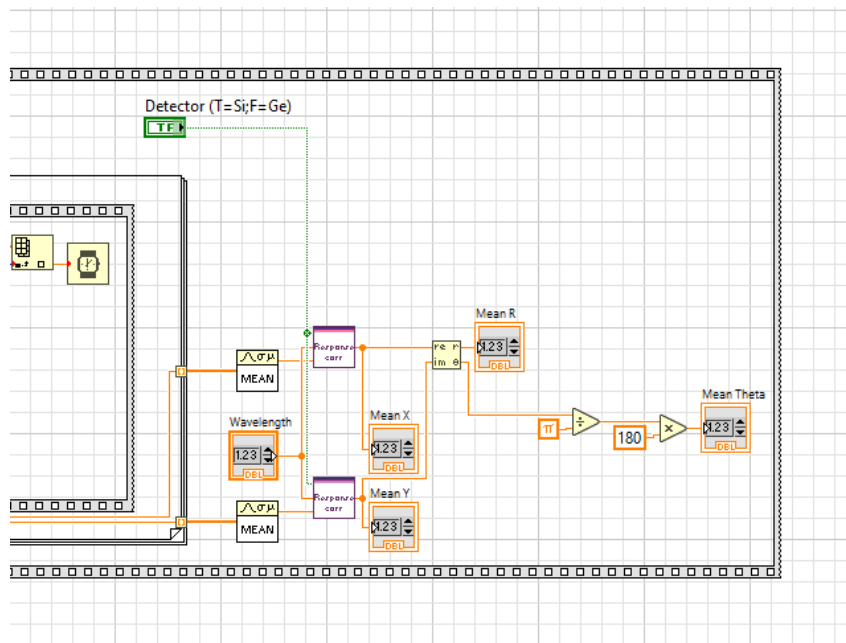


Figure 57: LIA acquire2/2.

B.9 LIA_Check_Overload

The LIA_Check_Overload VI is used to check if the signal input of the lock-in amplifier generates an overload error. The VI takes the VISA refnum of the lock-in amplifier.

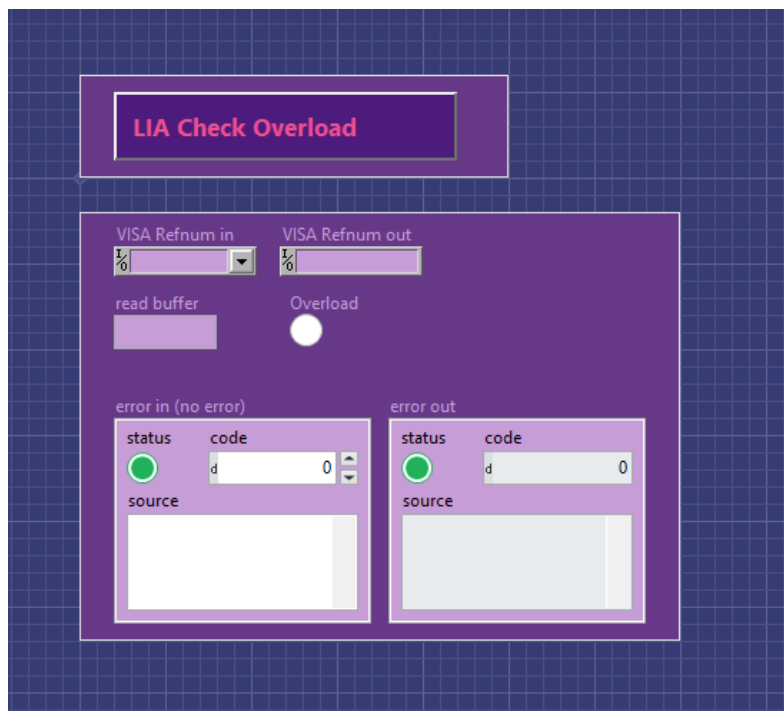


Figure 58: Front panel of the LIA_Check_Overload VI.

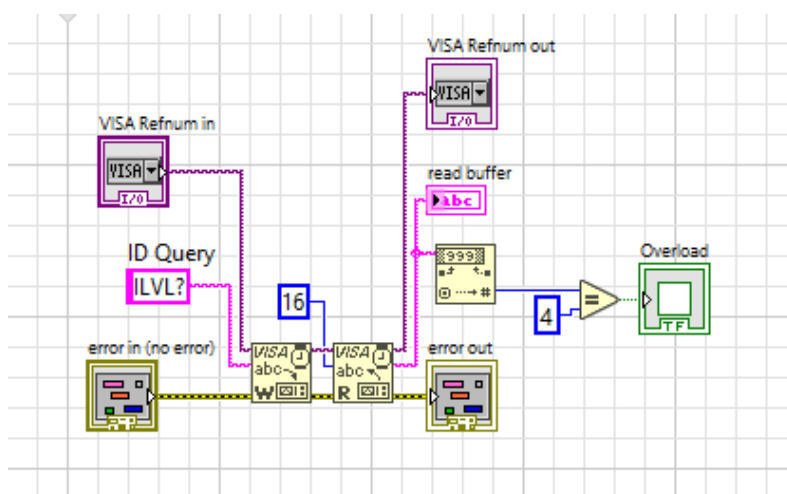


Figure 59: LIA_Check_Overload VI.

B.10 LIA_Filter_Setup

The LIA_Filter_Setup VI is used to set the filter settings of the lock-in amplifier. The VI takes the VISA refnum of the lock-in amplifier, a boolean to enable/disable the sync filter, an integer ring specifying the time constant, and an integer ring to specify the filter slope.

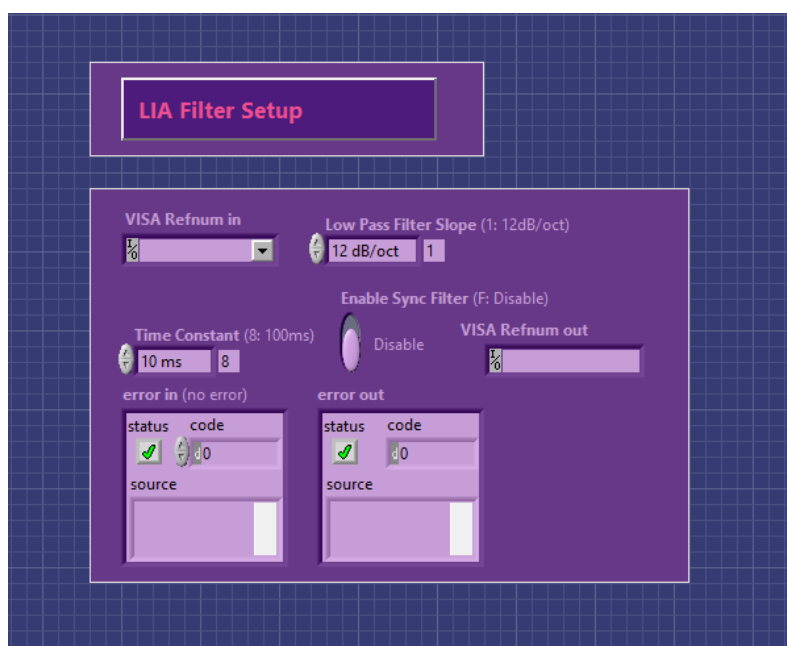


Figure 60: Front panel of the LIA_Filter_Setup VI.

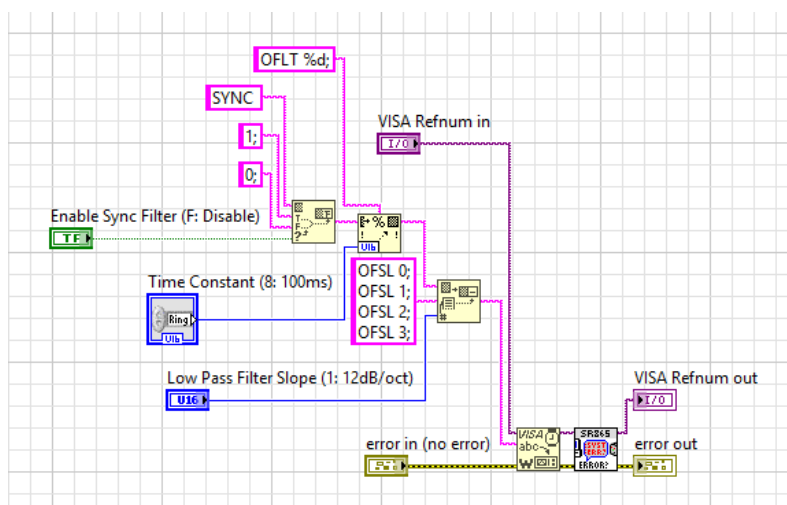


Figure 61: LIA_Filter_Setup VI.

B.11 LIA_Read_X_Y

The LIA_Read_X_Y VI is used to read the X and Y data channels of the lock-in amplifier. The VI takes the VISA refnum of the lock-in amplifier and two integer rings to specify, which two data channels are read.

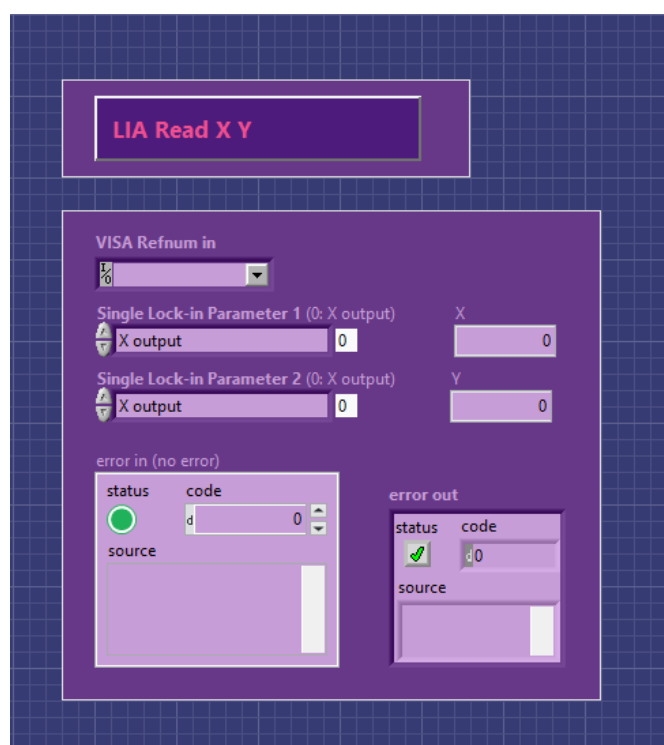


Figure 62: Front panel of the LIA_Read_X_Y VI.

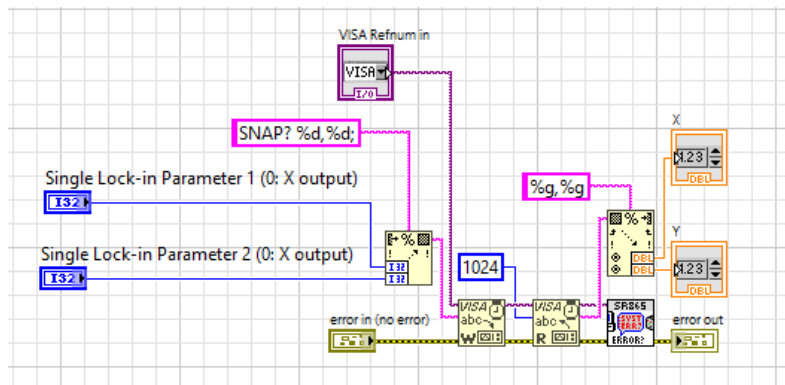


Figure 63: LIA_Read_X_Y VI.

B.12 LIA_Reference_Setup

The LIA_Reference_Setup VI is used to set the reference setting of the lock-in amplifier to use the external reference as a positive TTL signal with high impedance. The VI takes the VISA refnum of the lock-in amplifier.

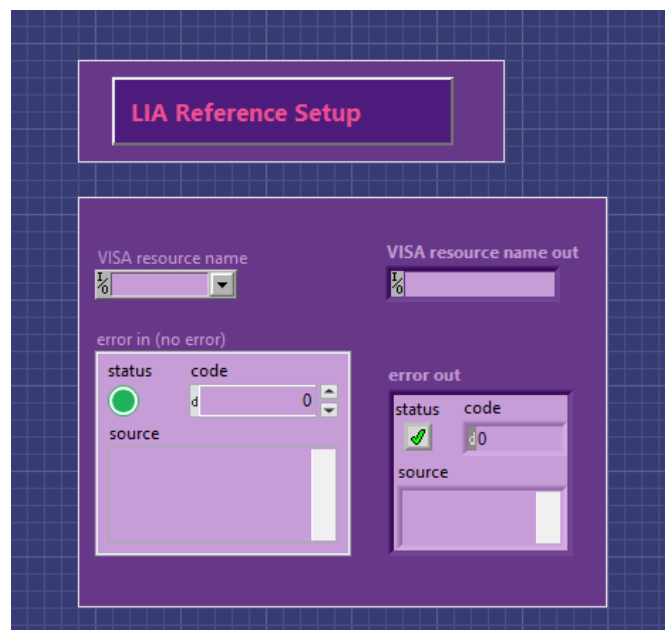


Figure 64: Front panel of the LIA_Reference_Setup VI.

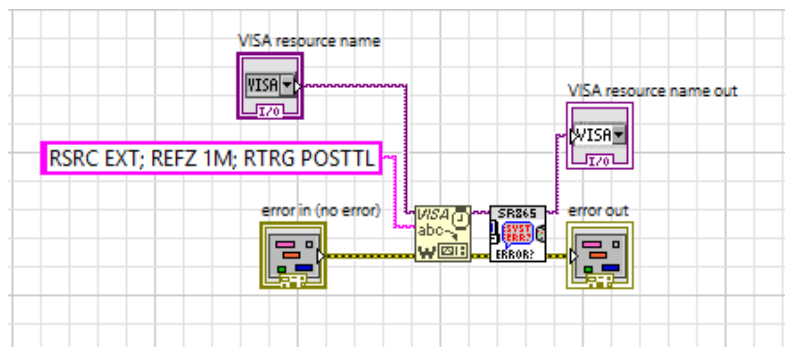


Figure 65: LIA_Reference_Setup VI.

B.13 LIA_Reference_Setup_internal

The LIA_Reference_Setup VI is used to set the reference setting of the lock-in amplifier to use the internal reference, set the frequency of the internal oscillator of the lock-in amplifier and use the BlazeX output of the lock-in amplifier. The VI takes the VISA refnum of the lock-in amplifier and the frequency at which the laser should be modulated.

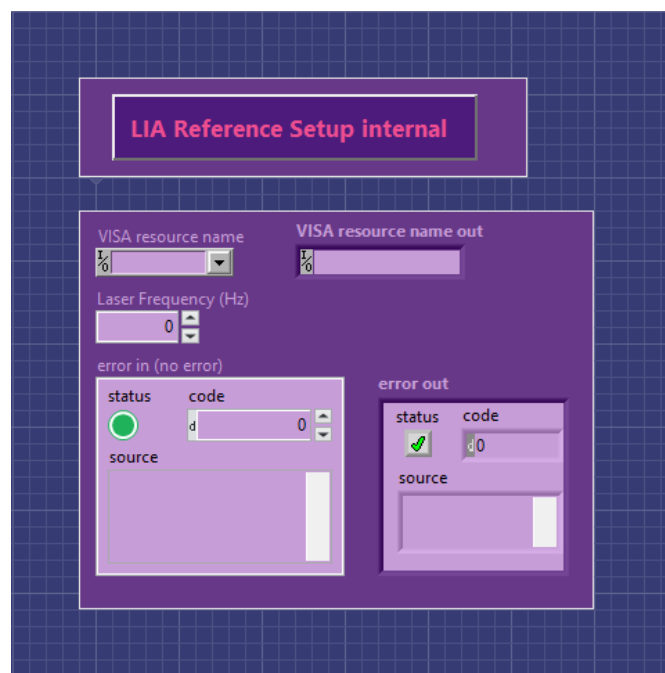


Figure 66: Front panel of the LIA_Reference_Setup_internal VI.

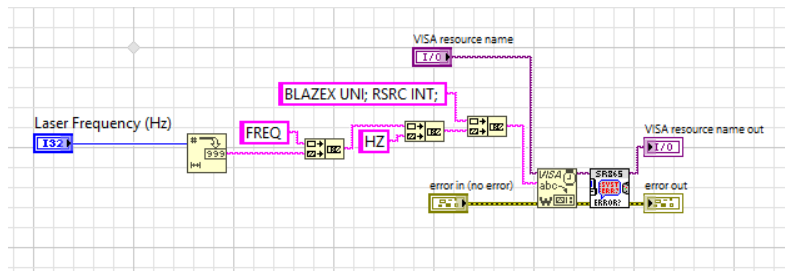


Figure 67: LIA_Reference_Setup_internal VI.

B.14 Wait_x_time_constant

The Wait_x_time_constant VI is used to a multiple of time constants. It takes an integer ring to specify the time constant of the lock-in amplifier and a multiplicator (DBL).

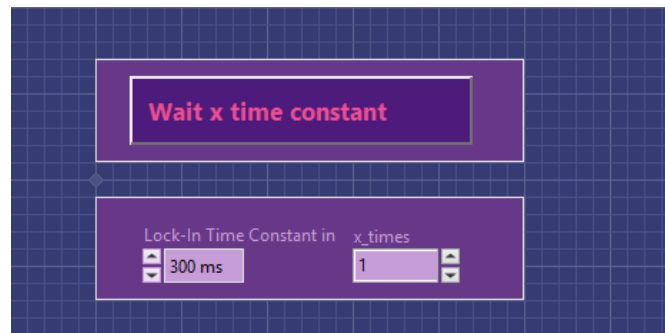


Figure 68: Front panel of the Wait_x_time_constant VI.

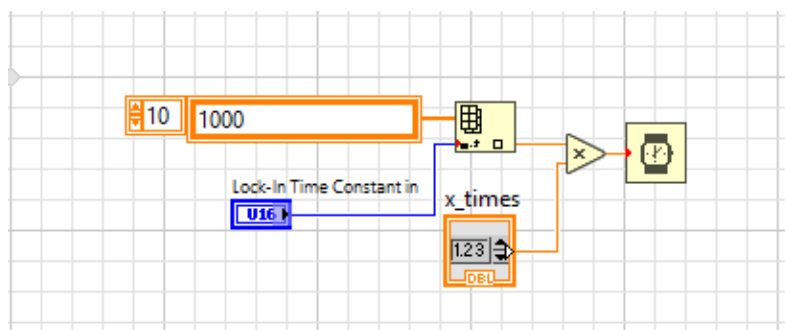


Figure 69: Wait_x_time_constant VI.

C Appendix: LabVIEW Main Program 'PIA-Launcher'

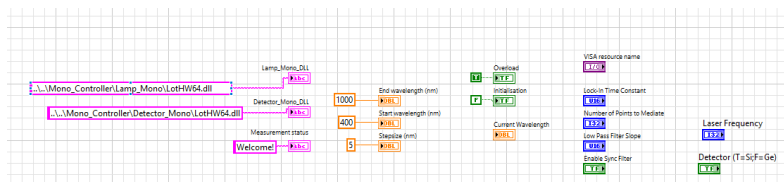


Figure 70: Variables defined outside the main loop.

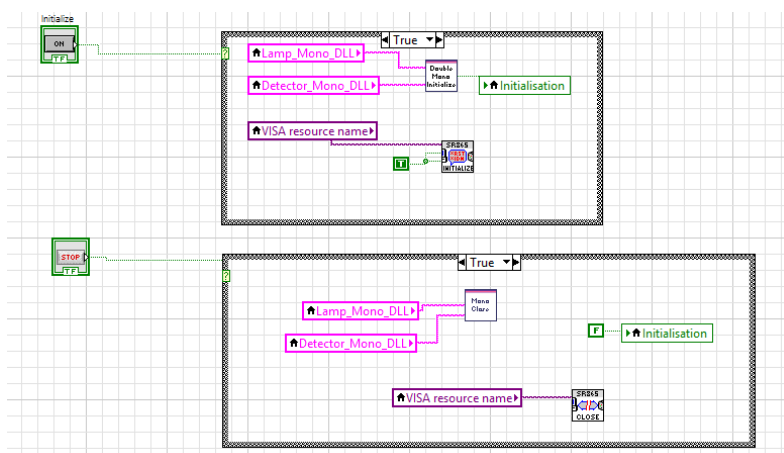


Figure 71: Initialize and Close functions of the program.

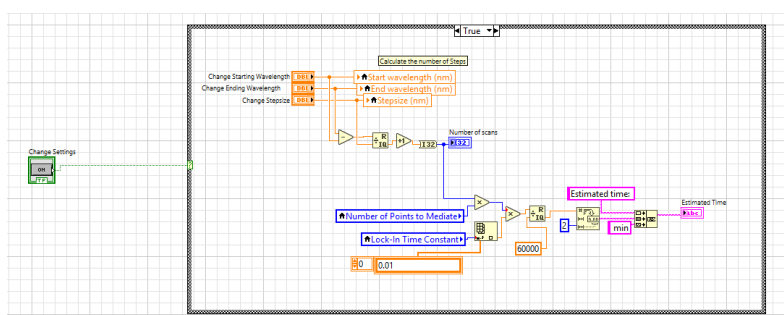


Figure 72: Changing the scanning parameters and calculate the number of scans and estimated time.

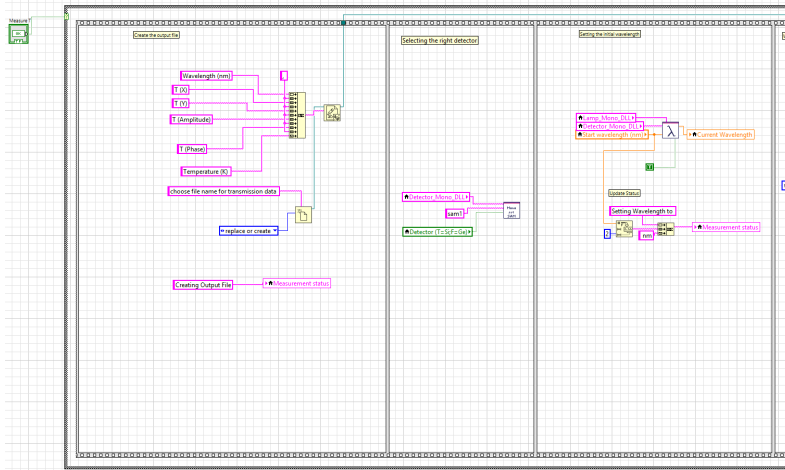


Figure 73: First three frames of the transmission subprogram.

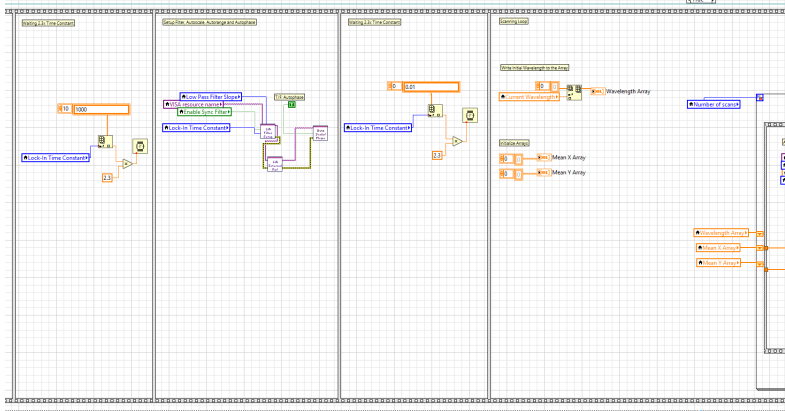


Figure 74: Frames 4-6 of the transmission subprogram.

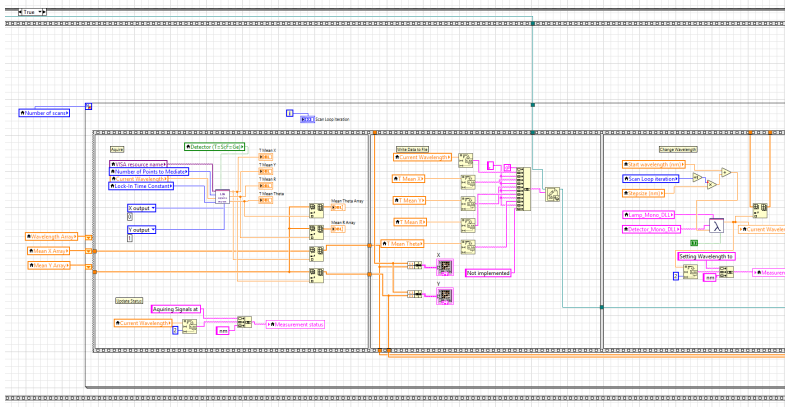


Figure 75: Frame 7 of the transmission subprogram with part 1 of the main scanning loop.

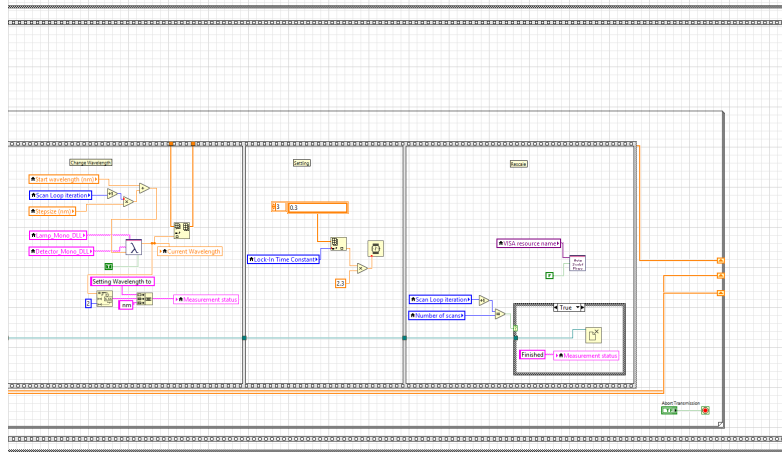


Figure 76: Frame 7 of the transmission subprogram with part 2 of the main scanning loop.

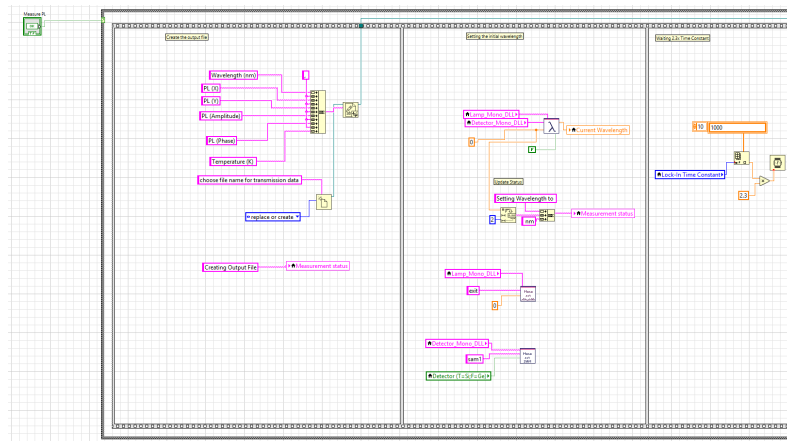


Figure 77: Frames 1-3 of the PL subprogram.

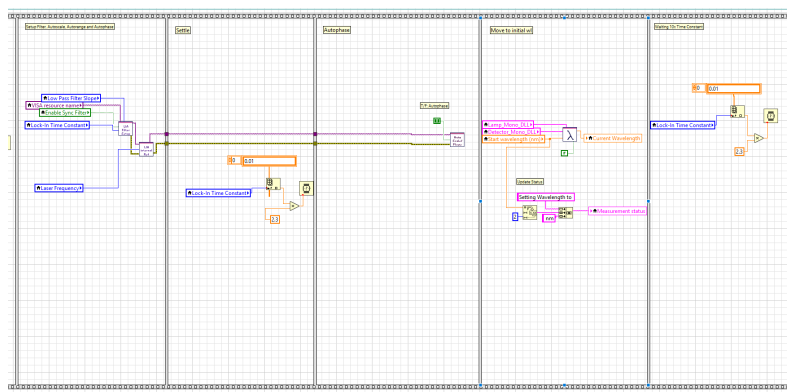


Figure 78: Frames 4-8 of the PL subprogram.

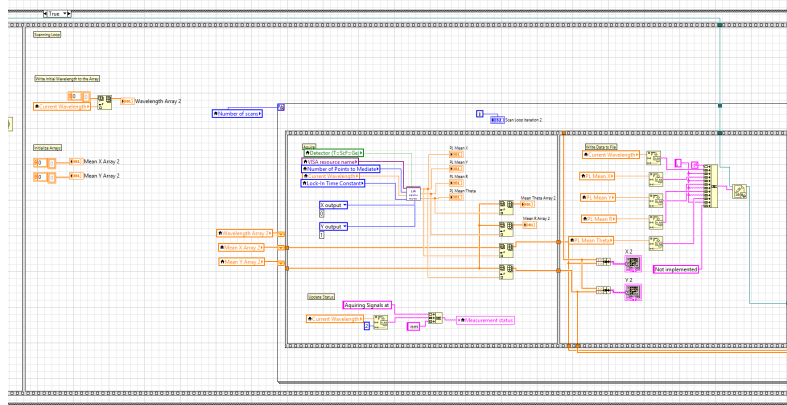


Figure 79: Frame 9 of the PL subprogram with part 1 of the main scanning loop.

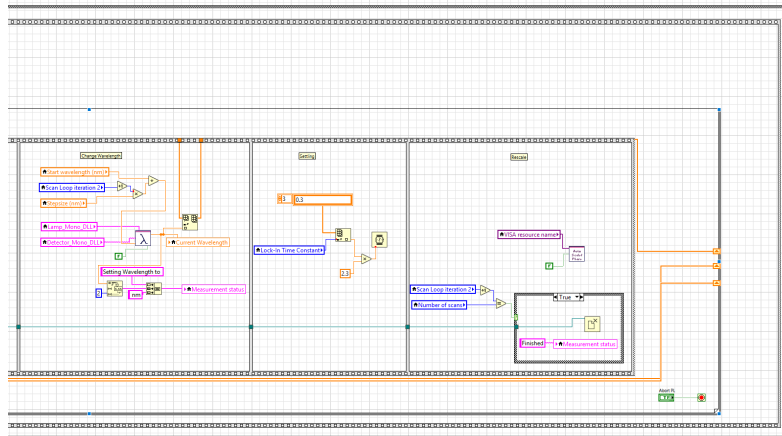


Figure 80: Frame 9 of the PL subprogram with part 2 of the main scanning loop.

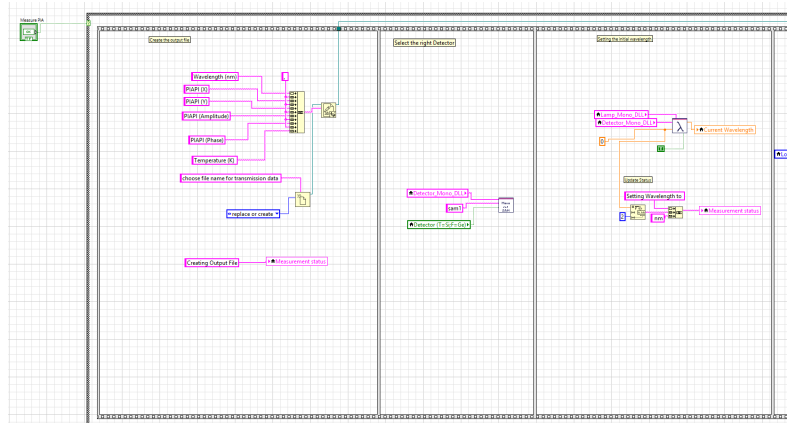


Figure 81: Frames 1-3 of the PIA+PL subprogram.

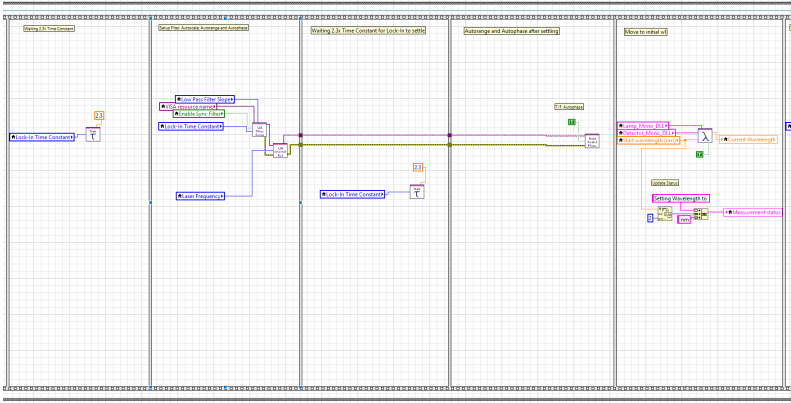


Figure 82: Frames 4-8 of the PIA+PL subprogram.

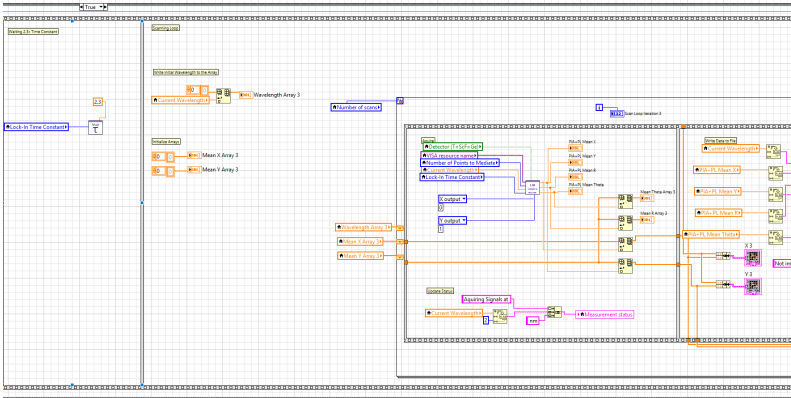


Figure 83: Frame 9 + 10 of the PL subprogram with part 1 of the main scanning loop.

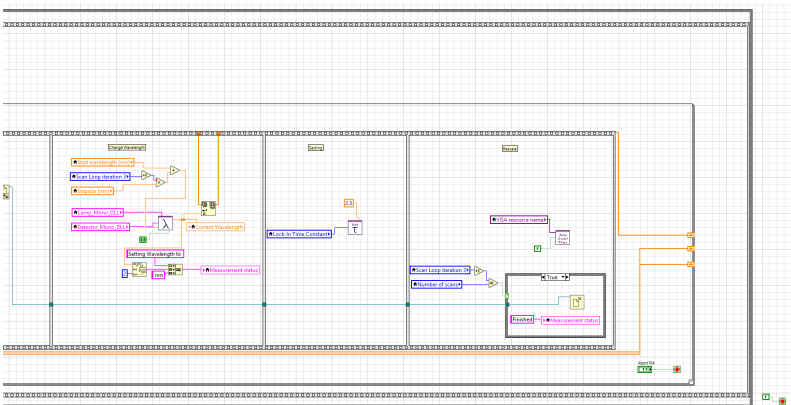


Figure 84: Frame 10 of the PL subprogram with part 2 of the main scanning loop.

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