

# THORLABS

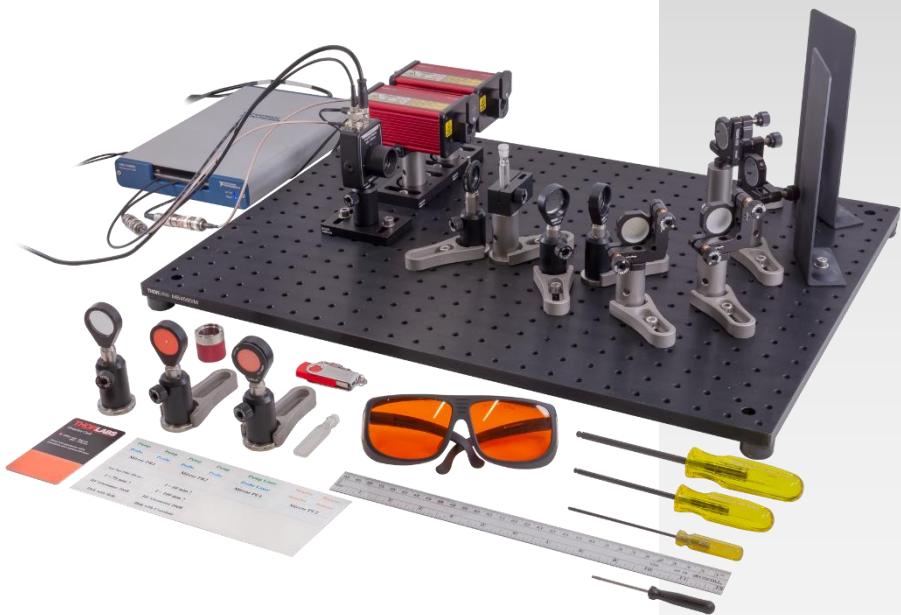
Discovery

**EDU-TRAS1**

**EDU-TRAS1/M**

## **Time-Resolved Absorption Spectroscopy Kit**

**Manual**





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# Chapter 1 Warning Symbols

Below is a list of warning symbols you may encounter in this manual or on your device.

Symbol	Description
	Caution: Risk of Danger
	Warning: Laser Radiation
	ESD Sensitive Equipment

## Chapter 2 Brief Description

### 2.1. Introduction

Optical spectroscopy has made a major contribution to the development of today's concept of atomic and molecular structure, and it is indispensable as an analysis procedure in research and industry. While optical spectroscopy measures the static optical properties of matter by continuous excitation with light, time-resolved spectroscopy focuses on the underlying process of electron photo-excitation and the analysis of photochemical reactions. Electronic transitions and the subsequent chemical reactions unfold within a few picoseconds up to hundreds of microseconds after photoexcitation. To monitor these processes, a typical approach includes acquiring spectra in multiple snapshots directly after light absorption in the studied material; this reveals the temporal evolution of these processes. As a result, time-resolved absorption spectroscopy is a modern tool for physicists and chemists to study a broad range of material properties and chemical reactions on the most fundamental level.

Thorlabs' time-resolved absorption spectroscopy kit uses two lasers to create very short pulses of light (2 ns - 140 ns) to investigate the excitation of the well-studied molecule Zinc-Tetraphenylporphyrin (ZnTPP) and subsequent charge transfer process to a fullerene. By varying the delay between an excitation pulse and a probe pulse, the absorption of the probe laser changes. The resulting signal, called the transient absorption intensity (TA)<sup>1</sup>, can be used to evaluate kinetic reaction models and mechanisms.

This kit teaches an advanced spectroscopy technique designed for a master's level lab courses in physics and chemistry. It educates scientists in nanosecond time-resolved spectroscopy, which builds on the knowledge of simple flash photolysis or spectroscopy experiments and leads up to ultrafast, very complex pico- to attosecond spectroscopy experiments.

### 2.2. Experimental Setup

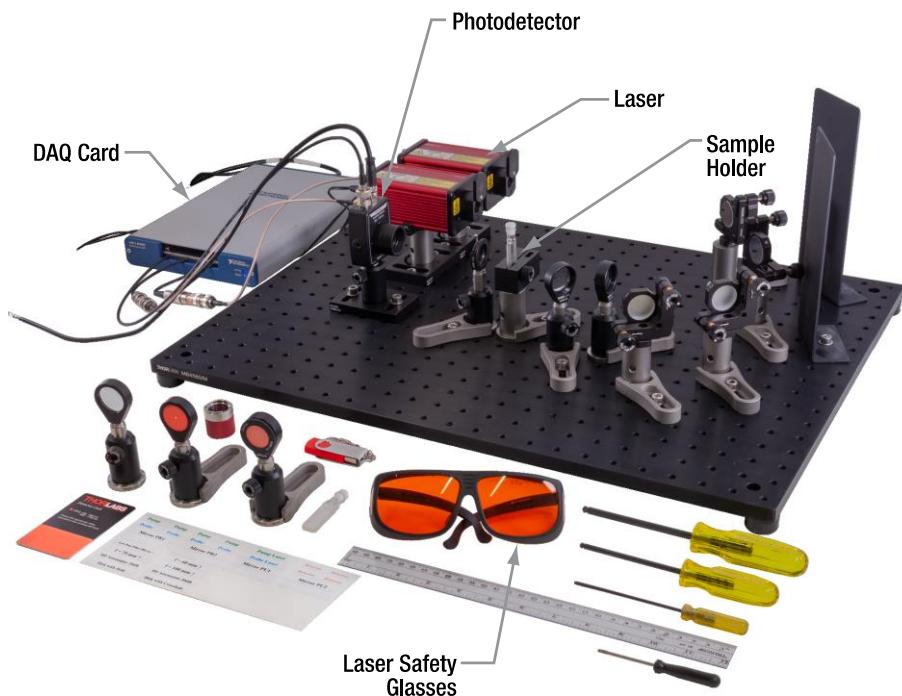
The experimental setup shown in Figure 1 consists of two nanosecond pulsed lasers: one pump laser for the molecule excitation and one probe laser for the analysis of excited states. The probe laser intensity is measured via a photodetector, and the signal routing is controlled by a data acquisition card (DAQ). Students start by overlapping the nanosecond pulsed laser beams at the sample position with two mirrors and one focusing lens for each laser. Laser safety goggles and beam alignment tools are also included.

Zinc-Tetraphenylporphyrin is a well-characterized molecule and was therefore chosen for this kit. A sample preparation scheme starting with raw chemicals is shown in Chapter 7. Purchasing references for the chemicals can be found on the kit web presentation<sup>2</sup>. A pre-mixed sample kit is available in certain countries; please check the webpage for more information.

<sup>1</sup> Transient means lasting only a short time.

<sup>2</sup> [https://www.thorlabs.com/newgroupage9.cfm?objectgroup\\_id=14444](https://www.thorlabs.com/newgroupage9.cfm?objectgroup_id=14444)

Each kit includes a USB stick with the EDU-TRAS1 software package, which is used to trigger the lasers and acquire data. The pump versus probe laser delay is also set within this software, and it saves the time-resolved transient absorption curves. Note that this software is a standalone installer<sup>3</sup> and does not require any licenses. Data can then be evaluated with any data processing software.



**Figure 1** Experimental Setup with Nanosecond-Pulsed Lasers, Cuvette Holder, Photodetector, Data Acquisition Card, and Laser Safety Goggles

## 2.3. Photochemical Process

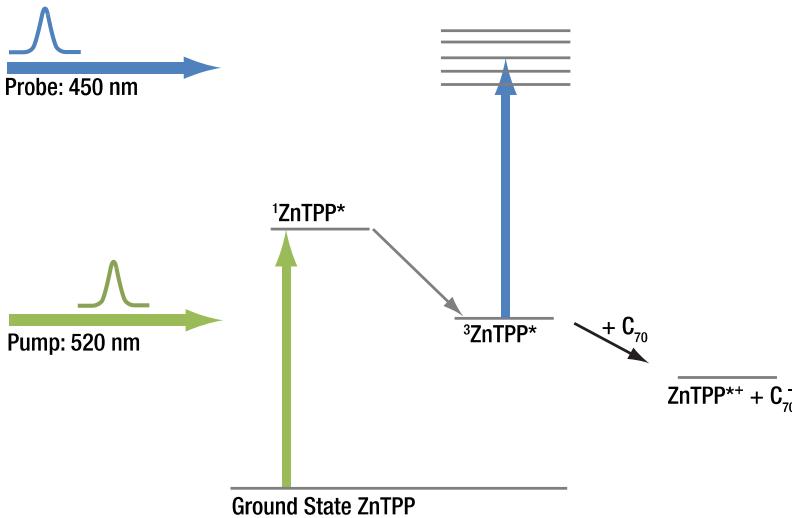
The rate of electron transfer from a donor to an acceptor molecule is of fundamental importance in light harvesting, which aims to improve the efficiency of solar energy conversion. With its high stability and functional optoelectronic properties, Zinc-Tetraphenylporphyrin (ZnTPP) is a molecule that is often used as an electron donor in

<sup>3</sup> This is a LabVIEW®-based executable file.

applications such as artificial photosynthesis, solar cells, nonlinear optical systems, and organic-based photovoltaic devices<sup>4</sup>.

The fundamental process investigated in this kit is the electron transfer from ZnTPP to a fullerene, which acts as an electron acceptor ( $C_{70}$ ). The transfer rate of this process is measured with a concentration-dependent series of ZnTPP to  $C_{70}$ . A concentration-dependent measurement is generally used to verify the reaction order, possible reaction paths and a reaction rate.

Figure 2 shows a simplified energy-level diagram of the molecules involved in the experiment. The pump laser excites ZnTPP molecules from the ground state to a singlet state ( $^1\text{ZnTPP}^*$ ) that almost immediately decays to a longer-living triplet state ( $^3\text{ZnTPP}^*$ ). This triplet state strongly absorbs the probe laser wavelength. In the presence of  $C_{70}$ , the  $^3\text{ZnTPP}^*$  state is depopulated due to an electron transfer process between the two molecules. This reduces the presence of  $^3\text{ZnTPP}^*$  and thus a reduced absorbance is measured.



**Figure 2 Simplified energy-level diagram of ZnTPP and  $C_{70}$ . Only the energy levels contributing to the Transient Absorption experiment are shown.**

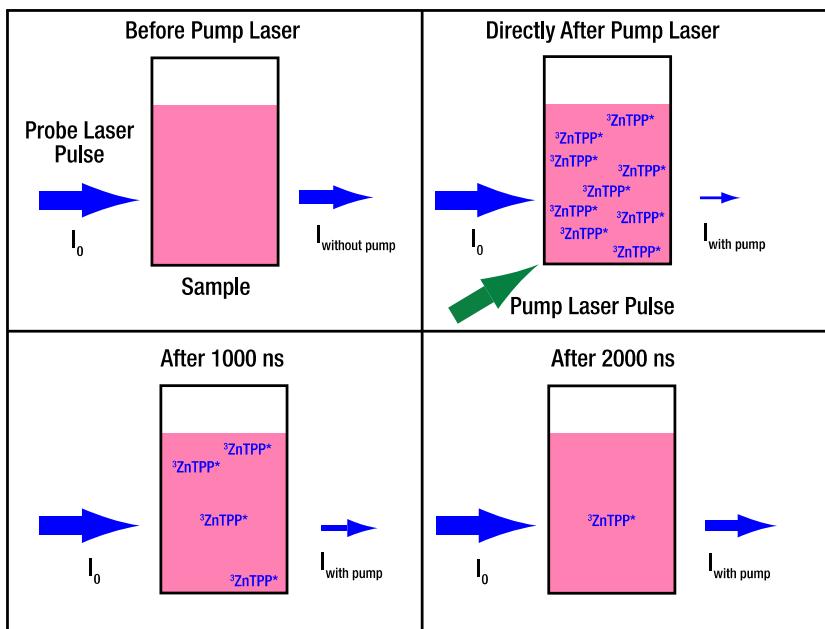
This kit investigates how the TA signal is affected by the pump beam focusing lens (see Chapter 10.1), varying ZnTPP concentrations (see Chapter 10.2), and the laser pulse width parameters (see Chapter 13.2).

<sup>4</sup> M.E. El-Khouly, O. Ito, P.M. Smith, and F. D'Souza, "Intermolecular and supramolecular photoinduced electron transfer processes of fullerene-porphyrin/phthalocyanine systems," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 5, no. 1, pp. 79 - 104, 2004.

## 2.4. Transient Absorption Measurement

The main goal of the transient absorption measurement is to examine how fast the  ${}^3\text{ZnTPP}^*$  state is depopulated after being populated by a pump laser pulse. This is done via an absorption measurement with a probe laser of a wavelength that is strongly absorbed by the  ${}^3\text{ZnTPP}^*$  triplet state (here: 450 nm). A photodetector measures the intensity of the probe laser after passing through the sample, and the absorbance of the sample can be determined from the detector voltages (see Chapter 5.1 for details). This measurement is repeated for different delays between the pump and probe pulses (see Chapter 6.1), which will determine the speed with which the  ${}^3\text{ZnTPP}^*$  state is depopulated.

The experiment is schematically shown in Figure 3. The  ${}^3\text{ZnTPP}^*$  concentration will be highest directly after the pump pulse hits the sample, and, as a result, the sample will absorb more of the probe laser pulse, resulting in a lower measured intensity behind the sample. Then, the excited state will decay over the span of several hundred nanoseconds, with the absorbance of the sample decreasing and the measured intensity increasing correspondingly.



**Figure 3** The blue arrows indicate the probe laser pulse train energy before ( $I_0$ ) and after passing the sample ( $I_{\text{with pump}}$ ). The thickness of the arrow correlates to the total energy / amount of photons. The  ${}^3\text{ZnTPP}^*$  concentration is highest directly after the pump laser absorption and decreases when time has passed. In turn, the intensity of the probe laser pulse train after passing the sample is higher with a lower  ${}^3\text{ZnTPP}^*$  concentration.

As the decay of  ${}^3\text{ZnTPP}^*$  is in the order of nanoseconds to microseconds, it is very difficult to measure this time dependence in one cycle. Data points would have to be recorded with a frequency of several 100 MHz to achieve sufficient resolution. Instead, the ZnTPP is repeatedly excited and a time series of transient absorption values is measured with a gradually shifting delay between the two pulses.

# Chapter 3 Safety

## 3.1. Laser Safety

Working with the included Class 3B lasers requires laser safety equipment. Contact your local laser safety officer to ensure the safety of the kit environment and protective eye wear. Up to date specifications for the lasers included in this kit can be found here:

[https://www.thorlabs.de/newgroupage9.cfm?objectgroup\\_id=10823&pn=NPL45B](https://www.thorlabs.de/newgroupage9.cfm?objectgroup_id=10823&pn=NPL45B)

[https://www.thorlabs.de/newgroupage9.cfm?objectgroup\\_id=10823&pn=NPL52C](https://www.thorlabs.de/newgroupage9.cfm?objectgroup_id=10823&pn=NPL52C)

An exemplary laser safety calculation according to European Norm (EN) can be found in Chapter 14.



**Warning: Laser Radiation** - This is a Class 3B laser system. Observe all safety precautions and wear protective eyewear appropriate for this type of device. Align system at lower output power if possible. Do not position device so that is difficult to access the switch and interlock.

VISIBLE LASER RADIATION  
WAVELENGTH: 405 nm TO 640 nm  
MAXIMUM AVERAGE POWER: 120 mW  
MAXIMUM PULSE: 650 nJ, 260 ns  
IEC 60825-1:2014

Caution – Use of controls or adjustments or performance of procedures other than those specified herein may result in hazardous radiation exposure.



**Caution: ESD Sensitive Component** - The components inside this instrument are ESD sensitive. Take all appropriate precautions to discharge personnel and equipment before making any connections to the unit.



**Caution: Components not Water Resistant** - This instrument should be kept clear of environments where liquid spills or condensing moisture are likely. It is not water resistant. To avoid damage to the instrument, do not expose it to spray, liquids, or solvents.



**Caution: Follow Intended Usage Guidelines**

Inputs and outputs must only be connected with shielded connection cables.

The safety of any system incorporating the equipment is the responsibility of the assembler of the system. If equipment is used in a manner not specified by the manufacturer, the protection provided by the equipment may be impaired. Only with written consent from Thorlabs may changes to single components be

carried out or components not supplied by Thorlabs be used. There are no user serviceable components inside this device.

The kit uses fluorescent detector cards which convert photons of the blue and green lasers in the red range, making the laser beams easily visible while wearing the laser safety goggles.

### 3.2. Chemicals

The chemicals used in this kit are commercially available and all safety classifications, i.e. Material Safety Data Sheets (SDS / MSDS), are described in the respective suppliers' documentation. All documents must be read, understood, and followed to perform the experiments described in this kit.

Handling these raw chemicals requires an equipped chemistry lab and access to waste disposal facilities.

Chemicals often have shipping restrictions, so not all chemicals might be available in your country. Thorlabs also offers a premixed sample kit (only available in specific countries). Please check the availability of the sample kit or raw chemicals before purchasing the kit. More information can be found on the kit website:

[https://www.thorlabs.com/newgroupage9.cfm?objectgroup\\_id=14444](https://www.thorlabs.com/newgroupage9.cfm?objectgroup_id=14444) .

The following data provides a quick overview and does not replace reading the complete Safety Data Sheet.

Benzonitrile Anhydrous, ≥99%	
CAS Number	100-47-0
Linear Formula	C <sub>6</sub> H <sub>5</sub> CN
Molecular Weight	103.12 g/Mol
Beilstein/REAXYS	506893
EC Number	202-855-7
MDL Number	MFCD00001770
eCl@ss	39031505
PubChem Substance ID	57648369
NACRES	NA.21

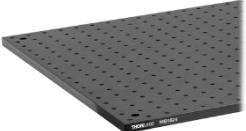
Zinc-Porphyrin	
CAS Number	14074-80-7
Empirical Formula (Hill Notation):	C <sub>44</sub> H <sub>28</sub> N <sub>4</sub> Zn
Molecular Weight	678.11 g/Mol
Beilstein/REAXYS	-
EC Number	-
MDL Number	MFCD00012155
eCl@ss	-
PubChem Substance ID	24855187
NACRES	NA.23

C <sub>70</sub> Fullerene (98%)	
CAS Number	115383-22-7
Empirical Formula (Hill Notation):	C <sub>70</sub>
Molecular Weight	840.75 g/Mol
Beilstein/REAXYS	-
EC Number	-
MDL Number	MFCD00146976
eCl@ss	-
PubChem Substance ID	24871859
NACRES	NA.23

## Chapter 4 Kit Components

In cases where the metric and imperial kits contain parts with different item numbers, metric part numbers and measurements are indicated by parentheses unless otherwise noted.

### 4.1. Breadboard

	
<b>1 x MB1824 (MB4560/M)</b> Aluminum Breadboard, 18" x 24" x 1/2" (45 cm x 60 cm x 1.27 cm)	<b>2 x RDF1</b> Rubber Damping Feet, Pack of 4

### 4.2. Light Sources

	
<b>1 x NPL45B</b> Nanosecond Pulse Laser Diode System, 450 nm, 5 - 39 ns Adjustable Pulse Width	<b>1 x NPL52C</b> Nanosecond Pulse Laser Diode System, 520 nm, 6 - 129 ns Adjustable Pulse Width

### 4.3. Optical and Mechanical Components

 <b>4 x KM100</b> Ø1" Kinematic Mirror Mount	 <b>4 x BB1-E02</b> Ø1" Broadband Dielectric Mirror	 <b>5 x RS2P8E (RS2P4M)</b> Ø1" (Ø25.0 mm) Pedestal Post, 8-32 (M4) Taps, 2" (50 mm) Long
 <b>2 x BA2F(M)</b> Flexure Clamping Base 2.00" x 3.00" x 0.48" (50.8 mm x 75 mm x 12.1 mm)	 <b>7 x CF125</b> Clamping Fork, 1.24" (31.5 mm)	 <b>2 x RS2P8 (RS50P4/M)</b> Ø1" Pillar Post, 8-32 (M4) Taps, 2" (50 mm) Length
 <b>4 x KCP1(M)</b> Centering Plate for Ø1" Kinematic Mirror Mount	 <b>5 x LMR1(M)</b> Ø1" Threaded Lens Mount with Retaining Ring	 <b>1 x LA1134-A</b> N-BK7 Plano-Convex Lens, Ø1", f = 60 mm, Anti-Reflection Coated

		
<p><b>1 x LA1608-A</b> N-BK7 Plano-Convex Lens, <math>\varnothing 1"</math>, f = 75 mm, Anti-Reflection Coated</p>	<p><b>1 x LA1509-A</b> N-BK7 Plano-Convex Lens, <math>\varnothing 1"</math>, f = 100 mm, Anti-Reflection Coated</p>	<p><b>1 x SM1L05</b> SM1 Lens Tube, 0.5" Threaded Depth, Retaining Ring Included</p>
		
<p><b>1 x FESH0500</b> <math>\varnothing 25</math> mm Shortpass Filter, Cut-Off WL = 500 <math>\pm</math> 3 nm</p>	<p><b>1 x IDA15 (IDA15/M)</b> Mounted Standard Iris, <math>\varnothing 15.0</math> mm Max Aperture – Single Item</p>	<p><b>1 x TR2 (TR50/M)</b> <math>\varnothing 1/2"</math> (12.7 mm) Post, 2" (50 mm) Long</p>
		
<p><b>7 x PH1.5 (PH40/M)</b> <math>\varnothing 1/2"</math> (12.7 mm) Post Holder, 1.5" (40 mm) Long</p>	<p><b>5 x TR1.5 (TR40/M)</b> <math>\varnothing 1/2"</math> (12.7 mm) Post, 1.5" (40 mm) Long</p>	<p><b>1 x TR1.5 (TR30/M)</b> <math>\varnothing 1/2"</math> (12.7 mm) Post, 1.5" (30 mm) Long</p>

 <b>6 x BE1(/M)</b> Ø1.25" (31.8 mm) Pedestal Base Adapter 1/4"-20 (M6) Thread	 <b>1 x BA2(/M)</b> Mounting Base, 2" x 3" x 3/8" (50 mm x 75 mm x 10 mm)	 <b>1 x Cuvette Holder</b>
 <b>1 x TS25H (TS6H/M)</b> Spring-Loaded Thumbscrew, 1/4"-20 (M6) Thread		

#### 4.4. Detector

 <b>1 x PDA36A2</b> Si Switchable Gain Detector, 350 - 1100 nm, 12 MHz Bandwidth, 13 mm <sup>2</sup> , Universal 8-32 / M4 Taps
-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------

## 4.5. Electronics

		
<p><b>1 x DAQ-Card</b> NI USB-6341 DAQ Card</p>	<p><b>1 x RG-174 BNC Coaxial Cable</b>, BNC Male to Terminal Pin/Crimp 24" (60 cm)</p>	<p><b>1 x RG-174 BNC Coaxial Cable</b>, BNC Female to Crimped End 6" (15 cm)</p>

## 4.6. Tools

		
<p><b>1 x VRC2</b> VIS/IR Detector Card, 400 - 640 nm, 800 - 1700 nm</p>	<p><b>1 x VRC2SM1</b> SM1-Threaded VIS/IR Alignment Disk 400 - 640 nm, 800 - 1700 nm</p>	<p><b>1 x VRC2D1</b> Ø1" VIS/IR Alignment Disk 400 - 640 nm, 800 - 1700 nm</p>

 <b>2 x TPSM1/(M)</b> Magnetic Laser Safety Screen, 7.87" x 2.95" (20 cm x 7.5 cm)	 <b>1 x CV2G07AE</b> Micro Cuvette 2 mm Thick, 2 Pack	 <b>1 x Ruler</b> 30 cm Long
 <b>1 x SPW606</b> SM1 Spanner Wrench, 1" Long	 <b>1 x Label Sheet</b>	 <b>1 x LG3</b> Laser Safety Glasses

**Imperial Kit**

Type	Quantity	Hex Keys: 3/16", 9/64", 5/64"
8-32 x 5/8" Setscrew	5	
1/4"-20 x 1/4" Cap Screw	3	
1/4"-20 x 3/8" Cap Screw	4	
1/4"-20 x 1/2" Cap Screw	10	
1/4"-20 x 5/8" Cap Screw	2	
1/4"-20 Washer	14	
 <b>1 x BD-9/64</b> Balldriver for 8-32 Cap Screws		 <b>1 x BD-3/16</b> Balldriver for 1/4"-20 Cap Screws
 <b>1 x BD-5/64</b> Balldriver for 5/64" Hex		

**Metric Kit**

Type	Quantity	Hex Keys: 5 mm, 3 mm, 2 mm
M4 x 16 mm Setscrew	5	
M6 x 6 mm Cap Screw	3	
M6 x 10 mm Cap Screw	4	
M6 x 12 mm Cap Screw	10	
M6 x 16 mm Cap Screw	2	
M6 Washer	14	
 <b>1 x BD-3M</b> Balldriver for M4 Cap Screws		 <b>1 x BD-5M</b> Balldriver for M6 Cap Screws
 <b>1 x BD-2M</b> Balldriver for M2.5 Cap Screws		

## Chapter 5 Theoretical Background and Processes

The theoretical background and processes involved in transient absorption are described in this chapter. The light absorption process in a material is described with Lambert-Beer's law and is the basis for the calculation of a transient absorption process, as shown in Section 5.1.

In the scope of this kit, a triplet state of ZnTPP is excited and its decay and deactivation via an electron acceptor is studied. The generation and deactivation paths are described in Section 5.2.

In Section 5.3, the time and concentration-dependent reaction rate is described, which introduces the decay time of the excited triplet.

The reaction paths created by introducing a second material as an electron transfer partner are shown in Section 5.4 and 5.5.

### 5.1. Transient Absorption

Transient Absorption spectroscopy measures the change in absorbance of a sample after excitation by light. This technique studies the kinetic details of chemical processes down to pico- or femtoseconds, enabling the detection of intermediate states of photochemical reactions and electron transfer processes.

The experiments in this kit calculate the transient absorption (denoted TA or  $\Delta A$ ) of a molecular system via a transmission measurement. From the time dependent transient absorption, the reaction rates and mechanisms can be determined.

Transient absorption is defined as the difference in absorbance  $\Delta A$  between two states of the system: absorbance of the probe laser by the sample directly following a pump laser pulse denoted  $A_{\text{with pump}}$  and absorbance of the probe laser without a pump laser pulse  $A_{\text{without pump}}$  (see Formula (1)). The measurements in this kit are performed at a fixed probe laser wavelength  $\lambda^5$ . The delay between pump and probe laser pulses is denoted  $\tau$ .

$$\Delta A(\lambda, \tau) = A(\lambda, \tau)_{\text{with pump}} - A(\lambda)_{\text{without pump}} \quad (1)$$

The TA signal  $\Delta A$  is calculated from these two measured values. By varying the delay  $\tau$  between pump and probe laser a TA decay curve is measured and used for evaluation.

The absorbance  $A$  of light in a substance follows Lambert-Beer's law<sup>6</sup>:

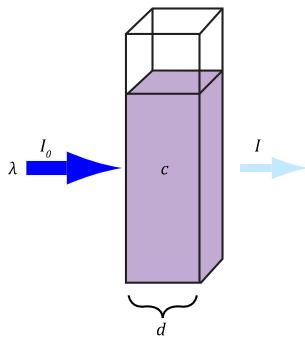
$$A = -\log\left(\frac{I}{I_0}\right) = d \cdot \sum_{i=1}^n \varepsilon_i \cdot c_i \quad (2)$$

Where the light path length through the sample is  $d$ , the molar extinction factor  $\varepsilon_i$  and the concentration  $c_i$  for all absorbing molecules  $i$ .

<sup>5</sup> A tunable pulsed probe laser source or multiple pulsed probe laser wavelengths can be used to gain further information about the underlying processes but are not included in this kit.

<sup>6</sup> The law is accurate only under certain sample and incident light conditions. Testing the validity of this law for the setup and sample configuration is omitted here.

The intensity  $I_0$  is the intensity of light before the sample and  $I$  is the intensity after passing through the sample as shown in Figure 4.



**Figure 4 Schematic of an absorption experiment.**

Inserting Formula (2) in (1) leads to formula (3).

$$\begin{aligned} \Delta A(\lambda, \tau) &= -\log \left( \frac{I(\lambda, \tau)_{\text{with pump}}}{I_0(\lambda)} \right) + \log \left( \frac{I(\lambda, \tau)_{\text{without pump}}}{I_0(\lambda)} \right) \\ &= \log(I_0(\lambda)) - \log(I(\lambda, \tau)_{\text{with pump}}) - \log(I_0(\lambda)) + \log(I(\lambda)_{\text{without pump}}) \\ &= -\log \left( \frac{I(\lambda, \tau)_{\text{with pump}}}{I(\lambda)_{\text{without pump}}} \right) \quad (3) \end{aligned}$$

In this kit, the probing is done with a fixed laser wavelength, this reduces Formula (3) to

$$\Delta A(\tau) = -\log \left( \frac{I(\tau)_{\text{with pump}}}{I_{\text{without pump}}} \right) \quad (4)$$

The transient absorption can thus be positive or negative. In the following sections, the various processes contributing to the transient absorption signal are described.

## 5.2. Transient Absorption Processes

The transient absorbance  $\Delta A$  has several contributing and competing processes<sup>7</sup>, which are schematically depicted in Figure 5:

1. **Stimulated Emission (SE):** The probing photon can interact with an excited molecule and lead to a stimulated relaxation back into the electronic ground state. This leads to the stimulated emission of a photon in the same direction and more detected photons in the probe beam, leading to a negative TA signal contribution.

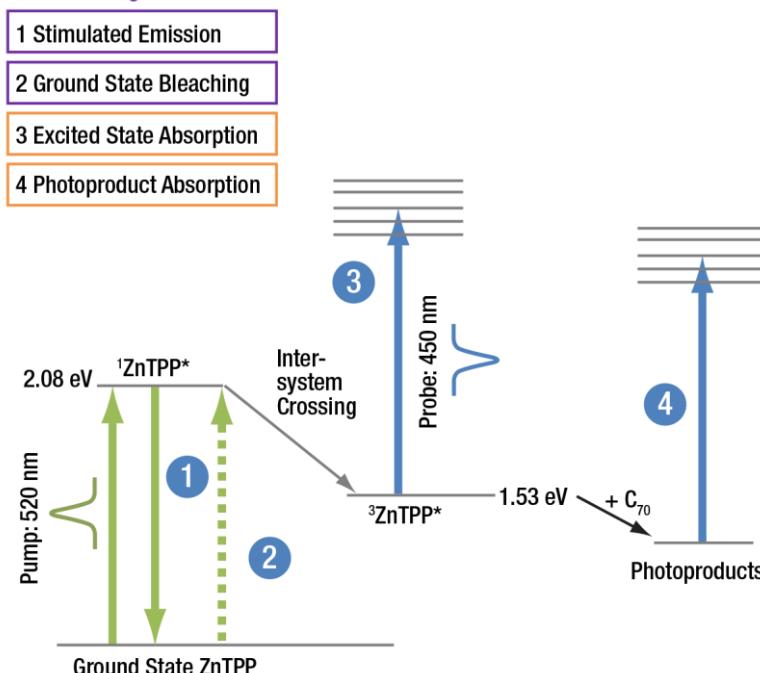
<sup>7</sup> R. Berera, R. van Grondelle, J. T. M. Kennis, "Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems," *Photosynthesis Research*, vol. 101, pp. 105 - 118, 2009.

2. **Ground-State-Bleaching (GSB):** After excitation with the pump laser pulse, fewer molecules are in the ground state, so the probability for further excitations from the ground state is decreased resulting in a negative TA signal contribution.
3. **Excited State Absorption (ESA):** Excited electrons can be further excited in higher states resulting in an absorption of the probe beam and a positive TA signal.
4. **Photoproduct<sup>8</sup> Absorption (PA):** The excited molecule can react, and a photoproduct is formed. The probe beam can be absorbed by the new photoproduct, resulting in a positive TA signal contribution.

#### Contributions to TA Signal

- Positive

- Negative



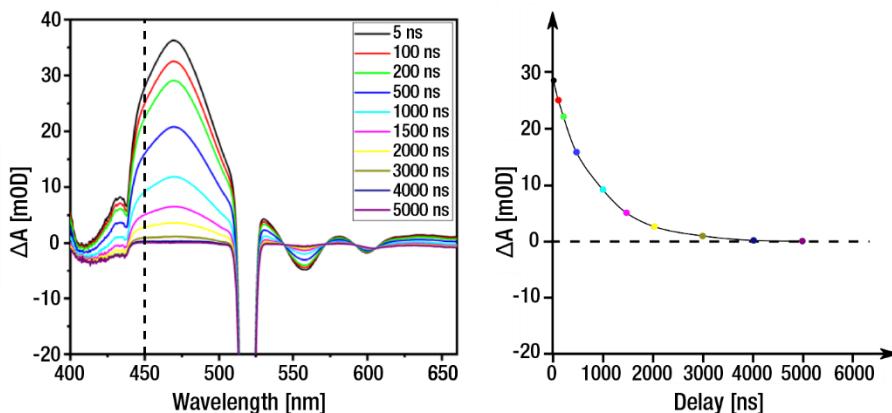
**Figure 5 Energy (Jablonski) diagram of possible excitation and deactivation paths in the transient absorption process. Processes can have positive or negative contributions to the measured TA signal. Process 1 and 2 (purple) reduce the TA signal whereas process 3 and 4 increase the TA signal.**

<sup>8</sup> In a photochemical reaction a molecule absorbs light and is excited. This excited chemical can have new properties and react with or change its structure to form a photoproduct. Famous examples are photosynthesis or photochemical etching in the fabrication of semiconductor chips.

Additionally, all contributions are (probe) wavelength dependent. Thus, the TA signal can be net positive or negative depending on the contribution of these effects. In this kit, the sample (ZnTPP) and the respective probe laser wavelength are chosen so that the positive contributions outweigh the negative contributions, creating a large net positive TA signal for demonstration purposes. An overview of the net TA signal with a tunable (wavelength) probe laser is shown in Figure 6.

In this kit, which has a 450 nm probing frequency, the dominating processes are ESA and PA since the overall TA signal is strongly positive. GSB can have some influence, but it is dominated by the other two processes.

The time scale of intersystem crossing (ISC<sup>9</sup>) of  $^1\text{ZnTPP}^*$  to  $^3\text{ZnTPP}^*$  is in the order of picoseconds and, therefore, too fast to be observed in the scope of this kit.



**Figure 6 TA Signal  $\Delta A$  for various probe wavelengths and delays  $\tau$  (5 ns - 5000 ns) between the pump and probe laser for ZnTPP in Benzonitrile. Provided by Jan Borstelmann, Tiago Buckup at CAM University of Heidelberg. The left plot shows the complete spectral data, while the right plot shows only the delay-dependent absorbance at 450 nm, which is the wavelength used in this kit (marked by the vertical dotted line in the left plot). At this wavelength, a positive TA signal is expected.**

### 5.3. Photoinduced Excitation of ZnTPP

In the first step the pump laser excites the ZnTPP via  $^1\text{ZnTPP}^*$  into a triplet state  $^3\text{ZnTPP}^*$ .

Typically, the rate of decay of a chromophore's triplet can be described as<sup>10</sup>:

<sup>9</sup>Intersystem crossing is a transition to a state with a different electron spin multiplicity.

<sup>10</sup>L. Pekkarinen and H. Linschitz, "Studies on Metastable States of Porphyrins. II. Spectra and Decay Kinetics of Tetraphenylporphine, Zinc Tetraphenylporphine and Bacteriochlorophyll<sup>1</sup>," *Journal of the American Chemical Society*, vol. 82, no. 10, pp. 2407 - 2411, 1960.

$$-\frac{d[C_T(t)]}{dt} = k_1 \cdot C_T(t) + k_2 \cdot (C_T(t))^2 + k_3 \cdot C_T(t) \cdot C_G(t) \quad (5)$$

$C_T(t)$  is the concentration of the excited  ${}^3\text{ZnTPP}^*$  triplet at a given time  $t$ .  $C_G(t)$  is the concentration of ZnTPP in the ground state, and the corresponding reaction rates are denoted  $k_i$ . The first term  $k_1 \cdot C_T(t)$  describes the relaxation back to the ground state and is the main mechanism of  ${}^3\text{ZnTPP}^*$  returning to the ground state (deactivation). The other two terms are bimolecular deactivation mechanisms where either an excited metastable state  $C_T(t)$  or the ground state  $C_G(t)$  takes part in the deactivation. The respective mechanisms for ZnTPP and C<sub>70</sub> are discussed in the following sections.

In typical experiments, the concentration of excited  ${}^3\text{ZnTPP}^*$  is much lower than the ground state concentration, so the term  $(C_T(t))^2 \ll C_T(t) \cdot C_G(t)$  is neglected for the following calculations.

The third term  $k_3 \cdot C_T(t) \cdot C_G(t)$  describes the deactivation of the excited  ${}^3\text{ZnTPP}^*$  by molecules of ZnTPP in the ground state. An additional assumption is that  $C_G(t)$  is not changed significantly by the excitation process (as comparatively few molecules are excited from the ground state) so that it becomes independent from time  $t$ , thus  $C_G(t)$  equals  $C_G$ . This reduces formula (5) to:

$$-\frac{d[C_T(t)]}{dt} = C_T(t) \cdot (k_1 + k_3 \cdot C_G) \quad (6)$$

The remaining reaction constants can be summarized to one term:  $k_o = k_1 + k_3 \cdot C_G$ , simplifying the differential equation further to a first order integrated rate law:

$$-\frac{d[C_T(t)]}{dt} = k_o \cdot C_T(t) \quad (6)$$

This type of differential equation is solved by an exponential function:

$$C_T(t) = C_T(0) \cdot e^{-k_o t} \quad (7)$$

This solution describes an exponential decay of the triplet state with a decay time  $T = \frac{1}{k_o}$ .

## 5.4. Quenching of States

Additional reactants can open new deactivation channels. This process is often referred to as quenching and includes a variety of processes (e.g. photoinduced electron transfer as described in the next section). Thus, a new term is added to the rate of decay shown in Equation 6.

$$-\frac{d[C_T(t)]}{dt} = k_o \cdot C_T(t) + k_q \cdot C_q \cdot C_T(t) \quad (8)$$

The reaction constant  $k_q$  and the concentration of quenching material  $C_q$  are denoted respectively. In this kit the concentration of C<sub>70</sub>, denoted  $C_{C70}$ , is a controlled quenching partner, but other quenching partners can be oxygen or other uncontrolled impurities.

Again, the reaction parameters can be summarized to a single term, which is called the apparent reaction constant:

$$k_{app} = k_0 + k_q \cdot C_q \quad (9)$$

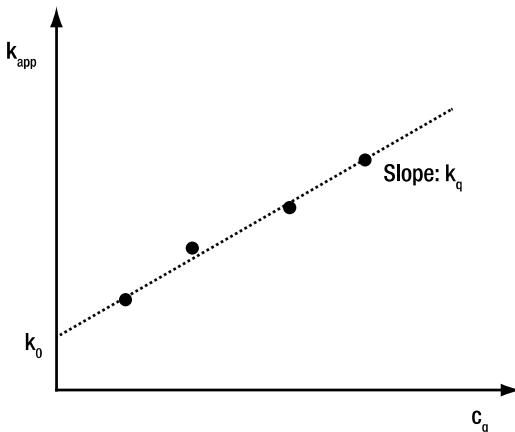
The solution of the differential equation (8) is of the same type as (7):

$$C_T(t) = C_T(0) \cdot e^{-k_{app} \cdot t}$$

Again, an exponential decay is described, and this time with a decay time  $T_{app} = \frac{1}{k_{app}}$ .

In the transient absorption experiment, this apparent decay time  $T_{app}$  is measured and the apparent reaction constant  $k_{app}$  is calculated from that. However, often it is of interest to determine the reaction constant  $k_q$  of the quenching reaction.

In order to separate  $k_q$  from  $k_0$ ,  $k_{app}$  is measured for various quenching partner concentrations of  $C_q$ . With the help of a graphical representation of  $k_{app}$  versus  $C_q$ , the reaction constant of the quenching partners  $k_q$  can be determined with a linear fit, as shown in Formula 9 and Figure 7. This information is used to describe the efficiency of the quenching material and contributes to the understanding of charge transfer efficiencies.



**Figure 7 Schematic plot used to determine the quenching reaction coefficient  $k_q$ .**

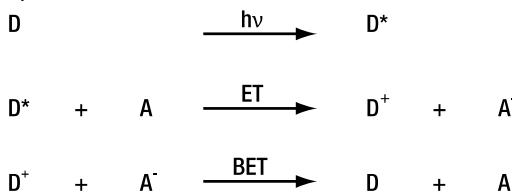
## 5.5. Photoinduced Electron Transfer Between ZnTPP and C<sub>70</sub>

Research on energy conversion systems and solar energy storage has gained importance in physical chemistry during the past decade. The process of photoinduced electron transfer (PET) converts solar energy / photons to chemical or electrical energy by charge separation<sup>11</sup>.

Intermolecular PET describes the transfer of electrons of an excited state induced by photons ( $D^*$ ) to an acceptor molecule (A) in the ground state. This leads to radical cations

<sup>11</sup> D. Meisel, "Electron Transfer in Heterogeneous System," in *Photochemical Conversion and Storage of Solar Energy*, edited by E. Pelizzetti and M. Schiavello (Springer, Dordrecht, 1991), pp. 15 - 26.

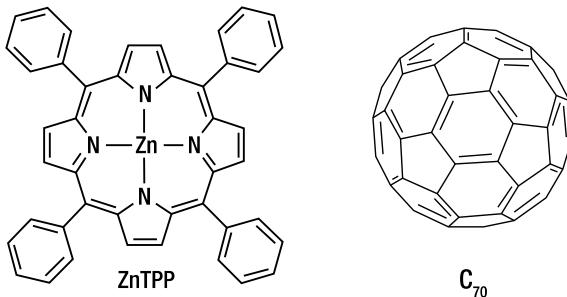
$D^+$  and radical anions  $A^-$ . In a back electron transfer (BET) these radicals change back to their ground states; see Figure 8. An intermolecular PET can also occur via photo-absorption of an acceptor.



**Figure 8 Reaction scheme for a molecule excitation.** From top to bottom, each line shows: a donor molecule  $D$  excited with light ( $\text{h}\nu$ ), intermolecular charge transfer (ET) to an acceptor molecule  $A$ , and back electron transfer (BET) to the ground state.

The efficiency of intermolecular PET has many variables; some examples include the energy levels of neighboring orbitals of  $D$  and  $A$ , steric hindrance, and the properties of the solvent.

The photochemical system of Porphyrin and Fullerenes (shown in Figure 9), which are known as electron donors and electron acceptors respectively, is a good starting point for learning about these processes.



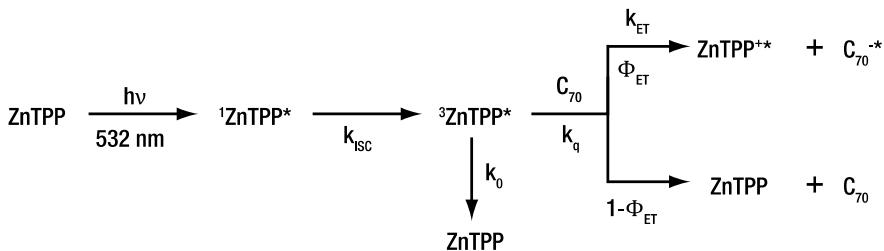
**Figure 9 Chemical structure of Zinc-Tetraphenylporphyrin (ZnTPP) and Fullerenes  $C_{70}$ .**

There are two dominant reaction paths, and the first is shown in Figure 10. The excitation of ZnTPP at 532 nm leads to an excited state  ${}^1\text{ZnTPP}^*$ , which decays to  ${}^3\text{ZnTPP}$ <sup>12,13</sup>. This very stable triplet with a lifetime of several hundred nanoseconds (characterized by the decay constant  $k_0$ ) can then either decay into the ground state ZnTPP ( $k_0$ ) with no further reactions or interact with present fullerenes ( $C_{70}$  in the scope of this kit) with the reaction

<sup>12</sup> T. Nojiri, A. Watanabe, and O. Ito, "Photoinduced Electron Transfer between  $C_{60}/C_{70}$  and Zinc Tetraphenylporphyrin in Polar Solvents," *Journal of Physical Chemistry A*, vol. 102, no. 27, pp. 5215 - 5219, 1998.

<sup>13</sup> A. Lukaszewicz et al., "Photophysical processes in electronic states of zinc tetraphenyl porphyrin accessed on one- and two-photon excitation in the sooret region," *Chemical Physics*, vol. 331, no. 2, pp. 359 - 372, 2007.

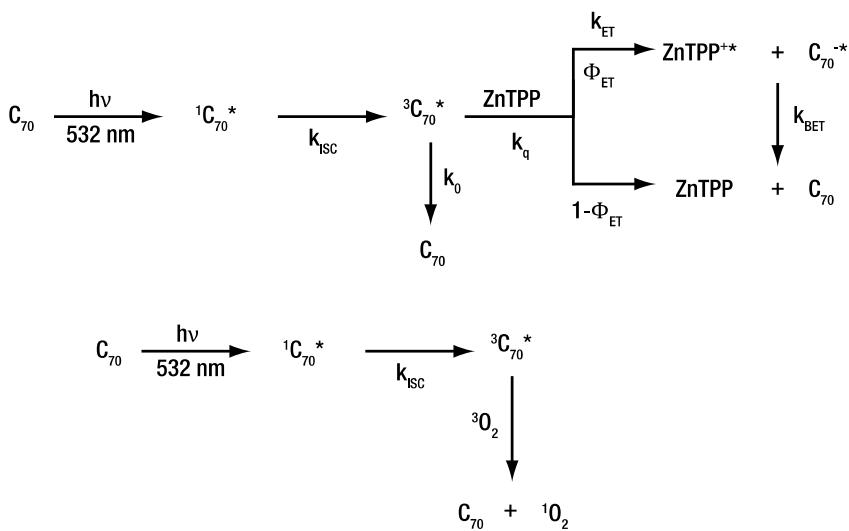
rate  $k_q$ . This path creates radical cations  $\text{ZnTPP}^{++}$  and anions  $\text{C}_{70}^{-*}$  with the reaction constant  $k_{\text{ET}}$  and the yield  $\Phi_{\text{ET}}$  with subsequent BET (k<sub>BET</sub>) to ZnTPP and  $\text{C}_{70}$  ( $1 - \Phi_{\text{ET}}$ ).



**Figure 10 First reaction path according to Nojiri et al.<sup>13</sup>**

With the excitation at 532 nm the fullerenes can also be excited, and a second reaction path opens up; see Figure 11. Molecular oxygen quenches the formed  $\text{C}_{70}$  triplets very efficiently<sup>14</sup>. In the scope of this kit we only operate in oxygenated atmosphere but the Benzonitrile is usually anhydrous, so a slow intake of oxygen over time (days) is visible in the results. The reaction pathway shown in Figure 11 is the dominant one for the oxygenated environment.

<sup>14</sup> M.E. El-Khouly, O. Ito, P.M. Smith, and F. D'Souza, "Intermolecular and supramolecular photoinduced electron transfer processes of fullerene-porphyrin/phthalocyanine systems," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 5, no. 1, pp. 79 - 104, 2004.

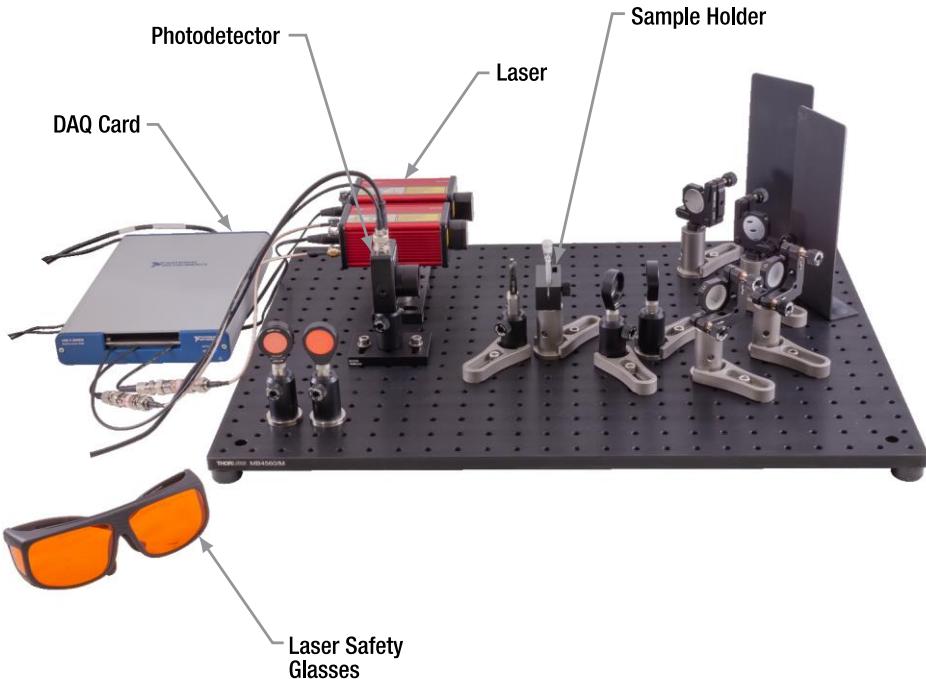


**Figure 11 Reaction path of excited Fullerenes (top) and extinction of the fullerene triplet by oxygen.**

The excitation wavelength in this kit (pump laser) is at 520 nm, chosen as close as possible to facilitate the excitation in the <sup>1</sup>ZnTPP\* state described in the literature.

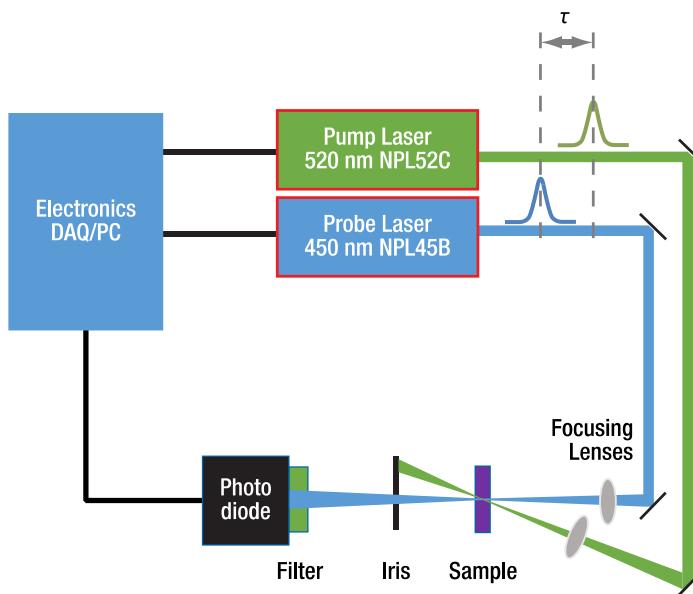
## Chapter 6 Experimental Setup

The assembled time-resolved transient absorption setup is shown in Figure 12. The laser pulses are generated electronically by the NPL52C (pump laser) and NPL45B (probe laser) nanosecond pulsed lasers. Both lasers have settings for pulse length and trigger inputs. Each laser beam is focused by a single lens and kinematic mirrors are used to overlap the beams inside the volume of a sample cuvette. The pump beam is blocked by an iris, and the probe laser is detected with a photodiode (PDA36A2) after passing a bandpass filter, which blocks ambient and pump laser light from reaching the detector. A schematic representation that includes the optical beam path is shown in Figure 13.



**Figure 12 Experimental Setup**

The pump laser NPL52C has a center wavelength of  $520 \pm 10$  nm with a variable pulse length of 6 to 129 ns and maximum pulse energy of 186 nJ. The probe laser NPL45B has a center wavelength of  $450 \pm 10$  nm, with a variable pulse length of 5 to 39 ns and a maximum pulse energy of 3 nJ.



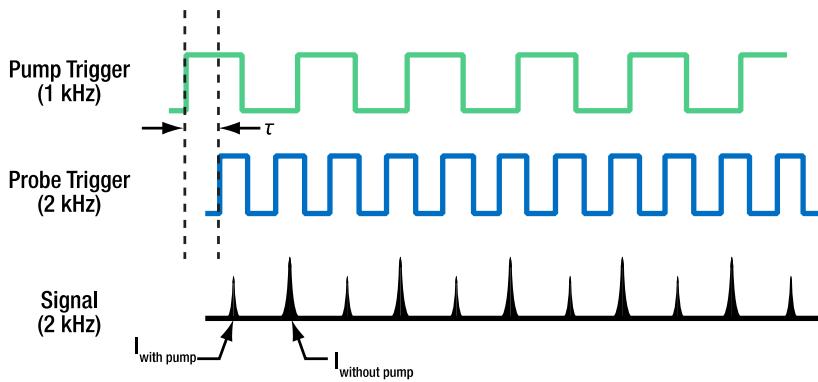
**Figure 13 Schematic representation of the time-resolved absorption setup.**

The control and data acquisition of the photodiode is performed with a digital acquisition card (DAQ) by NI. The USB-6341 card (included in the kit) is a plug and play device (USB 2.0) and must be connected to a standard Windows<sup>®</sup> (version 10 or higher) PC or laptop (not included). The software is based on a LabVIEW<sup>®</sup> code and a free installer for the executable file is provided.

## 6.1. Pulse and Acquisition Sequence

The software initiates the trigger and data acquisition sequence shown in Figure 14. The pump laser is only activated (triggered) after every second probe laser pulse, resulting in an alternating photodiode signal of  $I_{\text{with pump}}$  and  $I_{\text{without pump}}$ . In one sampling period, all  $I_{\text{with pump}}$  voltages are averaged and all  $I_{\text{without pump}}$  voltages are averaged, and one TA value is calculated according to formula (4).

Furthermore, the duty cycle of the trigger signal is 50% (half the time on, half the time off) but the lasers are only triggered once on the rising edge. The minimum delay step size is  $\tau = 10 \text{ ns}$ , which is given by the internal clock accuracy within the DAQ card.



**Figure 14 Standard trigger frequency sequence of the lasers and expected signals on the photodiode  $I_{\text{with pump}}$  and  $I_{\text{without pump}}$ .**

The laser pulses of the probe laser,  $I_{\text{with pump}}$  and  $I_{\text{without pump}}$ , are detected on the photodetector PDA36A2. The detector has a variable gain which is highly beneficial for measuring a broad range of intensities. The bandwidth (rise and fall times) of the photodetector is correlated with the gain. A higher gain (amplification of the signal) leads to a smaller bandwidth (slower rise and fall times), creating an artificially longer signal from a short pulse. The bandwidth at 10 dB gain is 1.6 MHz<sup>15</sup>. Thus, an incident probe pulse of 5 ns creates a voltage signal which is at least 625 ns long.

Gain Setting	Bandwidth	Gain
<b>0 dB</b>	12 MHz	$\sim 1 \times 10^3$ V/A
<b>10 dB</b>	1.6 MHz	$\sim 5 \times 10^3$ V/A
<b>20 dB</b>	1 MHz	$\sim 1 \times 10^4$ V/A
<b>30 dB</b>	260 kHz	$\sim 5 \times 10^4$ V/A
<b>40 dB</b>	90 kHz	$\sim 1 \times 10^5$ V/A
<b>50 dB</b>	28 kHz	$\sim 5 \times 10^5$ V/A
<b>60 dB</b>	9 kHz	$\sim 1 \times 10^6$ V/A
<b>70 dB</b>	3 kHz	$\sim 5 \times 10^6$ V/A

One could choose a faster detector (higher bandwidth) to sample the laser pulse more accurately, but this would ultimately require a much faster (higher sampling rate) and, thus, more expensive data acquisition card. The advantage of a slow photodiode is a signal that is much easier to acquire (basically hit the pulse) with a smaller sampling rate. The sampling scheme used in this kit is shown in Figure 15. This figure shows that a single data point is used to measure a pulse area (total pulse energy).

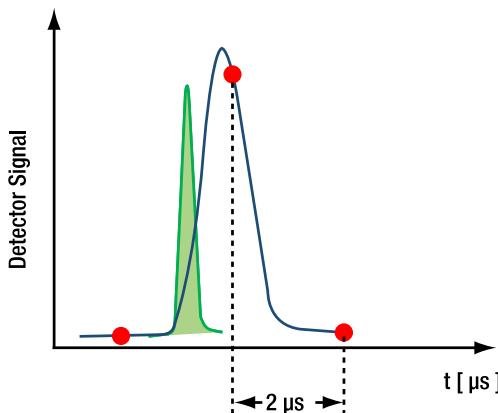
<sup>15</sup> <https://www.thorlabs.com/thorproduct.cfm?partnumber=PDA36A2>

There are two key assumptions to make this simplified measurement concept work for a transient absorption measurement:

1. A single voltage measurement of the probe pulse photodiode signal is proportional to the pulse energy (whole curve area integrated).
2. The laser pulse energy is proportional to the photodiode signal (peak area).

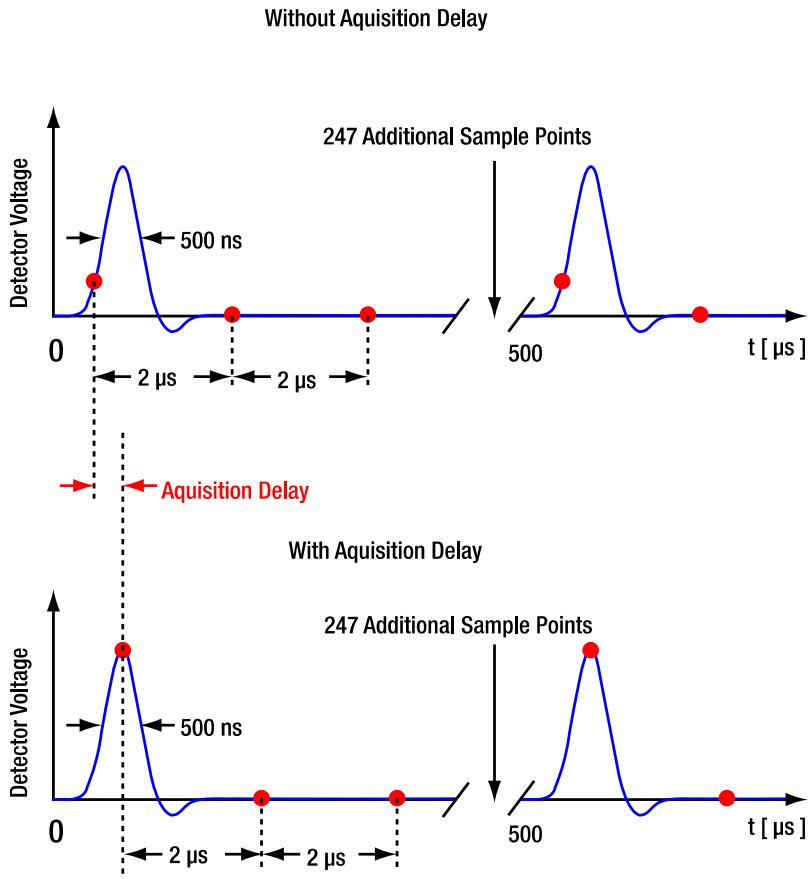
A rather easy test to verify these assumptions experimentally can be performed by using neutral density filters and observing the photodiode voltage in the measurement program, or by changing the pulse widths and measuring the detector voltage.

With these assumptions, all proportional factors in the experiment cancel out by dividing the two measured intensities (see formula (3)).



**Figure 15** The graph shows a short laser pulse (green) compared to the broad detector response (blue). Red dots represent sampling points of the DAQ card. Given the low sampling rate, a broad pulse is easier to detect.

The sampling rate of the DAQ card is 500 kilo samples per second (often denoted as kSa/s or kS/s) which corresponds to a data point taken every 2 μs. This leads to only one or a few data points on the photodiode output voltage pulse as shown in Figure 16. Since the detector signal at low gain setting (10 dB) is only ~0.5 μs, the sampling position plays a crucial role, otherwise signal could be hidden between sampling points. Therefore, a delay-to-acquisition time is implemented in the software and can be accessed in the settings tab. The software preset acquisition delay is set to a value that results in the sampling points being close to the photodiode response voltage maximum for all gain settings.



**Figure 16** Acquisition sampling rate scheme. The upper graph shows a measurement without the software acquisition delay, resulting in a sampling point (red) far away from the photodiode signal maximum. The lower graph shows a measurement with the adjusted delay-to-acquisition setting, resulting in a sampling point close to the maximum. Sampling points between the pulses are ignored for signal calculation.

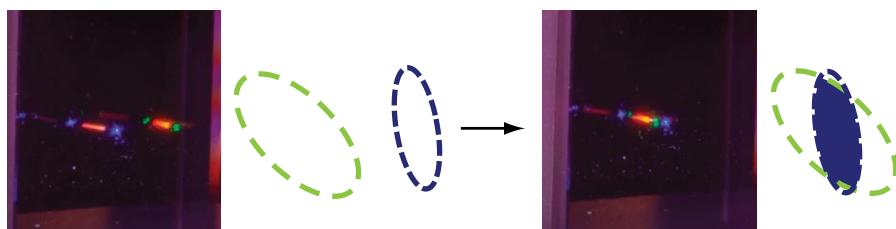
The actual pulse width of the photodiode signal varies with the gain setting, as mentioned above. This can be visualized on an oscilloscope or by using the software's zoom function in the signal acquisition tab; see Section 8.2. Gain settings are generally adjusted to the probe absorption as described in Chapter 10.

The delay between pump and probe laser  $\tau$  is set in the software and executed by the DAQ card. There are other techniques for generating such delays but often involve more advanced optical systems<sup>16</sup>.

## 6.2. Laser Overlap

The transient absorption signal is created by overlapping the two laser beams in the sample as shown in Figure 17. Defocusing and misalignment will rapidly drop the transient absorption signal, which makes learning to align the system and optimizing the transient absorption signal fundamental to this kit. An integral part of the learning experience is carrying out a beam walk to align the lasers, as well as using different focusing lenses. Note that this kit includes a sample holder with features, such as a groove for holding the viewing card, that help the user align the beams correctly.

The position of each laser beams is usually (and in this kit as well) adjusted with at least two kinematic mirrors. With the help of a two-mirror system, one can precisely adjust the beam height and angle. The lasers are first brought to the same height and horizontal orientation using the supplied fluorescent targets. The probe laser is set once (to always be on the detector center) and the pump laser is aligned subsequently to overlap with the probe laser. The overlap is fine-tuned by looking at the beams on a fluorescent card in the same plane as the cuvette center.



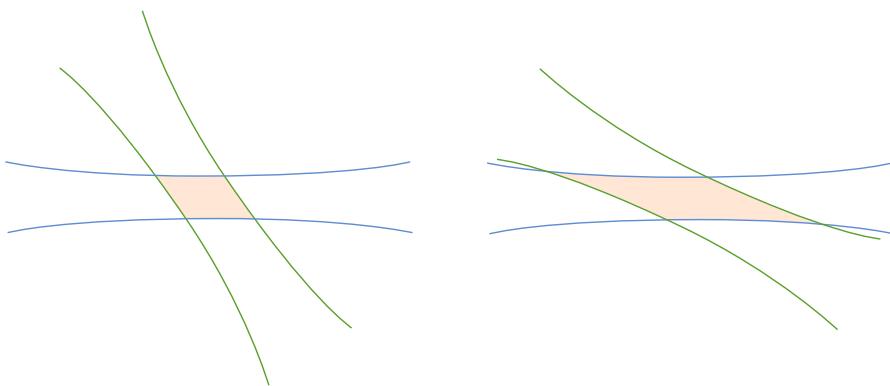
**Figure 17** Photo of the laser beams before alignment on the sample cuvette (left) and after alignment (right)<sup>17</sup>. The ellipses denote the cross-sections of the pump (green) and probe (blue) laser beams. The shaded area denotes the cross section of the overlap region.

The laser beams are focused on a small volume of the sample. The focus of the pump laser creates a high density of excited molecules. The focusing of the pump laser within this region creates a higher probability of absorption by these excited molecules, resulting

<sup>16</sup> A widely used technique in time-resolved absorption spectroscopy are optical delay lines such as shown here: [https://www.thorlabs.de/newgroupage9.cfm?objectgroup\\_id=5521](https://www.thorlabs.de/newgroupage9.cfm?objectgroup_id=5521). The educational kit uses electronically triggered signals to efficiently and economically delay pulses with the required accuracy.

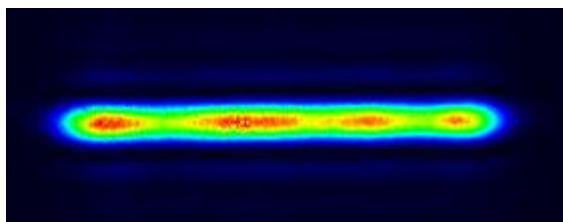
<sup>17</sup> The probe laser beam (blue/ purple) is not visible with the standard setting of 2 kHz and laser safety glasses, only with the provided fluorescent cards. This photo was taken by adjusting the repetition rate to 1 MHz with the dial on the back of the device (NPL45B) for a clear visualization. Warning: Increasing the repetition rate from several kHz to MHz will strongly increase the laser brightness and is not an intended alignment procedure.

in a higher TA signal than without focusing. The highest TA signal can thus be obtained by a small beam waist and large overlapping region. As shown in Figure 18, a small overlapping angle creates a larger overlapping region. Therefore, the setup is aligned with a narrow overlapping angle.



**Figure 18** A larger angle between the pump and probe beams (left image) results in a smaller overlapping region (red shaded area) than a smaller angle (right image).

Both nanosecond pulsed lasers have elliptical laser beam shapes and show strong non-uniform intensity profiles, as shown in Figure 19. These two effects can be diminished by using anamorphic optics to round the beam shapes and by other beam cleaning techniques. These additional optics are not essential in the scope of this kit and, therefore, are omitted.



**Figure 19** Typical intensity profile of the lasers used in this kit.

The focal lengths of the lenses are chosen to fit conveniently in the optical setup while not blocking each other's beam paths. By adjusting the distance between lens and sample, the user can create different focus spot sizes (beam waists). Due to the complex geometry and the non-Gaussian beam profiles of the lasers, the highest signal is not automatically reached by focusing both lasers to the same spot. Instead, the signal optimization (maximizing the signal) is done by manually adjusting the position of the pump laser's focusing lens while measuring the transient absorption signal.

### 6.3. Beam Polarization

Another important laser beam property to consider for ultrafast spectroscopy is the polarization of light. The pump beam polarization axis induces a dipole in the absorbing molecule along the same axis. To be absorbed, the probe beam polarization must be in the same plane as the excited dipole oscillation. The polarization axis of a laser can easily be rotated with  $\lambda/2$  wave plates, and, therefore, the transient absorption signal can be enhanced by matching the polarizations. The effect of the pump and probe beam polarizations plays a major role in femtosecond-picosecond dynamics due to molecular reorientation dynamics. In the nanosecond regime of this kit, molecules will rotate and change the dipole axis faster than the timing resolution of this experiment. This means that the molecule's orientation will change significantly during the duration of the probe pulse. Since the orientation change is random, there will be no net effect of the pump beam's polarization axis with the nanosecond lasers used here.

# Chapter 7 Sample Preparation

Thorlabs offers a sample kit in specific countries and a list of local vendors for raw materials are shown on the kit's website:

[https://www.thorlabs.com/newgroupage9.cfm?objectgroup\\_id=14444](https://www.thorlabs.com/newgroupage9.cfm?objectgroup_id=14444).

Check all local restrictions for purchasing, handling, and disposal of the aforementioned chemicals.

Benzonitrile has a very strong almond smell. Freshly opened shipping containers will have a distinct smell. This is not an indicator for spillage.

## 7.1. Chemicals

The following chemicals and volumes are needed for the experiments described in this manual. The preparation is calculated for 4 mL of all 6 concentrations. A minimum amount of 0.5 mL - 0.7 mL per sample is used in one cuvette. Scaling all ingredients down (and up) is possible but ultimately weighing becomes more difficult / inaccurate for smaller sample volumes.

Chemical	Abbreviation	CAS-Number	Min. Volume / Weight
Benzonitrile Anhydrous, ≥99%	BN	100-47-0	24 mL
Zinc-Porphyrin	ZnTPP	14074-80-7	7 mg
C <sub>70</sub> 98%	C <sub>70</sub>	115383-22-7	2.2 mg

## 7.2. Samples

The description shows the preparation of 6 samples:

Name	Volume	Concentration ZnTPP in BN	ZnTPP:C <sub>70</sub>
BZ08	4 mL	0.8 mMol/L	1:0
BZ04	4 mL	0.4 mMol/L	1:0
BZ02	4 mL	0.2 mMol/L	1:0
BZC01	4 mL	0.4 mMol/L	1:0.1
BZC05	4 mL	0.4 mMol/L	1:0.5
BZC1	4 mL	0.4 mMol/L	1:1

### 7.3. Lab Equipment

Device	Function / Specifications
Fume Hood	Using a fume hood is advised when handling Benzonitrile.
Balance	Accuracy of 0.1 g (0.01 g is Preferred)
Pipettes	Handling of 100 $\mu$ L and 1 - 10 mL Volumes
Ultrasonic Bath	No Heating, kHz Range
Screw Neck or Snap on Vials	Chemical Resistant (e.g. Glass) <sup>18</sup> , Six > 4 mL, Two > 20 mL
Gloves	Nitrile gloves are chemically resistant. More information on thickness and exposure time can be found in the SDS of Benzonitrile.
Eye Wear	Clear and Protective Against Splashes
Spatula	3 - 5 mm wide head. Porphyrin is a sticky powder and needs to be scratched from walls.

### 7.4. Step-by-Step Sample Preparation

The step by step instruction is aimed toward efficiency in handling. There might be other preparation procedures which aim for more accuracy.

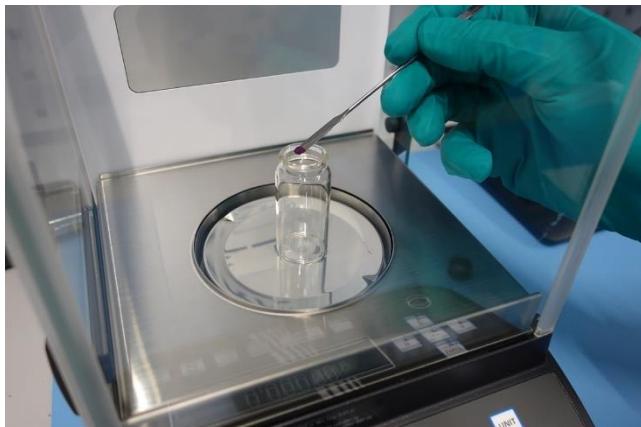
The table below shows an overview of the amount of chemicals used in each sample. Instead of weighing all components separately, it is easier and less prone to errors to create these samples from two base solutions.

Name	Concentration ZnTPP in BN [mMol/L]	ZnTPP [mg]	BN [mL]	C <sub>70</sub> [mg]	ZnTPP:C <sub>70</sub>
BZ08	0.8	2.17	4.00	0.00	1:0
BZ04	0.4	1.08	4.00	0.00	1:0
BZ02	0.2	0.54	4.00	0.00	1:0
BZC01	0.4	1.08	4.00	0.13	1:0.1
BZC05	0.4	1.08	4.00	0.67	1:0.5
BZC1	0.4	1.08	4.00	1.35	1:1
<b>SUM</b>		7.05	24	2.15	

<sup>18</sup> Glass vials are more precise for weighing than plastic vials.

## 1. Create the Zinc-Porphyrin Solution

- Put a vial (>20 mL) on the balance and press TARE to zero the balance.
- Create the base solution 0.8 mMol/L ZnTPP in BN by weighing 7 mg (no less) Zinc-Porphyrin in the vial with the spatula.



**Figure 20 Weighing Zinc-Porphyrin in the Vial**

- Read the scale and calculate the solvent volume accordingly.

$$\text{Volume [L]} = \frac{m [\text{g}]}{c \left[ \frac{\text{Mol}}{\text{L}} \right] \cdot n \left[ \frac{\text{g}}{\text{Mol}} \right]}$$

For example, if the scale reads 7 mg of ZnTPP, mix it with:

$$V[\text{Benzonitrile}] = \frac{0.007 \text{ g}}{0.0008 \frac{\text{Mol}}{\text{L}} \cdot 678.12 \frac{\text{g}}{\text{Mol}}} = 0.013 \text{ L} = 13 \text{ mL}$$

13 mL of Benzonitrile should be used to achieve a 0.8 mMol/L concentration. Use the pipettes to add the solvent.



**Figure 21 Zinc-Porphyrin Base Solution**

## 2. Create the C<sub>70</sub> Solution

- Put a vial (> 20 mL) on the balance and press TARE to zero the balance.
- Create a base solution of 0.8 mMol C<sub>70</sub> in Benzonitrile by weighing 2.15 mg (no less) of C<sub>70</sub>.



**Figure 22 Weighing C<sub>70</sub>**

- Read the scale and calculate the solvent volume accordingly.

$$V[\text{Benzonitrile}] = \frac{0.00281 \text{ g}}{0.0008 \frac{\text{Mol}}{\text{L}} \cdot 840.74 \frac{\text{g}}{\text{Mol}}} = 0.004 \text{ L} = 4 \text{ mL}$$

In this example, 4 mL of Benzonitrile is added to the C<sub>70</sub>.

- Close the lids or screw caps on your samples and put both solutions in the ultrasonic bath for 1 minute.



**Figure 23 Samples in Ultrasonic Bath**

### 3. Mix the Solutions

- Mix the 0.8 mMol/L ZnTPP and 0.8 mMol/L C<sub>70</sub> solutions with pure Benzonitrile in the following quantities to achieve the desired samples<sup>19</sup>:

Sample Concentration	0.8 mMol/L ZnTPP (Base Solution)	0.8 mMol/L C <sub>70</sub> (Base Solution)	Benzonitrile (Solvent)	Naming Scheme
0.8 mMol/L	4 mL	-	-	BZ08
0.4 mMol/L	2 mL	-	2 mL	BZ04
0.2 mMol/L	1 mL	-	3 mL	BZ02
0.4 mMol/L 1:1 ZnTPP:C <sub>70</sub>	2 mL	2 mL	-	BZC1
0.4 mMol/L 1:0.5 ZnTPP:C <sub>70</sub>	2 mL	1 mL	1 mL	BZC05
0.4 mMol/L 1:0.1 ZnTPP:C <sub>70</sub>	2 mL	1.8 mL	0.2 mL	BZC01

For example, to make the BZC1 sample, mix 2 mL of 0.8 mMol/L ZnTPP (base solution) and 2 mL of 0.8 mMol/L C<sub>70</sub> (base solution).

- Label the vials accordingly.



**Figure 24 Vials from Sample Kit**

Note: Working with that low amount of material can introduce deviation of the intended concentrations. Volumes can be scaled up easily, which improves accuracy but leads to higher material consumption.

<sup>19</sup> An experienced chemist might want to work with larger dilution series for a higher precision rather than absolute mixing of volumes.

**Storing and Degradation:**

Once mixed, all samples should be stored in a light-tight environment and are then good to use for several months. The expected transient absorption maximum values and decay times will change over time. A summary of influences and expected values can be found in Section 12.7.

The raw materials should be stored as shown in the table below:

Chemical	Storing
Benzonitrile Anhydrous, ≥99%	Chemical/Flame Safe Cabinet
Zinc-Porphyrin	Dry, Light-Tight
C <sub>70</sub> 98%	Dry, No Restrictions

Disposal of chemicals is described in the country specific SDS of the chemical (from the supplier) or mixture (<https://www.thorlabs.com/manuals.cfm>).

# Chapter 8 Software

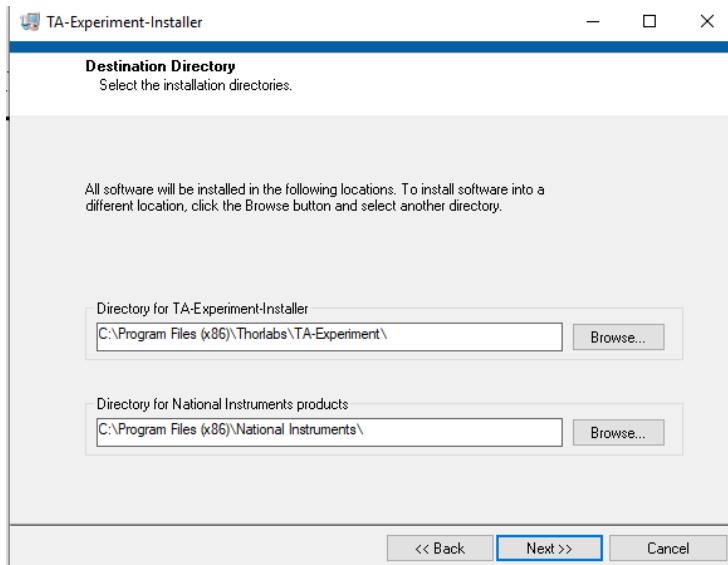
## 8.1. Installing the Software

The installer for the software is located on the USB stick included in the kit. Specifications can be found on the kit website<sup>20</sup>. Open the file setup.exe in the installer folder as shown in Figure 25.

bin	12/11/2020 1:06 PM	Dateiordner		
license	12/11/2020 1:06 PM	Dateiordner		
supportfiles	12/11/2020 1:06 PM	Dateiordner		
nidist.id	12/9/2020 8:21 PM	ID-Datei	1 KB	
setup	2/27/2020 11:44 AM	Anwendung	5,327 KB	
setup	12/9/2020 8:21 PM	Konfigurationsein...	33 KB	

**Figure 25 Setup File in the Software Folder on the USB stick (Marked by Red Rectangle)**

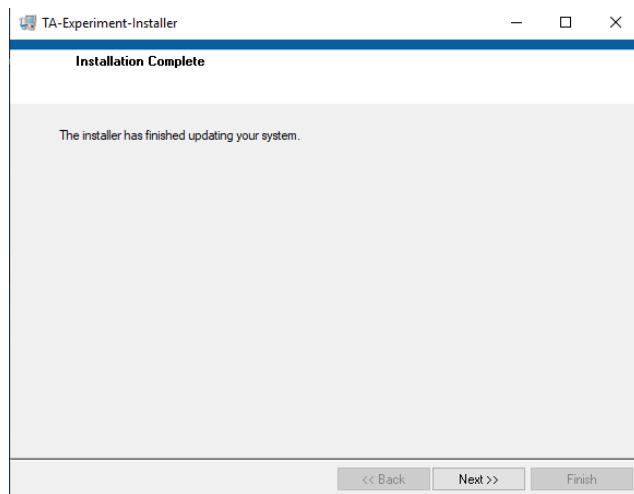
Choose the install path for the software and the required NI components, as shown in Figure 26, then click on “Next”.



**Figure 26 Choosing the Install Path**

In the next steps, accept the license agreement and start the installation. After the installation is completed (see Figure 27), a restart of the PC is recommended.

<sup>20</sup> [https://www.thorlabs.com/newgroupage9.cfm?objectgroup\\_id=14444](https://www.thorlabs.com/newgroupage9.cfm?objectgroup_id=14444)



**Figure 27 Installation Complete**

The software is started by opening the file “TA-Experiment.exe” from the desktop icon or in the install path (see Figure 28). The following sections describe all the elements and functions of the software.

Name	Änderungsdatum	Typ	Größe
TA-Experiment.alioses	10.06.2021 09:59	ALIASES-Datei	1 KB
TA-Experiment	10.06.2021 09:59	Anwendung	1.240 KB
TA-Experiment	10.06.2021 09:59	Konfigurationsein...	1 KB

**Figure 28 Install Folder (TA-Experiment.exe is Highlighted in Blue)**

## 8.2. The Signal Acquisition Tab

This tab is used to monitor the signal strength during alignment of the setup, as well as to set the parameters for a Transient Absorption measurement. It consists of three areas, as marked in Figure 29.



Figure 29 The Three Areas of the Signal Acquisition Tab

In the following, we will provide details on each of the three parts:

### 8.2.1. The Settings Panel

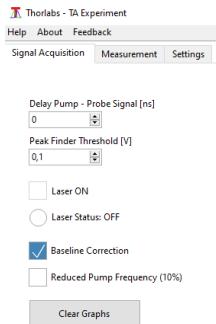


Figure 30 The Settings Panel of the Signal Acquisition Tab

The Settings Panel, shown in Figure 30, includes the following elements:

**Delay Pump-Probe Signal [ns]:** This parameter sets the delay between the pump and the probe pulse in ns. A value of 200 ns typically results in a high TA signal.

**Peak Finder Threshold [V]:** This parameter sets the threshold above which a peak is recognized. This should be set to about 0.1 V below the peaks displayed in the detector signal live feed; see Figure 31.

**Laser ON:** Activating this checkbox switches the triggers for both lasers, and the lasers will begin to emit. Always wear safety goggles when this checkbox is marked! The pump and probe laser are always activated simultaneously.



**Warning: Laser Radiation** - This is a Class 3B laser system. Observe all safety precautions and wear protective eyewear appropriate for this type of device.

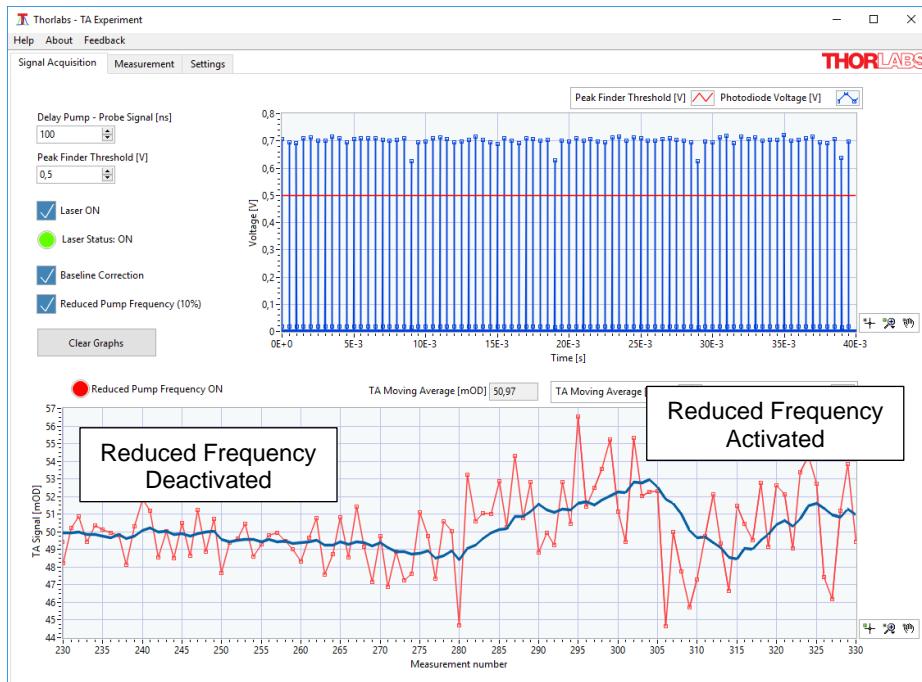
**Laser Status:** This element displays the current status of the lasers (ON or OFF). The round marker is colored green in the ON case and white in the OFF case.

**Baseline Correction:** The photodiode usually has a small offset voltage. When this checkbox is activated, this offset is automatically subtracted from the signal, moving the baseline to 0 V. This feature should usually be activated for all measurements. A baseline offset decreases the accuracy of the calculated the TA value.

**Reduced Pump Frequency (10%):** Activating this checkbox reduces the repetition rate of the pump laser to 100 Hz, which is 10% of its standard value. This is useful for beam adjustment, as the overall intensity of the laser is reduced, making it more safe but still clearly visible. **Laser safety goggles must still be used!**

**Important:** This checkbox should be deactivated for actual measurements. In Figure 31, you can see that the TA signal (lower graph) is much noisier when the Reduced Pump Frequency is activated.

**Clear Graphs:** Clicking this button restarts both the detector signal and the transient absorption live feeds. All data is cleared from the graphs.



**Figure 31 Comparison of TA signal with and without activation of the Reduced Pump Frequency feature. Please note the increased noise of the TA signal due to the reduced pump frequency on the right part of the curve.**

### 8.2.2. Detector Signal Live Feed

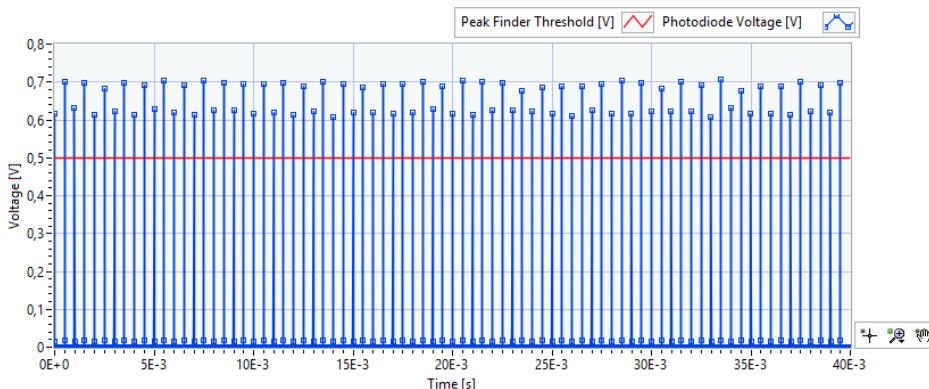
The detector signal live feed shows the voltage as measured by the photodiode and sampled by the DAQ card. The plot updates every 40 ms. If the probe laser hits the detector, you see single pulses (for the standard settings, there are always 80 pulses shown).

In Figure 32, you see a typical live feed for a completely adjusted setup. The blue line marks the detector signal, the blue squares are the sampling points of the DAQ card, and the horizontal red line marks the peak finder threshold, which can be adjusted in the Settings panel (see Section 8.2.1). This threshold must be below the peak maxima, otherwise the transient absorption signal will not be calculated, and an error message will be displayed<sup>21</sup>.

<sup>21</sup> The threshold function eliminates all data points below the threshold. This function is needed to reduce artifacts through noise being discarded before being introduced in any calculations. Reducing the threshold to zero will still give resulting spectra but is prone to wrong averaging of datapoints. Setting the threshold too high or too close to the peak position can introduce empty data points.

Please note that the pulses will not be stationary but will continuously shift slightly in position and height (by about 0.03 V). This is mainly due to imperfections of the lasers, which do not emit completely identical pulses. To avoid negative effects on the measurement, such as high noise, a single data point of the TA signal is calculated by averaging over several pulse pairs (pump on / pump off). Using the standard settings, 40 pulse pairs are used to form one TA signal data point.

The DAQ card has an input range of -10 V to + 10 V but the sensitivity is set to an input range of -1 V to 1 V in order to increase the resolution (matching the expected voltage range). As a result, if the signal from the photodiode exceeds 1 V, the transient absorption signal cannot be calculated correctly anymore. In this case, the warning **Measurement range [- 1V; 1V] exceeded** will appear above the graph. Reduce the signal by lowering the probe laser pulse width (for details, see Section 9.2.1), until the signal is about 0.9 V, at which point the warning will disappear again.

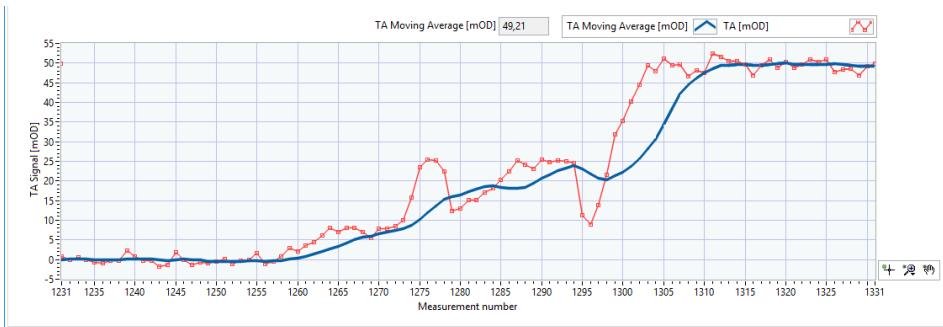


**Figure 32 Detector Signal Live Feed for a Well-Aligned Setup**

To the right of the graph, there is a small toolbar which allows you to zoom into the graph. This is described in more detail in Section 8.2.4.

### 8.2.3. Transient Absorption Live Feed

In the transient absorption live feed, the transient absorption signal is displayed. Each data point is calculated from 40 pulse pairs (using the standard settings), as described in Chapter 5.1. This results in about 3 data points per second, which are displayed as red squares connected by a red line, as shown in Figure 33. As the intensity difference between the pumped and unpumped state is small even for a well-adjusted setup, the TA signal shows significant noise. In order to facilitate the process of optimizing the setup for maximum TA signal, a rolling average of the last 10 data points is also displayed in the graph (as a blue line).



**Figure 33 The Transient Absorption Live Feed**

#### 8.2.4. Graph Manipulation Functions

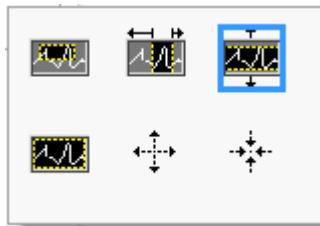
On the bottom right of every graph, there is a small toolbox which allows you to manipulate the graphs; see Figure 34.



**Figure 34 Graph Manipulation Toolbox**

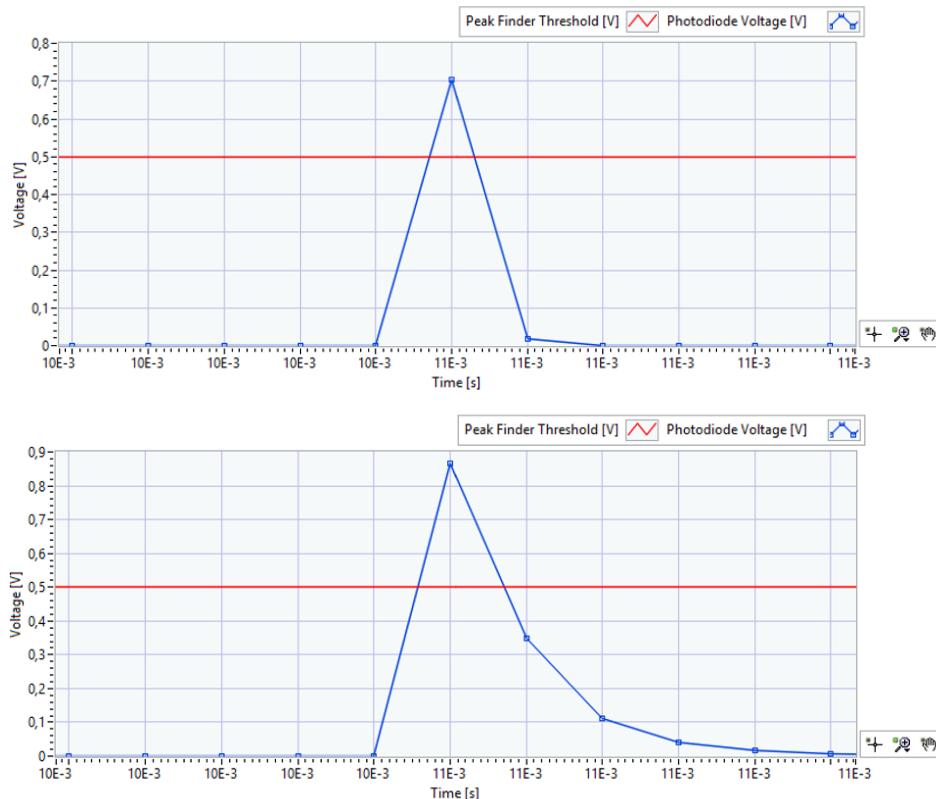
To use these features, you first need to right-click on the graph and deactivate the “Auto-scale x-axis” and “Auto-scale y-axis” options. The hand symbol on the right moves a graph via dragging. The magnifying glass symbol in the center opens a menu of zoom functions (see paragraph below), while the reticle symbol on the left sets the cursor back to normal.

The zoom functions are displayed in Figure 35. The symbol on the upper left draws out a rectangle on the graph and zooms into that region. The center and right symbols in the top line are for selecting a region of the x- and y-axis, respectively, to zoom into. The center and right symbols of the bottom line zoom out and in, respectively, by clicking onto the graph. Note that the zoom is centered on the cursor position. The lower left symbol resets the zoom level to the standard values. This can also be achieved by re-enabling the auto-scaling for both the x- and y-axes.



**Figure 35 Graph Zoom Functions**

An example application of the zoom functions is zooming into a single pulse (via the top center symbol) to see of how many data points it consists. In Figure 36 the live feed is shown for a single pulse with two different detector amplifications, highlighting how a larger amplification slows down the detector response.



**Figure 36** The same pulse is displayed with a 10 dB (top) and 40 dB (bottom) detector amplification. Note that a higher amplification increases the photodiode voltage signal but broadens the response signal due to a lower detector bandwidth.<sup>22</sup>

<sup>22</sup> Another detector pulse measurement technique would be to integrate (sum up) all data points from the curve. This is usually done with faster detectors and higher sampling rates, but it is also much more costly and, therefore, simplified in this kit.

## 8.3. The Measurement Tab

This tab is used to perform a measurement where the delay between the pump and probe pulses is gradually shifted and the TA signal is recorded for each delay step. The tab consists of three areas, as marked in Figure 37.

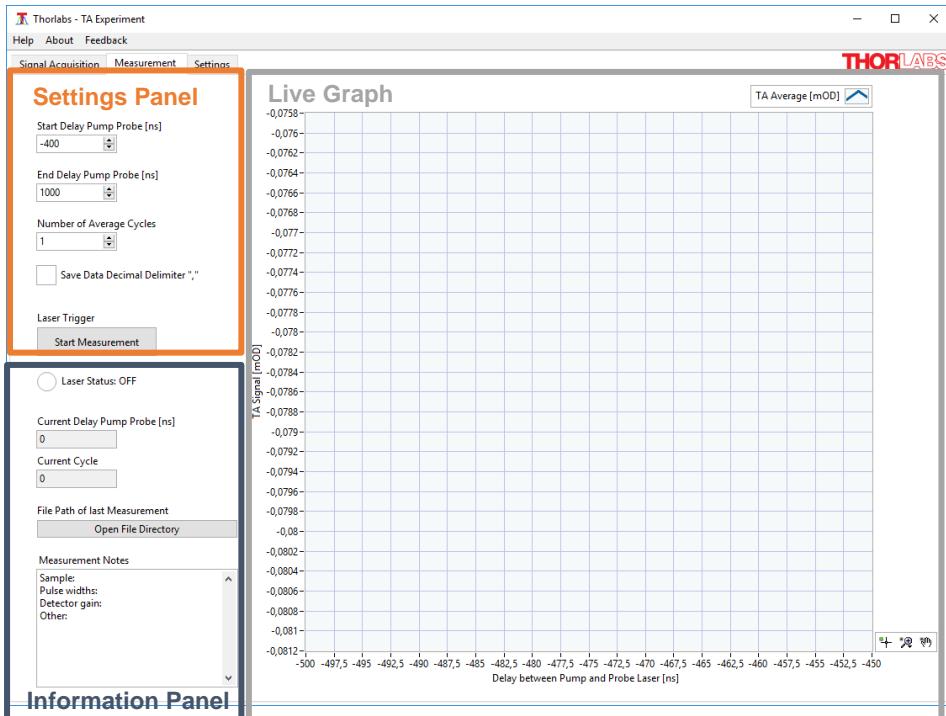
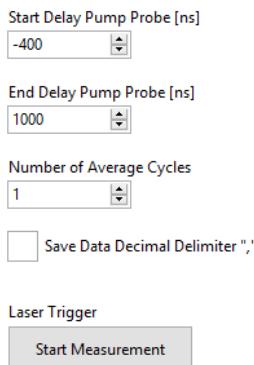


Figure 37 The Areas of the Measurement Timer Tab

### 8.3.1. The Settings Panel

In this panel, as shown in more detail in Figure 38, the settings for a time-resolved measurement are set before the measurement is started.



**Figure 38 The Settings Panel of the Measurement Timer Tab**

This panel contains the following elements:

**Start / End Delay Pump Probe [ns]:** In these two fields, the start and end delays of the measurement are set. Negative values, i.e. the probe pulse coming before the pump pulse, are possible. The range of possible values is -400 ns to 49000 ns in steps of 10 ns. The measurement range directly influences the measurement time, as the delay step width during the measurement is fixed at 10 ns. A typical range for a measurement of a ZnTPP sample is -400 ns to 5000 ns. This ensures that the whole exponential decay is recorded<sup>23</sup>.

**Number of Average Cycles [ns]:** This field sets an integer value for the number of curves that will be recorded and subsequently averaged during the measurement. This is very useful for improving the signal-to-noise ratio of the measurement because a single curve usually contains significant amounts of noise. Each completed curve, as well as the average of all curves that have been already completed, will be displayed. At the end of the measurement, two .csv save files are generated. One contains the average curve and the other contains all single traces (suffix "\_traces" added to the filename).

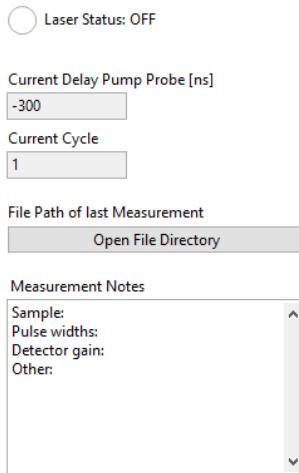
**Save Data Decimal Separator “,”:** With this checkbox you can choose between “.” and “,” as the decimal separator for the data in the result file. “.” is the standard for a deactivated checkbox, and “,” will be used if the checkbox is activated.

**Start Measurement:** Once you click this button, the measurement will start and all settings will be locked. You will be prompted to specify the name and path of your results file. The button will switch to “Abort measurement”. Aborting the measurement causes all data to be lost as partial measurements will not be saved.

<sup>23</sup> -400 ns is the lower limit to ensure the acquired data is correctly assigned to the state (with or without pump laser). A higher negative delay would flip the measured TA value.

### 8.3.2. The Information Panel

This panel, as shown in more detail in Figure 39, contains information about the parameters of a running measurement.



**Figure 39 The Information Panel of the Measurement Timer Tab**

It consists of the following elements:

**Laser Status:** This element displays the current status of the lasers (ON or OFF). The round marker is colored green in the ON case and white in the OFF case.

**Current Delay Pump Probe [ns]:** This shows the current delay in ns. This value should run from the start delay to the end delay in steps of 10 ns and jump back to the start value at the beginning of a new curve.

**Current Cycle [ns]:** If you have set an averaging value larger than 1, this value shows the number of the curve currently being measured.

**File Path of Last Measurement:** By clicking the **Open File Directory** button, you can open the file path you specified for the current measurement. If no measurement is running, the file path of the last completed measurement will be opened.

**Measurement Notes:** In this text box, you can add comments that will be saved in a .xml file that also contains the settings of your measurement for later reference. We recommend to fill in the Sample, Laser Pulse Widths and Detector Gain in this section, as those cannot be automatically determined by the software.

### 8.3.3. The Live Graph

In the graph, the following information is displayed during a running measurement:

- Curves of all completed cycles (in differently colored thin lines)
- The average of all completed curves (as a broader blue line)

Please be aware that the curve of a measurement cycle only appears after the cycle is finished, i.e. no data is displayed between the start of the measurement and the completion of the first cycle. During the measurement, students can observe how the noise of the average decreases with each completed single curve. Furthermore, one should check if all curves are roughly equal. Significantly deviating single curves are usually a sign for changing measurement parameters as described in Section 12.3. Figure 40 shows an example of a finished measurement.

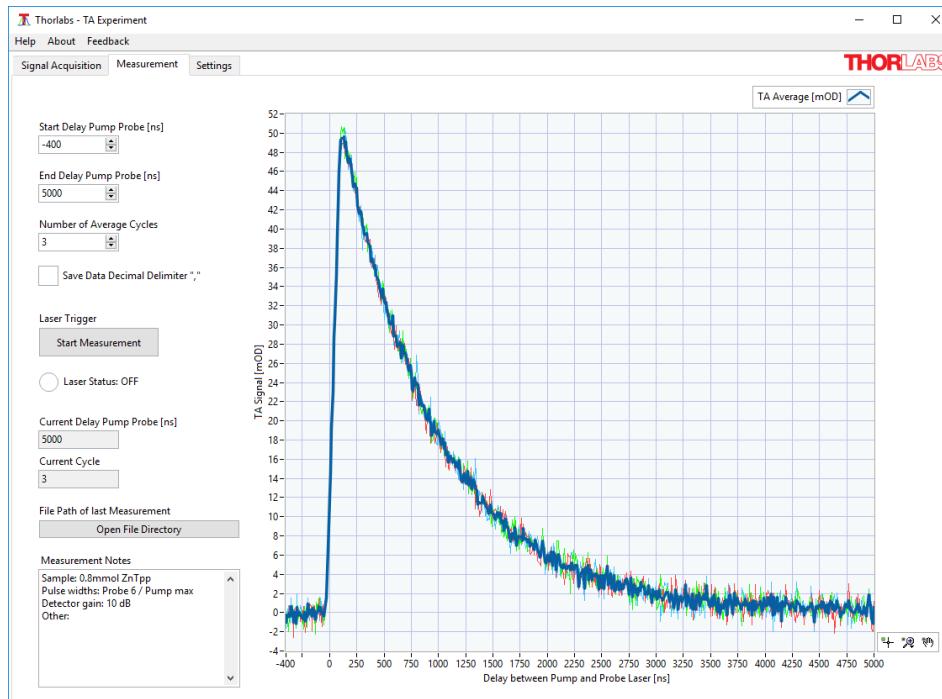
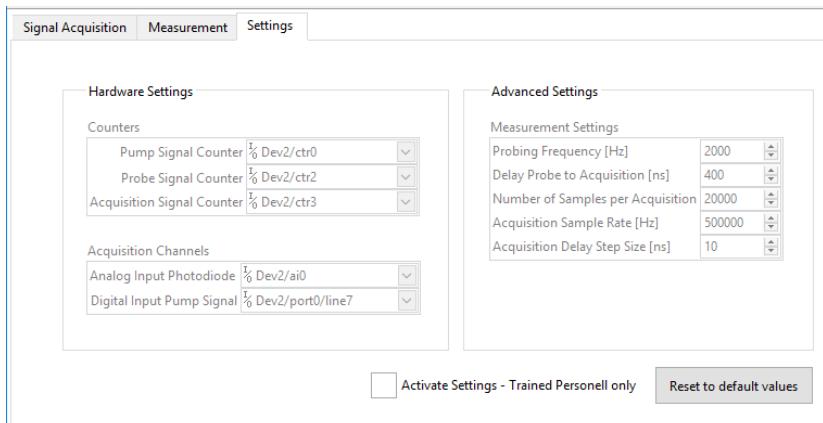


Figure 40 Example of a Completed Measurement

### 8.4. The Settings Tab

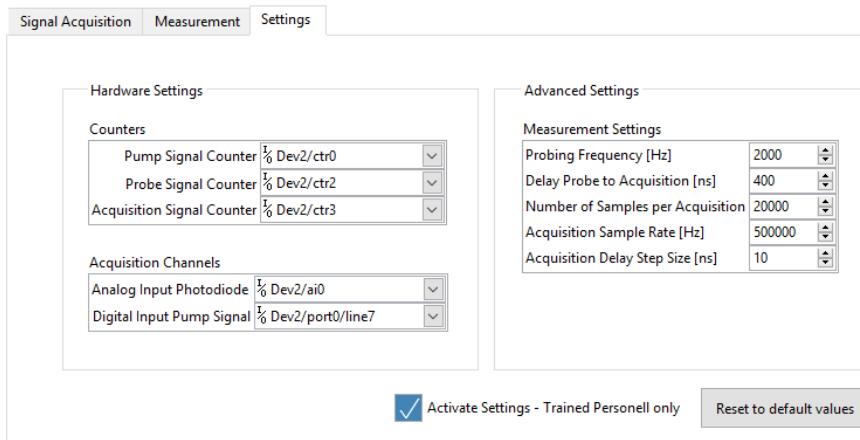
The settings tab contains some settings that govern measurement parameters. The standard settings are confirmed to work for the recommended samples and there is usually

no need to change them. As changing them can result in worsened performance of the experiment, they are locked upon starting the software, as shown in Figure 41.



**Figure 41 The Settings Tab in Locked Mode (Standard)**

However, in special situations or for a modified experiment, it can be helpful to have access to the settings. In this case, activate the **Activate Settings – Trained Personnel only** checkbox at the bottom of the tab. This will unlock the settings; see Figure 42. In the case of unwanted changes, the **Reset to default values** button returns the standard settings.



**Figure 42 The Settings in Unlocked Mode (Recommended Only for Experienced Users)**

In the following, the function of each setting is described, as well as situations where it might be useful to change them:

**Pump / Probe / Acquisition Signal Counter:** These three settings specify the trigger output channels for the pump probe trigger, as well as for the internal signal acquisition trigger. The part before the “/” sign is the name of the NI DAQ card in your system, which is automatically chosen upon software start (if you have two X-Series DAQ cards connected to your PC, you will be prompted to choose one). Usually, this will be “Dev1”. The part behind the “/” sign specifies the channel of the DAQ card on which the respective trigger should be put out. If you connect the cables to the DAQ card as described in Chapter 9.1.1, the standard settings will work.

**Analog Input Photodiode / Digital Input Pump Signal:** These two settings specify the input channels of the DAQ card. The same naming conventions as for the counter channels apply.

**Probing Frequency [Hz]:** This specifies the repetition rate of the probe laser. The pump laser repetition rate is always half of this value. Higher repetition rates result in more pulses to be averaged for a single data point of the TA signal, which can reduce the noise of the TA signal. However, this also increases the average power of the lasers, which is not recommended due to laser safety considerations.

**Delay Probe to Acquisition [ns]:** This delay ensures that the DAQ card samples near the peak maximum of the photodiode output signal (see Figure 16 for details). The standard value has been tested to be optimal for the components of the kit. Should you want to use a different DAQ card or lasers, it may be necessary to change this value.

**Number of Samples per Acquisition:** This value specifies how many samples of the DAQ card will be used for a single data point of the TA signal. A higher value leads to more averaging and therefore lower noise in the TA signal. However, this comes at the cost of increased measurement time. The standard value provides a good balance between noise and measurement time.

**Acquisition Sample Rate [Hz]:** This is the sample rate of the experiment. The standard value of 500 kHz is the maximum rate of the DAQ card included with the kit. This value should (only) be changed if a different DAQ card with a different maximum sample rate is used.

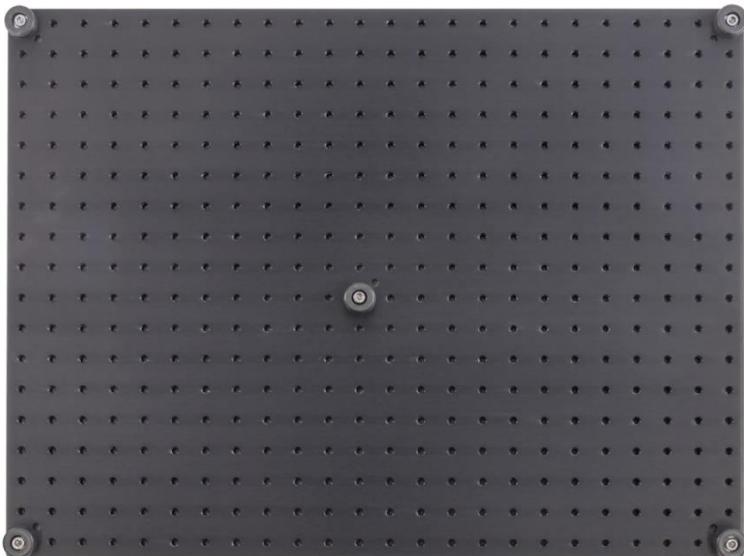
**Acquisition Delay Step Size [ns]:** This value specifies the step size in the delay-dependent measurement. A larger value reduces the measurement time at the expense of worse temporal resolution and vice versa. The standard (and minimum) value of 10 ns provides good resolution at reasonable measurements times.

# Chapter 9 Setup and Adjustment

## 9.1. Assembly of the Components

### 9.1.1. Breadboard

- Take the breadboard MB1824 (MB4560/M), turn it upside down (use Thorlabs Logo on side as reference), and attach 5 x RDF1 feet as shown in Figure 43 with 5 x 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screws.



*Figure 43 RDF1 Feet Attached to the Breadboard*

### 9.1.2. DAQ-Card

- Take the three BNC-to-DAQ connector cables and mark them with the labels from the label sheet according to Table 1.
- Remove the magnetic lid from the NI USB 6341 DAQ card.
- Connect the crimped ends of the BNC-to-DAQ connectors to the screw terminal of the DAQ card according to Table 1 (for definition of plug and jack; see Figure 44). Note: Crimped ends have a tight fit; rotate the crimped end to fit the screw terminal if necessary.

Cable	Label	Red Wire(s) to Port(s)	Black Wire to Port
BNC-Plug (Male) to Crimped End (2-Ended) 24" (60 cm)	Detector	1 (AI0+)	3 (AI GND)
BNC-Jack (Female) to Crimped End (2-Ended) 6" (15 cm)	Probe	93 (PFI14/P2.6)	92 (D GND)
BNC-Jack (Female) to Crimped End (3-Ended) 6.6" (17 cm)	Pump	89 (PFI12/P2.4) 72 (P0.7)	88 (D GND)

Table 1 Labels and Ports for BNC-DAQ Connection Cables

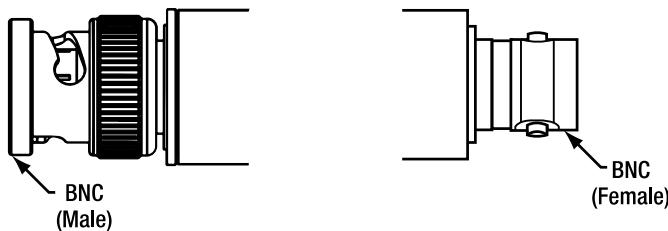


Figure 44 BNC Plug (Left) and Jack (Right)

- Unscrew the cable clamp, arrange the cables, and secure their position by screwing the cable clamp back on again. The DAQ card should then look similar to Figure 45.
- Close the DAQ card with the magnetic lid.
- Attach the power supply unit to the DAQ.

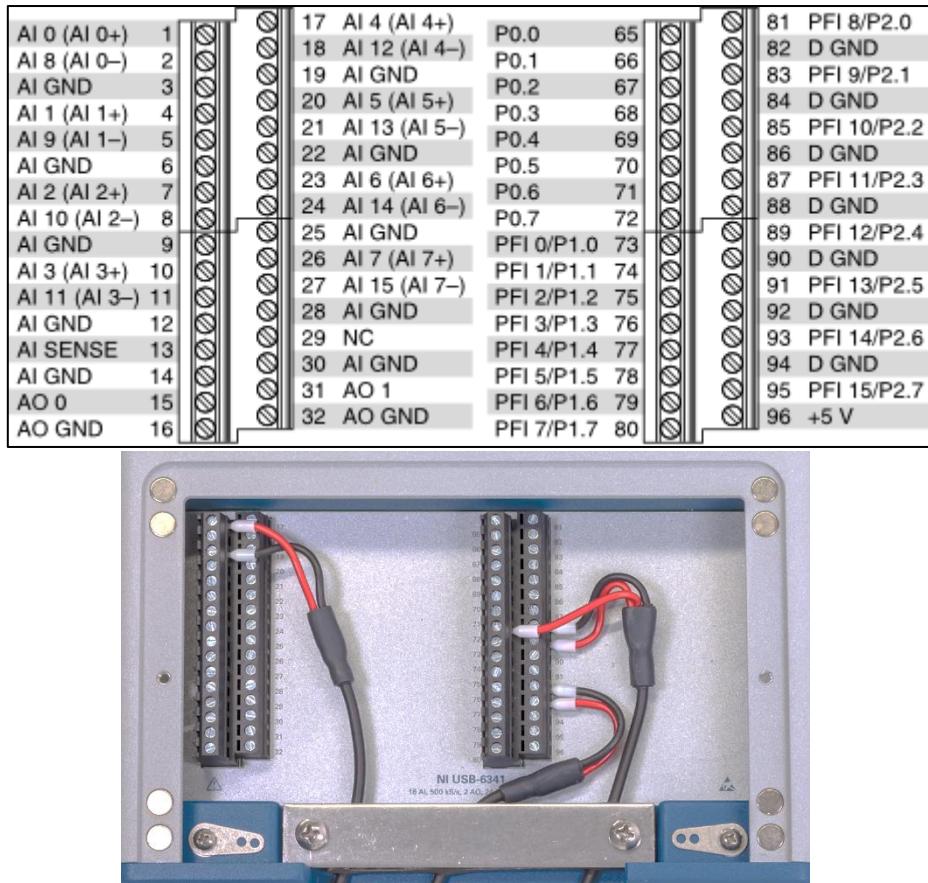


Figure 45 AQ card pinouts (top) and photo of the DAQ card after connecting all cables and clamping the strain relief down (bottom).

### 9.1.3. Lasers

- The NPL52C laser includes two ECM225 brackets. Take one bracket, insert an 8-32 x 1/4" (M4 x 6 mm) cap screw through the center counterbored hole, and connect the bracket to a RSP8 (RS50P4/M) post. Tighten the connection by using a ball driver through the hole of the post as a lever; see Figure 46.



**Figure 46 Tightening the connection between clamp and post.**

- Place a BA2F/(M) base on a level surface, loosen the 1/4"-20 screw at the side of the base and put the post into the base. Connect the base and post by retightening the screw.
- Loosen the locking screw on the side of the ECM225 bracket, then press the bracket to the bottom side (the one without part number and Thorlabs logo) of the NPL52C laser until it snaps in. Slide the laser in the bracket until the post is roughly centered under the laser, then tighten the locking screw of the bracket.
- The completed component is shown in Figure 47.
- Repeat all steps for the NPL45B laser.



**Figure 47 Mounted Laser**

#### 9.1.4. Mirrors

- Take four RS5P8E (RS2P4M) pedestal pillar posts.
- Attach a KCP1 (KCP1/M) Centering Plate for Kinematic Mirror Mounts to each pillar post with an 8-32 x 5/8" (M4 x 16 mm) set screw.
- Take the four KM100 mirror mounts, four 8-32 x 5/16" (M4 x 8 mm) cap screws, and four BB1-E02 mirrors. Connect a KM100 to each of the prepared posts by inserting the screw through one of the counterbored holes of the KM100 as shown in Figure 48, and tighten the screw against the KCP1 (KCP1/M) centering plate. Make sure that the front edges of the mirror holder and centering plate are parallel.
- For each KM100, loosen the locking screw, insert a BB1-E02 mirror, and secure the mirror by tightening the locking screw of the mount.
- The assembly steps for the mirror components are shown in Figure 48.



**Figure 48 Left:** KCP1 (KCP1/M) Centering Plate Assembly on RS5P8E (RS2P4M) pedestal pillar post. **Right:** Mirror Component attached to post.

#### 9.1.5. Lenses

- Take three PH1.5 (PH40/M) post holders and attach a BE1(M) Pedestal Base Adapter to each.
- Take three TR1.5 (TR40/M) posts and screw an LMR1(M) lens mount to each of these posts.
- Put these posts in the post holders.
- Remove the retaining ring from one of the LMR1(M) lens mounts, insert the anti-reflection coated plano-convex lens LA1134-A ( $f = 60$  mm) into the mount (flat

side of the lens should face the retaining lip of the mount; see Figure 49) and then secure it via the retaining ring. The completed component is shown in Figure 49.

- Repeat the previous step for the LA1509-A ( $f = 100$  mm) anti-reflection coated plano-convex lens and the LA1608-A ( $f = 75$  mm) anti-reflection coated plano-convex lens.
- Label the lens mounts with labels from the label sheet in order to make it easier to select the correct lenses later.

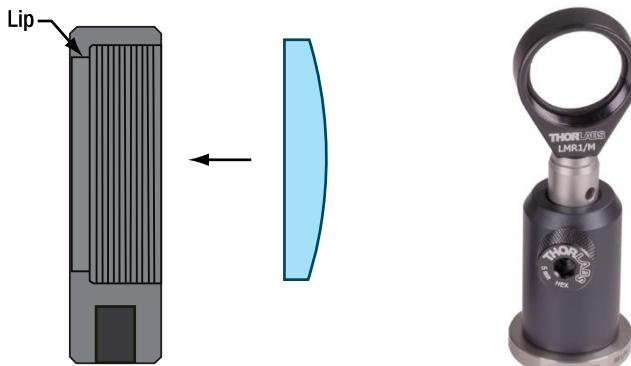


Figure 49 Lens Orientation (Left) and Assembled Lens Component (Right)

#### 9.1.6. Sample Holder

- Connect the sample holder to a RS2P8E (RS2P4M) post via an 8-32 x 1/4" (M4 x 6 mm) set screw. Use the threaded hole that is right below the sample cuvette position (i.e. the cuvette position that is crossed by the groove).
- Insert the TS25H (TS6H/M) thumbscrew in the thread on the side of the sample holder. The completed component is shown in Figure 50.



Figure 50 Sample Holder Component

### 9.1.7. Iris

- Take a TR2 (TR50/M) post and insert it into a PH1.5 (PH40/M) post holder. Attach a BE1(M) base adapter.
- Remove the setscrew from the post and connect the IDA15(/M) iris to the post. The completed component is shown in Figure 51.



*Figure 51 Iris Component*

### 9.1.8. Detector

- Connect a BA2(/M) base to a PH1.5 (PH40/M) post holder with a 1/4"-20 x 1/4". (M6 x 6 mm) Cap Screw.
- Connect the PDA36A2 detector to a TR1.5 (TR30/M) post and put it into the prepared post holder.
- Unscrew the retaining ring from the SM1L05 lens tube. Place the FESH0500 shortpass filter into the lens tube. The arrow on the filter mount should point towards the side of the lens tube with the external thread. Fix the filter with the retaining ring.
- Screw the lens tube onto the front of the detector. The completed component is shown in Figure 52.



**Figure 52 Detector Component**

### 9.1.9. Fluorescent Targets

- Connect two PH1.5 (PH40/M) post holders with BE1(/M) bases.
- Connect two LMR1(/M) lens mounts to TR1.5 (TR40/M) posts and place them into the prepared post holders.
- Remove the retaining ring from one LMR1(/M) and screw the VRC2SM1 fluorescent target (without hole) onto the mount.
- Remove the retaining ring from the other LMR1(/M), insert the VRC2D1 fluorescent target (with hole), and secure the target with the retaining ring.
- The completed target components are shown in Figure 53.



**Figure 53 Target Components**

## 9.2. Adjusting the Setup

In this section, the cable routing (see Figure 57) and the adjustment (see Figure 69) of the experiment is explained step-by-step. It might be helpful to look at the complete setup and cable routing before getting into the next section.

The core of the optical alignment procedure is a beam walk<sup>24</sup>, which is a technique that will align a laser beam to any path defined by two apertures. In this kit, it is used to align the pump and probe laser beams to the same height over the whole beam path. This ensures easy beam alignment and simplifies placement of optical components in the beam path.

In the first step, the probe laser, focusing lens, and detector are aligned. In the second step, the pump laser and its focusing lens are aligned to the same height as the probe laser. Then, the two beams are overlapped at the sample position.

### 9.2.1. Positioning and Connecting the Lasers

- Use the screw driver that comes with the laser and turn the pulse width of the NPL52C laser setting to minimum as shown in Figure 54.



Figure 54 NPL52C Settings

- Position the NPL52C laser (in the following called pump laser) on the left side of the far end of the breadboard, so that the post is centered on the 6th hole row from the left breadboard edge and on the 4th row from the far breadboard edge (top when viewed from above). The laser output should show to the right. Secure the position of the base with two 1/4"-20 x 3/8" (M6 x 10 mm) Cap Screws.

<sup>24</sup> More information on beam walks can be found on the Thorlabs website:  
[https://www.thorlabs.com/newgroupage9.cfm?objectgroup\\_id=14221](https://www.thorlabs.com/newgroupage9.cfm?objectgroup_id=14221)

- Use the screw driver to set the pulse width of the NPL45B laser to the highest position and the repetition rate to “D → User trigger” as shown in Figure 55.



**Figure 55 NPL45B Settings**

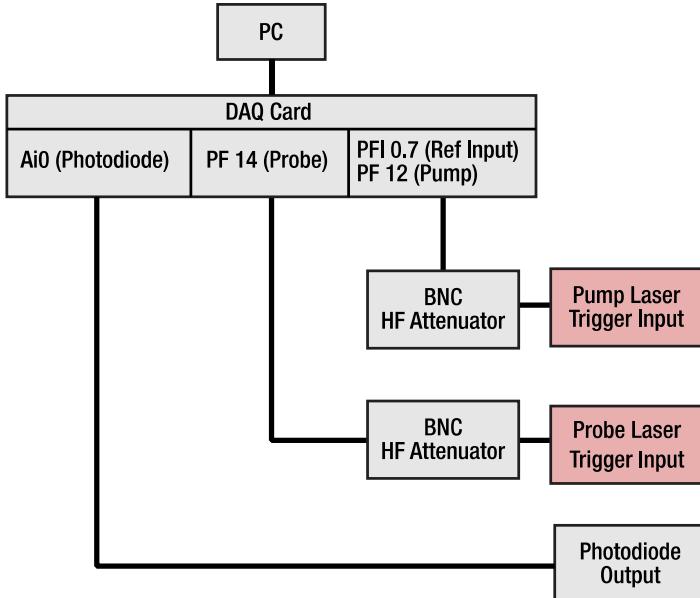
- Position the NPL45B laser (in the following called probe laser) parallel to the pump laser. The post should be centered on the 7th hole row counted from the far edge of the breadboard. Secure the position of the base with two 1/4"-20 x 3/8" (M6 x 10 mm) Cap Screws.
- The correct placement of the lasers is shown in Figure 56.



**Figure 56 Placement of the Lasers on the Breadboard**

- Connect both lasers to the power grid via the included power supplies.

- Connect the DAQ card output labeled “Probe” with an HF attenuator
- Connect the HF attenuator with the probe laser via a CA2812 SMA-to-BNC cable. A second “Probe” label can be used for this cable.
- Repeat the previous two steps for the pump laser.



**Figure 57 Complete Cable Routing**

### 9.2.2. Adjusting the Beam Path of the Probe Laser

In this section, the lasers will be turned on. **Always use laser safety goggles!**



**Warning: Laser Radiation** - This is a Class 3B laser system. Observe all safety precautions and wear protective eyewear appropriate for this type of device.

The probe laser should have a constant beam height after the second mirror and it should hit the target and detector under normal incidence, while being centered on the detector chip. To ensure this, follow the steps below.

- Put all four kinematic mirrors in the neutral position as shown below. If the thumb screw gets loose, use a hex key to hold the threading still and tighten the thumb screw.



**Figure 58 Neutral Position for the KM100 Kinematic Mount**

- Position a mirror component (from here on called PR1 mirror) on the 14th hole to the right of the probe laser post, (14 inches or 35 cm measured between the post centers). The mirror should be angled by 45° (so that the laser beam would be deflected towards the front edge of the breadboard) and its post should be centered over a breadboard hole. Secure the mirror position with a CF125 clamp and a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer. The long end of the clamp should point forward and right (as shown in Figure 59), in order to not block other elements later on.
- Use the ruler to set the post height of the fluorescent target with crosshairs (VRC2SM1) so that the target center is at 8.5 cm.
- Position the target close to the front edge of the breadboard, facing the PR1 mirror. The target post holder should be centered over the same row of breadboard holes as the post of the PR1 mirror, see Figure 59.

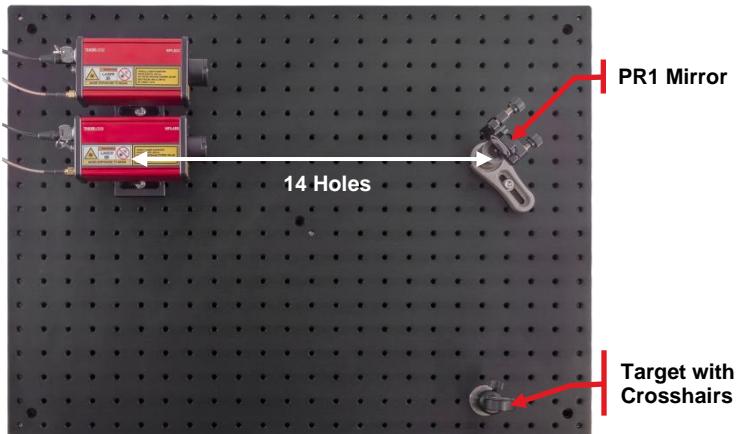


Figure 59 Placement of the First Mirror in the Probe Beam (PR1 Mirror)

- Switch on the probe laser by turning the key. Wait until the LED on the laser backside stops blinking (this can take 10 - 40 seconds), then open the shutter. Switch on the DAQ card and open the EDU-TRAS Software. Start triggering the laser by activating the corresponding checkbox in the software as described in Chapter 8.2.
- Use the laser viewing card to make sure that the laser hits the PR1 mirror roughly in the center. If it does not, slightly rotate the probe laser until it does<sup>25</sup>. For rotating the laser, loosen the M6 screw at the side of the BA2F(M) base. We recommend loosening it only slightly, as this allows for a more stable adjustment.
- The beam should now be visible on the target. If not, use the laser viewing card to follow the beam after the PR1 mirror and rotate the mirror until the spot is visible on the target (don't move the mirror component laterally). Then use the kinematic thumbscrews of the PR1-mirror to center the beam on the target. You may need to look at the setup from a different angle to be able to see the beam on the target.
- **LASER OFF** Position a second mirror component (from here on called PR2 mirror) 10 cm (4 holes on the breadboard) away from the first one, following the direction of the beam after the PR1 mirror. The PR2 mirror should also be angled by 45° (deflecting the laser towards the left edge of the breadboard) and its post should be centered over a breadboard hole. Secure its position with a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer and a CF125 clamp, pointing to the right of the mirror; see Figure 60.

<sup>25</sup> We recommend rotating the laser instead of moving the mirror in order to ensure right angle reflection at the mirror. This guarantees the correct overlap angles at the sample.

- Position the fluorescent target with crosshairs on the far-left side of the breadboard with its post centered on the same hole row as the PR2 mirror (see Position 1 in Figure 60).
- **LASER ON** The laser should now be visible on the target. If it is not, use the viewing card to find the laser spot and rotate the PR2 mirror (do not move it laterally), until the laser hits the target. Then, use the kinematic thumbscrews of the PR2 mirror to center the beam on the target.
- To perfectly align the laser on the hole row and ensure a constant beam height, we recommend using a beam walk, described in the following:
  - Remove the target with crosshairs from the breadboard and place the target with a hole at the same position. Adjust the post height until the laser is centered on the hole in the target. You have now ensured that both targets have the same height.
  - Remove the target with a hole and place the target with crosshairs at the same position. Position the target with a hole about 5 cm to the left of the PR2 mirror (Position 2 in Figure 60). Make sure it is centered on the same hole row as the PR2 mirror and the other target.
  - Use the kinematic thumbscrews of the PR1 mirror to center the beam on the hole of the first target.
  - After this adjustment, the laser spot should be visible on the second target, but not be centered anymore. Use the kinematic thumbscrews of the PR2 mirror to center it again (if the spot is not visible on the target, use the viewing card again).
  - Iteratively repeat the two steps above until the beam is centered on both targets; see Figure 61. The PR1 mirror is always used for adjusting the spot on the target with a hole, while the PR2 mirror is always used to adjust the spot on the target with crosshairs. After finishing the beam walk, remove the targets from the breadboard.

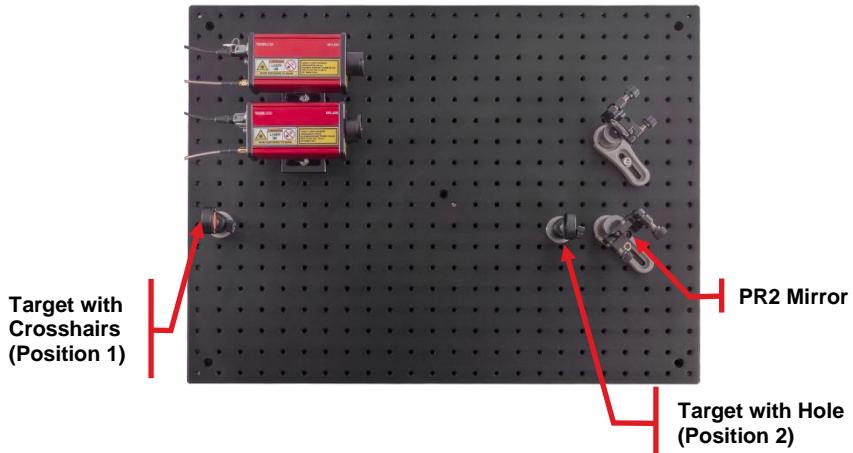


Figure 60 Setup for Beamwalk of the Probe Laser Beam.



Figure 61 Target with crosshairs (top) and target with a hole (bottom) after a successful beam walk.

- **LASER OFF** Position the sample holder on the 8th breadboard hole to the left of the PR2 mirror (8 inches or 20 cm measured between post centers). The post should be centered on a breadboard hole in the same row as the PR2 mirror and the side with the thumbscrew should point towards the mirror. Secure the position with a CF125 clamp and a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer, with the long end of the clamp pointing straight towards you.

- Remove the target with crosshairs from its lens mount. Remove the cap from the detector, then unscrew the retaining ring from the detector. Screw the target in front of the detector instead.
- Take the detector assembly and look at the gain setting on the side of the detector. Set the dial to 10 dB as shown below.



- Position the detector on the 6th breadboard hole (6 inches or 15cm measured between post centers) to the left of the sample holder.
- **LASER ON** Adjust the detector position and post height until the laser is centered on the target, then secure the position via two 1/4"-20 x 5/8" (M6 x 16 mm) Cap Screws plus washers. The setup after this step is shown in Figure 62.



**Figure 62 Placement of Sample Holder and Detector**

- Connect the detector to the power grid with the included power supply. Connect the "Detector" cable coming out of the DAQ card to the BNC port of the detector.

- Place the laser viewing card in the sample holder, such that the laser spot is visible on the fluorescent area. The holder is constructed such that the surface of the viewing card will be in the same plane as the center of the sample liquid during the actual experiment.
- Adjust the height of the 100 mm lens (center) to approximately 8.5 cm.
- **LASER OFF** Position the 100 mm lens halfway between the PR2 mirror and the sample holder. The side from which the retaining ring is visible should be pointing towards the mirror.
- **LASER ON** Move the lens on the axis between the mirror and the sample holder until you find the position where the spot on the viewing card is as small as possible, i.e. the probe laser is focused in the plane of the viewing card surface.
- Remove the viewing card and watch the spot on the fluorescent target in front of the detector. Move the lens perpendicular to the laser beam path until the spot is horizontally centered on the target again. Then, fix the position of the lens with a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer and a CF125 clamp pointing away from you and adjust the post height of the lens until the spot is also vertically centered on the target. This ensures that the beam is passing through the center of the lens.
- Switch on the detector and its power supply. Check that the green LED, which is located on the backside of the detector, is on.
- Remove the target from the detector and watch the signal in the Detector Signal Livefeed graph of the software (see Figure 29). Several sharp peaks should be visible<sup>26</sup>.
- Looking at the peak height and the scale of the detector signal, carefully adjust the detector position and height until the signal is maximized. If the peak height exceeds 1 V, reduce the detector gain temporarily for alignment to 0 dB. Keep in mind that inserting a sample will decrease the signal, so the gain needs to be set to 10 dB again. Reducing or increasing the probe laser pulse width can additionally be used. If the peaks are very broad and fluctuating, check the power of the detector (green status LED should be on) and alignment again. If the maximum peak height is below 0.1 V, increase the probe pulse width and the detector gain.
- The beam path of the probe laser is now set, and the setup should look like Figure 63.

<sup>26</sup> There will still be some signal in the detector live feed graph even if the detector is not switched on. Therefore, make sure that you see the laser pulse peaks before attempting to maximize the signal.

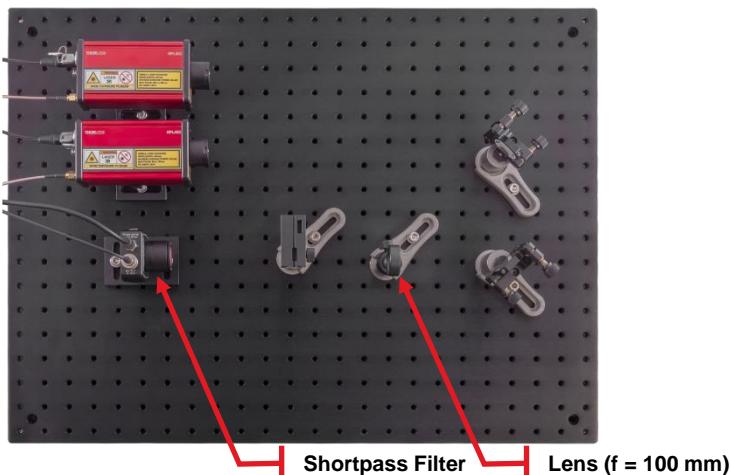


Figure 63 Complete Setup for Probe Laser

### 9.2.3. Adjusting the Beam Path of the Pump Laser

The pump beam adjustments follow a similar procedure as the probe beam:

- **LASER OFF** Position a mirror (called PU1) on the 12th breadboard hole (12 inches or 30 cm measured between post centers) to the right of the pump laser. Secure the mirror position with a CF125 clamp and a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer, with the long end of the clamp pointing to the right side; see Figure 64. Position the target with crosshairs at the end of the breadboard as shown in Figure 64.
- **LASER ON** Activate the **Reduce Pump Frequency (10%)** option in the software and open the shutter of the pump laser. Check the position of the laser beam on the PU1 mirror with the laser viewing card. Rotate the laser until the spot is centered on the mirror. The beam should now be visible on the target. If not, use the laser viewing card to follow the beam after the PU1 mirror and rotate the mirror until the spot is visible on the target (do not move the mirror component laterally). Then, use the kinematic thumbscrews of the PU1 mirror to center the beam on the target. You may need to look at the setup from a different angle to be able to see the beam on the target.

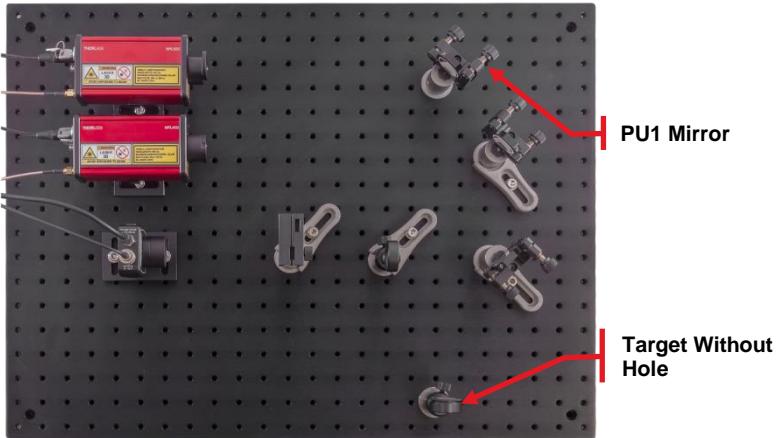
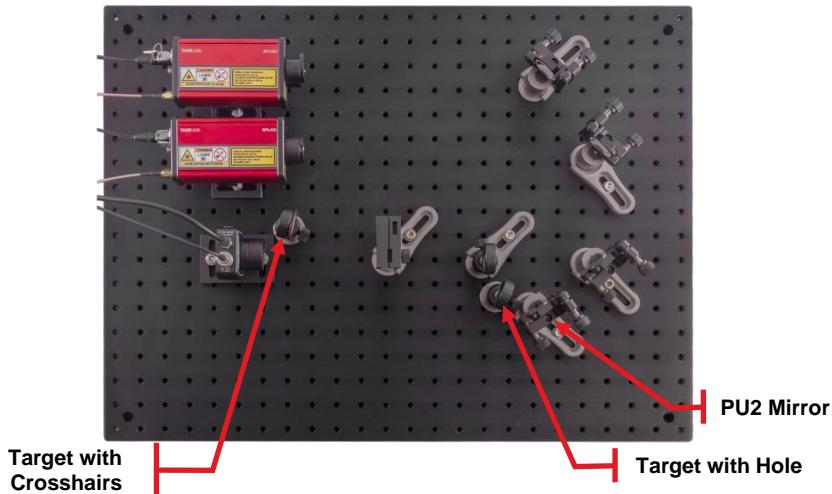


Figure 64 Setup After Placement of the PU1 Mirror

- **LASER OFF** Position the final mirror (called PU2) on the 9<sup>th</sup> breadboard hole along the beam path from the PU1 mirror (9 inches or 22.5 cm measured between the post centers). The PU2 mirror should be angled about 45°, so that the beam is deflected towards the left side of the breadboard, as shown in Figure 65. Secure the mirror position with a CF125 clamp and a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer.
- After the two mirrors are positioned, a beam walk is again required. This time, however, only a constant beam height after the PU2 mirror needs to be ensured. The other axis will be adjusted later to create an overlap between the pump and probe beam in the sample. Follow the steps below:
  - **BOTH LASERS ON** Place the laser viewing card into the sample holder.
  - Slightly loosen the CF125 clamp of the PU mirror, then rotate the mirror so that the pump and probe beam are roughly overlapping on the viewing card surface. Secure the clamp again. Using the kinematic screws of the PU2 mirror, move the pump laser spot until the small probe laser is centered in the larger pump laser spot.
  - Remove the viewing card and position the target with crosshairs in the beam path of the pump laser behind the sample holder so that the beam is centered horizontally. Use the upper thumbscrew of the PU2 mirror to center the target vertically.
  - Position the target with a hole about 5 cm away from the PU2 mirror and change its position until the beam is horizontally centered on the hole. The setup at this point is shown in Figure 65.
  - Use the upper thumbscrew of the PU1 mirror to center the beam vertically on the hole of the target with the hole.

- Use the upper thumbscrew of the PU2 mirror to center the beam vertically on the target with crosshairs.
- Iteratively repeat the two steps above until the beam is centered on both targets, then remove the targets from the breadboard.



**Figure 65 Setup for Beam walk of the Pump Laser Beam Height**

- Insert the laser viewing card into the sample holder. Position the 60 mm lens between the PU2 mirror and the sample holder. The side from which the retaining ring is visible should point towards the mirror. Move the lens along the beam path until the spot of the pump laser appears as focused as possible on the card.
- Move the lens perpendicular to the beam path until the pump and probe spots are vertically aligned on the viewing card. Then, fix the lens position with a CF125 clamp and a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer.



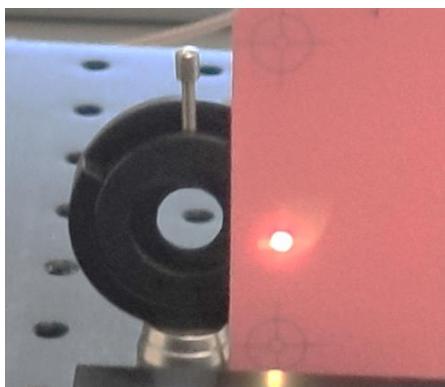
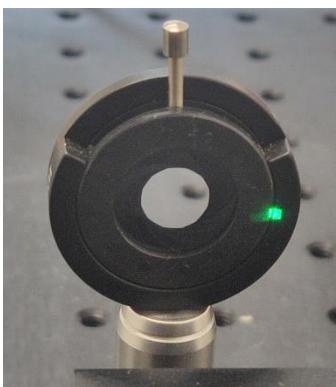
**Figure 66 Vertically Aligned Beam Spots**

- Adjust the post height of the lens until both spots overlap on the viewing card.



**Figure 67 Overlapping the Beam Spots**

- Remove the viewing card and place the iris component between the sample holder and the detector. Its purpose is to block the pump laser after the sample for laser safety. Therefore, the iris should be as close as possible to the sample holder.
- Use the laser viewing card to fine-tune the position and post height of the iris, such that the probe laser beam is centered on the iris. Then, secure the iris position with a CF125 clamp and a 1/4"-20 x 1/2" (M6 x 12 mm) Cap Screw plus washer. Close the iris completely and then open it slowly while observing the detector signal in the software. As soon as the signal is not increasing anymore, you have found the optimal opening diameter of the iris. Then, use the viewing card to check that the pump laser is blocked by the iris.



**Figure 68 Iris component in optimal position. The probe laser (not visible in the photo) passes the iris opening, while the pump laser (green spot in the left photo) is blocked by the iris. Please note that you should only be able to see the laser spot with the IR viewing card while wearing laser safety goggles (shown in the right photo). If you see the green spot, you are either not wearing goggles or using the wrong type.**

You have now completed the pre-alignment of the setup, which should look like Figure 69.

**Note:** From this point, only the PU2 mirror should be used for adjustments. The other three mirrors should remain completely unchanged.

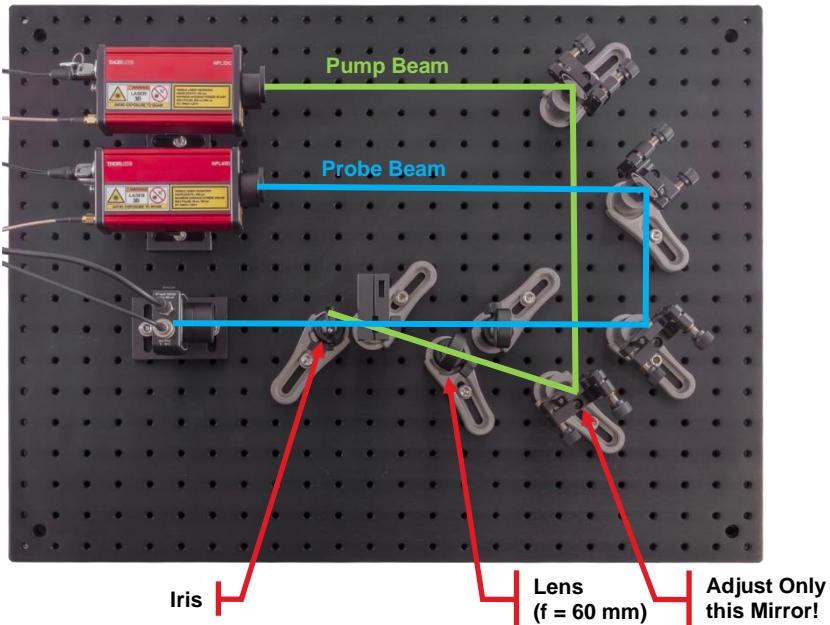


Figure 69 Final Setup

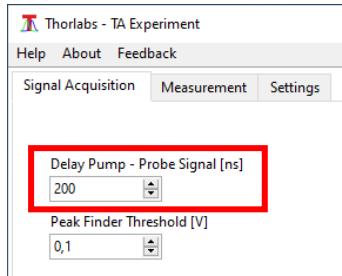
#### 9.2.4. Finding and Optimizing TA-Signal

A TA-signal is only measured when the foci of the pump and probe beam overlap inside the sample volume. To create this overlap, follow the steps below:

- Make sure that both laser shutters are open and that the **Reduce Pump Frequency** option is deactivated in the software.
- Set the pump beam width to the maximum position.

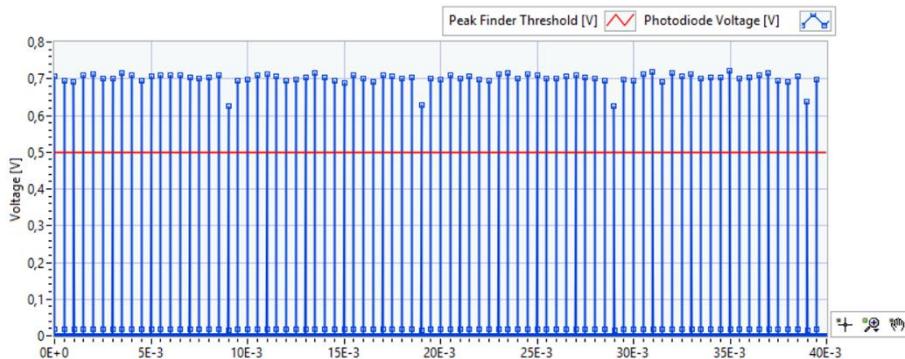


- Set the detector gain to 10 dB.
- Set the **Delay Pump – Probe** in the software acquisition tab to 200 ns. This value delays pump versus probe laser and is a requirement to get a TA signal once overlap is achieved.

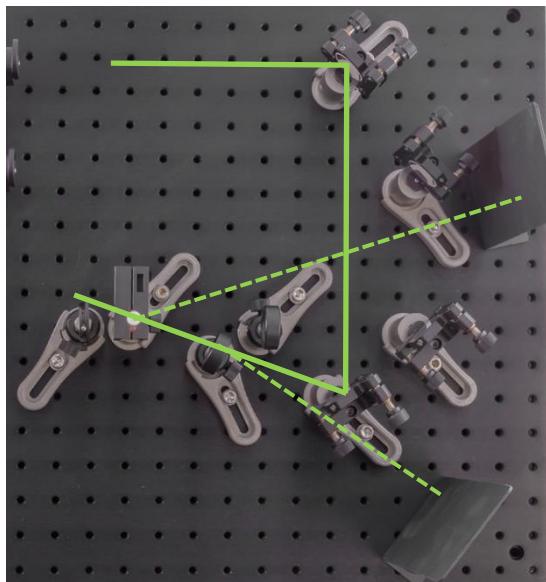


- Position a sample cuvette inside the sample holder and fix the cuvette with the thumbscrew. Use a sample solution that is expected to show high TA signals, such as the 0.8 mMol/L ZnTPP solution included in the sample kit.

- Adjust the probe laser pulse width with the screwdriver on the back of the laser to reach between 0.5 V - 0.9 V in the detector signal live feed.

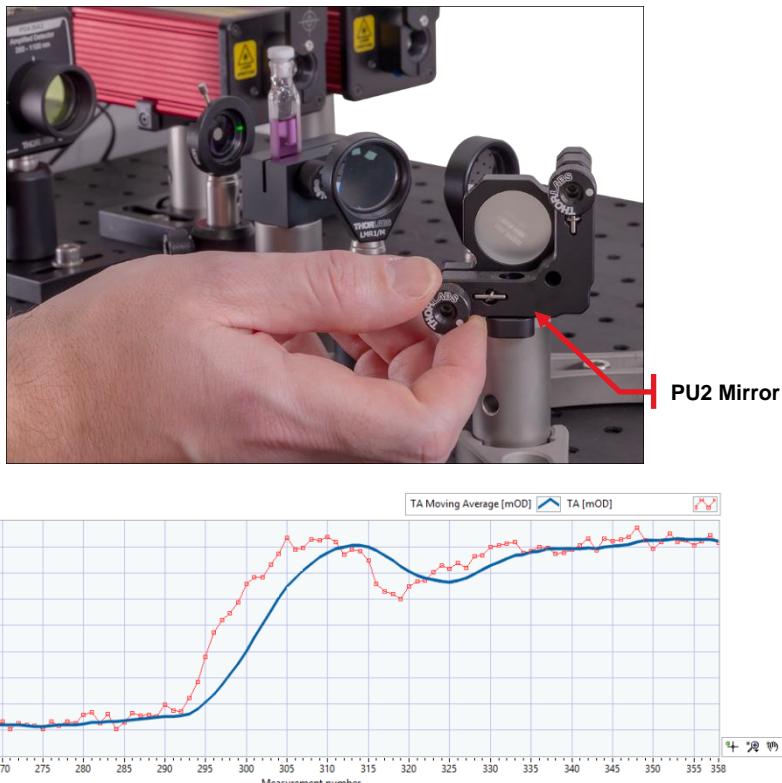


- Set the **Peak Finder Threshold** to a value that is about 0.2 V lower than the pulse signals displayed in the detector signal live feed.
- At this point, about 4% of the pump laser light will be reflected on the cuvette front surface. Follow the reflection with the help of the fluorescent viewing card and place one of the TPSM1/(M) screens at a suitable position to block this stray beam and secure its position with a 1/4"-20 x 1/4" (M6 x 6 mm) Cap Screw plus washer. Make sure that the screen is not interfering with any other beam.
- A second reflection is coming from the lens between the PU2 mirror and the sample holder. This one is much weaker due to the anti-reflection coating of the lens. To block this reflection (recommended), follow the same procedure as above using the second TPSM1/(M) screen. Depending on the lens orientation, the reflection might pass by the PU2 mirror holder or it may be reflected a second time on the PU2 mirror. Figure 70 shows an example of the positioning of the TPSM1/(M) screens.



**Figure 70 Using TPSM1(/M) Screens to Block Pump Laser Reflections (Dotted Lines)**

- Watch the TA signal in the lower graph of the software interface. The current TA signal, as well as an average of the last 10 data points, is shown.
- Carefully turn the lower kinematic screw of the PU2 mirror until you observe an increase of the TA signal. Start by slowly turn the screw in one direction. If a signal increase is not observed after one complete turn of the screw, go back to the original screw position and slowly turn it in the other direction. Once the signal starts to increase, maximize the signal with the lower kinematic screw, and then turn the upper kinematic screw of the PU2 mirror to further increase the signal.



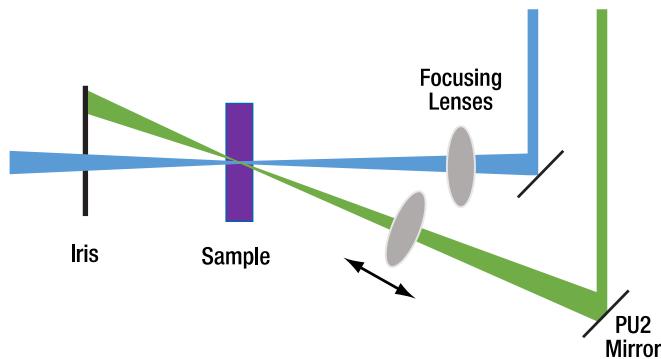
**Figure 71 Optimizing the TA Signal via the PU2 Mirror**

- If a signal above 0 is not observed, replace the sample cuvette by the laser viewing card and adjust the PU2 mirror until the spots of the probe and pump laser overlap. Then, re-insert the cuvette and try again.
- Once the signal has been maximized via the kinematic screws, record the maximum TA signal value. Note that this value should be between 5 mOD and 10 mOD. The next step should increase the signal up to 40 mOD. Note that the TA signal will vary with different samples, beam focus, and settings.

The next step is to manually adjust the position of the pump beam's focusing lens.

- Move the lens between the pump laser mirror (PU2) and sample holder a few millimeters towards the PU2 mirror. While moving the lens, keep an eye on the beam overlap at the sample cuvette. This will reduce the amount of fine adjustment. Then, use the lower kinematic screw of the PU2 mirror to maximize the TA signal again. If the beam overlap and TA signal are lost, insert the viewing card, move the lens perpendicular to the beam such that the beams overlap, and

start a new fine alignment. Remember to use the Pump 10% functionality in the software to reduce the pump beam intensity temporarily.



**Figure 72 Manually Adjusting the Pump Laser Focusing Mirror**

- Compare the maximum signal before and after moving the lens. If the signal increased, move the lens a bit further towards the PU2 mirror. If the signal decreased, move the lens towards the sample holder. Maximize the signal with the PU2 mirror kinematic screws again and compare the maximum signals.
- Repeat the step above until you have found the optimal position of the lens. A TA signal of more than 40 mOD for the 0.8 mMol/L ZnTPP sample is a good result. A value of about 70 mOD can be seen in ideal conditions (new sample, perfect alignment).

You have now ensured that the foci of the pump and probe laser overlap in the center of the sample liquid, and, therefore, established the setup configuration that should be used for the time-resolved absorption spectroscopy measurements.

# Chapter 10 Exercises and Examples

## 10.1. Setup Alignment

The overlap of the pump and probe laser is an important factor when aiming for a high transient absorption signal.

To test this, optimize the TA signal for two different focusing lenses in the pump beam and compare which one results in a higher signal.

### Experiment:

Device	Dial	Setting
NPL52C – Pump Laser	Pulse Width	16 → 129 ns (Maximum)
NPL45B – Probe Laser	Pulse Width	2 → 7 ns (as Start)
PDA36A2 – Detector	Gain	0 dB Without Sample (Alignment) 10 dB with Sample

- After adjusting the setup and optimizing the TA signal as described in Chapter 9.2.4 (with 0.8 mMol/L ZnTPP sample), note the maximum TA signal value.
- Switch off the lasers, remove the 60 mm lens between the PU2 mirror and sample holder.
- Position the 75 mm lens between the PU2 mirror and sample holder. The distance to the sample holder should be about 75 mm.
- Switch on the lasers and optimize the TA signal with the new lens as described in Chapter 9.2.4. Note the optimized TA value.

### Data Evaluation:

Compare the optimized TA signal strength for the two lenses. Which lens results in a higher signal? What could be the reason?

### Interpretation:

You should obtain a larger TA signal with the 60 mm lens, rather than with the 75 mm lens, because a higher overall intensity of the lasers is concentrated in the overlap region.

The details of the overlap are explained in Chapter 6.2. Due to the ellipticity of both laser foci, it is advantageous to make the focus of one laser as small as possible, thus ensuring it is mostly inside the focus of the other laser. A schematic comparison between a weakly and strongly focused pump laser is shown in Figure 73. Although the overlap region is slightly smaller in the strongly focused case, the power density of the pump is much higher, leading to a higher TA signal in this case.

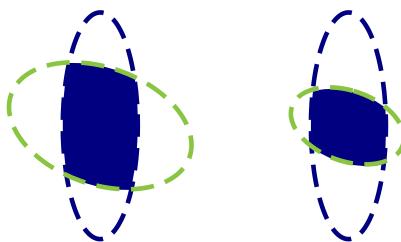


Figure 73 Focus Overlap for a Weakly Focused (Left) and Strongly Focused (Right) Pump Laser Beam (Green) and Fixed Probe Beam (Blue).

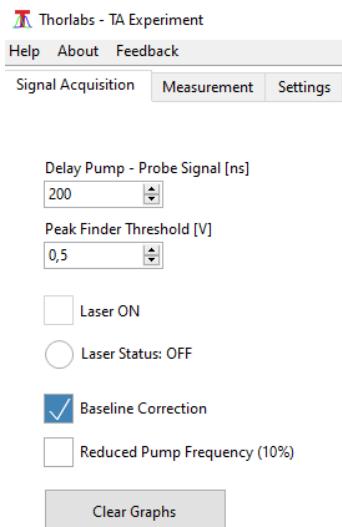
## 10.2. Measuring the Decay Time of the ZnTPP Excited State

After ensuring the overlap of the pump and probe beams inside the sample volume as described in Chapter 9.2.4, you can now measure the decay time of the excited state as follows:

### Experiment:

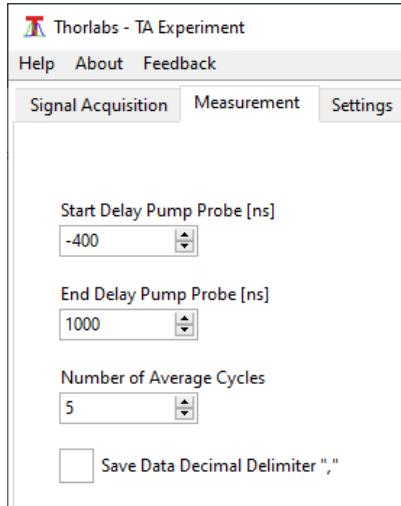
Device	Dial	Setting
NPL52C – Pump Laser	Pulse Width	16 → 129 ns (Maximum)
NPL45B – Probe Laser	Pulse Width	2 → 7 ns (Optimize)
PDA36A2 – Detector	Gain	0 dB Without Sample (Alignment) 10 dB with Sample

- Make sure that the 60 mm lens is installed in the pump beam path.
- Make the **Baseline Correction** checkbox is activated and **Reduced Pump Frequency (10%)** checkbox is deactivated, as shown in Figure 74. Then, switch to the Measurement Tab.



**Figure 74 Typical Settings Before Switching to Measurement Tab**

- Set the lower and upper delay boundaries. We recommend a range of -400 ns to 5000 ns.
- Set the Averaging. We recommend a value of 5 for a good balance between noise and measurement time. A measurement with the recommended parameters, as shown in Figure 75, will take about 10 minutes to complete.
- Set the Decimal separator that fits the data analysis software you intend to use later.



**Figure 75 Recommended Settings for Time Resolved Absorption Measurements**

- Start the measurement. You will be prompted to select a name and path for the result file.
- Once the measurement is started, the software displays the following information:
  - The measurement cycle you are currently in and the current delay between pump and probe cycle (see Figure 76).
  - All measured curves of this measurement (thin lines in various colors) and the average of all measured curves of the measurement (broad blue line); see Figure 77.
- The curves should show a sharp rise of the TA signal at a delay between 0 and 150 ns followed by an exponential decay as shown in Figure 76 and Figure 77.
- After the measurement is finished, the results are saved in a .csv file in the path specified at the start of the measurement. The averaged curve is saved as well as all single traces in a separate "\_traces.csv". Additionally, a ".xml" file is saved with measurement parameters and the editable info box during the measurement.

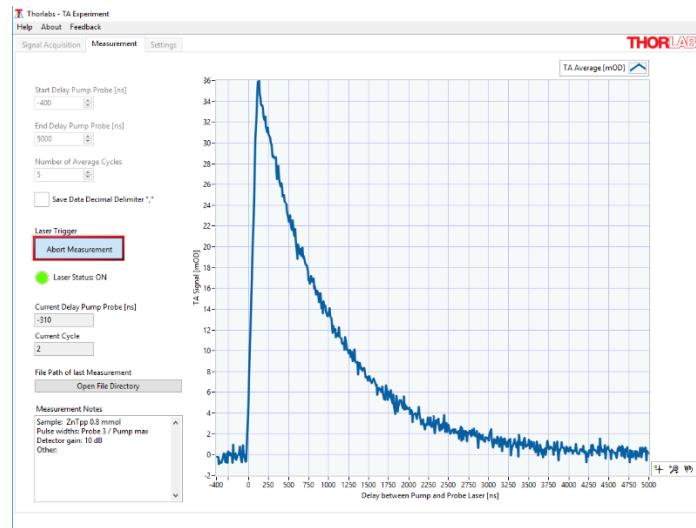


Figure 76 Screenshot During a Measurement

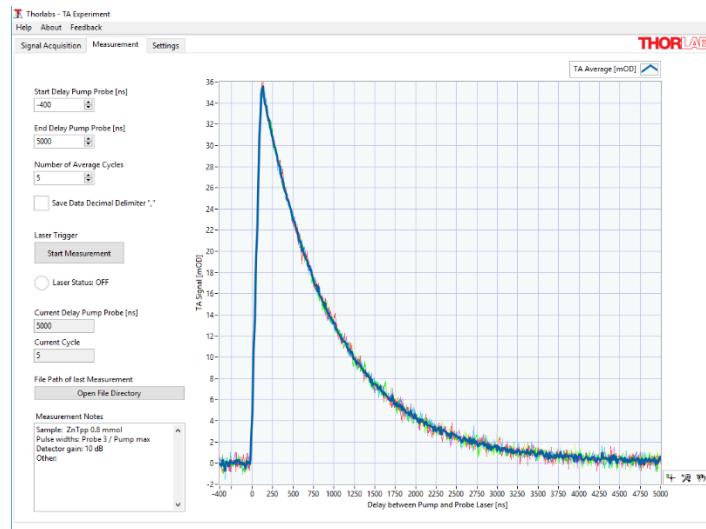
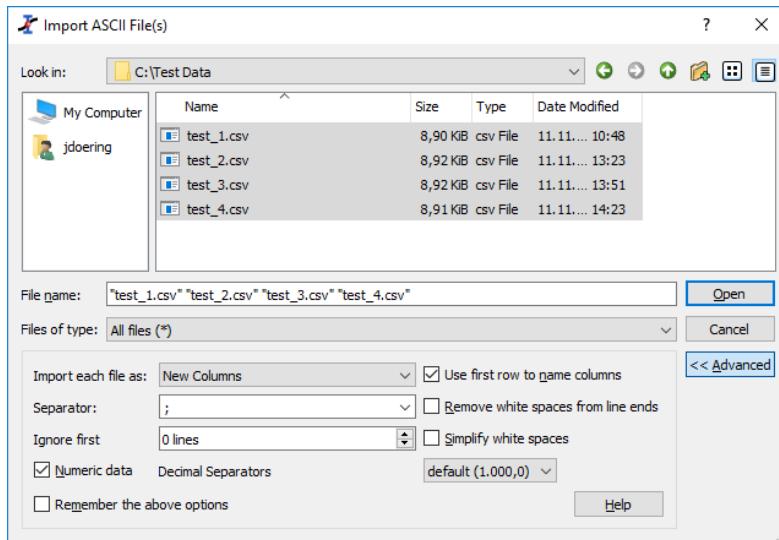


Figure 77 Screenshot of Finished Measurement

### 10.3. Data Analysis

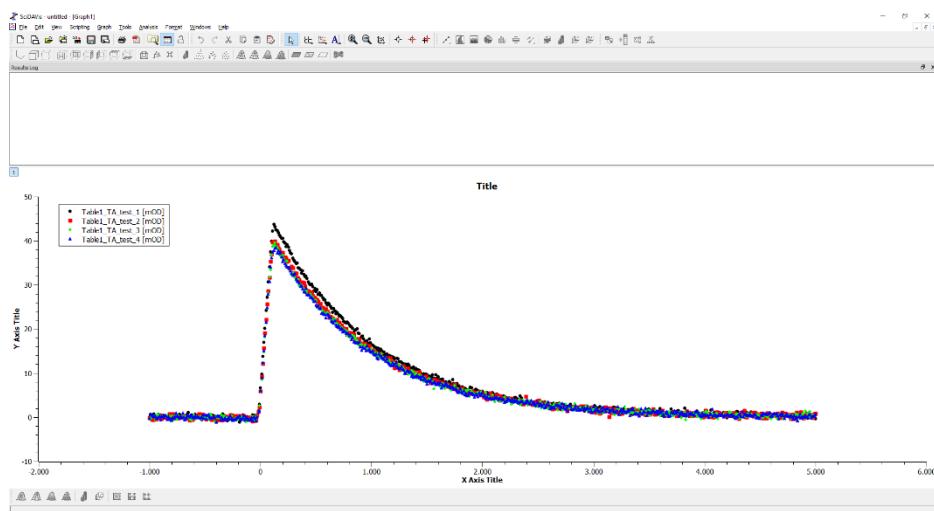
From the results of the measurement described in Chapter 10.2, one can obtain the lifetime of the ZnTPP excited state by fitting an exponential decay function to the data points. While any data plotter software can be used for this, we describe how the process works in the freeware program SciDAVis in the following:

- Start SciDAVis, a new project with an empty table is automatically created.
- Choose **File → Import ASCII** from the header bar.
- In the Import dialog window that opens, select all the measurement files that you want to plot and fill in the parameters as shown in Figure 78. The **Remember Settings** checkbox can be activated so the parameters only have to be changed once. Make sure to use the same decimal divider that was chosen in the measurement software.



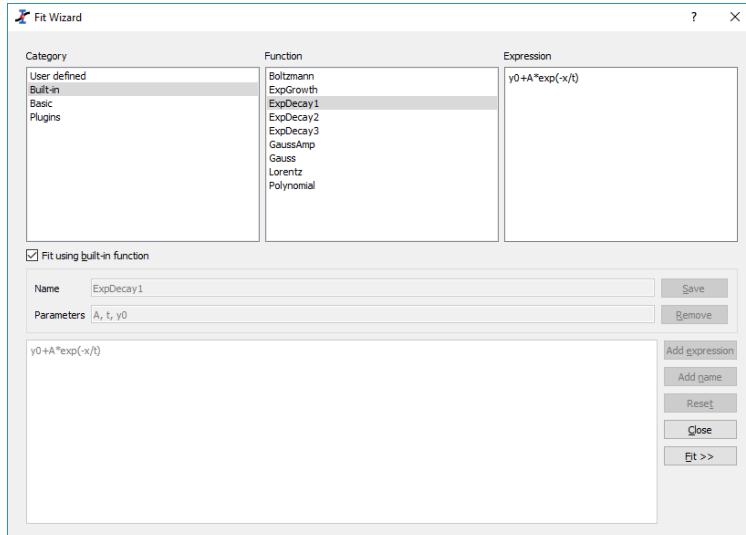
**Figure 78 Recommended Settings in Import Dialogue of SciDAVis**

- The ASCII import creates a separate x-column for each measurement. If you used the same start and end delays for all imported measurements, every x-column but the first can be deleted.
- The columns can be renamed via the description tab on the right side.
- Mark the whole table and choose **Plot → Scatter** from the header bar to create a plot from the measurement data. In the graph that opens you should see the exponentially decaying shape of the data curves, like the plot shown in Figure 79.



**Figure 79 Example Measurement Plotted in SciDAVis**

- Select **Analysis → Fit Wizard...** from the header bar. In the dialogue window that opens, select **Category: Built-In** and **Function: ExpDecay1**. This will fit an exponential function, similar to Formula (6) in Chapter 5.1, to the data points. Then check the **Fit using built-in function** box as shown in Figure 80 and press the **Fit>>** button.



**Figure 80 Fit Wizard Dialogue**

- In the next dialogue window, the start values for the fit parameters can be set as well as other fit settings as shown in Figure 81.
- You should give reasonable starting values for the three fit parameters, and the values in Figure 81 are usually a good choice for the reference sample provided with the kit. Here, **A** describes the starting TA signal of the exponential decay (usually between 10 and 60), **t** describes the decay time in nanoseconds (usually between 500 and 1000), and **y0** is the offset of the curve, which is close to 0.
- The **From x=** value should be the delay value of the data point with the highest TA-signal. This is usually between 100 ns and 150 ns, but needs to be checked for every new measurement.
- After clicking the **Fit** button, the fit is performed. The results are displayed in the dialogue window as well as in the result log. Furthermore, the fit is drawn in the plot, as shown in Figure 83.
- In addition, you have the option to create a new table containing the results by pressing the **Custom Output** button and then pressing the **Parameters Table** button in the next window; see Figure 82. An example for the created parameter table is shown in Figure 84.

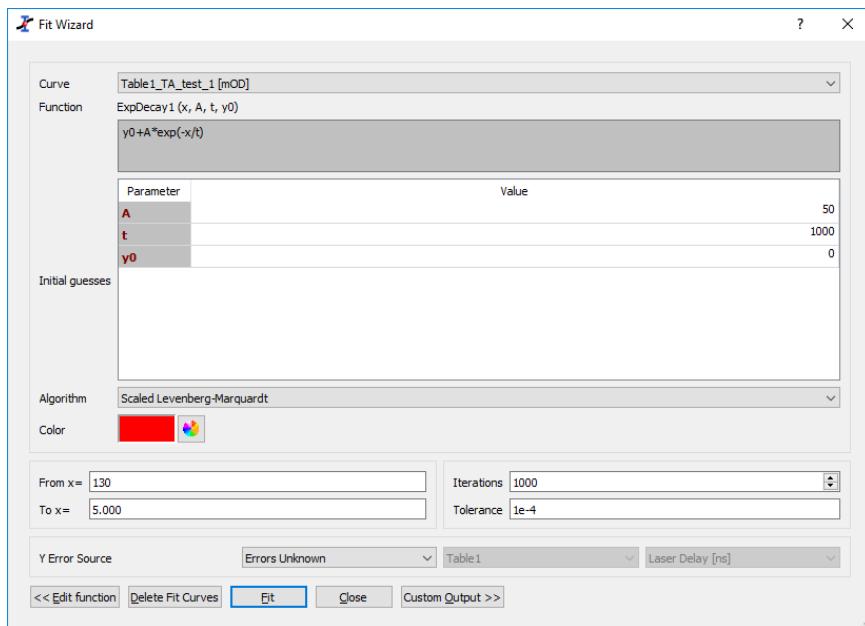


Figure 81 Fit Settings

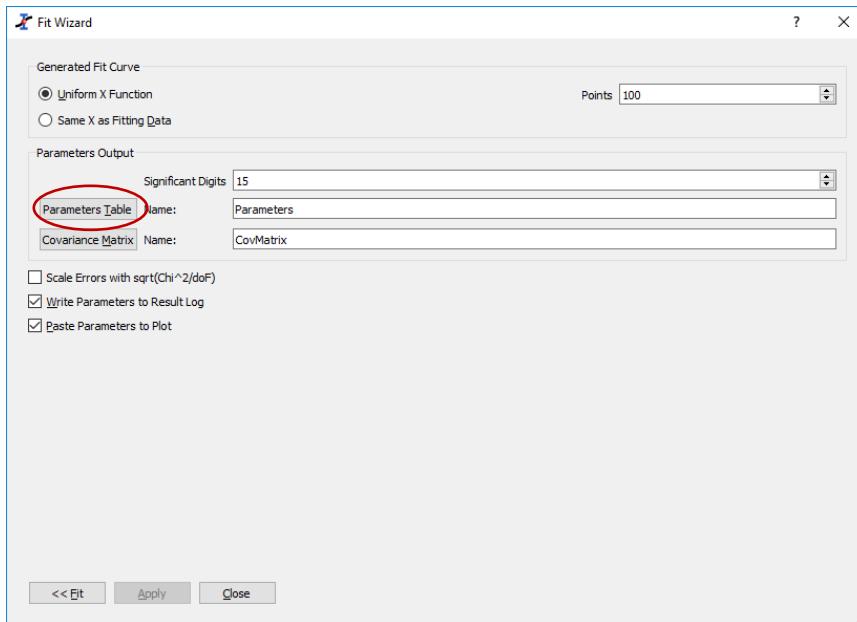


Figure 82 Custom output options in the fit wizard. The Parameters Table button is marked.

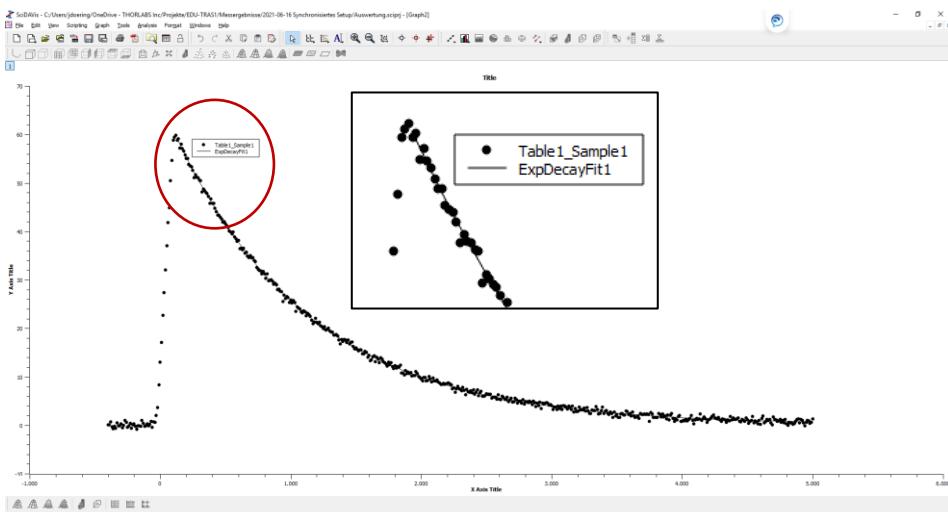


Figure 83 Example of the plot after fitting. As shown in the zoomed in inset, the fitted exponential function is added to the plot as a continuous line.

The screenshot shows a software window titled "Parameters9". On the left is a table with three rows of parameters:

Parameter[X]	Value[Y]	Error[yEr]
1 A	66,7434	0,153267
2 t	1.042,43	3,69766e-06
3 y0	0,115268	0,0426125

On the right side of the window, there are several configuration fields:

- Description:** Type: Text, Format: Text. Below these are "Selected column type: Text" and "Example: Hello world!".
- Apply:** A button at the top of the right panel.

**Figure 84 Example Parameter Table for a Fit**

## 10.4. Different Concentrations of ZnTPP

Up to now, you investigated a single sample with a fixed concentration of ZnTPP. In this section you will investigate the effect of the ZnTPP concentration on the experimental data by investigating three different samples.

- What effects on the signal do you observe for different concentrations?
- How can those effects be explained by setup parameters and/or reaction chemistry?

### Experiment:

- Prepare at least three solutions with different concentrations of ZnTPP. We recommend concentrations of 0.2 mMol/L, 0.4 mMol/L, and 0.8 mMol/L. For detailed instructions on sample preparation, see Chapter 7.
- Record a time resolved absorption curve as described in Section 10.2 for each of the concentrations (placeholder). Use the 0.4 mMol/L sample for the last measurement of the series.

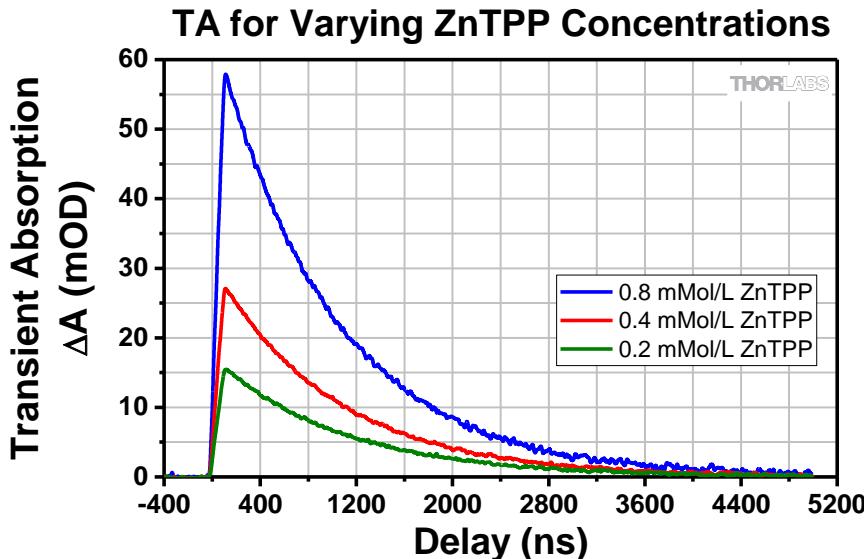
### Data Evaluation:

- Create a single plot with the curves for all measured concentrations as described in Section 10.3. What do you observe?
- Determine the fit parameters for all three curves as described in Section 10.2. Are there any trends in the data?
- Plot the lifetime over the concentration. What do you see?

- Is the single exponential fit adequate? Is a Y-axis offset needed as a free fit parameter needed?

### Interpretation:

The results of an example measurement are shown in Figure 85 and Table 2.



**Figure 85** Plotted Results of an Example Measurement for Three Different Concentrations of ZnTPP

ZnTPP Concentration [mMol/L]	Max. TA Signal $\Delta A$ [mOD]	T [ns]
0.2	17.32	1056.07
0.4	30.47	998.27
0.8	65.02	969.42

**Table 2** Fit Results of Example Measurement for Three Different Concentrations of ZnTPP

Notice the following relations:

- The maximum value of the TA signal increases with increasing concentration.
- The lifetime decreases with increasing concentration.

The first effect is intuitive. A higher concentration of ZnTPP in the sample means more molecules in the same sample volume. Therefore, the same pump laser pulse will excite more molecules into the triplet state (if the system is not saturated). This results in a higher absorption of the probe laser and in turn causes higher values of the TA signal.

The second effect is caused by adding another deactivation path. The concentration of ZnTPP influences the lifetime of the excited states due to increased triplet-triplet quenching; see Section 5.4. Thus, a lower lifetime is expected for higher concentrations.

Interpretation of fit functions and free parameters is an important learning experience. Depending on the field of the experimenter, one can go deeper into the topic. The question of whether a Y-axis offset parameter is needed in the fit depends on your data and cannot generally be answered. We expect no visible secondary reactions in the ZnTPP in Benzonitrile on the observed timescale excitation and, thus, fitting with an exponential fit without offset will be adequate.

## 10.5. Mixed C<sub>70</sub> and ZnTPP Samples

The next step is to investigate the influence of additional chemicals, in this case the electron acceptor C<sub>70</sub>, on the reaction chemistry. To this end, four or more samples with different ZnTPP- C<sub>70</sub> mixing ratios are measured.

- What effects on the signal do you observe for different mixing ratios?
- How can those effects be explained by setup parameters and/or reaction chemistry?

### Experiment:

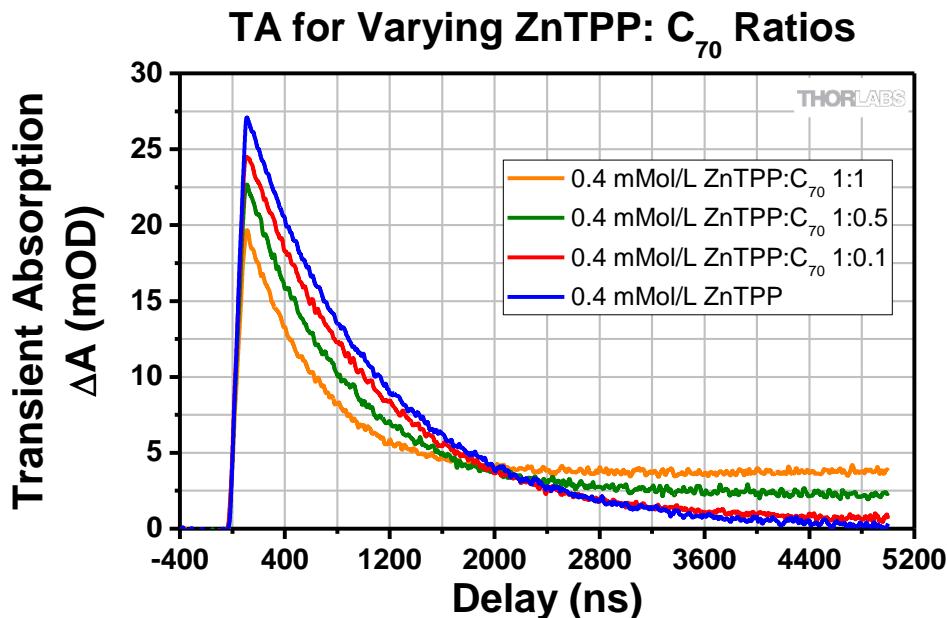
- Prepare at least four solutions with different mixing ratios of ZnTPP and C<sub>70</sub> for a fixed ZnTPP concentration (for details on the sample preparation, see Chapter 7). We recommend a ZnTPP concentration of 0.4 mMol/L and ZnTPP- C<sub>70</sub> ratios of 1:0, 1:0.1, 1:0.5, and 1:1.
- Record a time resolved absorption curve analogous to that in Section 10.2. for each of the mixing ratios.

### Data Evaluation:

- Create a single plot with the curves for all measured mixing ratios as described in Chapter 7.2. What do you observe?
- Determine the fit parameters for all curves as described in Chapter 10.2. Are there any trends in the data?
- Plot the lifetime over the mixing ratio. What do you see?
- Determine the reaction constant k from the plot. How do you do that?

### Interpretation:

- An example measurement is shown in Figure 86. Table 3 shows the fit parameters, and Figure 87 the reaction kinetic constant evaluation.



*Figure 86 Plotted Results of an Example Measurement for Four Different ZnTPP-to-C<sub>70</sub> Mixing Ratios*

ZnTPP-to-C <sub>70</sub> Mixing Ratio	Max. TA Signal ΔA [mOD]	T <sub>app</sub> [ns]	k <sub>app</sub> = 1/T <sub>app</sub> [10 <sup>6</sup> /s]
1:0	30.47	998.27	1.0017
1:0.1	27.43	946.90	1.0560
1:0.5	23.99	731.72	1.3666
1:1	19.94	536.04	1.8655

*Table 3 Fit Results of an Example Measurement for Four Different ZnTPP-to-C<sub>70</sub> Mixing Ratios*

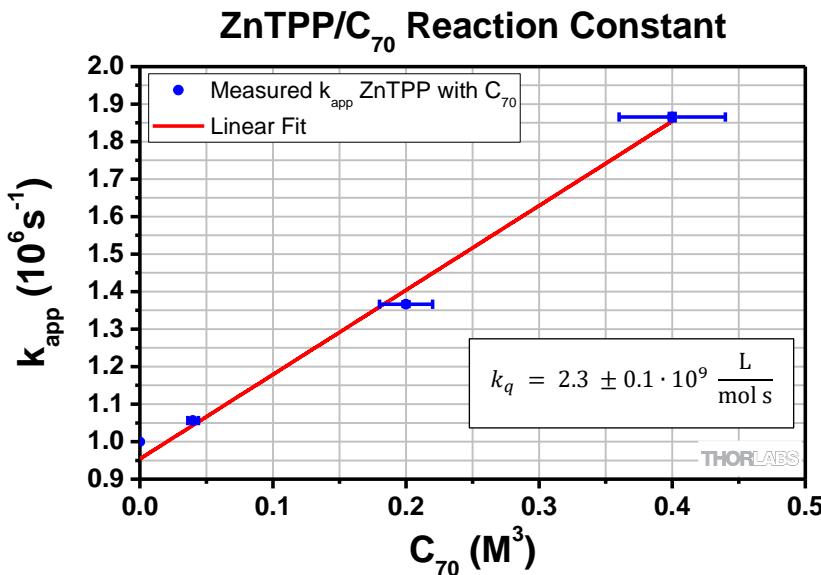


Figure 87 Plot and Calculation of Reaction Constant for C<sub>70</sub>/ZnTPP Measurement

Notice the following relations:

- The maximum value of the TA signal decreases with increasing amount of C<sub>70</sub> in the solution.
- The lifetime decreases with increasing amount of C<sub>70</sub> in the solution.

The first effect is caused by absorption of the pump beam by the C<sub>70</sub> molecules. The more C<sub>70</sub> is present, the more pump laser photons are absorbed by C<sub>70</sub>. In turn, less ZnTPP molecules are excited into the triplet state, reducing the absorption of the probe laser pulse. Thus, the difference between absorption in the pumped and unpumped state (the TA signal), decreases with increasing C<sub>70</sub> concentration.

The second effect is caused by the addition of a new reaction path. C<sub>70</sub> is a strong electron acceptor and reduces the lifetime of the excited ZnTPP state via Photoinduced Electron Transfer (PET). For details, see Section 5.5. Thus, a lower lifetime is expected for higher C<sub>70</sub> content.

The reaction constant k<sub>q</sub> can be calculated by plotting the inverse lifetimes over the C<sub>70</sub> concentrations as shown in Section 5.5 and applying a linear fit, as shown in Figure 87. The slope of the fit line is k<sub>q</sub> in units of  $10^9 \frac{\text{L}}{\text{mol s}}$ . In the case of the example measurement, the value  $k_q = 2.3 \pm 0.1 \cdot 10^9 \frac{\text{L}}{\text{mol s}}$  is in reasonable range of the literature values of

$k_q = 2.4 \cdot 10^9 \frac{\text{L}}{\text{mol s}}$  as measured by Nojiri et al.<sup>27</sup> (with different concentrations). As described in Section 11.2, the evaluated values  $T_1$  can vary for different reasons from the examples shown here. Therefore, the reaction constant  $k_q$  can vary between  $1 - 3 \frac{\text{L}}{\text{mol s}}$  depending on the sample preparation and condition.

<sup>27</sup> T. Nojiri, A. Watanabe, and O. Ito, "Photoinduced Electron Transfer between C<sub>60</sub>/C<sub>70</sub> and Zinc Tetraphenylporphyrin in Polar Solvents," *Journal of Physical Chemistry A*, vol. 102, no. 27, pp. 5215 - 5219, 1998.

# Chapter 11      Specifications and Tables

In this Chapter you can find specifications and data needed for the evaluation and interpretation of your measurements.

## 11.1. Nanosecond Pulse Lasers

In the following table typical pulse widths for the two lasers used are shown. An overview of the laser specifications can be found on the respective website:

[https://www.thorlabs.com/newgroupage9.cfm?objectgroup\\_id=10823](https://www.thorlabs.com/newgroupage9.cfm?objectgroup_id=10823)

Additional specifications can be found in the following sections.

### 11.1.1. NPL52C Laser

The center wavelength is  $520 \text{ nm} \pm 10 \text{ nm}$ . The pulse width can be set with the dial on the laser. The accuracy of the pulse width typically varies by  $\pm 1 \text{ ns}$  in the low pulse width range and by  $\pm 5 \text{ ns}$  in the high pulse width range.

Pulse Width Setting	Pulse Width (ns)	Average Power (mW) @ 50 kHz Rep. Rate
1	6	0.29
2	15	1.06
3	22	1.60
4	31	2.26
5	38	2.82
6	47	3.48
7	54	4.05
8	63	4.72
9	71	5.31
10	80	5.99
11	87	6.58
12	96	7.26
13	104	7.85
14	112	8.52
15	120	9.10
16	129	9.76

### 11.1.2. NPL45B Laser

Center wavelength 450 nm  $\pm$  10 nm. The accuracy of the pulse width typically varies by  $\pm$  1 ns in the low range pulse width range and by  $\pm$  3 ns in the high pulse width range.

Pulse Width Setting	Pulse Width (ns)	Average Power (a.u.)
1	5	0.66
2	7	1.36
3	10	1.80
4	12	2.17
5	14	2.47
6	17	2.84
7	19	3.15
8	21	3.46
9	23	3.79
10	26	4.10
11	28	4.45
12	30	4.76
13	33	5.04
14	35	5.35
15	37	5.66
16	39	5.97

## 11.2. Repeatability of Experiments

This section and Table 4 will provide an overview of additional measurement parameters and their influence on the results.

The largest influence on TA decay time  $T_1$  is the oxygen saturation of the sample. ZnTPP in anhydrous Benzonitrile will show decay times almost twice as high as oxygen saturated samples due to the added quenching partners. Newly prepared samples show decay times of 1300 ns compared to 900 ns after 24 hours stored in contact with air. To compare two samples, preparation and storage conditions should be very similar.

The largest influence on the maximum TA signal  $\Delta A$  (apart from misalignments) is degradation of ZnTPP. Samples will bleach (from violet to red) when stored in a bright (daylight / ceiling light) environment. Storing samples in light tight environment is therefore strongly recommended.

Other parameters tested only contribute to small changes in the  $T_1$  decay times. Tests showed that sample temperature, alignment accuracy, detector gain and, continuous measurement over 24-hour time frame only change the result within 0.7 % - 1.5 %.

Parameter	Configuration	Decay times $T_1$	Transient Absorption maximum $\Delta A$	Relative change of $T_1$
Oxygenation of Anhydrous Benzonitrile	New Sample (Prepared from Anhydrous ZnTPP)	1300 ns	85 mOD	65%
	After 1 Day Air Exposure	900 ns	80 mOD	
	After 1 Month Air/Light Exposure	850 ns	40 mOD	
Sample Temperature	10°C	923 ns	-	1.5%
	22°C	909 ns	-	
24h Measurement: Measuring the sample constantly over a span of 24 hours (not freshly prepared)	Min	917 ns	-	1.2%
	Max	928 ns	-	
Misalignments TA Signal 60 mOD vs TA signal 25 mOD	Aligned to 60 mOD	833 ns	60 mOD	1.3%
	Misaligned to 20 mOD	822 ns	20 mOD	
Detector Amplification 10 dB vs 40 dB	10 dB	858 ns	-	0.7%
	40 dB	864 ns	-	

Table 4 Additional Measurement Parameters

### 11.3. Chemical Stability and Optical Transmission

To examine the chemical stability of the involved reaction partners and solvents, an analysis of an absorption spectra in the UV and visible (UV-VIS) region is helpful.

The UV-VIS absorption spectra of ZnTPP, C<sub>70</sub>, and its mixture are shown in Figure 88. The ZnTPP spectral band at 420 nm is the so called Soret-band<sup>28</sup> and the smaller bands

<sup>28</sup> [https://en.wikipedia.org/wiki/Soret\\_peak](https://en.wikipedia.org/wiki/Soret_peak)

at 560 nm and 600 nm are Q-bands<sup>29</sup>. The comparison of chemically mixed and mathematically added spectra of the single components shown in Figure 88 shows almost identical form, which indicates that all molecules stay independent and do not form new reactants.

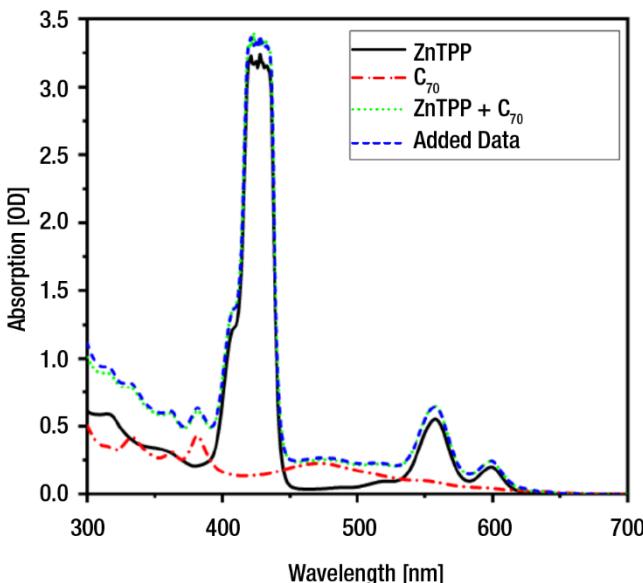


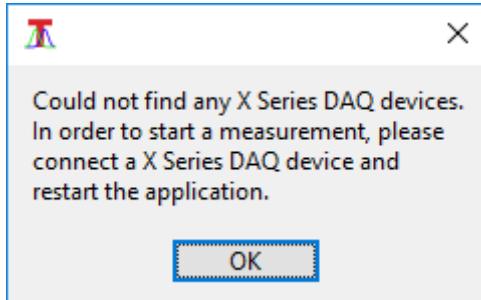
Figure 88 UV-VIS Spectra of the ZnTPP, C<sub>70</sub>, ZnTPP + C<sub>70</sub>, and calculated added-spectrum.

<sup>29</sup> A. Lukaszewicz et al., "Photophysical processes in electronic states of zinc tetraphenyl porphyrin accessed on one- and two-photon excitation in the soot region," *Chemical Physics*, vol. 331, no. 2, pp. 359 - 372, 2007.

# Chapter 12 Troubleshooting

## 12.1. DAQ Card Connection

**Problem:** When starting the software, the following error message occurs:



**Solution:** The DAQ card is not connected to the PC via USB or not switched on. If the DAQ card is connected and switched on, but the blue indicator LEDs on the front are both dark, then the PC did not recognize the card correctly. In this case, try using a different USB port on your PC.

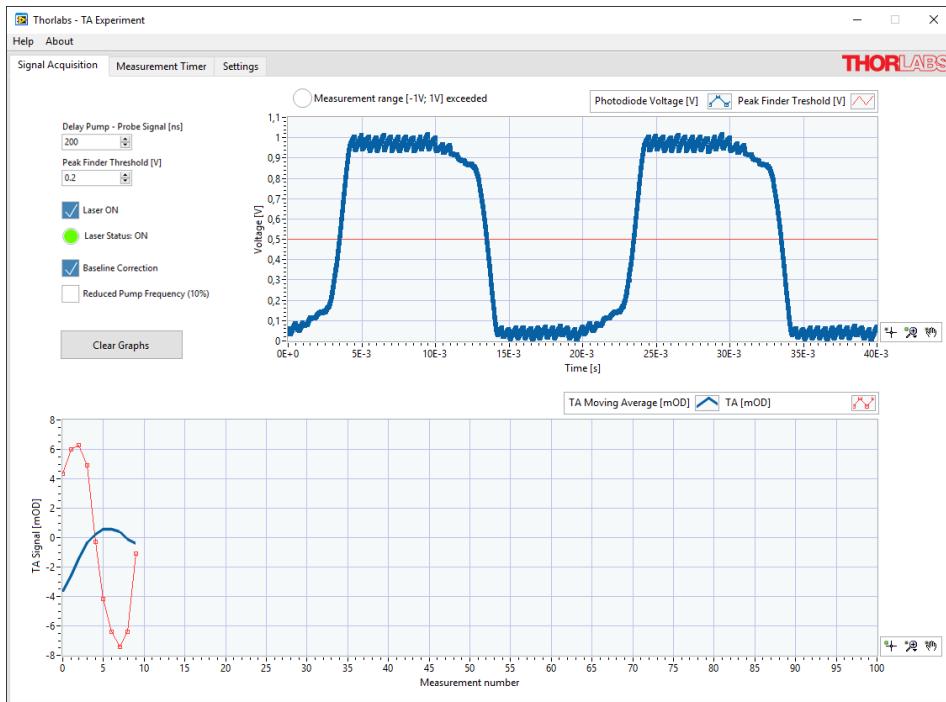
After establishing the connection with the DAQ card, the software has to be restarted to recognize the card correctly.

## 12.2. Photodiode Signal

**Problem:** Upon starting the trigger sequence in the software, no photodiode signal is displayed.

**Solution:** The photodiode signal is only coming from the probe laser. Follow the probe laser with the laser viewing card and check if it reaches the detector. You can remove the filter in front of the detector. If the beam does not reach the detector, new alignment is necessary as shown in Chapter 9.2.

If the probe laser is centered on the photodiode but still no typical 2 kHz periodic structure is visible (compare to Figure 29), the photodiode might be switched off. The photodiode has two “on” switches. One on the power supply and the other on the side of the device (green LED). A typical “signal” for a switched off photodiode is displayed in Figure 89.



**Figure 89 Typical signal when photodiode power is off.**

Another reason for an unusual signal is the input setting on the probe laser (NPL45B). To use the external trigger check if the repetition rate (REP RATE) is set to "D" user triggered (USER TRIG), see below.



Also, check the cable routing is as shown in Figure 57.

## 12.3. TA Signal

**Problem:** The beams are perfectly overlapped on the viewing card, but the TA signal is still zero after inserting a sample.

**Solution:** Try to fine-adjust the overlapping region with the adjusters of the PU2 kinematic mount as shown in Figure 71.

There is a small window of adjustment, which can only be optimized by rotating the kinematic thumbscrews of the PU2 mirror back and forth. Another way to check if the beams are overlapping is to hold the laser viewing card in front of the cuvette and behind the cuvette. When the beams are overlapping correctly, the distance between the two spots should be similar on both sides.

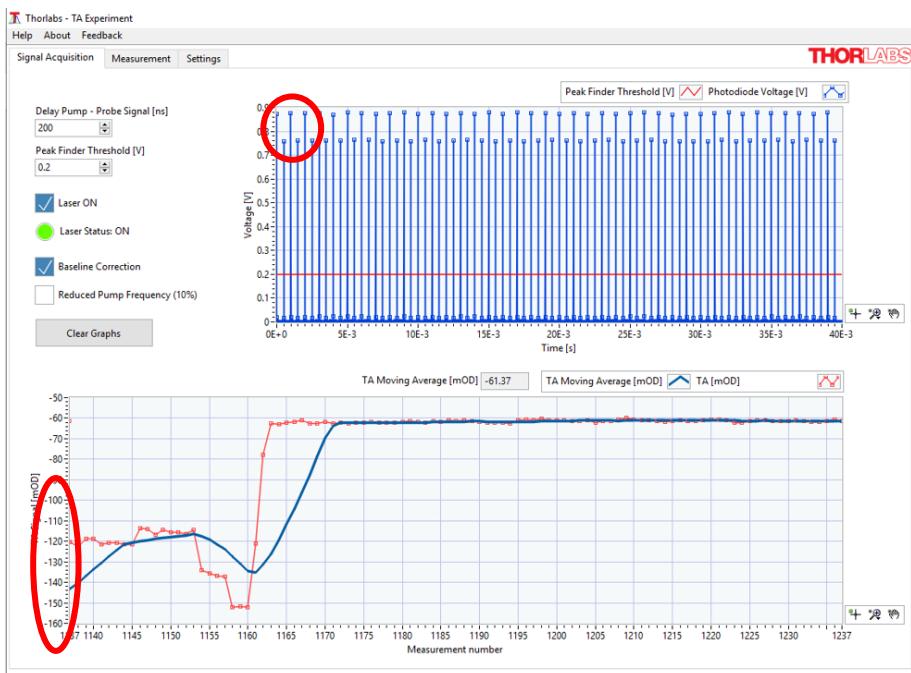
Getting the first signal might be challenging, but after some repetitions the alignment will get easier. Some additional quick checks / tips to look at:

- Set the delay to 200 ns in the acquisition tab window.
- Use highly concentrated samples (0.8 mMol/L ZnTPP in Benzonitrile).
- Check the peak-finder threshold voltage. The threshold must be below the voltage measured by the photodiode.
- Deactivate the **Pump 10 %** setting in the acquisition tab, which is only for visual alignment and results in a noisier TA signal.

## 12.4. Negative Transient Absorption Values

**Problem:** Negative TA signal values are measured. Some species or reaction pathways can lead to negative transient absorption values. However, in the scope of this kit, the lasers and sample are chosen to get a positive transient absorption value.

**Solution:** Obtaining negative TA values is a clear sign of pump beam intensity reaching the detector. When you look at formula (3), a higher intensity with pump ( $I_{\text{with Pump}}$ ) than intensity without pump ( $I_{\text{without Pump}}$ ) will lead to negative values. You can see this effect in Figure 90. Especially note that the first peak is larger than the second one.



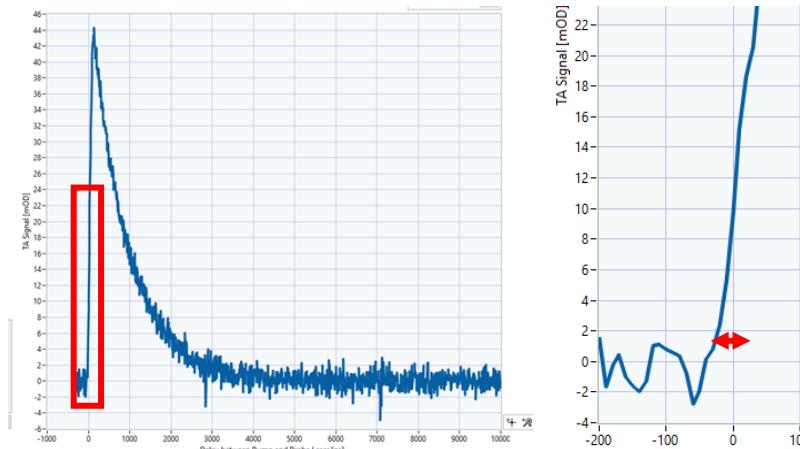
**Figure 90** If the pump beam is leaking into the detector, the first pulse of the detector voltage will be higher than that of the second and the TA signal will be negative (circled in red).

The setup is designed to block the pump beam with the iris and to block out unwanted wavelength with the filter in front of the detector. Disregarding these measures can introduce this artifact. The result will also be visible in the time dependent TA measurement in the form of a negative dip around -100 ns.

## 12.5. Negative Delay Values

**Problem:** The TA signal starts to ramp up at -30 ns. Why is that happening?

**Solution:** The DAQ card can only initialize its different clocks successively with a delay of approximately 30 ns. This delay in starting the internal process will lead to a small absolute delay. Since only the relative delay is important in the decay time calculation, this can be neglected.

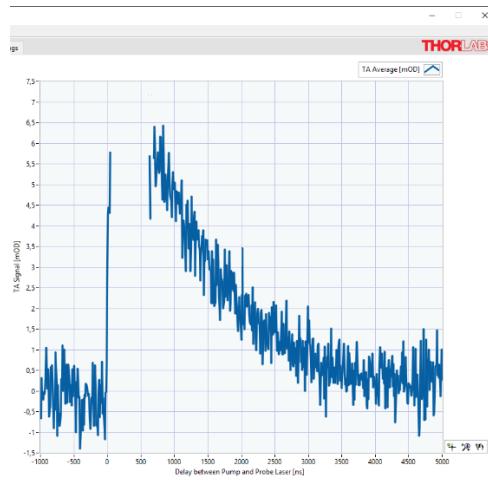


**Figure 91** TA signal is generated starting with -30 ns delay due to imperfect synchronization of trigger clocks in the data acquisition card. Left: An overview TA measurement. Right: Zoomed- in view on the rising edge of the TA signal, which is highlighted in red in the overview.

## 12.6. Missing Data Points in Measurement Tab

**Problem:** The variable-delay measurement shows missing data points, as displayed in Figure 92.

**Solution:** The peak finder threshold is probably set too close to the measured photodiode voltage. Decrease the peak finder threshold and restart the measurement.



**Figure 92** Missing data points due to a wrong threshold setting.

## 12.7. Fluctuating Measurements

**Problem:** Different cycles of a variable delay measurement deviate significantly from each other; see Figure 93.

**Solution:** Not mixing the components well enough when preparing a new sample can lead to concentration fluctuations in the sample. This in turn results in different TA signals and decay times for different measurements of the same sample. If you do a measurement with more than one averaging cycle and the curves of different cycles are differing from each other significantly, as shown in Figure 93, consider mixing the sample more.

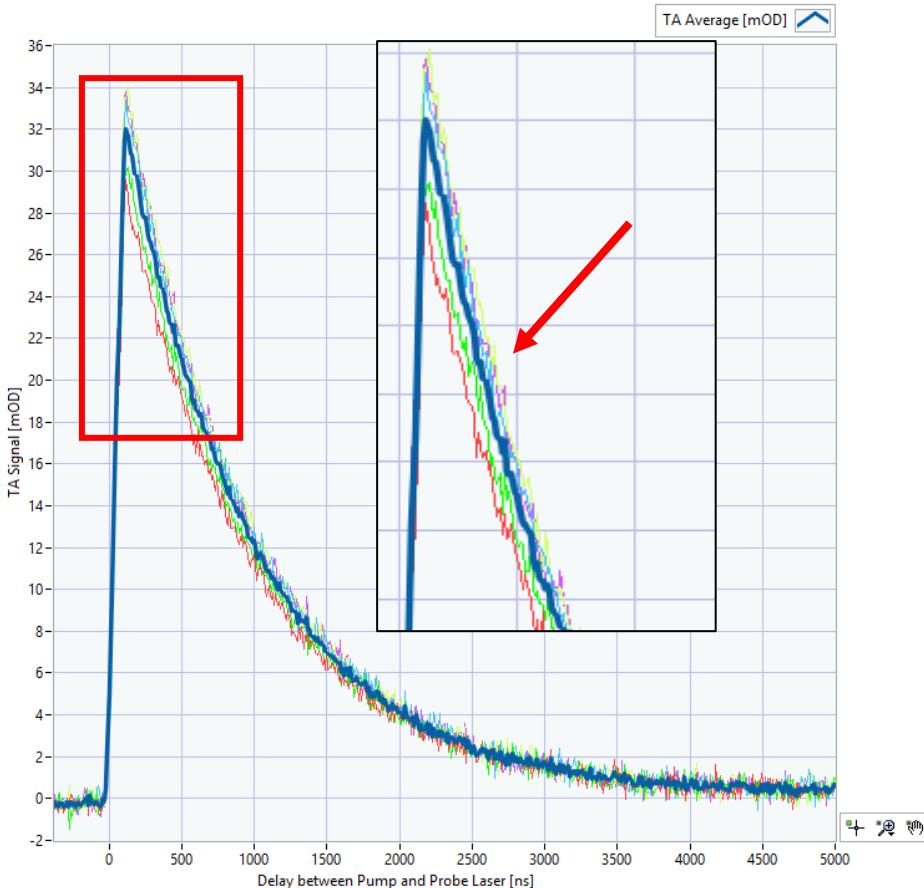


Figure 93 Stacked single measurements (thin lines) indicating concentration fluctuations.

# Chapter 13 Ideas for Additional Experiments

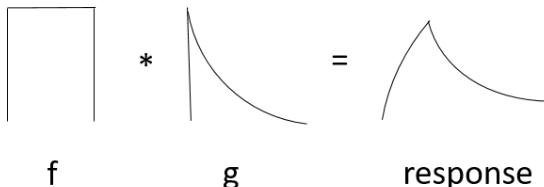
## 13.1. Convolution and Deconvolution

An additional learning exercise is the convolution and deconvolution of data. A standard pump-probe experiment starts with measuring the impulse response function (IRF). This IRF includes all intrinsic setup properties and is “mixed” or convoluted with the true signal. The IRF can be used to extract (deconvolve) the signal and obtain the true or more accurate values (e.g. decay times). This step is not part of this kit but the convolution and deconvolution functions of a signal can be easily explained. Also, the pulse width can be adjusted in the setup to show the impact of the convolution on the data.

Mathematically, the convolution of two functions  $f$  and  $g$  is defined as:

$$f(x) * g(x) = \int_{-\infty}^{\infty} f(\tau)g(x - \tau)d\tau$$

A schematic drawing with  $f$  as the IRF and  $g$  as a perfect decay leads to the response of the investigated system (the convoluted data we measure). Since ultimately, we are interested in the form of  $g$ , we would need the IRF to deconvolve the measured signal.



OriginLab® has a built-in feature for convolution and deconvolution of data. Other data handling software can be used for a more fundamental approach. A preparation exercise could include the following procedure:

Create a spreadsheet with two functions similar to the curves in Figure 94:

- Two rectangular probing signals.
- A (e.g. exponential) measurement signal.

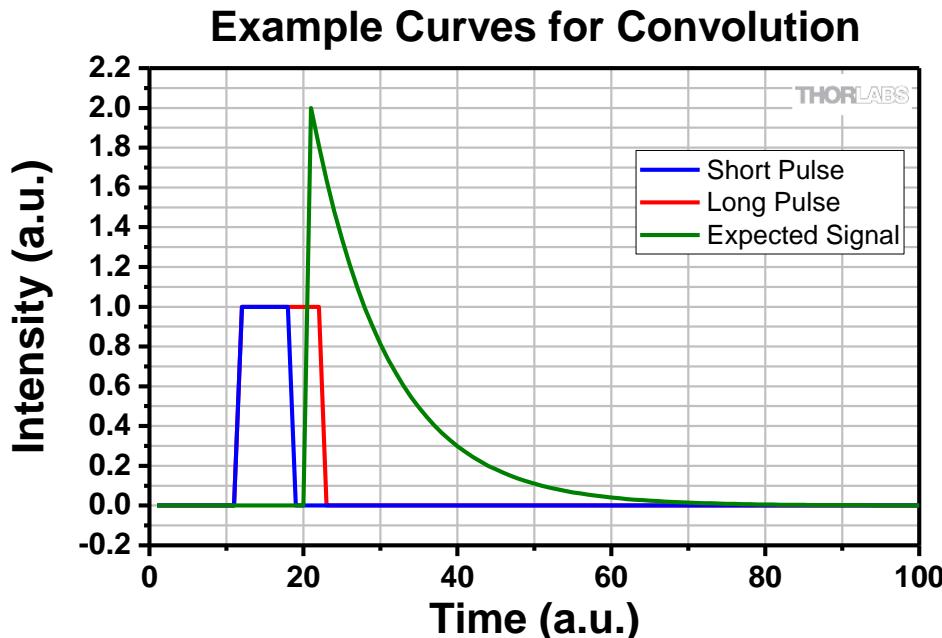


Figure 94 Artificially created pulses (red, blue) and an artificially expected exponential signal (green).

Convolute the two signals, for example, with Origin's preset function. Select from the menu bar: **Analyze -> Signal Processing -> FFT -> Convolution**. Set the exponential data as **Measured Signal** and the rectangular **Probing Pulse** as response.

This will result in a convoluted signal shown in Figure 95.

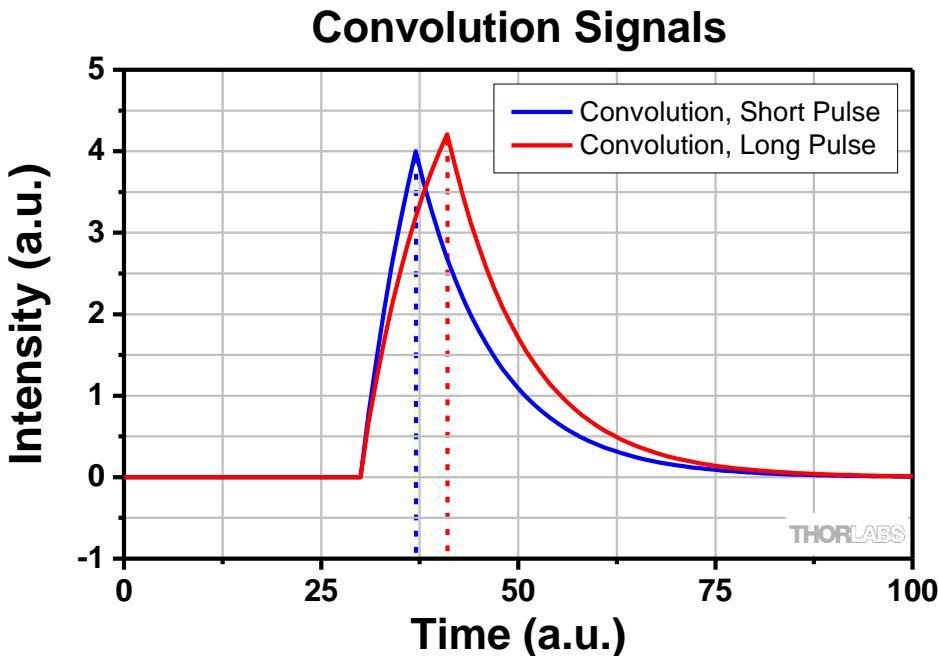


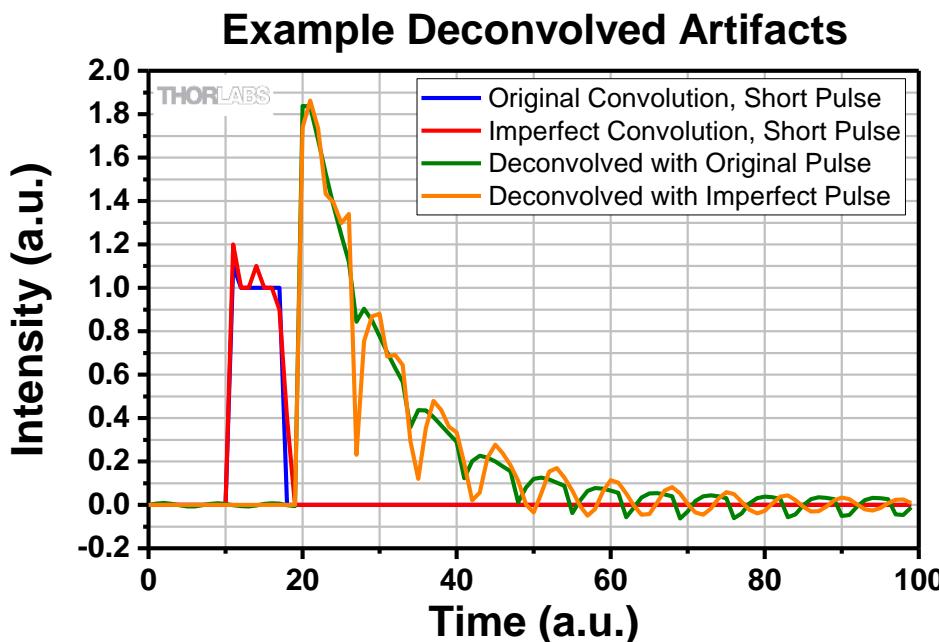
Figure 95 Convoluted signal of two rectangular probe pulses with different width and an exponential curve.

The calculations behind the convolution are explained in a lot of resources<sup>30</sup> and applying these will be important in the field of ultrafast spectroscopy.

The user can also deconvolve the signal with its original pulse form and a slightly deformed pulse form to see why deconvolution greatly depends on knowing the original probing pulse shape (IRF). An example can be found in Figure 96.

<sup>30</sup> Wikipedia (EN) has animated graphical visualizations of convolution and OriginLab® has a help segment. They can be found at the following websites, respectively:

<https://en.wikipedia.org/wiki/Convolution> and <https://www.originlab.com/doc/Tutorials/Convolution>.



**Figure 96 Deconvolution with the original pulse and an artificially imperfect pulse to demonstrate deconvolution artifacts.**

Measuring the actual pulse widths and shapes of the nanosecond lasers in this kit cannot be performed within the scope of this kit. The use of standard pulse width data for the lasers will not bring the same learning experience since the pulse shape will vary travelling through the setup. Resolving the pump pulse intensity profile after passing the sample on a very fast photodiode or using autocorrelation procedures might offer these accurate measurements. Since these methods are beyond the scope of this kit, a deconvolution process is best shown on prepared data instead of the measured data.

### 13.2. Laser Pulse Width

In the previous experiments the transient absorption was measured with a fixed pump pulse width. The pump laser was set to the maximum setting corresponding to 129 ns and the probe laser to one of the lower settings (approx. 5 - 20 ns). To adjust the pump laser pulse width, use the provided slotted screwdriver<sup>31</sup>.

<sup>31</sup> As an extra step the user can measure the exact pulse widths with Thorlabs' DET025A detector and visualize them on an oscilloscope (both not included in this kit). The typical pulse shape is shown in Figure 102.



**Figure 97 Image of the back side of the NPL52C. Adjust the laser pulse width with the provided slotted screwdriver.**

- Turn the pump laser pulse width down and observe the signal in the acquisition tab.
- What is the observed effect on the signal from the 0.4 mMol/L ZnTPP sample? Can you compare the slope in the region of 0 ns to 150 ns?
- What is the interpretation of the observed signal?
- How does this translate into measurement accuracy and resolution?

#### Experiment:

- Insert the cuvette with the 0.4 mMol/L ZnTPP sample into the sample holder. Adjust the laser overlap to maximize the TA signal as shown in Section 9.2.4. Check the voltage on the photodiode in the acquisition tab, activate the baseline correction, and adjust the photodiode gain if necessary. Start a timed measurement with a delay from -400 ns up to 1000 ns with five averages.
- Reduce the pump laser pulse width by four steps (insert and turn the slotted screwdriver counterclockwise in the dial shown above). If you are not sure where you are on the scale (hard to read with laser safety goggles), use the fluorescent laser card and turn the dial until you find the maximum intensity. The TA signal will decrease when reducing the pump pulse width. To counter the reduced TA signal and improve signal to noise ratio, increase the number of spectra to be averaged (7 - 10). Note the pump laser duration from Section 11.1.1.
- Reduce the pump laser intensity again by four steps. To counter the reduced TA signal and improve signal to noise ratio, set the averaging to 12.
- Alternative measurement: Measure the three different pump laser pulse widths starting with the smallest (position 8 / middle of the dial) with an averaging of 12. Increase the pump laser pulse width by four steps (position 12) and reduce the

TA signal to the previous level by misaligning the beam overlap. Then do the next measurement. Increase the pump laser pulse width by four steps (to position 16 / Maximum) and reduce the TA signal to the previous level.

### Data Evaluation:

- Plot all three measured curves in one graph.
- Alternative Measurement: Plot all three measured curves in one graph.

### Interpretation:

An example data plot can be seen in Figure 98 and Figure 99. The former shows a decreasing transient absorption signal with lower pump laser pulse width. The correlation is due to less ZnTPP molecules being excited in the first place; see Section 5.3.

The maximum of the plot is shifted to larger delays due to the convolution of the larger pulse width, as can be seen in Figure 95.

The alternative measurement shown in Figure 99 shows a steeper slope for reduced pump laser length (and same TA signal strength). The acquired data is a convolution of pump laser pulse width, probe laser pulse width, and the response signal of the transient absorption.

The pump and probe laser pulse width directly influence the acquired signal. Typical electron transfer processes are in the femtosecond region, thus many pump probe experiments and its laser pulse width will be in this region. Since there is a tradeoff between resolution and signal strength, the highest pump laser pulse width has been used throughout the experiments.

As shown in the Table 5, the pulse duration does not significantly influence the fit results. Thus, there is a tradeoff between shorter pulses (results in the observation of faster processes) and the overall maximum TA signal (creating a better signal to noise ratio and smaller measurement times).

Another takeaway is that the probing pulse duration, which can be set between 4 ns and 39 ns, does not influence the measured data significantly since it is much smaller than the pump laser pulse duration. The interested user can of course also analyze the probe pulse duration with a similar procedure by setting both pulse width to the smallest or largest possible values.

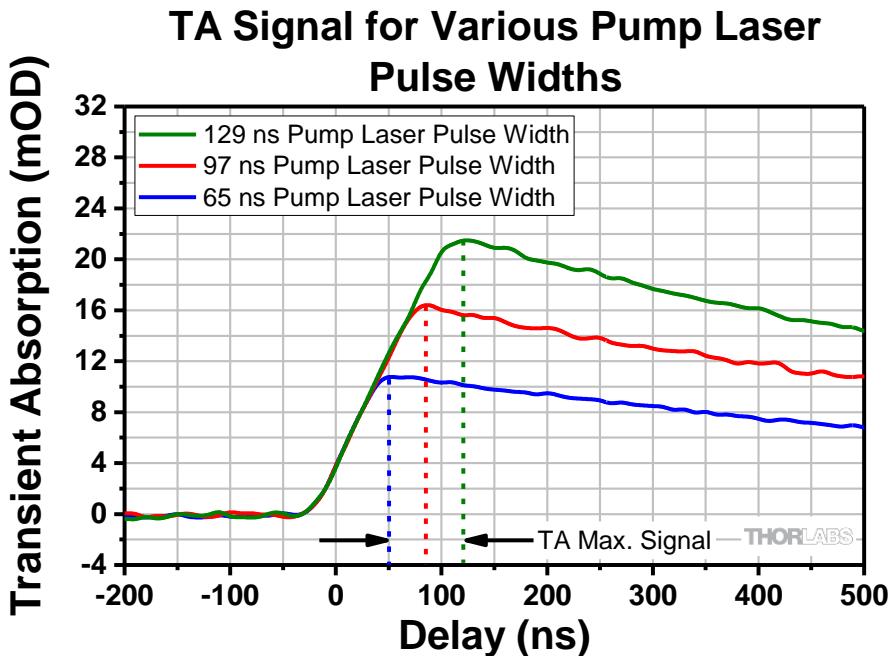


Figure 98 Graph of 0.4 mMol/L ZnTPP in Benzonitrile measured with three different pump laser pulse widths.

Fit of TA Measurement 0.4 mMol/L ZnTPP in Benzonitrile with:	TA Max. Position [ns]	TA Max. [mOD]	T [ns]	Standard Error of T [ns]
129 ns Pump Laser Pulse Width	110	21.82	933	4
97 ns Pump Laser Pulse Width	90	16.43	950	6
65 ns Pump Laser Pulse Width	50	11.06	941	6

Table 5 Resulting fit parameters for an exponential decay (without y-axis offset). The Standard Error (SE) of the fit is not the full picture of the error of the measurement. Repeating the measurement multiple times should be accounted as well in the evaluation of the error calculations.

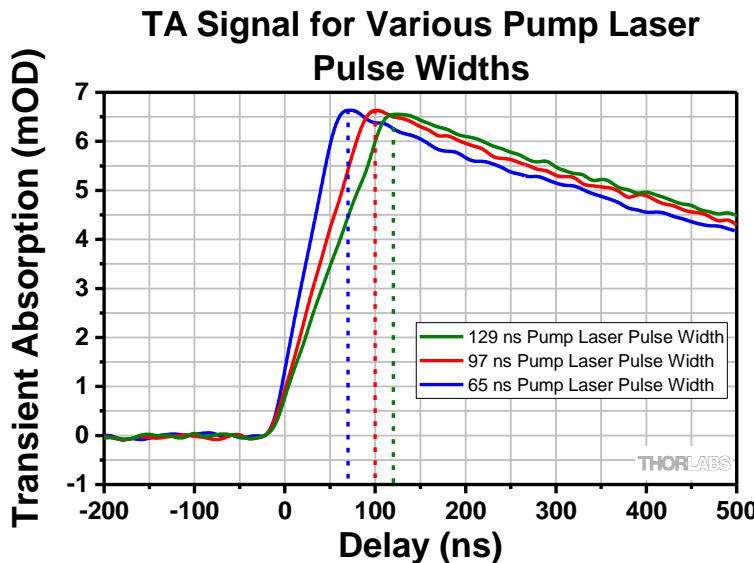
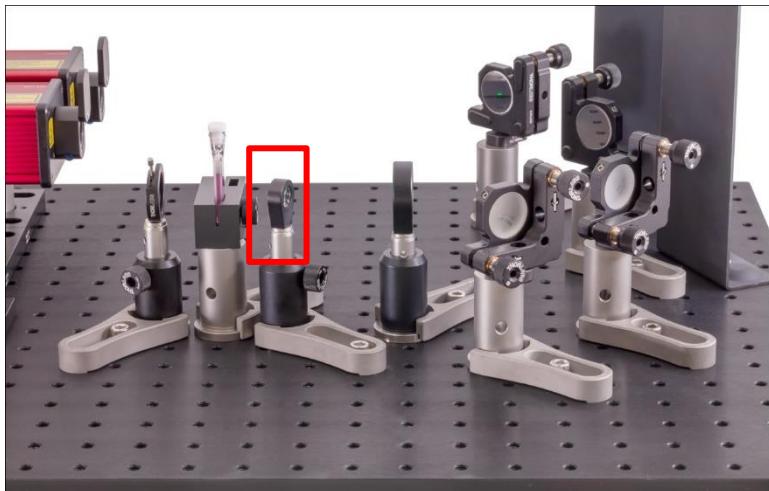


Figure 99 Graph of the transient absorption data of 0.4 mMol/L ZnTPP in Benzonitrile measured with three different pump laser pulse widths. The laser overlap was adjusted to equal the maximum TA signal (6.5 mOD) in each measurement to visualize the effect of the pulse widths.

### 13.3. Beam Focus Optimization

In this kit, the pump beam is focused with a Ø1" lens (focal length either 60 mm or 75 mm). To achieve an even higher transient absorption signal, one can go to lower focal length but must use a Ø0.5" lens due to geometrical restriction of the setup. Furthermore, the adjustment of the setup with a Ø0.5" lens is much harder due to beam clipping. An example of such a setup is shown in Figure 100.



**Figure 100 Setup with a Ø 0.5" lens ( $f = 40 \text{ mm}$ , Marked by Red Rectangle) in the Beam Path of the Pump Laser for Maximum TA Signal.**

If a collimated Gaussian beam with beam radius  $W_0$  hits a focusing lens with focal length  $f$ , the beam radius  $W_f$  of the beam waist (focus) after the lens can be calculated with the equation:

$$W_f = \lambda \frac{f}{\pi W_0}$$

So, a smaller focal length will result in a smaller beam waist. Since we want to squeeze more light into the probe laser beam waist, we can see a higher transient absorption signal with smaller pump beam focusing lens length.

Parts needed for test with smaller focusing lens and lower focal length:

1 x LMR05(M) half inch lens holder and  $f = 40 \text{ mm}$  or  $50 \text{ mm}$  Ø 0.5" lens. The distance to the sample holder does not allow for even smaller focal lengths.

## Chapter 14      Laser Safety Calculation

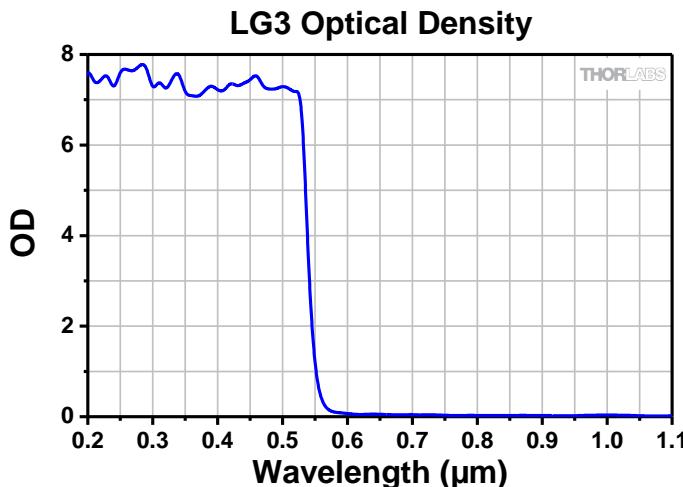
In this educational kit, we use two different lasers: the NPL45B and NPL52C nanosecond pulsed lasers. Each institution that uses this educational kit should have a laser safety officer to determine the safety requirements. However, here we give one approach to calculate the risk assessment based on the lasers used in this kit. In this chapter, we present:

- The laser class analysis for the NPL52C laser
- The laser safety glasses calculation for the NPL45B laser
- The laser safety glasses calculation for the NPL52C laser

The laser class of the NPL45B and NPL52C lasers is Class 3B, as described on the products' webpage and the documentation that ships with the units. However, we felt like it would be educational to present the actual calculation here. We only choose to demonstrate the analysis for the NPL52C laser, but the analysis for the NPL45B laser is fairly similar.

The laser safety glasses calculation explains why the LG3 Laser Safety Glasses were considered a suitable choice for both the NPL45B and NPL52C lasers. Below are the ratings and the optical density plot of the LG3 glasses (Figure 101).

LB-Rating Specs (EN 207)
180 to 315 nm (D LB7 + IR LB4)
>315 to 532 nm (DIRM LB6)



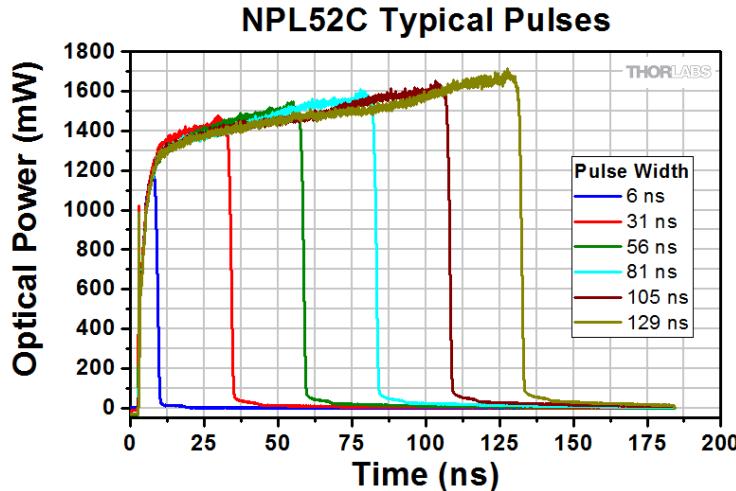
**Figure 101 Wavelength-Dependent Optical Density of the LG3 Material**

## 14.1. Laser Class Analysis for the NPL52C Laser

These are the specs of the laser as listed on the webpage:

Item Number	NPL52C
Center Wavelength	$520 \pm 10 \text{ nm}$
Pulse Width	$6 \pm 1 \text{ nm}$ to $129 \pm 5 \text{ ns}$
Pulse Energy	186 nJ
Peak Power	1500 mW
Beam Diameter	16.5 mm x 1.9 mm
Beam Divergence	3.7 mrad x 0.6 mrad
Maximum Rep. Frequency	50 kHz

Figure 102 shows typical pulse shapes for different pulse width settings.



**Figure 102 Typical Pulse Shapes for different pulse width settings of the NPL52C laser.**

The calculation we present here follows the EN60825-1:2014 norm (hereafter only referred to as “the norm”). We will not be able to give a detailed explanation of each quantity and correction factor. For that, please refer to the norm.

For this calculation, we essentially follow the example given in B.3.5 of the norm.

- The “time basis  $T$ ” describes the emission time that needs to be considered for the laser safety calculation (see 3.85 in the norm). For class 3B with wavelengths higher than 400 nm, the time basis is 100 seconds (see 4.3 e) of the norm).

In the following, we will verify that the laser does not exceed the maximum permissible exposure, the “MPE”, for laser class 3B. For pulsed lasers, however, there is not only one MPE we need to calculate. Instead, there are three different MPE values we have to look into:

- (i) for a single pulse,  $MPE_{\text{Single}}$
- (ii) for the average power of a pulse train,  $MPE_{\text{Single,T}}$
- (iii) for the entire pulse train,  $MPE_{\text{Single,Train}}$

We calculate each of these MPEs first and then compare to the actual properties of the laser.

Table 2 of the norm defines a time  $T_i$  in which we need to check if more than one pulse arrives. For the NPL52C laser’s wavelength, this time is defined as  $T_i = 5 \cdot 10^{-6}$  s (see Table 2 of the norm<sup>32)</sup>. The repetition rate of the NPL52C laser is 50 kHz. This means that a pulse arrives every  $\frac{1}{50} \text{ kHz} = 2 \cdot 10^{-5}$  s, and that only one pulse falls into the time  $T_i$ .

- a) Following 4.3 f) 1) of the norm, we examine the single pulse MPE. For that, Table 8 of the norm defines the MPE for wavelengths between 400 and 700 nm for pulse widths between  $10^{-9}$  seconds and 0.25 seconds. This value is given as 0.03 J (since the NPL52C laser’s pulse widths are smaller than 0.06 seconds, c.f. Table 8 of the norm).

$$MPE_{\text{Single}} = 0.03 \text{ J}$$

- b) Following 4.3 f) 2) of the norm, we examine the average power of a pulse train during the time  $T$ . As stated above,  $T = 100$  s. Table 8 of the norm then gives

$$MPE_T = 0.5 \text{ W}$$

Since the laser exhibits a periodic series of pulses, we do not need to average over shorter times. To make the comparison easier (see 4.3 f) 2) of the norm), the  $MPE_T$  is transformed so that it is valid for a single pulse by dividing by the repetition rate

$$MPE_{\text{Single,T}} = \frac{MPE_T}{\text{Rep Rate}} = \frac{0.5 \text{ W}}{50 \text{ kHz}} = 0.00001 \text{ J}$$

- c) Following 4.3 f) 3) of the norm, we consider the single pulse energy with correction factor  $C_5$ . Thus,

$$MPE_{\text{Single,Train}} = MPE_{\text{Single}} \cdot C_5$$

---

<sup>32</sup> Please note: in the EN60825-1:2007 norm, this value is  $T_i = 18 \cdot 10^{-6}$  s. However, the result of the calculation presented here would stay the same.

To calculate  $C_5$ , we follow 4.3 f) 3) of the norm: since our pulse widths of 6 ns to 129 ns are smaller than  $T_i$  and since the time basis  $T$  is larger than 0.25 s, the correction factor is calculated as

$$C_5 = 5 \cdot N^{-0.25}$$

where  $N$  is the number of pulses within the time  $T_2 = 10$  s (see table 9 of the norm).  $C_5$  is set to 0.4 if the formula above yields a smaller value than 0.4 (see 4.3 f) 3) of the norm). To calculate the number of pulses within 10 seconds, we use

$$N = 10 \text{ s} \cdot 50 \text{ kHz} = 5 \cdot 10^5 \text{ pulses}$$

Therefore,

$$C_5 = 5 \cdot N^{-0.25} = 0.188$$

Since this value is smaller than 0.4, we have to set

$$C_5 = 0.4$$

With this correction factor, we arrive at

$$\text{MPE}_{\text{Single,Train}} = \text{MPE}_{\text{Single}} \cdot C_5 = 0.03 \text{ J} \cdot 0.4 = 0.12 \text{ J}$$

All of the calculated MPEs refer to a single pulse which is why we can compare them. To assess whether or not our laser still falls within class 3B, we have to use the most restrictive case (which means the smallest number for the MPEs).

Comparing the values above, the MPE for class 3B for our laser is  $0.00001 \text{ J} = 1 \cdot 10^{-5} \text{ J}$ .

Next, we calculate the lasers energy  $Q$  for each pulse using the relation

$$Q = \text{Peak power} \cdot \text{Pulse width} = 1500 \text{ mW} \cdot 129 \text{ ns} = 1.94 \cdot 10^{-7} \text{ J}$$

Since  $1.94 \cdot 10^{-7} \text{ J} < 1 \cdot 10^{-5} \text{ J}$ , the NPL52C does not exceed the maximum permissible exposure for class 3B<sup>33</sup>.

In principle, the beam diameter and the beam divergence have to be considered too (see 4.3 c) and d) of the norm). However, the above calculation represents the strictest case with a point source of divergence  $\leq 1.5 \text{ mrad}$ . The NPL52C laser has a larger divergence which means that energy is actually distributed over a larger area. That, in turn, would result in a higher value of  $T_2$  (see table 9 of the norm) and an additional correction factor  $C_6$  which would only increase the maximum permissible energy. Since the actual energy of the laser pulse from NPL52C is already below the MBE in the strictest case as shown

<sup>33</sup> To be precise, this calculation does not mean that the laser is, in fact, a class 3B laser. For that, one would have to repeat the calculation with the time basis for the next lower class 3R. According to 4.3 e) 1) of the norm, the time basis for class 3R is 0.25 s. Such a calculation yields that the NPL52C exceeds the maximum permissible exposure for class 3R. Hence, the NPL52C is classified as a class 3B laser.

above, a calculation that includes the area and beam divergence would not raise the laser class.

## 14.2. Laser Safety Glasses Analysis for the NPL52C Laser

We recall the NPL52C laser's specs:

Item Number	NPL52C
Center Wavelength	520 ± 10 nm
Pulse Width	6 ± 1 nm to 129 ± 5 ns
Pulse Energy	186 nJ
Peak Power	1500 mW
Beam Diameter	16.5 mm x 1.9 mm
Beam Divergence	3.7 mrad x 0.6 mrad
Maximum Rep. Frequency	50 kHz

To pick a suitable scale number for the laser safety glasses, we use the EN 207:2017 norm (hereafter referred to as "the EN207-norm").

First, we recognize that the laser falls in the category of pulsed lasers, category **R** (pulse widths  $10^{-9}$  s to  $10^{-6}$  s), according to table 4 of the EN207-norm.

To determine the scale, we need to check the individual pulse as well as the average power. We follow B.3.3.2 of the norm.

### Individual Pulse:

The beam's energy density  $H$  is derived from the energy of the individual pulse  $Q$  and the beam area  $A$ . Note that the beam profile of the NPL52C laser is an ellipse with axes 16.5 mm and 1.9 mm. These values are given at  $1/e^2$ . This means that, on the major axis, the intensity has dropped to  $1/e^2 = 13.5\%$  after 8.25 mm. However, the EN207-norm asks for the drop to  $1/e$ . For a Gaussian profile, the  $1/e$  and  $1/e^2$  diameter differ by a factor of  $\sqrt{2}$ . Therefore, the relevant beam diameter is

- Beam diameter  $1/e$ : 11.7 mm x 1.3 mm

To make things simple but rigorous, we assume that all energy of the beam is located within a circular beam shape with diameter 1.3 mm. This is certainly a much stricter case than the actual beam profile. Thereby, we calculate the beam area as

$$A = \pi \cdot \left( \frac{1.3 \text{ mm}}{2} \right)^2 = 1.42 \cdot 10^{-6} \text{ m}^2$$

Then

$$H = \frac{Q}{A} = \frac{1500 \text{ mW} \cdot 129 \text{ ns}}{1.42 \cdot 10^{-6} \text{ m}^2} = 0.136 \frac{\text{J}}{\text{m}^2}$$

According to the EN207-norm, this energy density has to be multiplied with two correction factors,  $k$  and  $k_{T_l}$ .

$k$  calculates the number of laser pulses  $N$  that are emitted during the time of 5 seconds, following:

$$k = N^{0.25} = (50 \text{ kHz} \cdot 5 \text{ s})^{0.25} = 22.36$$

According to the EN207-norm, the previous formula may only be used when the time between two pulses is longer than the time  $T_i$  defined in table B.2 of the EN207-norm. For wavelengths between 400 nm and 1050 nm,  $T_i = 18 \cdot 10^{-6}$  s. Since  $1/50 \text{ kHz} = 2 \cdot 10^{-5}$  s  $> T_i$ , we can use the formula above. In addition, the EN207-norm states that  $k_{T_i} = 1$  in this case.

We can now derive the corrected energy density

$$H = H \cdot k_{T_i} \cdot k = 3.05 \frac{\text{J}}{\text{m}^2}$$

Next, we look up the required scale number from table 1 of the EN207-norm; see Figure 103. We choose the column that applies to our laser (wavelength range “315 - 1400 nm” and the laser’s category **R**) and pick the smallest number not less than the calculated value for  $H'$ . In this case, we require the scale number **R LB3**; see the red box in Figure 103.

	Max. Power Density ( $E$ , W/m <sup>2</sup> ) & Energy Density ( $H$ , J/m <sup>2</sup> ) in Specified Wavelength Range								
Wave-length Range	180 – 315 nm			>315 – 1400 nm			>1400 nm – 1000 μm		
	For Pulse Duration (seconds)								
Scale Number	T	D $> 3 \cdot 10^{-4}$	I, R $10^{-9}$ to $3 \cdot 10^{-4}$	M $< 10^{-9}$	D $> 5 \cdot 10^{-4}$	I, R $10^{-9}$ to $5 \cdot 10^{-4}$	M $< 10^{-9}$	D $> 0.1$	I, R $10^{-9}$ to 0.1
LB1	$10^{-1}$	0.01	$3 \cdot 10^2$	$3 \cdot 10^{11}$	$10^2$	0.05	$1.5 \cdot 10^3$	$10^4$	$10^3$
LB2	$10^{-2}$	0.1	$3 \cdot 10^3$	$3 \cdot 10^{12}$	$10^3$	0.5	$1.5 \cdot 10^2$	$10^5$	$10^4$
LB3	$10^{-3}$	1	$3 \cdot 10^4$	$3 \cdot 10^{13}$	$10^4$	5	0.15	$10^6$	$10^5$
LB4	$10^{-4}$	10	$3 \cdot 10^5$	$3 \cdot 10^{14}$	$10^5$	50	1.5	$10^7$	$10^6$
LB5	$10^{-5}$	$10^2$	$3 \cdot 10^6$	$3 \cdot 10^{15}$	$10^6$	$5 \cdot 10^2$	15	$10^8$	$10^7$
LB6	$10^{-6}$	$10^3$	$3 \cdot 10^7$	$3 \cdot 10^{16}$	$10^7$	$5 \cdot 10^3$	$1.5 \cdot 10^2$	$10^9$	$10^8$
LB7	$10^{-7}$	$10^4$	$3 \cdot 10^8$	$3 \cdot 10^{17}$	$10^8$	$5 \cdot 10^4$	$1.5 \cdot 10^3$	$10^{10}$	$10^9$
LB8	$10^{-8}$	$10^5$	$3 \cdot 10^9$	$3 \cdot 10^{18}$	$10^9$	$5 \cdot 10^5$	$1.5 \cdot 10^4$	$10^{11}$	$10^{10}$
LB9	$10^{-9}$	$10^6$	$3 \cdot 10^{10}$	$3 \cdot 10^{19}$	$10^{10}$	$5 \cdot 10^6$	$1.5 \cdot 10^5$	$10^{12}$	$10^{11}$
LB10	$10^{-10}$	$10^7$	$3 \cdot 10^{11}$	$3 \cdot 10^{20}$	$10^{11}$	$5 \cdot 10^7$	$1.5 \cdot 10^6$	$10^{13}$	$10^{12}$

Figure 103 Table 1 of the EN207:2017 Norm.

## Average Power:

The average power density  $E_m$  of the laser beam is derived from the average laser power  $P_m$  and the beam area  $A$ ; see B.3.3.3 of the EN207-norm. Thereby

$$E_m = \frac{P_m}{A} = \frac{1500 \text{ mW} \cdot 129 \text{ ns} \cdot 50 \text{ kHz}}{1.42 \cdot 10^{-6} \text{ m}^2} = 6824.7 \frac{\text{W}}{\text{m}^2}$$

Again, we look up the scale number in table 1 of the EN207-norm and find that the NPL52C laser requires a scale number of **D LB3**; see green box in Figure 103.

**Conclusion:** The laser safety glasses LG3, rated DIRM LB6, are suitable for the NPL52C.<sup>34</sup>

Note: It may be surprising that the laser safety glasses calculation does not include the lenses that are included in this kit. In particular, we use a lens for each laser to focus it into the sample. Placing your eye into that focus -- is that not the worst case? The answer here is no! The most dangerous beam characteristics for a laser in the visible range are for a perfectly parallel laser. In the visible range, the cornea and the eye's lens are almost completely transparent. Therefore, a perfectly parallel beam would be the most dangerous since it would be focused onto one small point on the eye's backside, the retina.

In short: by assuming a perfectly parallel beam, we already cover the worst case and do not need to consider the lenses in the setup. While they do focus light, they cannot result in a higher intensity on the retina than the parallel beam.

## 14.3. Laser Safety Class Analysis for the NPL45B Laser

The NPL45B laser's specs are:

Item Number	NPL45B
Center Wavelength	$450 \pm 10 \text{ nm}$
Pulse Width	$5 \pm 1 \text{ nm}$ to $39 \pm 3 \text{ ns}$
Pulse Energy	3 nJ
Peak Power	75 mW
Beam Diameter	3.3 mm x 1.6 mm
Beam Divergence	0.5 mrad x 0.25 mrad
Maximum Rep. Frequency	10 kHz

To pick a suitable scale number for the laser safety glasses, we use the EN 207:2017 norm (hereafter referred to as "the EN207-norm").

First, we recognize that the laser falls in the category of pulsed lasers, category **R** (pulse widths  $10^{-9}$  s to  $10^{-6}$  s), according to table 4 of the EN207-norm.

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<sup>34</sup> DIRM LB6 means that the glasses are classified as D LB6, I LB6, R LB6 and M LB6. Based on the calculation above, we require at least **R LB3** and **D LB3**. Since LB6 is higher than LB3, the LG3 laser safety glasses are suitable for the NPL52C laser.

To determine the scale, we need to check the individual pulse as well as the average power. We follow B.3.3.2 of the EN207-norm.

### Individual Pulse:

The beam's energy density  $H$  is derived from the energy of the individual pulse  $Q$  and the beam area  $A$ . Note that the beam profile of the NPL45B laser is an ellipse with axes 3.3 mm and 1.6 mm (full beam width). These values are given at  $1/e^2$ . This means that, on the major axis, the intensity has dropped to  $1/e^2 = 13.5\%$  after 1.65 mm. However, the norm asks for the drop to  $1/e$ . For a Gaussian profile, the  $1/e$  and  $1/e^2$  diameter differ by a factor of  $\sqrt{2}$ . Therefore, the relevant beam diameter is

- Beam diameter  $1/e$ : 2.33 mm x 1.13 mm

To make things simple but rigorous, we assume that all energy of the beam is located within a circular beam shape with diameter 1.2 mm. This is certainly a much stricter case than the actual beam profile. Thereby, we calculate the beam area as

$$A = \pi \cdot \left( \frac{1.13 \text{ mm}}{2} \right)^2 = 1.01 \cdot 10^{-6} \text{ m}^2$$

Then

$$H = \frac{Q}{A} = \frac{75 \text{ mW} \cdot 39 \text{ ns}}{1.14 \cdot 10^{-6} \text{ m}^2} = 2.91 \cdot 10^{-3} \frac{\text{J}}{\text{m}^2}$$

According to the EN207-norm, this energy density has to be multiplied with two correction factors,  $k$  and  $k_{T_i}$ .

In contrast to the calculation of the NPL52C laser,  $k$  cannot be calculated as before. Since  $1/10 \text{ MHz} = 1 \cdot 10^{-7} \text{ s} < T_i$  with  $T_i = 18 \cdot 10^{-6} \text{ s}$  according to table B.2 of the EN207-norm, the factor  $k$  is given as

$$k = (5 \text{ s} \cdot 55.56 \cdot 10^3 \text{ Hz})^{0.25} = 22.96$$

The maximum frequency that is applied here is taken from table B.2 of the EN207-norm. The factor  $k_{T_i}$  is given as the number of pulses during the time  $T_i = 18 \cdot 10^{-6} \text{ s}$ . Therefore

$$k_{T_i} = 10 \text{ MHz} \cdot 18 \cdot 10^{-6} \text{ s} = 180 \text{ pulses}$$

We can now derive the corrected energy density

$$H' = H \cdot k_{T_i} \cdot k = 12.02 \frac{\text{J}}{\text{m}^2}$$

Next, we look up the required scale number from table 1 of the EN207-norm; see Figure 103. We choose the column that applies to our laser (wavelength range "315-1400 nm" and the laser's category **R**) and pick the smallest number not less than the calculated value for  $H'$ . In this case, we require the scale number **R LB4**; see the blue box in Figure 103.

**Average Power:**

The average power density  $E_m$  of the laser beam is derived from the average laser power and the beam area; see B.3.3.3 of the EN207-norm. Thereby

$$E_m = \frac{P_m}{A} = \frac{75 \text{ mW} \cdot 39 \text{ ns} \cdot 10 \text{ MHz}}{1,01 \cdot 10^{-6} \text{ m}^2} = 29095.5 \frac{\text{W}}{\text{m}^2}$$

Again, we look up the scale number in table 1 of the EN207-norm and find that the NPL45B laser requires a scale number of D LB5; see the yellow box in Figure 103.

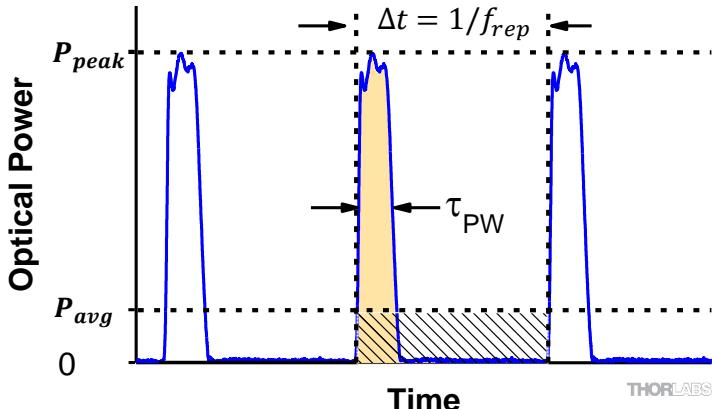
**Conclusion:** The laser safety glasses LG3, rated DIRM LB6, are suitable for the NPL45B laser.<sup>35</sup>

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<sup>35</sup> DIRM LB6 means that the glasses are classified as D LB6, I LB6, R LB6 and M LB6. Based on the calculation above, we require at least R LB4 and D LB5. Since LB6 is higher than LB4 and LB5, the LG3 laser safety glasses are suitable for NPL45B laser.

# Chapter 15      Laser Pulse Definition

## 15.1. Pulse Parameters



**Figure 104 Schematic of Pulse Parameters**

Figure 104 shows the parameters used to describe pulsed laser emission. Pulse Energy ( $E$ ) is the shaded area under the pulse curve. Pulse energy is, equivalently, the area of the diagonally hatched region.

Parameter	Symbol	Units	Description
Pulse Energy	$E$	Joules [J]	A measure of one pulse's total emission, which is the only light emitted by the laser over the entire period. The pulse energy equals the shaded area, which is equivalent to the area covered by diagonal hash marks.
Period	$\Delta t$	Seconds [s]	The amount of time between the start of one pulse and the start of the next.
Average Power	$P_{avg}$	Watts [W]	The height on the optical power axis, if the energy emitted by the pulse were uniformly spread over the entire period.
Instantaneous Power	$P$	Watts [W]	The optical power at a single, specific point in time.
Peak Power	$P_{peak}$	Watts [W]	The maximum instantaneous optical power output by the laser.
Pulse Width	$\tau_{PW}$	Seconds [s]	A measure of the time between the beginning and end of the pulse, typically based on the full width half maximum (FWHM) of the pulse shape. Also called <b>pulse duration</b> .
Repetition Rate	$f_{rep}$	Hertz [Hz]	The frequency with which pulses are emitted. Equal to the reciprocal of the period.

## 15.2. Equations

- *Period and repetition rate are reciprocal:*  $\Delta t = \frac{1}{f_{rep}}$  and  $f_{rep} = \frac{1}{\Delta t}$
  - *Pulse energy calculated from average power:*  $E = \frac{P_{avg}}{f_{rep}} = P_{avg} \cdot \Delta t$
  - *Average power calculated from pulse energy:*  $P_{avg} = \frac{E}{\Delta t} = E \cdot f_{rep}$
  - *Peak pulse power estimated from pulse energy:*  $P_{peak} \approx \frac{E}{\tau_{PW}}$
  - *Peak power and average power calculated from each other:*
- $$P_{peak} = \frac{P_{avg}}{f_{rep} \cdot \tau_{PW}} = \frac{P_{avg} \cdot \Delta t}{\tau_{PW}} \quad \text{and} \quad P_{avg} = P_{peak} \cdot f_{rep} \cdot \tau_{PW} = \frac{P_{peak} \cdot \tau_{PW}}{\Delta t}$$
- *Peak power calculated from average power and duty cycle*<sup>36</sup>:

$$P_{peak} = \frac{P_{avg}}{\tau_{PW}/\Delta t} = \frac{P_{avg}}{\text{duty cycle}}$$

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<sup>36</sup> Duty cycle  $\tau/\Delta t$  is the fraction of time during which there is a laser pulse emission.

## **Chapter 16      Acknowledgements**

This kit grew out of a collaboration with Tiago Buckup from the group of Marcus Motzkus Group at Heidelberg University. Their motivation was to teach students about the pump-probe-methodology. Since they found no teaching kit on ultra-fast time-resolved spectroscopy, they partnered with Thorlabs to use our nano-second lasers. In particular, we thank Tiago Buckup for developing the prototype and finding ideal samples that allow nonhazardous experiments. The feedback from his students and his practical courses helped tremendously to improve the provided teaching material.

**Do you also have ideas for an experiment which you either have implemented already or want to implement? Please contact us at [techsupport@thorlabs.com](mailto:techsupport@thorlabs.com).  
We are happy to enter into partnerships!**

## Chapter 17      Regulatory

As required by the WEEE (Waste Electrical and Electronic Equipment Directive) of the European Community and the corresponding national laws, Thorlabs offers all end users in the EC the possibility to return "end of life" units without incurring disposal charges.

- This offer is valid for Thorlabs electrical and electronic equipment:
- Sold after August 13, 2005
- Marked correspondingly with the crossed out "wheelie bin" logo (see right)
- Sold to a company or institute within the EC
- Currently owned by a company or institute within the EC
- Still complete, not disassembled and not contaminated

As the WEEE directive applies to self-contained operational electrical and electronic products, this end of life take back service does not refer to other Thorlabs products, such as:

- Pure OEM products, that means assemblies to be built into a unit by the user (e.g. OEM laser driver cards)
- Components
- Mechanics and optics
- Left over parts of units disassembled by the user (PCB's, housings etc.).

If you wish to return a Thorlabs unit for waste recovery, please contact Thorlabs or your nearest dealer for further information.

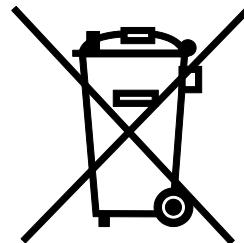
### ***Waste Treatment is Your Own Responsibility***

If you do not return an "end of life" unit to Thorlabs, you must hand it to a company specialized in waste recovery. Do not dispose of the unit in a litter bin or at a public waste disposal site.

### ***Ecological Background***

It is well known that WEEE pollutes the environment by releasing toxic products during decomposition. The aim of the European RoHS directive is to reduce the content of toxic substances in electronic products in the future.

The intent of the WEEE directive is to enforce the recycling of WEEE. A controlled recycling of end of life products will thereby avoid negative impacts on the environment.



**Wheelie Bin Logo**

## Chapter 18      Thorlabs Worldwide Contacts

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### **USA, Canada, and South America**

Thorlabs, Inc.  
[sales@thorlabs.com](mailto:sales@thorlabs.com)  
[techsupport@thorlabs.com](mailto:techsupport@thorlabs.com)

### **Europe**

Thorlabs GmbH  
[europe@thorlabs.com](mailto:europe@thorlabs.com)

### **France**

Thorlabs SAS  
[sales.fr@thorlabs.com](mailto:sales.fr@thorlabs.com)

### **Japan**

Thorlabs Japan, Inc.  
[sales@thorlabs.jp](mailto:sales@thorlabs.jp)

### **UK and Ireland**

Thorlabs Ltd.  
[sales.uk@thorlabs.com](mailto:sales.uk@thorlabs.com)  
[techsupport.uk@thorlabs.com](mailto:techsupport.uk@thorlabs.com)

### **Scandinavia**

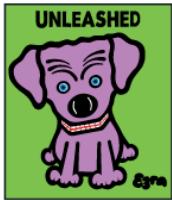
Thorlabs Sweden AB  
[scandinavia@thorlabs.com](mailto:scandinavia@thorlabs.com)

### **Brazil**

Thorlabs Vendas de Fotônicos Ltda.  
[brasil@thorlabs.com](mailto:brasil@thorlabs.com)

### **China**

Thorlabs China  
[chinasales@thorlabs.com](mailto:chinasales@thorlabs.com)



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[www.thorlabs.com](http://www.thorlabs.com)