Vernier Flash Photolysis Spectrometer

(order code: VSP-FP)

Educational Flash Photolysis Spectrometer

Reference Manual

(version: 4/6/2021)

This manual has been provided for information only and product specifications are subject to change without notice. Any change will be reflected in future printings.

Ultrafast Systems,

8330 Consumer Ct,

Sarasota FL, 34240, USA

Repair Information

If you have watched the related product video(s), followed the troubleshooting steps, and are still having trouble with your Vernier Flash Photolysis Spectrometer, contact Vernier Technical Support at support@vernier.com or call 888-837-6437. Support specialists will work with you to determine if the unit needs to be sent in for repair. At that time, a Return Merchandise Authorization (RMA) number will be issued and instructions will be communicated on how to return the unit for repair.

Table of Contents

1 Preface

This document contains user information for the Vernier Flash Photolysis Spectrometer. Vernier Flash Photolysis Spectrometer is conceived to be a simple, user-friendly device for demonstrating to chemistry students the fundamental principles of Chemical Kinetics. Every process labeled as "chemical" occurs as the result of chemical bonds being broken or formed, i.e. nuclei change their spatial positions with respect to each other. Chemical Kinetics is one of the major divisions of Physical Chemistry and is basically the quantitative study of the rates and mechanisms of chemical reactions. Chemical change can be induced in a variety of ways; the one employed in Vernier Flash Photolysis Spectrometer is by absorption of light. Thus, the instrument serves also as a way of introducing the student to the concepts and practice of Photochemistry.

Read this Documentation carefully before operating the spectrometer for the first time. Special attention should be given to Section 2: General Safety on page 5.

2 General Safety

The Vernier Flash Photolysis Spectrometer is designed and manufactured for kinetic analysis of chemical specimen by means of ultrafast transient absorption spectrometry. And it is not sold, nor intended for, nor should ever be used for any other purpose. The product should be used solely in accordance with the instructions provided.

Hazards

Take extra caution when operating or servicing this equipment:

- If this equipment is used in a manner not specified in this manual, the protection provided by this equipment may be impaired.
- Handle the cuvette with care. Check the cuvette for damage or cracks and replace any damaged ones immediately.
- Use extreme caution in handling the cuvette when it is filled with liquid. Always remove the cuvette before changing contents. Never fill or refill the cuvette when it is in the sample holder.
- The optimal operation temperature of Vernier Flash Photolysis Spectrometer is at or near room temperature.
- Due to the relatively small size and light weight of Vernier Flash Photolysis Spectrometer, make sure it is securely fastened to the work surface, and provide free space of 10 cm around the unit. This is to reduce chance of overheating and provide ample space to disconnect the USB cable, if necessary.

Electrical Safety

Observe these general warnings when operating or servicing this equipment:

- Read all warnings on the unit and in the operating instructions.
- Vernier Flash Photolysis Spectrometer uses a large capacitor to charge the Xe flash lamp. Dangerous voltage levels are expected to persist even after unplugging the unit.
- Do not disassemble or open the spectrometer case. Doing so may damage the excitation light source and risk electric shock.
- Do not use this equipment in or near water.

- Dry the exterior of the cuvette prior to placing it in the holder. Using a cuvette with a wet exterior or one that is leaking liquid can result in the severe malfunction, shorting of electrical components or electric shock.

Declaration of Safety

Ultrafast Systems declared that Vernier Flash Photolysis Spectrometer is in conformity with the essential requirements and other relevant provisions of the CE, FCC.

3 Product Specifications

Table 1: Product specifications of Vernier Flash Photolysis Spectrometer

For indoor use only

General Specifications	
Footprint (L x W)	4.25” x 5.5”
Weight	2 lbs
UL94	V-0
UL796	Meets requirements
USB cable	28 AWG shielded
Power source	PC USB connection Supplied current: 500 mA Supplied voltage: 5 V
Altitude	Up to 2500 m
Operating temperature	15 to 40 °C
Operating relative humidity	10 to 70% (non-condensing)
Spectrometer Specifications	
Spectral coverage	450 to 750 nm
Spectral resolution	Depends on the filter used. Typically, ~10 nm
Temporal resolution	~100 µs
Time window	≥ 15 ms
Detector Specifications	
Detector type	Silicon PIN
Active area	3.6 x 3.6 mm (13 mm^2)
Wavelength range	350 to 1100 nm
Rise time	14 ns
Bias voltage	10 V
Dark current (with 1 MΩ load)	0.35 nA

2.125

Manufacturer: Ultrafast Systems
Kronos Model: KR-6
Input: 5V DC
Max Current: 0.5 A

1.00

Made in the U.S.A.

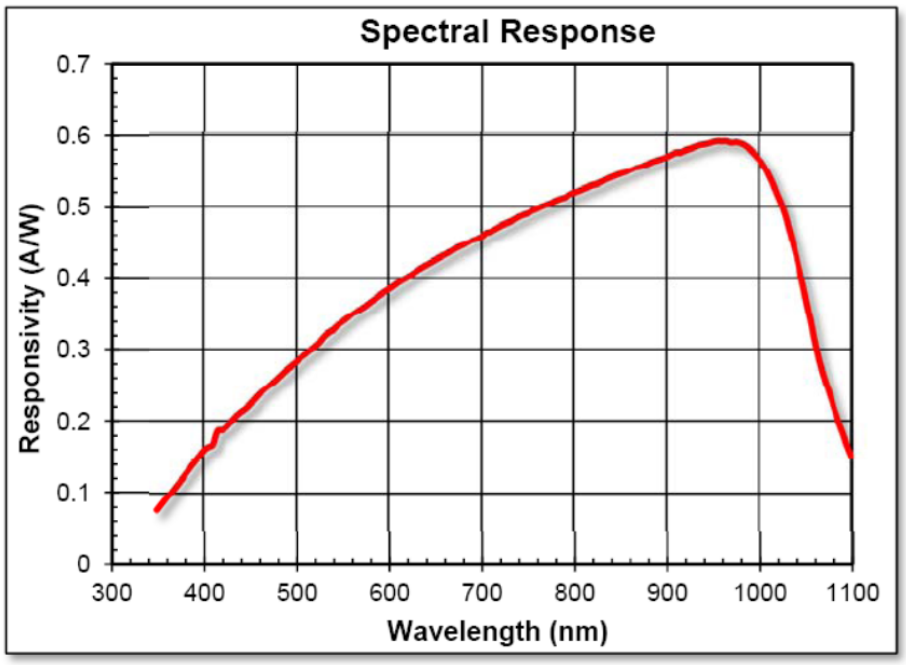

Figure 1: Spectral response of detector

Vernier Flash Photolysis Spectrometer produces a 2-dimensional Time-Current data matrix in a form of an ASCII (.CSV file) which can be easily processed with free or commercially available spreadsheet or graphing software, e.g. Logger *Pro*.

4 Unpacking and Inspection

The Vernier Flash Photolysis Spectrometer is carefully packaged at the factory to minimize the possibility of damage during shipping. Inspect the box for external signs of damage or mishandling. Inspect the contents for damage. If there is visible damage to the instrument upon receipt, inform the shipping company and Ultrafast Systems immediately.

5 Hardware

The Vernier Flash Photolysis Spectrometer is shown in Figure 2a, highlighting the simple design that makes Vernier Flash Photolysis Spectrometer very easy to use. Holes are machined into the housing, which allows rapid replacements of standard square filters and cuvettes. The detection filters are mounted in a customized holder. Figure 2b shows the simplified optical layout of the Vernier Flash Photolysis Spectrometer.

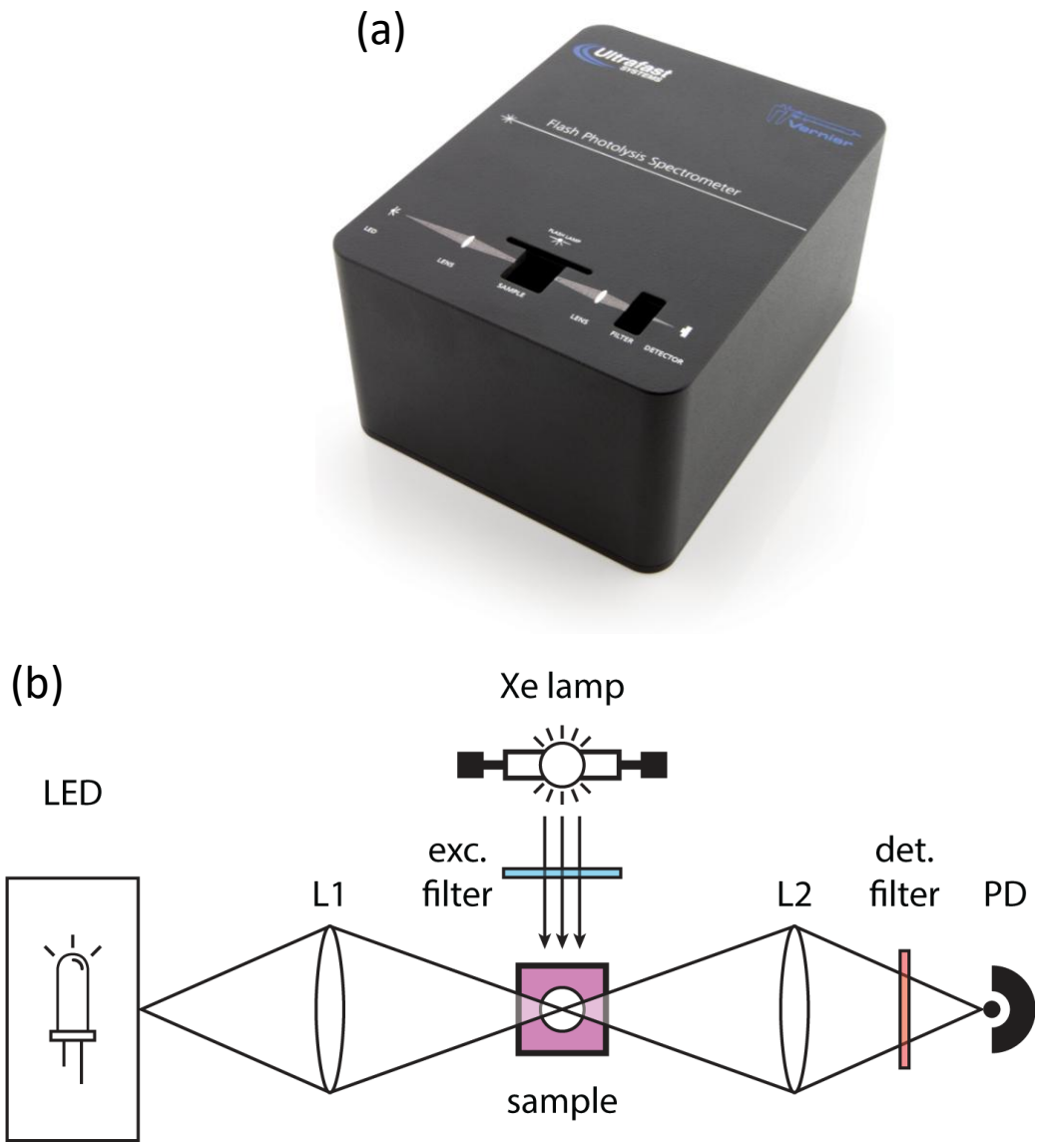

Figure 2: Photograph of Vernier Flash Photolysis Spectrometer (a) without components inserted, and (b) Schematic optical layout of the Vernier Flash Photolysis Spectrometer

Table 2: Vernier Flash Photolysis Spectrometer optical components

VERNIER FLASH PHOTOLYSIS SPECTROMETER
LED: LED probe source
Xe lamp: Xe flash lamp pump source
sample: 10mm × 10mm cuvette holder
L1, L2: lenses

PD: Silicon photodiode
Exc. filter: Holder for 25mm × 25mm × 2mm filters (for excitation wavelength selectivity)
Det. filter: Holder for 0.5”-diameter filters (for detection wavelength selectivity)

Table 3: Excitation colored glass filters included with the Vernier Flash Photolysis Spectrometer

Excitation colored glass filters
CG-BG-3
CG-BG-39

Table 4: Detection dielectric interference filters included with the Vernier Flash Photolysis Spectrometer with center wavelengths listed

Detection dielectric interference filters, 10 nm bandwidth, center lines at (nm):	
450	600
480	620
500	640
520	660
540	680
560	700
580	

6 Software

Table 5: UI elements in the Vernier Flash Photolysis Spectrometer software

ELEMENT	**DESCRIPTION**
Photodiode I_0	Amount of probe light reaching the photodiode (Probe intensity, y-axis)
Range	Related to detector gain and LED intensity. **Absorption mode** Leave it on Auto **Emission mode** Adjust the range slider to achieve sufficient signal-to-noise
Absorption/Emission	Select either Absorption or Emission experiment modes
Run	Starts measurement
Save	Save data in CSV format (first column: time, in units of seconds; second column: light intensity, in units of amperes)
Exit	Exit the program
Average	Number of scans to average across
Time window	Time scan range (x-axis). Use smaller time windows for faster processes.

Figure 3 shows the Vernier Flash Photolysis Spectrometer UI. By default, the software will adjust the axis scales automatically: the Y-axis range will adjust to display the signal only, showing the large spike around time = 0. The default X-axis setting is “Auto Scale”. To change this, right click anywhere on the plot and choose the desired option. Alternatively, you can use the graph controls on the top right of the screen, just above the graph display.

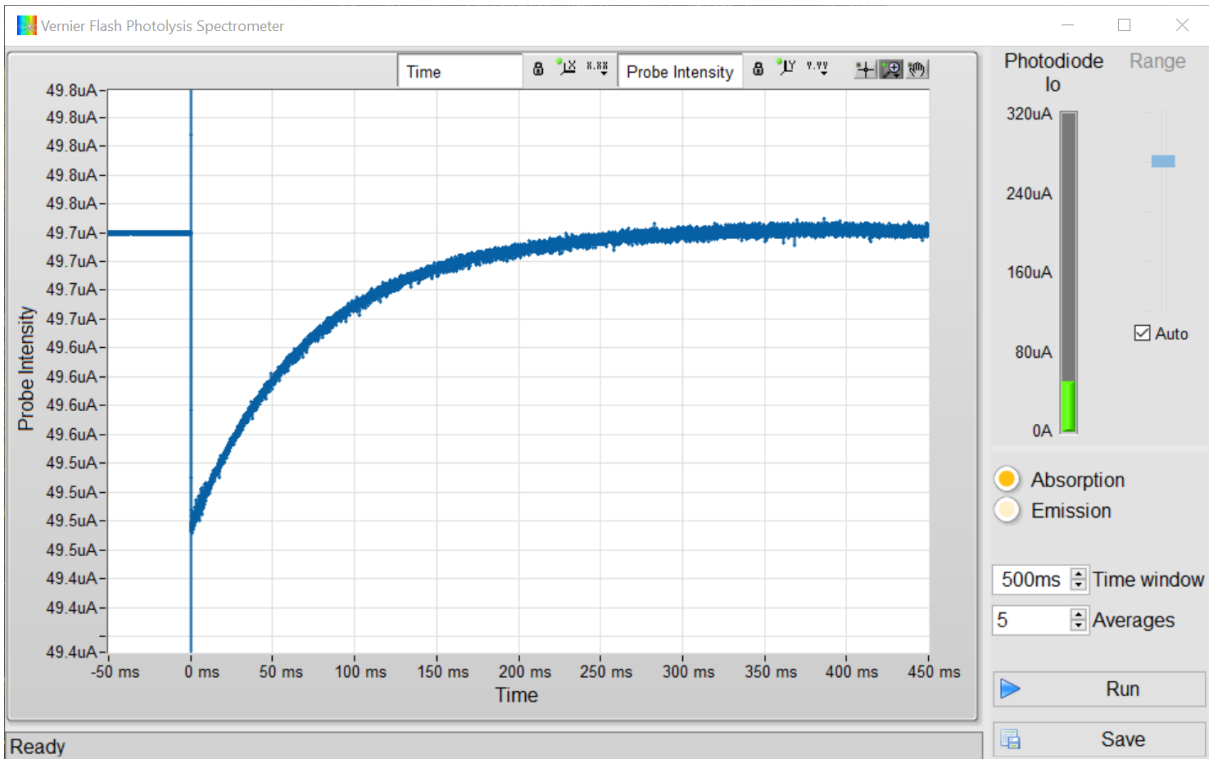

Figure 3: Screenshot of the Vernier Flash Photolysis Spectrometer software

Table 6: Graph controls in Vernier Flash Photolysis Spectrometer

ELEMENT		DESCRIPTION
		Axis Auto Scale mode OFF and ON.
		Autoscale axis once
		Pan graph
		Select between graph zoom modes:
		Select X and Y region to zoom in
		Select X region to zoom in, keep Y limits unchanged
		Select Y region to zoom in, keep X limits unchanged (default)
		Autoscale both X and Y axes once to fit graph

ELEMENT		DESCRIPTION
		Zoom out and in

Table 6 shows the graph controls on the top of the screen allow you to zoom in the graph after measurements have been completed. By default, cursor mode on the graph is y-axis zoom.

7 Using Vernier Flash Photolysis Spectrometer

7.1 Setting Up Vernier Flash Photolysis Spectrometer

The Vernier Flash Photolysis Spectrometer is initialized by follow the steps below:

1. Connect Vernier Flash Photolysis Spectrometer to the PC via a USB cable.
2. Wait until Windows recognizes the new USB device.
3. Start the Vernier Flash Photolysis Spectrometer software. Refer to the Appendix if Vernier Flash Photolysis Spectrometer does not initialize the correct COM port.

7.2 Preparing Vernier Flash Photolysis Spectrometer for Experiments

Before performing any experiments, look for a white glow in the Vernier Flash Photolysis Spectrometer interior. This means Vernier Flash Photolysis Spectrometer is powered up. Remove any samples and allow the LED probe light to be incident on the photodiode and check that the photodiode meter displays a value. This will be I_0, i.e., the baseline intensity before any pump-induced changes.

In absorption mode during data acquisition, the Vernier Flash Photolysis Spectrometer will wait for approximately 2 sec between flashes to allow enough time for the flash capacitors to recharge.

7.3 Choosing the Excitation and Detection Wavelengths

Vernier Flash Photolysis Spectrometer uses a Xe lamp and LED for the pump and probe light, respectively. Both are broadband light sources and their spectra is shown in Figure 4. By using an appropriate filter, you can select which wavelength to pump (excite) the sample with, and what range of wavelengths is measured by the detector. The filters isolate the wavelength of interest by transmitting said wavelengths and blocking the others.

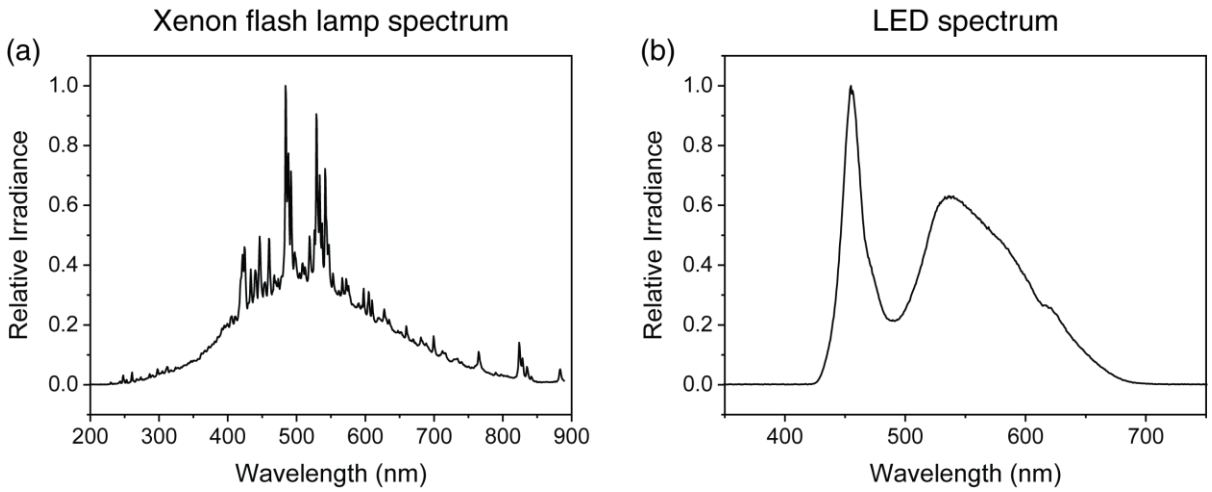

Figure 4: Spectra of Vernier Flash Photolysis Spectrometer light sources: (a) Xenon flash lamp for the pump, and (b) LED for the probe

The excitation wavelength range is manually selected by using a 25mm × 25mm square colored glass filter. The labeled narrow rectangular slit on top of the Vernier Flash Photolysis Spectrometer housing accommodates a 2 mm thick square filter. Figure 5 shows the transmission spectra of the two colored glass filters included with Vernier Flash Photolysis Spectrometer. Any incident light within the high transmittance regions can pass through the filters easily. For example, CG-BG-3 has high transmittance around 350 nm and allows the Xe lamp to function as a UV/blue light source. If you wish to pump with a separate wavelength region (e.g. 500 nm), simply use CG-BG-39, which is transparent in that region.

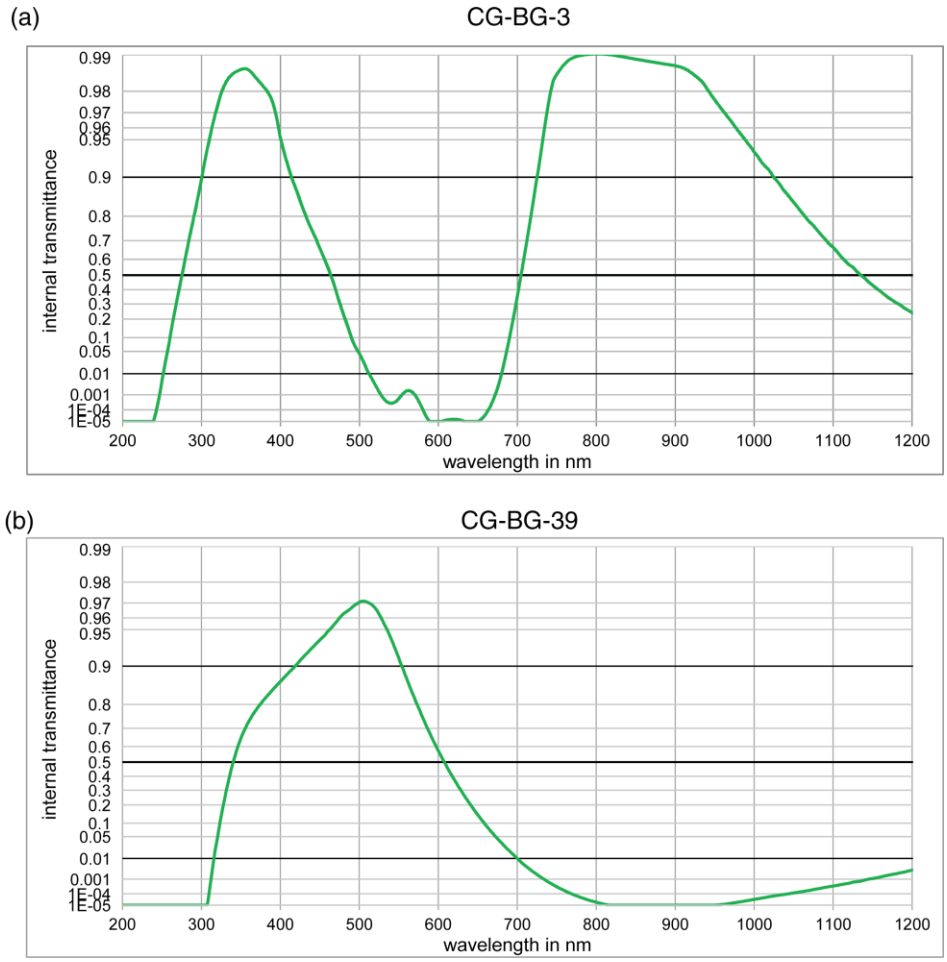

Figure 5: Transmission spectrum of (a) CG-BG-3 filter and (b) CG-BG-39 excitation colored glass filters

The detection wavelength range is manually selected by using a 0.5”-diameter dielectric interference filter individually mounted in holders. The labeled broad rectangular slit on top of the Vernier Flash Photolysis Spectrometer housing accommodates one such filter mount. Figure 6 shows the transmission spectrum of the 600 nm dielectric interference filter included with Vernier Flash Photolysis Spectrometer. These filters have a bandwidth, or full width at half maximum of 10 nm (in this scenario, 595 nm to 605 nm).

Functioning the same way as colored glass filters, any incident light within this bandwidth has high transmittance. Any wavelength below 590 nm and above 610 nm is strongly attenuated. This allows you to probe the kinetics that occur within this region. If you wish to probe a separate wavelength region, simply use another dielectric filter that transmit those wavelengths.

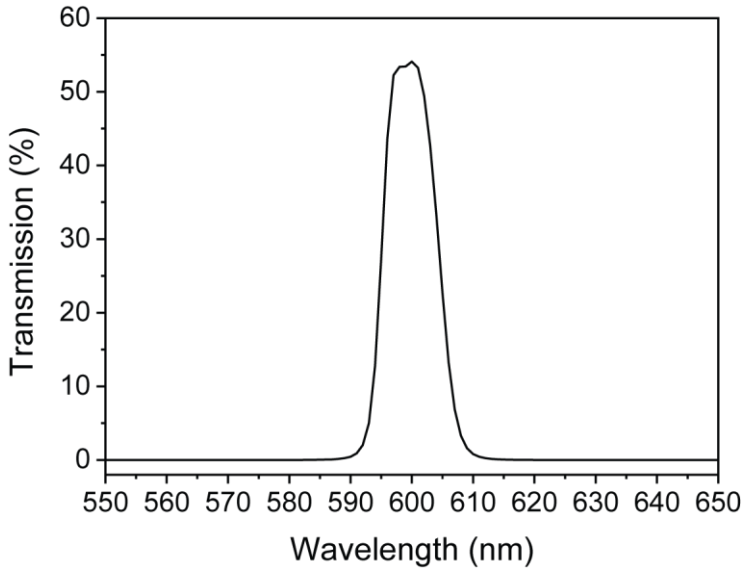

Figure 6: Transmission spectrum of 600 nm detection dielectric interference filter.

7.4 Acquiring Data

Place a filled cuvette into the sample area and select the appropriate parameters for averaging and time window. For absorption measurements, click on the Absorption radio button. Make sure the Range is set to Auto. A tick should be present in the check box, otherwise, click it to enable Auto. Do not disable Auto Range for absorption measurements, as the software will automatically adjust the detector gain and LED intensity. In absorption mode, both LED and Xe light sources will be activated.

For emission measurements, click on the Emission radio button. Make sure the Range is not set to Auto, i.e., the check box should be empty. In this mode, only the Xe source will be activated. Trial and error is required to select the appropriate Range using the slider to obtain good signal-to-noise.

Click on the <Run> button and allow the measurement to complete. You may notice a large spike (an artifact) in the first 50 µs present in the absorption kinetics. This is mainly due to electromagnetic interference in the circuitry and is intrinsic to the equipment. Since the temporal resolution of the Vernier Flash Photolysis Spectrometer is around 100 µs, you can safely reject the artifact and simply use the datapoints after the artifact.

Click on the <Save> button to save the data as a CSV file that can be processed in graphing or spreadsheet software. The file contains two columns: the first column is the time data, in units of milliseconds; the second column is the probe intensity data, in units of current (amperes). A sample graph is shown in Figure 7.

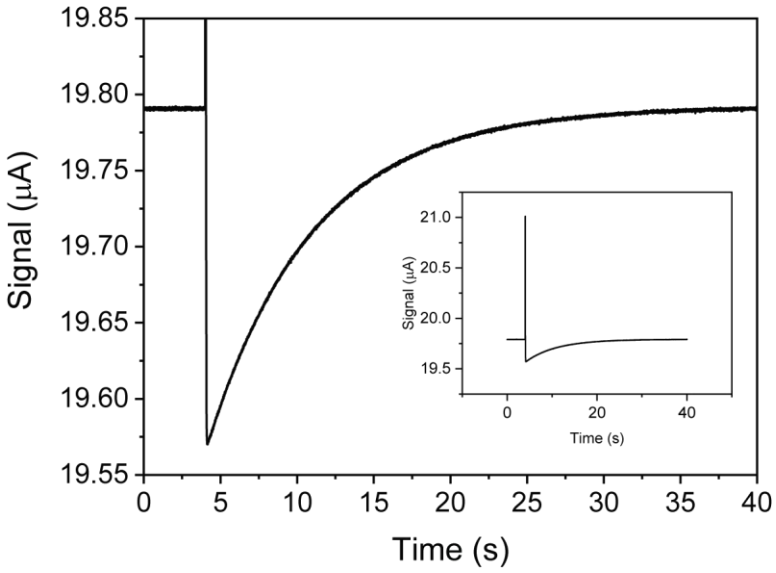

Figure 7: Example of a signal-time kinetic trace produced by Vernier Flash Photolysis Spectrometer. The inset shows the full curve; note the strong spike due to EMI

8 Familiarizing with the Reference Samples

Table 7: Various reference samples used for different experiments in Vernier Flash Photolysis Spectrometer

Experiment	**Chemical**	**Supplier**	**Product ID**	**Excitation wavelength (nm)**	**Detection wavelength (nm)**	**Additional chemicals**
Base catalysis of cis-trans isomerization of Congo Red	Congo Red	Sigma-Aldrich	C6277	< 500 nm	600 nm	Sodium hydroxide, ethanol
Activation Energy of One Spiropyran	1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-2*H*-indole)	Sigma-Aldrich	273619	<400 nm	600 nm	Toluene
Isomerization of Mercury Dithizonate	Mercury dithizonate	Sigma-Aldrich	M4128	< 500 nm	600 nm	Trifluoroacetic acid, ethanol

Table 7 shows the various standard experiments that are possible with Vernier Flash Photolysis Spectrometer. This section serves to provide information and details of these experiments.

8.1 Base Catalysis of the cis-trans Isomerization of Congo Red

Background

Congo Red (CR) is a diazo dye that is a derivative of azobenzene and, as can be seen from the skeletal structure in Figure 8, CR has two identically substituted azobenzene moieties.

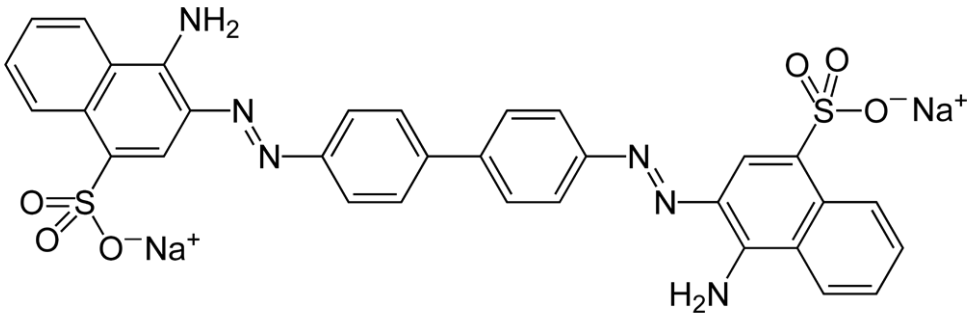

Figure 8: Skeletal structure of Congo Red, molecular weight = 696.67

The absorption spectrum of a solution of CR in its trans-ground state in 20% water/ethanol is shown in Figure 9. The dye absorbs strongly throughout the visible range with a maximum near 510 nm. Note that the absorbance is very weak at 600 nm.

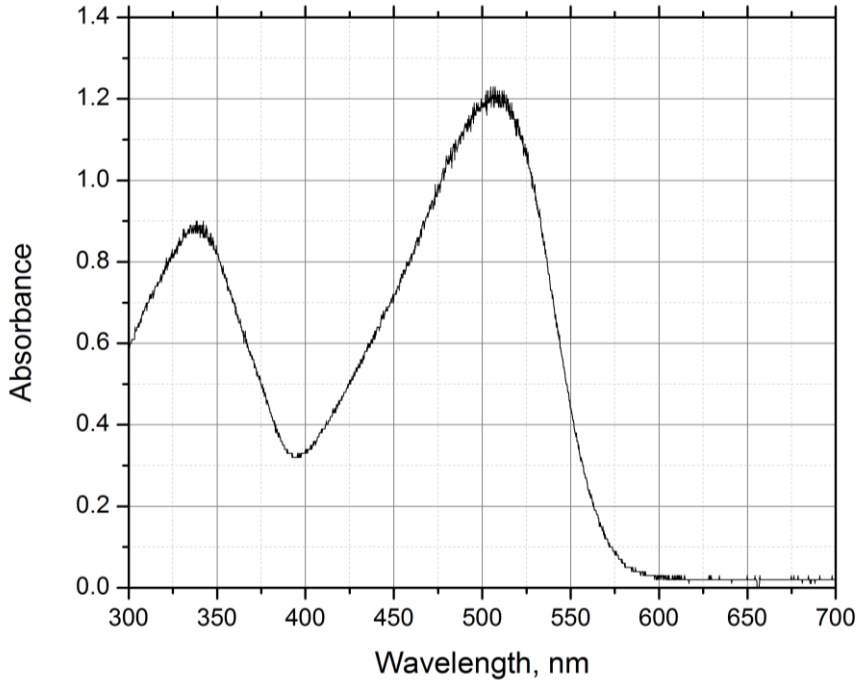

Figure 9: Ground state absorption spectrum of Congo Red (trans conf.) in 20% water/ethanol.

When light within the broad visible band is absorbed by the dye, some ground state molecules are converted into an excited state in which the electronic structure of the dye is changed. This shift in electron density causes the –N=N- bond to have significantly less double-bond character, and because of this, the molecule becomes torsionally flexible. Thus, in its attempt to rid itself of the energy imparted by the absorption of a photon, CR flips rapidly from a trans-excited state to a cis-ground state that is a higher energy state than the trans-ground state. This cis-state is therefore metastable with respect to the trans-ground state, and in fluid media at room temperature, a cis-trans isomerization will occur with the result that CR in its initial state is regenerated. Overall then, all that happens is that light energy is converted to heat in the solution.

However, this photoreaction provides an opportunity for the student to follow the progress of a thermal cis-trans isomerization and measure its rate on timescales that cannot be achieved by traditional mixing methods. Moreover, the rate is found to be catalyzed by both acids and bases, and the student is required to find the bimolecular rate constant for catalysis by OH^- ions.

Experimental Procedure

Obtain and wear goggles. Ensure you have connected the Vernier Flash Photolysis Spectrometer to your computer using the Vernier Flash Photolysis Spectrometer software. Prepare 100 mL of 20% water in ethanol using de-ionized or distilled water. It may be convenient to use 190 proof ethanol, which is 5% in water, and add the requisite volume of water to bring it to 20%. Note that the exact percentage of water is not important, but the water must be pure. Add small quantities of solid CR to the water-alcohol mixture until the color is a light red. Again the amount of dye is not important; you need to have just enough to generate a quantity of the cis-photoproduct to provide an absorbance that has a good signal-to-noise ratio in the Vernier Flash Photolysis Spectrometer. A useful check is to transfer some of the solution to the 10 mm x 10 mm cuvette and place it in the sample position with the 580 nm band pass filter inserted in front of the detector. If the I0 reading on the lower-left of the Vernier Flash Photolysis Spectrometer software is about 20% lower than the value without the cuvette in the sample position (or with an empty cuvette), the solution is adequate for the purpose.

Remove 50 mL of the prepared dye solution and add sufficient 0.1 M NaOH solution in water to bring it to 2 mM in NaOH (the amount of water you add here is not significant in the total).

Now you have two equivalent solutions of dye in the solvent mixture, one of which is 2 mM in OH- ions.

By mixing appropriate amounts of the two solutions, prepare 5 mL amounts that range from 0 to 0.1 mM in OH- ions. These solutions all contain the same CR concentration in the same water/ethanol mixture.

Starting with the 0 mM sample, transfer about 4 mL to a clean, dry cuvette. Place the cuvette in the sample position. Insert CG-BG-3 into the excitation filter slot and the 580 nm dielectric filter into the detection filter slot. Make sure Range is set to Auto (checked box). Click the <Run> button with the averages window set to 1. You should see a time profile similar to that in Figure 10, where the y-axis is Probe Intensity in amperes and the x-axis is Time in seconds.

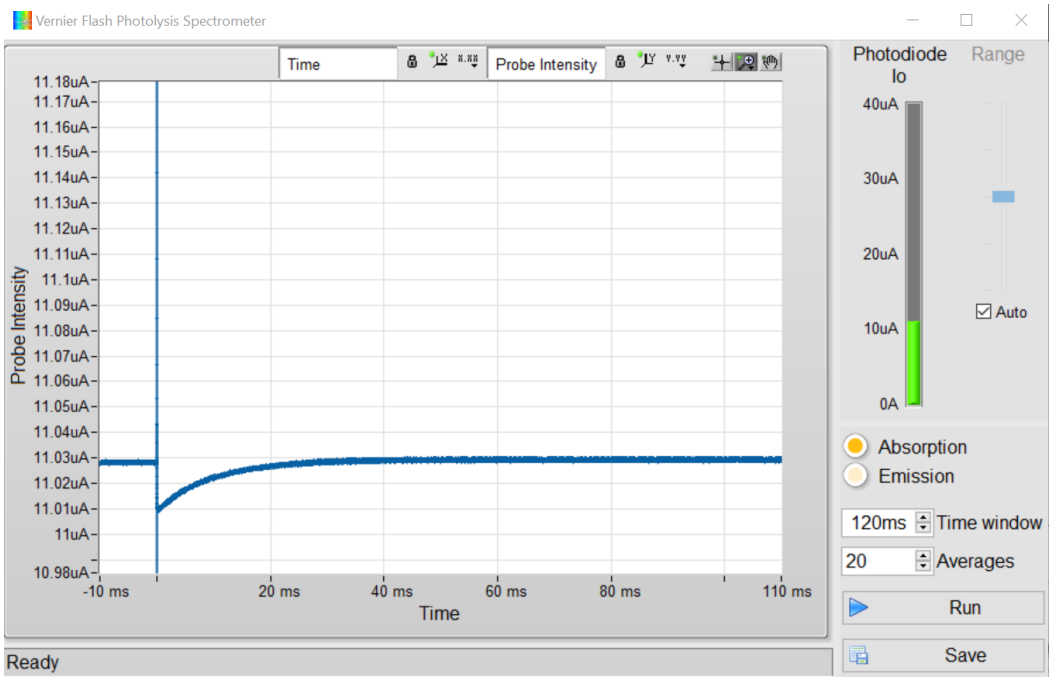

Figure 10: Kinetic profile of Congo Red in 20% water in ethanol.

In Figure 10, you can see that the flash at t = 0 causes a vertical (on these time scales) drop in the Probe Intensity reading; ignoring the large spike and looking at data after 100 µs, it drops from ~19.8 µA prior to the flash to ~19.6 µA after. Subsequently, the value increases over hundreds of milliseconds. The flash induces the changes outlined earlier, and very quickly, at shorter times than software can follow, the ground state of the cis-form is generated. The ground state of the cis-form absorbs light passing through the 580 nm filter, and the detector registers a drop in transmission. Then, the cis-form returns to the trans-form over many milliseconds, and it is the rate of this process that you are required to extract from the data set.

Repeat data collection with the averages set to 10 (or more) and save the resulting data.

Do the same procedure for the other samples you have prepared, and save their averaged data sets. As you go through the series, you see that the recovery rate increases; to account for this, you will need to adjust the time window setting and the time scale in order to obtain curves that use as much of the time window as possible.

Following the steps in Section 10.1: Transient Optical Spectroscopy on page 26, process the saved data to evaluate the rate constants for the cis-trans conversion of CR as a function of [OH-], you will obtain a curve similar to the one shown in Figure 11. You should find that the decays follow an exponential rate law with a constant that is a linear function of [OH-] and the slope of the line (or the best fit of the regression) is the bimolecular rate constant for the catalytic process.

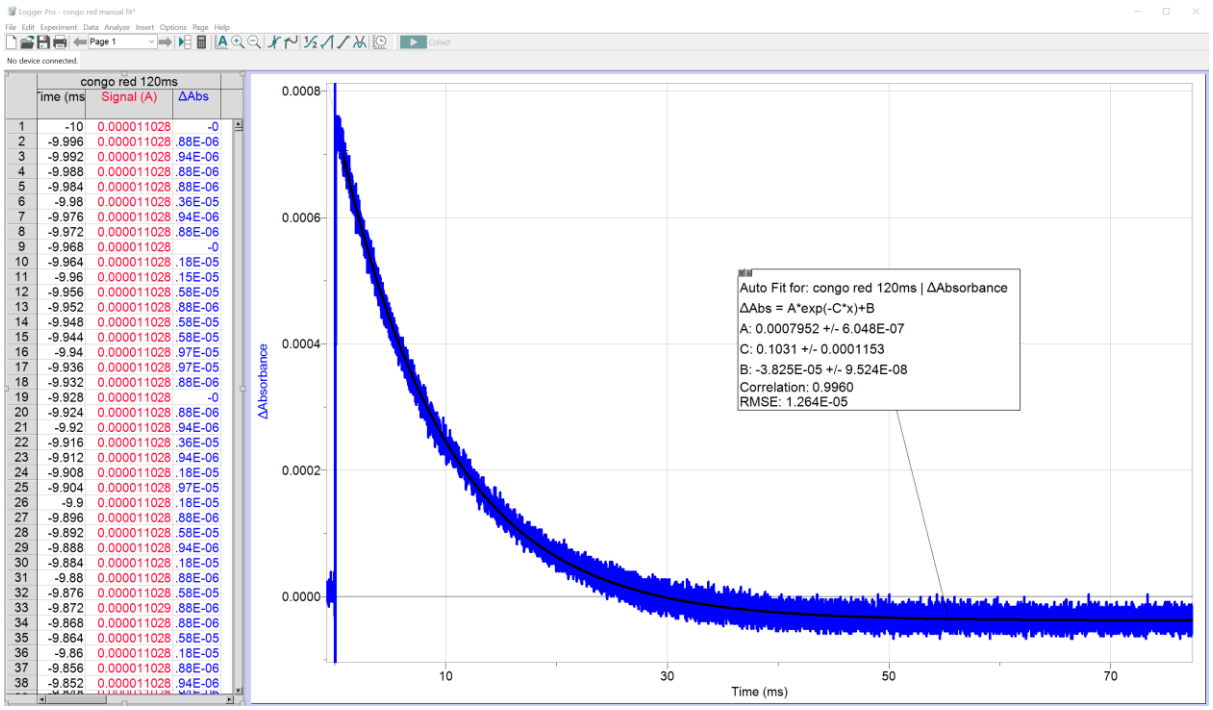

Figure 11: Calculated and fitted ΔA plot

8.2 Determination of the Activation Energy of the Thermal Back Reaction of One Spiropyran in Toluene

This section uses a scientific publication for reference: Piard, Jonathan, "Influence of the Solvent on the Thermal Back Reaction of One Spiropyran" *Journal of Chemical Education*. 2014, **91**, 2105-2111.

Background

6-NO_2-BIPS is a type of spiropyran molecule that is colorless in its normal form (N isomer) and undergoes a photochemical ring-opening reaction to yield an isomeric colored merocyanine form (MC isomer) when irradiated with UV light. It has been proposed that the MC isomer is a zwitterion, as shown in Figure 12.

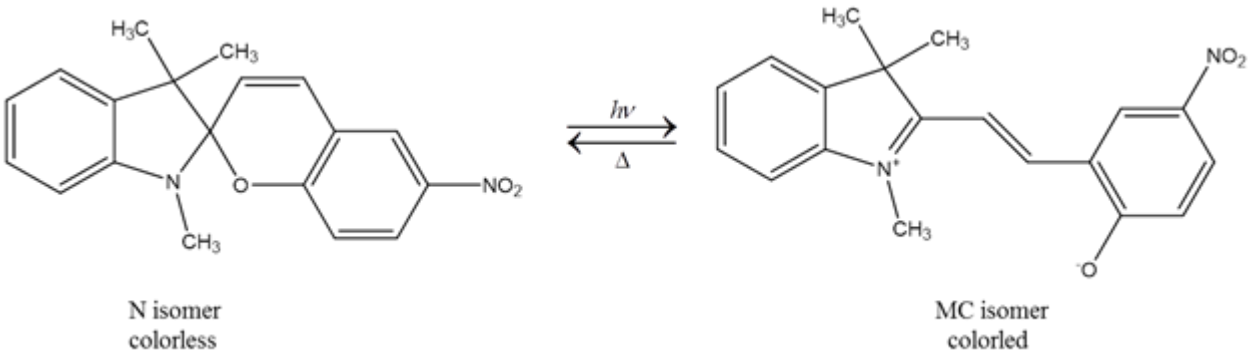

Figure 12: Structure and photochromic reaction of 6-NO_2-BIPS

The N isomer is the thermodynamically more stable isomer and absorbs in the UV region, whereas the MC isomer absorbs in both the UV and visible regions. The MC isomer exhibits a strong and characteristic absorption band between 550 and 650 nm. Upon UV irradiation of 6-NO2-BIPS, the formation of the MC isomer is induced. The increase in the concentration of the MC isomer results in

the increase of absorbance in the visible region of the absorption spectrum. The MC isomer spontaneously returns to the N isomer once the UV irradiation is stopped. The kinetics of this back reaction process can be characterized by measuring the visible absorption at 600 nm of the MC isomer as a function of time. In this experiment, the kinetics of the back reaction will be measured for a range of temperatures in order to determine the activation energy, Ea, of the back reaction. The activation energy can be determined from the slope of ln(τ) as a function of 1/T according to the Arrhenius equation:

$$k = \frac{1}{\tau} = A \exp\left[-\left(\frac{E_a}{RT}\right)\right]$$

where k is the rate constant, τ is the time constant of the back reaction, T is the temperature in Kelvin, A is the pre-exponential factor in reciprocal time units, and R is the universal gas constant. The literature reported value for E_a = 62.5 kJ mol^{-1}.

Experimental Procedures

Prepare the solution by taking 0.032 mg of 6-NO2-BIPS and dissolving it in approximately 20 mL of toluene to give a 5.0 × 10-6 mol L-1 solution. The concentration was chosen such that the absorbance at λ = 300 nm in a 1 cm cuvette of the UV absorption peak was 0.5 at room temperature (see Figure 13). This avoids any dimerization processes as well as allows the UV irradiation to propagate through the entire sample. If using a common UV-visible spectrometer in an undergraduate laboratory, λ_{max} should not exceed 1.

Ensure you have connected the Vernier Flash Photolysis Spectrometer to your computer using the Vernier Flash Photolysis Spectrometer software. Insert the CG-BG-3 dielectric filter and the 600 nm band pass filter. Fill the provided cuvette with 4 mL of the 6-NO2-BIPS/toluene solution.

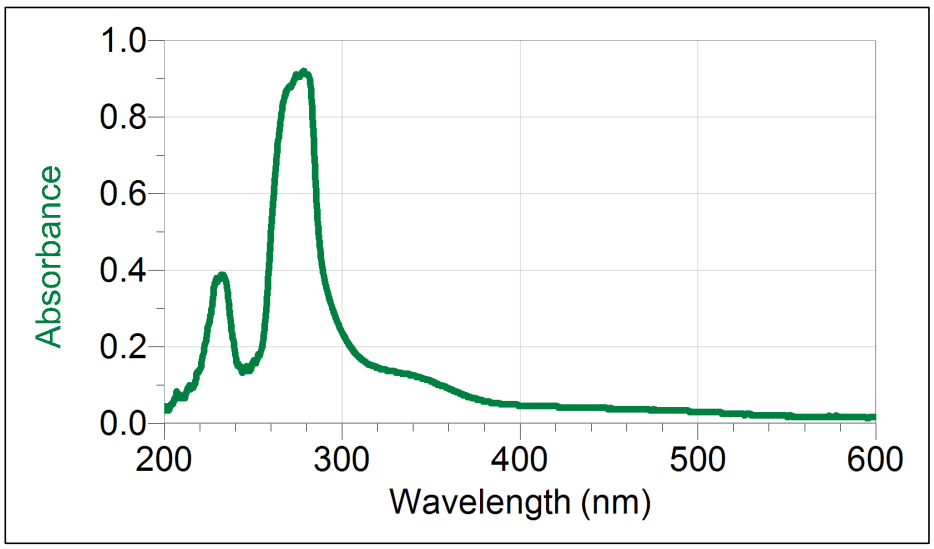

Figure 13: Ground state absorption spectrum of One Spiropyran in toluene.

Fill the provided cuvette with 4 ml of the 6-NO_2-BIPS/Toluene solution.

Prepare a hot bath of water that can be temperature controlled, and use a thermometer to monitor the temperature. The bottom half of the cuvette should be placed into the hot bath to allow the solution to come into thermal equilibrium with the water. For five different temperatures between 30°C and 60°C, remove the cuvette once it is in thermal equilibrium and place the cuvette in the Flash Photolysis Spectrometer. Set the time window appropriately and take one measurement,

returning the cuvette to the hot bath afterwards. See Figure 14 for an example of measurements done at five varying temperatures. For multiple measurements at the same temperature, return the cuvette to the hot bath in between measurements; this will ensure that the solution is at thermal equilibrium with the warm water for each measurement.

An example of the generated absorbance vs. time profile is shown in Figure 15 for a temperature of 55°C. Also shown in this plot is the fitted exponential decay function (red line) generated using Logger Pro software. This fit will provide the lifetime of the back reaction, which in this example is 1.33 seconds. Once lifetimes at five different temperatures are obtained, a plot like the one in Figure 16 can be generated. Using Logger Pro, a line is fit through the five data points and the slope of this line is used to calculate the activation energy, Ea, of the back reaction.

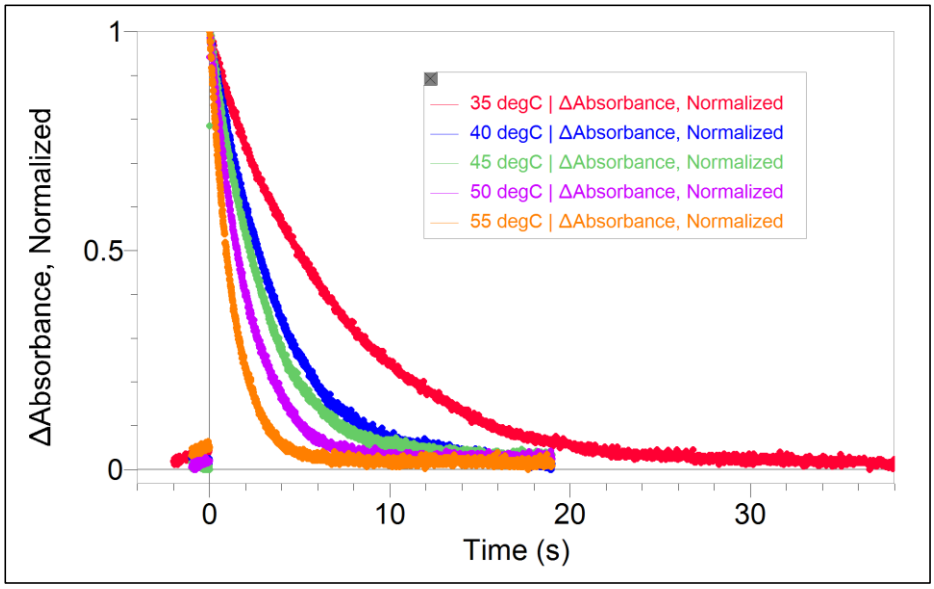

Figure 14: Transient absorption of Spiropyran in Toluene at 600 nm detection wavelength.

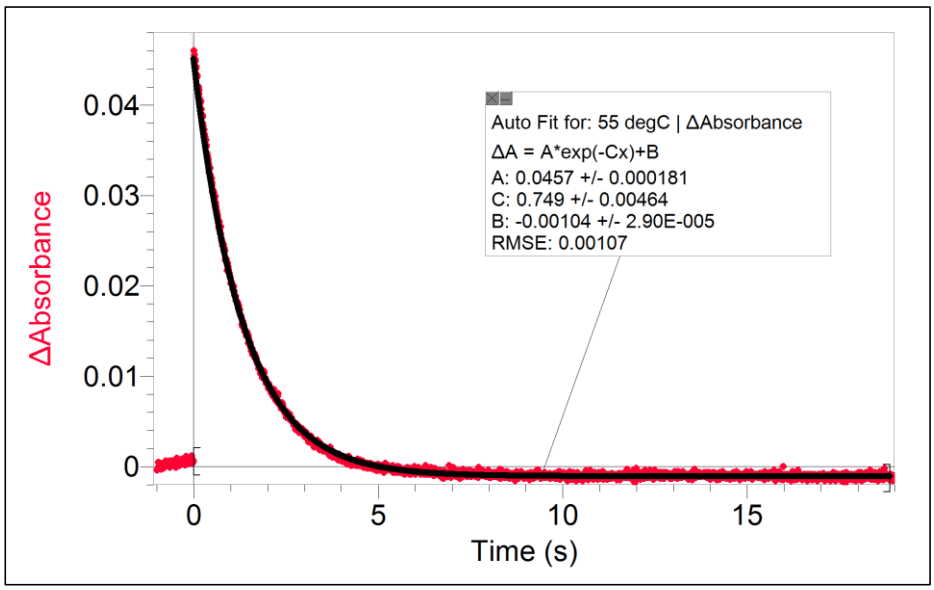

Figure 15: Example decay and exponential fit for 55°C measurement.

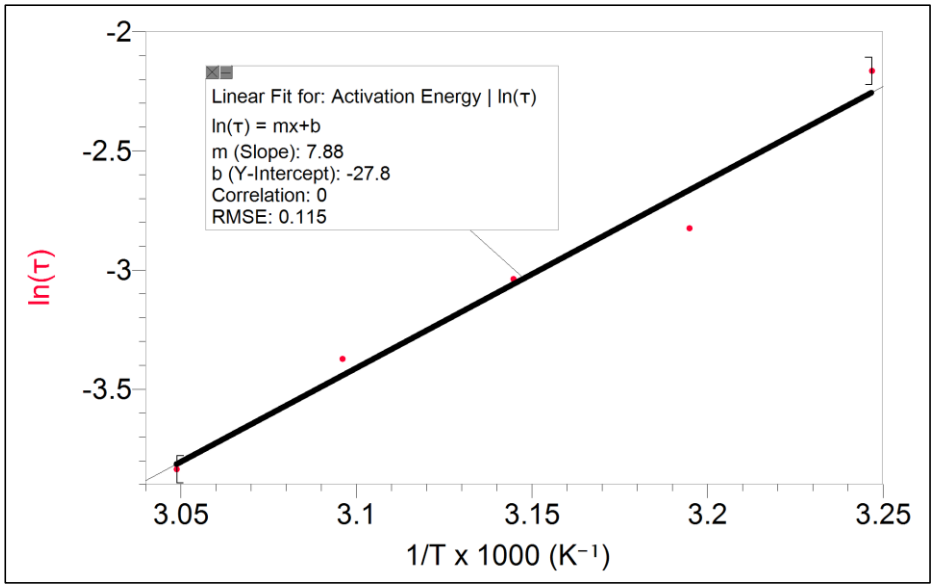

Figure 16: Actual data example of ln(τ) as a function of 1000/T.

8.3 Isomerization of Mercury Dithizonate

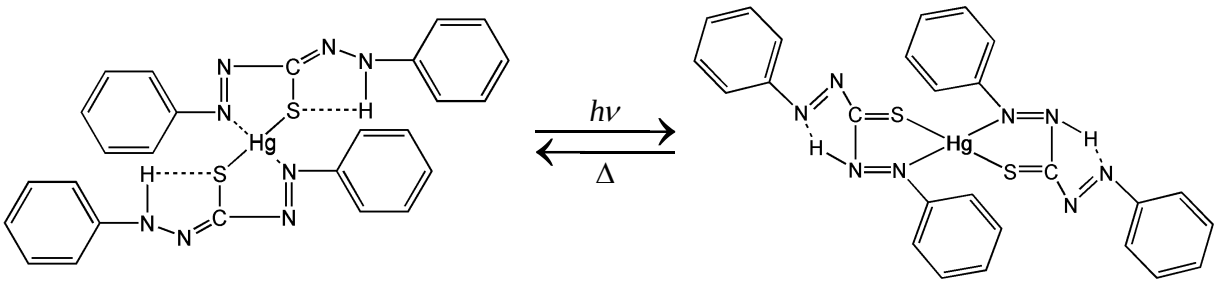

Figure 17: Photoinduced isomerization of mercury dithizonate

This photoisomerization event occurs within the flash lamp profile (i.e., "instantaneously" on our time scale). The trans-to-cis back reaction occurs in the dark period following the flash, and the color reverts thermally with a lifetime of ~650 ms. This inversion of color can be catalyzed by acids and bases. In this experiment, the solution of the HgDz complex is excited by the flash lamp and the decay of the transient absorption at 600 nm is monitored as a function of time after the flash.

The decay is exponential in time with a rate that is first order in the concentration of an acid such as trifluoroacetic acid (TFA). The experimental conditions are such that the TFA is at a much higher concentration than the photo-produced trans-isomer of the complex and so the conditions correspond to the pseudo-order situation as described in the kinetics theory section (Section 10.3). A plot of the observed rate constant as a function of acid concentration is linear with a slope that provides the bimolecular rate constant for the catalysis process.

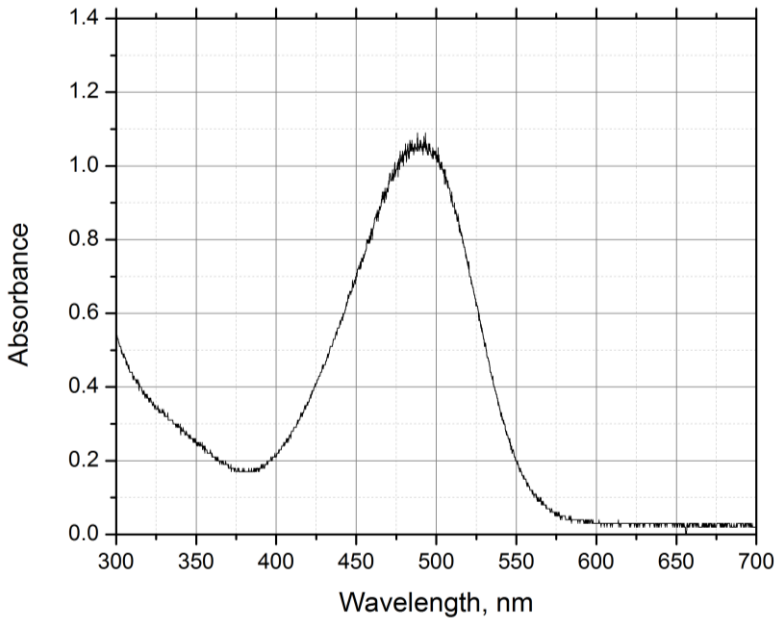

Figure 18: *Ground state absorption spectrum of mercury dithizonate (trans conf.) in ethanol*

Procedure

Obtain and wear goggles. Prepare a 25 mL stock solution of HgDz in ethanol with sufficient solute to provide absorbance of ~1 in a standard cm2 at 500 nm (roughly 10-5 M). Prepare 25 mL of 0.01 M stock solution of TFA in ethanol. Prepare at least five sample solutions, each containing 3 mL of HgDz stock, aliquots of TFA stock in the range of 0–1 mL, and sufficient ethanol to bring total volume to 4.0 mL. These sample solutions will all have the same concentration of HgDz and varying concentrations of TFA in the range 0–0.02 M TFA. Place ~4 mL of the [TFA] = 0 M sample solution in a 10 mm x 25 mm rectangular borosilicate cuvette with all faces polished and proceed to photoexcitation. Ensure you have connected the Vernier Flash Photolysis Spectrometer to your computer using the Vernier Flash Photolysis Spectrometer software. Insert the CG-BG-3 dielectric filter and the 600 nm band pass filter.

Photoexcitation of an air-saturated ethanol solution of the Hg complex with the dithizone ligand in the cis-form induces cis-to-trans isomerization, and the compound changes color from orange to blue (λmax = 605 nm).

In Figure 18b, you can see that the flash at t = 0 causes a vertical (on these time scales) drop in the Probe Intensity reading; ignoring the large spike and looking at data after 100 µs, it drops from ~29.98 µA prior to the flash to ~29.85 µA after the flash. Subsequently, the value increases over hundreds of milliseconds. The flash induces the changes outlined earlier, and very quickly, at shorter times than software can follow, the ground state of the cis-form is generated. After reviewing the scanned data, the half-life for this sample is ~300 ms. Importing the data into data-analysis software such as Logger Pro will allow for the determination of the trans-cis isomerization rate constant with greater accuracy. Repeating this process at the various concentrations of TFA will show a linear dependence of the lifetime on acid concentration.

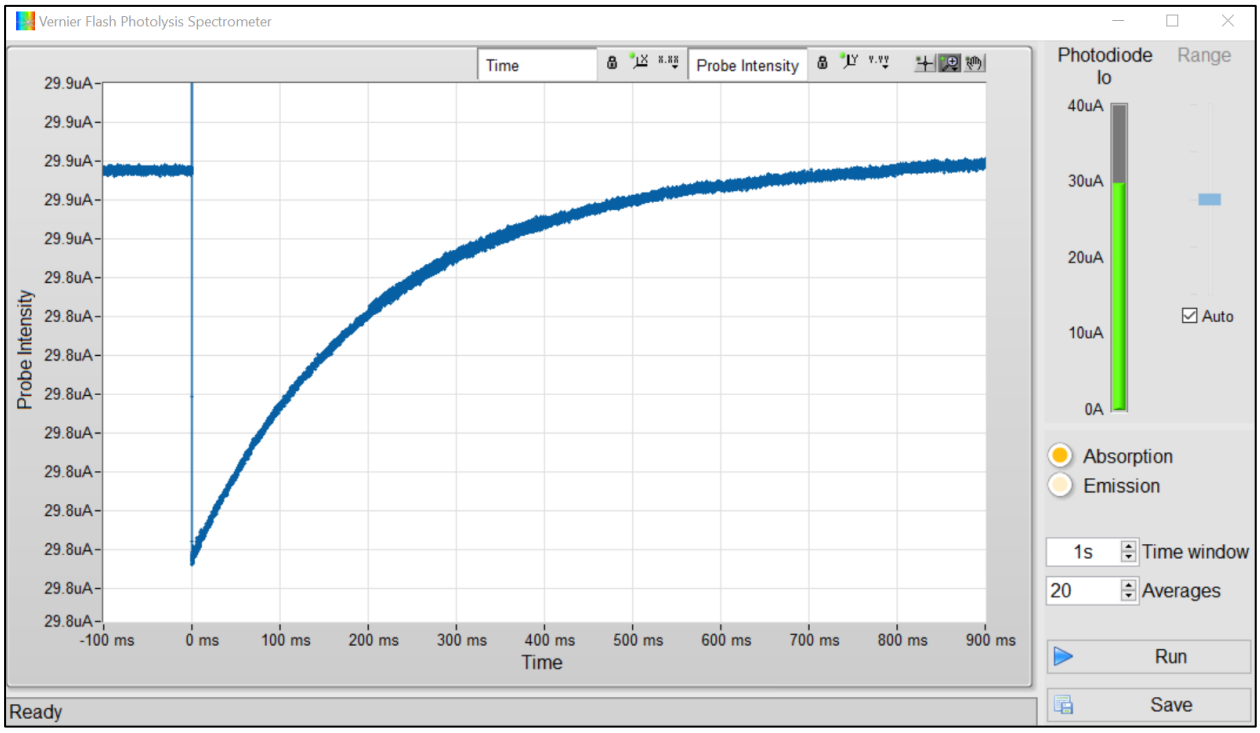

Figure 18b: *Kinetic profile of mercury dithizonate in ethanol*

9 Daily Operations of Vernier Flash Photolysis Spectrometer

Start-Up

1. Switch on the Vernier Flash Photolysis Spectrometer. The LED will start immediately, and you should be able to see a white glow inside the enclosure.
2. Start the Vernier Flash Photolysis Spectrometer software.

Choose Experiment Mode and Set Parameters

1. Choose Absorption or Emission mode for your experiments.
2. Set the number of times to average and the time window.

Finding the Signal

1. Place the appropriate excitation and detection filters for your sample. A prior UV/vis absorption measurement would help determine which are appropriate.
2. Prepare your sample and place it in the Vernier Flash Photolysis Spectrometer sample holder.

Acquiring Data

1. Click on the <Run> button and allow the scan to complete.
2. Click on the <Save> button to export data.

Shutdown

1. Remove the sample and any filters added.
2. Click on the <Exit> button to close the Vernier Flash Photolysis Spectrometer software.
3. Unplug the USB connector.

10 Basic theory

This section aims to provide some background for the user to be aware of flash photolysis spectroscopy. It does not aim to be a comprehensive guide on the intricacies of the technique and its physics. For more details and on how to interpret the data, the user is encouraged to read books on optical spectroscopy and scientific literature.

Most chemical reactions that occur via a series of simple, or elementary processes, which can proceed at different rates. An elementary process is a single step reaction where there are no chemically-identifiable intermediates. Elementary processes are best used to understand the fundamental principles of photochemical kinetics. For a given complex reaction, its rate will be determined by the rate of the slowest of the participating elementary reactions. The major advantage of using photons to initiate reactions is that in this way it is relatively straightforward to initiate elementary processes.

10.1 Transient Optical Spectroscopy

Optical spectroscopy is a general term used to describe measurements done with light, and how matter interacts with light. Depending on the type of processes that occur, their features and timescales, spectroscopists will choose different instruments to perform such experiments. The most basic optical spectroscopic techniques are steady state measurements. While lacking temporal information, they provide immense spectral information that prompts measurements that record the temporal change of the sample. Such experiments measure the transient changes of the sample's properties, such as absorbance.

Transient absorption (TA) measurements can range from 'slow' to 'ultrafast', because different processes that occur at different 'speeds', or more accurately, 'timescales'. The faster the processes, the shorter the excitation and probe sources need to be, and the higher the cost. Femtosecond TA provides information in the sub-picosecond timescales that are useful to extract information such as carrier cooling, exciton generation, etc., but has a limited time window due to its nature. One of its 'slow' counterparts is flash photolysis, where no specialized equipment is required. To perform such measurements, a reasonably fast pulsed light source and an appropriate detector is sufficient.

TA spectroscopy is also known as pump-probe spectroscopy: the pump excites the sample and generates photogenerated carriers that is the interrogated by the probe light. The goal is to measure the pump-induced probe change, either transmitted through or reflected off the sample. By taking the difference between the transmitted and initial signal, and doing a logarithmic calculation, the differential absorption spectrum [ΔA(λ)] can be obtained,

$$\Delta A(t) = -\log\left[\frac{I_{\mathrm{pump-on}}(t)}{I_{\mathrm{pump-off}}(t)}\right]$$

In such measurements, kinetics data is represented in signal vs relative time units, e.g. delay time or similar. The data is relative to a quantity called 'time zero'. Time zero is a misnomer: it does not describe time; instead, it describes the pump-probe delay corresponding to the pump and probe pulses overlapping in time at the target, i.e., the sample.

This time zero in flash photolysis is arbitrarily set since it is essentially a single shot measurement. A distinct feature of time zero is the sudden increase in signal, assuming the pump and probe beams are also overlapping in space. Depending on the user, it can be just before the signal amplitude rises, or when the signal is maximum. This manual uses the former definition.

10.2 Photochemistry

Materials in this section have been adapted from "A Qualitative Theory of Molecular Organic Photochemistry" (http://www.columbia.edu/itc/chemistry/photochem/courseworks/06MMP_Chapter6.pdf). The paper serves as a good introduction to photochemistry. Interested and curious readers are strongly encouraged to read it in its entirety.

When light of a certain energy is incident on a sample (e.g., molecule) that is equivalent to a difference between two optically allowed states, an optical transition occurs. If these two states are the ground and first excited state, the sample absorbs the light and becomes an electronically[1] excited molecule.

Here, the molecule (**R**, reactant) absorbs the energy ($h\nu$) and undergoes a photophysical process to an excited molecule (***R**). The excited molecule can then relax back to the ground state non-radiatively (photophysical). It can also undergo photochemical processes to form a product (**P**) in a single step or via an intermediate (**I**). One can think of photophysical processes that do not change the sample and reversible, whereas photochemical processes results in a different chemical outcome and generally irreversible.

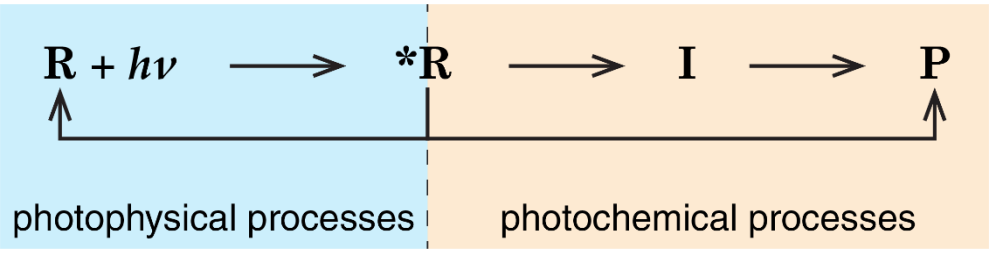

Figure 179: Photophysical and photochemical sequence in light-matter interactions

In photophysical processes, the radiative – fluorescence and phosphorescence – recombination kinetics can be detected using methods such as fluorescence spectroscopy. Ultrafast Systems offer the Halcyone system to perform these measurements. On the other hand, in photochemical processes, the intermediates and products are likely to absorb light themselves in different spectral regions from the reactant. Thus, by performing TA measurements on different detection wavelengths, the kinetic process of the chemical sequence can be followed.

Since the intermediates are often short-lived (< 1 millisecond), it is necessary for high time resolution to capture such processes. As previously mentioned, faster processes (sub-nanosecond) requires more specialized setups such as nanosecond or femtosecond TA. Ultrafast Systems offers the EOS and Helios systems to perform these measurements.

10.3 Chemical Kinetics

10.3.1 Stoichiometry

Every chemical change can be represented by a stoichiometric, or balanced, equation in symbolic form. For example, the acid-base reaction between sulfuric acid and a metal hydroxide is represented by

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \quad (1)$$

[1] Note that the word electronic here refers to the electronic states of the molecule (as compared to vibrational), and not circuits or devices.

This equation tells us nothing about the mechanism of the process; it simply expresses the overall chemical equivalency.

10.3.2 Reaction Rate

The rate of a chemical reaction is expressed as the variation with time of the concentration of either reactants or products. In solution phase reactions, as studied here, the units of reaction rate are concentration units per second, i.e. mole per liter per second, M s^{-1}.

In the (elementary) reaction,

$$A + B \rightarrow C \qquad (2)$$

The rate (change in concentration as a function of time) is expressed in the form of a derivative

$$\text{Rate} = -\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{\mathrm{d}[C]}{\mathrm{d}t} \qquad (3)$$

For the rate to be a positive quantity, the derivatives of $[A]$ and $[B]$ with time are negative because the concentrations of these reactants decrease as time proceeds. The square brackets ([]) is a standard way to show that the concentration is in M s^{-1}.

In the case of the symbolic elementary reaction

$$2A \rightarrow C \qquad (4)$$

which could represent a dimerization process, where reactant A is removed at twice as quickly compared to product formation, the rate is given by

$$Rate = -\frac{1}{2}\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{\mathrm{d}[C]}{\mathrm{d}t} \qquad (5)$$

10.3.3 Rate Expression and Rate Constant

Empirical observations of the rates of chemical processes led to the Law of Mass Action, "The rate of a chemical reaction is directly proportional to the active masses of the reacting species." For reactions taking place in dilute homogeneous solution the term "active masses" can be replaced by molar concentrations (mole L^{-1}, or M).

For the *elementary* reaction, where P is the product,

$$A + B \rightarrow P \qquad (6)$$

the mathematical formulation of the Mass Action Law is

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} \propto [A][B] \qquad (7)$$

and replacing the proportionality sign with a constant of proportionality or rate constant, k, the rate expression, or rate equation can be obtained,

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][B] \qquad (8)$$

This equation tells us that since the concentrations of the reactants decrease during the reaction, then the rate (but not the rate constant) decreases with time elapsed. Thus, the rate constant provides the spectroscopist with a useful measure of the velocity of a reaction, an important quantity to determine when studying chemical kinetics.

10.3.4 Order of Reaction

In the previous rate equation (Equation 8) the concentrations of A and B both appear to the first power, i.e., this reaction is first order with respect to both [A] and [B], and overall second order reaction.

In the dimerization reaction for the elementary process (Equation 4), the rate expression is will be

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][A] = k[A]^2 \qquad (9)$$

For this reaction, it is second order in [A] and overall second order.

Also, the symbolic elementary process

$$A \rightarrow P \qquad (10)$$

would be expected to have a rate equation

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A] \qquad (11)$$

and the reaction is first order in [A] and overall first order. Orders higher than 2, fractional and zero orders are found in special cases. These are not considered here because they are not relevant to Vernier Flash Photolysis Spectrometer.

NOTE: It is important to realize that assignment of order by inspection is only valid for elementary reactions; it does not apply for stoichiometric equations.

10.3.5 Experimental Approach

The data that are obtained in a kinetics experiment could look something like those shown in Figure . The change in concentration of reactant A (open circles) and product B (filled circles) as a function of time can be observed; M is the generic species (A or B).

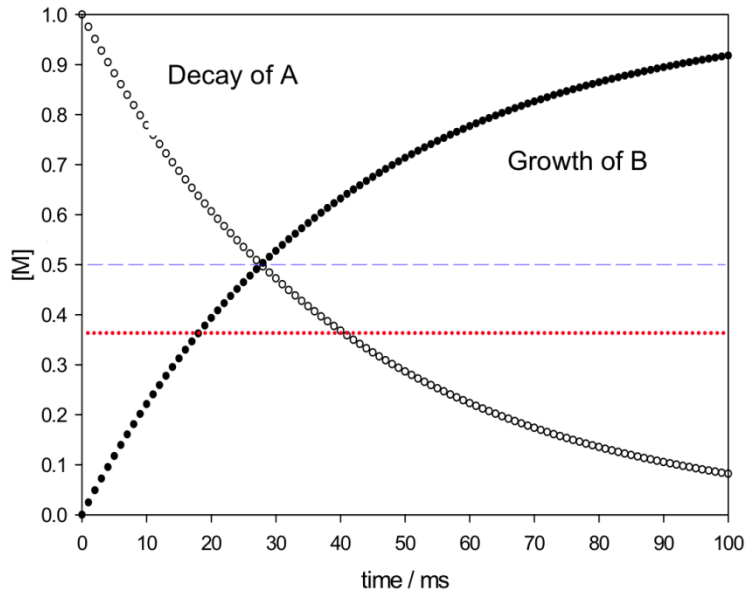

Figure 20: Concentration time profiles of reactant and product.

The blue line is drawn at the point of 50% reaction (half of the initial concentration of A has been converted into B). By inspection this occurs after an elapsed time of about 28 milliseconds. This

represents the half-life, or half time, of the reaction. The red line is drawn when $1/e$ (~37%) of the initial concentration of A has been converted to B; this represents the reaction lifetime.

10.3.6 Relationship between Rate Constant, Half-life and Lifetime

Consider a first order reaction ($A \rightarrow P$) in Equation 10, with its associated rate equation in Equation 11. Setting $[A]_0$ as the initial concentration of A and solving the differential equation yields the expression

$$[A] = [A]_0 \exp(-kt) \qquad (12)$$

which shows that the concentration of A decreases exponentially with time (see the decay trace of A in Figure). Since the argument of the exponential term must be dimensionless, it is clear that the units of k, the first order rate constant, are time^{-1}, and conventionally, time is measured in seconds, or sub-multiples of seconds such as ms, µs, ns, etc.

At the half-life point, $[A]_{50\%} = 0.5[A]_0$ and $\exp(-kt_{1/2}) = \frac{1}{2}$,

where $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$ and a measurement of $t_{1/2}$ leads to the rate constant. In this reaction, the half-life point only depends on k.

The lifetime of a reaction, usually written as τ, defined as the inverse of the rate constant, $\tau = \frac{1}{k}$. Thus Equation 12 can be written as

$$[A] = [A]_0 \exp\left(-\frac{t}{\tau}\right) \qquad (13)$$

and at $t = \tau$,

$$[A] = [A]_0 \exp(-1) = 0.368[A]_0 \qquad (14)$$

or, at the lifetime point, the concentration of A has fallen to $\frac{1}{e}$ (~37%) of its initial value.

Note that in processes that are overall first order, the half-life and the lifetime are independent of time and initial concentration.

Such overall first order reactions could be the spontaneous decay of an electronically excited state of a molecule that has been generated by the absorption of photons (see later). In this case the product(s) could be the original ground state of the molecule, or an isomer thereof (cis-trans photoisomerization). Such reactions are termed unimolecular because there is only one molecule involved and are overall first order.

Now let us consider the elementary process ($A + B \rightarrow P$) in Equation 6, which is bimolecular since it requires a molecule of A and B each. Upon inspection, this reaction is expected to show overall second order kinetics. Instead, the actual order observed in the experiment will be determined by the reaction conditions.

Under conditions where the initial concentrations of A and B are equal, the rate equation is as in Equation 8. Integrating this differential equation and setting [A] = [B] yields

$$[A]^{-1} = [A]_0^{-1} = kt \qquad (15)$$

This is also the result for the case of the reaction $2A \rightarrow P$.

At the half-life time point, were $[A] = 0.5[A]_0$,

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} = kt_{1/2}$$

In this overall second order reaction, half-life time also depends on the initial concentration, unlike the overall first order reaction.

10.3.7 Pseudo-first Order

Consider the bimolecular elementary process ($A + B \rightarrow P$) in Equation 6, where [B] $\gg$ [A]. Thus, changes in concentration of B is negligible compared to A, which goes from 100% to zero during the reaction. The rate equation (Equation 8) can be simplified to

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][B]_0 = k'[A] \qquad (16)$$

where $k' = k[B]_0$.

Integrating this differential equation yields

$$[A] = [A]_0 \exp(-k't) \qquad (17)$$

Thus, this bimolecular process is seen to be first order in A and overall first order. This is referred to as "pseudo-first order" by some spectroscopists, but the important thing to realize is that the process behaves in a first order manner in the experiment. This behavior can be detected by evaluating the first order rate constant at different initial concentrations of B, when it will be found to depend linearly on [B].

11 Maintenance and Troubleshooting

11.1 Maintenance

Vernier Flash Photolysis Spectrometer does not contain any consumable items or spare parts. The exterior of Vernier Flash Photolysis Spectrometer can be cleaned with a soft cloth moisten with ethanol. Never use acetone. Replace the lids to ensure no contaminants or dust will fall into the modules. Avoid cleaning inside the modules due to the risk of optics and crystal contamination, and accidental misalignment. If absolutely necessary, ensure sufficient ventilation to minimize fume concentration in the modules.

Clean optical surfaces allow for optimal reflection or transmission of laser power. Contaminants on the optics can reduce the efficiency of the system. Touching the polished surface of the optics in anyway, even with new gloves, can cause contamination. It is crucial that optics are handled at the ground edges only. Exercise caution when handling optics and when cleaning them. Always inspect the optics before and after cleaning them. Use a magnification device and a bright light to spot small defects and contaminants.

Clean optics in increasing level of contact. Use non-contact methods by blowing off dust and other contaminants with compressed air. Be careful not to use excessive pressure that might cause the optics to slip or crack.

If blowing is not sufficient to remove remnant contaminations, e.g. oils, spectroscopic-grade methanol is the recommended solvent for cleaning optics. Other solvents and poorer grades can leave residues or degrade the optical coatings. Always read the associated data sheets and MSDS sheets prior to using any solvent.

Prepare a single piece of high-quality lens tissue, folded neatly, and lightly moistened with the solvent. Gently use the tissue for *one* wipe and *one* direction only and discard it immediately. Use a new tissue for subsequent passes. Reusing the tissue or reversing direction can drag contaminants back across the cleaned surface, causing residual streaks and potential damage.

11.2 Troubleshooting

This section aims to provide the user with some solutions to common problems.

If the problem is…	**Here's what to do…**
There is no white glow in the Vernier Flash Photolysis Spectrometer when the USB is plugged in.	Plug the USB connector in snugly and check that the computer can detect the Vernier Flash Photolysis Spectrometer. It will appear as a COM port connection.
There is no light detected on the photodiode (PD level is zero or very low).	Check that the instrument is plugged in and turned on, and there is no obstruction in the light path. You can verify the unit is turned on by watching for a white glow emitted by the LED light. Remove any filters that were placed in the slit before the detector.
There is a signal, but it is noisy or fluctuating significantly.	1. Remove the sample and filters and check that the photodiode reads a strong baseline intensity. Contact your local representative or Ultrafast Systems if no light is detected. 2. Try to average across more scans if the baseline intensity falls within the

	recommended range. 3. Ensure the Range is set to Auto (checked box) when performing absorption measurements. For emission measurements, ensure Auto is turned off (unchecked box) and play around with the slider and clicking run.
The photodiode reads the baseline correctly, but when I place my sample inside and do a measurement, I see no observable change.	Check the photoresponse of your sample and that appropriate filters are placed in the slit. Make sure to familiarize yourself with Section 8: Acquiring Data on page 15 prior to performing measurements.
I can reliably measure the reference samples and get consistent data, but when I place my sample for measurements, I do not see any signal.	The sample response could be too weak or fast for the Vernier Flash Photolysis Spectrometer to detect. If you have access to a laser pump-probe setup like the EOS or Helios, you can try to perform your measurements there.

12 Appendix

The Vernier Flash Photolysis Spectrometer software has an advanced settings window for experienced spectroscopists. The settings can be accessed by pressing **CTRL + SHIFT + C** on the keyboard from the main window of the Vernier Flash Photolysis Spectrometer software.

In this window, you can change the COM port and the default graphing unit from current to ΔA. Changing the latter will instruct the software to automatically perform calculations to convert the light intensity data. Teaching lab instructors and technicians should ensure this setting is always set to display current for educational purposes. Students should be able to calculate it themselves.

13 Warranty

Ultrafast Systems warrants that the spectrometer system (the Product), that is the subject of this sale, (a) conforms to Ultrafast Systems' published specifications and (b) is free from defects in materials and workmanship.

The Product is warranted to conform to Ultrafast Systems' published specifications and to be free from defects in materials and workmanship for a period of five years from the date of installation. If the Product is found to be defective during the warranty period, the Product will either be repaired or replaced at Ultrafast Systems' option.

To exercise this warranty, contact Vernier Software & Technology.

Limitation of Warranty

The foregoing warranty shall not apply to defects resulting from:

1. Unauthorized repair or modification that was performed without written approval by Ultrafast Systems.
2. Operation outside the environmental specifications of the Product, leading to the Product being subjected to unusual physical, thermal or electrical stress.

This warranty does not apply to misuse, abuse, accident or negligence in use, improper installation storage, transportation or handling not specifically authorized by Ultrafast Systems.

This warranty does not apply to fuses, batteries, or damage from battery leakage.

This warranty is in lieu of all other warranties, expressed or implied, including any implied warranty of merchantability or fitness for a particular use. Ultrafast Systems shall not be liable for any indirect, special, or consequential damages resulting from the purchase or use of its products.

14 Notice

14.1 Confidentiality & Proprietary Rights

14.1.1 Reservation of Title

The Ultrafast Systems programs and all materials furnished or produced in connection with them ("Related Materials") contain trade secrets of Ultrafast Systems and are for use only in the manner expressly permitted. Ultrafast Systems claims and reserves all rights and benefits afforded under law in the Programs provided by Ultrafast Systems.

Ultrafast Systems shall retain full ownership of Intellectual Property Rights in and to all development, process, align or assembly technologies developed and other derivative work that may be developed by Ultrafast Systems. Customer shall not challenge or cause any third party to challenge the rights of Ultrafast Systems.

14.1.2 Preservation of Secrecy and Confidentiality and Restrictions to Access

Customer shall protect the Ultrafast Systems Programs and Related Materials as trade secrets of Ultrafast Systems and shall devote its best efforts to ensure that all its personnel protect the Ultrafast Systems Programs as trade secrets of Ultrafast Systems. Customer shall not at any time disclose Ultrafast Systems' trade secrets to any other person, firm, organization, or employee that does not need (consistent with Customer's right of use hereunder) to obtain access to the Ultrafast Systems Programs and Related Materials. These restrictions shall not apply to information (1) generally known to the public or obtainable from public sources; (2) readily apparent from the keyboard operations, visual display, or output reports of the Programs; 3) previously in the possession of Customer or subsequently developed or acquired without reliance on the Ultrafast Systems Programs; or (4) approved by Ultrafast Systems for release without restriction.

14.2 Service Information

The user should not attempt any maintenance or service of the system or optional equipment beyond the procedures outlined in this manual. Any problem that cannot be resolved should be referred to Ultrafast Systems.