

Vernier Flash Photolysis Spectrometer

(order code: VSP-FP)

Educational Flash Photolysis Spectrometer

Reference Manual

(version: 12/14/2015)

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1 General Information

1.1 Introduction

The Vernier Flash Photolysis Spectrometer is designed to be a simple, user-friendly device for demonstrating to chemistry students the fundamental principles of chemical kinetics. Every process that we label 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 the 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.

1.2 Specifications

1.2.1 Spectrometer Specifications

Spectral Coverage

450–750 nm

Spectral Resolution

Determined by an interference filter used. Typically ~10 nm

Temporal Resolution

~100 μ s

Time Window

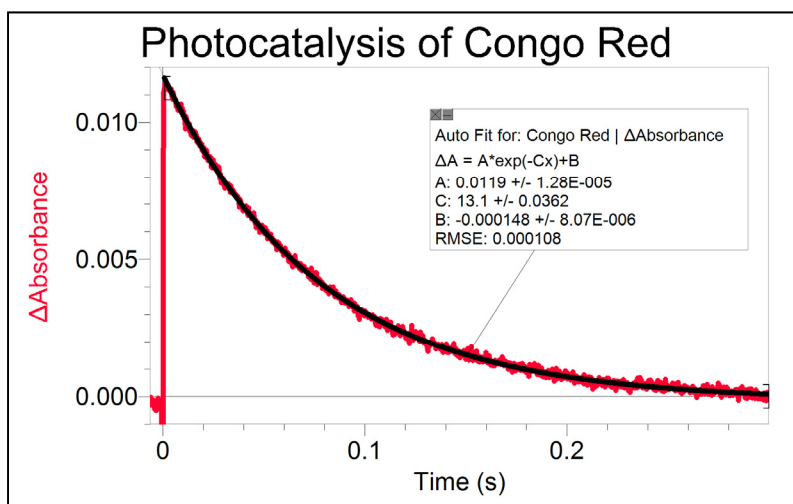
\geq 15 ms

Software

The Vernier Flash Photolysis Spectrometer comes with data-acquisition software necessary to collect the signal waveform from the photodetector. Subsequent data processing, such as conversion of the acquired voltage waveform into temporal profile of ΔA and fitting the ΔA profile to an appropriate function in order to extract the rate constants, can be done by exporting the data into Vernier Logger Pro software or Microsoft® Excel®.

Data Format

The Vernier Flash Photolysis Spectrometer produces ΔA vs. time data in a form of an ASCII CSV file that can be easily processed with Logger Pro.



	Congo Red			Congo Red - Run 2			T
	Time (s)	Signal (V)	ΔA	Time (s)	Signal (V)	Abs	
168	0.017	0.822	0.009	0.017	0.823	0.009	
169	0.017	0.822	0.009	0.017	0.823	0.009	
170	0.017	0.822	0.009	0.017	0.824	0.009	
171	0.017	0.822	0.009	0.017	0.823	0.009	
172	0.018	0.822	0.009	0.018	0.824	0.008	
173	0.018	0.822	0.009	0.018	0.823	0.009	
174	0.018	0.822	0.009	0.018	0.824	0.009	
175	0.018	0.823	0.009	0.018	0.824	0.009	
176	0.019	0.822	0.009	0.019	0.823	0.009	
177	0.019	0.822	0.009	0.019	0.824	0.009	
178	0.019	0.822	0.009	0.019	0.823	0.009	
179	0.019	0.823	0.009	0.019	0.824	0.009	
180	0.020	0.823	0.009	0.020	0.823	0.009	
181	0.020	0.823	0.009	0.020	0.824	0.009	
182	0.020	0.823	0.009	0.020	0.824	0.008	
183	0.020	0.823	0.009	0.020	0.824	0.008	
184	0.021	0.823	0.009	0.021	0.824	0.008	
185	0.021	0.823	0.009	0.021	0.824	0.008	
186	0.021	0.823	0.009	0.021	0.824	0.008	
187	0.021	0.823	0.009	0.021	0.824	0.008	
188	0.022	0.823	0.009	0.022	0.824	0.008	
189	0.022	0.823	0.009	0.022	0.824	0.008	
190	0.022	0.823	0.009	0.022	0.825	0.008	
191	0.022	0.824	0.009	0.022	0.825	0.008	

Figure 1: Examples of Vernier Flash Photolysis Spectrometer data processed in Logger Pro

1.2.2 Equipment Specifications

Weight: 10 lbs

Footprint: 8" x 8" (20.3 cm x 20.3 cm)

UL94 rating: V-0

Meets UL796 requirements

Voltage range: 100–120 V & 210–240 V

Frequency range: 50 Hz & 60 Hz

Power rating: 50 W maximum

DC battery: A23 12 V

USB cable: 28 AWG shielded

AC power cable: 18 AWG 300 V

1.2.3 Detector Specifications

All measurements were performed with a 50 Ω load unless stated otherwise.

Detector		Silicon PIN
Active area		3.6 x 3.6 mm (13 mm ²)
Wavelength range	λ	350 to 1100 nm
Peak wavelength	λ_p	970 nm
Rise time	t_r	14 ns
Bias voltage	V_R	10 V
Dark current (with 1 M Ω load)	I_D	0.35 nA
Output voltage	V_{OUT}	0 to 10 V

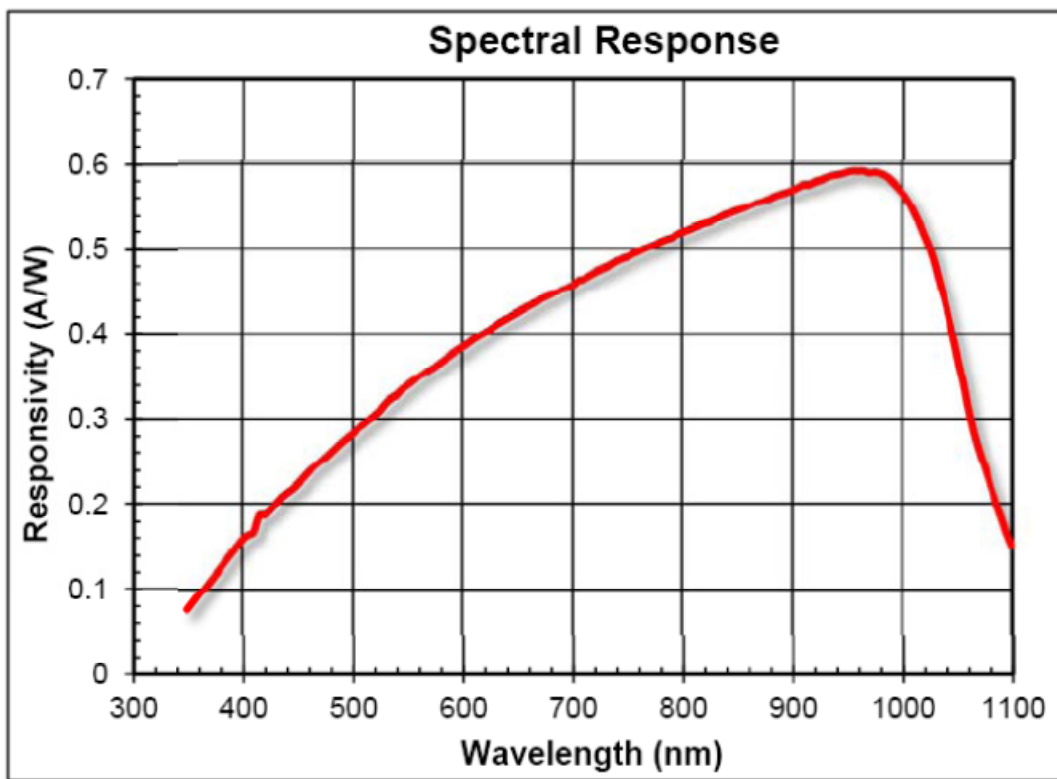


Figure 2: Detector responsivity vs. wavelength

2 Safety Information

The Vernier Flash Photolysis Spectrometer is designed and manufactured for kinetic analysis of a chemical specimen by means of transient absorption spectrometry. 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.

- Use a compliant surge protector when exposing equipment to voltage. Failure to do so may result in damaging the unit.
- Do not use this equipment in or near water.
- Use extreme caution in handling the cuvette when it is filled with liquid. Never fill or refill the cuvette when it is in the sample holder. Failure to use a cuvette with a dry outer surface or a cuvette that is leaking liquid can result in the flash housing to malfunction or short.
- This system is designed to work optimally at room temperature or an approximation of room temperature.
- Do not disassemble the spectrometer case. Doing so may result in damaging the excitation light source and electric shock.

If the spectrometer does not appear to be functioning properly, do not attempt to repair it yourself. Please contact Vernier Technical Support for assistance.

Every effort has been made to ensure that the information in this manual is accurate. All information in this document is subject to change without notice. Ultrafast Systems makes no representation or warranty, either expressed or implied, with respect to this document. In no event will Ultrafast Systems be liable for any direct, indirect, special, incidental, or consequential damages resulting from any defects in this documentation.

If this equipment is used in a manner not specified in this manual, the protection provided by this equipment may be impaired.

The following are definitions of the Warnings, Cautions, and Notes that are used throughout this manual to call your attention to important information regarding your safety, the safety and preservation of your equipment, or an important tip.



WARNING

Situation has the potential to cause bodily harm or death.



CAUTION

Situation has the potential to cause damage to property or equipment.

NOTE

Additional information the user or operator should consider.

3 Layout and Basic Principles of Operation

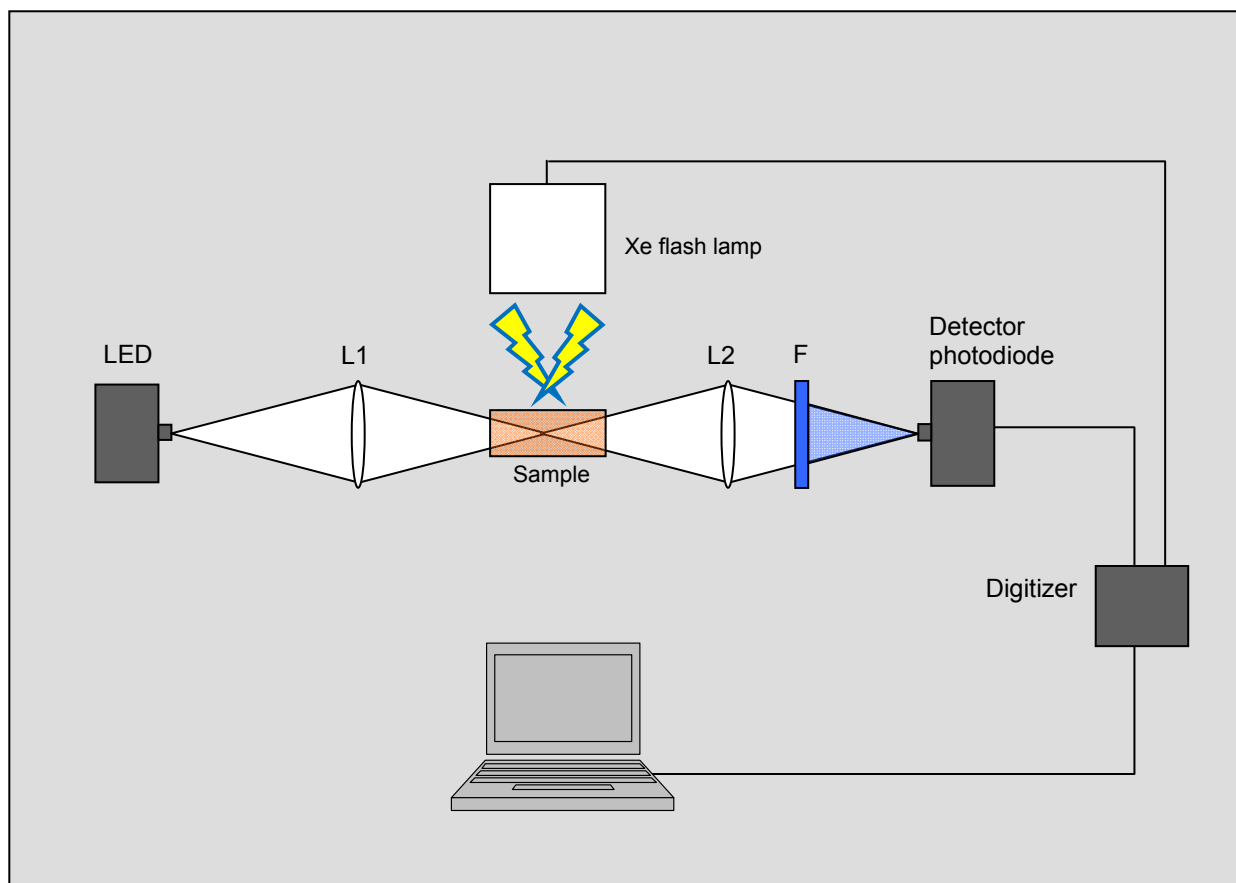


Figure 3: Schematic of the Vernier Flash Photolysis Spectrometer

A white light LED is utilized for probing the spectral changes taking place after the sample has been exposed to an excitation flash. The white light is sent through a sample cuvette via lens L1 and subsequently delivered to the photodetector diode by passing through an optical interference filter and objective lens L2. The optical interference filter is used to select the desired wavelength out of the broad emission spectrum of the LED. While the continuous wave (CW) output from the LED is being monitored by the photodiode, the photoexcitation flash is sent through the sample. The photo-induced transient species cause the absorption of the sample to deviate from what it was before the excitation flash. This results in changes in the intensity of the LED light passing through the sample. These changes are detected by the monitoring photodiode. The output voltage waveform from the photodiode is collected and digitized by an internal DAQ device and transferred to the computer for further manipulation.

4 Hardware Description

4.1 Turning the Spectrometer On and Off

- Connect the power cord to the AC input located at the rear of the Vernier Flash Photolysis Spectrometer.
- Connect the Vernier Flash Photolysis Spectrometer to the computer via a USB cable.
- Wait until Windows® recognizes the new USB device.
- Start the Vernier Flash Photolysis Spectrometer Software.

NOTE

The 12 V battery that powers the photodiode can be accessed by removing the battery compartment lid on the side of the housing.

4.2 Optical Filters

A 600 nm interference filter is included with the Vernier Flash Photolysis Spectrometer. Insert the filter into the filter housing that is also included. These filters select the wavelength monitored by the photodiode. Additional filters can be purchased from any filter company. The size that fits the housing is 12.5 mm (OD), 9.0 mm (ID).

4.3 Software Description

The user interface of the Vernier Flash Photolysis Spectrometer Software is rather intuitive (Figure 4). The I_0 value (PD level, V) at the top-right of the screen reflects the amount of probe light reaching the detector photodiode. Please keep in mind that at 2500 mV the detector will saturate, and your signal will be distorted. A typical I_0 should not be larger than 2 V for absorption measurements. If the I_0 values are lower than 500 mV or higher than 2000 mV, please contact Vernier Technical Support. For emission measurements, the LED light turns off and the I_0 value should drop close to zero (<10 mV).

During data acquisition, the Vernier Flash Photolysis Spectrometer will wait for approximately 2 seconds between flashes to allow enough time for the flash capacitors to recharge. By default, the software will adjust the axis scales automatically: the y-axis range will adjust to display the signal only, cutting off the large scattered flash pulse 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 of the screen (Figure 4).

The data are saved in CSV (comma delimited values) ASCII format. The first column is time in milliseconds and the second column is light intensity in millivolts.

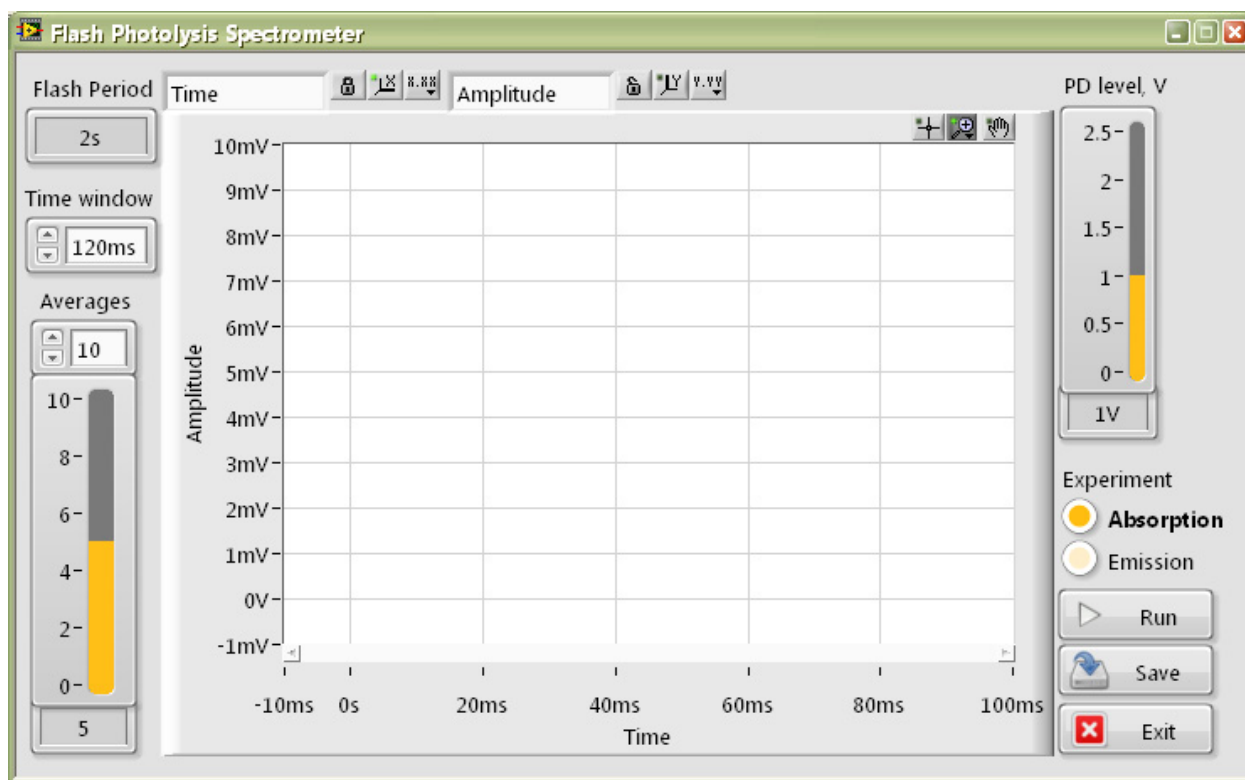



Figure 4: Screenshot of Vernier Flash Photolysis Spectrometer Software


4.3.1 Graph Controls


Graph controls on the top of the screen allow you to zoom in the graph after measurements have been completed. By default, the cursor mode on the graph is y-axis zoom, with the following graph controls:

 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.

 Default, select Y region to zoom in, keep X limits unchanged.

 Autoscale both x- and y-axes once to fit graph.

 Zoom in;  Zoom out.

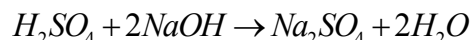
5 The Basic Principles of Chemical Kinetics

Most chemical reactions that occur, either in nature or in the laboratory, are complex. That is, they occur via a series of simple, or elementary, processes, which can proceed at different rates. An elementary process is a single-step reaction in which there are no chemically-identifiable intermediates. 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 and it is these that are best used to understand the fundamental principles of chemical kinetics.

Now some necessary definitions:

5.1 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



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

5.2 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, Ms^{-1} .

In the (elementary) reaction



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

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} \text{ Ms}^{-1} \quad \text{Equation 2}$$

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.

In the case of the symbolic elementary reaction



which could represent a dimerization process, the rate is given by

$$\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = \frac{d[C]}{dt} \quad \text{Equation 4}$$

since A is removed twice as quickly as the product is formed.

5.3 The Rate Expression and the Rate Constant

Empirical observations of the rates of chemical processes led to the Law of Mass Action which states that

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



the mathematical formulation of the Mass Action Law is

$$-\frac{d[A]}{dt} \propto [A][B] \text{ Ms}^{-1} \quad \text{Equation 6}$$

and replacing the proportionality sign with a constant of proportionality, *k*, we find

$$-\frac{d[A]}{dt} = k[A][B] \text{ Ms}^{-1} \quad \text{Equation 7}$$

Equation 7 is known as the rate expression, or rate equation, and the proportionality constant is referred to as the rate constant. This equation tells us that since the concentrations of the reactants decrease during the course of the reaction, then the rate (but not the rate constant) decreases with time

elapsed. Thus the rate constant provides the experimenter with a useful measure of the velocity of a reaction, and it is this quantity that we usually seek in a study of chemical kinetics.

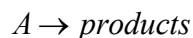
5.4 Order of Reaction

In Equation 7, the concentrations of A and B both appear to the first power, and we say that this reaction is first order in [A] and first order in [B], and that it is second order overall. However the rate expression for the elementary process 3 will be

$$-\frac{d[A]}{dt} = k[A][A] = k[A]^2 \text{ Ms}^{-1} \quad \text{Equation 8}$$

For this reaction it is seen that the concentration of A appears as the 2nd power, and we say that the reaction is second order in [A] and second order overall.

Also, the symbolic elementary process



would be expected to have a rate expression such as

$$-\frac{d[A]}{dt} = k[A] \text{ Ms}^{-1} \quad \text{Equation 9}$$

and the reaction would be said to be first order in [A] (and first order overall). Orders higher than 2 and also fractional and zero orders are found in special cases. These are not considered here because of lack of relevance to the Vernier Flash Photolysis Spectrometer concept.

SPECIAL NOTE: It is important to realize that assignment of order by inspection is only valid for elementary reactions; we cannot do this for stoichiometric equations.

5.5 The Experimental Approach

The data that are obtained in a kinetics experiment could look something like those presented in Figure 5, which shows the change in concentration of reactant A (open circles) and product B (filled circles) as a function of time; M is the generic species (A or B).

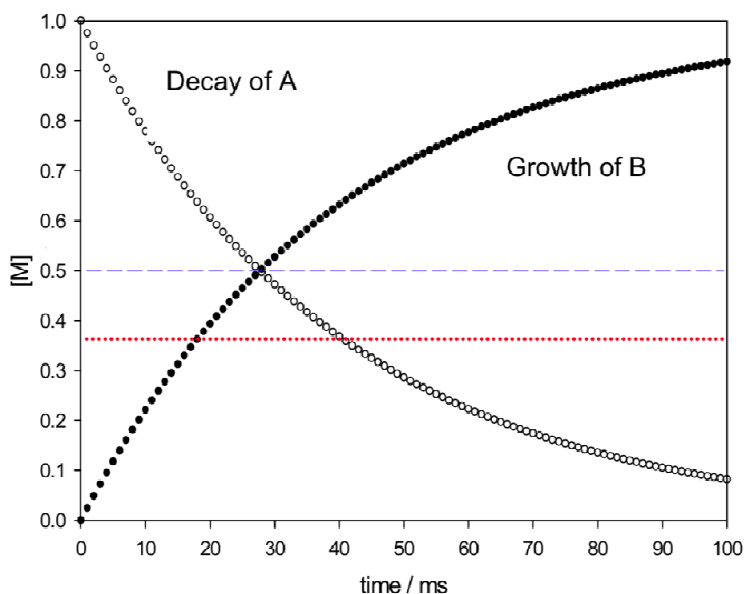
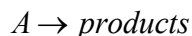


Figure 5: Concentration time profiles of reactant and product

On the plot you can see a pair of horizontal lines, one blue (at 0.5) and one red (at 0.37). The blue one 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 about 37% of the initial concentration of A has been converted to B; this represents the reaction **life time**.

5.6 The Relationships Between Rate Constant, Half Life, and Life Time

First, we shall consider a first order reaction symbolized by



The rate of this reaction is as written in Equation 9 as

$$-\frac{d[A]}{dt} = k[A] \text{ Ms}^{-1}$$

Setting $[A]_0$ as the initial concentration of A, the integrated form of this differential rate equation is given as

$$[A] = [A]_0 \exp(-kt) \quad \text{Equation 10}$$

which shows us that the concentration of A decreases as an exponential function of time. The shape of the decrease of $[A]$ curve in the above Figure 5 is exponential in time. 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 , or ns.

At the half-life point,

$$[A]_{50\%} = 0.5[A]_0 \text{ and } \exp(-kt_{1/2}) = 1/2,$$

whence $t_{1/2} = \ln 2 / k = 0.693 / k$ and a measurement of $t_{1/2}$ leads to the rate constant.

The lifetime of a reaction, usually written as τ , is defined as the inverse of the rate constant, $\tau = 1 / k$.

Thus Equation 10 can be written as

$$[A] = [A]_0 \exp(-t / \tau) \quad \text{Equation 11}$$

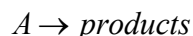
and at $t = \tau$,

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

or, at the life-time point, the concentration of A has fallen to 36.8% (about 37%) of its initial value.

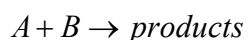
Note that in processes that are first order overall, the half life and the life time are independent of time and initial concentration.

So far we have considered only the reaction that can be written



This implies that we are considering the spontaneous conversion of some compound into another, chemically distinct, species. Such a process could be the spontaneous decay of an electronically excited state of a molecule that has been generated by the absorption of photons (see Section 6.3). 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. Such reactions will show first order kinetics overall.

Now let us consider the elementary process



Clearly this is now bimolecular because it requires a molecule of A and a molecule of B to react together. At first sight, we would expect this process to show second order kinetics overall, but, as we shall see, the order actually observed in an experiment will be determined by the reaction conditions.

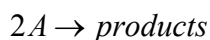
Under conditions where the initial concentrations of A and B are equal, the rate equation is as in Equation 7, viz

$$-\frac{d[A]}{dt} = k[A][B]$$

Integrating this and setting $[A] = [B]$ leads to

$$[A]^{-1} - [A]_0^{-1} = kt \quad \text{Equation 12}$$

This is also the result for the case of the reaction



At the half-time point $[A] = 0.5[A]_0$ then

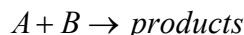
$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} = kt_{1/2}$$

$$\text{or } t_{1/2} = 1/k[A]_0$$

Thus we see that the half time depends on the initial concentration, unlike the first order case.

5.7 Pseudo Order

In the bimolecular elementary process



If the initial concentration of one of the reacting species, say B, is very much higher than that of the other, A, then changes in concentration of B through reaction become negligible compared to those of A, which go from 100% to zero during the course of the reaction. Then the rate equation

$$-\frac{d[A]}{dt} = k[A][B]$$

becomes

$$-\frac{d[A]}{dt} = k[B]_0[A] = k'[A]$$

$$\text{where } k' = k[B]_0$$

Upon integration this becomes

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

This bimolecular process is seen to be first order in A and first order overall. This is referred to as “pseudo-first order” by some practitioners, 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 the behavior will be found to depend linearly on $[B]$.

6 Data Treatment

6.1 Data Acquisition

The Vernier Flash Photolysis Spectrometer Software will produce a file containing two columns of numbers in CSV format. One column (#1) is time, the other (#2) is voltage from the detector. On the computer screen, you will observe the waveform built from these columns. These are your raw data. Once you have acquired the data files you will need to transfer them to the *Logger Pro* or Excel for analysis. For Figure 6, the raw data were imported into *Logger Pro*. In cases where the voltage has been generated from an emission experiment (no probe beam), the kinetic analysis can proceed with the raw data as displayed. In an absorption experiment, further processing is necessary before kinetic analysis can proceed. In an absorption experiment, the detector monitors the intensity of light transmitted by the sample as a function of time prior to, during, and after the firing of the photoflash.

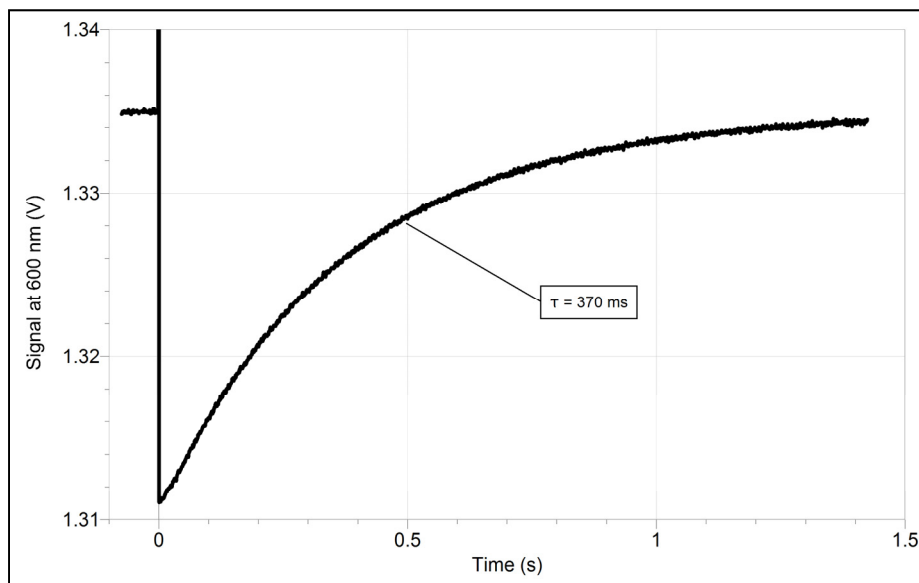


Figure 6: Example of a voltage-time waveform after importing into *Logger Pro*

	Congo red in EtOH			with 1 mM NaOH		Time (s)
	Time (s)	Signal (V)	ΔA	Time (s)	Signal (V)	
1						
2	-0.0751	1.33481	6.18E-005	-0.0751	1.317503	
3	-0.07435	1.334886	3.71E-005	-0.07435	1.317459	-0
4	-0.0736	1.334832	5.47E-005	-0.0736	1.31771	
5	-0.07285	1.334983	5.53E-006	-0.07285	1.317594	-0
6	-0.0721	1.334904	3.12E-005	-0.0721	1.317572	
7	-0.07135	1.334958	1.37E-005	-0.07135	1.317672	-0
8	-0.0706	1.334983	5.53E-006	-0.0706	1.317522	
9	-0.06985	1.335011	-3.58E-006	-0.06985	1.31754	-0
10	-0.0691	1.334964	1.17E-005	-0.0691	1.317569	
11	-0.06835	1.335001	-3.25E-007	-0.06835	1.317459	-0
12	-0.0676	1.334876	4.03E-005	-0.0676	1.317443	
13	-0.06685	1.334889	3.61E-005	-0.06685	1.31749	-0
14	-0.0661	1.335001	-3.25E-007	-0.0661	1.317656	
15	-0.06535	1.33497	9.76E-006	-0.06535	1.317581	-0
16	-0.0646	1.334873	4.13E-005	-0.0646	1.317763	
17	-0.06385	1.334879	3.94E-005	-0.06385	1.317487	-0
18	-0.0631	1.334926	2.41E-005	-0.0631	1.317565	
19	-0.06235	1.335001	-3.25E-007	-0.06235	1.31749	-0
20	-0.0616	1.334942	1.89E-005	-0.0616	1.317509	
21	-0.06085	1.33508	-2.60E-005	-0.06085	1.317559	-0
22	-0.0601	1.334992	2.60E-006	-0.0601	1.317547	
23	-0.05935	1.334961	1.27E-005	-0.05935	1.317443	-0
24	-0.0586	1.334973	8.78E-006	-0.0586	1.317518	
25	-0.05785	1.334911	2.90E-005	-0.05785	1.317556	-0
26	-0.0571	1.334817	5.95E-005	-0.0571	1.317681	
27	-0.05635	1.334936	2.08E-005	-0.05635	1.317653	-0

Figure 7: Time and voltage (raw data) and absorbance (calculated)

Viewing the trace in Figure 6, you see that at the left side (for about 400 ms before time zero) the voltage level is stable with an average of 1.335 V. This corresponds to the intensity of the transmitted beam prior to the firing of the flash lamp. We define this voltage as I_0 . The table in Figure 7 displays a portion of the data plotted in Figure 6. Note that the time goes from negative to positive, as on Figure 6, and that the first 10 voltage values are ~ 1.335 , our I_0 value as shown in Figure 6. During the flash the voltage dips to 0.024 volts and eventually, as seen clearly on Figure 6, it returns to the initial level. This tells us that a species that absorbs light at the observation wavelength is generated by the flash, and thus the resulting solution transmits less of the monitoring beam.

Except under certain conditions, the transmitted intensity is not directly proportional to concentration of the generated transient. We need to process the raw data to obtain absorbance ($A(t)$), which is proportional to concentration through the relationship

$$A(t) = \log \frac{I_0}{I_r(t)} = \epsilon c(t) l \quad \text{Equation 13}$$

where I_r is the transmitted voltage at a given time, ϵ is the molar decadic extinction coefficient of the generated transient, and l is the optical path length. Most spreadsheet software allows you to write a simple transform, with $I_0 = 1.335$ V in the example shown here, to convert the data in column 2 ('Signal') to that in column 3 (' ΔA '). Logger *Pro* allows you to do this by creating a calculated column. After having done this, you can generate and display an absorbance vs. time graph.

6.2 Kinetic Analysis

The light-generated species in the suggested experiments are formed on a time scale much shorter than response time of the Vernier Flash Photolysis Spectrometer (~100 microseconds). Therefore we are only interested in studying the decay part of kinetic profiles. One important thing to consider when analyzing the kinetic profiles acquired with Vernier Flash Photolysis Spectrometer is the scattered excitation light recorded by the photodetector (Figure 8).

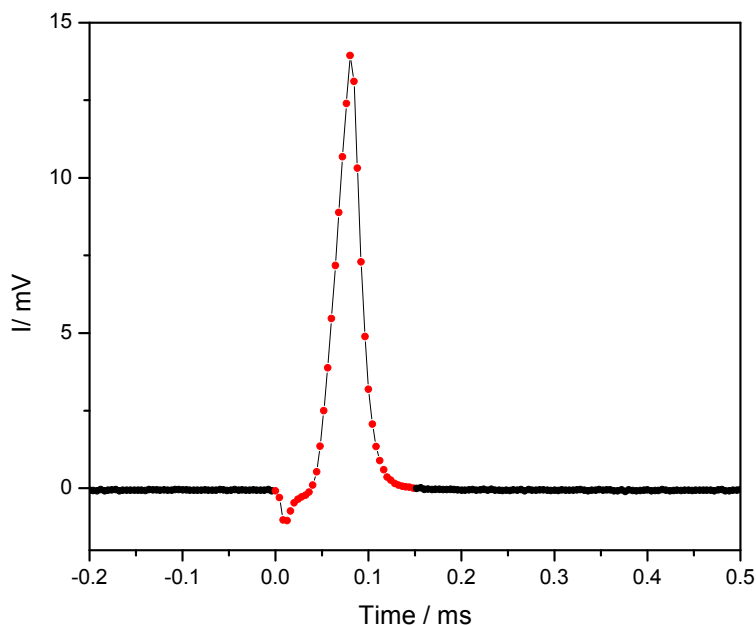


Figure 8: Example of a temporal profile of the scattered excitation light

In Figure 8, it can be seen that the scattered excitation light effect on the kinetic profile diminishes within the first 150 μ s. Therefore it is safe to exclude only the first 150 μ s along with the pre-trigger points (negative time) from the waveform to be analyzed (Figure 9).

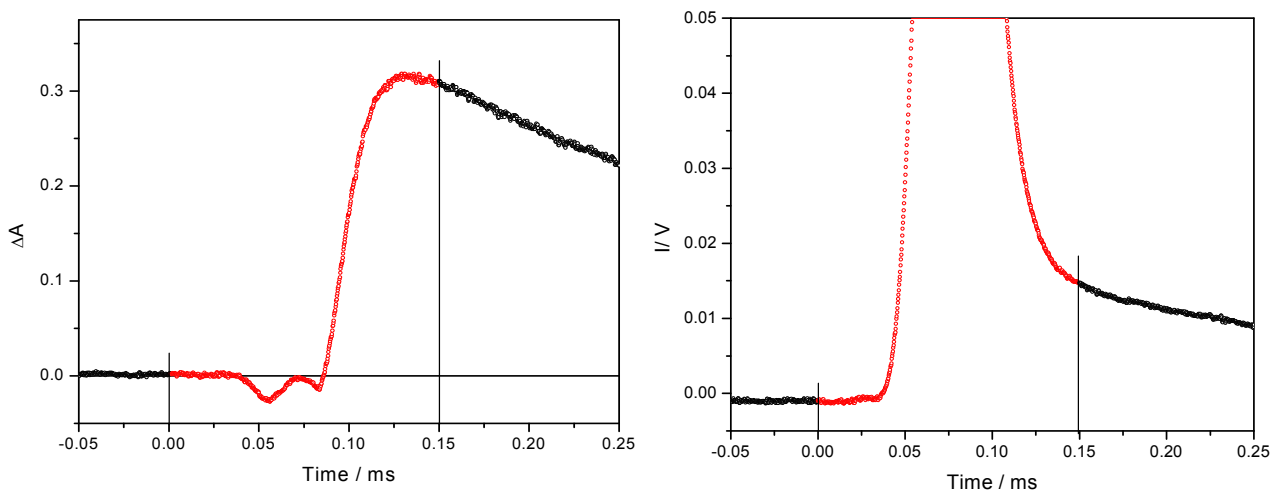


Figure 9: Absorption (left) and emission (right) kinetic profile including the scattered excitation light picked up by the detector

The processed ΔA vs. time data (Figure 10) can now be fitted by the algorithms representing first order and second order behavior. To do this you will need to write transforms derived from Equations 11 and 12, and test the data against the transformed data. In many spreadsheet programs, including *Logger Pro*, the requirement for the fitting transform is to express the absorbance as a function of time with rate constant, initial intensity, and any significant baseline offset as fitting parameters.

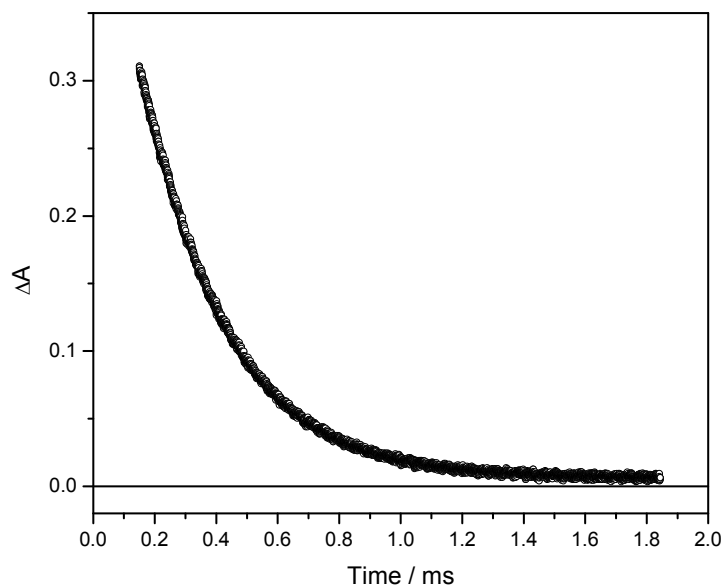


Figure 10: Decay portion of the ΔA -time profile

6.3 The Basics of Photochemistry

Light, as is true for all types of electromagnetic radiation, is a form of energy. A beam of light can be thought of as a train of energetic particles that we call photons. The light to which our eyes are sensitive is in the spectral range of about 350 nm (violet) to 800 nm (red). The amount of energy contained by a photon is in inverse proportion to the wavelength. The energy content of the shorter wavelengths (200–500 nm) is sufficient to break chemical bonds and even the longer wavelengths can have chemical consequences.

Useful relationships are provided in the following equations, where E is the photon energy:

$$E(J) = h(Js) * \nu(s^{-1}) \quad \text{Equation 14}$$

$$E(J) = h(Js) * c(ms^{-1}) / \lambda(m) \quad \text{Equation 15}$$

When a photon comes within close approach of a molecule, if its energy (see Equation 14) is equivalent to that of another state of the molecule, the whole of the photon energy can be given to the molecule with annihilation of the photon. We say that the molecule has absorbed the light, meaning the energy of the photon has become transferred to the molecule. In doing so, the molecule changes its nature—its electronic configuration is altered from that in the ground state—an *excited electronic state* has been generated. This electronic change is usually accompanied by changes to the motions of the nuclei, resulting in vibrational (and torsional) excitations. Since it is the electronic configuration of a molecule that governs its chemical properties, excited electronic states show different chemical properties from their parent ground states. It is the study of the chemical nature of molecules in excited states that is the essence of *photochemistry*.

Molecules that have been promoted to excited states by absorption of photons are intrinsically unstable. They seek to reduce their energy content and reach a lower energy condition. One of the ways to do this is to lose the energy in a radiative process such as fluorescence or phosphorescence. Often, these emissions can be observed, and in such cases, the observation provides us with a means to measure the rates of decay of the excited species. Another way to reduce energy is by chemical transformations in which chemical bonds are broken or formed. These new species may also be unstable and react further to produce another generation of products. The intermediates in the sequence and the eventual final products are likely to absorb light themselves in spectral regions that are different from the parent compound. We can follow the process of the chemical sequence by the use of spectrophotometric methods. Since the life times of the intermediates are often very short (ms, μ s, ns, and less) and their reactions are fast, it is necessary for the methods to be capable of high time resolution. The experiments with the Vernier Flash Photolysis Spectrometer are designed to demonstrate the use of time-resolved techniques in a straightforward and cost-effective way.

7 Flash Photolysis Experiments

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

Excitation wavelength: <500 nm

Observation wavelength: 600 nm

Chemicals needed

- Congo red (CR)
- Sodium hydroxide
- Ethanol, commercial grade for solvent

Background

Congo red (CR) is a diazo dye that is a derivative of azobenzene. As can be seen from the skeletal structure in Figure 11, CR has two identically substituted azobenzene moieties.

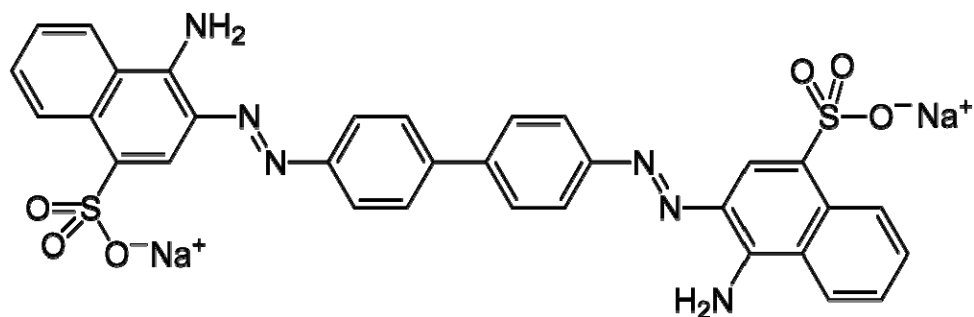


Figure 11: Congo red, MW=696.67

The absorption spectrum of a solution of CR in its trans-ground state (as depicted in Figure 13) in 20% water/ethanol is shown in Figure 12. The dye absorbs strongly throughout the visible range with a maximum near 510 nm. Note that the absorbance is very weak at 600 nm.

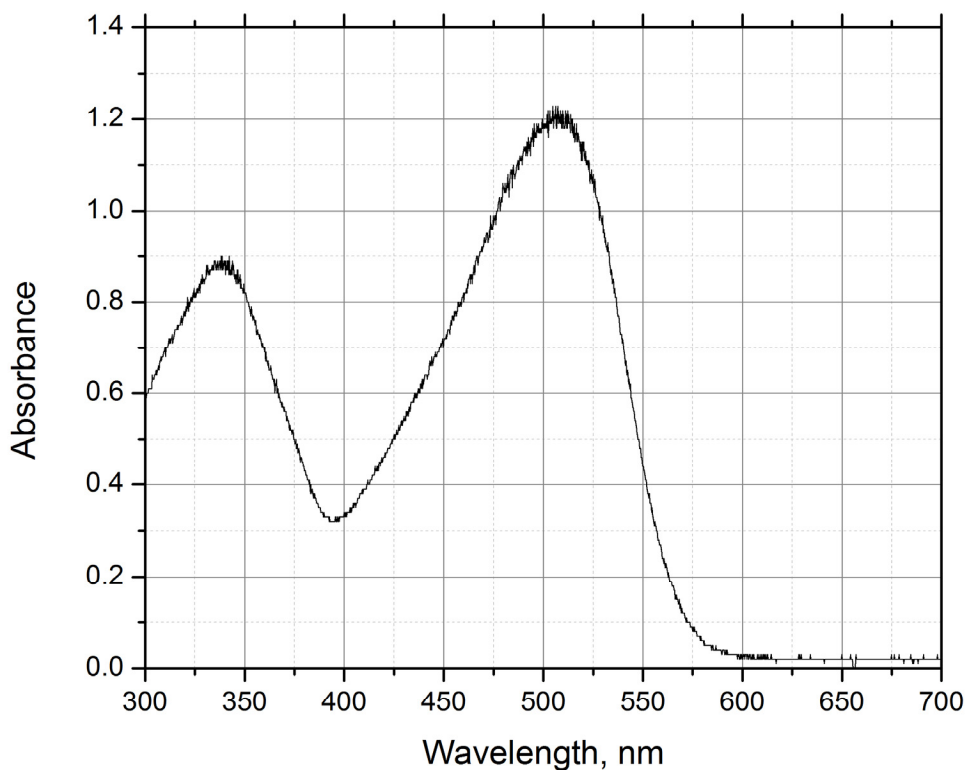


Figure 12: Ground state absorption spectrum of Congo red (*trans conf.*) in 20% water in ethanol

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.

Procedure

Obtain and wear goggles. 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 600 nm band pass filter inserted in front of the detector. If the I_0 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 3 mL to a clean, dry cuvette. Place the cuvette in the sample position and confirm that Averages is set to 1. Then, click the Start button. You should see a time profile similar to that in Figure 10, where the y-axis is Amplitude in mV and the x-axis is in ms.

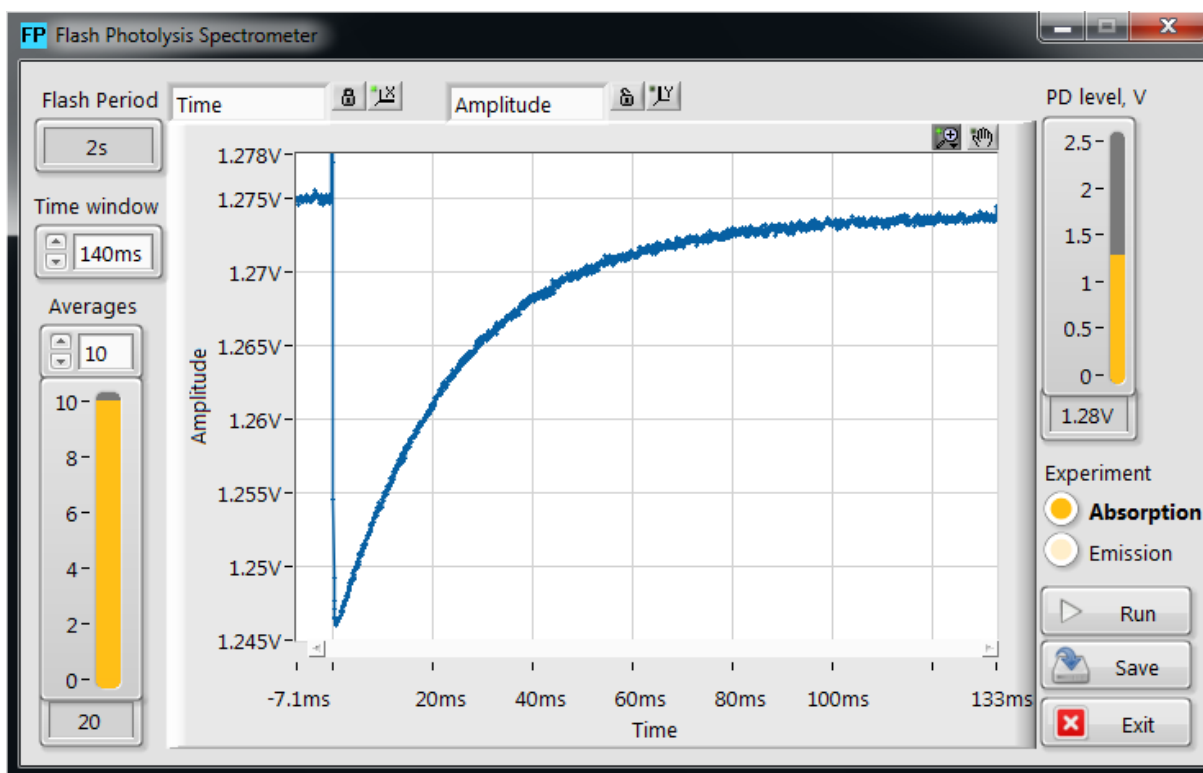


Figure 13: Kinetic profile of Congo red in 20% water in ethanol

In Figure 14, you can see that the flash at $t = 0$ causes a vertical (on these time scales) drop in the mV reading; it drops from ~ 1.275 V prior to the flash to ~ 1.245 V 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 600 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.

The samples that you have examined have been stored as comma-separated values (CSV) files. Import the data into *Logger Pro* to evaluate the rate constants for the cis-trans conversion of CR as a function of $[\text{OH}^-]$. You should find that the decays follow an exponential rate law with a constant that is a linear function of $[\text{OH}^-]$ and the slope of the line (or the best fit of the regression) is the bimolecular rate constant for the catalytic process.

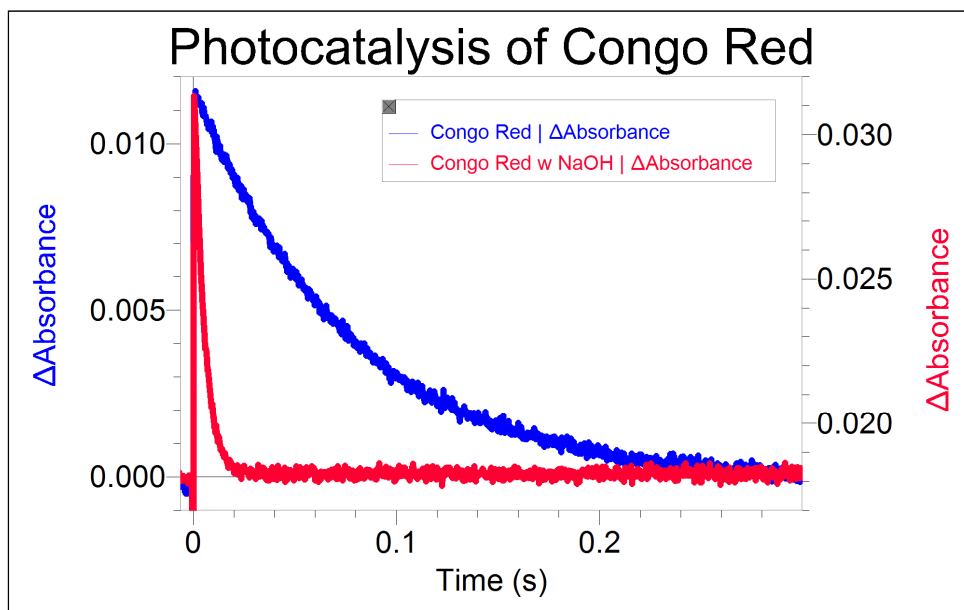


Figure 14: Absorption kinetic profile of Congo red in 20% water in ethanol with 2 mM OH⁻ ions

7.2 Isomerization of Mercury Dithizonate

Excitation wavelength: <500 nm

Observation wavelength: 600 nm

Chemicals needed

- Mercury dithizonate (HgDz)
- Trifluoroacetic acid (TFA)
- Ethanol, commercial grade for solvent

Background

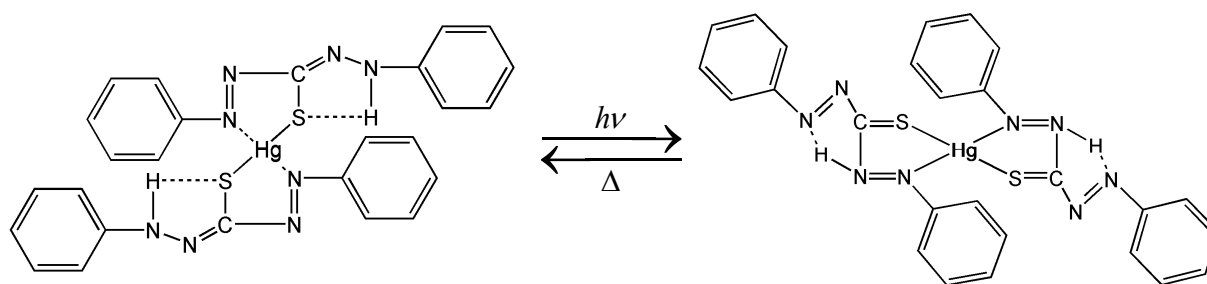


Figure 15: Photoinduced isomerization of mercury dithizonate

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 5.7). 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.

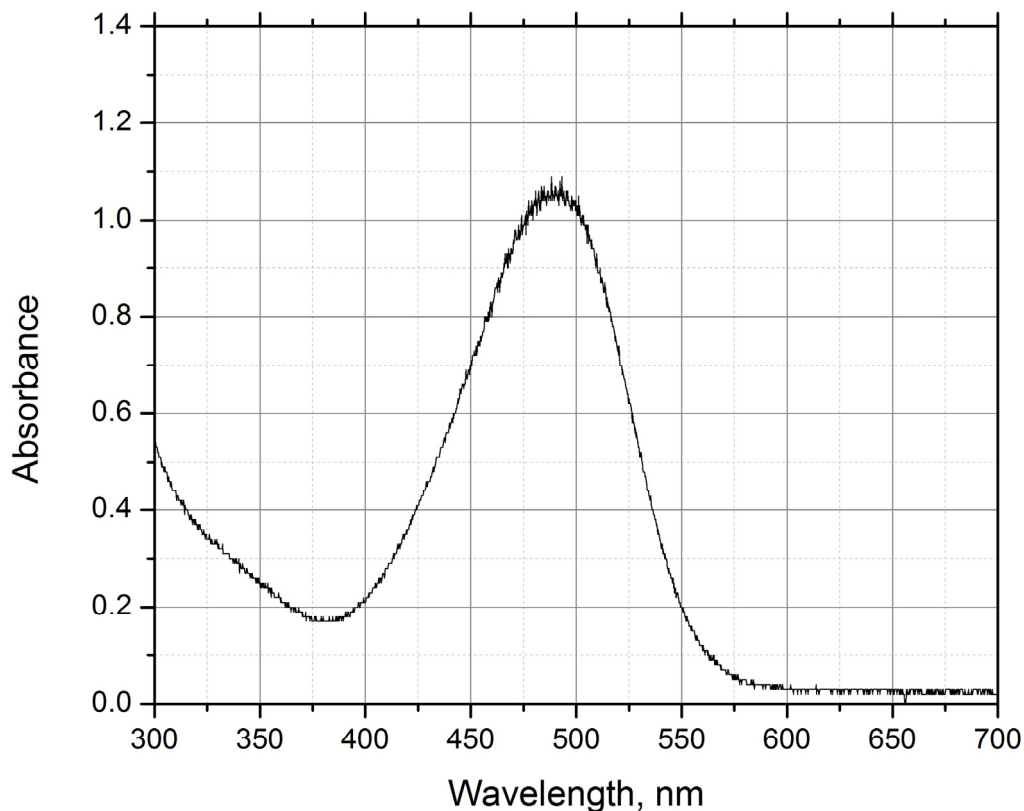


Figure 16: Ground state absorption spectrum of mercury dithizonate (*trans conf.*) in ethanol

Procedure

Obtain and wear goggles. Prepare a 25 mL stock solution of HgDz in ethanol with sufficient solute to provide absorbance of $\sim 1/\text{cm}$ at 500 nm (roughly 10^{-5} M). Prepare 25 mL of 0.01 M stock solution of TFA in ethanol. Prepare at least 5 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 $[\text{TFA}] = 0$ M sample solution in a 10 mm x 25 mm rectangular borosilicate cuvette with all faces polished and proceed to photoexcitation.

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 ($\lambda_{\text{max}} = 605$ nm).

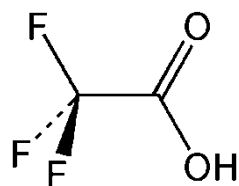


Figure 17: Trifluoroacetic acid (TFA); MW = 114.03

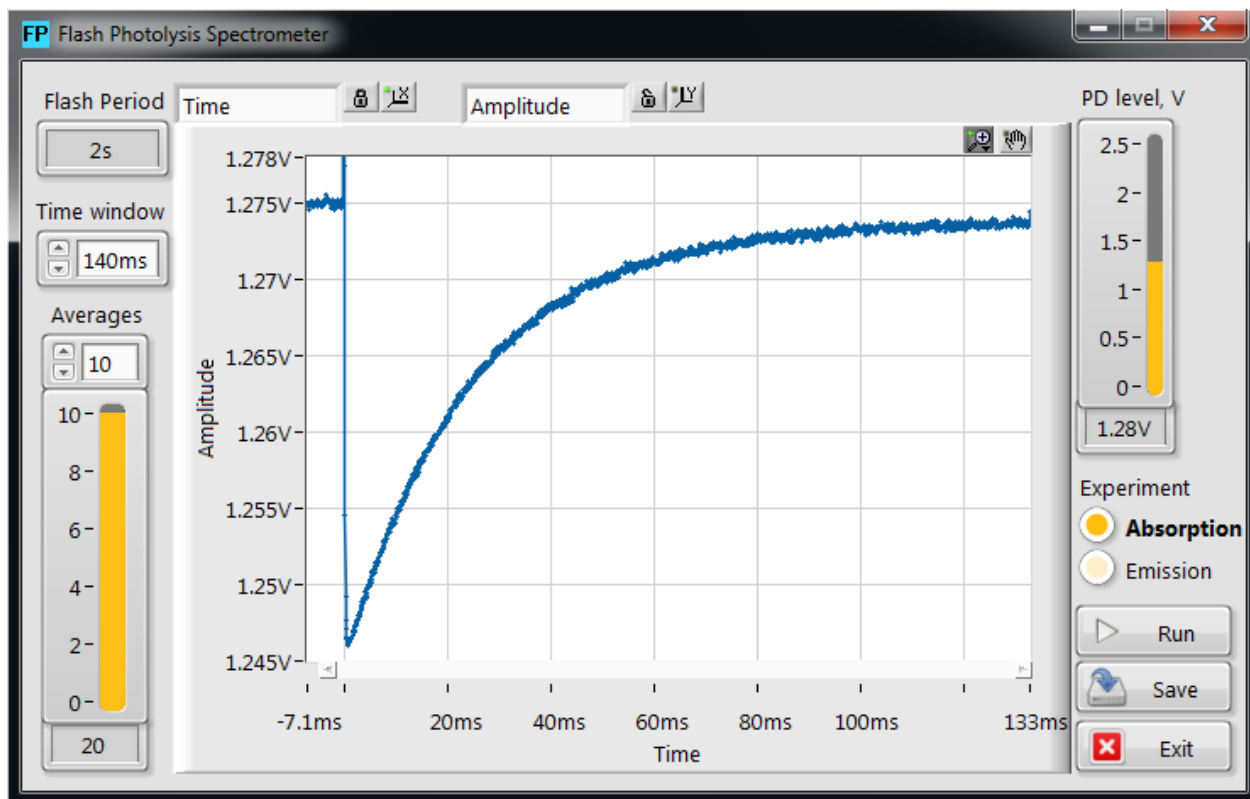


Figure 18: Kinetic profile of mercury dithizonate in ethanol

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

Excitation wavelength: <400 nm

Observation wavelength: 600 nm

Chemicals needed

- 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-2*H*-indole) (6-NO₂-BIPS)
- Toluene

Background¹

6-NO₂-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 19.

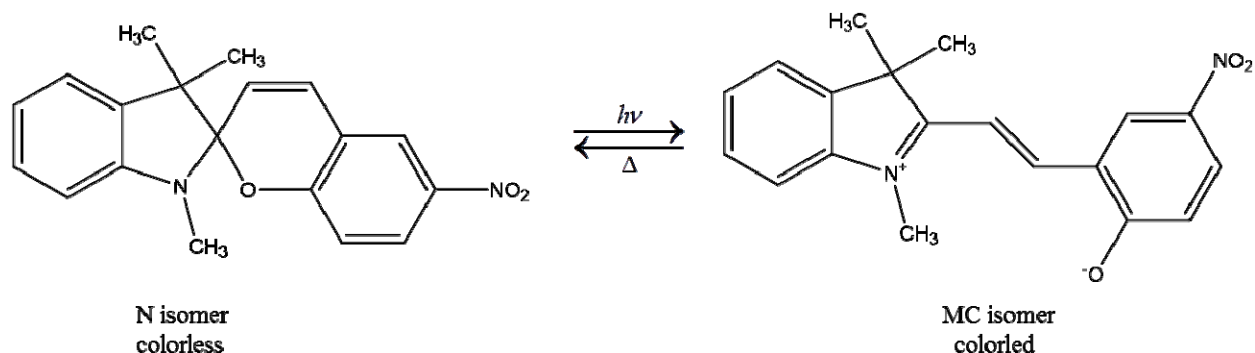


Figure 19: Structure and photochromic reaction of 6-NO₂-BIPS

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

¹ Reference: Piard, Jonathan, "Influence of the Solvent on the Thermal Back Reaction of One Spiropyran" *Journal of Chemical Education*. 2014, **91**, 2105–2111.

this experiment, the kinetics of the back reaction will be measured for a range of temperatures in order to determine the activation energy, E_a , of the back reaction. The activation energy can be determined from the slope of $\ln(\tau)$ as a function of $1/T$ according to the Arrhenius equation:

$$k = \frac{1}{\tau} = Ae^{-\left(\frac{E_a}{RT}\right)}$$

where k is the rate constant, τ is the time constant of the back reaction process, 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 $E_a = 62.5 \text{ kJ mol}^{-1}$.

Procedure

Prepare the solution by taking 0.032 mg of 6-NO₂-BIPS and dissolving it in approximately 20 mL of toluene to give a $5.0 \times 10^{-6} \text{ mol L}^{-1}$ solution. The concentration was chosen such that the absorbance at $\lambda = 300\text{nm}$ in a 1 cm cuvette of the UV absorption peak was 0.5 at room temperature (see Figure 16). 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.

Fill the provided cuvette with 4 ml of the 6-NO₂-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. Remove the cuvette once it is in thermal equilibrium with 5 different temperatures between 30 and 60 °C (Figure 21 shows an example of measurements done at five varying temperatures.) 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. 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 22 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 23 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, E_a , of the back reaction.

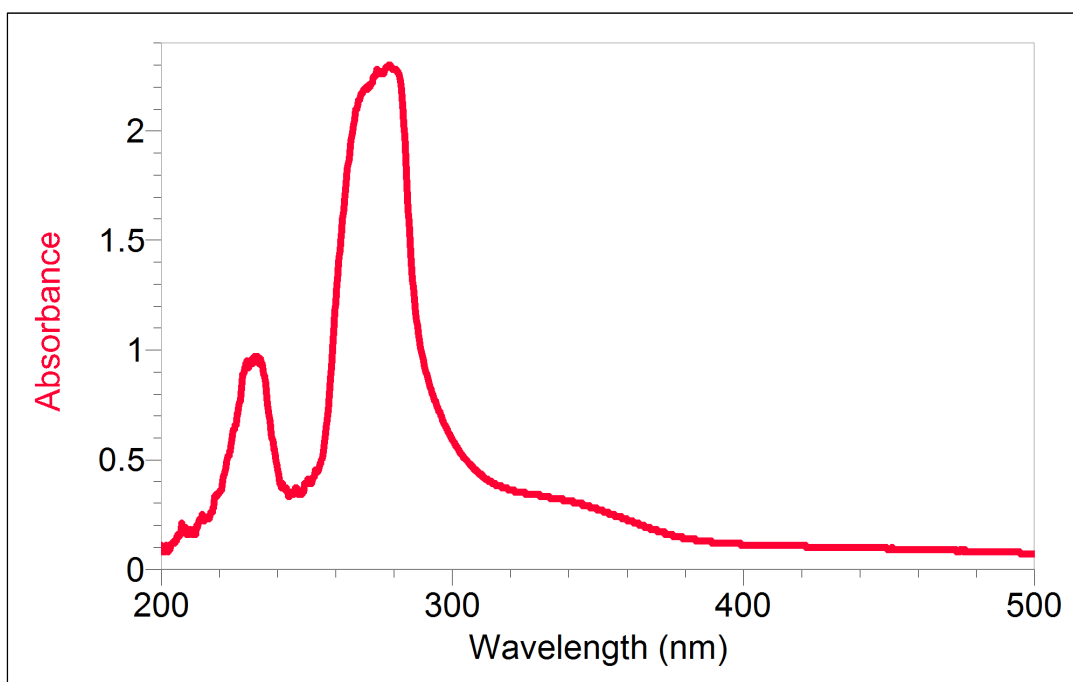


Figure 20: Ground state absorption spectrum of one spiropyran in toluene

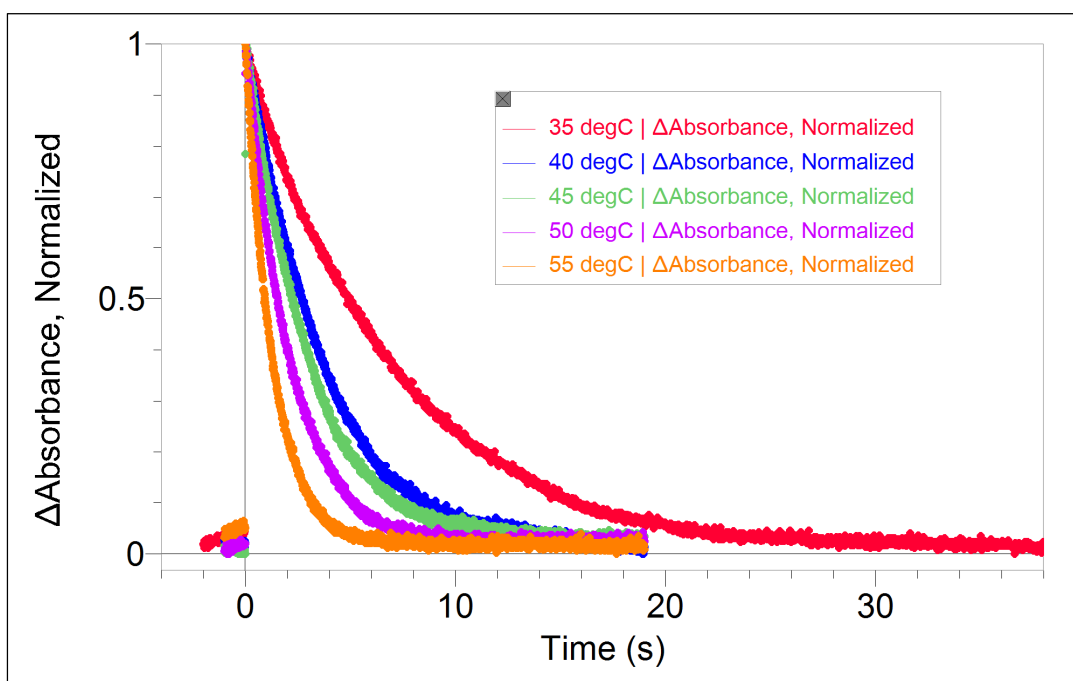


Figure 21: Transient absorption at 600 nm of spiropyran in toluene

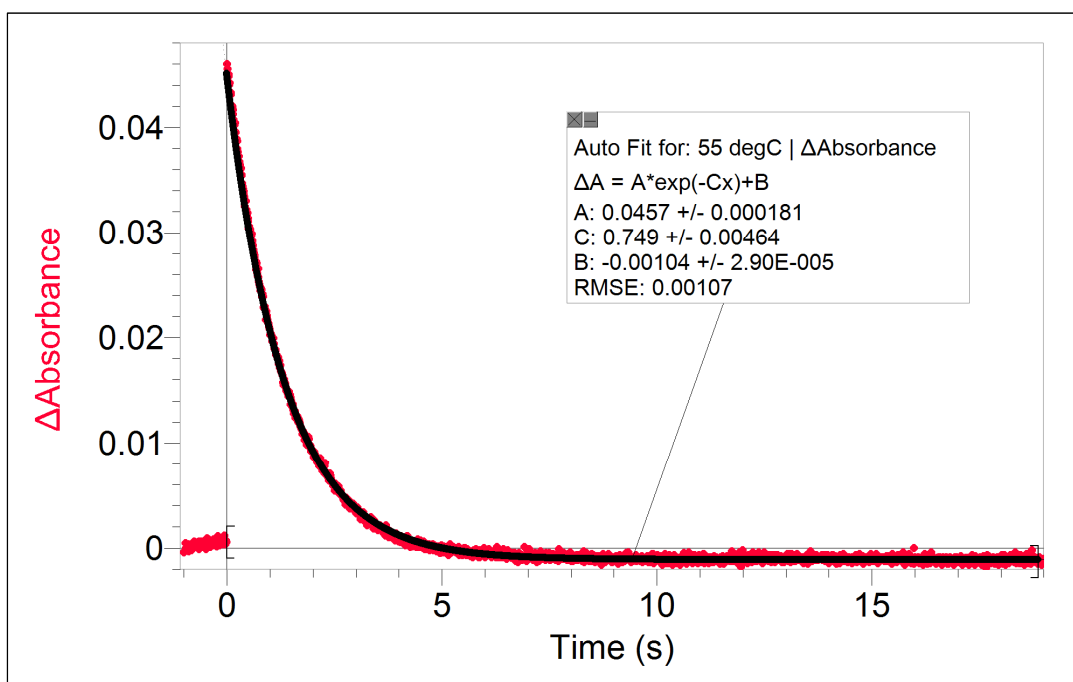


Figure 22: Example decay and exponential fit for 55°C measurement

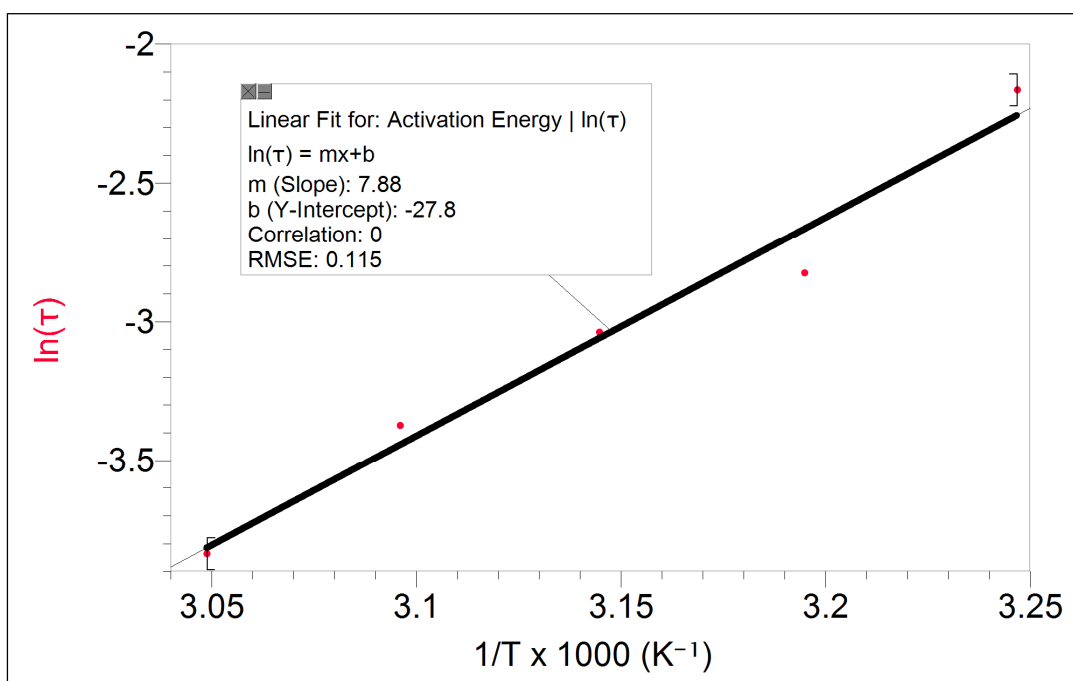


Figure 23: Actual data example of $\ln(\tau)$ as a function of $1000/T$.

8 Appendix

8.1 Spectra of Flash Lamp and White Light LED

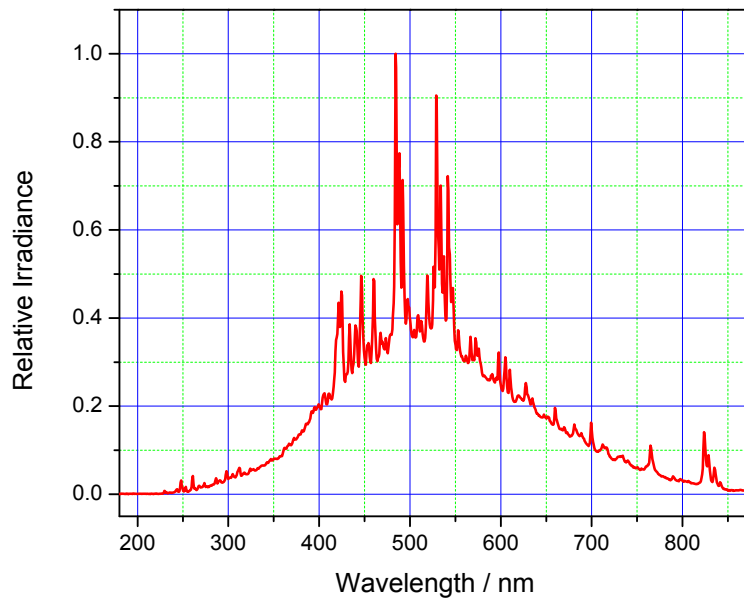


Figure 24: Emission spectrum of xenon flash lamp

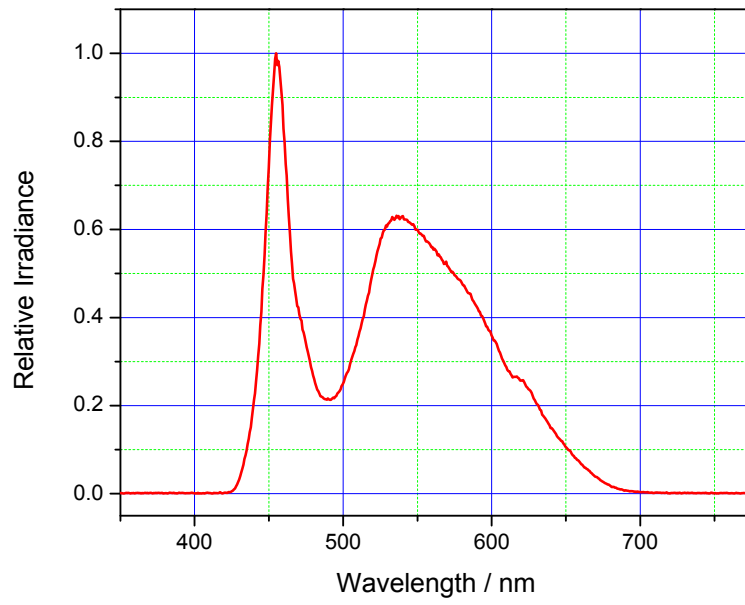


Figure 25: Emission spectrum of white light LED

8.2 Spectra of Optical Filters

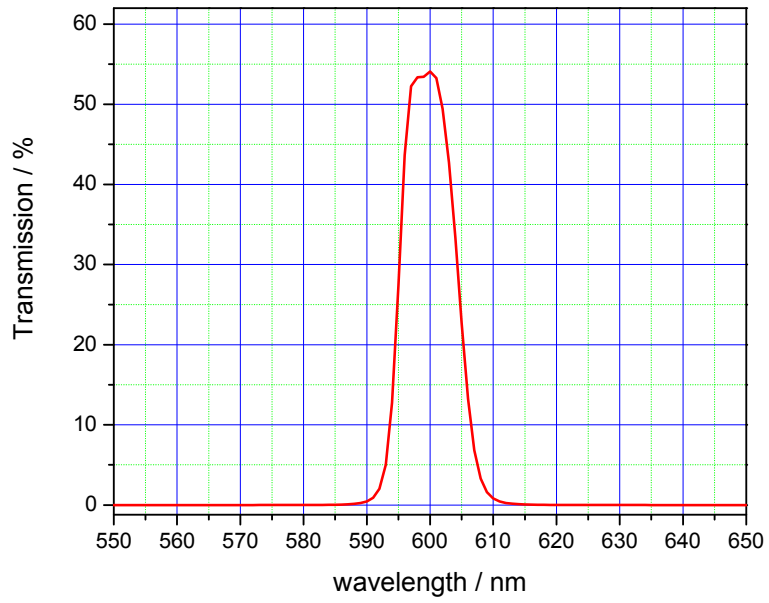


Figure 26: Transmission spectrum of 600 nm bandpass filter