

Laser Flash Photolysis

Purpose: A reactive free radical ketyl is produced from the photochemical reaction of excited state benzophenone with isopropanol. The rate constant for the dimerization of this reactive intermediate is determined as a function of pH.

Pre-lab: Print the instructions for using the Ocean Optics diode array spectrophotometer, which are on the lab Web site.

Introduction¹

Photochemical reactions are very important in many areas chemistry. Examples in atmospheric environmental chemistry include the production of ozone in the stratosphere, the decomposition of chlorofluorocarbons in the stratosphere, and the oxidation of sulfur species with photochemically generated hydroxyl radicals in the troposphere. An example in aqueous environmental chemistry is the speciation of Fe(II) and Fe(III). Photochemistry is very useful in synthetic chemistry. Often photochemically driven reactions provide different products than thermally driven reactions. An example from synthetic chemistry is the use of photochemically generated methylene singlet and triplet intermediates. Absorption of light by molecules produces electronic excited states. Electronically excited molecules can be very reactive. As a consequence, photochemical reactions are often very rapid. Fast reaction techniques are required to study these processes.

Flash Photolysis

Flash photolysis is a commonly used fast reaction technique for photochemical reactions. For reactions with a moderate rate, flash lamps provide sufficient time response. An example of a typical flash lamp is the xenon lamp in a standard camera. For very fast reactions, however, the slow decay time of the light emission from a flash lamp covers the progress of the reaction. In general the pulse width of the light source must be much shorter than the half-time of the chemical reaction. The pulse width of xenon flash lamps, such as those used in photography, is in the microsecond time scale. For faster reactions, specially designed lasers must be used that have pulse widths in the nanosecond range. Using ultra-fast pulsed lasers allows processes in the sub-femtosecond time scale to be studied. In our laser flash-photolysis system the lasers have pulse widths in the 10 nanosecond range, which allows a wide range of photochemical processes to be studied.

One disadvantage of laser driven systems is that ultraviolet lasers have a fixed wavelength. Reactants in photochemical reactions can have a wide variety of absorption wavelengths, some of which may not be accessible to a given laser source. Therefore, several different types of lasers are often necessary to provide coverage of the UV range of common organic and inorganic reactants. Our instrument uses a Nd-YAG laser or an excimer laser.

Nd-YAG is the acronym for a neodymium-yttrium aluminum garnet solid-state laser. Nd-YAG is a synthetic "mineral" that is excited by flash lamps to produce light in the IR region of the spectrum at 1064 nm. To convert the IR light into the visible and then the UV region a special optical trick is used. Certain substances have non-linear optical properties in intense laser irradiation that combines the photons; doubling and then tripling and then quadrupling the photon frequency are possible. Potassium hydrogen phosphate is such a substance. Doubled output is at 532 nm, which is in the green region of the spectrum. Tripled output is at 355 nm and quadrupled

at 266 nm. However, at each successive step the available power is greatly diminished. Output at 355 nm works well for many conjugated aromatic compounds.

Eximer lasers use gas phase chemical reactions to provide highly excited diatomic molecules that emit light. The chemical reaction is initiated by an intense electrical discharge. The reaction used is normally between xenon and either fluorine or chlorine, producing either XeF or XeCl. The diatomic product is produced in a highly excited state with a lifetime in the nanosecond range. In dropping back down to the ground state, light is emitted in a short pulse. XeCl provides laser emission at 308 nm with a 0.3 nm spectral width and a pulse width of about 10 nsec.

Monitoring Fast Reactions

Many different techniques are available for monitoring the progress of photochemical reactions. Conductivity, IR, Raman, mass spectrometry, and chemiluminescence are all used. However, the most commonly used technique is UV/Visible spectrophotometry. A typical UV/Visible spectrometer can be used. However, the signal acquisition must be very fast. The signal from the photodetector is digitized using a very fast digital oscilloscope. This instrument is capable of collecting data at 2 GHz, that is 2×10^9 samples per second. However, the signal response of the detector and the amplifier electronics usually limit the time resolution to a slower sampling rate. Flash photolysis experiments are monitored at a single wavelength. However, it is often desired to determine the UV/Visible absorption spectrum of the products.

There is not time enough to scan the wavelength of the monochromator of a traditional spectrophotometer during the acquisition of each time point. Diode array spectrometers are often used to acquire all the data points in a spectrum at one time. Unfortunately, the time response of diode array detectors is not sufficient for fast pulse studies. However, the experiment can easily be repeated at a series of wavelengths to piece together the spectrum of the products as a function of time. The only requirement is that enough time is allowed between experiments that the solution can return to equilibrium, usually by diffusion of reactants into the optical path of the laser. Of course, each pulse of the laser consumes reactants, so the starting concentrations must be much greater than the amount of reactants consumed during each laser pulse.

Photoreduction of Benzophenone^{1,2,3}

The electronic energy level diagram for a typical molecule is shown in Figure 1. The closely spaced horizontal lines represent the different vibrational states of the given electronic state.

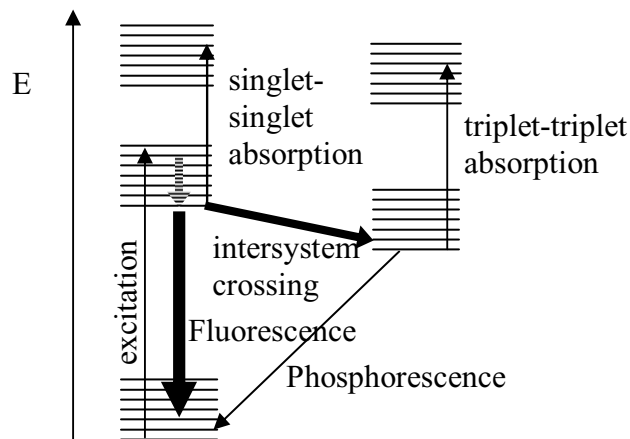


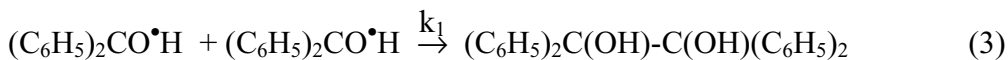
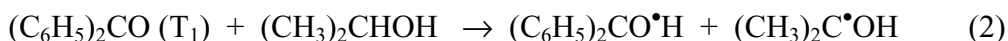
Figure 1. Typical electronic energy level diagram.

One of the goals of this experiment is to construct such a diagram for benzophenone. Benzophenone undergoes rapid intersystem crossing to the triplet state, which has a long half-life. Fluorescence is not observed for benzophenone. Phosphorescence is observed at liquid nitrogen temperature, while only very weak phosphorescence is observed at room-temperature (in water and isooctane). At room temperature, photochemical reactions and nonradiative processes are responsible for the quenching of the phosphorescence.

In this experiment, the laser flash is used to produce excited triplet state benzophenone.



The reaction is done in 50:50 isopropanol-water as a solvent. The α -hydrogen of isopropanol is transferred to the very reactive excited state to produce the protonated benzophenone ketyl $(\text{C}_6\text{H}_5)_2\text{CO}^{\bullet}\text{H}$, which is a free radical. Dimerization of the free radicals gives the reaction product, benzpinacol.

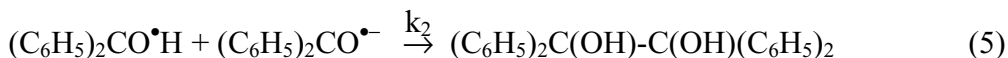


The k_1 rate constant is measured in acidic solution. The other product of the initial proton transfer from isopropanol, $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$, is a protonated acetone ketyl. This free radical may disproportionate to form acetone and isopropyl alcohol, or the free radical may also react with benzophenone to produce another molecule of the protonated benzophenone ketyl $(\text{C}_6\text{H}_5)_2\text{CO}^{\bullet}\text{H}$.

Reaction 3 is monitored by following the disappearance of the absorption of the protonated ketyl $(\text{C}_6\text{H}_5)_2\text{CO}^{\bullet}\text{H}$ at 545 nm. However, the protonated benzophenone ketyl $(\text{C}_6\text{H}_5)_2\text{CO}^{\bullet}\text{H}$ is a weak acid. In basic solution, the protonated ketyl is deprotonated:



At pH values greater than 8 the production of product is through the following reaction rather than reaction 3:



The deprotonated benzophenone ketyl, $(\text{C}_6\text{H}_5)_2\text{CO}^{\bullet-}$, has an absorbance maximum at 630 nm. Kinetics studies in basic solution use 630 nm to follow the time course of the reaction.

Kinetics Studies

Reaction 3 is a second order reaction. The rate law is given by

$$-\frac{d[\text{AH}]}{dt} = k_1 [\text{AH}]^2 \quad (6)$$

where AH is the protonated benzophenone ketyl. Integration of equation 6 gives:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_1 t \quad (7)$$

According to equation 7, for a second-order reaction a plot of $1/[A]$ versus t should yield a straight line. This form is appropriate for this experiment in acidic solution at 545 nm.

In basic solution, reaction 5 is first order in $(C_6H_5)_2CO^{\bullet}H$ and $(C_6H_5)_2CO^{\bullet-}$:

$$-\frac{d[A^{\bullet-}]}{dt} = k_2 [AH][A^{\bullet-}] \quad (8)$$

where $A^{\bullet-}$ is the deprotonated form. The concentration of the deprotonated form can be calculated from the acid dissociation constant for the equilibrium in reaction 4:

$$K_a = \frac{[H^+][A^{\bullet-}]}{[AH]} \quad (9)$$

$$[AH] = \frac{[H^+][A^{\bullet-}]}{K_a} \quad (10)$$

The K_a for the protonated benzophenone ketyl is 6×10^{-10} . If the acid-base reaction is much faster than the photochemical reaction, equation 10 can be substituted into equation 8 giving:

$$-\frac{d[A^{\bullet-}]}{dt} = \frac{k_2 [H^+]}{K_a} [A^{\bullet-}]^2 \quad (11)$$

Defining k_{obs} as

$$k_{obs} = \frac{k_2 [H^+]}{K_a} \quad (12)$$

gives an effective second order rate law:

$$-\frac{d[A^{\bullet-}]}{dt} = k_{obs} [A^{\bullet-}]^2 \quad (13)$$

In basic solution at 630 nm, k_{obs} can be calculated by a plot of $1/[A^{\bullet-}]$ versus t .

The rate constant for reaction 5 can be determined from k_{obs} by a plot of k_{obs} versus pH. From equation 12 and

$$\log k_{obs} = \log(k_2/K_a) + \log [H^+] \quad (14)$$

giving

$$\log k_{obs} = \log(k_2/K_a) - \text{pH} \quad (15)$$

A plot of the log of k_{obs} should give a line with a slope of -1 , Figure 1. The intercept can be used to calculate k_2 . The value of k_1 should not depend on pH, so that in acidic solution the plot should have zero slope.

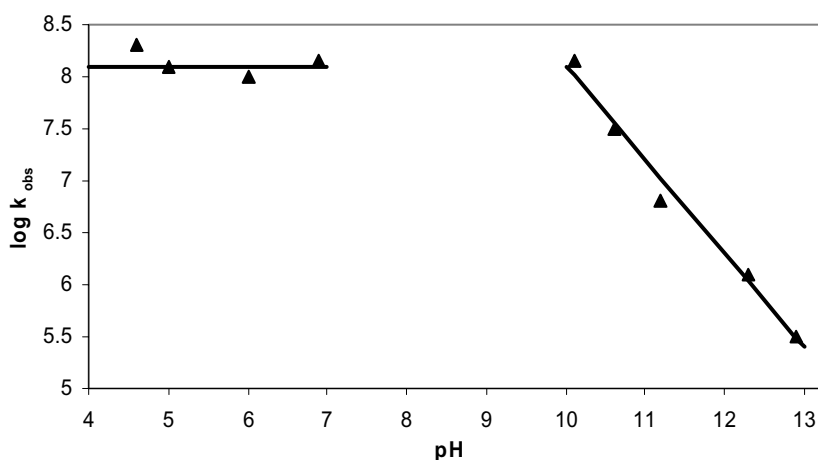


Figure 1. pH dependence of the observed rate constant, as $\log k_{\text{obs}}$ or $\log k_1$.^{1,2}

Absorbance Measurements

The absorbance of a substance is given by the Beer-Lambert Law:

$$A = a b [A] \quad (16)$$

where a is the molar absorption coefficient, b the length of the optical path within the solution, and $[A]$ is the concentrations. (Please note that $[A]$, in brackets, is the concentration of species A , while A , without brackets, is the absorbance of the solution.) If other species that absorb at the same wavelength are in solution that are not involved in the reaction, then a constant background absorbance must be added to find the total absorbance of the solution:

$$A_{\text{tot}} = A + A_{\text{background}} = a b [A] + A_{\text{background}} \quad (17)$$

This equation can be solved to find the concentration of the species of interest:

$$[A] = \frac{A_{\text{tot}} - A_{\text{background}}}{a b} \quad (18)$$

If the molar extinction coefficient is not known the absorbance can be used directly in curve fitting. For a first order reaction:

$$\ln [A] = -k t + \ln [A]_o \quad \text{or} \quad \ln \frac{A_{\text{tot}} - A_{\text{background}}}{a b} = -k t + \ln [A]_o \quad (19)$$

The curve fit can then be done with $\ln(A_{\text{tot}} - A_{\text{background}})$ as the y-variable:

$$\ln (A_{\text{tot}} - A_{\text{background}}) = -k t + \ln [A]_o + \ln (a b) \quad (20)$$

The constants a and b just become part of the intercept for the curve fit:

$$\ln (A_{\text{tot}} - A_{\text{background}}) = -k t + \text{cst} \quad \text{with cst} = \ln [A]_o + \ln (a b) \quad (21)$$

For a second order reaction:

$$\frac{1}{[A]} - \frac{1}{[A]_o} = k t \quad \text{or} \quad \frac{1}{A_{\text{tot}} - A_{\text{background}}} - \frac{1}{A_{\text{tot}}(0) - A_{\text{background}}} = k t \quad (22)$$

Where $A_{\text{tot}}(0)$ is the initial absorbance of the solution. The curve fit can then be done with $1/(A_{\text{tot}} - A_{\text{background}})$ as the y-variable:

$$\frac{1}{A_{\text{tot}} - A_{\text{background}}} = \frac{k}{a b} t + \frac{1}{A_{\text{tot}}(0) - A_{\text{background}}} \quad (23)$$

Unfortunately, the slope does not give the rate constant directly. But the rate constant is proportional to the slope. As long as this proportionality is kept in mind, the slope can be considered as an effective rate constant for comparison from solution to solution.

Procedure

Three separate experiments will be performed and the results combined to get an energy level diagram for benzophenone and the rate constants for either reaction 3 or 5. The experiments are outlined below, with detailed instructions to follow.'

Outline:

1. Each student will determine the rate constant for the reduction of benzophenone at a given pH. The results from the class will be pooled to plot the rates constants as a function of pH.
2. Determine the absorbance spectrum of benzophenone using an Ocean Optics Spectrophotometer.

Detailed Instructions

Prepare a stock solution of about 2.5×10^{-3} M benzophenone in isooctane in a 10-mL volumetric flask. Isooctane is 2,2,4-trimethylpentane. Remember not to stick anything into the stock bottle of isooctane to avoid contamination. Two significant figures are sufficient for the accuracy of the solutions. Prepare a 5.0×10^{-3} M benzophenone in isopropanol (2-propanol) solution. Again be careful not to introduce any contaminants into the solvent stock bottles.

Step 1. Laser Flash Photolysis of Benzophenone

If you are assigned a basic solution, prepare a stock solution of potassium hydroxide in water at the concentration assigned. This concentration will be in the range of 0.1-0.001 M. For neutral or acidic solutions, prepare a buffer using phthalate, acetate, or phosphate using standard concentrations. Lange's Handbook is a good source for buffer concentrations. Use volumetric pipettes and volumetric flasks for this purpose. A stock solution of 0.1 M KOH will be available. The reaction is faster at lower pH so you will need to adjust the sampling rate accordingly. Mix 5 mL of the isopropanol-benzophenone stock solution with 5 mL of your assigned aqueous buffer or potassium hydroxide solution. Degas this sample for at least 30 min in a long-necked

fluorescence cuvette (if available) as instructed below. Follow the attached instructions to determine the rate constant for the reaction.

Step 2. Absorbance Spectrum of Benzophenone in Isooctane.

Determine the absorbance spectrum of the 2.5×10^{-3} M stock benzophenone in isooctane solution. Print and save your spectrum. Use a quartz cuvette. Determine the absorbance spectrum using a HP Diode Array spectrophotometer. Degassing is not necessary. The instructions for using the instrument are on the lab Web site. This high-concentration spectrum is useful for determining the wavelengths for weak transitions. However, this solution will have some transitions with absorbances above 1.5. Such bands will be distorted because spectrophotometers have a maximum absorbance limit near 1.5 to 2. Dilute the 2.5×10^{-3} M stock benzophenone in isooctane solution by a factor of 200 with iso-octane. To do the dilution, use a micropipettor and a 10-mL erlenmeyer flask or beaker. The exact concentrations are not at all critical; you just want to make a solution with a maximum absorbance less than about 1. Remember not to stick anything into the stock bottle of isooctane to avoid contamination. If the absorbances are above 1, dilute accordingly. Print and save your spectrum.

Degassing:

Method 1: Using a long-necked fluorescence cuvette, fill the cuvette to 2/3 full. Insert a Teflon needle through a small rubber septum. Attach the rubber septum to the top of the cuvette stem. Insert a short needle through the septum to allow the sparging gas to escape. Attach a plastic syringe valve to the end of the Teflon needle. Attach the syringe valve to a source of dry nitrogen. Allow the nitrogen to slowly bubble through the solution for 20-30 minutes. Turn off the nitrogen flow, close the syringe valve, and remove the exit needle quickly to avoid reintroduction of oxygen.

Method 2: Using a standard fluorescence cuvette, fill the cuvette to 2/3 full. Cut off the end of a small balloon. Stretch the balloon over the top of the cuvette. Pierce the balloon with two syringe needles. Attach one of the needles to a source of dry nitrogen. Allow the nitrogen to slowly bubble through the solution for 20-30 minutes. Remove the two needles and turn off the nitrogen flow.

Calculations

Part 1: Manual Data Analysis

Using the automated data analysis software ruins all the fun of doing kinetics calculations. In this part of the calculations you will construct a spread sheet to repeat the automatic calculations. Transfer your raw data file into Excel. The first column is the absorbance data and the second column is the time in microseconds. Scan down the absorbance column to find the data point that corresponds to the beginning of the flash (the absorbance will be a maximum). Delete the data up to this point. Make a new column for the time in seconds, beginning at $t=0$, and a column for the corrected absorbance, $A_{\text{tot}} - A_{\text{background}}$. You will be changing the value of $A_{\text{background}}$ a lot, just as you did for the automatic curve fitting, so use a separate cell for this value. Use a trial value for

$A_{\text{background}}$ that is the average (very roughly) of the last 20 or so data points. Scan down the corrected absorbance column and note the cell where the data becomes so noisy that the values drop below zero. Do your data plotting and curve fitting up to this cell.

Use Eq. 21 and 23 to make appropriate plots to verify the order of the reaction. Determine the effective rate constant, $k_1/(a-b)$ or $k_{\text{obs}}/(a-b)$, and compare to the value you determined using the automated software.

Part 2: Using the rate constants for the Data Analysis Software

Make a plot of the log of the rate constant, either k_1 or k_{obs} , versus pH using the pooled data from the class. Calculate k_2 . Report the uncertainty in k_2 from the curve fitting.

Part 3: Energy Level Diagram

Absorbance spectra: Converting wavelengths to cm^{-1} , draw an energy level diagram, to scale, showing all of the detected excited electronic states. Your diagram should be similar to Figure 1. The excited state bands will overlap (that's OK), and all the excited states will be singlets as shown on the left side of the diagram in Figure 1. (You need to study the fluorescence emission spectrum to determine the energies of the triplet states.) Label with an arrow the energy in the excited state that is excited by the laser. To help you draw the diagram, fill in the following table. See the following section for additional hints on how to construct your energy level diagram.

Transition	Start of absorption band		End of absorption band	
	λ	cm^{-1}	λ	cm^{-1}
First excited state				
Second excited state				
Third excited state if present				
Fourth excited state if present				
Fifth excited state if present				
Laser excitation				

Literature Cited

1. "Flash Photolysis Experimental Manual," Applied Photophysics, Ltd., London, England.
2. A. Beckett, G. Porter, *Trans. Faraday Soc.*, **1963**, 59, 2038.
3. G. Porter, F. Wilkinson, *Trans. Faraday Soc.*, **1961**, 57, 1686.

Spectral Deconvolution and Energy level Diagrams

Here is an example that will help you draw the energy level diagram from your spectrum. A typical example spectrum is given in Figure 3.

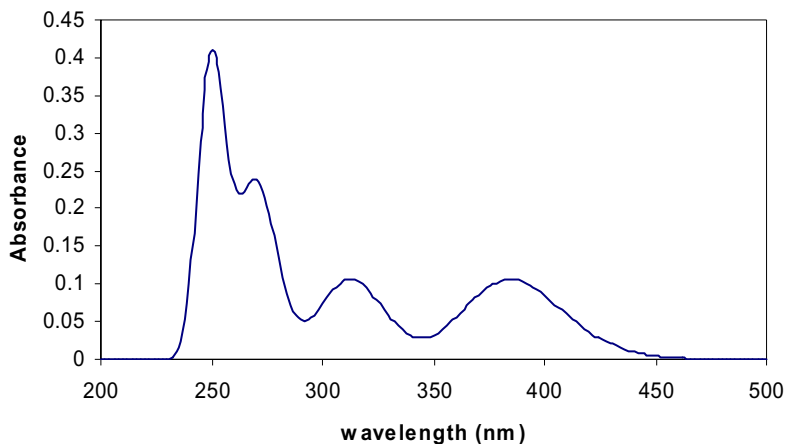


Figure 3. Example spectrum

The first step is to convert the wavelengths to energy units or units like cm^{-1} that are directly proportional to energy, Figure 4. Then each transition is resolved by approximating each transition as a simple Gaussian peak. This process is often done by least squares fitting programs, which in this context is called spectral deconvolution. For the purposes of this lab, the deconvolution process can just be done by eye with a pencil. Often the actual number of transitions is not completely clear, but you do the best you can with the information available. Each transition is a different electronic state, in other words the electrons are in different sets of molecular orbitals.

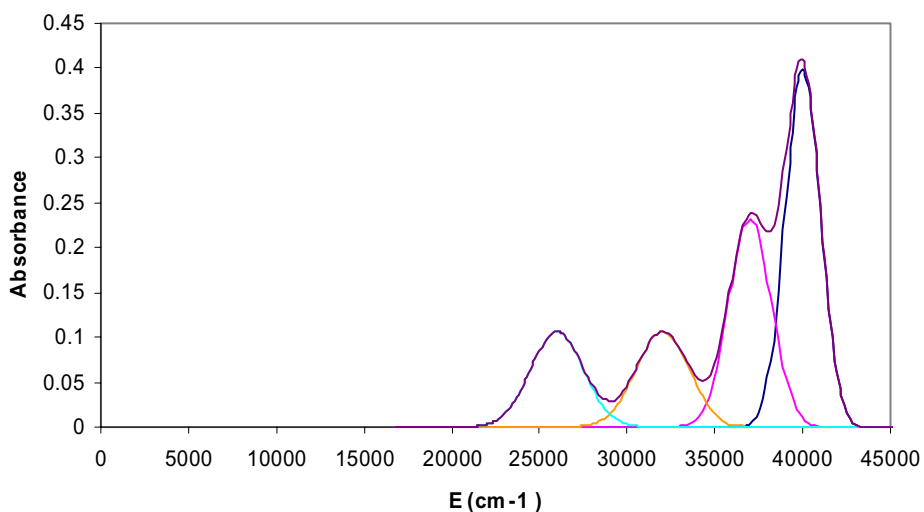


Figure 4. Spectrum with the wavelength axis converted to wavenumbers (cm^{-1}).

The process of drawing the energy level diagram can be illustrated simply by rotating the absorbance spectrum on its side and using the spectral transitions to delineate the energy levels into bands. It is common for the transitions to overlap. Table 1 provides the energies that are needed for this process. The wavelengths or wavenumbers at the start and end of each band are read by eye directly from the deconvoluted spectra, plotted versus either wavelength or wavenumber. The resulting energy level diagram is shown in Figure 5.

Table 1. The start and end of each band are read from the deconvoluted spectrum. The values are approximate and are often read in nm from the original spectrum and converted to wavenumbers.

Transition	Start of absorption band		End of absorption band	
	λ	cm-1	λ	cm-1
First excited state	440	22700	340	29400
Second excited state	350	28600	280	35700
Third excited state	295	33900	250	40000
Fourth excited state	270	37000	235	42600

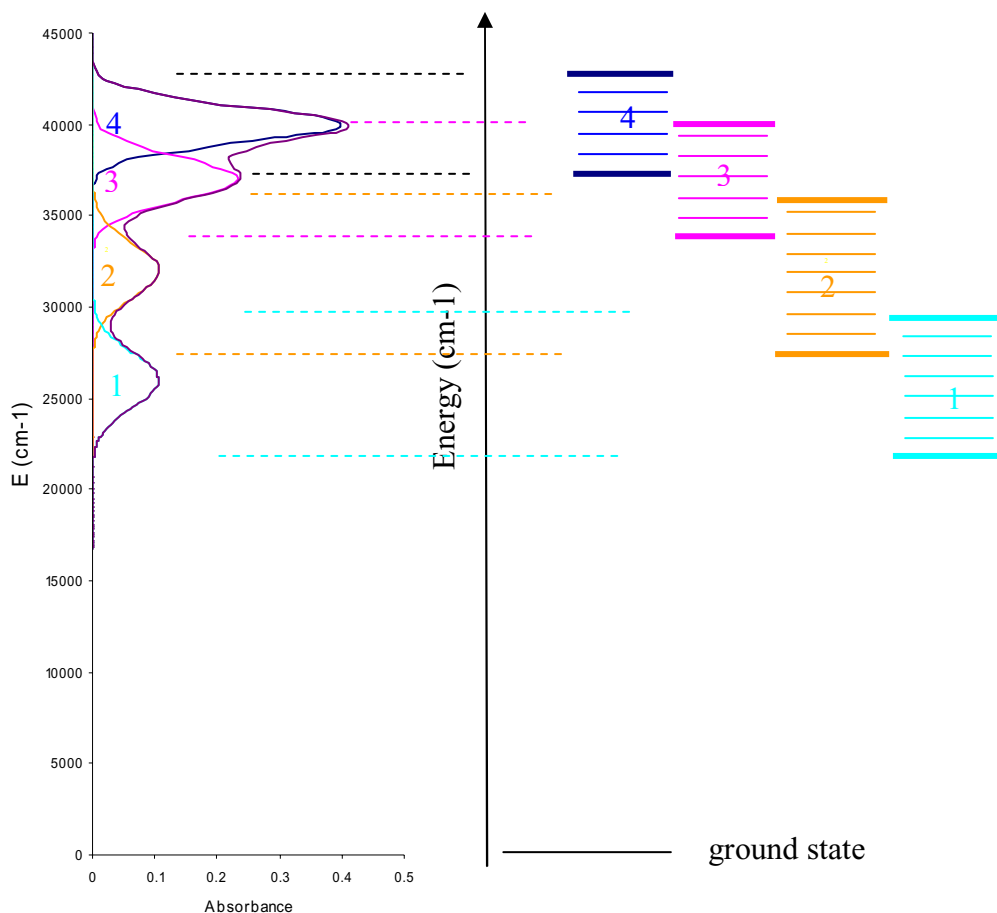


Figure 5. The process for drawing the energy level diagram can be illustrated by picturing the spectrum tilted on its side. The different excited state bands are offset for clarity (they are all singlet states if the ground state is a singlet).

Each electronic transition is really a set of transitions to different vibrational states of the same electronic state. The set of vibrational transitions to a given electronic state form a band of states given by the width of the electronic transition. The vibrational bands are often drawn as a series of lines, Figures 1 and 5. These lines correspond to the different vibrational transitions. For our current purposes, the spacing between the lines is arbitrary since the wavenumber resolution in solution UV/visible spectra is usually not sufficient to discern the vibrational lines.

Complex molecules have many vibrational frequencies. The gas phase high resolution spectrum of benzene is shown in Figure 6 with many well resolved vibrational transitions. In rare circumstances vibrational fine structure can also be resolved in solution absorbance spectra, Figure 7. This appearance depends on the vibrational frequencies, the line width, and the resolution of the spectrophotometer. Only very large vibrational frequencies are typically observable in solution. The vibrational frequency corresponds to the spacing between the closely spaced peaks. It is not uncommon for aromatic hydrocarbons like anthracene to show vibrational fine structure.

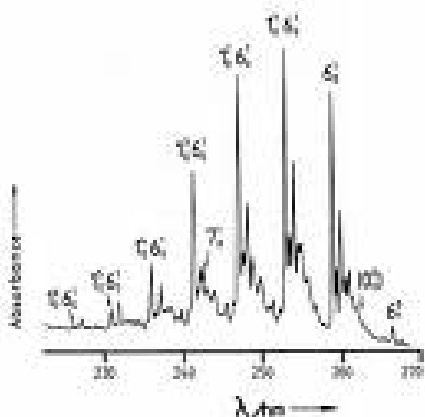


Figure 6(9): Low resolution $\tilde{S}^0 A_{1g} - \tilde{S}^0 A_{1g}$ absorption spectrum of a 1 cm path of benzene vapour above the liquid at room temperature and atmospheric pressure

Figure 6. High resolution gas phase spectrum of benzene. In solution, the spectrum of benzene has a similar appearance to Figure 7, with only the largest vibrational spacings observable. (source: www.ch.ic.ac.uk)

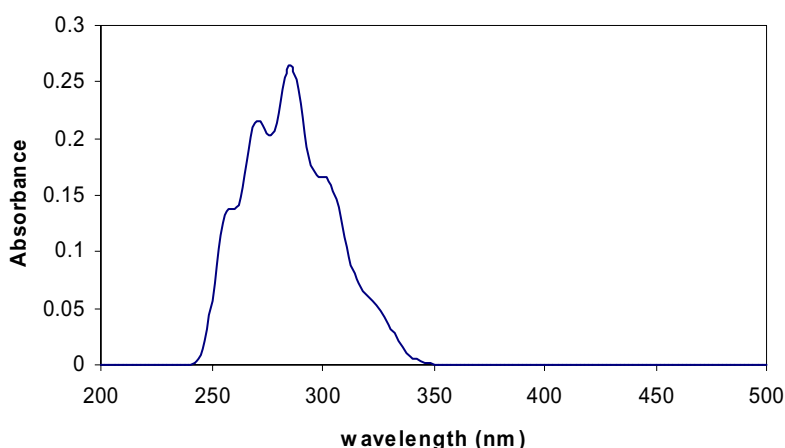


Figure 7. Vibrational fine structure can sometimes be resolved in low resolution UV/Visible absorbance spectra. A single electronic band is shown with poorly resolved vibrational transitions. A complete spectrum would show additional electronic transitions.

However, how can you tell when the “bumps” on your spectra correspond to different electronic transitions as in Figure 3, or vibrational fine structure as in Figure 7? The different vibrational transitions in Figure 7 are equally spaced with a small spacing. For example, a vibrational frequency of 2000 cm^{-1} corresponds to a spacing of about 15 nm for a 300 nm electronic transition. On the other hand, the wavelength difference in absorbance maxima for different electronic states is usually much bigger than these small vibrational spacings.

In illustrating the drawing of an energy level diagram from the absorbance spectrum, the wavelength axis for the absorbance spectrum was first converted to wavenumbers as in Figure 4. This intermediate step is not required, however. Table I contains all the information to construct the energy level diagram. So the conversion of the absorption spectrum from a wavelength to a wavenumber axis is not normally done in actual practice.

Luzchem Laser Flash Photolysis System and Quantel Brilliant R Nd-YAG laser Instructions

System Preparation

Twenty minutes before you wish to use the system, turn on the laser power supply. To do this, turn the key on the power supply consol that sits on the floor. Ten minutes before you wish to begin, turn on the xenon lamp; in any event, make sure to turn on the xenon lamp before you turn on the main system power on the Luzchem LFP consol. To turn on the xenon lamp, use the switch on the upper electronics cabinet (with a black cover) at the back right hand side. The xenon lamp is the light source for the monitoring spectrophotometer. When you are ready to start, turn on the main LFP electronics consol using the toggle switch on the front of the lower electronics consol. The Tektronics digital oscilloscope should turn on automatically at this point. Start up the computer system and from the pull up Start menu choose Mlfp. Click the red OK.

In the Mlfp application, click on the Program Prefs button. Check that the following settings are set:

200	Target I_{zero}
1.00	Transmission at I_{zero} calibration
1200	Monochromator grating
0.75	Fluorescence correction factor
10	Frequency divider
195	Delay(usec)

The target I_{zero} is the desired photodetector reference current for 100% transmittance:

$$\%T = \frac{I}{I_{zero}} 100$$

where I is the photodetector current for the sample. This %T value is then used to calculate the absorbance, $A = 2 - \log \%T$. The Monochromator grating setting is the number of grooves per inch, which is necessary to calculate the dispersion and then the proper angle of the grating to set the wavelength of interest. The flash lamp on the laser is factory set at 10 pulses per second. However, the optical switch on the laser, or Q-switch, may be set to allow output from the laser at a smaller rate. The Frequency divider setting of 10 means that the Q-switch allows only one in ten of these pulses to be output from the laser. In other words, with the Frequency divider at 10, the pulse rate from the laser is one pulse per second in free-running mode. The reason the flash lamp needs to run at a fixed rate is for temperature and therefore output power stability. Click on Return to return to the main LFP window. In the next dialog, click on Continue if you didn't make any changes in the preferences.

Starting the Laser

Never use a high-power laser without active supervision of a Faculty member

One flash is all that is necessary to permanently and completely destroy an eye

Turn On the laser warning sign. This switch is on the wall, next to the switch for the room lights. Close the room door so that others will not walk into the room by accident while the laser

is flashing. Pull the safety curtain across the door. Make sure that you are using the required special goggles for UV light protection at the chosen wavelength of the laser.

If you are unsure if you are using the proper goggles, do not turn on the laser. Regular lab safety goggles are never sufficient. Make sure that you have checked with a Faculty member, and that they know that you are currently using the laser.

Failure to follow laser safety procedures will mean immediate revocation of your ability to use any high-powered laser at Colby and a zero on the corresponding laboratory report. Laser safety goggles must be worn at all times in the laser lab.

Place your sample in the cuvette holder and make sure that the sample compartment light shield is closed. You should not look at the sample when the laser is in operation. This laser is a **Class 4 laser**, which means that even stray reflections can cause an eye injury. You don't need to look directly into the beam to get a severe eye injury. Direct contact of the beam with clothing or your skin will cause a very painful burn.

On the laser keypad, use the arrow key to select Configuration 2. Then press the Ready button and then the Start button for the Flash lamp. You will hear the flash lamp circuitry fire the lamp at 10 pulses per second. A notice will be displayed that the user must wait for 8 seconds to allow the system to stabilize. After eight seconds, press the Q-switch Start button.

Choosing the Data Acquisition Settings

In the main MLFP control panel, check the following settings. These settings are a good starting point for benzophenone in 50:50 isopropanol-water with the potassium hydroxide concentration at 0.01 M.

Monochromator λ	630 nm (or 545 nm for neutral or acidic)
Number of shots	3
Volts per division	5 mv
Time per division	4 ms
Bandwidth	20 MHz
Number of points	625
Laser wavelength	355 nm
Target Izero	200
Izero lower limit	100
Izero high limit	450
Acquisition delay	0
Fluorescence factor	0.75

Neither Correction button should be depressed.

The monochromator λ is the wavelength that you want to monitor. If you are doing a run at $\text{pH} < 9$, you will want this set to 535 nm instead. The number of shots determines the number of runs that will be averaged together to gain better signal-to-noise. This setting can be set to 1 if the single-shot signal-to-noise is very good. The Volts per division is the vertical scale sensitivity of the digital oscilloscope. If the signal trace is too small, you should set the Volts per division to a smaller number, and visa-versa if the kinetics traces starts off the top of the screen. The Time per division needs to be set for the experiment at hand. You need to acquire a time course for the

reaction that fills the majority of the oscilloscope screen, horizontally. However, the time course should get back to the baseline by the end of the oscilloscope trace.

The Bandwidth setting determines the effective rise time of the electronics amplifiers and the oscilloscope. For slow reactions, the 20 MHz setting is sufficient and provides considerable improvement in signal-to-noise through filtering. However, for fast transients, the Bandwidth must be set to a higher value. If the Bandwidth is not set properly, the resulting rate constants will be too small. For rough guidance, the inverse of the bandwidth should be at least five times shorter than the half-time of the reaction you are studying. For example at 20MHz,

$$\text{Rise time} \approx 1/20 \times 10^6 \text{ sec}^{-1} = 5 \times 10^{-6} \text{ sec} = 5 \mu\text{sec}$$

So a 20 MHz bandwidth should suffice for half-times of 25 μsec or longer. A bandwidth of 150 MHz gives a usable range of half-times down to 50 nsec. The best way to tell if you have set the Bandwidth properly is to do a run at a higher bandwidth and compare the resulting rate constant. The values won't match exactly, since the run at higher bandwidth will be much more noisy. However, the result at higher bandwidth should be at worst within a factor of two or three.

The Number of points is the number of time data points that will be collected during each transient. The Laser wavelength setting is not used by the Kinetics or Curve Fitting program, the setting is just included in the data label for later information.

The Target I_{zero} setting is specified on the Program preferences page. The I_{zero} low and high limits are used as a check on data quality. If the measured I_{zero} is outside of the specified range, the data trace will be rejected. This problem may occur if the photomultiplier gain is set incorrectly, or if the solution in the cuvette has changed to cause a big shift in background absorbance. If the PMT Control mode is set to Software and if a data trace is rejected, the program will automatically adjust the gain. If the PMT Control mode is set to Manual, you must change the photomultiplier gain by hand to ensure that the I_{zero} falls within the limits that you chose.

The photomultiplier gain is set by adjusting the photomultiplier voltage. In Software mode, the program will make this setting for you. However, for wavelengths around 600 nm, the sensitivity of the system is very low. In Software mode, the maximum voltage is 850 V. For use around 600 nm, the photomultiplier voltage must be set manually to 1000 V. Press the Ctrl and F12 function keys on the computer keyboard. Click Yes in the next warning dialog box. A dialog box will appear where you can set the voltage to 1000 V. Back in the main screen, set the PMT Control mode to Manual. Pull the red slider on the PMT voltage to 1000.

Running and Optimizing the Data Acquisition Settings

To do a run, click on the Go button. After the number of shots that you specified have been acquired a dialog box will appear asking if you want to take any more. If the signal-to-noise is sufficient, click on No. In the file dialog box, select the PChem folder and save your file with a unique name that includes your initials. Inspect the data. The time course should fill the screen both horizontally and vertically, with the signal attaining the baseline at the end of the trace. To adjust the vertical presentation, choose a new Volts per division. To adjust the horizontal presentation, choose a new Time per division. You may want to gently shake the cuvette to ensure that the concentrations of the reactants in the optical path are at equilibrium. To rerun the experiment, just click Go again. If the time course looks good you can proceed to the Curve Fitting application.

Data Analysis

Click on the Fitting button. In the File dialog box, navigate to your file, click on the file name, and click Open. In the data analysis window, you need to make three settings. Use the mouse to drag the yellow vertical line to the start of your transient. Use the mouse to drag the red vertical line to a point where the transient has almost attained the baseline. Use the mouse to drag the blue horizontal line to the long-time tail of your transient. Select the appropriate kinetics fit using the menu at the bottom-right of the window. For the disappearance of the benzophenone ketyl radical, you should choose 2nd order. For fluorescence or phosphorescence studies you would choose 1st order. Click on the "Try This Fit" button. If the resulting curve fit closely approximates your transient, click on the Continue button. If the curve fit does not work out well, you need to redo the three settings to help guide the initial guesses for the non-linear curve-fitting algorithm. For 2nd order reactions, you may find that the baseline setting is the most sensitive. Long lived background luminescence, index of refraction changes due to heating, depletion of several species or the absorbance of products of the reaction may make the apparent baseline different from the true baseline. Moving the blue baseline setting lower than the apparent baseline may be necessary to get a good 2nd order fit for the initial part of the kinetics time-course.

After finishing the curve fitting, a window will be displayed summarizing the results of the experiment. Record the rate constant, the life-time (if displayed), and the uncertainty in the fit results. The uncertainty for the rate constant is labeled as "SDV k".

Notice also the `STRAIGHT` line plot in the lower right-hand corner. This plot shows the results of a conventional fit of either $\ln [A]$ or $1/[A]$ versus time. This plot should obviously show minimal deviation from a straight line if the correct kinetic order has been chosen. For calculating the rate constant, however, the non-linear fit is better, since non-linear least squares curve fitting better accounts for the effective of noise. Print your results and Quit.

Turning off the Instrument

Press the Q-switch Stop button on the laser keypad. Press the Flash lamp Stop button. Turn off the laser power supply, using the key. Turn off the Laser warning sign. Turn off the xenon lamp power supply. Turn off the LFP console. You don't need to log out or shut down the computer. Make sure the Laser lab door is locked when you leave. Inform your supervising faculty member that you have completed your work.

It is very important that you turn on and off the laser warning sign appropriately. If the sign is left on all the time, students will tend to ignore it. If the sign is never turned on, obviously, people unfamiliar with the laboratory may inadvertently be hurt.

Turn off the laser warning sign when the laser is off