

Appendix for Chapter 2

Appendix 2.1 Calculation of the sensitivity

In section 2.1, we wrote an expression for the absorption coefficient (2.8a). We rewrite the equation here in terms of absorbance as:

$$A = \sigma NL' = \frac{L}{c} \left(\frac{1}{\tau_{abs}} - \frac{1}{\tau_{vac}} \right) = \frac{L}{c} \times \frac{\Delta\tau}{\tau_{vac}} \times \frac{1}{\tau_{abs}} \quad (2.8 \text{ b})$$

At the beginning of our experiments, we collect ten ringdown signals and calculate both the standard deviation and average of the ringdown constants. Depending on the alignment of the optical cavity, values for $\Delta\tau/\tau$ range from 0.1-0.7 %. The distance between the CRD mirrors is determined by the length of the ringdown cell ($L = 40\text{-}70$ cm); the reflectivity of our mirrors (R) range from 0.9995-0.9999%. A diagram of the ringdown cells and a list of CRD mirrors are provided in Appendix 2.3.2.

Suppose $L = 70$ cm, $\Delta\tau/\tau = 0.4\%$, and $1/\tau = 67000$ (corresponding to a ringdown time of 15 μs). The sensitivity or minimum absorbance is:

$$\begin{aligned} A &= \frac{70}{3 \times 10^{10}} \times \frac{0.4}{100} \times 67000 = 6.3 \times 10^{-7} \text{ minimum absorbance/pass} \quad (\text{A-2.1}) \\ &= 0.63 \text{ ppm/pass} \end{aligned}$$

Sensitivity is often reported as the value for which the observed absorption has a signal-to-noise ratio (S/N) = 3 or 5. The calculated A_{min} is multiplied by the desired S/N accordingly.

The sensitivity can also be reported to take into account the length of the sample cell and the number of ringdown signals averaged for data analysis:

$$\frac{A}{L} = 8.9 \times 10^{-9} \text{ min absorbance/cm}$$

$$\frac{A}{L} \times \sqrt{\frac{\# \text{ avg ringdowns}}{\text{repetition rate of laser}}} = \frac{A}{L} \times \sqrt{\frac{10}{5 \text{ Hz}}} = 1.26 \times 10^{-8} \text{ min absorbance/cm/Hz}^{\frac{1}{2}}$$

(A-2.2 a-b)

Thus, special attention should be given to the units for comparison of sensitivities of different apparatuses.

Appendix 2.2 Photos and alignment of the Raman cell

This section provides instructions on how to align the Raman cell with a HeNe laser. The HeNe light is guided into the Raman cell through the entrance port and is reflected back and forth in the cell n number of times before exiting the cell. Alignment is easier once the components of the Raman cell are understood.

The Raman cell in our apparatus consists of a 2-m stainless steel tube with mirror/flange attachments at each end. Blueprints of the Raman cell have been published.¹ A basic diagram of the Raman cell is shown in Fig. A-2.1. The viewport consists of a window connected to a metal piece (copper gasket seal). The metal piece lowers a contraption with two small mirrors into the Raman cell. The contraption is high enough that it does not interfere with the passing light beam. The mirrors are angled such that the entrance and exit of the Raman cell can be viewed from inside the cell.

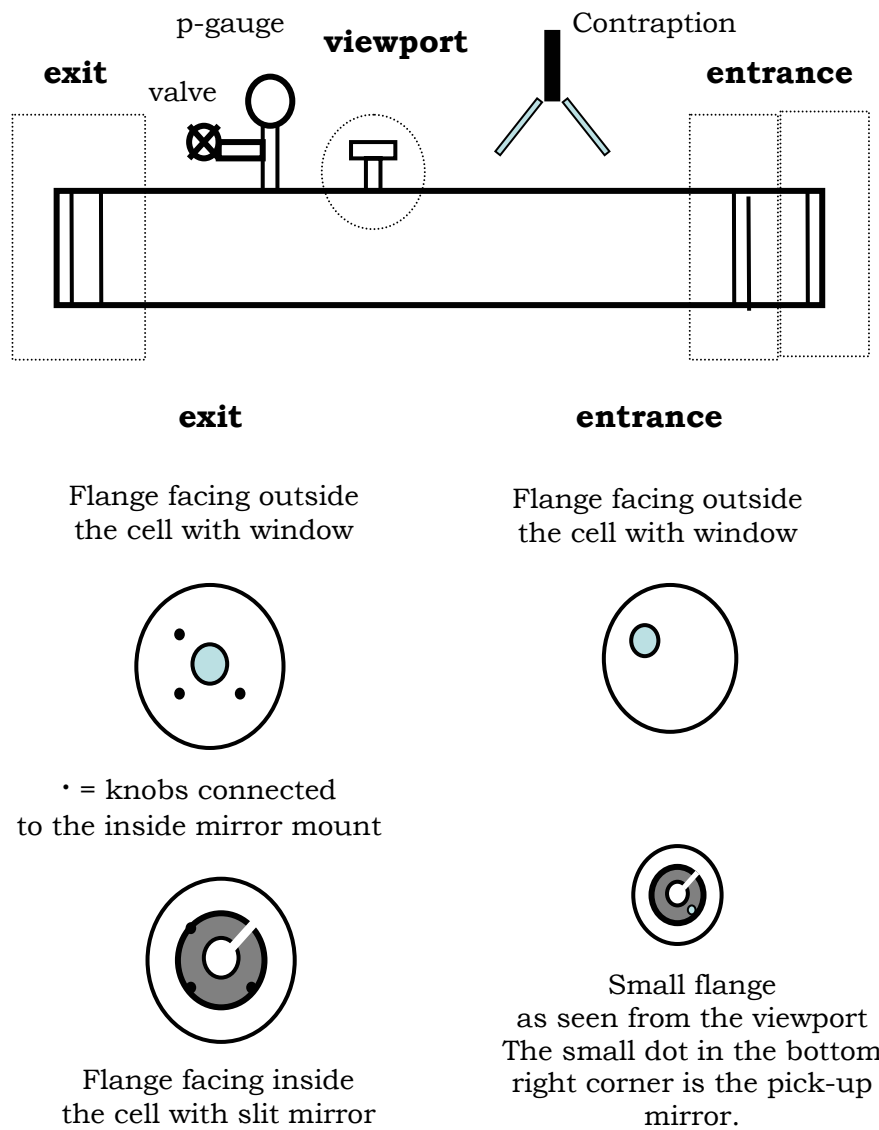


Figure A-2.1 Diagram of the 2-m stainless steel Raman cell used in the laboratory. Individual components are highlighted, including the exit and entrance flanges and the viewport.

The metal flange that bolts to the exit side of the cell (o-ring seal) has attachments on both sides of the flange. A small flange holding a BK7 window (o-ring seal) is attached to the center of the flange surface facing outside the cell. A mirror mount holding a modified 3-inch diameter silver-coated mirror is attached to the flange surface facing inside the cell.

The knobs to the mirror mount are bored through the flange such that adjustments can be made from outside the cell.

The metal flange that bolts to the entrance side of the cell (o-ring seal) has a BK7 window (o-ring seal) located in the upper left corner of the flange surface facing outside the cell. Removal of the flange reveals a small flange inside the cell, directly attached to the stainless steel tube by four long screws. A tiny mirror mount for the "pick-up" mirror is located at the bottom of the screws. A larger mirror mount, supporting a 3-inch slit silver-coated mirror identical to the one on the exit flange, is on small flange itself (Fig. A-2.2).

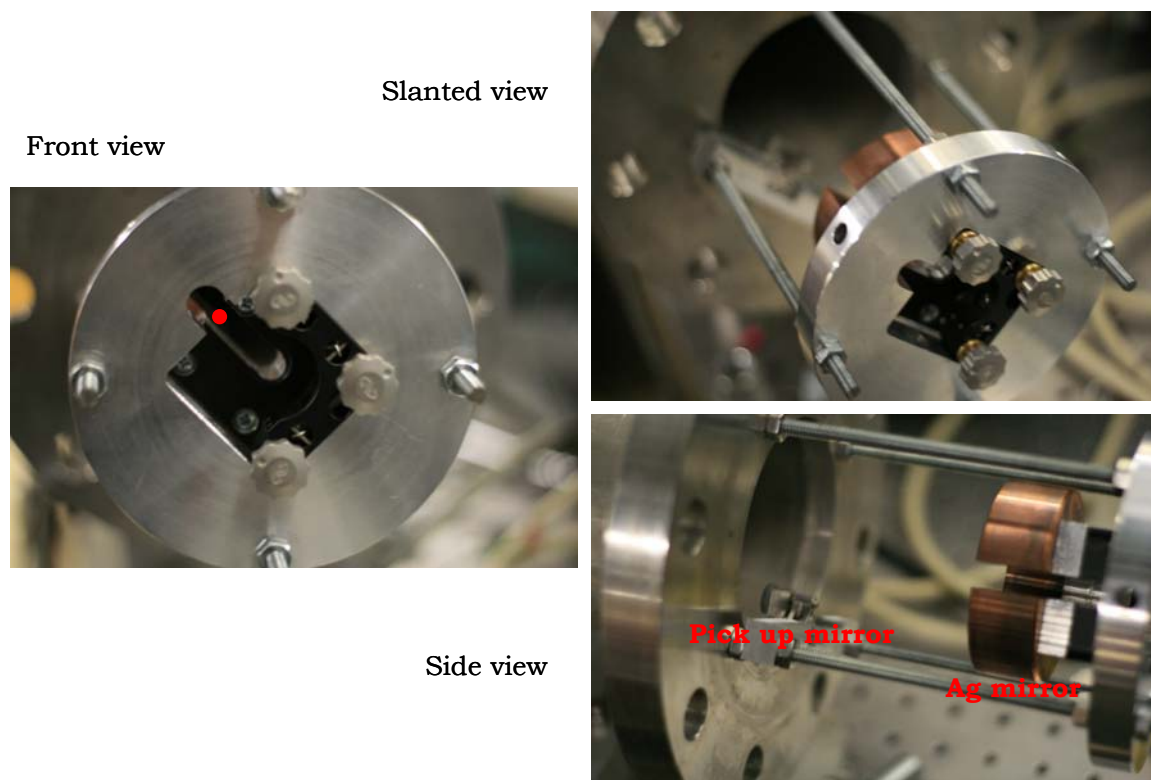


Figure A-2.2. Photos of the small flange on the entrance side of the Raman cell. The photo of the front view of the small flange shows a circular shape cutout. One would assume that the cutout is centered with the window on the entrance flange. Closer examination however shows that there is a slight misalignment of the two pieces and the “center” of the window is the marked red spot in the photograph.

Alignment of the Raman cell is recommended for two people. The procedure is as follows:

1. Remove the entrance and exit flanges. Use two mirrors to guide a HeNe laser beam directly through the cell, preferably traveling through the marked spot (Fig. A-2.2). As the cell is 2-m long, the HeNe beam tends to hit the inner walls. Vertical alignment of the HeNe beam is recommended before horizontal alignment. The two mirrors will be called the "HeNe mirrors" in the following instructions.
2. Re-attach the exit flange. To minimize leaks, grease the o-rings with Apiezon L. From the viewport, check to see whether the beam is hitting the silver mirror mounted to the exit flange. Adjust the HeNe mirrors accordingly. Arrange two irises to mark the HeNe beam pathway. From this point on, do NOT touch the HeNe mirrors.
3. There are two mirrors mounted on the entrance side, the pick-up mirror and the silver coated mirror. The Raman cell can be aligned like a Herriot cell for $n(\text{odd})$ passes. The beam is reflected by the silver-coated mirrors on the exit and entrance sides until the last pass, in which the beam hits the pick up mirror and is guided outside the Raman cell through a window. Difficulty in the alignment differs greatly on the choice of configuration.

For conversion to second order Stokes, a 3-pass configuration is sufficient. Simply, adjust the mirror mount on the exit flange such that the HeNe beam is directed towards the pick-up mirror. This can be observed through the viewport. For a 3-pass configuration, the silver-coated mirror on the entrance port never has to be touched.

4. Adjust the pick-up mirror mount such that the beam is traveling through the center of the window on the exit side. The HeNe beam should be visible outside the Raman cell. Put the entrance flange back on the Raman cell.

5. Once HeNe alignment is completed, pump down the cell and do a leak test of the Raman cell. Water from the air can contaminate the cell. If the cell is not leaking, fill the cell with hydrogen gas (~200 psi). Replace the HeNe laser with the laser of interest and align with the same irises. Minor adjustments may have to be made, but Stokes and anti-Stokes outputs, in addition to the origin laser beam (Rayleigh-scattered light), should be observed from the exit of the Raman cell.

In the CRD experiments, visible light from the dye laser is injected into the Raman cell. The conversion efficiency of the visible light to NIR light is inversely proportional to the diameter of the beam. The silver mirrors are however easily damaged by focused light. Telescope lens (- and + focal lens) can be arranged such that the laser beam is large entering the cell but focuses in the middle of the cell. While the alignment can be done with a HeNe laser, re-check the focal point with the dye laser output before directing the dye laser light into the cell.

Appendix 2.3 Details of the pulsed CRDS apparatus


A-2.3.1 Overview of the Labview programs


Our data collection and analysis programs are written in Labview version 8.5. The current programs are outlined here. Codes for the programs can be found on the Okumura acquisition computer, under folder "Noyes 105 Data Programs."

The main data collection program is called "mainprogram_excimer2.vi." The front panel is shown in Fig. A-2.3. Each Boolean option opens a subprogram that carries out the selected function. The "Diagnostic" option opens the "readboard.vi" subprogram to collect and analyze ringdown signals. The "Move the dye laser" option opens the "movedyelaser2_dr.vi" subprogram to change the wavelength of the dye laser and thus the wavelength of the NIR light used in the CRDS experiments. The "Excimer on and off" option controls firing of the excimer laser. Finally, the "Scan region" option utilizes all listed subprograms to collect CRD spectra.


The "readboard.vi" subprogram works directly with the digitizer board (Gage CompuScope 14100) installed on the acquisition computer to collect decay signals from the detector of our CRDS apparatus. The subprogram serves as an interface to the digital oscilloscope such that the voltage scale and sampling rate can be adjusted. Data collection begins when the program receives a trigger TTL pulse from delay generator (BNC 555). The delay generator controls firing of all lasers in the CRDS apparatus (Appendix 2.3.5). The ringdown signal is collected and fit to an exponential decay. Both the ringdown constant and its inverse are reported. The number of acquisitions can also be adjusted in the subprogram.

Main Data Collection Program for CRDS Noyes 105


Diagnostics
 For diagnostics (i.e. check alignment at one wavelength point), click on the button and then run the main program. The diagnostics subprogram will open. Follow the instructions. Before closing the diagnostics program, go to Edit and select: Make Current Values Default in this subprogram. Save and exit the subprogram.

Move the dye laser
 The current position of the dye laser is: nm wavenumber first Stokes second Stokes
 642.5 15564.2 11409.2 7254.202

To move the dye laser, click on the button and then run the main program. The moving dye laser subprogram will open. Follow the instructions. Before closing the moving subprogram, go to Edit and select: Make Current Values Default in this subprogram. Save and exit the subprogram. Note: to refresh the current dye laser position in the main program, just run the main program without highlighting any of the buttons.

Excimer on and off
 Click on the button on the left to turn the excimer on. (Make sure the delay generators are turned on: The delay generator SRS DG536 should be set to external trigger control and channel CD output should be set to Variable Mode). status code
 **Remember you can adjust the external trigger from the YAG to the excimer DDG
 Delay time (s) between trigger from YAG output and firing the excimer
 0
 Enter the GPIB address of SRS DG536 Trigger: enter 0-50 Ohm, 1-High impedance Pulse width (s)
 15 0 0.00015

(make sure to click run button after each choice selection)

Scan region
 If you are ready to scan the region, enter the following information and click on the button before running the main program. Make sure to first run the Diagnostics program as this subprogram controls the board settings. Note: Once the scanning begins, a plot of the spectrum will appear below. A second screen (the diagnostics) will open so the user can observe fits to the ringdown while collecting data.


Start Position of Scan (nm) wavenumber first Stokes second Stokes
 633.0900 15564.2 11409.2 7254.202


End Position of Scan (nm) wavenumber 2 first Stokes 2 second Stokes 2
 627.5300 15820.53 11665.53 7510.532

steps in each scan step size motor stepsize (nm)
 200 0.000159601

The scan will automatically be saved to the C:\CRDS folder. (with header: #avg ringdowns, time interval, and any notes you would like to save)

Notes to be saved to the datascan text file
 N205 + O3


Click if you want to save the ringdowns during your scan


If you need to stop once scanning has begun, click here: 2


index of refraction (air)
 1.00029

index of refraction (air)
 1.00029

Now suppose you want to take a scan and have the excimer on and off during that one scan. Then turn off the excimer button on the top and click the following button.

Excimer scan on/off
 if we feel that the response rate for the excimer to turn on is slow, we can wait a bit, before we start collecting data (ms)
 0

after we turn the excimer off, we might want to wait again, before we start collecting data (ms)
 0

Figure A-2.3. A snapshot of the front panel of the main data collection program "mainprogram_excimer2.vi". Spectra with the excimer on and off are plotted below the panel, such that the user can observe the spectra as data is collected

The subprogram "movedyelaser2_dr.vi" controls the position of the dye laser through DAQ card (NI USB-6008). The DAQ card sends a TTL pulse to a step motor connected to the grating of the dye laser. The step motor rotates counter or counterclockwise, according to high or low voltage input from the computer. Given two dye laser positions (nm), the subprogram calculates how many TTL pulses need to be sent to the step motor to adjust the grating of the dye laser accordingly. Details of the

circuit connecting the DAQ card to the dye laser step motor are available in Appendix 2.3.4.

Collection of CRD spectra is more involved. Before any scan, the settings in "readboard.vi" should be selected and saved in the file. The gage board settings cannot be changed once the scan is started. To collect a spectrum with the excimer continuously on, the front panel options "scan region" and the "excimer on and off" should be highlighted simultaneously. To collect a spectrum with the excimer off, the "excimer on and off" button should not be highlighted. The beginning and end wavelengths of the scan and the step size of the scan are manually entered in the front panel. The wavelengths refer to the position of the dye laser. Thus, for scans in the NIR region, the appropriate wavelengths in the visible must be selected. For example, to scan the 7000-7100 cm^{-1} range, the difference in indexes of refraction for air and vacuum must be taken into account (Appendix 2.3.3) before calculating the corresponding wavelengths of light in the visible, 653.4-648.7 nm.

$$\begin{aligned}
 &7000 - 7100 \text{ cm}^{-1} \xrightarrow{\text{correct index of refraction}} 6995 - 7105 \text{ cm}^{-1} \\
 &\frac{10^7}{6995 + 2 * 4155(\text{Stokes})} = 653.4 \text{ nm} \\
 &\frac{10^7}{7105 + 2 * 4155(\text{Stokes})} = 648.7 \text{ nm}
 \end{aligned}
 \tag{A-2.3}$$

The step size of the scan refers to the number of TTL pulses that are sent to the step motor before data collection. The "motor stepsize" on the front panel provides the effective nm-wavelength scale for one TTL pulse.

The program automatically saves a text file with all the wavelengths and inverse ringdown time constants at each scanning point. The averaged

ringdown signals for each scanning point can also be saved in separate text files by selecting "Click if you want to save the ringdowns during your scan" on the front panel. Once all the options have been selected or entered, the main program can be run. The program will ask the user to check the gage board settings and scanning range before initiating the scan.

The main program calls the "movedyelaser2_dr.vi" to move the position of the dye laser to the starting wavelength of the scan. The "readboard.vi" collects and fits the ringdown signals. The "corrected" dye laser position (see Appendix 2.3.3) and inverse ringdown constant are plotted on the main screen. The "movedyelaser2_dr.vi" then moves the dye laser by the user-selected step size. The process repeats until the end of the scanning range. If the scan has to be stopped during the middle of the experiment, the "Stop" Boolean button, and not the "Stop" of the "mainprogram_excimer_2.vi," should be selected.

To collect simultaneous spectra during a photolysis experiment for excimer on and off, select the "excimer scan on/off" button located at the bottom of the front panel. The Boolean "Excimer on and off" button should not be selected. Instructions for other inputs remain the same. Once the scan is started, the main program uses an additional subprogram to control the firing of the excimer laser. Specific details of the external control of the excimer are reserved until Appendix 2.3.5. To briefly summarize, the computer controls a delay generator connected to the excimer such that the excimer fires at a specified time before the ringdown signal is collected by the detector. At each scanning wavelength, the main program turns the excimer on and collects the ringdown signals using "readboard.vi." After the averaged ringdown

signal has been collected, the computer turns off the excimer and repeats the collection of ringdown signals.

We mainly use the previous program for data collection. When we switch laser dyes, we use the Labview program "Calibration of the dye laser.vi" to calibrate the position of the dye laser in the visible region. Specifics of the calibration procedure are provided in Appendix 2.3.3. The program has a very similar format to the main data collection program. The main difference is that the program collects optogalvanic spectra rather than CRD spectra. Thus, the "readboard.vi" is replaced by "optogalvanic.vi", which analyzes optogalvanic signals by integrating the areas beneath the signals.

Smaller subprograms are stored in the "Noyes 105 Data Programs" folder. Most do simple calculations such as determination of the residence time given the voltage of the flow meters. One program compares CRD background spectra with a reference water spectrum to calculate the concentration of water in the cell. Labview significantly eases the daily operation of the apparatus; thus future lab members should continue to update and add to the current collection of programs and subprograms.

A-2.3.2 Components of the optical cavity

A diagram of the optical cavity was shown in Fig. 2.5. We use a variety of ringdown cells in our laboratory. For long residence time experiments, we use long multi-port Pyrex cells (Fig. A-2.4). For photolysis experiments, we use stainless steel cells with quartz windows of various sizes (Fig. A-2.5). We also use multiple CRD mirrors to scan different regions of interest. A list of the current CRD mirrors in the laboratory is provided in Table A-2.1. 1" Teflon adapters are used to mount smaller diameter (0.8 ") mirrors into our 1" Newport mirror mounts.

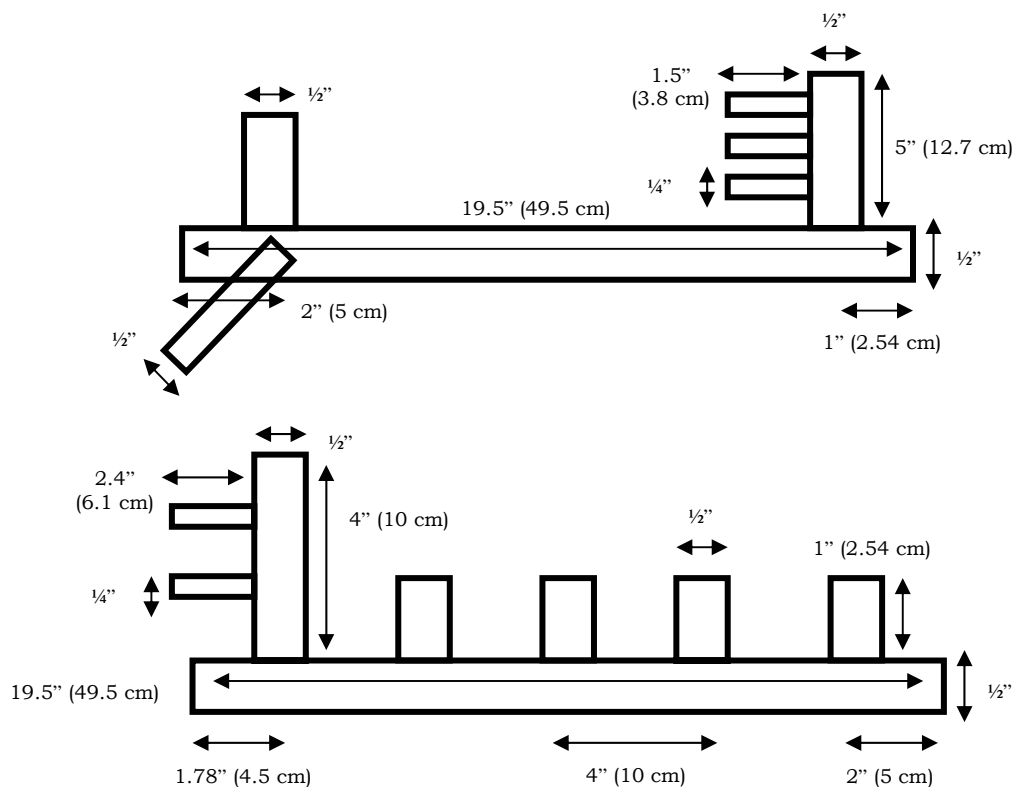


Figure A-2.4. Schematic of Pyrex cells used for long residence time CRD experiments.

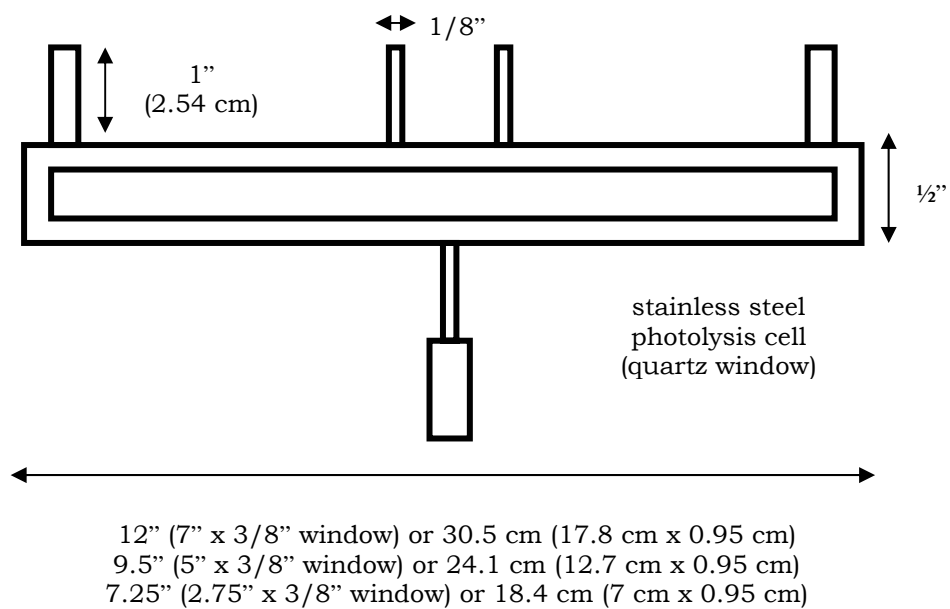


Figure A-2.5. Schematic of stainless steel cells with quartz windows used for CRD photolysis experiments

Company	Center	Reflectivity	Diameter
LGR	490 nm	99.995 %	0.8"
Newport	623 nm	99.97 %	1"
Nova Wave	690 nm	99.9975 %	1"
LGR	950 nm	99.99 %	0.8"
Newport	1060 nm/9434 cm ⁻¹	99.97 %	1"
LGR	1200 nm/8333 cm ⁻¹	99.99 %	0.8"
LGR	1315 nm/7600 cm ⁻¹	99.985 %	1"
LGR	1330 nm/7519 cm ⁻¹	99.99 %	1"
Layertec	1390 nm/7194 cm ⁻¹	99.99 %	1"
ATF	1390 nm/7194 cm ⁻¹	n/a	1"
LGR	1400 nm/7143 cm ⁻¹	99.995 %	1"
Nova Wave	1550 nm/ 6452 cm ⁻¹	99.9975 %	1"
Newport	1550 nm/6452 cm ⁻¹	99.97 %	1"
LGR	2800 nm/3571 cm ⁻¹	99.98 %	0.8"
LGR	2900 nm/3448 cm ⁻¹	99.96 %	0.8"
LGR	3200 nm/3125 cm ⁻¹	99.94 %	0.8"
LGR	3300 nm/3030 cm ⁻¹	99.98 %	0.8"

Table A-2.1. List of CRD mirrors in the laboratory. The experiments in this work utilize the CRD mirrors in the NIR region (6400 - 8600 cm⁻¹).

On-axis alignment of the optical cavity is done with a HeNe laser (Fig. 2.4). The procedure is listed below:

1. Turn on the HeNe laser. A second mirror is inserted before the optical cavity along the path of the NIR beam. Mount the ringdown cell (Fig. 2.5) but wait to put on the metal flanges with the CRD mirrors.
2. If the irises have already been set to define a straight path through the ringdown cell, use the two mirrors to align the HeNe beam through the irises. Otherwise, align the beam such that the HeNe goes through the center of the ringdown cell. Fix the irises. Do not touch the HeNe laser beyond this point.

3. The detector (Thorlabs PDA 400) is mounted to a two-dimensional micrometer translational stage. Although the detector consists of an InGaAs photodiode, it can still detect light from the HeNe laser. Insert a focal lens between the detector and exit of the ringdown cell such that the beam focuses before or after the surface of the photodiode. Adjust the vertical and horizontal positions of the detector to maximize the HeNe signal on an oscilloscope.

4. The CRD mirrors should be cleaned before alignment. The "drag-drop" method with methanol works well for most NIR CRD mirrors. On the side of the ringdown cell closest to the detector, mount the metal flange with the first CRD mirror. The reflective or coated surface should face inward. Part of the HeNe beam will be reflected. Use the mirror mount on the flange to direct the HeNe beam through the irises. Run the purge gas slowly to protect the CRD mirror from water in the air.

5. Mount the second flange with the second CRD mirror on the cell. Turn off the purge gas. Although the HeNe beam is hitting the non-coated side of the mirror, part of the beam will be reflected. Use the mirror mounts to direct the HeNe beam through the irises.

6. After both mirrors have been mounted, evacuate the cell. Turn off the HeNe laser and remove any mirrors blocking the pathway of the NIR light. Turn on the Nd:YAG and dye laser. Use an NIR card and a set of mirrors to align the NIR beam through the same irises. A ringdown signal should be observed on the oscilloscope. Adjustments can be made to the mirrors along the NIR pathway to achieve a good ringdown signal, i.e., a ringdown signal with a single exponential decay. The positions of the CRD mirrors can also change upon pressure change. Minor corrections can be made by adjusting the CRD mirror mounts. The Labview

"readboard.vi" program is used to analyze the ringdown signals on the computer.

A.2.3.3 Calibration of the spectra

Calibration of NIR spectra involves two stages. First, the position of the dye laser is calibrated in the visible region using an optogalvanic spectroscopy apparatus. Second, the exact Stokes shift of the hydrogen gas is determined for calibration in the NIR region using our pulsed CRDS apparatus. We begin our discussion with the first stage of calibration.

There are three parameters of interest in the Labview data collection program with respect to the calibration of the wavelength of the dye laser:

- 1) the current dye laser wavelength (nm), which is stored in a file: "dyelaserposition.txt"
- 2) the step size of the dye laser motor (nm/TTL pulse), which is stored in a file: "stepsize.txt"
- 3) the index of refraction, which is stored in a file: "indexofrefraction.txt"

The first two parameters calibrate the wavelength of the dye laser output, as the beam is propagated through the air. We use the optogalvanic apparatus to adjust the two parameters.

Optogalvanic spectroscopy has been reviewed by Barbieri and Beverini.^{2,3} The methodology is quick, inexpensive, and spectrally precise. The approach can be better understood by examining a diagram of the apparatus (Fig. A-2.6). In principle, any gas can be used. We use neon (Ne) gas due to the high number of atomic lines in the visible region and the NIST database of the Ne line positions.⁴ The diagram shows a circuit

with a simple \$0.40 neon lamp. The signal-to-noise (S/N) can be vastly improved by using a hollow cathode tube filled with neon. The basic components and underlying science of the apparatus remain the same.

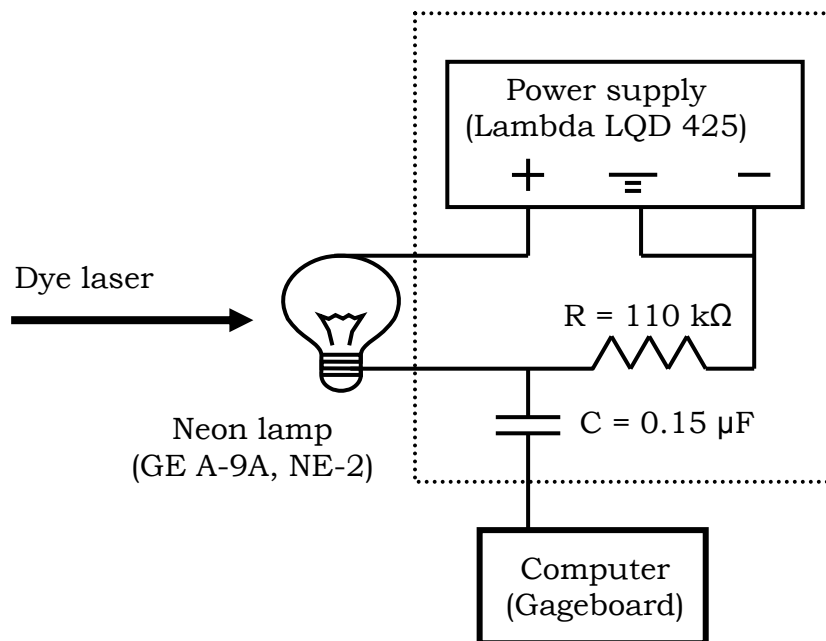


Figure A-2.6. Diagram of a basic optogalvanic apparatus that can be made from a cheap neon lamp. For better S/N, the neon lamp is replaced with a hollow cathode tube filled with neon and another homemade optogalvanic circuit (dashed square). The essential components of the two apparatuses remain the same.

The power supply provides current to the lamp. The Ne lamp begins to glow orange, as the gas is discharged. When light is shined on the neon discharge, populations of the excited and ground state neon atoms are affected. These effects are observed externally by changes in the conductivity of the lamp in the circuit. The change in the current can be measured directly by probing the voltage across the resistor (R). The change becomes more pronounced when the light is resonant with an atomic transition of neon. Cartoon depictions of the signal are shown in Fig. A-2.7.

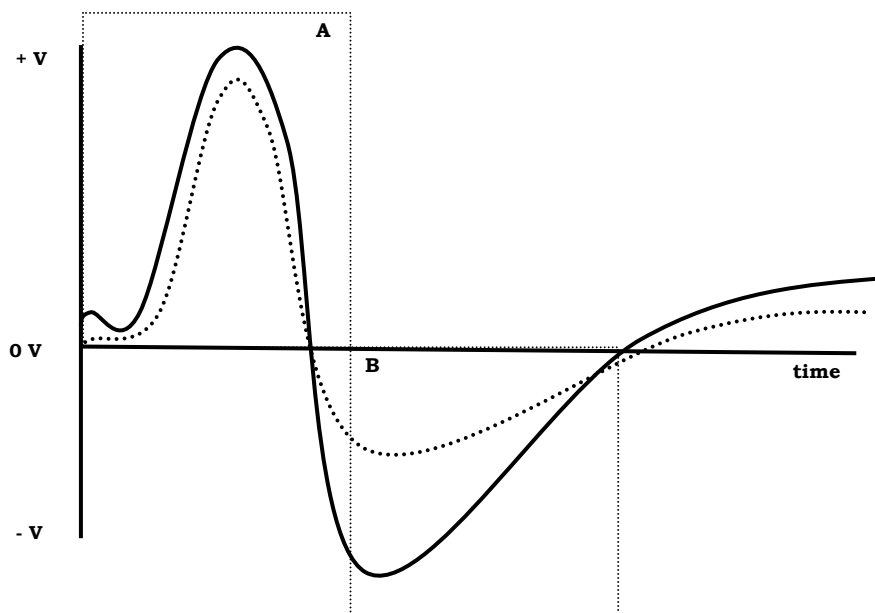


Figure A-2.7. Carton depictions of the voltage readout from an optogalvanic apparatus when the light is resonant (dark line) and non-resonant (dotted line) with a neon transition. The area underneath the voltage signal can be positive or negative depending on the sampling window. Sampling window A results in a positive sum or peak while sampling window B results in a negative sum or peak. Sampling window B results in a better S/N peak.

Elucidation of the time response is beyond the scope of this work. We instead probe the circuit for large changes in the voltage to identify the neon transitions. As the Ne transitions are known to high accuracy, the signals can be used to calibrate the dye laser position. We therefore use the Labview program "Calibration of the dye laser.vi" to scan the dye laser and collect signal from the optogalvanic apparatus at each scanning point.

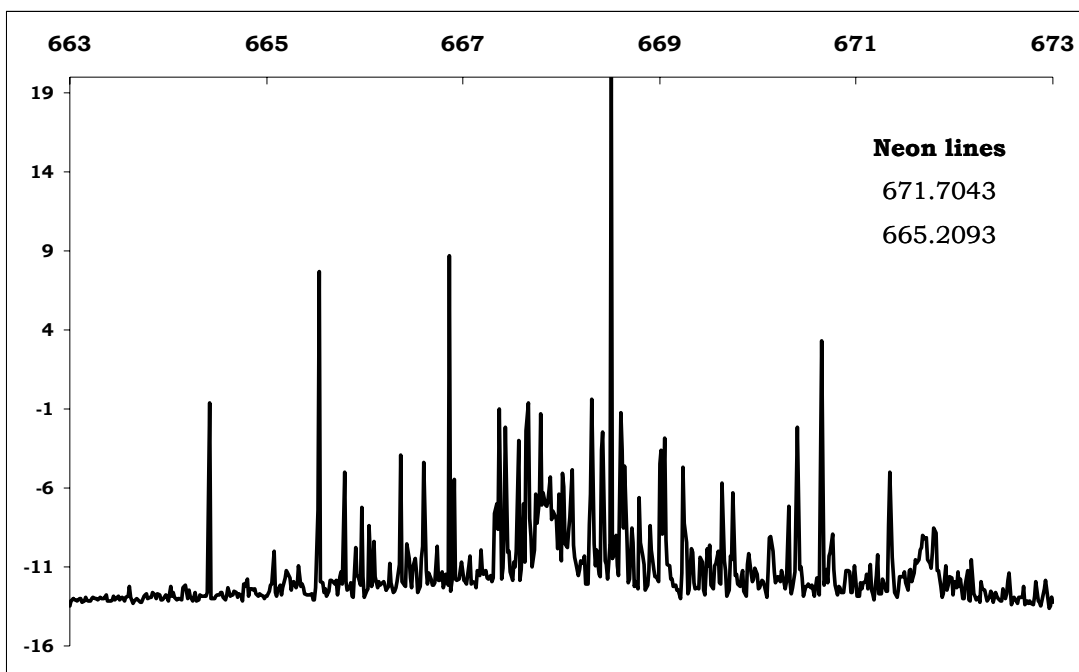
The optogalvanic signal is processed in the Labview subprogram "optogalvanic.vi" using a simple box integrator. The area underneath the voltage signal is calculated and plotted against the wavelength. Areas underneath negative voltage signal is considered "negative." Depending on the shape of the signal and sampling window, the resultant sums can

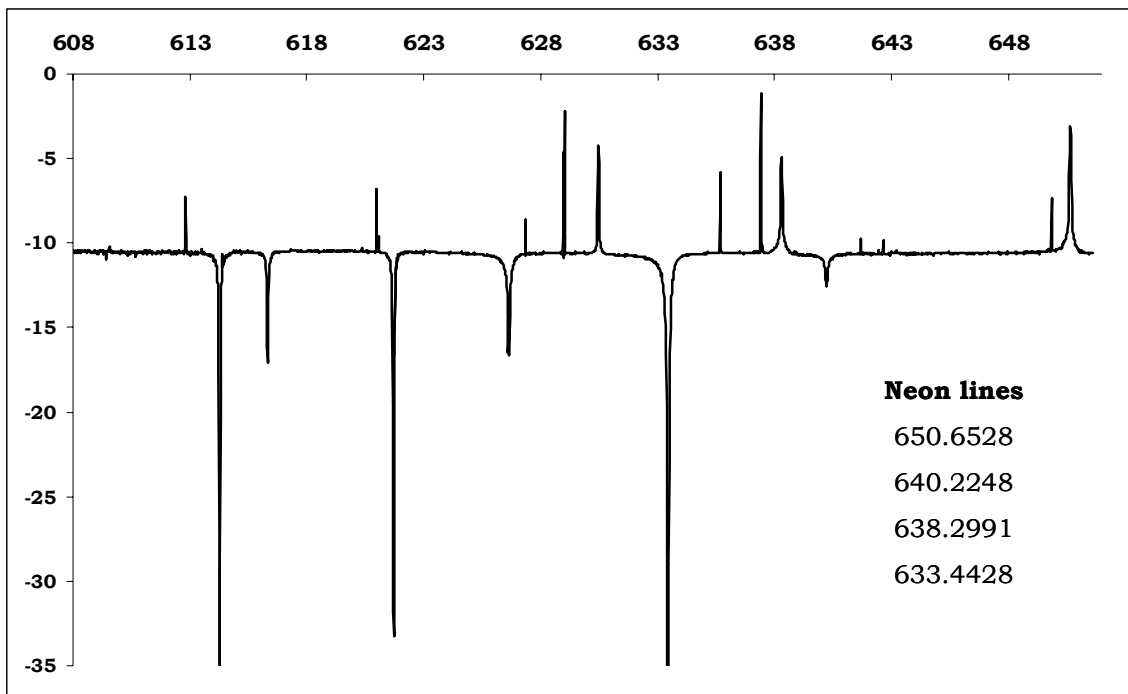
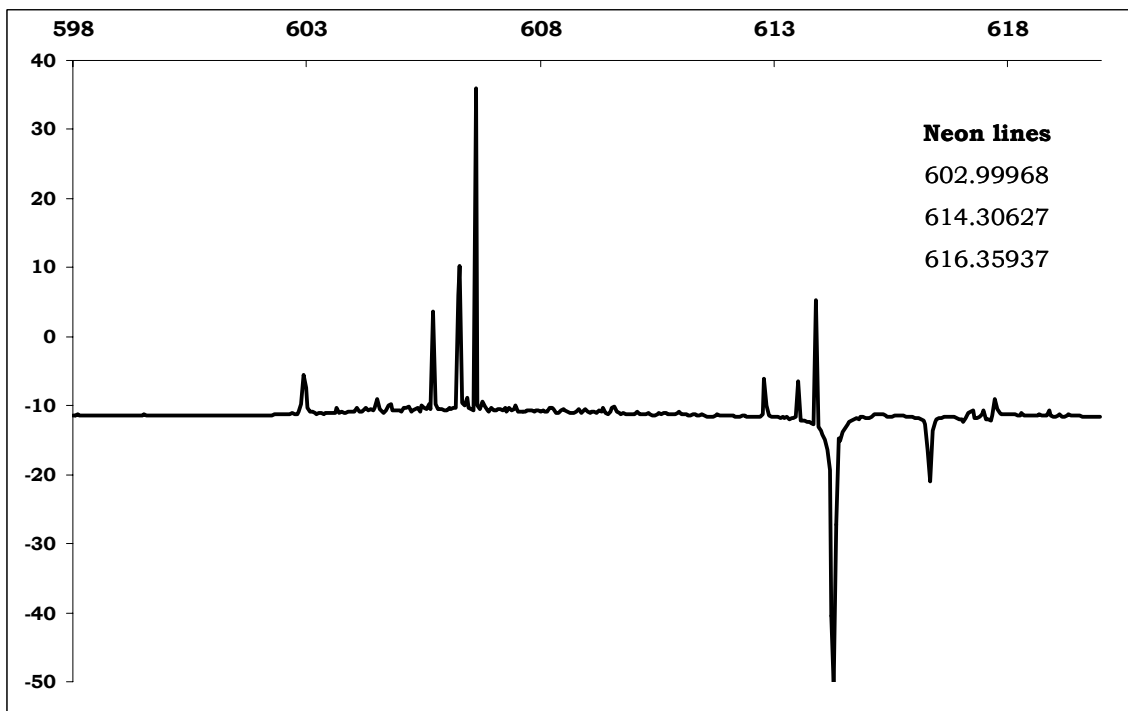
be positive or negative (Fig A-2.7). The peak position, however, should not change. To maximize the S/N of the peak, the sampling window should be chosen to contain the largest absolute change in the voltage signal. Optogalvanic spectra collected in various visible regions are shown in Fig. A-2.8. Recipes for the laser dyes used in the dye laser for each scan are listed in Table A-2.2.

Laser Dye	Wavelength Range	Oscillator & Amplifier
Oxazine 720	664 - 672 nm	117.5 mg/0.87 L & 69.3 mg/0.82 L
DCM	620 - 653 nm	22 mg/0.9 L & 158.3 mg/0.9 L
Rhodamine perchlorate 640	608 - 622 nm	192 mg/0.9 L & 101 mg/0.9 L
Rh 640	603 - 613 nm	143 mg/1.0 L & 19.0 mg/1.0 L
Rh 610 + Rh 640	594 - 610 nm	19.2 mg Rh640 + 34.1 mg Rh 610/0.9 L & 9.6 mg Rh 640 + 16.8 mg Rh610/0.9L
Rhodamine chloride 610	583 - 597 nm	96 mg/0.9 L & 33.7 mg/0.9 L

Table A-2.2. List of the dye laser recipes used in the experiments. The solvent for all mixtures is high grade methanol (water < 0.1%).

Ox 720 laser dye



DCM laser dye**Rh 640 laser dye**

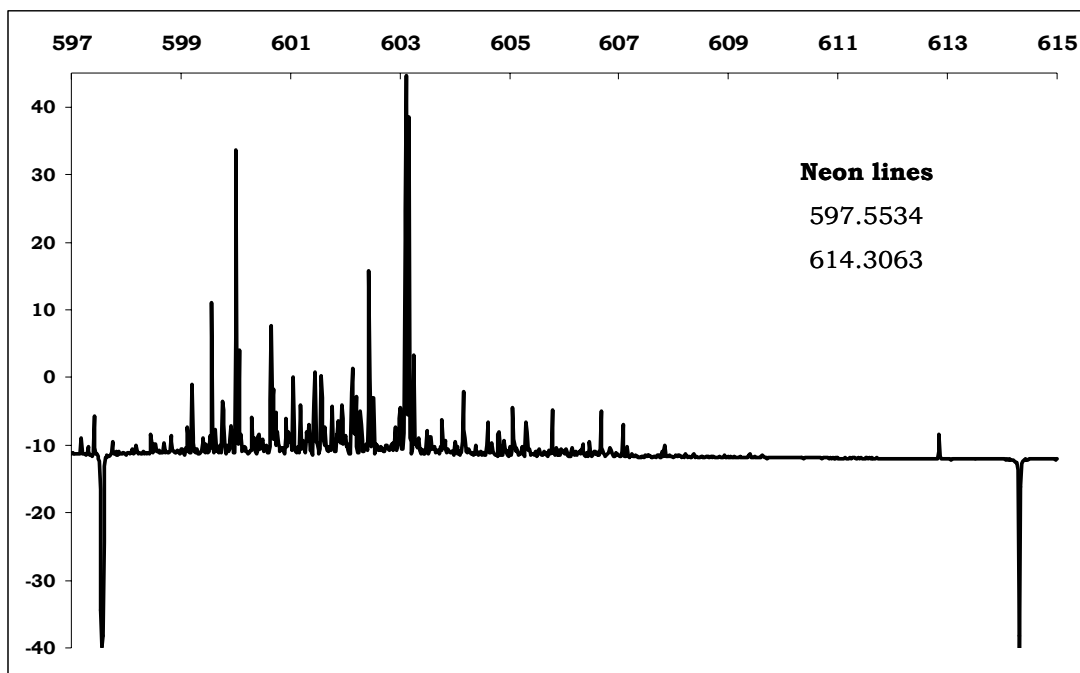
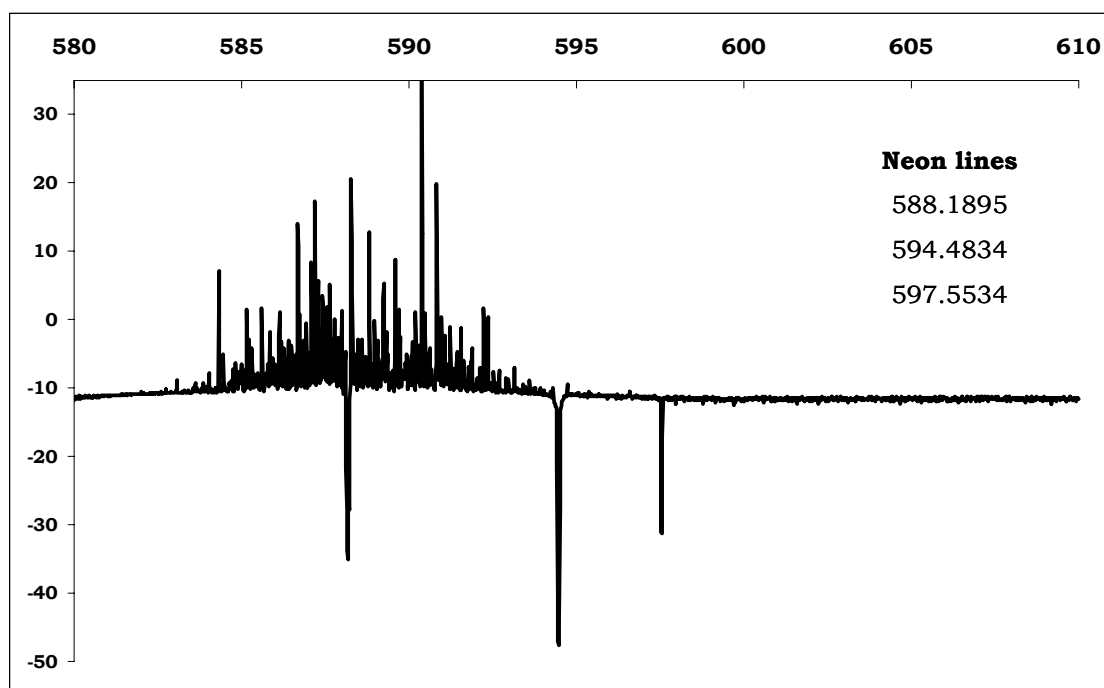
Rh 610 + Rh 640 laser dye**Rh 610 laser dye**

Figure A-2.8. Optogalvanic spectra collected in the visible regions using different laser dyes. The frequency axes and the neon lines are all in units of nm. The y-axis is arbitrary, as depending on the alignment, the relative intensities of the bands change. The line positions however are unaffected.

Each peak in the optogalvanic spectra can be fit with a Gaussian line shape to calculate the center of the peak:

$$y = Ae^{-\frac{(x-b)^2}{2c^2}} \quad (\text{A-2.4})$$

where A = amplitude of the peak, b = center of the peak, and c = width of the peak. The centers of the peak are compared to the Ne lines from the NIST database. Ideally, we analyze three peaks evenly spaced across the scanning range; however, as long as the lines are far apart, the analysis works well with even two lines. If there is a systematic difference between the data and NIST frequencies, we move the laser to the peak of interest and adjust the parameter "current dye laser position" to the equivalent NIST frequency. If the differences are not systematic, we adjust, in addition, the parameter controlling the step size of the motor. We first move the laser to the peak of interest and correct the "current dye laser position" as before; we then adjust the "step size of the motor" by:

$$\text{new step size} = \frac{|NIST \text{ peak 1} - NIST \text{ peak 2}|}{\frac{|data \text{ peak 1} - data \text{ peak 2}|}{\text{current step size}}} \quad (\text{A-2.5})$$

The parameters described above involve corrections to the dye laser output as it propagates through the air. Many of our experiments, however, are done under vacuum. We must take into account the difference between the indexes of refraction of air ($n_{air} \neq 1$) and vacuum ($n_{vac} = 1$).

$$\lambda_{vac} \nu = c \rightarrow \frac{\lambda_{vac} \nu}{n_{air}} = \frac{c}{n_{air}} \rightarrow \lambda_{dye} \nu = \frac{c}{n_{air}} \quad (\text{A-2.6})$$

In the Labview program "Calibration of the dye laser.vi," we process all positions based on the wavelength of the dye laser λ_{dye} . For vacuum experiments, we switch to the "mainprogram_excimer2.vi." The program multiplies the wavelength by n_{air} and reports the "dye laser" positions as the corrected value. The value of n_{air} depends on the relative water composition of the air (1.00029 ~ 1.00033). Our current parameter for the index of refraction is set to 1.0029.

The best calibration method involves obtaining a reference spectrum in the experimental apparatus under similar temperature and pressure conditions. This is the second stage of our calibration process. Most of the pulsed CRDS experiments are conducted in the NIR region (7000-8700 cm^{-1}). Water lines are therefore used for calibration. The "mainprogram_excimer2.vi" program records the "corrected" dye laser position and the inverse of the ringdown constants for each wavelength position during a CRD scan. To convert the frequency-axis (nm) to wavenumbers (cm^{-1}) in the NIR region, the "corrected" dye laser positions are converted to wavenumbers in an Excel spreadsheet. The second order Stokes shift is then manually subtracted from the frequencies. We compare our CRD spectrum of water to the PNNL database⁵ or Hitran⁶ to determine the Stokes shift. The absolute lines positions are known to < 0.1 cm^{-1} . In our experiments, the Stokes shift of hydrogen ranges from 4155.15-4155.30 cm^{-1} .

A.2.3.4 Laser maintenance

The Continuum manuals for both the Nd:YAG and dye lasers (NY61 and TDL 51 respectively) and the Laser Physik manual for the excimer laser (LPF 220) review the physical phenomena leading to light generation in great detail and provide protocols for laser alignment and maintenance.

We outline here only the issues that are not discussed in the manuals but are still needed for operation of the lasers.

NY61 Nd:YAG laser

The laser head consists of three major components: the housing, the flow tube, and the YAG rods. While most laser housings consist of silver or gold cavities, the NY61 cavity consists of an aluminum housing, packed with barium sulfate powder. The packing is directly related to the efficiency of the YAG power and needs to be replaced every 5-10 years. If the rubber silicone o-rings fail and water contaminates the powder, the packing needs to be replaced immediately. The flow tube is made of 5% Samarium-doped quartz. It not only absorbs UV light but also fluoresces pink light to contribute to the overall YAG power (~10-15%). Over time, the quartz material gets baked by the UV light and also needs to be replaced. In Fig. A-2.9, a photo of a damaged flow cell is shown. Finally, the YAG rods need to be polished and recoated every 5-10 years for peak laser performance.

For problems with low laser power, the protocols in the laser manual on laser alignment or replacement of the flashlamps should be first followed. If the efficiency of the laser power continues to decrease and there is no obvious damage to the optics, the laser head should be resent to the manufacturer (Continuum) or another laser refurbishing company (e.g. Kentek) for evaluation.

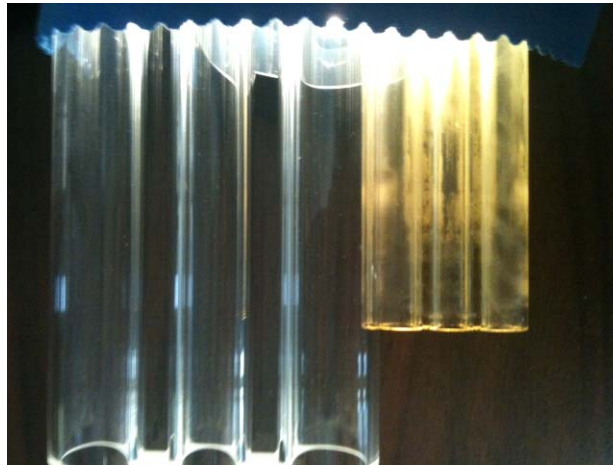


Figure A-2.9. Photo of the three-bore flow cell of the laser head of the NY 61 Nd:YAG laser. The material on the left is not made out of the 5% Samarium-doped quartz. However, it illustrates how translucent the material should be. The flow cell on the right has been used in a laser head for extended time. While the flow cell is still intact, the quartz has been baked such that the material has a cloudy appearance.

The Nd:YAG laser also has problems with the control unit (CU601). The laser program crashes after the flashlamp count exceeds a billion counts. The program must be reset, or the laser cannot be fired.

To reset the program, we follow the below procedure:

1. Open switch #8 on the red dip switch component located on the mother board (#503-9900) inside the CU.
2. Reset the key switch to start the countdown display.
3. In the service mode, use the "Parameter Select" button to cycle through each parameter. Set each parameter to the following: Pulse div min = 0, Pulse div max = 11, Rep rate min = half the operating rep rate = 10 Hz, and Rep rate max = operating rep rate = 20 Hz.

4. Reset switch #8 to the closed position and reset the key switch to restart the CU.

While this protocol allows operation of the Nd:YAG laser, the laser can only be externally triggered. TTL pulses must be sent to the control unit to trigger the firing of the flashlamp and Q-switch. For the flashlamp, the signal can be either a positive or negative-going 5V TTL pulse (width 10 μ s); for the Q-switch, the signal must be a negative-going 5V TTL pulse (width 10 μ s). These signals are supplied by a delay generator. Exact details are available in Appendix 2.3.5. A homemade box connected to a 5V power supply is used as an interface between the delay generator outputs and the inputs for the control unit box, a BNC cable for “ext Q-switch” and a blue 9-pin connector for “externals.” A switchbox has also been added to the Q-switch input BNC cable. This is useful for “single shot” procedures for alignment of the Nd:YAG laser.

TDL 51 dye laser

External control of the step motor connected to the grating of the dye laser is crucial for experimental scans. The step motor needs a 5V TTL pulse to rotate and a 5/0 V line voltage to determine the direction of rotation. In our laboratory, we use a DAQ card (NI USB 6008) to provide both signals to the step motor. There are two connections to the dye laser, one 25-pin connector for movement of the dye laser and one 15-pin connector for safety interlock of the dye laser. We interface the DAQ card to these connectors via a 37-pin connector and circuit box.

In a senior lab member's notebook, we found a printout of an unidentified connector that sounded very similar to the input of our dye laser step motor (Fig. A-2.10). From the printout, we made a homemade box to interface the DAQ card with the dye laser connection (Fig. A-2.11).

The essential connections for movement of the step motor are pins 34-37, or on the DAQ card, lines P0.3, P0.2, A00, and P0.0, respectively. Outputs from the pins are connected to a TTL integrated component (IC) SN74128N (NOR 50 Ω line driver). A subprogram of the Labview program "movedyelaser2_dr.vi" controls the DAQ card such that outputs of the pins can switch from 0 to 5 V rapidly. The outputs of pin 36 (0/5 V) and pin 37 (0 V) work together to create a TTL pulse, while the outputs of pin 34 (0V) and pin 35 (0/5 V) work together to determine the direction of rotation. When pin 35 is 0 V, the IC output is 5 V and the step motor rotates such that the wavelength of the dye laser grows shorter. When pin 35 is 5 V, the IC output is 0 V and the step motor rotates such that the wavelength of the dye laser grows longer.

Only two of the pins, 31 and 33, are currently connected to the 15-pin connector of the dye laser. They both provide 5 V lines to the dye laser and behave as safety interlocks. If the step motor moves the grating of the dye laser to the edge, the dye laser shuts down the motor such that the grating is not damaged. The computer program can receive signals from the dye laser stating whether the grating is at the edge or not. These safety connections are currently not set up, as we have never moved the motor beyond the grating range.

J1-indexer connector

Pin #1_Step + : This input causes the motor to be incremented one microstep for each pulse it receives. This pulse or pulse train input must be TTL (0 to 5 VDC @ 20 ma) level and have a minimum of one μ s pulse width. There is no maximum pulse width. Velocity of the motor will be proportional to the frequency of the input pulse train, and distance will be in equal (in μ s) to the number of pulses received. This input is optically isolated. Return is Step- (J1 pin 2)

Pin # 2_Step - : This input provides a return for the Step + input. This input is optically isolated and should not be connected to logic ground (J1 pin 8 and J2 pin 8)

Pin # 3_Dir + : The state of this input determines the direction the motor will move when step pulses are received on the Step + input. This is a TTL level input with a logic high (5 V @ 20 ma) corresponding to CW motion of the motor and a logic low (0 V) corresponding to CCW motion. This input must be defined 80 μ s before a step pulse is received and must remain in that state for the duration of the move. This input is optically isolated. Return is Dir- (J1 pin 4).

Pin #4_Dir - : This input provides a return for the Dir + input. This input is optically isolated and should not be connected to logic ground (J1 pin 8 and J2 pin 8)

Pin #5_Res Sel C: The state of this input along with the state of J1 pins 6 and 7 determines the resolution of the DB Drive. The state of this input is read only at power-up. Changes in state to this input is read only at power-up. Changes in state to this input after power-up will have no effect.

Pin #6_Res Sel B: The state of this input along with the state of J1 pins 5 and 7 determines the resolution of the DB Drive. The state of this input is read only at power-up. Changes in state to this input is read only at power-up. Changes in state to this input after power-up will have no effect.

Pin #7_Res Sel A: The state of this input along with the state of J1 pins 5 and 6 determines the resolution of the DB Drive. The state of this input is read only at power-up. Changes in state to this input is read only at power-up. Changes in state to this input after power-up will have no effect.

Pin #8_Logic Gnd: This input provides a ground for configuring the state of the resolution select inputs. This is internally connected to the logic ground input on J2 pin 8. This input should never be connected to earth ground.

Figure A-2.10. Description of a connector to the step motor of the dye laser.

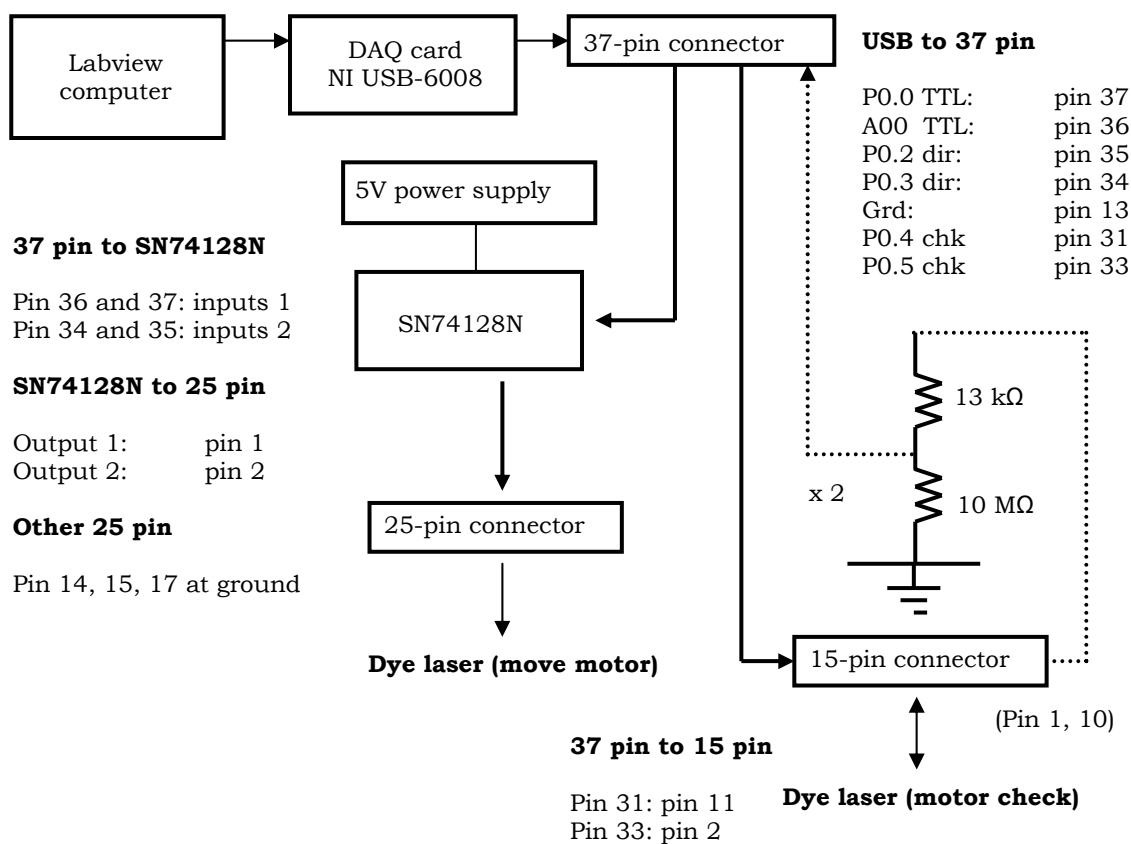


Figure A-2.11. Schematics of the connections between the dye laser and DAQ card/computer. The dotted lines are currently not connected. The 25-pin connector is for moving the step motor of the dye laser. The 15-pin connector is for safety checks of the step motor and dye laser grating.

LPF 200 Fluorine excimer

The excimer can be operated at multiple wavelengths, as long as the gas mixture is fluorine-based. The internal program for the excimer laser however can only fill the chamber with the 193-nm gas mixture recipe. To operate the laser at other wavelengths, the fill must be done manually. The following protocol is used:

1. Close all gas cylinder valves. Purge each gas line connected to the excimer three times.
2. Do not touch the halogen line. Remove all other lines and cap off all gas ports on the excimer.
3. Select "New Fill" and execute. The chamber should pump down to ~30 mbar. The program then tries to fill the chamber with gas from the gas ports. However, as all the ports are closed and the halogen cylinder is closed, an error message appears. Push the "break" button.
4. Open the fluorine cylinder. Push F7 to inject a fixed amount of halogen into the chamber. Repeat to fill the chamber with X mbar of gas. The overall pressure reads: "30 + X" mbar. If necessary, the injection can be interrupted by pushing the "break" button. Close the fluorine cylinder when finished.
5. All other gases must be added via the inert gas port. They can be added in any order, although it is recommended that the rare gas and then inert gas are added. Connect the cylinder of interest to the inert gas port. Purge the line three times. Then open the cylinder of interest. Push F6 to inject a fixed amount of the gas into the chamber. Repeat as necessary. If needed, the injection can be interrupted with the "break" button. Close the cylinder. Purge the lines three times before removal. Add all gases accordingly.

We have mostly used 193-nm and 248-nm fills. For operation of the excimer at 193 nm, the gas mixture consists of 100 mbar fluorine, 150 mbar argon, and 2750 mbar neon, while for operation of the excimer at

248 nm, the gas mixture consists of 80 mbar fluorine, 100 mbar krypton, and 2870 mbar neon.

A.2.3.5 Delay generators for control of the laser firing

Controlling the timing between the firing of the Nd:YAG and excimer lasers is critical for kinetic experiments. We also need to trigger the Labview program "readboard.vi" to collect the ringdown signal at the appropriate time. We achieve these conditions by using two delay generators (Fig. A-2.12). The flashlamps of the NY 61 Nd:YAG laser are specified for 20 Hz rep rate. If we run the experiments at 20 Hz, the triggering of the Nd:YAG, excimer, and data collection program is straightforward (Fig. A-2.13). The first delay generator is internally operated at 20 Hz. Channel A controls the firing of the flashlamp of the Nd:YAG laser. This channel defines the zero of the timing control. Channel B controls firing of the Q-switch. The output of the Nd:YAG laser is optimized by adjusting the time delay for channel B (~280 μ s). Channel C triggers the data collection on the computer. The time delay for Channel C is relatively close to the Q-switch firing (Channel B). We collect a few data points before the NIR light reaches the detector to get a better measurement of the baseline.

Finally, Channel D is used to trigger the excimer. There are two separate issues that need to be discussed. First, we need to control when the excimer fires with respect to the Nd:YAG or probe laser. Second, we want to be able to turn the excimer laser on and off during the same experimental scan. With respect to the first issue, the excimer laser light travels a different path to the ringdown cell than the Nd:YAG laser. To define the zero of the kinetic measurements, we measure the exact time that the two laser pulses overlap in the ringdown cell. This is done by observing the NIR CRD signal. The excimer laser causes a small spike in

the ringdown signal. The delay time of Channel D (x) can be adjusted such that the spike lies on the rise of the CRD signal. This defines the zero point of the kinetics experiments. For example, to do a 10 μs delay experiment, the Channel D delay time is adjusted to " $x-10$ " μs . As channel A defines the zero of the timing control, the delay time of Channel A can be set to 10 ms. We can then fire the excimer <10 ms before the NIR pulse reaches the cell to probe the sample of interest.

With respect to the second issue, channel D triggers the second delay generator to send a TTL pulse to the excimer. The excimer only fires upon receiving a TTL pulse with amplitude >3 V and width >15 μs . We therefore also connect the second delay generator to the computer. A subprogram of Labview program "Excimer on and off" is used to rapidly change the amplitude of the TTL pulse from 1 or 4 V to turn the excimer off and on respectively during the course of a scan.

Operating the laser at 20 Hz allows the maximum number of ringdown signals to be collected per second by the CRDS apparatus for averaging. There are however situations in which the gases reside in the ringdown cell for over 50 ms. In the kinetic experiments, we often operate at 5 Hz to guarantee that all gases have been flushed from the ringdown cell before the next excimer pulse initiates chemistry. Triggering all the equipment becomes more difficult, as the Nd:YAG flashlamp must still operate at 20 Hz. We therefore use a combination of TTL ICs to achieve these settings: SN7414 (inverter) and SN7407 (driver) for the excimer channel and SN7400 (NAND) and SN7407 (driver) for the Q-Switch channel. The driver IC is an open-collector. Open-collector devices sink currents in their logic 0 state; thus, an external pull-up resistor is needed to hold the signal line high until the device sinks enough current to pull the line back low. In the circuit, we add a resistor between the

common voltage and output of the ICs. In Fig. A-2.14, we show the schematic of the pulses used to operate the Nd:YAG flashlamp and excimer lasers at 5 Hz.

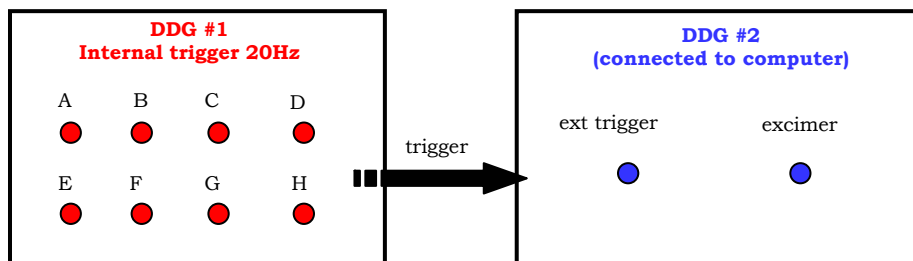


Figure A-2.12. Timing of the lasers and data collection program is controlled by two delay generators. The first delay generator is operated at 20 Hz. The second delay generator is externally triggered by an output from the first delay generator.

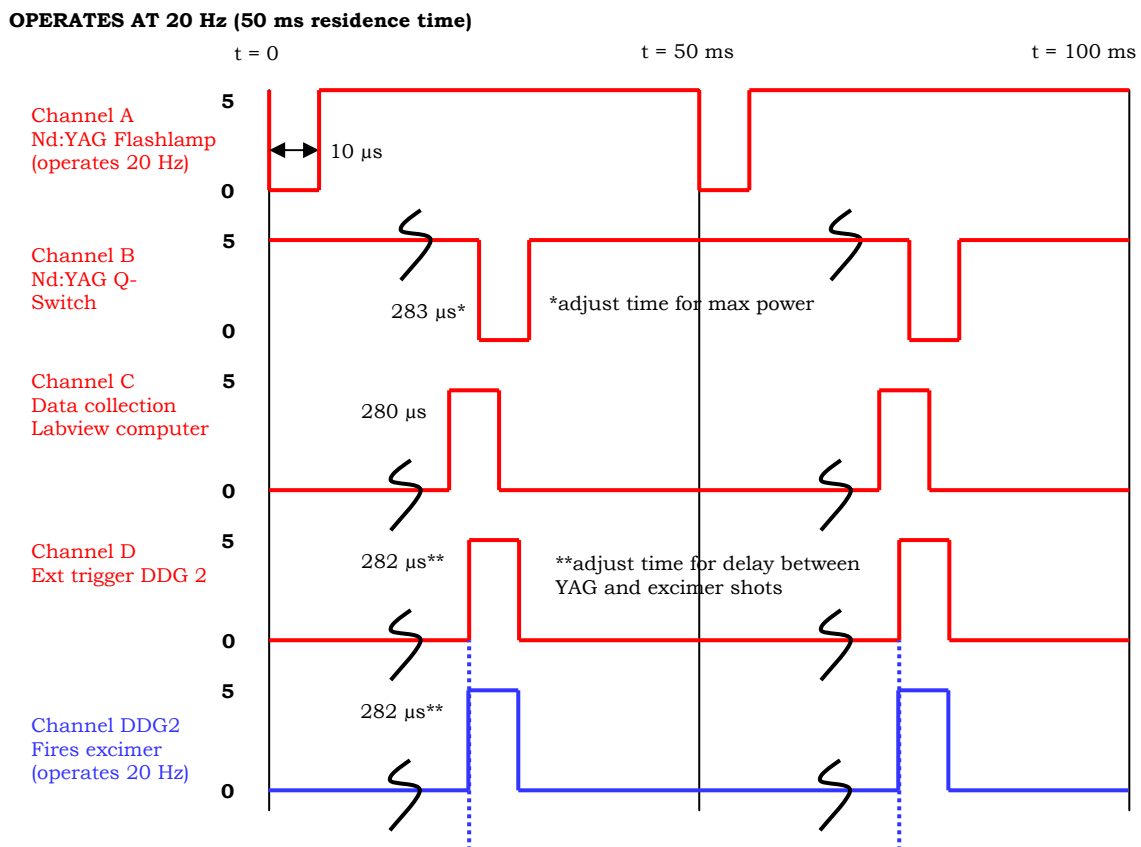
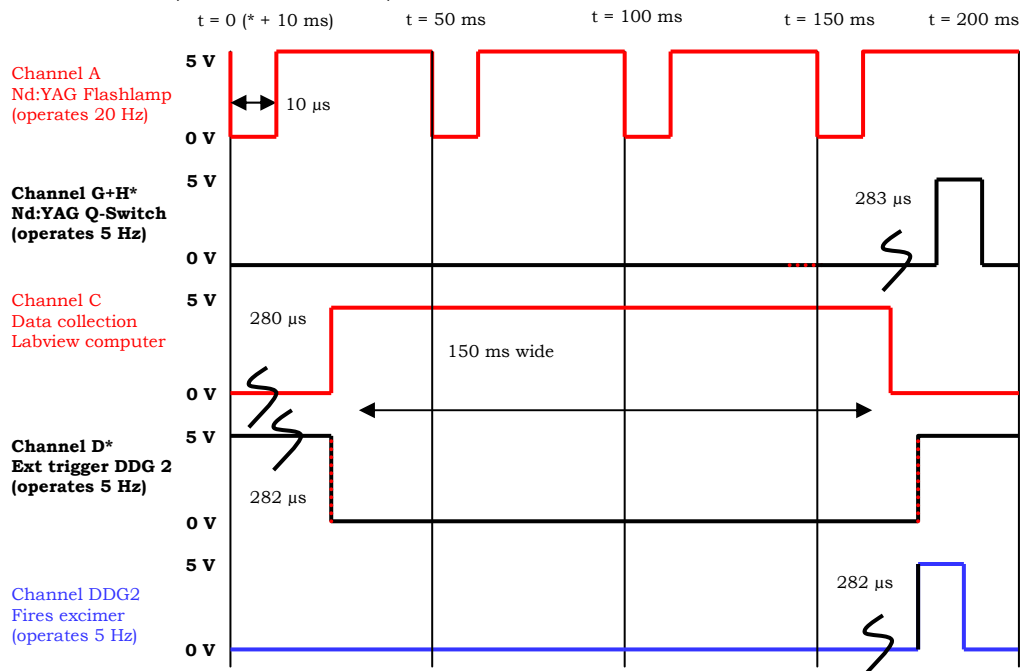


Figure A-2.13. Schematic of the outputs from different channels of the delay generators for experiments at 20 Hz rep rate or 50 ms residence time.

a.

OPERATES AT 5 Hz (200 ms residence time)



b.

Q-switch for Nd:YAG at 5 Hz

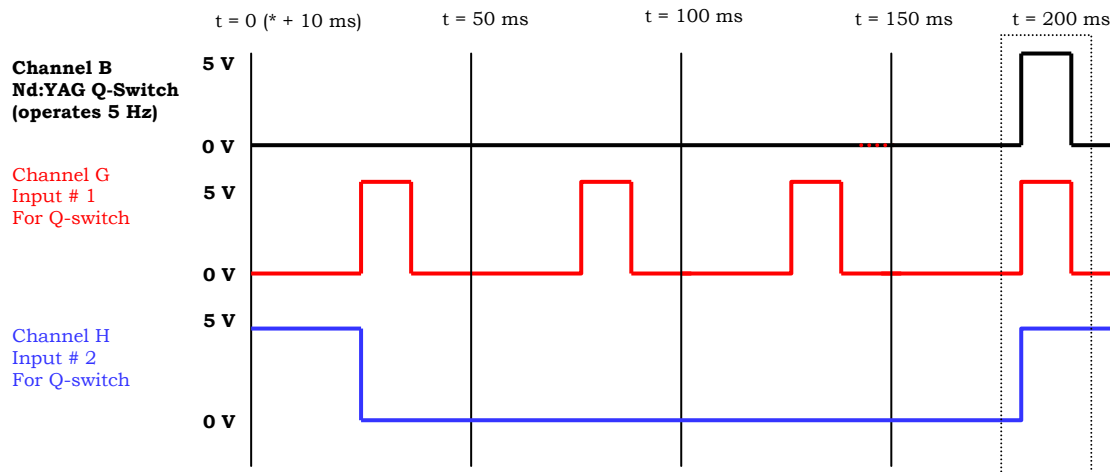


Figure A-2.14. Schematic of the different channel outputs for the delay generators for operation at 5 Hz rep rate or 200 ms residence time. Schematic (a) summarizes all the channels. The Q-switch and excimer channels (black) go through an TTL IC component before they are connected to the dye laser or second delay generator, respectively. The circuit for channel D (excimer) is straightforward as the original TTL pulse is just inverted. The circuit for the Q-switch is more complicated, as it involves two channels G and H, which go through the NAND TTL IC. The original G and H inputs are shown in figure (b). Note that the delay time for channel A, and thus all other channels, can be adjusted by 10 ms to provide a larger time window for the kinetic experiments.

Appendix 2.4 Lab safety and procedures

My advisor once gave a laboratory safety seminar to the first year graduate students in chemistry. After a graphic description of laser light striking the eyeball, one of the students remarked, "I don't want to work in a dangerous lab. I'm going to join an inorganic chemistry group." We are always asked by incoming students and undergraduates how dangerous our laboratory is. Compared to many areas of research, our area of research is very safe. We use less hazardous chemicals and solvents. The laser dyes are mutagenic, but we do not handle them often, and when we do handle them, we wear protective gloves. It is more the nature of the danger that is unfamiliar to most incoming students. Thus, we include here a brief overview of the safety issues in our laboratory. There are many topics not discussed here, e.g., emergency eye wash, showers, fire escape, etc. Every person working in the laboratory should review general safety protocols with the safety officer and other lab members.

Lasers

Lasers are very safe when used correctly. The power and wavelength of the laser should be known by the user before operation. Goggles are wavelength-specific and should be chosen to minimize eye exposure to the most intense wavelengths of laser light. The laser pathway should be well-defined and not designed at eyelevel. If any metal construction is involved, the reflected and scattered light should be contained. Communication is the best protection for persons sharing a laboratory with a laser. Be aware when a laser is being fired in the laboratory.

Gas samples

Gas samples are like any other chemical. Some are toxic; others are harmless. The Material-Safety-Datasheets (MSDS) for gases should be checked before any experiment. Some gases can only be transported by specific materials. The material of the line, Swagelok pieces, and o-rings in the connectors should all be checked. When using toxic gases, it is also important to leak check the gas lines before opening the cylinder. There are several ways to leak check a system, including a helium leak detector, methanol/acetone vapor check, and Snoop spray. While many of the gases are invisible and have no smell, some toxic gases such as ozone and halogen have distinct sharp odors. If there is a leak, close the gas cylinder immediately and evacuate the area.

Gases are usually transported to the laboratory in large cylinders. Every cylinder has a CGA number. The CGA number of the pressure regulator should always match the CGA number of the cylinder. For safety reasons, pressure regulators associated with toxic or flammable species are reverse-threaded and have notches on the input. Sometimes we purchase small lecture bottles of gas and make our own high pressure gas cylinder mixture (Fig. A-2.15). Areas exposed to high pressure (>1 atm) are made of metal. Electronics such as low pressure readouts are also protected.

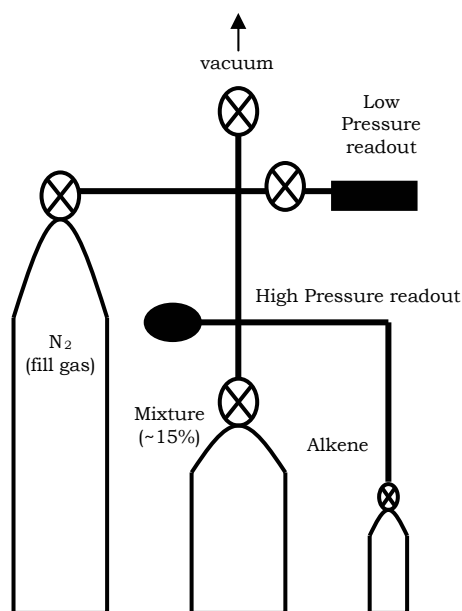


Figure A-2.15. Schematic of the preparation of the alkene/ N_2 cylinder at high pressure. All connected lines and the mixture cylinder are evacuated. After the vacuum line is closed, the valves to the mixture cylinder, alkene lecture bottle, and low pressure readout are opened. After the desired amount of alkene is injected into the mixture cylinder, the valve to the mixture cylinder is closed. The remaining alkene in the line is recollected by placing a liquid nitrogen bath on the alkene lecture bottle. After valves to the alkene lecture bottle and low pressure readout are closed, the valve to the nitrogen (fill gas) cylinder is opened. The valve to the mixing cylinder is slowly opened and filled to the desired total pressure.

Baths and liquid nitrogen

Solid and liquid samples are also used in the experiments. We utilize different temperature baths for the samples (Table A-2.3). The MSDS of the sample should always be checked before choosing the appropriate bath, as there is always a possibility that the container holding the sample may break. We also use baths on the gas lines to remove water and on the vacuum trap to prevent reactive or corrosive species from reaching the mechanical vacuum pump.

Liquid nitrogen is the most common bath used in the laboratory. We use it on the helium purge lines for the CRDS experiments. Nitrogen gas lines are often utilized for atmospheric experiments. Liquid nitrogen should not be used on those lines. Instead, a dry ice/acetone bath or a

sieve trap should be used to remove water contaminants. Similar considerations should be made for the bath of the vacuum trap.

If ozone is used in the experiment, a heated trap, filled with copper scrubs, should be added, in addition to a bath, to the vacuum line. Concentrated ozone can cause explosions. The combination of heat and copper eliminates excess ozone. Trapped ozone gives a violet-colored glow. If ozone becomes trapped, stop the ozone source and let the trap warm up slowly, with plenty of head volume. Due to similar concerns, care should be taken to not condense flammable hydrocarbons and oxygen in the same trap.

Bath	Temperature
Liquid nitrogen	< -196 °C
Methanol in Neslab ULT 80 Chiller	25 °C ~-70°C
Dry ice/acetone	-60 °C
Salt water/liquid nitrogen	-10 ~-20°C
Ice bath	0 °C

Table A-2.3. Common baths used in our laboratory.

Liquid nitrogen is also used to store samples in bubblers overnight. The bubbler must be leak tight. If there is a leak, air can enter the bubbler and condense. When the bubbler is removed from the liquid nitrogen, the condensed air is immediately warmed and becomes a gas again. As there is not enough head volume for the extra gas, the bubbler explodes. To avoid this problem, flow helium gas through the bubbler to remove all head gas and fill the bubbler with helium (>1 am) before liquid nitrogen storage. The freezing point of helium is below the temperature of liquid nitrogen. Thus, even if there is a minor leak, the helium should leak out of the bubbler before any air enters the bubbler. A relatively tall liquid nitrogen storage dewar is used for storage such that the valves of the

bubbler (usually made of Teflon) remain above the liquid nitrogen level and do not contract from the cold temperatures.

Before an experimental run, the bubbler is evacuated while it is under liquid nitrogen in the hood. When the bubbler or sample is removed from the liquid nitrogen dewar, we check the bubbler for liquid. If any liquid is observed in the sample, the bubbler is quickly lowered back into the liquid nitrogen. Helium gas is then run over the sample to slowly warm up the liquid. Similar precautions should be taken with freeze-pump-thaw liquid procedures. The bubbler should not be filled with too much liquid, as the inner glass tube of the bubbler can break upon rapid liquid contraction and expansion.

High voltages

The main danger in a physical chemistry laboratory is the high voltage equipment. Before taking apart any equipment, make sure that the power has been turned off, and the equipment has been unplugged. Many lasers such as the Nd:YAG laser involve high capacitor banks. Even if the equipment is turned off, the capacitors take time to discharge. For emergencies, be aware of the main circuit breaker for the laboratory, so all power can be turned off immediately.

Appendix 2.5 References

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