# PHYSICAL CHEMISTRY LABORATORY MANUAL



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# Physical Chemistry Laboratory Manual

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# 1: Safety Laboratory Exercise

## Exercise 1. Safety in the laboratory


## Profs. Stockwell and Morris


## August 2016

## Purpose

Students will become aware of laboratory hazards, safety rules, safety equipment and responsibilities.

## Report

The report for this exercise will consist of the following:
Your quizes for each of the safety modules taken,
A paragraph on what you find in the Material Safety Data Sheet for Toluene,
A Material Safety Data Sheet for a compound of your choice,
A paragraph on what you find in the assigned Material Safety Data Sheet for the compound of your choice,
A 1-2 page summary on one of the examples of a saftey disaster given below,
A map of the Physical Chemistry Laboratory and exteriar hallway showing safety equipment and exits,

## Core Safety Rules to be Followed at ALL TIMES

1. No one, including professors, should work in the laboratory alone.
2. Proper clothing must be worn.
3. Use the prescribed amounts of material. Do not waste.
4. Report broken equipment immediately.
5. No smoking in the laboratory.
6. No eating or drinking in the laboratory.
7. Eye protection - Safety goggles or eyeglasses must be worn at all times.
8. Reactions that produce toxic vapors must be carried out in the fume hood.
9. Wash with lots of water in the event of a strong acid or base burn.
10. Treat everyone with courtesy and respect.

## More General Rules

### Electrical Hazards

If you ever have to maintain an electrical apparatus or computer it should be unplugged from any power source. It is not safe to simply turn it off. If you must place electrical test probes in a solution use one hand to avoid any possibility of conducting an electric current through your heart.
Heating mantles, used to heat solutions, are to be plugged into the variable transformers and never directly into the power outlets.

### Laser and Radiation Hazards

Do not look into the beam of a laser even if the beam has a very low power. Shiny watches and/or jewelry are not okay in a laser lab under any conditions because they may reflect stray radiation into someone's eyes. Certain types of UV lamps can damage

eyes and produce a sunburn effect on the skin.

## Vacuum and High Pressure

Special glass vessels without cracks or scratches, with thick walls, are preferred when constructing vacuum apparatus. They should be wrapped in tape to prevent glass from flying if the vessel implodes.

When you place a regulator onto a gas cylinder you want to secure it firmly but not so that you risk twisting the neck off the cylinder. Whenever you turn it on you want to stand away from the direct line between the regulator and the cylinder in case the regulator was installed incorrectly and flies off the cylinder.

# Procedure

## Part 1:

Take the safety training course at: http://labsafetyworkspace.org

* The course list is at: http://labsafetyworkspace.org/training-course-list.

* Take the course: Introduction to Laboratory Safety.

* Print and attach your certificate of completion to your report.

* You will have to register but the course is free.

## Part 2:

**Find and describe Material Safety Data Sheets (MSDS).**
Your best source of safety information on chemicals is a Material Safety Data Sheet (MSDS). The MSDS describes the properties of a laboratory or industrial chemical and chemical mixtures. It is concerned with safety and product stewardship. It is especially for workers and safety personnel. It gives important warnings and procedures for safe handling of the substance. The information may include melting and boiling points, hazards, toxicity, health effects, first aid and other useful things such as storage and disposal information. See:

There are many sources for MSDS. A list is at http://ehs.okstate.edu/links/msds.htm.
Click at the link marked MSDS Library (Air Liquide) https://industry.airliquide.us/resources/safety-data-sheets. You will come to a page marked "Click here to find the safety data sheet you need" and click here. That will give you a search box.

Enter the chemical in the search form and perform the search. Try searching for “Toluene” and be sure you click on the menue to set "Begins With". You will come to a page with a number of choices. Select the entrywith just Toluene and write a paragraph describing the entry that you find.

Do a similar search on another chemical that you believe has some dangers. Write another paragraph describing the MSDA that you find for this chemical. Print the first page of this MSDS that you find and include it with your report.

Fill free to try the other sources of MSDS on the Oklahoma State University list.

## Part 3:

Prepare a 1-2 page summary of one of the examples (the topics can be selected randomly) and they will be expected to discuss in detail next week. There are some fundamental chemical concepts in play with both of these types of the explosions and fires that are interesting to explore. The first is a very tragic example of why safety should be followed at all costs.

UCLA Chemist Fatality:
http://www.rsc.org/chemistryworld/2013/05/ucla-chemist-trial-safety-violations-linked-sheri-sangji-death

And
http://cen.acs.org/articles/90/web/2012/01/Systemic-FailuresCited-UCLA-Lab-Fatality.html

Propane plant in Florida:
http://www.cnn.com/2013/07/30/us/florida-propane-explosion

Fertilizer plant in Texas
http://www.cnn.com/2013/06/27/us/texas-explosion/index.html

## Part 4:

**Survey the Physical Chemistry Laboratory and the surrounding hall way for safety equipment.**

Make a map on the attached worksheet. Identify the layout of the Physical Chemistry Laboratory and hallway outside in order to draw a map. On the map show the location of the following: fire blankets, fire extinguishers, fume hoods, spill kits, eye wash, safety shower and first-aid kits. There are containers in the lab to throw away all sharp objects, broken glass, and hazardous chemicals. Identify them on the map and use them. The chemical spill kits for acids, bases and solvents are in the hallway along with other fire extinguishers. List these on your map too.

# FORM

# Map of Howard University Physical Chemistry Laboratory

with Surrounding Hallway.

## Name:_____

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# 2: Chemical Literature

## Using Scientific Literature

In this initial exercise you will learn more about searching the scientific literature. You need not follow the standard format for labs for your report (this applies to this report only). Next week's quiz will include material from this discussion.

## Goal

The goal of scientific research is to produce new knowledge that others may use. Performing a literature search can save you much work and even embarrassment in the long run. Google, Wikipedia and other similar resources are very useful. However you need go beyond these for serious scientific research.

## Why We Need Peer Review

This video presents an outstanding explanation of why media reports of science are often completely wrong. This is why we need the scientific peer review process.

Watch: Scientific Studies: Last Week Tonight with John Oliver (HBO)
https://www.youtube.com/watch?v=0Rnq1NpHdmw

## Structure of a Typical Scientific Paper

- Although each scientific paper may be a little different, most papers follow the following template.
- Abstract
- Short Introduction describing the purpose, relevant theory and derived equations.
- Experimental with a short description of the apparatus and procedures.
- Results including sample calculations, tabulated results with error bounds.
- Conclusions with a discussion of error, precision and accuracy as appropriate. Compares results with any other available literature values and discusses error and accuracy.
- References. A citation of all sources including books, peer reviewed journals and the internet.

## Peer Reviewed Scientific Journals

Peer reviewed scientific journals remain the most important source of information for scientists. Examples include the New England Journal of Medicine, Nature, Science, the Journal of the American Chemical Society. Peer review refers to the process where papers are submitted to journals. The papers are sent anonymously to other scientists who review the papers for importance, errors, length, readability and other things. Reviewers make recommendation to editors who reject or accept them depending upon the reviews. Peer review is the "gold standard" of the scientific process although mistakes are often made. It does not guarantee that the paper is correct but it catches obvious errors and fraud (usually)

## Other Primary Sources

Preprints (papers sent to journals and under peer review are now often available before their acceptance by journals but beware! Some many never appear due to errors found during peer review.

## The "Gray Literature"

- Masters and Ph.D. Dissertations
- Government Reports

- Proceedings from scientific meetings
- Patents

## Secondary Literature

The secondary literature presents results that are compiled from the primary sources. Textbooks are a form of secondary literature with which you are probably most familiar. Other important sources include indexes and abstracts. These include sources such as Chemical Abstracts, Medline and Web of Science. Other excellent sources include review journals such as Chemical Reviews and Reviews of Geophysics; and data collections such as the CRC Handbook.

## Chemical Abstracts and SciFinder Scholar

Chemical abstracts is the most respected source of chemical information and guide to the literature. The print version began in 1907 and the electronic version began in 1967. It covers almost anything in the primary literature that can be construed to be new research in chemistry or chemical engineering. This means that it also includes much about the literature in biology, environment, geology, materials, medicine and physics. Coverage is global and it tries to include all languages. You can search it in many ways including by keywords, title and authors. SciFinder Scholar is an electronic version of chemical abstracts.

## MEDLINE® (Medical Literature Analysis and Retrieval System Online)

MEDLINE is a leading bibliographic database for medicine, medicinal chemistry and the life sciences. Given the importance of chemistry for medicine, MEDLINE includes a significant amount of abstracts in most areas of chemistry. An advantage of MEDLINE is that it's free and available to the general public. MEDLINE contains citations of over 15 million journal articles. It begins in about 1950 (there is some older material) to the present. There are citations from approximately 5,000 journals in 37 languages. MEDLINE is a subset of PubMed® which is, in turn, one of the databases provided by US National Library of Medicine 's National Center for Biotechnology Information (Source US National Library of Medicine website; see below).

### Instructions for MEDLINE®

1) MEDLINE: Go to the US National Library of Medicine (National Institutes of Health) website:
http://www.nlm.nih.gov/

2) Go to PubMed in upper left-hand corner.

3) Try an author search first. Type a name of one of our faculty in the search box at the top and submit. If no articles appear try again. If too many appear try a list of two names or more. Now you will find fewer citations. For example suppose that you are looking for a paper written by Fujita AND Stockwell. Arrive at a more reasonble number of abstracts. View one of the abstracts by clicking on its title.

4) Now try a subject search. It works just like the author search.

## Google Scholar

A Google search engine focused on the scholarly literature. Works mostly like Google; see the site at: http://scholar.google.com/

## American Chemical Society

To see a list of journals published by the ACS go to: http://pubs.acs.org/action/showPublications?display=journals
Search these journals at: http://portal.acs.org/portal/acs/corg/content

## Science - American Association for the Advancement of Science

http://www.sciencemag.org/

# Beware of Science Fraud

Approximately one published scientific paper per day is retracted due to some form of misconduct that ranges from plagiarism to fabricating results. Two percent of scientists say they have fudged their data in publications. Do not commit fraud in your labatory reports or during your professional career.

Read: What's Behind Big Science Frauds?
By Adam Marcus and Ivan Oransky May 22, 2015 in the New Your Times.
http://www.nytimes.com/2015/05/23/opinion/whats-behind-big-science-frauds.html?_r=0

# Assignment - To Do

In this initial exercise you will perform a literature search by using an online abstract service. Most operate in more or less the same way. Given the health profession orientation of many in our class you can use MEDLINE® OR the other sites listed above.

## Complete Table 1

Complete Table 1 using MEDLINE to perform the search, or use or another one of the databases listed above. Be sure to put you name and the database you used and write down how many citations you find for your search.

Name_____ Database_____

Table 1. Subject / Keyword Search Results – The quotes are necessary where shown.

| Search Term | Number of Citations |
|---|---|
| Thermodynamics | |
| "Quantum Mechanics" | |
| Enzyme | |
| Protein | |
| Thermodynamics AND Enzyme | |
| "Quantum mechanics" AND Enzyme | |
| Kinetics | |
| Kinetics AND Enzyme | |
| Kinetics AND Thermodynamics | |
| Spectroscopy | |
| Spectroscopy AND Enzyme | |
| "X-Ray Crystallography" | |
| Hydrogen Peroxide | |
| H2O2 | |

## Discuss the Results for Table 1.

Notice that many of the searchs in Table 1 are linked, such as the search for Enzyme and the search for Thermodynamics AND Enzyme. Write a paragraph that discusses the differences between the connected search terms. Include in your report.

## Find a Paper by Using a Search Strategy

The best databases include links so that you can download papers. However costs are usually involved. Howard University has several subscriptions that are free to you when used within the university. Come up with a total of three search terms. These may be authors or key words or some combination of these and list in the Report section. Use the search terms to find a recent research article in a primary peer reviewed journal. You many need to revise the search terms depending on your results. Try to find a paper that includes all or most of the standard paper components that we discussed in class (Abstract, Experimental (or methods), Results, Discussion and References). Do not worry if the paper does not contain an Appendix because its not included in the typical paper. Download the paper to your computer.

Each student will find a unique paper. You must use a defensible search strategy; just using a paper that you happen to have does not count.
After you find a paper, **Reseserve It** by writing down its reference on the reservation sheet on my door.

## Write a Paragraph Explainging Your Search Strategy

To get credit for this part you must successfully explain in your report how you found your paper from the databases. From your report I need to be able to find it from your description.

Include in your discussion a list of your search terms such as:
Term 1. Thermodynamics; Term 2. Kinetics; Term 3. Enzyme

## Discuss the Paper Briefly

For the primary research paper that you found discuss its format. How well does it present its results? I am not looking for a detailed review, just a short assessment that should be expressed in two or three paragraphs. If you were the reviewer would you recommend major changes (why or why not)?

## More Questions to Answer in Your Report

1. What is the difference between the primary and secondary scientific literature?
2. Discuss the differences between a paper in a peer-reviewed journal, a review article and a textbook.
3. Given the same paper, would scientists believe it more if it were published in Nature or a Federal Government Report? Why?
4. Discuss the peer review process. What are its virtues? Can you imagine any serious problems and deficiencies?
5. Suppose you are new to a specialized research area but familiar with the overall subject. Would it be better to begin your search with a paper in a peer reviewed journal, a review article or a textbook? Defend you answer.
6. Compare the Example Databases to Google and the Wikipedia. What are their relative strengths and weaknesses?

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# 3: Experimental Error and Statistics

## Density, Experimental Error and Data Analysis

### Purpose

The purpose of this laboratory is to collect datasets that will be used to show the random and systematic errors associated with any measurement. The student will make learn about data analysis. Density measurements will be used as the first example. Density is chosen because it is a familiar concept and this allows the student to focus on the new concepts of experimental error in this laboratory.

### Introduction

Density, and extensive and intensive properties
Mass and volume are extensive properties. Extensive properties depend on the amount of substance present in a sample. Usually an intensive property results if two extensive properties are divided. An intensive property is a characteristic of a substance and does not depend on the amount present.
Density (d) is an example of an intensive property derived from two extensive properties, mass (m) and volume (V).

$$d = \frac{m}{V}$$

Although there are many ways to measure density for specialized applications, in this laboratory we will measure density by measuring the mass and volumes of samples and then calculating the density.

### Experimental Error

No measurement is perfectly exact and in fact all measurements have random errors systematic errors. Suppose that the same measurement was repeated a large number of times. Random error prevents the measurement from giving you the same value every time. Figure 1 is a distribution that shows the general result for a repeated measurement. The x-axis shows the measured values as the experiment was repeated. The y-axis shows the number of times the experiment yielded a particular measured value.

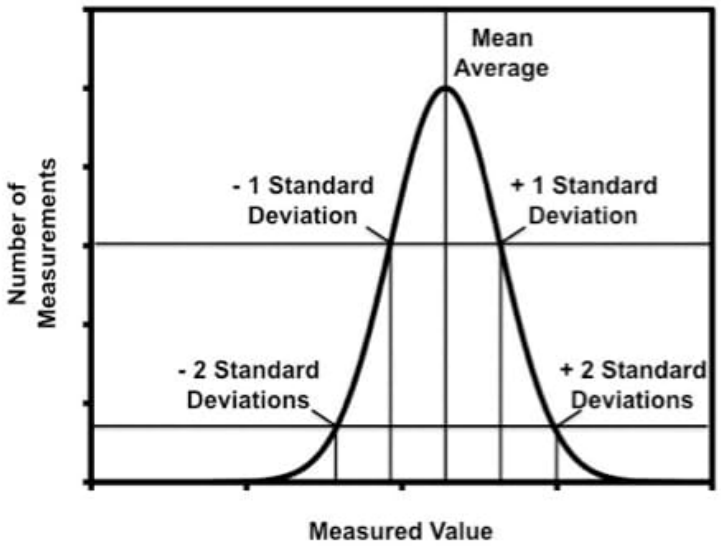



Figure 1. An experiment was repeated many times. The measured values are plotted on the x-axis and the number of times a given value was measured is plotted on the y-axis. The standard deviation is .

Random error leads to the Gaussian (or normal distribution) shown in Figure 1. The mean average is the most frequently measured value. The mean, $\overline{x}$, is given by:

$$\overline{x} = \frac{\sum x_i}{N}$$

where: $x_i$ are the measured values and N is the total number of measurements. The standard deviation of the mean, $\sigma$, is given by:

$$\sigma = \sqrt{\frac{\sum (x_i - \overline{x})^2}{N-1}}$$

An apparatus or a procedure for a measurement may have systematic errors. The difference between random and systematic error is that systematic errors can lead to bias whereas random errors contribute to imprecision. For example the measurement may have a bias that tends to yield higher or lower values than the “true” value, Figure 2.

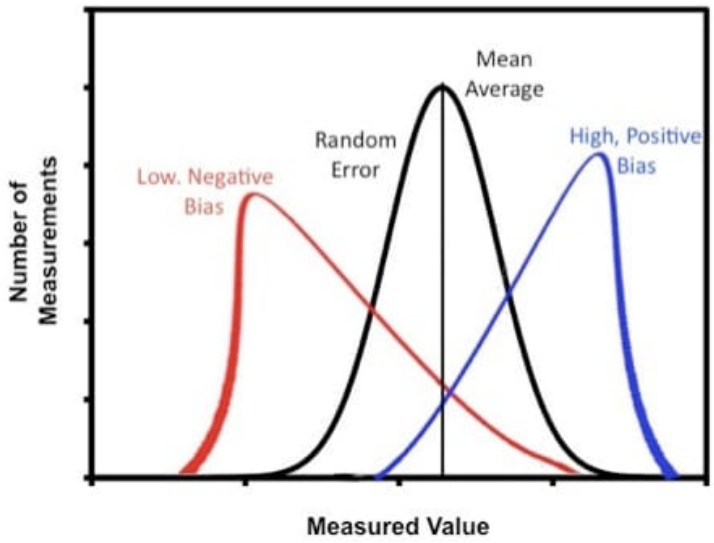



Figure 2: An experiment was repeated many times. The distribution in red shows low or negative bias. The distribution in blue shows high or negative bias. The curve in black is the normal distribution due to random error. The mean average or “true” value is marked on the normal distribution.

Systematic errors may be fixed (e.g. constant in magnitude) or proportional in magnitude to concentration or other experimental variables. Since the averaging of of a very large number of replicate measurements will reduce the random error, the total error for a system of measurements will tend towards the systematic error as the number of replicate measurements increases. You may be able to test this result based on a comparison of all data generated by the class.

## Experimental Procedure

You will measure the volume and mass of three substances that were chosen to be somewhat difficult. Your grade does not depend on getting the “right” density but it does depend on your learning about measurements. The substances are navy beans, Styrofoam and ice.

1) Navy Beans: Each group will take a clean and dry 250 ml beaker, weigh it on a top-loading balance and record its mass. Remove the beaker from the balance and then weigh it again. Weigh the beaker a total of 5 times. Ask yourself if you always get the same results.

Add 50 ml of beans to the beaker, weigh it and record the total mass. Pour out the beans back to the stock of beans and stir the stock of beans so that you will not be weighing all the same beans again. Measure another 50 ml of beans and weigh. Do not try to get the same mass as the first by adding, subtracting, shaking the beaker... doing these kinds of things introduces systematic bias and will ruin the experiments. Repeat this procedure for a total of 10 times.

Repeat for 100 ml of beans. Repeat this for a total of 10 times with volumes of 100 ml of beans.

Repeat for 150 ml of beans. Repeat this for a total of 10 times with volumes of 150 ml of beans.

Repeat for 200 ml of beans. Repeat this for a total of 10 times with volumes of 200 ml of beans.

2) Styrofoam: Repeat the procedure above but substitute Styrofoam for the navy beans.

3) Ice: Repeat the procedure above but substitute ice for the navy beans. Make sure that you use a paper towel to dry the ice before weighing it and do not handle it with your fingers (Why not?). This is difficult but do the best you can to remove the water. You may find that there is some systematic bias in the ice measurements. Describe the sources and types of error in your lab report.

4) Data Pooling: We will pool our data across all groups and be sure to submit your data to the instructors at the end of the lab period.

## Data Analysis – Error and Distributions

The data will be provided in an Excel spreadsheet and you will calculate the density of the beans, Styrofoam and ice from the measurements. Keep four significant digits in these calculations.

Calculate the average mass of the beaker. The mean average, $\overline{x}$, is given by:

$$\overline{x} = \frac{\sum x_i}{N}$$

where: $x_i$ are the measured values and N is the total number of measurements. Determine the standard deviation of the mass measurements for the empty beaker with the formula,

$$\sigma = \sqrt{\frac{\sum (x_i - \overline{x})^2}{N-1}}$$

Calculate the density for all of the mass measurements from the following formula,

$$d = \frac{m_i - m_b}{V}$$

where $m_i$ is the measured total mass, $m_b$ is the mass of the empty beaker and $V$ is the volume (50, 100, 150 and 200 ml). For the mass of the beaker use its average mass. You will get a set of densities for navy beans, Styrofoam and ice. For example a sample dataset for navy beans is given below.

***Table 1:*** *Volume and mass measurements, and calculated densities for navy beans.*

| Volume (ml) | Mass (g) | Density (g / ml) | Volume (ml) | Mass (g) | Density (g / ml) |
|---|---|---|---|---|---|
| 0.000 | 114.0 | | | | |
| 50.00 | 154.0 | 0.800 | 150.0 | 248.0 | 0.893 |
| 50.00 | 154.2 | 0.804 | 150.0 | 242.2 | 0.855 |
| 50.00 | 160.2 | 0.924 | 150.0 | 239.2 | 0.835 |
| 50.00 | 158.2 | 0.884 | 150.0 | 248.2 | 0.895 |
| 50.00 | 158.0 | 0.880 | 150.0 | 242.3 | 0.855 |
| 50.00 | 152.1 | 0.762 | 150.0 | 240.5 | 0.843 |
| 100.0 | 197.0 | 0.830 | 200.0 | 276.8 | 0.814 |
| 100.0 | 204.2 | 0.902 | 200.0 | 280.4 | 0.832 |

| Volume (ml) | Mass (g) | Density (g / ml) | Volume (ml) | Mass (g) | Density (g / ml) |
|---|---|---|---|---|---|
| 100.0 | 199.8 | 0.858 | 200.0 | 282.0 | 0.840 |
| 100.0 | 195.9 | 0.819 | 200.0 | 282.2 | 0.841 |
| 100.0 | 201.5 | 0.875 | 200.0 | 283.8 | 0.849 |
| 100.0 | 203.1 | 0.891 | 200.0 | 279.2 | 0.826 |

Calculate the mean average and the standard deviation for the densities of the beans, Styrofoam and ice. For example, the average and the standard deviation of the limited dataset above are 0.85 g/ml and 0.038 g/ml, respectively.

Next take the density for each substance and sort it (there is an Excel command for this). Below is an example from the sample dataset.

*Table 2: The calculated densities for navy beans are arranged from low to high values.*

| Density (g / ml) | Density (g / ml) |
|---|---|
| 0.762 | 0.849 |
| 0.800 | 0.855 |
| 0.804 | 0.855 |
| 0.814 | 0.858 |
| 0.819 | 0.875 |
| 0.826 | 0.880 |
| 0.830 | 0.884 |
| 0.832 | 0.891 |
| 0.835 | 0.893 |
| 0.840 | 0.895 |
| 0.841 | 0.902 |
| 0.843 | 0.924 |

This is the same data as above. The data as been sorted from low to high values.

Sort the data into bins consisting of equal data ranges. See the example below. You will have to adjust the size range of the bin to get a good understanding of the distribution. Describe the thought process used to determine your bin sizes. WARNING: We do NOT expect that everyone thinks the exact same way.

*Table 3. The calculated densities for navy beans sorted into bins consisting of a range 0.03 g/ml per bin.*

| Density Range (g / ml) | Number of Values in the Range |
|---|---|
| <0.799 | 1 |
| 0.80-0.8299 | 5 |
| 0.83-0.8599 | 10 |

| Density Range (g / ml) | Number of Values in the Range |
|---|---|
| 0.86-0.8899 | 3 |
| 0.89-0.9199 | 4 |
| >0.92 | 1 |

Make a plot of the density range and the number of values similar to Figure 3 for each substance. Fit a polynomial curve to the bars to see the distribution better.

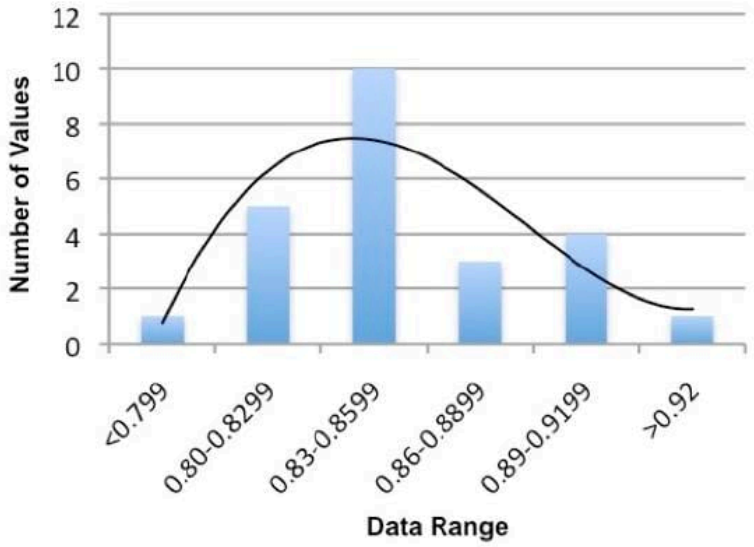



*Figure 3. A plot of the distribution derived from Table 3. Note that it is not too far from the normal distribution. There may be a small systematic negative bias in the measurements.*

## Data Analysis – Part 2 – Analysis by Linear Regression

Read the handout “Error, Accuracy, Precision and Linear Regression”. There is another method to treat the measurements that usually results in more accurate results. This method is linear regression.

An Excel spreadsheet for linear regression is supplied. An advantage of the spreadsheet is that it gives the best fit slope, intercept and their standard deviations. The standard deviations are not available from the standard version of Excel, you have to buy an extra Excel statistical package to have them.

Make three copies of the original spreadsheet for linear regression and save the original in case you mess up one of the copies. Paste all of the volume and mass measurements for each substance into a copy of the Excel spreadsheet. Include values made with the empty beaker and enter the volume as zero for these.

Copy the regression plots along with the best fit slope, intercept and their standard deviations into your laboratory report. You should add labels to the axes of the plots, Figure 4. The slope is the density for each substance and the standard deviation of the slope is the standard deviation of the density. Compare the values calculated by linear regression with the results from Part 1. Is the standard deviation of the density larger or smaller than the one calculated in Part 1?

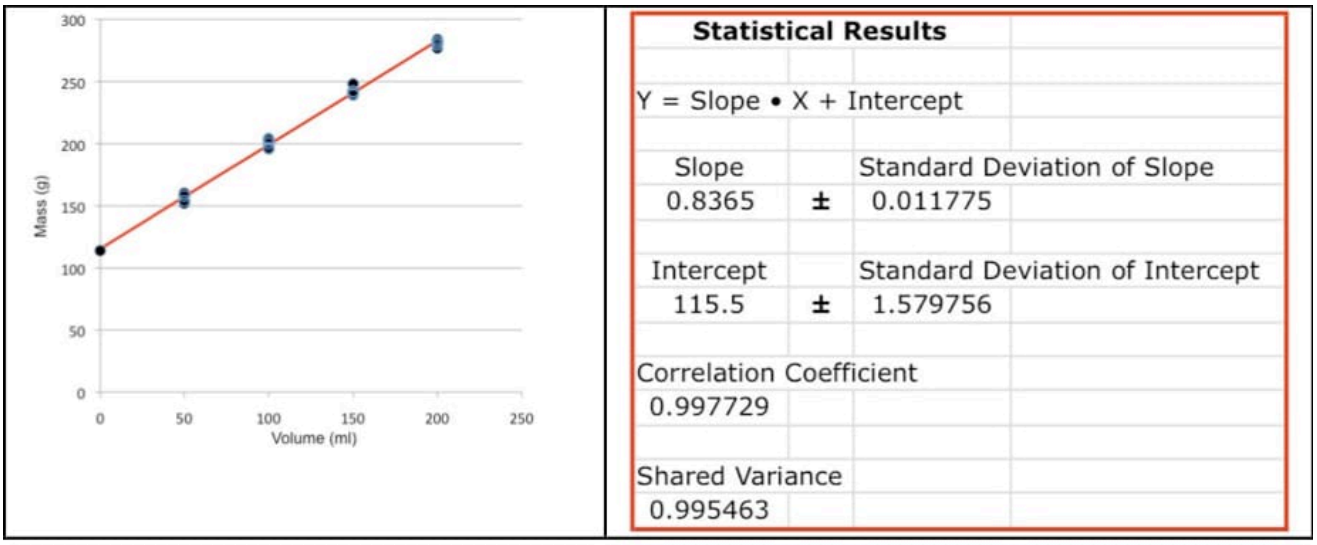



*Figure 4: A plot of the linear regression of all data from Table 1 showing the best-fit line. The statistical results from the spreadsheet for linear regression are shown on the right.*

## Part 2 - Calibration of a UV-Visible Spectrometer

### Purpose

In this laboratory you will learn the general theory of calibration. To perform the calibrations you need to understand the concepts of significant figures, measurement error, accuracy, precision, propagation of errors, graphing and linear regression.

### Introduction

It is easy to buy any number of measuring devices: thermometers, scales to measure your weight, watches and timers, laboratory instruments etc. To often, at least at home, people just trust the numbers coming out of the measuring devices. Chemists make measurements with some devices that they have used for centuries, such as volumetric glassware (pipettes, graduated cylinders, etc.) and chemical balances and with modern spectrometers. In a medical laboratory or in a hospital the results may be disastrous if the numbers are not accurate. How do can you know that the measurements correspond to reality? Calibration of the measurement device is required. **Calibration is the process that correlates an instrument's response with known standards.** In this laboratory you will perform a calibrations of a UV-Vis spectrometer.

**Calibration of a UV-Visible Spectrometer**

1. First you will use an Ocean Optics visible spectrometer and a hydrogen discharge lamp. Turn on the hydrogen lamp and examine its spectrum. Use the green cursor to read the wavelengths of the hydrogen lines.

- One of the spectra should be read at a low enough integration time so that none of the lines "peak out".
- The second spectra should be recorded at a higher integration time so that you can see lines with lower intensity.
- Each group will make their own spectral measurements.

2. Repeat this procedure for argon and mercury **using the same spectrometer that you used for your group's hydrogen spectra.**
3. Make one calibration curve for your spectrometer using your data that includes both your hydrogen and argon data.

Make a table in Excel with your wavelengths measured lines and the known lines. Note that there will be differences between the wavelengths of the peaks as measured by the spectrometer and their known wavelengths. For hydrogen the known lines are 656.3, 486.1, 434.1 and 410.2 nm. You can check these spectral lines and find the ones for argon at: http://physics.nist.gov/PhysRefData/ASD/index.html. Note that H I and Ar I are the atoms of H and Ar, respectively.

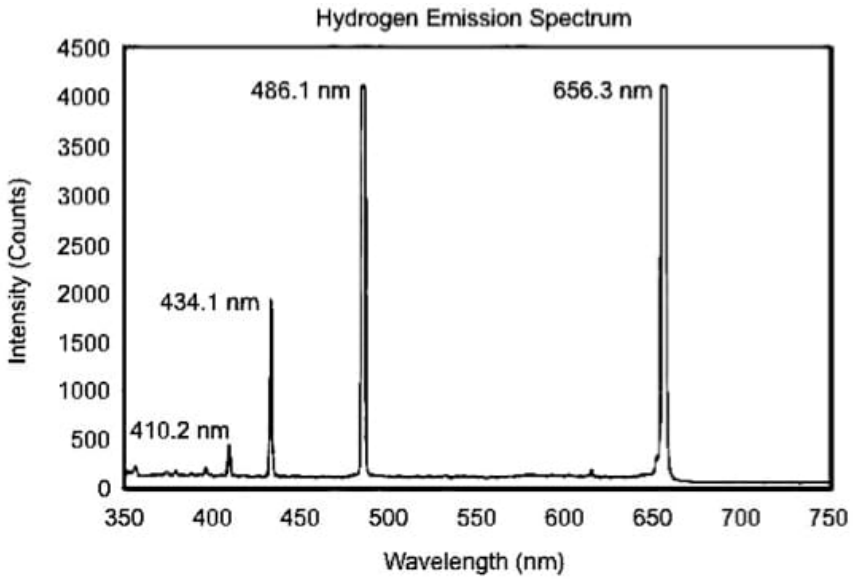



Figure 5: A plot of the known emission lines for hydrogen.

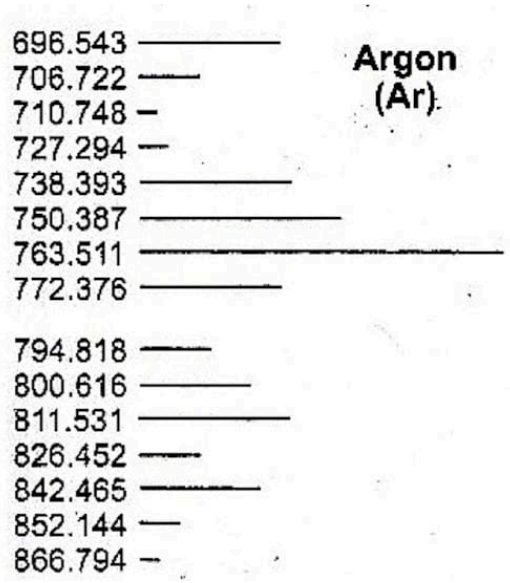



Figure 6: A plot of the known emission lines for argon.

4. Plot the points and determine slope and intercept as you have done in the precious sections. It is strongly suggested that you use the known lines as the “y-axis” and your measured lines as the “x-axis”.
5. Copy the hydrogen lines into the Linear Regression Spreadsheet and calculate the slope, standard deviation of slope, intercept, standard deviation of intercept, the correlation coefficient and the shared variance for these data. The equation that you will get is the following:

    Calibrated Wavelengths = slope * measure wavelength + intercept

6. Copy the statistical results and the plot of the calibration curve for the wavelength scale into your laboratory report in the Results section.

See Also: http://www.astronomyknowhow.com/hydrogen-alpha.htm

## Report

You may combine this section with the first part on density to create one report. Comment on the

bias of all the measurements.

### The Linear Regression Spreadsheet is Available at:

Linear_Regression.xls

A weighted least squares regression spreadsheet is available at:

Linear_Regression_Weighted.xls

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# 4: Numerical Data Analysis

## Physical Chemistry Laboratory Fall 2016

## Numerical Data Analysis

### Professor Vernon Morris

Numerical analysis involves the practical use of mathematical calculations. Much like the Babylonian approximation of $\sqrt{2}$ (which turned out to have tremendous practical applications), modern numerical analysis does not seek exact answers, because exact answers are often impossible to obtain in practice. The current “arguments” revolving around “Climate Science” are a great example of this. The naysayers tend to focus on the existence of uncertainty as a reason to doubt everything. In fact, the constraints on the uncertainty are precisely why we should be paying great heed! Numerical analysis is concerned with obtaining approximate solutions while maintaining reasonable – as accurately as possible – bounds on errors.

Numerical analysis naturally finds applications throughout engineering and the physical sciences. The current century finds that life sciences, social sciences, and the arts have adopted various elements of numerical analysis and statistics as fundamental to their practice.

The overall goal of the field of numerical analysis is the design and quantitative study of techniques to give approximate but accurate solutions to hard problems, the variety of which is suggested by the following:

- Advanced numerical methods are essential in making highly accurate numerical weather prediction commonplace. (Consider the availability and specificity of the upcoming winter and seasonal forecasts compared to when you were in grade school.)
- Computing the trajectory of a spacecraft requires the accurate numerical solution of a system of ordinary differential equations. Recently, a rocket was not just launched but landed in vertical position. Others have been retrieved a sea on ships.
- Car companies can improve the crash safety and autonomous operations of their vehicles by using computer simulations. Such simulations essentially consist of solving partial differential equations numerically.
- Hedge funds (private investment funds) use tools from all fields of numerical analysis to attempt to calculate the value of stocks and derivatives more precisely than other market participants. (Google “Voodoo” economics sometime!)
- Airlines use sophisticated optimization algorithms to decide ticket prices, airplane and crew assignments and fuel needs. Historically, such algorithms were developed within the overlapping field of operations research.
- Insurance companies use numerical programs for actuarial analysis.

## Purpose

The purpose of this assignment is to provide you with some experience exploring and analyzing data numerically, i.e. without using an information visualization system. You will be provided a data set (that can be imported into Excel) about the ambient atmosphere. You should explore and analyze this data using Excel or any other graphing or visualization tools with which you are familiar (e.g. Mathematica, MATLAB, S-Plus). Your goal here is to perform an exploratory analysis of the data set, to better understand the data set and its characteristics, and to develop insights about the environmental data.

## Report

The report that you turn in should consist of five things.

1. First, list (bullet list of items) five "insights", chunks of knowledge, or deeper questions that you either encountered or gained while exploring the data. An insight could be some understanding of the data and its characteristics that is not relatively obvious or intuitive. It is something that most people might not realize initially. Note that an insight or knowledge chunk simply may be a deeper question that arose in your mind while exploring the data and your cursory analysis may not have been sufficient to answer the question.
2. Plot the time series of the key environmental variable(s) supplied to you by the instructor. Based on your visual inspection,

describe the temporal behaviors of each parameter and their apparent relationships to each other.

3. Perform and report on the outcomes of the following statistical techniques

    a. Determine the median and geometric means of each environmental parameter for all daytime hours, all nighttime hours, for the average day (24 hours) and over the entire observational period. Compute and report the average deviation and variance for each statistical measure.
    b. Pick out the two groups (e.g. daytime, nighttime, full day, full observational period, or another descriptive measure of the data set) whose means are closest to each other. Do a two-sample t-test on the two groups you picked, using the Excel function described on the t-test page. Report the P-value and propose a plausible explanation what it means.
    c. Do a two-sample t-test on the two groups in your data set with means that are the furthest apart. Report the P-value and propose a plausible explanation for what it means.
    d. Perform a Pearson Correlation for all pairs of time-dependent variables from the data set. Report the R-values and propose a plausible explanation for what it indicates.

4. Attempt to “fit” the data with a mathematical function (e.g. linear, 2nd-degree polynomial, 3rd-degree polynomial). Which functions worked the best and for which parameters? What do you think is the purpose of such an exercise? What advice would you give someone who needs to fit a similar data set?
5. Write two paragraphs about challenges or problems that you encountered in doing the analysis this way. Did anything limit or frustrate you? If nothing did, perhaps there was something that was more difficult than you thought it should be. Nothing is perfect, so you should be able to list some potential issues here.

## Down Load Data for Analysis Here

3_AirConc_200507.xls

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# 5: INTRODUCTION TO COMPUTATIONAL TOOLS FOR P-CHEM

5.1: Pre-Lab Assignment

5.2: Python, Jupyter Notebooks, and Google CoLab

5.3: Chem Compute for Molecular Electronic Structure Calculations

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# 5.1: Pre-Lab Assignment

📅 **Due:** This assignment must be completed before 1:00 PM on your first lab meeting day (see syllabus schedule).

🕒 **Time:** Plan at least two hours to complete this assignment. If you run into technical challenges, this will take additional time.

🎯 **Purpose**: Learn to use Python, Jupyter Notebooks, and Google CoLab so that you arrive to our first meeting prepared to complete your first in-class activity.

---

## Pre-Lab assignment for our first meeting

*This assumes you have completed the Orientation Module and have enrolled in our Google Classroom.*
To prepare for the first laboratory meeting, please do the following prior to the laboratory period:

- Read this entire module - follow the instructions within the module to complete the tasks listed below.
  - Complete and submit the Google CoLab assignment: *A. Introduction to Python and Jupyter Notebooks (in Google CoLab)*.
  - Create an account on ChemCompute
- Bring your working computer to the meeting.
- This session is a "Dry Lab": We will meet in a classroom, thus lab attire is not necessary for this session.

**Be sure you complete the assignment above and submit it on Google Classroom before the deadline!**

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# 5.2: Python, Jupyter Notebooks, and Google CoLab

**Goal**: gain proficiency with python, jupyter notebooks, and Google CoLab so that you can use these tools for data analysis.

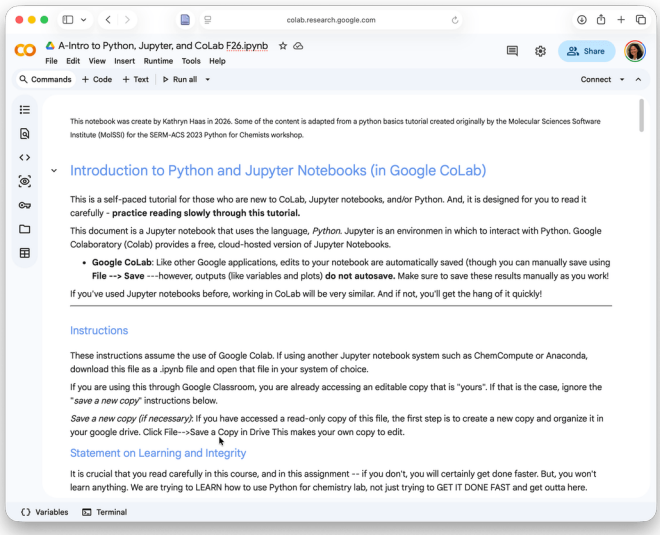
Python is a coding language that computers understand. It is more human-friendly when it it done in a Jupyter notebook. And Google CoLab is a free platform for Jupyter Notebooks.

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To get started with python, complete the tutorial provided in your google classroom. A link to the "viewable" Google CoLab tutorials are below for anyone outside our course who would like to use it. But, for students enrolled in this course, please go to your Google Classroom and complete the assignments there.

A. **Pre-semester warm up (due before our first meeting):** Intro to Python, Jupyter, and CoLab
B. **Practice with Python for data analysis (we will do this in class)**: Practice with Python In Class

This is a preview of the first tutorial:




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# 5.3: Chem Compute for Molecular Electronic Structure Calculations

**Goal**: prepare to use computational tools through the Chem Compute website. We will use them later this semester, but lets get the ball rolling on account set up now.

---

ChemCompute (https://chemcompute.org/) is a website that gives us free access to molecular electronic structure tools. We will primarily use the GAMESS quantum Chemistry package.  To prepare for the semester, sign up for an account using your Duke University credentials.

1. Go to the ChemCompute website (https://chemcompute.org/).
2. Click **Register** in the top left corner (expand the menu in the top left of it is hidden).
3. Choose LOG IN WITH YOUR UNIVERSITY (you must check boxes to indicate that you read and accept the acceptable use policy and indicate that you are not a spy).
4. Use your Duke NetID (the same credentials that you use to log into Duke email) to sign up.

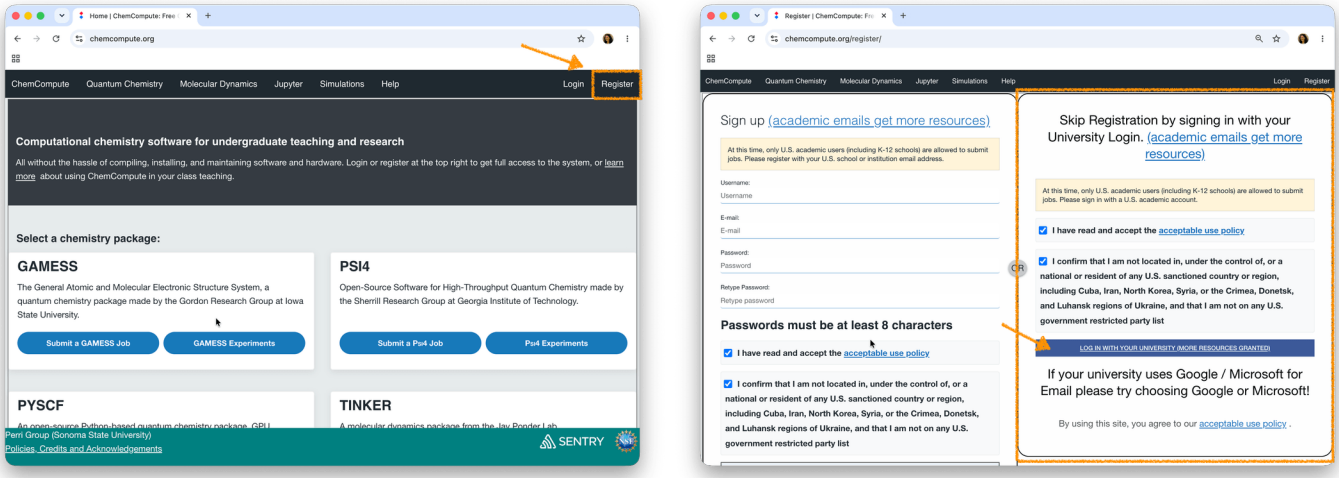



Figure 5.3.1: How to sign up for ChemCompute account using your ".edu" University Credentials. (Kathryn Haas; CC-NC-BY-SA)

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# 6: Computation of Thermodynamic Quantities

## Computation of Thermodynamic Quantities Based on Molecular Structure Calculations

## Introduction:

The thermochemistry of common substances is largely known through carefully measured experiment. Thermochemical data for substances are available in data tables in both written and digital formats (e.g. Chemical and Engineering Data Reference Tables, CRC Handbook). Knowledge of the standard values of state functions such as the heat of formation, heat capacity, molar entropy, and free energy are useful in determining appropriate reaction conditions. This laboratory assignment is designed to provide a basic introduction to modern methods of computational thermochemistry, to thermochemical data, and to a comparison of the accuracy of computed values to experimental data. Note that this laboratory can be done in shifts, since there are only three machines with Spartan loaded in the PChem lab.

## Objectives:

1. Learn to use computational chemistry software to optimize geometries and to model molecular behavior.
2. Perform computations of thermodynamic functions using equipartition theory and compare to literature values.
3. Evaluate the performance of various theoretical models used in computational chemistry with regards to thermochemistry

## Procedure:

(Equipment Required: Computer with Spartan)
For this lab, you will compute IR vibrational frequencies and thermodynamic state function values for different molecules using several theoretical techniques. You will then compare the results to literature values for ideal and real gases as well as compare the performance of different theoretical models.

### Running Spartan for Thermochemical Calculations.

1. Make a new file.
2. Build molecule by selecting atoms and clicking on screen.
3. Go to Setup Calculations, Select “Single Point Energy”, depending on your case: molecular mechanics, semi-empirical, and Hartree-Fock (HF/3-21G), check IR and thermodynamics. You need not change anything else.
4. Go to submit and “submit”.
5. Use Monitor to see if model is executing. (Should be very fast so might not be necessary).
6. Go to display and record thermodynamic values. Record the “contributions” to enthalpy, entropy, Cv … Note that Total Enthalpy = Total vibration + ideal gas + translation + rotation.
7. Go to display spectra and write down the vibrational frequencies.

### Computational Thermochemistry Simulations

1. Build and minimize molecular models for $CH_2O$, HCN, $CO_2$ and $CH_4$ using molecular mechanics, semi-empirical, and Hartree-Fock (HF/3-21G*).
2. Tabulate the thermochemical data for each simulation.
3. Tabulate the vibrational (IR) data for each simulation.
4. Perform a literature search to identify the thermodynamic constants and the vibrational frequencies of each molecule. Evaluate the % error, bias, and average absolute error for the thermodynamic constants and separately for the vibrational bands from literature values.
5. Compare and discuss the differences between the calculated thermodynamic values for the enthalpy, entropy and molar heat

capacity and their corresponding literature values for each molecule. [You should construct a simple table of values]

6. Discuss the trends that you observe. For example, what was the trend in the %error for each constant as a function of computational method? What about the other statistical measures?
7. Compare and discuss the differences between the calculated thermodynamic values for the vibrational frequencies for each molecule. [You should construct a simple table of values here as well] Discuss the trends that you observe. For example, what was the trend in errors for each constant as a function of computational method? How did the errors vary by molecular size? How did the errors vary as a function of vibrational mode?
8. Compute the vibrational contributions to the molar heat capacities of hydrogen cyanide and methane using a) the computed values of the vibrational frequencies and b) the literature values of the vibrational frequencies. To what do you attribute the differences in these quantities? Represent your data in tabulated form. Explain the trends and discuss the results. HINT: Use the vibrational temperatures for each gas to compute the molar heat capacities and note that the total vibrational heat capacity is equal to the sum of the heat capacities for the individual vibrational degrees of freedom.

The vibrational temperature, $\Theta_{vib}$, is defined by the equation:

$$\Theta_{vib} = \frac{hc\nu}{k}$$

where h is Planck's constant, c is the speed of light, v is the frequency and k is Boltzmann's constant.

The vibrational contribution to the molar heat capacity from a given vibrational degree of freedom of frequency ν is given by:

$$(C_v)_{vib} = N \times R \times \left(\frac{\Theta_{vib}}{T}\right)^2 \times \frac{\exp\left(\Theta_{vib}/T\right)}{\left\{\exp\left(\Theta_{vib}/T\right) - 1\right\}^2}$$

where N is the number of moles, R is the ideal gas constant and T is temperature.

The total contribution to the heat capacity at constant volume from all vibrational degrees of freedom is:

$$C_{vib,Total} = \sum (C_v)_{vib}$$

where the summation is over all vibrational degrees of freedom, 3N-5 (linear molecules) or 3N-6 (non-linear molecules)

9. The speed of sound in any gas can be computed from the expression:

$$v_{sound} = \left\{\left(\frac{C_p}{C_v}\right) \times \frac{RT}{M}\right\}^{1/2}$$

Where $C_p$ is the heat capacity at constant pressure, $C_v$ is the heat capacity at constant volume and M is the molecular mass of the gas. Use your computed values of molar $C_V$ and $C_P$ to derive a theoretical speed of sound for each of your gases and compare to each other and to their literature values. Evaluate the %error, bias, and average absolute error for the theoretical and "literature-derived" molar heat capacities. What trends, if any, do you observe both amongst the four gases (within a particular theoretical framework) and between individual gases computed across the framework. For the "literature-derived" sound velocities, use the tabulated values of the molar CP and CV at the standard temperature and pressure values of 298 K and 1 atmosphere.

## To Calculate and Display the Distribution of Electrons

1. Setup the molecules as above.
2. Make a new file.
3. Build molecule by selecting atoms and clicking on screen.
4. Go to Setup Calculations, Select "Single Point Energy", and Hartree-Fock (HF/3-21G), check IR and thermodynamics. You need not change anything else.
5. Here you only need to run the Hartree-Fock (HF/3-21G),
6. Go into "Setup" menu and choose "Surfaces"
7. Click "Add" and choose Surface = density; property = Potential; click "OK"; close window.
8. Go to submit and "submit".
9. Use Monitor to see if model is executing. (Should be very fast so might not be necessary).
10. When completed go to "Results" menu and choose "Surfaces"; click on the box and see the potential surface around your

molecule.
11. The red regions of the surface indicate the more electronegative regions of the molecule while the blue regions indicate the lower electronegative regions.

## To Display the Vibrational Modes

12. Go to “Results” menu and choose IR. Check the box to display the entire spectrum. Click on the boxes to see the molecule vibrate in each of its modes.

Computational Thermochemistry Exercises
Inorganic Molecules.

1. Build $H_2$ and run.
2. Build HCl and run.
3. Build HF and run.
4. Compare the electron distribution for these three molecules. What does this say about electronegativity?
5. Examine the vibrations for the three molecules and compare. Which molecule has the greatest vibrational frequency? Is there any relationship to the electronegativity?

## Organic Molecules

1. Build benzene and run.
2. Build chlorobenzene and run.
3. Build toluene and run.
4. Build $C_6H_5$-O-$CH_3$ and run.
5. Compare the electron distribution for these three molecules. What does this say about electronegativity and the ability of groups to extract or donate charge to the ring?
6. Examine the vibrations for the four molecules and compare. Is there any thing interesting that you can say?

## Lab Report

- In the lab write-up, be sure to include responses to the following questions as you discuss and analyze your results.
- What difference does the computational technique make on computed values?
- Does molecular bonding appear to play a role in computational accuracy?
- What differences are there between the computed values and literature values?
- How does one account for the difference among computed values?
- How does one account for the difference between computed and literature values?
- Propose at least two instances where computed data may be useful in an experimental laboratory setting.
- For $H_2$, HCl and HF compare the electron distribution for these three molecules. What does this say about electronegativity?
- For $H_2$, HCl and HF examine the vibrations for the three molecules and compare. Which molecule has the greatest vibrational frequency?Is there any relationship between the vibrational frequency to the electronegativity difference between the elements?
- For the four aromatic molecules compare the electron distributions. What does this say about electronegativity and the ability of the groups to extract or donate charge to the ring?
- For the four aromatic molecules examine the vibrations for the three molecules and compare. Is there any thing interesting that you can say?

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# 7: Equation of State

## Equation of State Experiment -- Temperature and Pressure Measurements of an Ideal Gas During Heating Within a Closed Container

### EXPERIMENT DESCRIPTION: The Ideal Gas Equation of State

### Purpose

The ideal gas equation of state (pV = mRT) provides a simple relationship between pressure, temperature, mass, and volume for gases at relatively low pressures and high temperatures. This experiment illustrates the application of the ideal gas equation and other equations of state to relate the properties of several gases contained in a rigid vessel with changes in temperature.

### Assignment

A stainless steel pressure vessel with a volume of 1 liter will be instrumented with a pressure transducer and thermocouple to measure the gage pressure and temperature, respectively, of the air inside the vessel. You will need to select your vessel and confirm its volume. **How do you determine the volume of the vessel?** Use the Pasco™ temperature and pressure transducers to connect to the vessel and secure so that it is air-tight. **Check with your instructor for how to determine if a fitting is air tight.** Please consult the laboratory instructor regarding the appropriate compression fittings. **What is a compression fitting? How does it differ from other types of pipe fittings?**

The pressure transducer produces a voltage signal that can be related to the gage pressure in the cylinder by a calibration curve that is supplied with the instrument. Note that atmospheric pressure in Washington, DC is approximately 13.6 psia. The calibration curve for the pressure transducer is given by the following equation:

$$p = 4.3087(V \cdot V) - (13.1176\,V) + 10.7276$$

where V equals the voltage output (volts) from pressure transducer, and p equals the absolute pressure (kPa).

The thermocouple in the pressure vessel is connected in series with a second thermocouple that is located in an ice bath that provides a reference temperature. The thermocouple pair produces a voltage signal that is related to the temperature (T) of the air in the pressure vessel by the following expression:

$$T = T_{ref} + \frac{V}{S}$$

where $T_{ref}$ equals the ice bath reference temperature (0°C), V equals the voltage (volts) measured across the thermocouple pair, and S equals the thermocouple constant, 42.4 μV/°C.

A signal processor displays and records the voltage signals from both the pressure transducer and the thermocouple during the course of an experimental trial. In addition, the signal processor records the data in a data file that can be downloaded to other programs for data analysis and plotting.

The steps you should follow to carry out the experiment are as follows:

1. Turn on the signal analyzer. Identify the location of the "start" and "pause" buttons.
2. Make sure the pressure readings and ranges are appropriate. The signal analyzer should display two different plots of pressure and time and temperature and time. You will need to combine these data to plot pressure versus temperature at the same times for your system over a range of different temperatures.
3. Check to verify that your hot plate is operating.
4. Temperature profiles (repeat as needed in order to generate reliable statistics)

- Press "start" to begin reading data, and then heat the pressure vessel by placing it on the hot plate. Continue heating the vessel until the temperature plateaus (The pressure will reach approximately 400 kPa).
- Create a slush using crushed dry ice or a liquid nitrogen slurry to cool the vessel to temperatures of at least -40oC. Record the data as above.

  NOTE: Review the handling of cryogenics below before proceeding.

- Repeat for at least three gases

  NOTE: DO NOT place a hot vessel into the cryogen or an extremely cold vessel into the heat bath.

5. Save the data appearing on the display onto a disk (ask the instructor for help if needed). Choose a meaningful name such as "yourname_LabTemp.dat" for the files. You may have to save two sets of data--one for temperature and another for pressure.
6. Using the data obtained in both the cooling and heating experiments, construct a P-T curve for the entire range of temperatures.

## Handling of Cryogens

**Cryogenic Materials** will be defined here as any material used for cooling baths that has a melting point, boiling point or sustained temperature below -20°C. This includes dry ice (solid $CO_2$), dry ice-isopropanol mixture, frozen slush baths prepared from liquid nitrogen and organic liquids (methanol, ethanol, hexane, toluene, etc.) and liquid nitrogen.

### Handling Procedure:

When cryogenic liquids are transferred to containers located above waist-height of the operator the liquid must first be poured from the storage Dewar into a small, easily handled, insulated container (such as a glass Dewar flask) and then poured into the final container. The operator must wear a face shield in addition to safety glasses when pouring cryogenic liquids above waist-level. All containers with evacuated wall space (Dewar flasks) and evacuated round-bottom flasks that have volume of greater than 500 ml. must be wrapped with tape or surrounded by protective net to contain flying glass in case the container should break while being cooled with cyrogenic liquid. Only round bottom flasks should be used for freezing and thawing of organic liquids. Evacuated flasks containing liquids frozen at cryogenic temperatures must be contained in another vessel (a beaker or open dish capable of holding the entire contents of the flask at all times).

### Preparation of a Dry Ice Slurry:

The best low temperature baths are made with as a high a percentage as possible of the coolant (dry ice here, or ice in general). Approximately the amount of dry ice that will be needed should be crushed and placed in the container (usually a dewar or equivalent). To this you should add the acetone or isopropanol slowly. This is most conveniently done with a squeeze bottle. Add only enough to cover the dry ice. If you need a looser slurry, this can be accomplished by addition of more solvent.

Loose slurries can be made in the following way:

A suitable container, usually a Dewar flask is filled about one-fourth to one-third full of the solvent. Acetone and isopropanol are both often used, but isopropanol is less volatile, less toxic, and is less flammable. A little crushed dry ice is added to the solvent and vigorous bubbling will result. As the dry ice sublimes and the solvent cools, the bubbling will become less violent. A little more dry ice can be added at this point. It should be remembered that the temperature of this bath will not be as low as with the previous recipe.

Dry ice can be added to either bath as needed to maintain the low temperature. When finished using the slurry, allow the dry ice to sublime completely, pour the solvent into a bottle indicating the solvent is for cold baths only. Loosely cap the container for about 24 hours or overnight to prevent a degassing mishap.

## Analysis

- Using the initial values of the measured pressure and temperature, the volume of the vessel, calculate, from the ideal equation of state, the mass of air in the vessel. Assuming the volume and mass are constant during the heating process,

calculate the temperature of the air (from the ideal gas equation) for each of the pressure values--remember that the recorded values of the pressure are absolute. Plot the experimental and calculated temperatures as a function of the measured pressure. Clearly label the graphs. Compare the experimental results with the theoretical results. What might be responsible for the differences?

- Plot the P vs T curves for each graph and compare the slopes to the value nR/V. Perform an error analysis based on the comparison of the theoretical and observed values. What differences to you see? Which gas or molecular characteristics might be responsible for the differences?
- Which of your gases might best be described by a van der Waals equation of state? Compare your P vs T curve to a the van der Waals P vs T curve over the same range of T and P for each potential van der Waals gas. Discuss the similarities and differences. What might be responsible for the differences?
- Extract an estimate of the van der Waals constant from your graphs. How do they compare to the literature values? How might you improve your results?

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# 8: Heat Capacity Ratios for Gases (Cp/Cv)

## Measuring the Ratio of the Heat Capacity at Constant Pressure to the Heat Capacity at Constant Volume for a Gas (Cp/Cv)

### Introduction

The equipartition theorem states that any quadratic energy term such as kinetic energy contributes equality to the internal energy of a system in thermal equilibrium. This means that for a gas each degree of freedom contributes ½ RT to the internal energy on a molar basis (R is the ideal gas constant)

An atom of a monoatomic gas can move in three independent directions so the gas has three degrees of freedom due to its translational motion. Therefore its internal energy, U, follows the equation U = 3/2 RT. The heat capacity at constant volume, $C_v$, is the derivative of the internal energy with respect to the temperature, so for our monoatomic gas, $C_v$ = 3/2 R.

The heat capacity at constant pressure can be estimated because the difference between the molar $C_p$ and $C_v$ is R; $C_p - C_v = R$. Although this is strictly true for an ideal gas it is a good approximation for real gases.

The rotation of gas molecules adds additional degrees of freedom. A linear molecule rotates along two independent axes. Therefore a linear molecule has two rotational degrees of freedom. The total number of degrees of freedom for a linear molecule is 5 so its internal energy is U = 5/2 RT, its molar heat capacity at constant volume is $C_v$ = 5/2 R and its molar heat capacity at constant pressure will be $C_p$ = 7/2 R.

A nonlinear molecule rotates along three independent axes. Therefore a linear molecule has three rotational degrees of freedom. The total number of degrees of freedom for a linear molecule is 6 so its internal energy is U = 3 RT, its molar heat capacity at constant volume is $C_v$ = 3 R and its molar heat capacity at constant pressure will be $C_p$ = 4 R.

Vibrations may add to the heat capacity but only if they are thermally accessible. The vibrational temperature, $\Theta_{vib}$, is defined by the equation:

$$\Theta_{vib} = \frac{hc\nu}{k}$$

where h is Planck's constant, c is the speed of light, v is the frequency and k is Boltzmann's constant. The vibrational contribution to the molar heat capacity from a given vibrational degree of freedom of frequency ν is given by:

$$(C_v)_{vib} = N \times R \times \left(\frac{\Theta_{vib}}{T}\right)^2 \times \frac{\exp\left(\Theta_{vib}/T\right)}{\left\{\exp\left(\Theta_{vib}/T\right) - 1\right\}^2}$$

where N is the number of moles, R is the ideal gas constant and T is temperature. The total contribution to the heat capacity at constant volume from all vibrational degrees of freedom is:

$$C_{vib,Total} = \sum (C_v)_{vib}$$

where the summation is over all vibrational degrees of freedom, 3N-5 (linear molecules) or 3N-6 (non-linear molecules)

### Experimental

You have a large bottle fitted with a gas inlet and a pressure gauge attached to a stopper in the neck of the bottle, Figure 1.

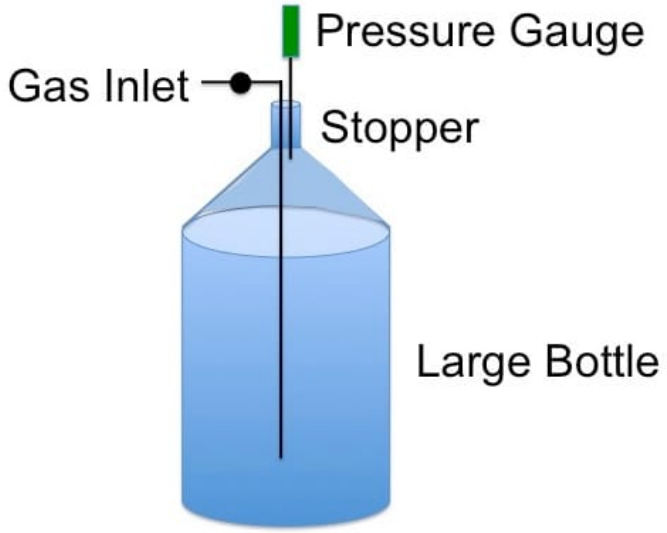



**Figure 1. Setup for measuring the ratio of Cp/Cv for gases.**

Now you begin with the gas at atmospheric pressure (760 Torr) and then add gas to increase the pressure inside the bottle by a small amount, say 1.5% (11.4 Torr).

Now very quickly pop the stopper from the bottleneck and return it very quickly to its original position, Figure 2.

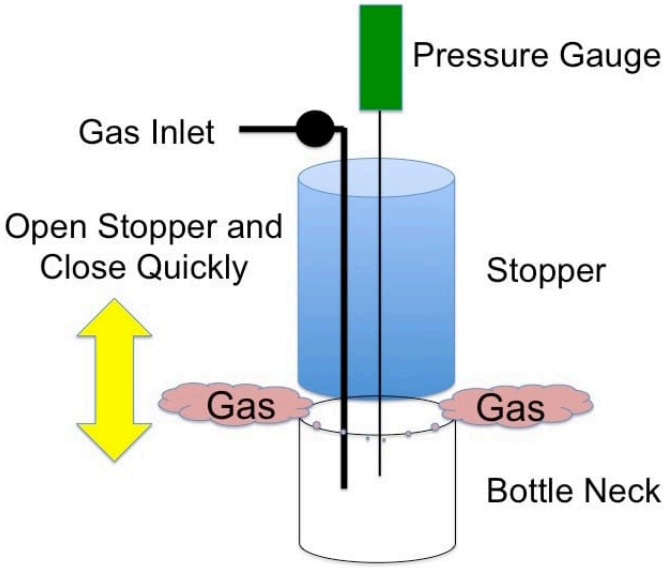



**Figure 2. Remove the stopper very quickly.**

Before reading further pause for a moment and consider the following two questions. What happens to the pressure and temperature in the bottle when you remove the stopper? How will the pressure and temperature change over the next few minutes? Note that the bottle is not thermally isolated from its surroundings.

First the gas returns to the ambient atmospheric pressure when you remove the stopper from the bottle and gas escapes. Assuming you remove the stopper and return it quickly, this process is adiabatic. An adiabatic process is a process where heat is not transferred (dq = 0). When the gas expands it does work against its surroundings and it cools a little.

Second after a few minutes the gas returns to the original ambient temperature because the bottle is not thermally isolated. What does this do to its pressure? The pressure rises because of the ideal gas law, PV=nRT. Rearranging we have P=nRT/V. As the temperature of the gas returns to ambient the pressure rises.

The extent of the pressure increase is related to the ratio of the gas's heat capacity at constant pressure to its heat capacity at constant volume. This ratio is given by:

$$\frac{C_p}{C_v} = \frac{\ln P_1 - \ln P_2}{\ln P_1 - \ln P_3}$$

Where $P_1$ is the initial pressure of the gas, $P_2$ is the ambient pressure of the room and $P_3$ is the final pressure reached after the stopper is popped.

## Procedure

Construct an apparatus as described above. Gases will be assigned in class and may include nitrogen, oxygen, helium, argon and carbon dioxide. Perform the experiment 10 times for each assign gas. Calculate the mean and standard deviations for your measurements. Compare your measurements of Cp/Cv with available literature values and values calculated from the Equipartition of Energy Theorem.

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# 9: Blackbody Radiation

## CHEM 174 Physical Chemistry Laboratory II

## Blackbody Radiation

### Classical mechanics failed as scientists examined nature on smaller and smaller spatial scales. There where five experimental observations that were of particular importance for the development of quantum mechanics.

## First Experiments that Established Quantum Mechanics

1. Blackbody Radiation
2. Photoelectric Effect
3. Atomic and Molecular Spectroscopy
4. Heat Capacities at Low Temperature
5. Electron Diffraction

Blackbody radiation was one of the first experiments that lead to quantum mechanics. It started with the simple observation that when you heat a metal that it first becomes red, followed by yellow and then white hot as the temperature increases. Now, imagine a cube with a tiny pinhole that leads to a very irregular cavity inside the cube. As the Figure 1 shows, any light reaching the pinhole is very likely to be absorbed before it can exit the pinhole.

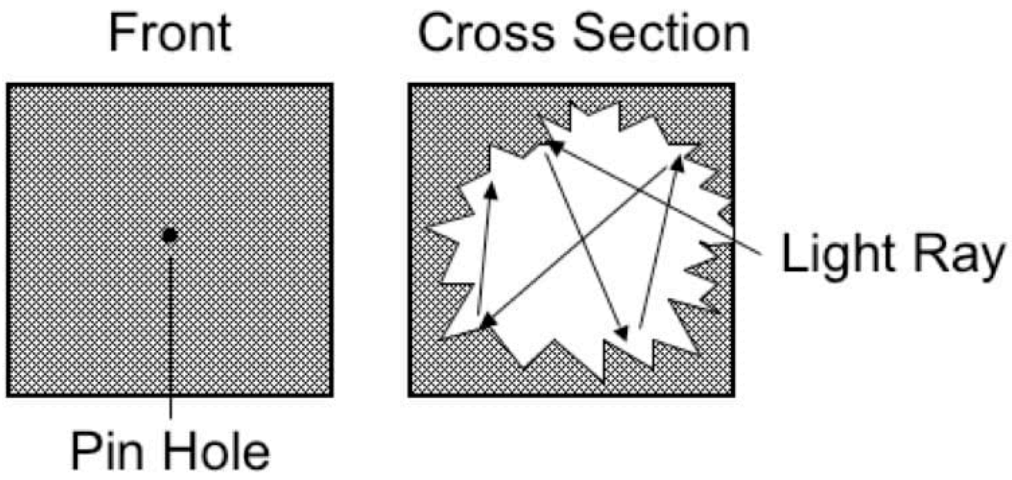



Figure 1. An idealized blackbody radiator

Any object in thermal equilibrium is constantly emitting and absorbing radiation. Kirchhoff's Law states that a body that radiates strongly at some wavelength also absorbs radiation strongly at the same wavelength. Therefore an ideal blackbody radiator is both a perfect absorber and emitter of radiation. Many thermal sources, such as the sun, a flame, an incandescent light bulb, the Earth, approximate blackbody radiators. However, if you use only classical physics, the radiation from a blackbody radiator is impossible to describe correctly without quantum mechanics.

Careful measurements that used experimental approximations to the ideal blackbody radiator showed that the radiation distribution depends only on the temperature of the body. The hotter the temperature the greater the radiation and the lower the wavelength of the peak, Figure 2.

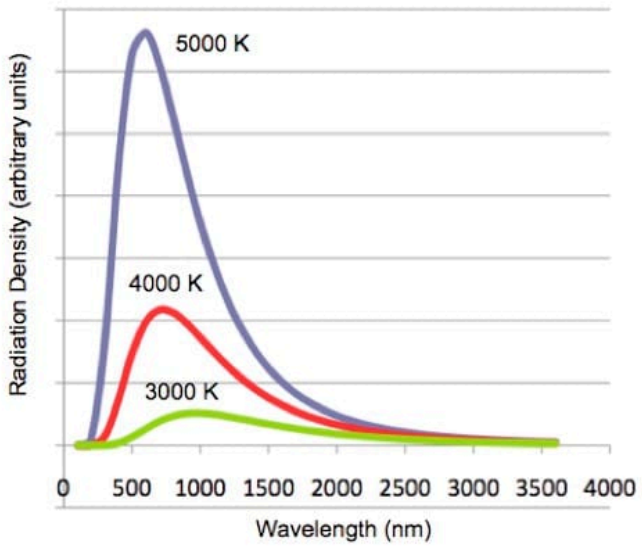



Figure 2. Blackbody radiation for three different temperatures.

The radiation distribution B(T) is:

Equation (1)

$$B_\lambda(T) = \frac{3.74 \times 10^{-16} \lambda^{-5}}{\pi\left(\exp\left(1.45 \times 10^{-2}/(\lambda T)\right) - 1\right)}$$

The radiation peak, $\lambda_{max}$, is equal to:

Equation (2)

$$\lambda_{max}(nm) = \frac{2.897 \times 10^6\,(nmK)}{T\,(K)}$$

For a blackbody the power emitted per unit area, M, is:

Equation (3)

$$M = \sigma T^4$$
$$\sigma = 5.67 \times 10^{-8} W m^{-2} K^{-4}$$

A first attempt to explain these observations was made by Lord Rayleigh. He assumed that the thermal motions of atoms that compose the walls of the blackbody excite “oscillators” of the electromagnetic field. (For a very rough mental picture of his oscillators, think of the electromagnetic field as a vast series of strings on a musical instrument.) Next he applied the equipartition principle from statistical thermodynamics. The assumption was that all of the oscillators share equally in the energy supplied by the walls. According to the equipartition principle each oscillator gets kinetic energy of ½ kT and potential energy of ½ kT for a total of kT where: k is Boltzmann’s Constant (the gas constant divided by Avogadro's number and the temperature, T. Even the oscillators with the highest frequencies such as x-rays and even more are excited. This reasoning led to the Rayleigh-Jeans Law where σ is the radiation density:

Equation (4)

$$dE = \delta d\lambda$$
$$\delta = \frac{8\pi kT}{\lambda^4}$$

The accumulation of energy in the highest frequencies leads to a severe problem with the Rayleigh-Jeans Law. As the wavelength

gets shorter that amount of radiation becomes greater and greater, Figure 3. Everything in this world glows in the dark according to the Rayleigh-Jeans Law. If it were not for quantum effects a lighted match should emit x-rays intensely and even more gamma-rays! This incorrect prediction is called the “ultraviolet catastrophe.”

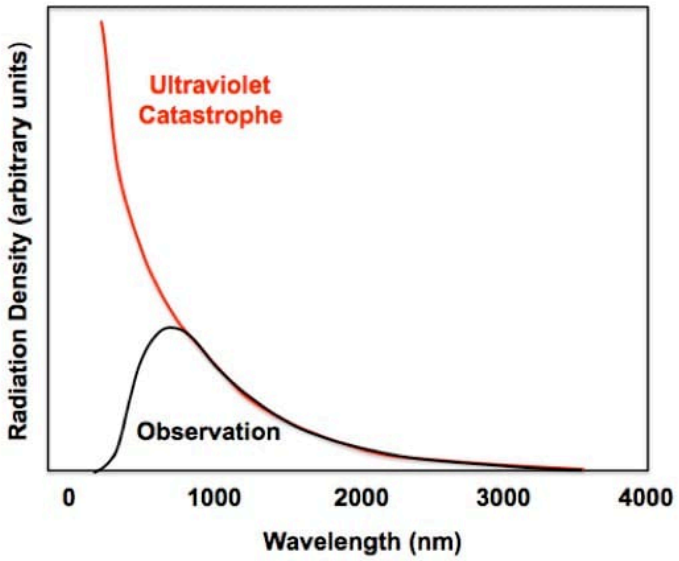



Figure 3. The ultraviolet catastrophe predicted by the Rayleigh-Jeans Law

The ultraviolet catastrophe makes no sense! Max Planck solved the problem by assuming that the energy appears in discreet (quantized) packages. He assumed that the energy, E, of an oscillator was equal to an integer multiplied by a constant, h (Planck’s constant), times the frequency of the oscillator.

Equation (5)

$$E = nh\nu$$
$$n = 0, 1, 2, 3...$$

If Equation 5 is correct than oscillators are excited only if they can get energy of at least kT. But as the frequency ν becomes greater it becomes more difficult for an oscillator to receive enough energy from the blackbody’s walls. The maximum oscillator frequency excited depends only on the temperature of the walls. The net effect of assuming that energy is quantized eliminates the contribution of high-frequency oscillators to the emitted radiation and this eliminates the ultraviolet catastrophe. The blackbody radiation predicted from the quantum theory of Max Planck conforms to Equations 1 – 3.

In this laboratory you will investigate the effect of temperature on the location of the peak of the blackbody radiation curve.

## Procedure

Required Equipment
Ocean Optics UV-Vis Spectrometer
Blackbody Radiator Experimental Setup
Candle

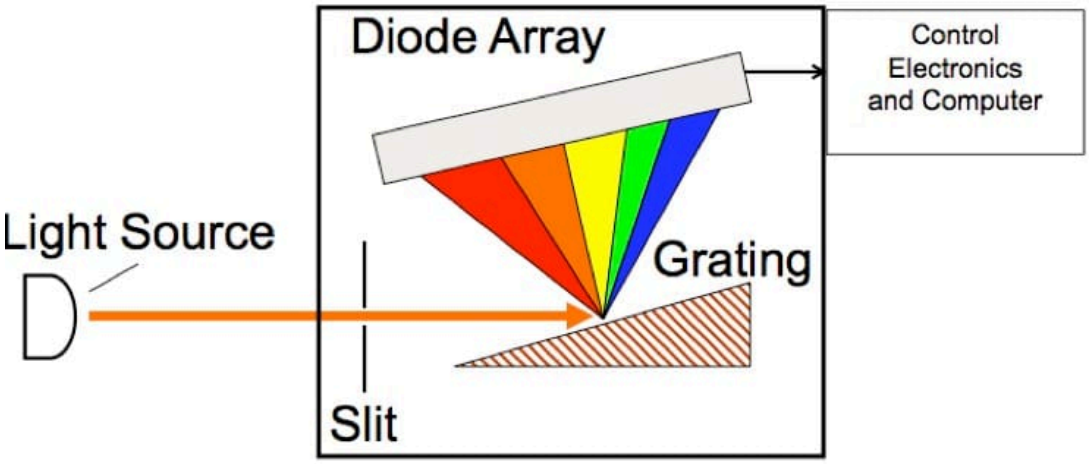



Figure 4. Schematic diagram of Ocean Optics UV-Vis spectrometer

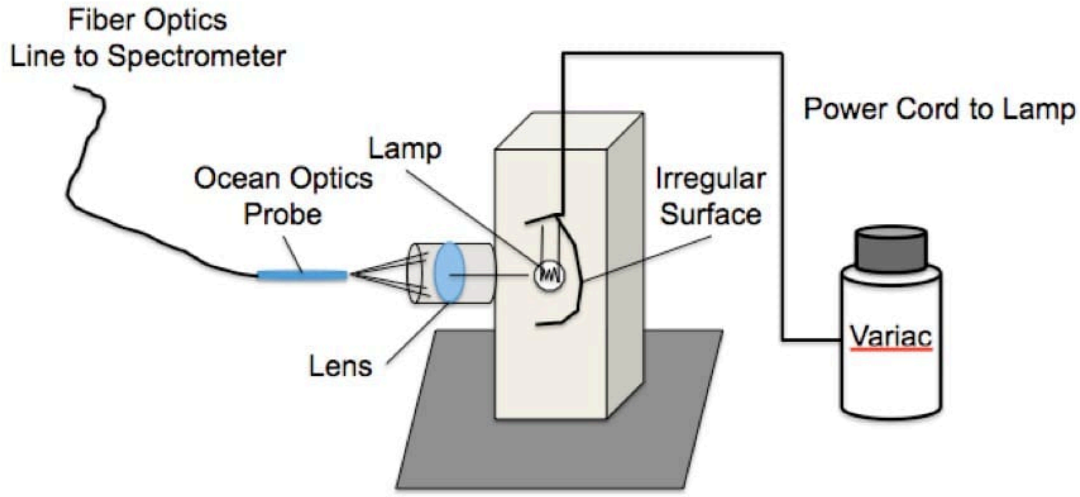



Figure 5. Blackbody radiator experimental setup

## Blackbody Radiation Measurements

The procedure is to make at observations of the emission spectrum of the light emitted from the blackbody radiation setup with the Ocean Optics UV-Vis Spectrometer. Vary the setting of the power Variac and take spectra.

## Candle Radiation Measurements

The procedure is to make at observations of the emission spectrum of the light emitted from a candle flame with the Ocean Optics UV-Vis Spectrometer. Take spectra of different sections of the flame (lower blue, middle, upper most...). **Be careful, do not put the lens of the optical probe in the candle flame.**

## Calculations

- Use the calibration equations given in class to correct the measured wavelength scale using the calibration equation that you got from the calibration laboratory to get the true wavelengths for the blackbody and candle spectra.

- Plot each of the blackbody radiation spectra. The x-axis will be the true wavelength in nm and the y-axis will be emission intensity.
- Determine the peak of the radiation distribution, λmax, for all your spectra.
- Plot the peak of the radiation distribution, λmax, as a function of the variac setting.
- Use Equation (2) to calculate the temperature of the blackbody for each variac setting. Plot the temperature (y-axis) as a function of the variac setting (x-axis).
- Taking the temperatures calculated in step 5, use Equation (3) to calculate the power per unit area emitted by the blackbody for each variac setting. Plot the power per unit area (y-axis) as a function of the variac setting (x-axis).
- Discuss your blackbody results in view of Equation (1).
- Use the blackbody equations to estimate the temperature of the various sections of the flame.

## Report

Please follow the standard format for a scientific paper given in the syllabus and discussed in lecture. It includes the following.

- Abstract – A summery of the entire experiment
- Short Introduction describing the purpose and any relevant theory you find.
- Experimental with a short description of the apparatus and procedures.
- Results please tabulate your observations.
- Discussion and Conclusions Can you find other relevant observations? Compare your results with other available observations. Please discuss the answers to the questions (below) here.
- References. Cite all sources including books, peer reviewed journals and the internet. I am happiest when you find more than two.
- Appendix with a photocopy of the raw data as you entered them in your notebook. I do not need copies of all the spectrometer data, an example first page of one spectrum would be good (total 1 page).

# Reference


- Atkins, P. and J. De Paula, Physical Chemistry, Eighth Edition W. H. Freeman, 2006.


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# 10: Atomic Spectroscopy

## CHEM 174 Physical Chemistry Laboratory II

## Atomic Spectra

### The Hydrogen-Like Atom

A hydrogen-like atom is composed of a single electron and a nucleus with an arbitrary number of protons. In this laboratory the relationship between the wavelengths of light emitted from atoms and changes in quantum numbers will be explored.

Schrödinger's equation in three dimensions is:

Equation (1)

$$\widehat{H}\psi = E\psi$$
$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r,\theta,\varphi)$$

Where: $\widehat{H}$ is the Hamiltonian, $\psi$ is the wavefunction, E represents the possible energy levels, $\hbar$ is Planck's constant, h, divided by 2π, m is the particle's mass. r, θ, φ are the spatial coordinates and V(r,θ,φ) is the potential energy.

A nucleus with an atomic number Z has a charge of $Z_e$ where: e is the unit of elementary charge (the charge on a single proton or electron). Coulomb's Law gives the force between an electron and the nucleus of an atom. Therefore the potential energy of an electron separated from the nucleus by a distance r is given by Equation (2) where $\varepsilon_o$ is the vacuum permittivity:

Equation (2)

$$V = -\frac{Ze^2}{4\pi\epsilon_o r}$$

Equation (3) is Schrödinger equation for the internal motion of an electron relative to its nucleus.

Equation (3)

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_o r}\psi = E\psi$$
$$\mu = \frac{1}{m_e} + \frac{1}{m_N}$$

Where $m_e$ is the mass of the electron and $m_N$ is the mass of the nucleus.

The solution of Equation (3) yields the energy levels given by Equation (4).

Equation (4)

$$E_n = \frac{Z^2\mu e^4}{32\pi^2\epsilon_o^2\hbar^2 n^2}$$

if:

$$R_H = \frac{\mu e^4}{32\pi^2 \epsilon_o^2 \hbar^2}$$

Then:

$$E_n = \frac{Z^2 R_H}{n^2}$$

$R_H$ in Equation (4) is known as the Rydberg constant, $R_H$ = 109,677 $cm^{-1}$. Energy levels for the hydrogen-like atom are plotted in Figure 1.

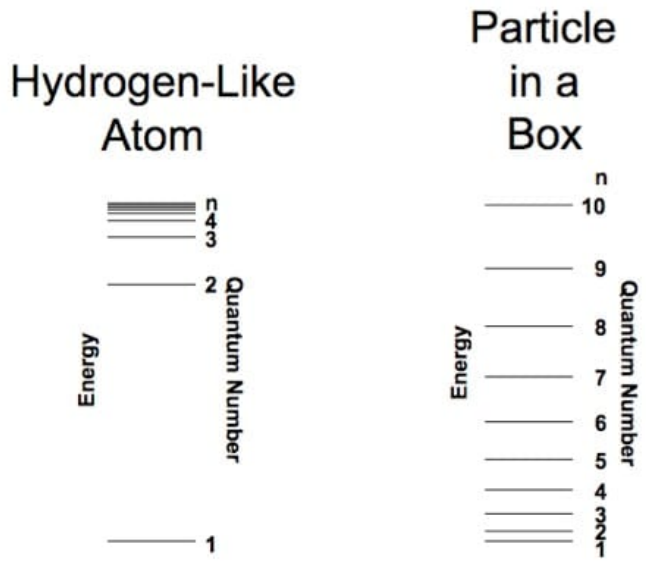



**Figure 1. The energy levels of a hydrogen-like atom are shown compared with the energy levels of the particle in a box.**

If an electron in an atom is excited to a higher energy level by passing an electric current a photon will be emitted when it falls to a lower energy level. The energy difference between the initial energy level and the final energy level is given by Equation (5). In Equation (5) $n_f$ is the final energy level (lower energy) and $n_i$ is the initial energy level (higher energy).

Equation (5)

$$E_n = Z^2 R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

or

$$\frac{1}{\lambda_n} = Z^2 R_H' \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

A series of lines arises when electrons fall from higher energy levels to the same lower energy level, Figure 2. For the hydrogen atom when the final quantum number ($n_f$) is 1 you have the Lyman series, when $n_f$ = 2 you have the Balmer series and when $n_f$ = 3 you have the Paschen series. The series that you can see in the visible is the Balmer series.

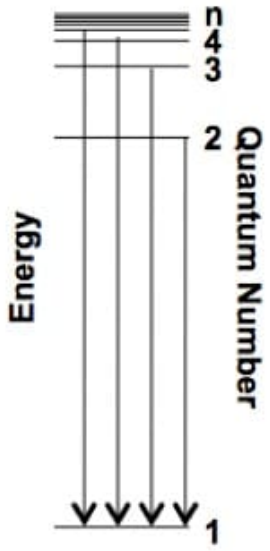



**Figure 2. The Lyman Series is the series where $n_f$ = 1, the excited electron falls into the ground state.**

## Procedure

1. Calculate the Rydberg constant in $cm^{-1}$ from the hydrogen lines in the Balmer series. These lines are the ones that you used in previous laboratories: 410.17, 434.05, 486.13 and 656.28 nm.

    - First, convert the units of the emitted lines from wavelengths to $cm^{-1}$:

        Equation (6)

        $$\frac{1}{\lambda\,(cm)} = \frac{1}{\lambda(nm) \times 10^{7} cm}$$

    - Note that the final quantum number for the Balmer series is 2. Therefore the initial quantum numbers must be greater than 2. The initial quantum numbers are 3, 4, 5 and 6. Match the initial quantum number with the correct emission above. To do this correctly think about which transition is the most energetic and with transition is the least.

    - Now use Excel or similar application to plot $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$; as the x-axis and $\frac{1}{\lambda_n(cm)}$; as the y-axis. You will get a very straight line.

    - Determine the slope and intercept. The slope is the Rydberg constant. Note that it should be near $R_H$ = 109,677 $cm^{-1}$.

2. Recalibrate your spectrometer using the calibration standard provided. The optical probe may be attached to the calibration standard by a screw fitting. The standard provides a mixture of Ar and Hg lines. The known wavelengths are given on the back of the calibration standard. Take a few spectra at different intensities. Make a new calibration curve using as many of the lines that you can identify from the calibration standard.

3. Take emission spectra of the Hg lamp at different intensities.

    - Correct the measured emission line wavelengths of Hg using your new calibration curve.

    - Convert the units of the emitted lines from wavelengths to $cm^{-1}$ by using Equation (6).

    - Identify as many of the spectral lines as you can by using the NIST database at: http://physics.nist.gov/PhysRefData/ASD/index.html

4. Take emission spectra of the Ne lamp at different intensities. Repeat all of the steps in part 3 for Ne.

5. Take emission spectra of the Ar lamp at different intensities. Repeat all of the steps in part 3 for Ar.

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# 11: UV-Vis Absorption Spectroscopy

## CHEM 174 Physical Chemistry Laboratory II

## Visible Absorption Spectroscopy and Beer's Law

### Theory: Beers Law

Beer's law describes how radiation interacts with matter. A completely transparent container contains some compound and there is an incident monochromatic radiation beam of intensity Io. The greater the concentration of the compound and the longer the path length, L, the lower the intensity of the emerging beam, I.

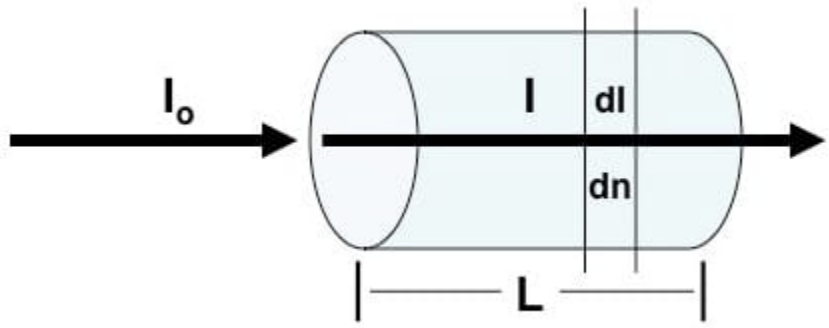



Figure 1. A cell containing a substance that absorbs radiation and the definition of terms needed to derive Beer's Law.

A more precise way of saying this is that "successive increments in the number of identical absorbing molecules in the path of a beam of monochromatic radiation absorb equal fractions of the radiant energy transversing them" (Ewing, 1969). Mathematically dI is the change of radiation intensity at intensity I caused by the absorbance of dn molecules with σ as a proportionally constant.

$$\frac{dI}{dn} = -\sigma I$$

This equation can be rearranged and integrated between the limits of $I_o$ to I and 0 to N where N is the total number of molecules transversed.

$$\int_{I_o}^{I} \frac{dI}{I} = -\sigma \int_{0}^{N} dn$$

$$\ln(I) - \ln(I_o) = -\sigma N$$

$$\ln\left(\frac{I_o}{I}\right) = \sigma N$$

The absorbance, A, is defined as:

$$A = \ln\left(\frac{I_o}{I}\right)$$

The number N is more conveniently written as the product of the concentration [C] and the path length, L. Beer's Law is then:

$$A = [C]\,\sigma L$$

If [C] is expressed in molecules $cm^{-3}$ and L in cm than σ is the absorption cross section per molecule cm2. Note: Divide a concentration in moles $liter^{-1}$ by $1 \times 10^3$ to convert to moles $cm^{-3}$.

## Electronic Absorption and Dipole Strength

Molecules only absorb photons that lead to a change of state. Visible radiation typically corresponds to changes in electronic states. For example the figure below shows two different electronic states, $\psi_m$ and $\psi_n$, rotational states represented by the horizontal lined and two possible transitions between the electronic states.

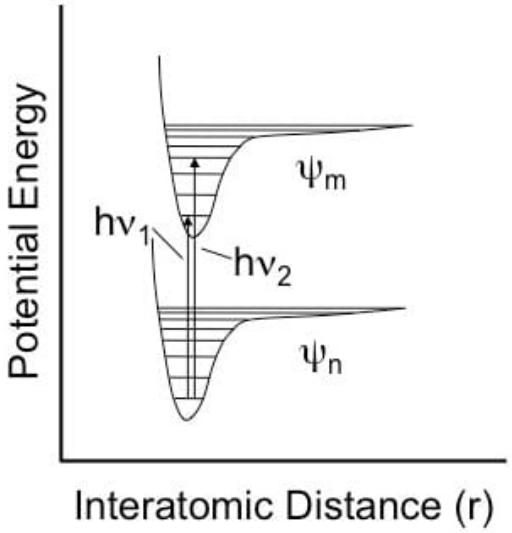



*Figure 2. Absorption of visible or ultraviolet radiation between two stable electronic states.*

In general the stronger absorbances are related to stronger dipole moments and a greater degree of overlap between the lower and upper states. The strength of the transition is proportional to the following integral where is the dipole moment operator.

$$f \propto \int_z \psi_n \widehat{d_e} \psi_m dz$$

In this lab we will quantitatively determine the absorption cross sections for Congo Red. This compound is an acid base indicator that is blue-violet in acidic solutions and red at higher pH. "Its spectral properties can be approximated by the quantum mechanical particle in a box" (see the lab lecture). Congo Red is composed of four aromatic rings and two –N=N- groups. Its structure is given below.

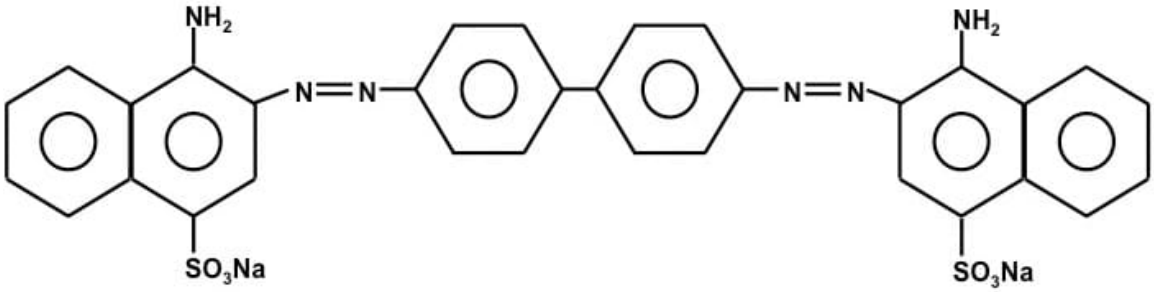



*Figure 3. The chemical structure of Congo Red. The molecular weight of Congo Red is 696.67 g mole$^{-1}$.*

## Procedure

1. An aqueous stock solution (Red) of Congo Red solution has been prepared at pH 7 with a concentration of about 7.5 × 10$^{-5}$ moles liter$^{-1}$.
2. Prepare series of dilute solutions by quantitatively diluting the Red stock solution to make 5 or 6 solutions. Use a 1 or 2 ml pipet to transfer different increments of the solution to small volumetric flasks and fill with distilled water.

Note: In the following work completely clean the cuvette between samples. Use the same spectrometer settings and the same cuvette for the background and the Congo Red solutions.

3. Fill a cuvette with distilled water and record a spectrum. This spectrum will be your first background spectrum ($I_o$).
4. Record a spectrum of the stock Congo Red solution.
5. Wash the cuvette and fill it with distilled water and record a spectrum. This spectrum will be your second background spectrum ($I_o$).
6. Repeat steps 3 to 5 for each of the more dilute solutions.
7. Finally after running all the solutions fill the cuvette with distilled water and record one more background spectrum.
8. An acidified (Blue-Violet) aqueous stock solution of Congo Red solution has been prepared with a concentration of about $1.5 \times 10^{-7}$ moles liter$^{-1}$. A small amount of acetic acid with used to acidify the solution. Prepare series of dilute solutions by quantitatively diluting the Blue-Violet stock solution to make 5 or 6 solutions. Use a 1 or 2 ml pipet to transfer different increments of the solution to small volumetric flasks and fill with distilled water.

Repeat all the steps to take spectra for the blue violet Congo Red solution.

## Calculations

Calculate absorbance spectra for the dye solutions by taking the natural log of the ratio between the background spectra and the Congo Red solutions.

$$A = \ln\left(\frac{I_o}{I}\right)$$

For the background spectrum (Io) average the background taken before and after the Congo Red spectrum.

Correct the wavelength scale using the calibrations you developed during the calibration laboratory.

Plot the spectra. Make one set of plots for the Red Congo Red solution and another set of plots for the Blue-Violet Congo Red solution.

For both sets of solutions determine the numerical value of the extinction coefficient for the maximum absorption peak, $\lambda_{max}$, by plotting the absorbance as a function of the concentration for both sets of solutions. Determine the slope of the best-fit line and the correlation coefficient for both plots. The slope is the product of the maximum extinction coefficient and the path length (1 cm). Divide the slope by 1 cm to get the maximum extinction coefficient and its unit will be liter mole$^{-1}$ cm$^{-1}$.

Convert the extinction coefficient (liter mole$^{-1}$ cm$^{-1}$) to the cross section of one molecule $\sigma_{max}$. Multiply by the conversion factors $10^3$ cm$^3$/ 1 liter and 1 mole / $6.02 \times 10^{23}$ molecules. The units should now be in cm$^2$ molecule$^{-1}$.

Take the ratio of $\sigma_{max}$ to the measured absorbance at $\lambda_{max}$. Multiply the absorbances for each spectra by this ratio to determine the cross sections for all the wavelengths.

Average the spectra after you calculated the cross sections to get a single spectrum of cross sections. Calculate the average and the standard deviation of the cross sections as a function of the wavelengths for the Red and for the Blue-Violet Congo Red solutions.

## Questions for Discussion Section in Your Report

1. Why is it necessary to calibrate the wavelength scale but not the light intensity measurement for this experiment?
2. Which form of Congo Red has the greatest $\sigma_{max}$?

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# 12: Particle in a Box

## CHEM 174 Physical Chemistry Laboratory II

## Dye Color, the Particle in a Box and

## Determination of the Length of a Molecular System

### Purpose

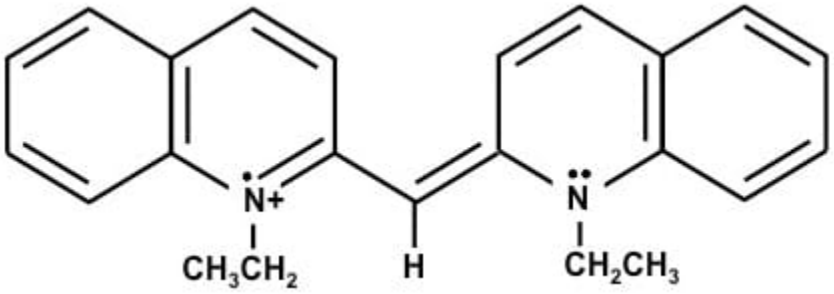
The objectives of this experiment include:
• Learning more about how organic compounds absorb radiation.
• Why compounds have color.
• How spectroscopic measurements may be used to derive some molecular properties (in this case the length of a conjugated pi-bonded system in dye molecules).

### Introduction

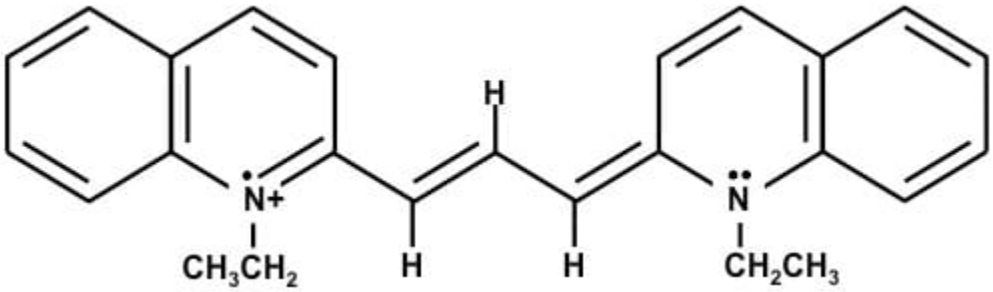
White light is a mixture of all wavelengths of the visible spectrum. Color results when a compound absorbs light in a portion of the visible spectrum and transmits (or reflects) the remainder. Absorption of blue light produces the color red while the absorption of red light produces the color blue-green. Therefore to understand how organic dyes produce color it is necessary to understand how these compounds absorb light.

Consider the following series of cyanine dyes (I- is not shown in each case below):

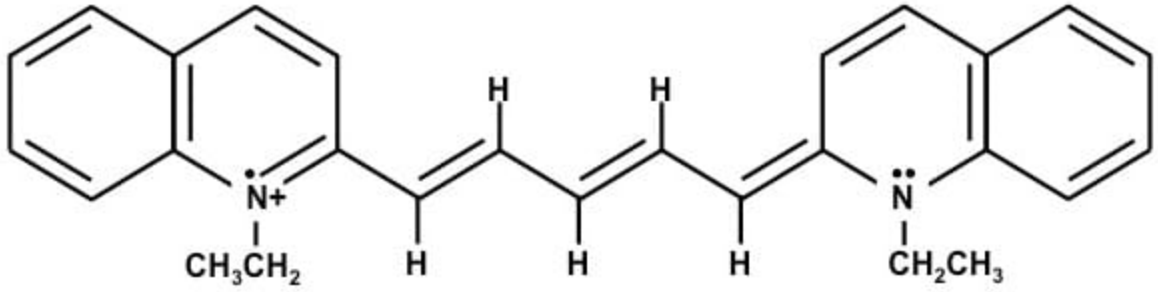
1,1'-Diethyl-2,2'-cyanine iodide – (Dye A)



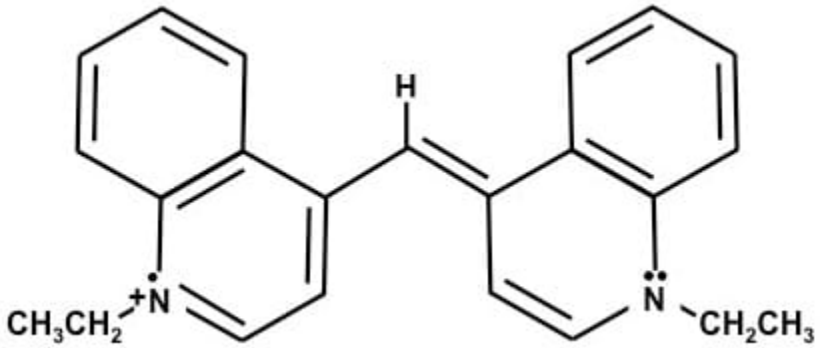

1,1'-Diethyl-2,2'-carbocyanine iodide – (Dye B)



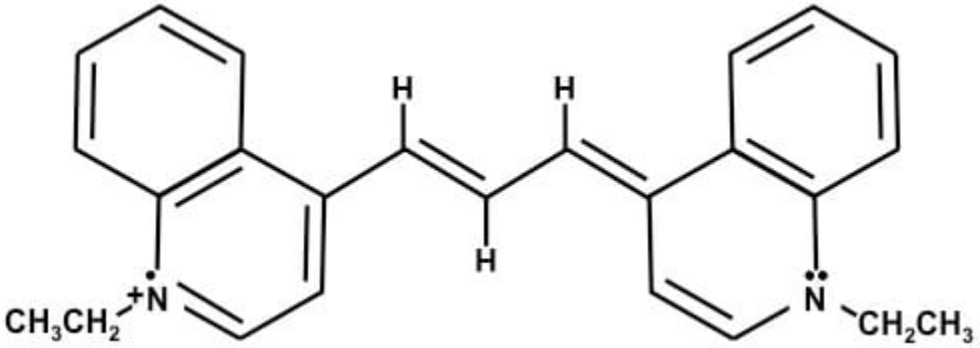

1,1'-Diethyl-2,2'-dicarbocyanine iodide – (Dye C)



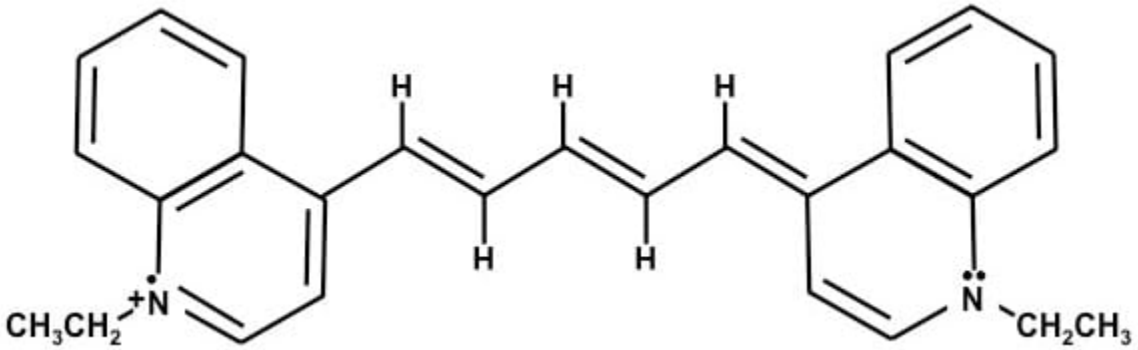
1,1'-Diethyl-4,4'-cyanine iodide – (Dye D)



1,1'-Diethyl-4,4'carbocyanine iodide – (Dye E)



1,1'-Diethyl-4,4'-dicarbocyanine iodide – (Dye F)



The chemical structures are resonance structures; the positive charge can be equally well represented as residing on either nitrogen atom. In reality the pi electrons may be considered to reside across the system of conjugated pi-bond system that extends from one nitrogen atom to the other, Figure 1. The conjugated pi-bonded system extends above and below the plane of the sigma bonds.

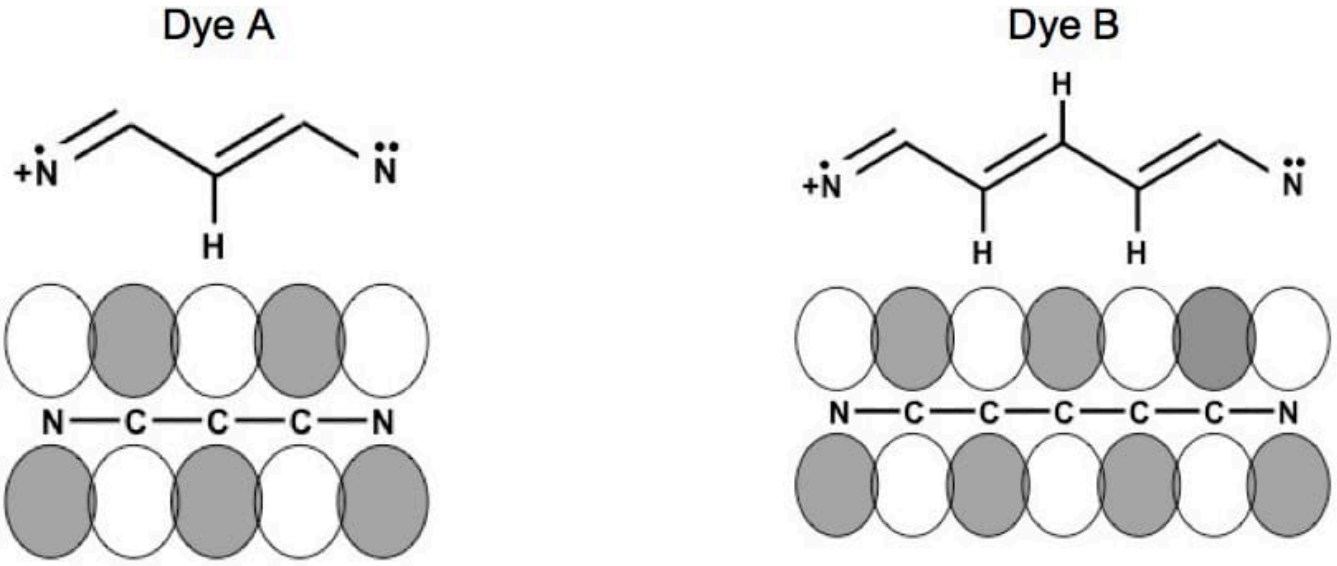



Figure 1. Conjugated pi-bonded system for dyes A and B.

Electrons change energy levels when radiation is absorbed. Schrödinger's equation is used to calculate the energy levels, Equation (1).

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V\left(x\right)\psi=E\psi$$

where: $\hbar$is Planck's constant divided by 2π , $m$ is the particle's mass, $V\left(x\right)$ is the system's potential energy, $\psi$ is the wave function and $E$ represents the possible energy levels.

The potential energy of a system needs to be defined to calculate the energy levels. Figure 2 shows the potential energy of the conjugated pi-bonded systems for dyes A and B. Figure 2 shows that there is a potential energy barrier at the nitrogen atoms and there are "wells" at each atom; however to a reasonable degree of accuracy the potential energy of the conjugated pi-bonded system can be approximated by a particle in a box potential.

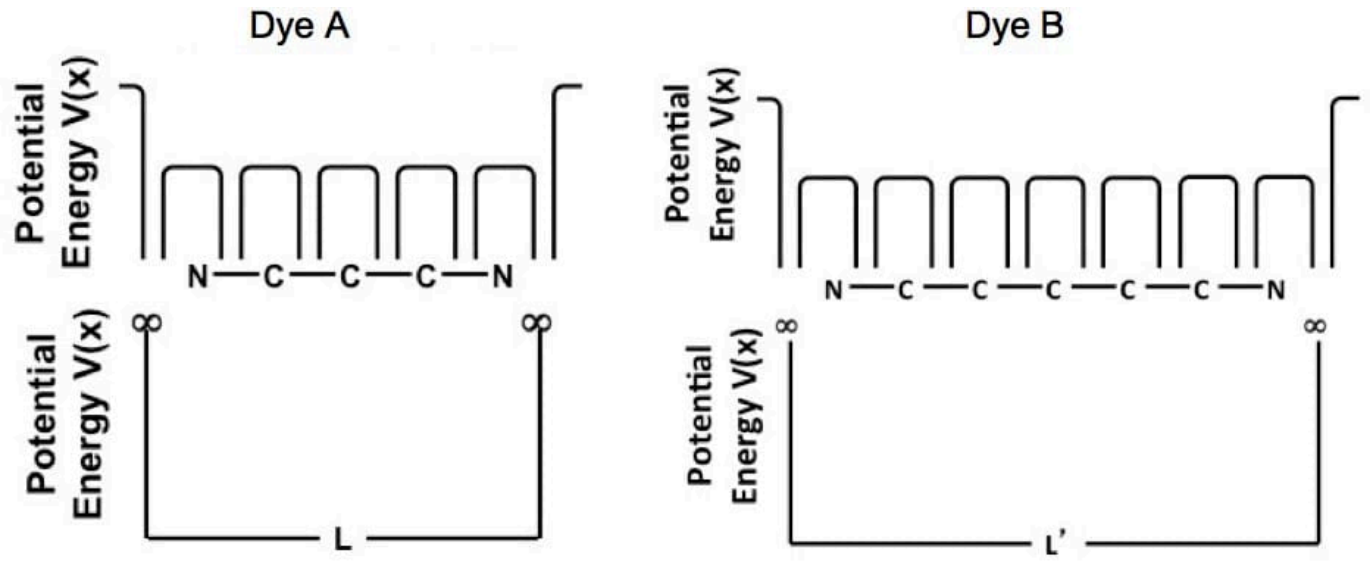



Figure 2. Potential energy of the conjugated pi-bond system for dyes A and B.

The solution of Schrödinger's equation for the particle in a box yields the energy levels given by Equation (2).

$$E = n^2 \frac{h^2}{8mL^2}$$
$$n = 1, 2, 3...$$

where: $E$ represents the possible energy levels $h$ is Planck's constant, $m$ is the particle's mass and $L$ is the length of the box.

**Pauli Exclusion Principle and Packing Electrons into the Particle in a Box**

Dye A has 6 electrons and dye B has 8 electrons in their respective pi-bond systems. If the particle in a box is used to represent these molecules then the pi electrons need to be distributed into the box. The Pauli exclusion principle and the energy levels establish the electron distribution.

An electron is a fermion and the Pauli Principle states that the total wave function for a system of fermions must be antisymmetric when particles are interchanged. Suppose the total wave function is ψ(q1,q2,q3,...) where q1,q2,q3,... are the coordinates / quantum numbers of electrons 1, 2, 3,... If electrons 1 and 2 are exchanged:

$$\psi(q_1, q_2, q_3, q_4, ...) = -\psi(q_2, q_1, q_3, q_4, ...)$$

Suppose there were two electrons with the same set of quantum numbers (q1), then the total wave function would be ψ(q1,q1,q3,...). If the two electrons with the same set of quantum numbers were switched then Equation (4) results.

$$\psi(q_1, q_1, q_3, q_4, ...) = -\psi(q_1, q_1, q_3, q_4, ...)$$

For any function, f(x), if f(x) = -f(x) then f(x) must be equal to zero. If ψ(q1,q1,q3,...) is equal to zero then probability of any two electrons having the same identical set of quantum numbers is zero.

In the case of electrons in the particle in a box there are two quantum numbers, n and spin. The quantum number n = 1, 2, 3... and the spin of an electron can be either up (+1/2) or down (-1/2). So each level of the particle in a box can contain two electrons, one spin up and the other spin down. Figure 3 shows how pi electrons for dye A (a 6 electron system) and dye B (a 8 electron system) are contained in the box when it is in the ground state. Note that the energy levels are more closely spaced due to the fact that dye B is represented by a larger box.

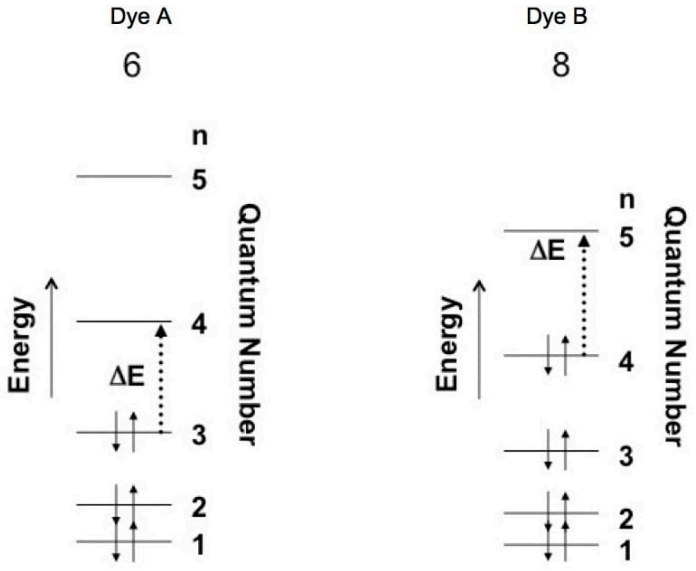



Figure 3. Assignment of electrons into particle in a box model for dyes A and B. The figure also shows the change in state caused by the absorption of a photon.
Dye A Dye B

**Absorption of Energy**

The change in energy associated with an electron jumping from one state to another is given by equation (5).

$$\Delta E = \frac{h^2}{8mL^2}\left(n_f^2 - n_i^2\right)$$

where: ΔE is the change in energy, h is Planck's constant, m is the mass of the electron, L is the length of the box and ni and nf are the initial and final quantum numbers.

Three things need to be considered to calculate the energy changes from Equation 5. For the dyes studied in this experiment the number of electrons (N) is an even number, p. There will be two electrons per energy level because of the Pauli Exclusion Principle. The principle quantum number changes by +1. Mathematically:

Equations (6 - 9)

$$p = n_i = \frac{N}{2}$$

$$n_f = n_i + 1$$

$$\Delta E = \frac{h^2}{8mL^2}\left[(p+1)^2 - p^2\right]$$

$$\Delta E = \frac{h^2}{8mL^2}(2p+1)$$

Remembering that:

$$\lambda_{abs} = \frac{hc}{\Delta E}$$

where $\lambda_{abs}$ is the wavelength of the absorbed radiation and c is the speed of light, the following equations result.

$$\lambda_{abs} = \frac{8mL^2c}{h(2p+1)}$$

or Equation (11)

$$L = \sqrt{\frac{\lambda_{abs}h(2p+1)}{8mc}}$$

In the experiment the length of the conjugated pi-system will be calculated for each dye from measurements of λabs and Equation (11).

## Safety

All six dyes: 1,1'-Diethyl-4,4'-cyanine iodide, 1,1'-Diethyl-4,4'-carbocyanine iodide, 1,1'-Diethyl4,4'-dicarbocyanine iodide, 1,1'-Diethyl-2,2'-cyanine iodide, 1,1'-Diethyl-2,2'-carbocyanine iodide and 1,1'-Diethyl-2,2'-dicarbocyanine iodide and methanol are considered highly toxic and irritate the skin. Do not get the dye solutions or methanol on your skin or in your eyes. Wear eye protection.

# Procedure

1. Solutions of dyes A – F in methanol have been prepared.

   Note: In the following work completely clean the cuvette between samples. Use the same spectrometer settings and the same cuvette for the background and the dye solutions. Also do not cross contaminate the dye solutions by the using same pipette to transfer different dye solutions.

2. Fill a cuvette with methanol and record a spectrum. This spectrum will be your background spectrum (Io) for this dye.
3. Add a drop or two dye A solution. You should just be able to see a little color.

4. Wash the cuvette. Go back to step 3
5. Repeat steps 3 – 5 until spectra have been recorded for all the dye solutions.

## Calculations

- Calculate absorbance spectra for the dye solutions by taking the natural log of the ratio between the background spectra and the dye solutions.

$$A = \ln\left(\frac{I_o}{I}\right)$$

- Correct the wavelength scale using the calibrations given in the class handout.
- Make plots of the absorbance spectra for dyes A – F. You may combine the plots in one or two page graphs.

Fill out the worksheet given below as you do the following.

- Identify the color of each dye.
- Identify the wavelength of the maximum absorbance, λmax, for each dye.
- Count the number of pi-electrons, N.
- Calculate the length of the conjugated pi-system, L, for each of the dyes from the measured $\lambda_{max}$ and Equation (11). Provide a sample calculation in your report.
- Count the number of bonds in the conjugated pi-system for each dye.
- Assume that each bond has a length of 0.139 nm and estimate the length of the box from the number of bonds. Provide a sample calculation in your report
- Evaluate and tabulate the difference between the length of the box calculated from Equation (11) and the length estimated from the number of bonds for each dye.

## Report and Questions

1. For the recalibration include a plot of the known wavelengths as a function of the measured wavelengths and the linear fit with your report.
2. Discuss the observed colors and the absorption spectra. What is the relationship between the dye colors and the spectra?
3. Make two plots of $\lambda_{max}$ as a function of the length of the box calculated from Equation (11): one plot for dyes A – C and another for D – F.
4. Discuss the difference between the length of the box calculated from Equation (11) and the length estimated from the number of bonds. Is the difference usually positive or negative? Suggest reasons for this difference.

## Reference

McRae, E.G. and M. Kasha (1958). J. Chem. Phys. 28, 721.
Pope, M., C.E. Swenberg, Electronic Processes in Organic Crystals, (Oxford University Press, New York, 1982), Chapter 1D.
New Mexico State University, Department of Chemistry
http://www.chemistry.nmsu.edu/studntres/chem435/Lab5/

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## Worksheet for particle in a box; include with your report.

Name_____

| Dye | Color | $\lambda_{max}$(nm) | Number of pi- electrons N | Experimental box length (nm) | Number of bonds in conjugated system | Predicted box length (nm) | D Experime |
|---|---|---|---|---|---|---|---|
| A | | | | | | | |
| B | | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | | | | | | | |
| D | | | | | | | |
| E | | | | | | | |
| F | | | | | | | |

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# 13: Fourier Transform Infrared Spectroscopy (FTIR)

## CHEM 174 Physical Chemistry Laboratory II

## Fourier Transform Infrared Spectroscopy (FTIR)

### How a Fourier Transform Infrared Spectrometer Works

There are many advantages to a Fourier Transform Infrared Spectrometer (FTIR): higher resolution at lower cost, relatively less time to collect spectra, for reacting systems the spectra are easier to interpret and FTIR can be used in a mode (photoacoustic) where samples do not have to be optically thin.

A Fourier Transform Infrared Spectrometer (FTIR) is a based on the interferometer. The interferometer in an FTIR works on the same principles as the one used in the Michelson–Morley experiment. The Michelson–Morley showed that the speed of light is the same in all directions; a key finding supporting special relativity. Figure 1 shows a schematic of an interferometer.

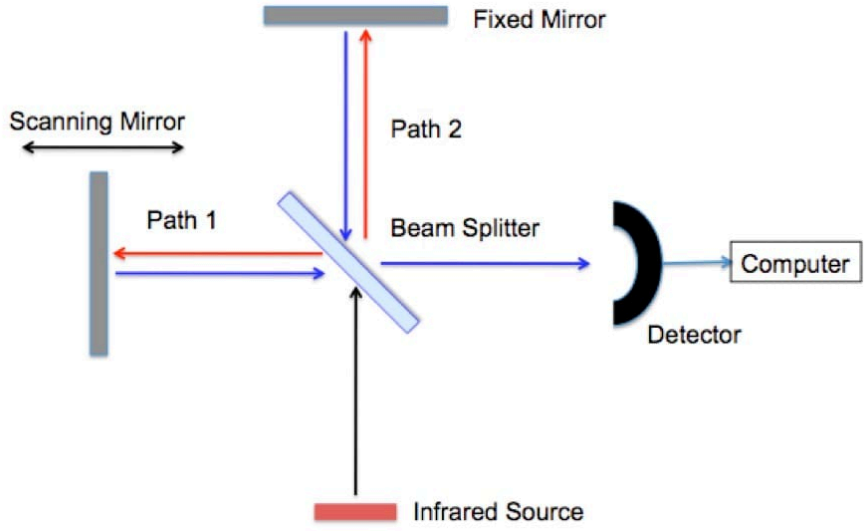



Figure 1. A schematic of an interferometer used in a Fourier Transfer Infrared Spectrometer (FTIR).

Infrared radiation is typically generated by passing electricity through a conducting ceramic bar (glow bar). First the radiation reaches a “beam splitter”. The beam splitter is a partially coated mirror that reflects half of the infrared radiation and passes the remaining half. The radiation follows either path 1 or path 2 to mirrors that return it to the beam splitter where the beams recombine and they are reflected in to an infrared detector. Remember that the radiation is a wave, Figure 2. The signal seen at the detector at any moment in time depends on the difference between path 1 and path 2.

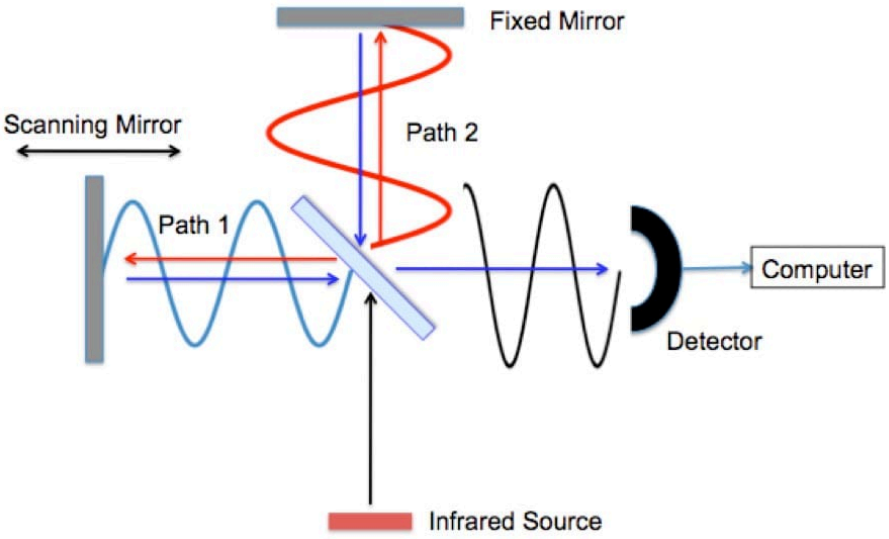



Figure 2. FTIR interferometer with radiation waves drawn in.

Suppose for a moment that we use a laser that emits a single wavelength as the radiation source. Next suppose that the lengths of path 1 and path 2 are both even multiples of the laser's radiation wavelength. When the radiation returns to the beam splitter it arrives "in phase", the beams reinforce each other when they recombine and a strong signal will be seen at the detector, Figure 1A. This process is called "constructive interference".

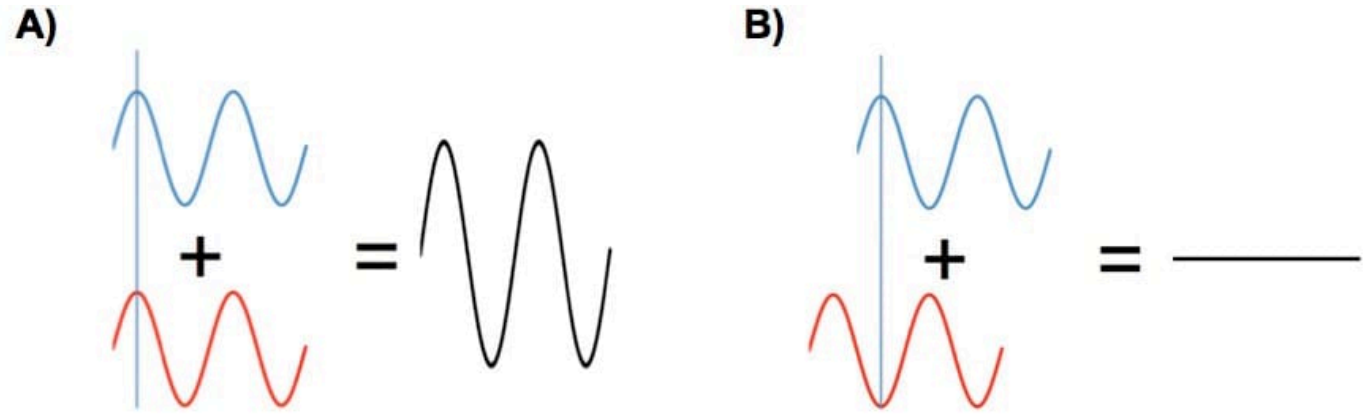



Figure 3. (A) Constructive interference by two recombining radiation beams. (B) Destructive interference by two recombining radiation beams.

Suppose that the scanning mirror on path 1 is moved a distance equal to half of the wavelength of the laser radiation. Now when the beams recombine at the beam splitter they will "out of phase" and destructively interfere cancelling each other and no signal will be seen at the detector. If the scanning mirror is scanned at a constant rate a sinusoidal signal is generated at the detector.

The frequency of the detector signal depends on the speed of the mirror and wavelength of the radiation. Let infrared radiation with a frequency of 1000 $cm^{-1}$ pass through the interferometer and move the scanning mirror with a speed of 1 cm $s^{-1}$. There will be 1000 waves of infrared radiation per centimeter for this frequency (this is why $cm^{-1}$ is called sometimes "wave-numbers"). If the mirror is moved a total of 1 cm then there will be 1000 cycles of constructive and destructive interference. For these conditions the frequency of the detector signal will be 1000 $cm^{-1}$ × 1 cm $s^{-1}$ = 1000 $s^{-1}$. The important point is that the scanning information has coded the wavelength of the infrared radiation so that the detector can measure frequency and intensity at the same time. An infrared detector is very capable of detecting the intensity and the frequency of an infrared signal with an audio frequency.

When multiple frequencies pass through the interferometer, the signal at the detector is the sum of the coded frequencies. A glow bar is a ceramic that emits infrared radiation when heated by an electric current. It is an excellent approximation to a blackbody radiator, Figure 4A. When this radiation passes through the interferometer the signals add, “the superposition”, of all the signals is observed at the detector, Figure 4B. Figure 4B is called an “interferogram”. Note that the information contained in a spectrum and the interferogram is identical.

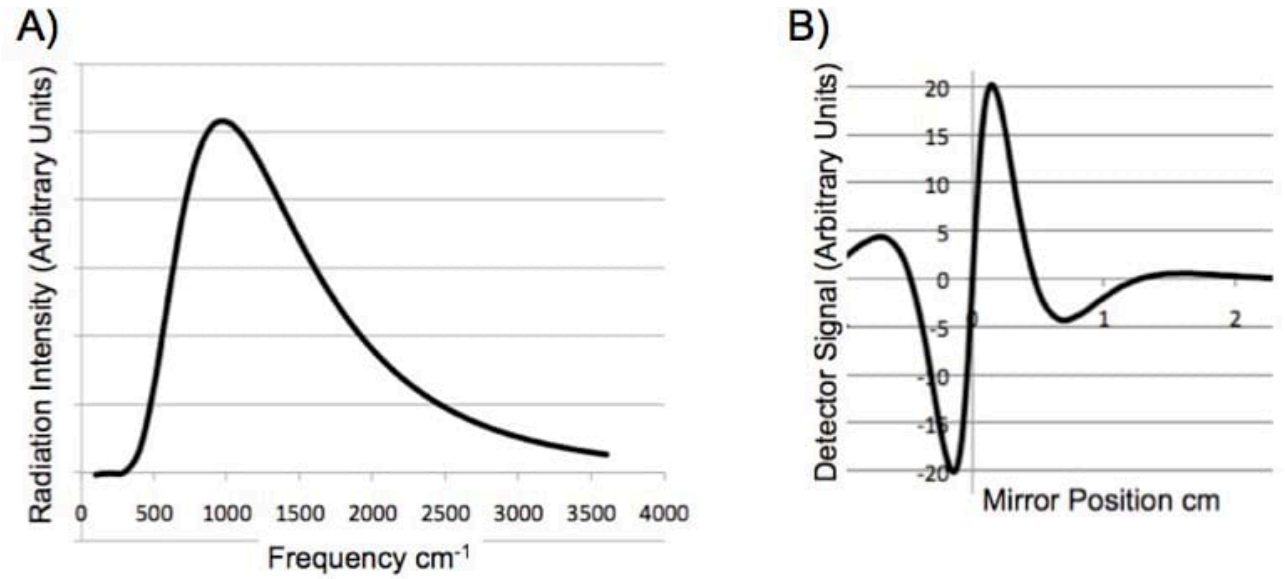



Figure 4. (A) Blackbody radiation spectrum of a glow bar. (B) The signal seen at the detector of an FTIR as a function of the scanning mirror position.

Although the information contained in a spectrum and the interferogram is identical chemists find it difficult to interpret interferogram in terms of molecular structure. The interferogram measured by the FTIR must be converted back to a spectrum. This transformation is accomplished by applying the Fourier transform to the interferogram. Equation (1) shows the Fourier transform.

$$\tilde{f}(\nu) = \int_{-x}^{x} f(x)\, e^{-2i\pi\nu x} dx$$

where: $f(x)$ is the signal measured at the detector which is a function of the mirror position, $x$, $\tilde{f}(\nu)$ is the spectrum which is a function of frequency, $\nu$. Figure 5 shows a sample function and its Fourier transform.

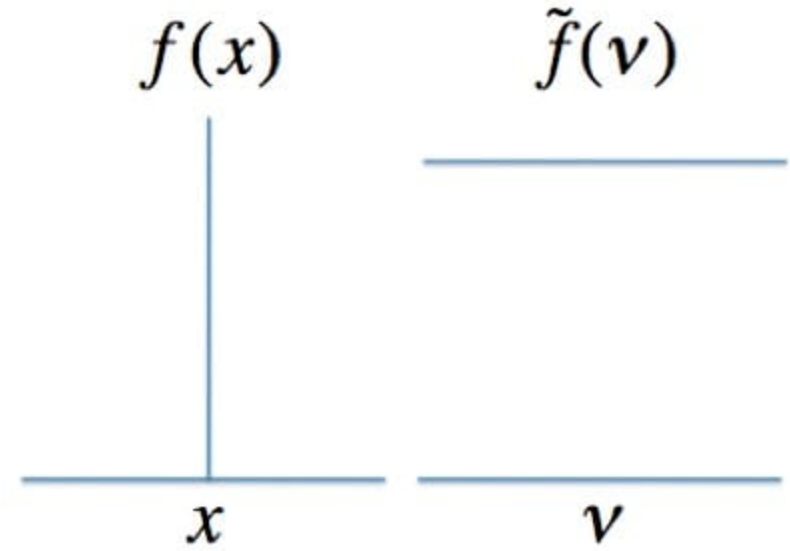


Figure 5. The Fourier transform of a delta function, $f(x)$, is a horizontal line, $\tilde{f}(\nu)$. The more highly $f(x)$ is defined in space the less defined is $\tilde{f}(\nu)$. The Heisenberg Uncertainty Principle is a consequence of this relationship.

To calculate a spectrum from an interferogram considerable computational resources are required and therefore Fourier transformation methods came into widespread use only after the invention of modern computers.

## Procedure

This report will be combined with the next laboratory session. Please take the spectra as a group and discuss together. But please – each person will submit their own individual report.

For all of the spectra gathered save ASCII copies to disk and take with you.

1. Record a spectrum of a standard polyethylene sample.
2. Record a gas-phase spectrum of air using an evacuated cell as the reference.
3. Record a gas-phase spectrum of acetaldehyde using an air filled cell as the reference. Expose to UV light for an hour and run a second spectrum.
4. Record a liquid-phase spectrum of acetaldehyde using attenuated total reflection (ATR) with air as the reference.
5. Record a spectrum of solid Congo Red using ATR with air as the reference.

## Analysis

This report will be combined with the next laboratory. For all of the spectra gathered save ASCII copies to disk and take with you.

1. Use the measured IR lines of the standard polyethylene sample to check the wavelength calibration.
2. Identify as many of the IR bands/lines for as many atmospheric gases as you can in the air spectrum. Do you expect to see Ar, $O_2$ and $N_2$?
3. Discuss the bands found in the IR spectra of acetaldehyde. What differences do you see between the gas and liquid-phase spectra?
4. For the gas-phase acetaldehyde sample what are the differences in the spectra before and after the sample was exposed to UV radiation? If there are differences, what happened?
5. Discuss the IR spectrum of Congo Red. Is there any relationship between the pi-chain and the observed IR spectrum? What are the differences in the functional groups between the particle-in-a-box-experiment dyes (Laboratory 13) and the Congo Red dye? Are these groups in Congo Red seen in its IR spectra?

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# 14: Nano-Particles and Quantum Dots

## CHEM 174 Physical Chemistry Laboratory II

## Nano-Particles, Quantum Dots and Emission Spectroscopy

### Introduction

Nano-technology is the science and engineering of devices with a size range between 1 to 100 nm. Substances in this size range may have properties that are different than those in the bulk. For example the semiconductor cadmium phosphide in the bulk is black but smaller particles can be red, orange, yellow or white depending upon their size (Brown et al., 2009). The smallest particles are white.

Quantum dots are very small aggregates of semiconductor material that contain $10^3$ to $10^5$ atoms and are between 1 to 10 nm in diameter. For quantum dots prepared from a given substance, their color and electrical properties can be tuned by varying their size. They have potential applications in biology and medicine, photovoltaic electricity generation, light sources and display devices and computing. Their applications to biological problems are among the most significant. Organic dyes have a long history of applications to problems in microscopy, analysis and the treatment of disease. Quantum dots can be engineered to specifications much more precisely than traditional organic dyes. They provide a very intense light when excited and they are very stable, they may persist for months in a biological system. Applications include, tagging of cells and their real-time observation of cells over long time periods, in-vitro imaging of cells (Dahan et al. 2003; Ballou et al., 2004) and the delivery of gene-silencing molecules into cells (Newswise, 2008). The latter is an example of a potential therapeutic application of quantum dots. The major potential drawbacks are toxicity and other environmental effects that are not yet well known.

### Semiconductors

Covalent bonds are formed from the overlap of atomic orbitals. When the bonds are formed both bonding and anti-bonding molecular orbitals are formed. For every bonding molecular orbital there is an anti-bonding molecular orbital formed. When a p-orbital overlaps with another p-orbital three bonding molecular orbital and three anti-bonding molecular orbitals are formed. In a crystal the bonding molecular orbitals constitute the valence band and anti-bonding orbitals constitute the conduction band. The difference in energy between the valence band and the conduction band is called the band gap, Figure 1.

In metals the band gap is very low and there is a population of electrons in the conduction band. These are the electrons that conduct electricity. The band gap is greater in semiconductors and few electrons are found in the conduction band. The absorption of a photon may promote an electron from the valence band to the conduction band. This excitation of the electron from the valence band creates “hole” in the valence band. Conversely the recombination of an electron and a hole may result in light emission; this is the basis of the light-emitting diode, Figure 2.

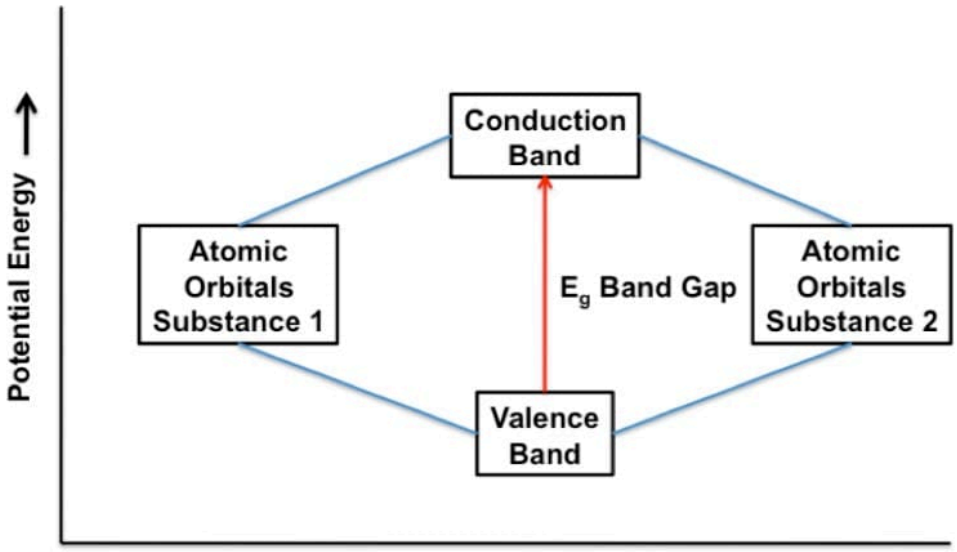



Figure 1. The figure shows the formation of bonding (valence band) and anti-bonding molecular orbitals (conduction band) from atomic orbitals. The band gap is the potential energy difference between the valence and conduction band.

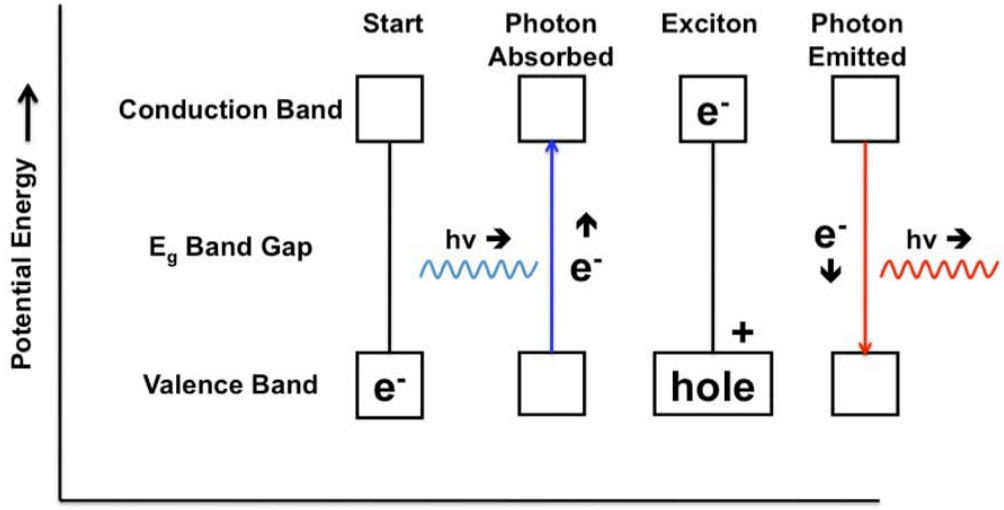



Figure 2. An electron is initially in the ground state. Next a photon with energy at least equal to the band gap is absorbed and the electron is promoted from the valence band to the conduction bond. A hole is left behind. (Note that while there is a net positive charge left behind, it is not correct to call the hole positive.) The electron and hole pair together is called an exciton. Finally the electron will return to valence band and a photon is emitted.

## Quantum Mechanics

In the laboratory "Dye Color, the Particle in a Box and Determination of the Length of a Molecular System," the quantum mechanics of a particle in a linear box was presented. Schrödinger's equation in one dimension is Equation (1)

$$\widehat{H}\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

where: $\widehat{H}$ is the Hamiltonian, $\psi$ is the wavefunction, $E$ represents the possible energy levels, $\hbar$ is Planck's constant, $h$, divided by $2\pi$, $m$ is the particle's mass, $x$ is the spatial dimension and $V(x)$ is the potential energy.

For the particle in a box of length, $L$, the boundary conditions are $V(0) = +\infty$, $V(L) = +\infty$ and $V(x) = 0$ for $0 < x < L$. Solution of Equation (1) for these boundary conditions yields the energy levels given by Equation (2).

$$E = n^2 \frac{h^2}{8mL^2}$$
$$n = 1, 2, 3...$$

where: $n$ are integers (quantum numbers).

The particle in a box can be extended to a three-dimensional sphere. The Hamiltonian for a spherical particle in a box is given by Equation (3).

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

In spherical coordinates the boundary condition is $V(r) = 0$ for $0 \leq r < R$ and $V(r) = +\infty$ for $r \geq R$ where: $R$ is the radius of a sphere. The energy levels of a spherical particle in a box are given by Equation (4).

$$E = n^2 \frac{h^2}{8mR^2}$$
$$n = 1, 2, 3...$$

The approximate Hamiltonian for an exciton is similar to that for the spherical particle in a box but both the electron and the hole are confined within the quantum dot. In addition there is an electrostatic interaction between the electron and the hole that follows Coulomb's Law (Atkins and de Paula, 2006).

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{4\pi\varepsilon\left|r_e - r_h\right|}$$

where: $m_e$ is the mass of the electron, $m_h$ is the mass of the hole, $e$ is the charge of an electron, $\varepsilon$ is the permittivity of the semiconductor and $|r_e - r_h|$ is the absolute value of the distance between the electron and the hole. The boundary conditions for exciton are the same as for the spherical particle in a box. The solution for the energy of an exciton, $E_{ex}$, is given by the following equation, (Atkins and de Paula, 2006).

$$E_{ex} = \frac{h^2}{8R^2}\left(\frac{1}{m_e} - \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\epsilon R}$$

The band gap energy, $E_g$, is:

$$E_g = -\frac{1.8e^2}{4\pi\epsilon R}$$

$$E_g = \frac{E'}{R}$$

where

$$E' = -\frac{1.8e^2}{4\pi\epsilon}$$

$$E_{ex} = \frac{h^2}{8R^2}\left(\frac{1}{m_e} - \frac{1}{m_h}\right) + \frac{E'}{R}$$

## Exciton Creation and Emission

In this experiment quantum dots will be excited by blue light photons, emitted from a diode source, to form excitons. The excitons decay and when the electron recombines with the hole a photon with energy equal to $E_{ex}$ is emitted. If the wavelength of the emitted photon is measured the radius of the quantum dot can be calculated starting with Equation (9) and Equation (10).

$$E = \frac{hc}{\lambda}$$

Equating Equations (9) and (10) yields the following Equation (11).

$$\frac{hc}{\lambda} = \frac{h^2}{8R^2}\left(\frac{1}{m_e} - \frac{1}{m_h}\right) - \frac{E'}{R}$$

To determine the radius of the quantum dot from the wavelength of the exciton emission, multiply each term in Equation (11) by R2 and rearrange to a quadratic form that may be solved by using the quadratic equation.

$$\frac{hcR^2}{\lambda} - E'R - \frac{h^2}{8}\left(\frac{1}{m_e} - \frac{1}{m_h}\right) = 0$$

Let:

$$a = \frac{hcR^2}{\lambda}$$
$$b = -E'R$$
$$c = -\frac{h^2}{8}\left(\frac{1}{m_e} - \frac{1}{m_h}\right)$$

Then:

$$R = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

or

$$R = \lambda \times \left(\frac{E' + \sqrt{E'^2 + \frac{h^3c}{2\lambda}\left(\frac{1}{m_e} - \frac{1}{m_h}\right)}}{2hc}\right)$$

You may want to check the derivation of the final expression from the quadratic equation.

In your calculations use the following values:

| Quantity | Value |
|---|---|
| h | $6.626 \times 10^{-34}$ J s |
| c | $2.998 \times 10^{+8}$ m $s^{-1}$ |
| $m_e$ | $9.109 \times 10^{-31}$ kg |
| $m_h$ | $6.830 \times 10^{-30}$ kg |
| E' | $8.750 \times 10^{-28}$ J m |

## Procedure

Required Equipment
Quantum dots (Four different sizes are provided in vials of solution).
Ocean Optics UV-Vis Spectrometer
Red and Blue Light Emitting Diodes
Backlight for Absorption Measurements

You will measure both absorption spectra and emission spectra of the quantum dots. You will use the emission spectra to calculate the radii of the four different sizes of quantum dots.

## Absorption Spectra

1. Use the Ocean Optics spectrometer to take a background spectrum of the background light source, Figure 3.
2. Place the vials containing the quantum dots in front of the background light source.
3. Use the Ocean Optics spectrometer to record a spectrum of each vial.
4. For your report plot the spectra for each vial as absorption spectra $A = \ln\left(\frac{I_o}{I}\right)$. Use the background spectrum as your Io.

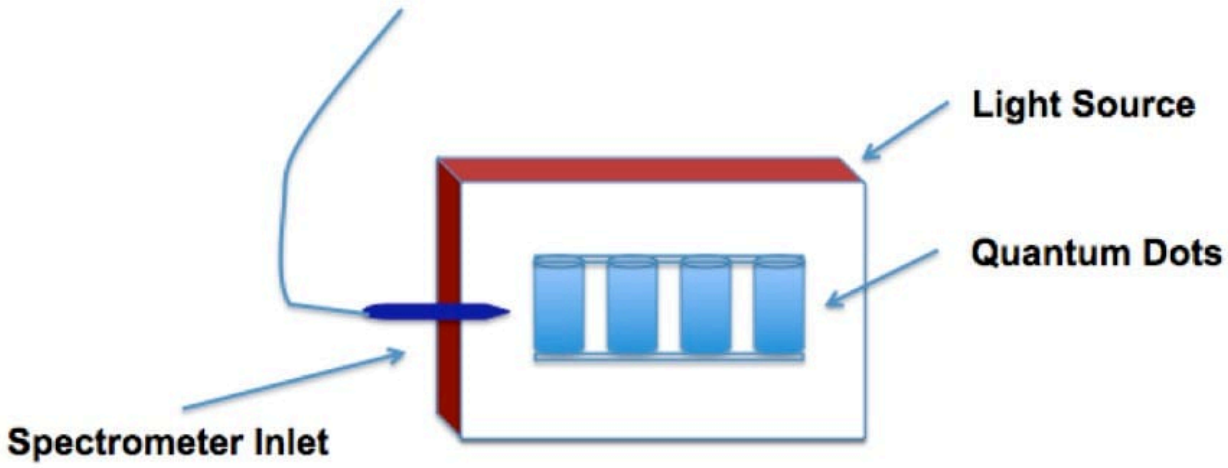



Figure 3. This figure shows the placement of light source, quantum dots and spectrometer inlet for absorption spectra.

## Emission Spectra

1. Use a blue light emitting diode to excite the quantum dots. Use the Ocean Optics spectrometer to take a spectrum of the blue light emitting diode. Do not point the diode directly into the spectrometer optical fiber. Rather reflect the light in to the spectrometer by using a white surface such as a piece of paper.
2. Place the blue light emitting diode below a vial and turn it on, Figure 4.
3. Use the Ocean Optics spectrometer to record an emission spectrum of the vial.
4. Repeat steps 3 and 4 until you have done all four vials.

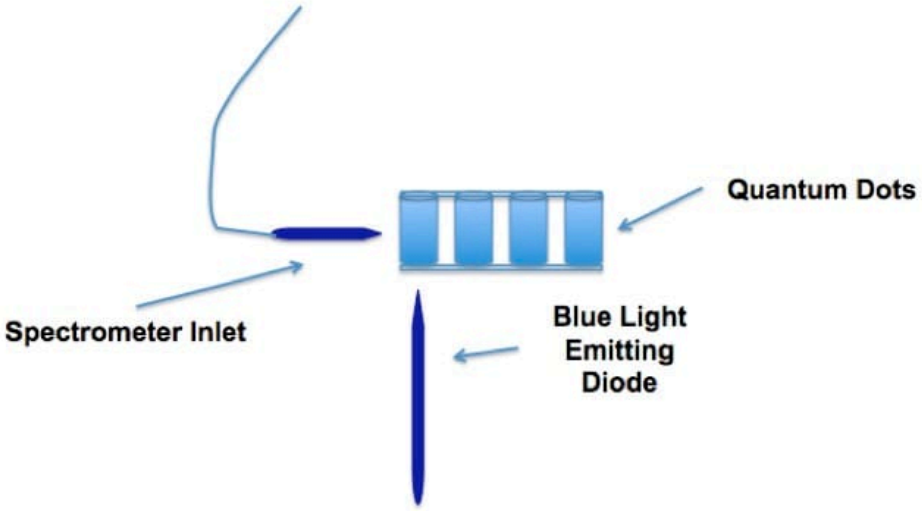



Figure 4. This figure shows the placement of blue light emitting diode, quantum dots and spectrometer inlet for emission spectra of the excitons.

## Calculations, Questions and Report

Use your wavelength calibration curve to determine the calibrated wavelength scale for all of your measured spectra. This includes the absorption spectra, the light emitting diode spectrum and the exciton emission data. For the absorption spectra and the exciton spectra you can label these according to their trace color seen in the vials.

Use the background spectrum and the four spectra obtained under the section “Absorption Spectra” to calculate the absorption spectrum for each vial of quantum dots. Plot the absorbance spectrum for each of the vials of quantum dots using the calibrated wavelength scale and include in your report.

For the data obtained under the section “Emission Spectra” first make a plot of the emission spectrum of the blue light emitting diode using the calibrated wavelength scale. Plot the emission spectrum for each of the vials of quantum dots of quantum dots using the calibrated wavelength scale and include in your report.

For the exciton emission spectra, find the wavelength of the maximum emission for each of the vials. Use Equation (14) to calculate the radius of the four sizes of quantum dots. Summarize your results in a Table such as the following.

| Solution Color | Peak Wavelength (nm) | Radius (nm) |
|---|---|---|
| Color | ###.# | #.### |

Make a plot of quantum dot radius (y-axis) as a function of the peak wavelength of the emitted light (x-axis).

In the discussion and conclusions section consider the following. (1) What happens to the wavelength of light emitted as the radius of the quantum dot increases? (2) Examine the absorption spectra. From the absorption spectra discuss why a blue light emitting diode creates an exciton and why the red light emitting diode does not for the quantum dots used in this experiment.

## References


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# 15: Kinetics of Hydrogen Peroxide Decomposition

## CHEM 174 Physical Chemistry Laboratory II

## Hydrogen Peroxide Decomposition

### Introduction

The composition of our world is controlled by detailed chemical mechanisms and their rates. Extremely complex mechanisms determine the characteristics of everything from living cells to the atmosphere. For example, chemists are creating mechanisms for the reactions of organic compounds in the polluted urban atmosphere that include almost two million elementary reactions. The goal of chemical kinetics is to better understand the mechanisms and rates of chemical reactions. In this laboratory you will learn some methods that can be applied to understand the mechanisms of many kinds of reactions.

Hydrogen peroxide is an oxidant that is ubiquitous in the environment that is formed by atmospheric processes (Stockwell et al., 1997). Hydrogen peroxide is injurious to cells because it attacks unsaturated fatty acids (lipids) found in cell membranes and consequently cells produce a powerful catalyst, catalase, that decomposes H2O2 (Keusch). Catalase is a catalyst (rather than just another reactant) because it reacts both as an electron donor and as an electron acceptor. Catalase is an example of a enzyme, a biological catalyst.

There are many other compounds that decompose hydrogen peroxide such as iodide ion under acidic conditions. The decomposition is characterized by the stoichiometric reaction 15.1.

$$2I^- + 2H^+ + H_2O_2 \rightarrow I_2 + 2H_2O \tag{15.1}$$

If the solution is relatively acidic (with a pH is less than about 3) the rate of reaction 15.1 is independent of the pH. Assume that the rate of the reaction under acidic conditions is given by Equation 15.2.

$$Rate = k\left[I^-\right]^a\left[H_2O_2\right]^b \tag{15.2}$$

where $k$ is the rate coefficient, $[I^-]$ is the iodide concentration, $[H_2O_2]$ is the hydrogen peroxide concentration and $a$ and $b$ are the order of the reaction with respect to iodide and hydrogen peroxide, respectively. We will learn something about kinetics by experimentally determining a and b and by estimating k as a pseudo rate coefficient. This laboratory is based on a similar experiment (Hutton, 1968).

### Measuring the order of the reaction with respect to the iodide and hydrogen concentrations, “a” and “b”

We could mix many different concentrations of iodide and hydrogen peroxide and measure the rate but the data analysis would be very difficult and confusing. Suppose that we measured the rate using some baseline concentrations of iodide and hydrogen peroxide, $[I^-]_o$ and $[H_2O_2]_o$ respectively. The baseline rate will be called $Rate_o$ as in equation (3).

$$Rate_o = k\left[I^-\right]_o^a\left[H_2O_2\right]_o^b \tag{15.3}$$

constant at $[H_2O_2]_o$. The ratio between the new rate and the baseline rate is give by equation 15.4.

$$\frac{Rate}{Rate_o} = \frac{k\left[I^-\right]^a\left[H_2O_2\right]_o^b}{k\left[I^-\right]_o^a\left[H_2O_2\right]_o^b} \tag{15.4}$$

Equation 15.4 simplifies to equation 15.5.

$$\frac{Rate}{Rate_o} = \left(\frac{[I^-]}{[I^-]_o}\right)^a \tag{15.5}$$

A typical experimental “trick” is to find a way of linearizing the experiment so that its’ results can be fit by a straight line as given by equation (6).

$$y = slope \cdot x + constant \tag{15.6}$$

where y in the dependent variable and x is the independent value. In this case linear regression can be used to determine an experimental value. We will do that here by taking the natural logarithms of both sides of equation (6).

$$\ln\left(\frac{Rate}{Rate_o}\right) = a \ln\left(\frac{[I^-]}{[I^-]_o}\right)$$

Therefore if we measure the reaction rate at some concentration of iodide and then make several more measurements at differing concentrations of iodide and plot $\ln\left(\frac{Rate}{Rate_o}\right)$ as a function of $\ln\left(\frac{[I^-]}{[I^-]_o}\right)$ the slope will be equal to $a$, the order of the reaction with respect to the iodide concentration.

We can follow similar reasoning to measure $b$, the order of the reaction with respect to the hydrogen peroxide concentration.

$$\ln\left(\frac{Rate}{Rate_o}\right) = b \ln\left(\frac{[H_2O_2]}{[H_2O_2]_o}\right)$$

## Measuring the reaction rate

How can the reaction rate of reaction (1) be measured? Thiosulfate ion reacts with iodine to convert it back to iodide as shown in reaction (9) and it does not react to any significant extent with anything else in the solution.

$$I_2 + 2\ S_2O_3^{=} \rightarrow 2\ I^- + S_4O_6^{=}$$

Iodine concentrations remain low as long as there is thiosulfate in the solution. After the thiosulfate is consumed iodine concentrations will increase and in the presence of starch a blue colored complex will form. We can measure the rate of reaction (1) by adding a known amount of a standard sodium thiosulfate solution and some starch to the reacting solution. The time required for the solution to turn blue is measured. The rate is given by equation (10).

$$\text{Rate} = \text{Moles } H_2O_2 \text{ reacted / Time (s)} = \text{Moles thiosulfate reacted / Time to turn blue}$$

The formula of sodium thiosulfate is $Na_2S_2O_3$. Sodium thiosulfate may absorb water or react with impurities in solution. Therefore to measure the rate coefficient accurately we should do several different titrations of the sodium thiosulfate solution to accurately establish its’ concentration. However we can make estimates by simply assuming the formula to calculate the thiosulfate concentration. This uncertainty does not affect the determination of reaction order at all but it does affect the determination of the rate coefficient.

### Estimating a pseudo rate coefficient

We will estimate a pseudo rate coefficient with respect to iodide and another pseudo rate coefficient with respect to hydrogen peroxide.

To estimate a pseudo rate coefficient with respect to iodide. use the data were the iodide was varied and the hydrogen peroxide concentration was kept constant. Under these conditions we may define $k'$, where $k' = k\,[H_2O_2]^b$ and the expression for the reaction rate becomes:

$$Rate = k'\,[I^-]^a$$

If the measured reaction rate, $Rate$, is plotted as a function of $[I^-]^a$ then $k'$ can be determined from the slope.

To estimate a pseudo rate coefficient with respect to hydrogen peroxide, use the data were the hydrogen peroxide was varied

and the iodide concentration was kept constant. Define this pseudo rate coefficient, $k''$, as $k'' = k\left[I^-\right]^a$ and the expression for the reaction rate becomes:

$$Rate = k''\left[H_2O_2\right]^b$$

If the measured reaction rate, $Rate$, is plotted as a function of $\left[H_2O_2\right]^b$ then $k''$ can be determined from the slope.

## Temperature Dependence of Rate Coefficients

The temperature dependence of rate coefficients for many reactions is given by the Arrhenius equation:

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

where $A$ is the preexponential factor, $E_a$ is the activation energy, $R$ is the ideal gas constant and $T$ is the temperature. In applying this equation be certain the units of $E_a$ and $R$ are consistent. Substituting the Arrhenius equation into the general rate equation for the reaction of hydrogen peroxide with iodide yields,

$$Rate = A\exp\left(\frac{-E_a}{RT}\right) \times \left[I^-\right]^a\left[H_2O_2\right]^b$$

Take the natural logarithm of both sides.

$$\ln\left(Rate\right) = \frac{-E_a}{RT} + \ln\left(A\left[I^-\right]^a\left[H_2O_2\right]^b\right)$$

Therefore if we measure the reaction rate at several temperatures at the same concentration of iodide and hydrogen peroxide and then plot $\ln\left(Rate\right)$ as the dependent axis (y-axis) and $\frac{1}{T}$ as the independent axis (x-axis) the slope will be equal to $\frac{-E_a}{R}$.

## Procedure Part 1:

Prepare a KI solution with a concentration that is about 0.3 M. Use an analytical balance to accurately weigh 25 g of KI. Use a volumetric flask to dilute to 500 ml. Calculate the concentration.

Prepare a $H_2O_2$ solution with a concentration that is about 0.1 M. Dissolve about 6 ml of 30% hydrogen peroxide in 500 ml distilled water. You do not need to calculate the concentration.

Prepare a sodium thiosulfate solution with a concentration that is about 0.02 M. $S_2O_3^=$ Use an analytical balance to accurately weigh 1.5 g of $Na_2S_2O_3$. Use a volumetric flask to dilute to 500 ml. Calculate the approximate concentration.

Make a 500 ml buffer solution with 0.5 M of acetic acid and 0.5 M sodium acetate.

To see the colors of the reaction products do the following:

Record your observations as you do the following. Place about 5 ml of the KI solution in a test tube. Add a few drops of the hydrogen peroxide solution.

Divide the mixture of KI and hydrogen peroxide between three test tubes. Label as I, 2 and 3.
Test tube 1) Keep as a reference.
Test tube 2) Add a couple drops of starch solution.
Test tube 3) Add a couple drops of sodium thiosulfate solution and observe. Add a couple of drops of starch solution and observe again.

Keep these test tubes as a reference as you perform the kinetics measurements.

*Table 1. Experimental Solutions for Part 1.*

| | (1) Distilled Water (ml) | (2) Buffer (ml) | (3) KI Solution (ml) | (4) Starch Solution (ml) | (5) Na2S2O3 Solution (ml) | (6) More Distilled Water (ml) | (7) $H_2O_2$ Solution (ml) |
|---|---|---|---|---|---|---|---|
| | KI Variation | | | | | | |
| A | 300 | 25 | 5 | 2 | 25 | To make 475 | 25 |
| B | 300 | 25 | 10 | 2 | 25 | To make 475 | 25 |
| C | 300 | 25 | 15 | 2 | 25 | To make 475 | 25 |
| D | 300 | 25 | 20 | 2 | 25 | To make 475 | 25 |
| E | 300 | 25 | 25 | 2 | 25 | To make 475 | 25 |
| | | | | | | | |
| | $H_2O_2$ Variation | | | | | | |
| E | 300 | 25 | 25 | 2 | 25 | To Make 475 | 25 |
| F | 300 | 25 | 25 | 2 | 25 | To Make 450 | 50 |
| G | 300 | 25 | 25 | 2 | 25 | To Make 425 | 75 |
| H | 300 | 25 | 25 | 2 | 25 | To Make 400 | 100 |
| I | 300 | 25 | 25 | 2 | 25 | To Make 375 | 125 |

First note the temperature of the solutions and record in your notebook. Mix the solutions 1 – 6 together to make solution A but do not add the hydrogen peroxide. Measure the volumes of the KI and of sodium thiosulfate as accurately as possible. Pour the solution into a 500 ml beaker. Accurately measure the volume of the hydrogen peroxide solution. Mix solution A and the hydrogen peroxide solution and determine the time from mixing until the solution turns to a light blue. Record the time to the nearest second. Repeat for all solutions in Table 1. You do not need to repeat solution E, it is listed in Table 1 to indicate that it is part of both the hydrogen peroxide and potassium iodide variations.

## Data Summary Sheet

| | Time (Min) | Measured Temperature C° |
|---|---|---|
| A | | |
| B | | |
| C | | |
| D | | |
| E | | |
| F | | |
| G | | |
| H | | |
| I | | |

## Part 2 Temperature VariationTable 2 gives the composition of the reaction mixture.

*Table 2. Experimental Solutions for Temperature Variation. Part 2.*

| | Temperature C° | Distilled Water (ml) | Buffer (ml) | KI Solution (ml) | Starch Solution (ml) | Na2S2O3 Solution (ml) | More Distilled Water (ml) | H2O2 Solution (ml) |
|---|---|---|---|---|---|---|---|---|
| E1 | 25 | 300 | 25 | 25 | 2 | 25 | To make 475 | 25 |
| E2 | 30 | 300 | 25 | 25 | 2 | 25 | To make 475 | 25 |
| E3 | 35 | 300 | 25 | 25 | 2 | 25 | To make 475 | 25 |
| E4 | 40 | 300 | 25 | 25 | 2 | 25 | To Make 475 | 25 |
| E5 | 45 | 300 | 25 | 25 | 2 | 25 | To Make 475 | 25 |
| E6 | 50 | 300 | 25 | 25 | 2 | 25 | To Make 475 | 25 |

First perform the experiment at room temperature. Repeat the experiment near 30, 35, 40, 45 and 50 °C. For all measurements mix solutions 1 – 6 together but do not add the hydrogen peroxide. Measure the volumes of the KI and of sodium thiosulfate as accurately as possible. Pour the solution into a 500 ml flask. Either perform at room temperature or place in a water bath to warm to the desired temperature. There will be three warm water baths available. Do not heat the hydrogen peroxide to avoid decomposition.

Accurately measure the volume of the hydrogen peroxide solution. Mix the solution and the hydrogen peroxide solution and determine the time from mixing until the solution turns to a light blue – brown color. Record the time to the nearest second. Record the temperature of the final solution and record in your notebook.

Each group will perform a measurement at room temperature and near 30, 35, 40, 45 and 50 °C (five total measurements per group).

Data Summary Sheet for Part 2.

| | Time (Min) | Measured Temperature C° |
|---|---|---|
| E1 | | |
| E2 | | |
| E3 | | |
| E4 | | |
| E5 | | |
| E6 | | |

Calculations and Graphs
In your report organize the results of your calculations in tables and show example calculations.

Iodide variation

Use solution E as the baseline solution. Note that the ratios, $[I^-]/[I^-]_o$, for solutions A – E are 1, 2, 3. 4 and 5, respectively. Calculate the ratio of the measured rates (measured times for the solutions to turn blue ($Rate/Rate_o$). Take the natural logs and plot $\ln([I^-]/[I^-]_o)$ as the independent variable (x-axis) and plot $\ln(Rate/Rate_o)$ as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the order of the reaction with respect to iodide from slope. Also determine the $r^2$ (shared variance) of the fit.

Hydrogen peroxide variation
Use solution E as the baseline solution. Note that the ratios, $[H_2O_2]/[H_2O_2]_o$, for solutions E – I are 1, 2, 3. 4 and 5, respectively. Calculate the ratio of the measured rates (measured times for the solutions to turn blue ($Rate/Rate_o$). Take the natural logs and plot $\ln([H_2O_2]/[H_2O_2]_o)$ as the independent variable (x-axis) and plot $\ln(Rate/Rate_o)$ as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the order of the reaction with respect to hydrogen peroxide from the slope. Also determine the $r^2$ (shared variance) of the fit.

Estimate the pseudo rate coefficients
For solutions A – E calculate the reaction rate (Rate) in terms of moles of hydrogen peroxide per second and calculate $[I^-]^a$. Plot $[I^-]^a$ as the independent variable (x-axis) and plot the Rate as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the pseudo rate coefficient from the slope. Also determine the $r^2$ (shared variance) of the fit.

For solutions E – I calculate the reaction rate (Rate) in terms of moles of hydrogen peroxide per second and calculate $[H_2O_2]^b$. Plot $[H_2O_2]^b$ as the independent variable (x-axis) and plot the Rate as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the pseudo rate coefficient from the slope. Also determine the $r^2$ (shared variance) of the fit.

Temperature Variation
For Part 2 plot the natural logarithm of the reaction time as a function of 1/T to determine the activation energy of the rate coefficient. Use Kelvin (K) as your temperature unit.

## Report

Structure the report as discussed in class and include a discussion of the following questions in your conclusions section.

1. To determine the reaction order of KI or $H_2O_2$ why is it not necessary to know the either the initial or actual concentrations of KI or $H_2O_2$ during the experiment?
2. What are the major uncertainties in the results for the reaction orders? What are the major sources of error for the pseudo rate coefficient. What are the r and shared variance ($r^2$)?
3. Suggest a reaction mechanism from the data. Can you distinguish between the following two elementary reaction mechanisms on the basis of your data?

| | Scheme I | Scheme II |
|---|---|---|
| Step 1: | $H_2O_2 + H^+ \rightarrow H_3O_2^+$ | $H_2O_2 + I^- \rightarrow OI^- + H_2O$ |
| Step 2: | $H_3O_2^+ + I^- \rightarrow HOI + H_2O$ | $OI^- + H^+ \rightarrow HOI$ |

| | | |
|---|---|---|
| Step 3: | $HOI + I^- \rightarrow I_2 + OH^-$ | $HOI + I^- \rightarrow I_2 + OH^-$ |
| Step 4: | $OH^- + H^+ \rightarrow H_2O$ | $OH^- + H^+ \rightarrow H_2O$ |

4. Why is the ionic strength kept constant?
5. What are the lessons that can be transferred from this laboratory exercise to life sciences research?

## References


Hutton, W., "General Chemistry Laboratory Text with Qualitative Analysis," Experiment 14, Kinetics of the Reaction Between Hydrogen Peroxide and Iodide Ion, Charles E. Merrill Publishing Company Columbus, Ohio (1968).

Keusch, P. Enzyme Kinetics, Enzymatic Decomposition of Hydrogen Peroxide, http://www.uniregensburg.de/Fakultae...ylab_kat-e.htm

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# 16: MOLECULAR SPECTROSCOPY OF IODINE

16.1: Prelaboratory Assignment
16.2: Introduction
16.3: Potential Energy Curves
16.4: Experimental Part I - Absorption Spectrum of Iodine Vapor
16.5: Experimental Part II - Emission Spectrum of Iodine Vapor
16.6: References and Additional Reading

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# 16.1: Prelaboratory Assignment

Complete the general pre-lab assignment and submit your assignment on Canvas. In addition, please read the following (Duke Students click here):

## Pre-Laboratory Reading

1. McQuarrie and Simon, Chapter 13, sections 13.1, 13.6–13.7; Chapter 15, sections 15.1–15.2, 15.5–15.6
2. Alberty, R.A. and Silbey, R.J. "Physical Chemistry," 2nd ed. (and 4th ed.), Wiley, NY, 1996, Chapter 14, Sections 14.1–14.3, 14.8–14.10

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# 16.2: Introduction

This module uses a simple homodiatomic molecule, $I_2$, to demonstrate that molecules have quantized vibrational and electronic states, and that the transitions between electronic and vibrational states can be coupled.

**This is a two part module consisting of the following:**

I. Collection and analysis of the Absorption Spectrum of Iodine Vapor
II. Collection and analysis of the Emission Spectrum of Iodine Vapor

Chemists use spectroscopy to determine fundamental properties of molecules, and to monitor interesting chemical and physical changes. In this module, you will use linear spectroscopy to monitor the absorption and emission of iodine vapor. This is a demonstration of how scientists use sensitive spectroscopic methods to determine the structure and properties of molecules.

Iodine is purple in color. At room temperature, it is in equilibrium between a solid and gaseous state (see Figure). You can probably draw the Lewis structure and molecular orbital diagram of $I_2$.

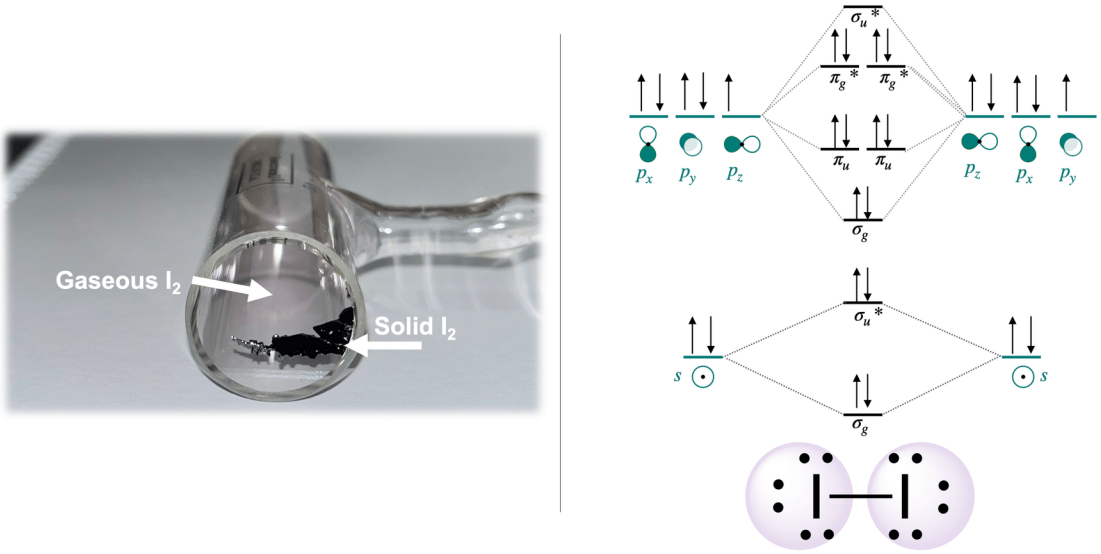



Figure 16.2.1: Left; A spectroscopic cell containing $I_2$. Right; A Lewis dot structure and an approximate valence molecular orbital diagram for $I_2$ (CC-BY-NC-SA; Kathryn Haas)

To know what a molecule is at the atomic scale we must use instruments that are more sensitive than our eyes. We know from the Lewis dot structure of $I_2$ that it consists of two iodine atoms with a single bond between them. But the simple Lewis structure, and rigid dumbbell model that comes to mind, does not describe the dynamics of the iodine molecule.

Consider this for example:

- Using the simple models you learned in Gen. Chem (Lewis dot stuctures or simple MO diagrams), how many electronic transitions should we expect between the HOMO and LUMO of iodine?

You might expect just one electronic absorption from the HOMO to the LUMO. However, the UV-vis absorption spectrum shows many different closely spaced absorptions, and the emission spectrum also shows several wavelengths of light upon excitation.

The fine structure of the electronic absorption and emission spectra are due to the many vibrational states that occur in $I_2$ when it is in its ground and excited electronic states. In other words, the iodine atoms move in space with respect to each other, which effects the energy of the initial state. Furthermore, the electron excitation alters the bonding in the molecule, effecting vibrational states.

The vibronic structure in a UV-Visible absorption spectrum reveals the vibrational energy levels in the excited electronic states of iodine. From these levels a detailed description of the inter-atomic potential between the iodine atoms in these excited states can be obtained. And, the vibronic structure in the emission spectrum from the excited states of iodine reveals the ground state vibrational levels, from which the ground state potential energy curve can be constructed. Finally, comparison of the ground and excited state potentials determined in this way reveals how the bond length changes and how the vibrational potential softens (or stiffens) on electronic excitation.

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# 16.3: Potential Energy Curves

## Harmonic Oscillator

Within the Born-Oppenheimer approximation, each electronic state in a diatomic molecule has a characteristic nuclear potential surface V(R) describing the interatomic potential energy as a function of interatomic distance R. For a bound diatomic molecule with low vibrational energy this interatomic potential V(R) is similar to that of a harmonic oscillator

$$V\left(R\right)=\frac{1}{2}k\left(R-R_e\right)^2 \tag{16.3.1}$$

where R-$R_e$ is the deviation of the interatomic separation from the equilibrium value $R_e$, and k is a force constant describing the strength of the "harmonic spring" that binds the diatomic molecule together.

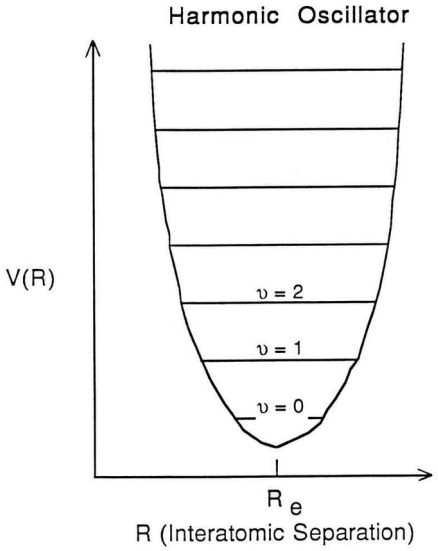



Figure 16.3.1: The potential energy V(R) and vibrational energy levels for a harmonic oscillator. (CC-NC-BY_DUKE CHEM)

The potential energy curve V(R) for a harmonic oscillator is a parabola, and the energy levels are equally spaced, as shown in Figure 5.3.1. The vibrational energy $E_\upsilon$ increases linearly with the vibrational quantum number $\upsilon$ according to the equation

$$E_\upsilon=h\nu\left(\upsilon+\frac{1}{2}\right) \tag{16.3.2}$$

where h is Planck's constant and $\nu$ is the vibrational frequency. The vibrational frequency $\nu$ is related to the force constant k and the reduced mass $\mu$ through the relation

$$\nu=\frac{1}{2\pi}\sqrt{\left(\frac{k}{\mu}\right)} \tag{16.3.3}$$

where $\mu=\frac{m_1m_2}{m_1+m_2}$ for a diatomic molecule where $m_1$ and $m_2$ are the atomic masses of the atoms.

***However, the chemical bonds in real diatomic molecules are not harmonic oscillators***.

## Anharmonic Oscillator

As a chemical bond stretches it gets weaker, ultimately resulting in dissociation as R approaches $\infty$. Also, as the bond shortens, interatomic repulsions raise the potential more rapidly than in the harmonic potential. Thus, the potential V(R) for a real diatomic

molecule is anharmonic, and this results in a decrease in the vibrational energy spacings with increasing vibrational energy.

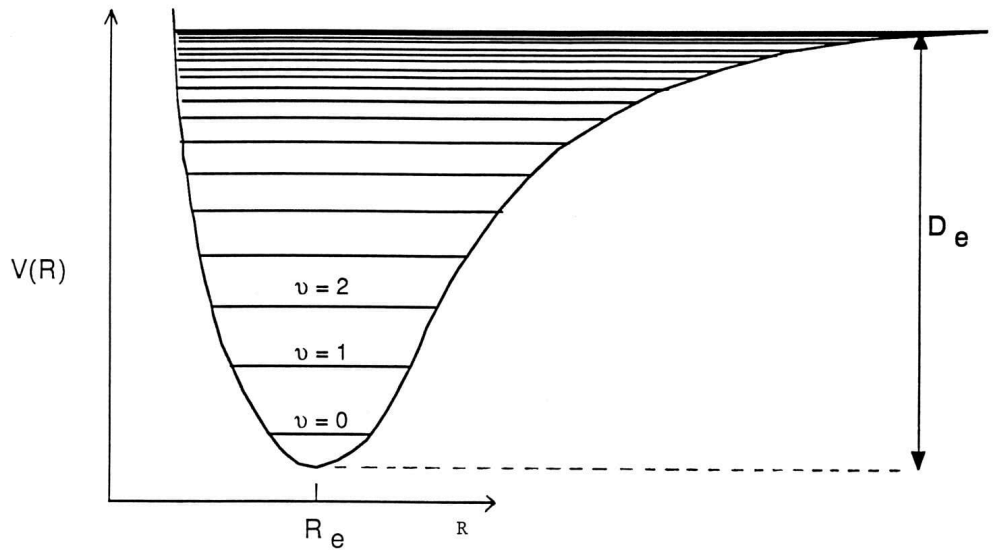



Figure 16.3.2: A typical Morse potential for a diatomic molecule. (CC-NC-BY-DUKE CHEM)

In fact, the difference in energy between neighboring vibrational energy levels approaches zero as the vibrational energy approaches the dissociation energy. Figure 5.3.2 shows schematically a typical anharmonic potential energy surface along with its vibrational energy levels.

## Vibrational energies of an anharmonic oscillator

The vibrational energy levels of an anharmonic oscillator can be described by a power series expansion in $\upsilon + \frac{1}{2}$

$$G_\upsilon = \omega_e \left(\upsilon + \frac{1}{2}\right) - \omega_e \chi_e \left(\upsilon + \frac{1}{2}\right)^2 + \ldots \tag{16.3.4}$$

where $G_\upsilon$ is the energy of quantum level $\upsilon$ in $cm^{-1}$, $\omega_e$ is the "harmonic frequency" of the oscillator in $cm^{-1}$, and $\chi_e$ is called the anharmonicity parameter. For the iodine states of interest in this experiment we can truncate the expansion at the second term, as indicated in equation 5.3.4. The difference between successive vibrational energies is then given by

$$\Delta G_{(\upsilon)} = \left|G_{(\upsilon+1)} - G_{(\upsilon)}\right| = \omega_e - 2\omega_e \chi_e \left(\upsilon + 1\right) \tag{16.3.5}$$

By measuring $G_\upsilon$ for a given state, and plotting the change in vibrational energy spacing $\Delta G_{(\upsilon)}$ with respect to $\upsilon + 1$, both $\omega_e$ and $\omega_e \chi_e$ can be found. According to equation 5.3.5, this plot should be a straight line with a slope of $-2\omega_e \chi_e$ and an intercept equal to $\omega_e$. (Such a plot is called a Birge-Sponer plot. Hertha Sponer was a well-known and highly respected professor of physics at Duke University, one of only a few women physicists at major research universities during the first half of the twentieth century.)

## The Morse Potential

The Morse potential is a simple empirical potential with only two adjustable parameters that incorporates all of these features. In particular it gives rise to the two-term expression for $G_\upsilon$ in equation 5.3.4, with the vibrational energies converging on the dissociation energy $D_e$ (See Figure 5.3.2). The **Morse Potential** has the functional form

$$V\left(R\right) = D_e \left[1 - e^{-a(R-R_e)}\right]^2 \tag{16.3.6}$$

where the Dissociation energy $D_e$ and Morse parameter, a, are related to the parameters $\omega_e$ and $\omega_e \chi_e$ by

$$a = \sqrt{\frac{8\pi^2 c\mu\omega_e\chi_e}{h}} \tag{16.3.7}$$

$$D_e = \frac{\omega_e}{4\chi_e}$$

Thus, for this potential, the constants, a, and $D_e$ can be determined from a measurement of $\omega_e$ and $\omega_e\chi_e$. While other empirical potential functions provide a better representation of the true shape of the potential for many electronic states of diatomic molecules, for the electronic states of iodine considered here the Morse potential works quite well.

## Ground (X) and excited (B) states of iodine

In general, different electronic states have different potentials and different average interatomic separations. For some excited electronic states, the potential may not even have a minimum, or "bound" region. Excitation to one of these "repulsive" potentials would result directly in the dissociation of the molecule, and consequently the absorption spectrum would have no structure. In this experiment, you will focus on electronic transitions between the vibrational levels of two bound electronic states, the ground X $^1\Sigma_g$ state and the excited $B^3\Pi_u$ state. Other electronic states of the iodine molecule will not be discussed here. The potential surfaces for the X and B states can be described by Morse functions. As the molecule dissociates along the ground state X surface, it will separate into two iodine atoms (I + I) in their ground $^2P_{\frac{3}{2}}$ electronic states. However, in the electronically excited B state, dissociation leads to one iodine atom in its ground electronic $^2P_{\frac{3}{2}}$ state, and the other in an excited $^2P_{\frac{1}{2}}$ electronic state (I + I*) (see Figure 5.3.3 below). The energy for the electronic excitation of an iodine atom E(I*) is known quite accurately from atomic spectroscopy, the value being 7603 cm$^{-1}$. This energy is just the separation in energy between the iodine molecule X and B state potential curves in the limit where R approaches $\infty$ (See Figure 5.3.3).

Electronic transitions caused by absorption or emission of light will occur between the various ground state vibrational levels $(v'')$ and the excited state vibrational levels $(v')$. Such transitions involving changes in both vibrational and electronic states are often called vibronic transitions. By convention the various parameters associated with the excited state are designated by $'$ and the parameters for the ground state are designated by $''$, as shown in Figure 5.3.3. The frequency of a vibronic transition (in cm$^{-1}$) between a ground vibrational state level $(v'')$ and an excited state vibrational level $(v')$ will be given by

$$\nu_{(v'',v')} = \nu_{el} + G_{(v')} - G_{(v'')} \tag{16.3.8}$$

where $\nu_{el}$ is the difference in electronic energies of the two potentials at their respective minima, $R_e'$ and $R_e''$ (see Figure 5.3.3). Note that the energy $\nu_{el}$, the dissociation energies $D_e'$ and $R_e''$, and the atomic excitation energy of the iodine atom E(I*) are related through the equation

$$D_e'' = \nu_{el} + D_e' - E\,(I^*) \tag{16.3.9}$$

This can be seen in Figure 5.3.3.

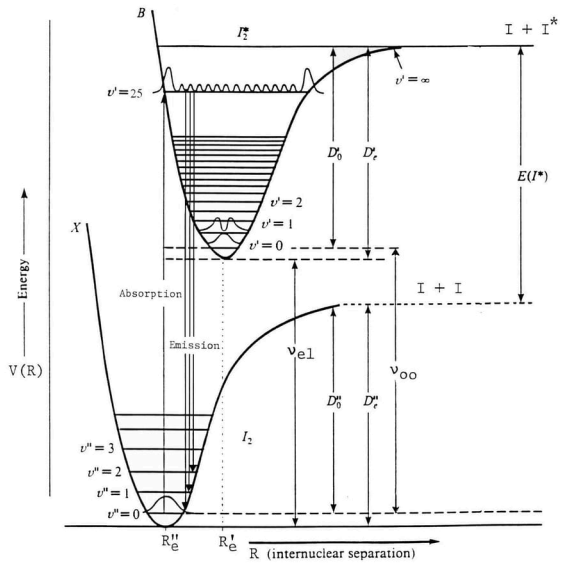



Figure 16.3.3: Schematic representation of the ground (X) and excited (B) states of iodine. Various electronic transitions are indicated by arrows. (CC-NC-BY-DUKE CHEM)

In an absorption experiment, one usually identifies a series of bands (a "progression") that originate from a single ground state vibrational level $v''$, say $v'' = 0$, and end in a series of different excited state vibrational levels. These bands are then assigned to the appropriate $v'$ quantum numbers (not a trivial task!). If one then calculates the spacing between these bands, it can be seen from equation 5.3.8 that this will yield a linear equation just like equation 5.3.5, but where the independent variable is $(v' + 1)$. From the slope and intercept of this plot the values of $\omega'_e$ and $\chi'_e$ can be determined, and from these the values of the Morse parameters $a'$ and $D'_e$ for the excited state can be calculated using equations 5.3.7.

In an emission experiment, one usually pumps a single excited state $v'$, and then observes a band progression of transitions back to a number of different ground states $v''$. These bands can then be assigned, and the separation between them plotted in the form of equation 5.3.5, with $(v' + 1)$ as the independent variable. This allows the ground state parameters $\omega''_e$, $\chi''_e$, $a''$, and $D''_e$ to be determined.

Consider the molecular potential-energy curves shown in Figure 5.3.3. They relate to different electronic states of the same molecule. Some of the vibrational energy levels of each electronic state are marked, together with some of the vibrational wavefunctions. Before absorption of light occurs, the molecule is most likely to be in the ground vibrational state of the lower electronic state, $v'' = 0$, and so we shall concentrate on that initial level. The form of the lowest vibrational wavefunction shows that the most probable location of the nuclei is near their equilibrium separation $R''_e$. However, at room temperature the $v'' = 1$ and $v'' = 2$ levels of iodine also have significant thermal populations and so electronic transitions originating from the $v'' = 1$ and $v'' = 2$ levels can also be seen; these are known as **hot bands**.

When an electronic transition occurs, the molecule is excited to the state represented by the upper curve in Figure 5.3.3. According to the Franck-Condon principle, the vibronic transitions occur so fast (on the order of femtoseconds or less) that the nuclear framework remains constant during the actual transition. We may, therefore, imagine the nuclear wavefunction of the molecule as rising up the vertical lines shown in Figure 5.3.3. This is the origin of the term *vertical transition*, which is used to denote an electronic transition that occurs without change of nuclear geometry.

The vertical transition cuts through several vibrational levels of the upper electronic state. The level marked $v' = 25$ is the one in which the nuclei are most probably at the separation $R''_e$ because the wavefunction has maximum amplitude there. Therefore this is the most probable level for the termination of the excitation. It is not, however the only vibrational level at which the transition may end, because several of its neighbors also have a high probability of having nuclei at the separation $R''_e$. Therefore transitions take place to all vibrational levels in this region, but with greatest probability to the level with the wavefunction that overlaps the initial vibrational state wavefunction most favorably. Transitions from the $v'' = 0$ state of iodine would tend to "miss" upper-level vibrational states with low values of $v'$. For this reason, these transitions are weak or not observed.

As stated above, the excited state vibrational wavefunctions which have the greatest Franck-Condon overlap with the $v'' = 0$ ground state level, are those with the greatest amplitude near $R''_e$. For these levels the maximum amplitude in the vibrational wavefunction occurs at the inner "classical turning point" or the edge of the potential well. Such wavefunctions lie at high values

of $v'$ as shown in Figure 5.3.3. Thus we see that the vibrational structure of the spectrum depends on the relative displacement of the two molecular potential energy curves, and a long *progression* of vibrations (a lot of vibrational structure in the spectrum) is stimulated if the two electronic states are significantly displaced.

This Franck-Condon principle can be used to estimate the shift in the potential minimum on excitation, i.e. $R_e'' - R_e'$. The strongest absorption transition (from $v'' = 0$) will be to some particular excited state level $v^{*\prime}$. The separation, $R^{*\prime}$, at the inner turning point of this exited state level can be identified. Assuming the shapes of both the ground and excited state potential curves are known, the two curves can be overlaid so that the minimum in the ground state $R_e''$ overlaps vertically with the excited state turning point value $R^{*\prime}$. The displacement, $R_e' - R_e''$, can then be read from the plots, or calculated analytically (see references 1 and 4).

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# 16.4: Experimental Part I - Absorption Spectrum of Iodine Vapor

The ELN template for this entire experiment is available here: ELN for Iodine

## Collect the Absorption Spectrum of Iodine Vapor

**Here is the Basic procedure for using the Agilent 100 Series UV-Visible spectrophotometer in the Molecular Spectroscopy of Iodine experiment.**

There are two sample holders in the instrument. The Sample is placed in the front holder; and, the Reference is placed in the back holder (if applicable).

With both sample and reference holders empty and the cover closed, turn on the instrument with the switch at the front, lower left. Wait two minutes before proceeding further.

## Validate the Wavelength Accuracy of the UV-Vis Spectrometer

4.07: UV-vis procedure and instructions for data analysis

## Collect the Absorption Spectrum of Iodine Vapor

1. Load the Scan Software by clicking the  icon on the Windows main screen. In a few moments the scan software main screen will appear and will begin to communicate with the instrument. You can follow the progress by monitoring the display at the lower left of the screen. When the traffic light at the top center of the screen turns green, the system is ready. You will see absorbance at the upper left and wavelength at the upper right of the screen.

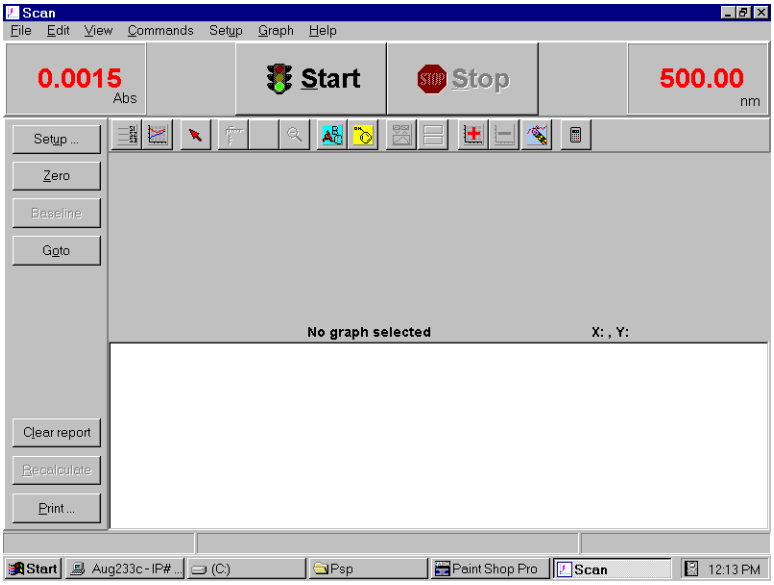



Figure 16.4.4: The Scan Module Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the  button and wait for the setup screen to appear. Select, first, the Cary tab to begin setting

parameters for your sample runs. Under Xmode, the Mode should be set to nanometers and your scan range from 620 to 490. Under Ymode, the Mode should be set to absorbance and the range from 0.02 to 0.25. The Ave time should be 0.1 seconds and the Data interval should be set to 0.1 nm. This will yield a Scan Rate of 60 nm/min.

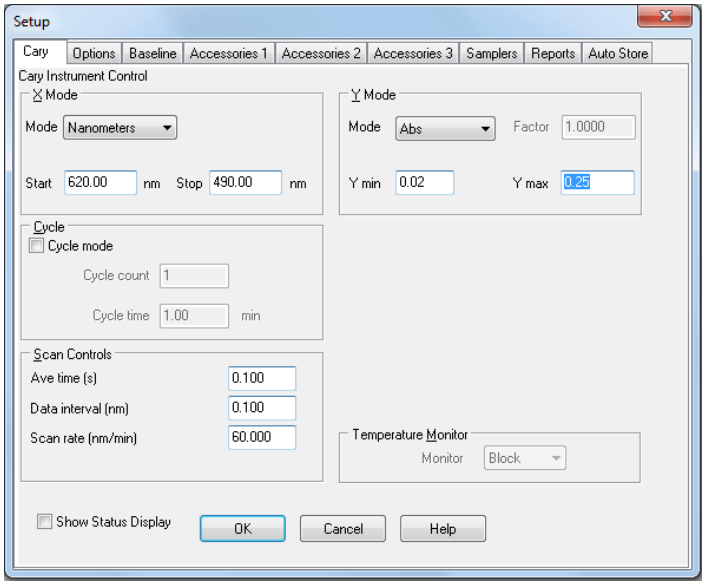



Figure 16.4.5: The Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

3. Select the Options tab on the setup screen and set the Spectral Band Width (SBW) to **0.2 nm**. Select Double Beam Mode. Select UV-Vis as the source and be sure the Source changeover is set to 350 nm. Under Display options you can choose Individual data.

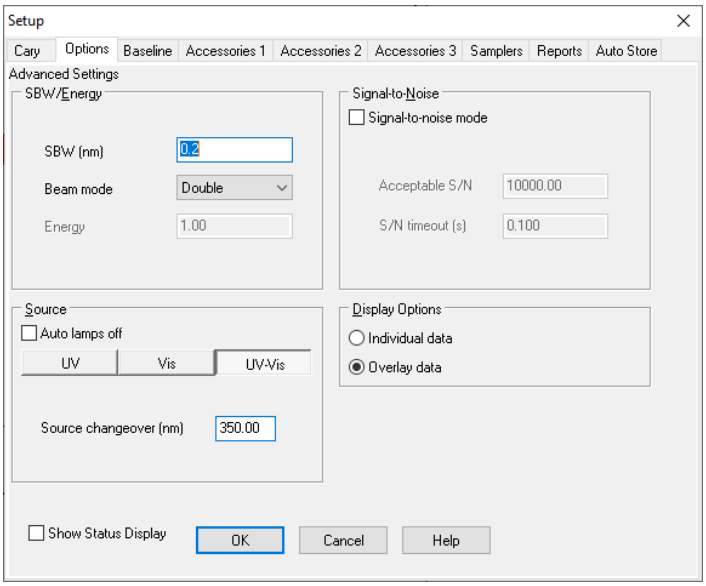



Figure 16.4.6: The Options Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

4. Select the Reports tab. Put your names in the Name box and the title of the experiment in the Comment box. Under Options, check Data Form, Graph, Focused trace. and % Page Height 50. Be sure the Include XY pairs table is not checked. Click Peak Information. Under Peak Table, put a check in All peaks, set the Threshold to 0.0200, and put Peaks in the Peak Type box. Click OK to return to the Setup screen. Choose Select for ASCII (csv). Click OK to return to the main screen.

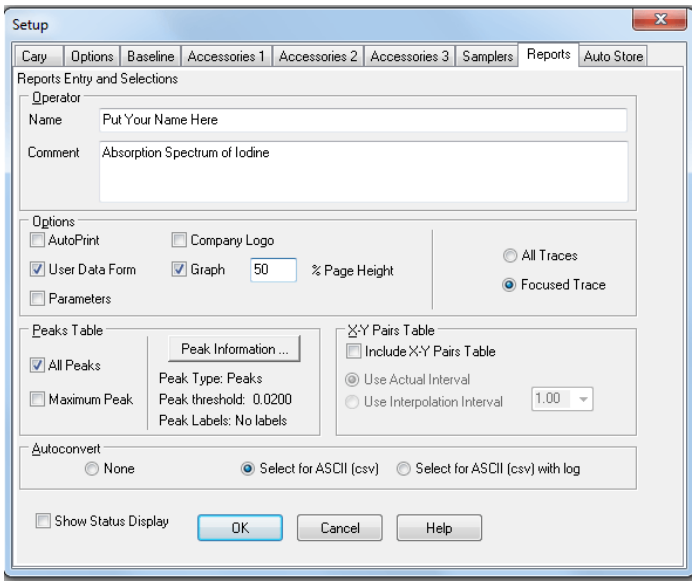



Figure 16.4.7: The Reports Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

5. Remove the 1 cm cuvette holder from the Sample (front) beam of the instrument and replace it with the 10 cm sample cell holder. Place your iodine vapor sample in the Sample holder and close the cover. Click 

to begin your run. You will be prompted for a filename. After naming the file you will be prompted for a sample name. Place the name of the sample (Iodine) in this box. As the run proceeds you will see the spectrum generated in real time on the screen.

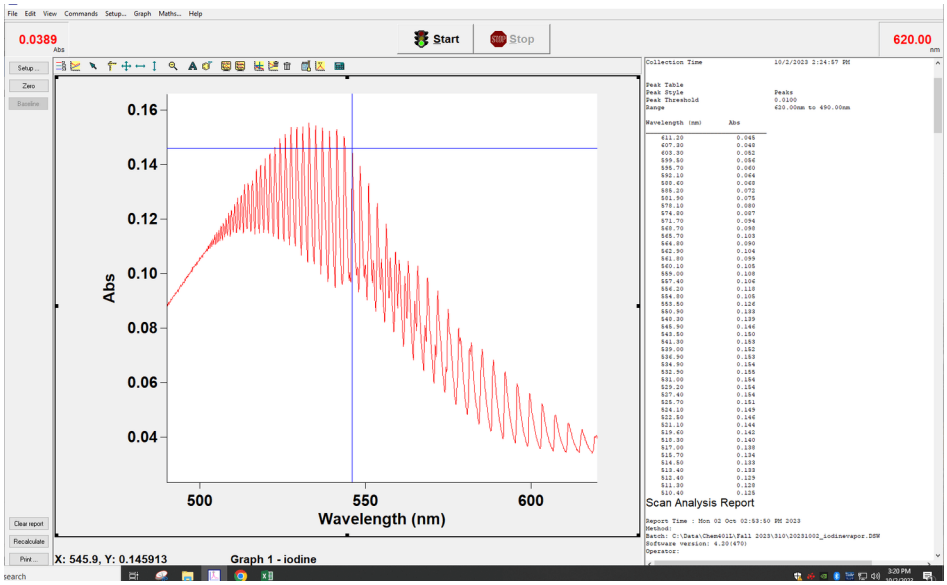



Figure 16.4.8: The Absorption Spectrum of Iodine Vapor. (CC-NC-BY-DUKE CHEM)

6. At the conclusion of the run, find the $v'' = 0 \quad to \quad v' = 25$ transition that is expected to occur at 545.5 nm. Add an annotation to the spectrum to indicate this peak on your spectrum. Also locate the wavelength showing the largest absorption intensity and label it on your spectrum (see note below).

**Note**

Since the baseline is not straight, the peak of largest absorption intensity is found by consideration of both the base and the peak height.

7. Remove the sample and sample holder and replace the 1 cm cuvet sample holder in the instrument, using the screw to secure it properly.
8. Be sure you have screenshots of the needed results, and the Excel spreadsheet generated at the end of the run. Exit the software and turn off the instrument.

## Instructions for Data Analysis (Part I Absorption Spectra of Iodine)

**Note**

- Do not forget to make corrections to the wavelengths based on the results of the validation experiment.
- Be careful not to confuse peaks originating from $v'' = 0$ with those of "hot bands" originating from $v'' > 0$.
- You may consult your instructors and classmates during data analysis, however all work submitted for grading should be your own.

1. Given that the $v'' = 0$ to $v' = 25$ transition occurs at 545.5 nm, assign the peaks in the spectrum according to their $v'$ values.
2. Choose 20 peaks:
   - Convert their wavelengths to wavenumbers. These are the values of $G_v$.
   - Calculate $\Delta G_{(v)}$ (see Equation 5.3.5)
3. Using MATLAB or another program, plot $\Delta G'_{(v)}$ (wavenumbers) vs $(v' + 1)$ (see Equation 5.3.5). Perform a linear least squares regression and overlay the fitted line on the plot of the data.
4. From the intercept calculate $\omega'_e$ using Equation 5.3.5.
5. From the slope calculate $\chi'_e$ using Equation 5.3.5.
6. From Equation 5.3.7 calculate $D'_e$.
7. Estimate your error in measuring the peak positions. Using the standard deviation of the slope and intercept, and Equation 5.3.5, calculate the uncertainties in $\omega'_e$, $\chi'_e$ and $D'_e$.
8. Calculate the Morse parameter, $a'$ from equation Equation 5.3.7.
9. Compare your results with literature values (Ref. 8, p. 540, and Ref. 4).

### Discussion Questions

**Note**

For the following questions, you will need to have already done the data analysis for Part II.

Include responses to the following in your ELN.

1. Determine the value of $\nu_{00}$ (the energy of the transition from $v'' = 0$ to $v' = 0$ is notated by the symbol $\nu_{00}$).
   - Use Equation 5.3.4, which is copied below for convenience, to find $G_{(v'=0)}$ and $G_{(v\'=0)}$:
     $G_v = \omega_e \left(v + \frac{1}{2}\right) - \omega_e \chi_e \left(v + \frac{1}{2}\right)^2 + \ldots$ parameters.
   - Using Equation 5.3.8.: $\nu_{(v'',v')} = \nu_{el} + G_{(v')} - G_{(v'')}$ .
2. Why do the vibrational spacings get narrower as V(R) increases?
3. Why is the Morse potential asymmetric?
4. Why are some of the transitions called "Hot Bands"?
5. How would you calculate $\chi''_e$ and $D''_e$ using the hot bands?. (See reference 6 for help.)
6. What are the units of the Morse parameter, a, in Equation 5.3.7?

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# 16.5: Experimental Part II - Emission Spectrum of Iodine Vapor

In this part of the experiment you will use a HeNe laser at 543.5 nm to excite iodine to the B state, and a monochromator and photomultiplier to measure the spectrum of the emission back to the ground X state. It is worth noting that this technique of "laser-induced fluorescence" is an important spectroscopic tool, not only for physical chemists, but also for analytical chemists. The sensitivity is extremely high, and this has led to a wide variety of applications. These include the measurement of trace amounts of osmium and iridium in rock samples as part of an effort to test a theory for the sudden destruction of the dinosaurs by a catastrophic collision of the earth with an asteroid!

## Laser Safety

Since the laser used in this experiment can be harmful, and the apparatus is relatively expensive, a number of safety precautions must be taken.

### Safety and Other Precautions

1. **Don't look into the laser!** This is a class IIIa/3R laser. If the beam is directed into your eye it will damage your eye before you can blink. However you will still want to avoid looking directly into the beam, or having the beam be directed at you. Any glass that the laser hits will reflect about 5% of the beam intensity. This specular reflection may accidentally be directed toward your eyes. **Therefore, do not move items into or out of the laser path with the laser on. Wear laser goggles whenever the laser is on.**
2. Don't vent the cell. There is no danger to you if you vent it, but you won't be able to do the experiment until the cell is evacuated again.
3. Don't kill the PMT. The Photomultiplier Tube (PMT) is an extremely sensitive light detector. If you can see the light, that's enough light to overload the PMT if there is voltage on it. Read and understand the experimental procedure before applying any voltage to the PMT. Do not turn on the voltage to the PMT if it is exposed to significant amounts of light. Also, turn up the voltage slowly as you look for signal. As long as the observed signal stays below 0.2 V the PMT will not be damaged. Again, no physical damage to you will result from overloading the PMT, only financial.

### Note

The Helium-Neon laser frequency of 543.5 nm corresponds to one of the larger absorption peaks from the absorption spectrum obtained in Part I of the experiment. Notice that absorptions close to 543 nm in the absorption spectrum (Part I) are among the most intense absorptions.

## Preparation of Gas Sample Cell

- A cell containing solid iodine ($I_2$) will be put under high vacuum to vaporize the $I_2$ for spectroscopic analysis.

### Vacuum-Line Start-Up

Some of the following may be completed by the TA before the lab period.

1. Check that all external valves on the working and main manifold are closed to the outside atmosphere.
2. Attach an empty $N_2$ trap to the main manifold. *Hold this trap in place until a vacuum has formed.*
3. Turn on the floor vacuum pump to start generating a vacuum.
4. Turn on all valves in the manifold that are connected to gages (marked with purple tape).

5. Turn on the diffusion pump.
    - Ensure that the floor pump is on BEFORE the diffusion pump. Otherwise, the diffusion pump will generate heat and the oil within the pump will oxidize, causing long-term damage to the diffusion pump.
6. Turn on Digivac electronic monitor. Use this to actively monitor the pressure at the end of the main manifold.
7. Check the analog pressure gauge on the diffusion pump to ensure the pressure is stable.
    - Throughout the experiment, the pressure should remain near 10 mtorr if the system is closed and stable.
8. Fill a 4L dewar with liquid $N_2$ from the shared Chemistry department supply.
9. Place a second dewar underneath the $N_2$ trap on the Main Manifold and fill with liquid $N_2$ such that the $N_2$ trap is submerged in liquid $N_2$.
10. Place the iodine trap on the main manifold and place a third (small) dewar under the trap such that the trap is submerged.
11. Check the level of $N_2$ as the experiment progresses. Refill if necessary to ensure the trap remains cold.
12. Check to ensure the pressure at the end of the main manifold is near 10 mtorr before proceeding.

1. Use the high vacuum line, with help from your TA, to evacuate the iodine vapor cell that will be used in the emission experiment.



Figure 16.5.1: A sample cell containing solid iodine is placed in a liquid nitrogen dewar and evacuated using the main manifold of a high vacuum line. (CC-BY-SA; Kathryn Haas, Duke Chem)

2. Once the cell is well evacuated, place it on the sample holder on the laser table. The cell should be in the path of the laser and there should be nothing obstructing the light path.

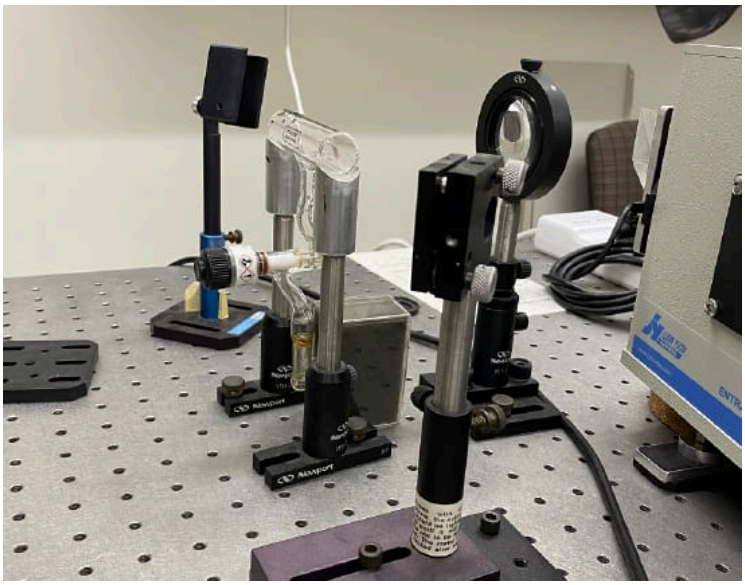


Figure 16.5.2: A sample cell is positioned on the sample cell holder in the path of the laser. The valve on the sample chamber is positioned toward the laser and away from the detector, as shown. (CC-BY-SA; Kathryn Haas, Duke Chem)

### Vacuum Line Shutdown

1. Turn off the diffusion pump. Wait 5 mins for the pump to cool.
    - The pump should be cool before any oxygen is introduced to the system to prevent oil in the pump from oxidizing.
2. Close all valves with purple tape.
3. Turn off Digivac monitor.
4. Turn off the floor pump.
5. Pick an external valve and open it to release the vacuum and open both the working manifold and the main manifold to the air.
    - Do this quickly after step 4. The system should not be left under vacuum without an active vacuum pump.
6. Remove $N_2$ trap and transfer it to the fume hood to safely evaporate excess HCl/DCl gas.
    1. Do this quickly after step 5. Leaving the $N_2$ trap cold after the vacuum has been released may cause liquid $O_2$ to condense, which is highly volatile.

## Instrument Configuration

The figure below shows a schematic diagram of the instrument set up.

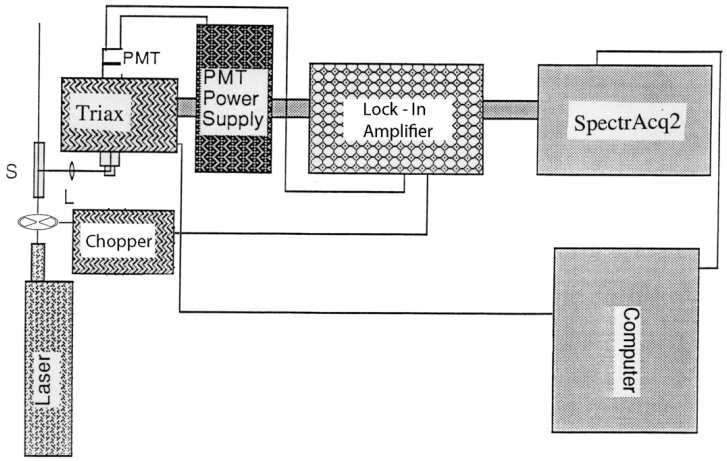



Figure 16.5.1: Instrumentation used for Laser Fluorescence Experiments. (CC-NC-BY-DUKE CHEM)

**Laser**: A Research Electro-Optics, Inc. HeNe laser (model 30968), which emits visible light (543.5 nm), is used to pump primarily transitions from $\upsilon'' = 0$.

**Monochromator**: A Triax 320 monochromator is used to disperse the emission signal from the sample. The entrance and exit slits of the monochromator control the signal intensity and resolution. It is best to use very narrow slits when looking for signal of unknown intensity so you don't overload the photomultiplier tube (PMT) detector with too much light. The PMT is mounted on the exit slit, which should be set to the same width as the entrance slit. There is a slide shutter on the exit port. The manual control unit (CD-2a) can be used for tuning the monochromator when you are setting up the experiment. The monochromator is computer controlled during data collection.

**PMT Power Supply**: The PMT power supply allows you to introduce a voltage to the PMT. Typically you will use a voltage off 1100 volts for this specific PMT. Depending on the available time, your TA may show you the effect of PMT voltage on the observed signal.

**Lock-In Amplifier**: In association with Stanford Research Systems (SRS) chopper an SRS510 Lock-in Amplifier is used to improve the signal to noise ratio of the emission spectrum. The interested student should read the Bentham Instruments introduction to the principles of a lock-in amplifier in the Course Documents section of your Sakai site, or at http://www.bentham.co.uk/pdf/F225.pdf.

**Spectra Acq2**: This is an analog to digital (A/D) converter which takes the analog signal (current from the PMT) and converts it to a digital signal that the SynerJY computer software can read and process.

# Operating the Laser Spectrometer

1. Turn on the Chopper using the power switch on the back of the power supply. It should already be set to approximately 500 Hz. If necessary, adjust settings using the frequency adjust controls to bring it to approximately 500 Hz.

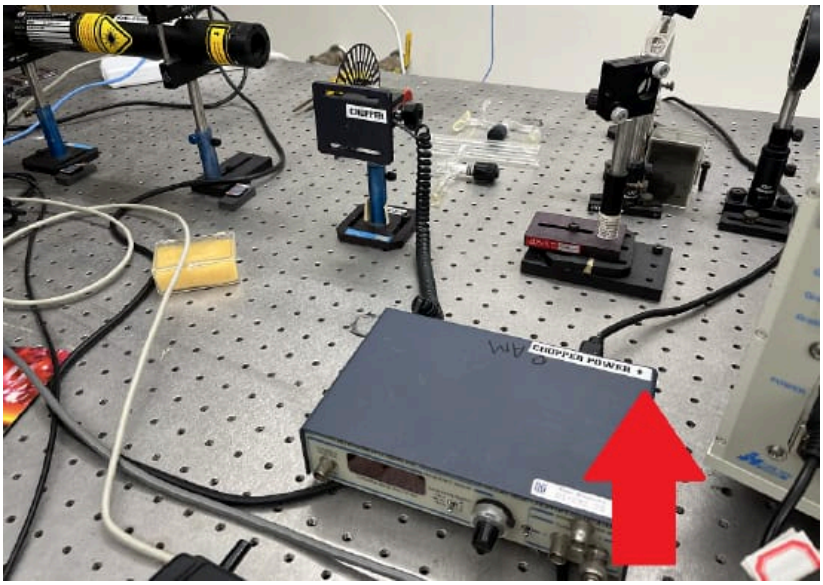



Figure 16.5.3: The chopper and its power supply are labeled. Turn on the chopper using the switch on the back side of the power supply. (CC-BY-SA; Kathryn Haas, Duke Chem)

2. Turn on the power for Amplifier and Photomultiplier Tube (PMT).
   a. Turn on the Pre-Amp power supply using the toggle switch on the box.
   b. Turn on the Lock-in Amplifier using the black switch on the front right of the box.
   c. Turn on the PMT Power Supply, but do NOT apply voltage yet.



Figure 16.5.4: **a) The Pre-Amp power supply** is the black box in the center of the picture; it is turned off using the silver toggle switch. **b) the Lock-in Amplifier** is the box on the left of the photo; it is powered on using the black toggle switch at the bottom right of the control panel. **c) The PMT power supply** is the box on the right; it is powered on using the press button at the bottom right. Do NOT touch the black switch to apply voltage to the PMT until the lights in the room are off. (CC-BY-SA; Kathryn Haas, Duke Chem)

3. Turn off the lights in the room.
4. With the lights off, turn on the laser (key on the laser power supply). Notice that while the laser beam itself is green (543.5 nm), the emitted light, seen as a beam along the length of the sample cell, is in the yellow orange, that is, at lower energy (higher wavelength) than the exiting laser. Of course what you see in the cell is the sum of all wavelengths of emitted light. To resolve that into a spectrum, you will send that light into the monochromator and scan an appropriate wavelength range.
5. Click the SynerJY icon ( 

 ) on the computer screen to load the SynerJY software.
6. From the **Collect** menu choose **Experiment Setup**.

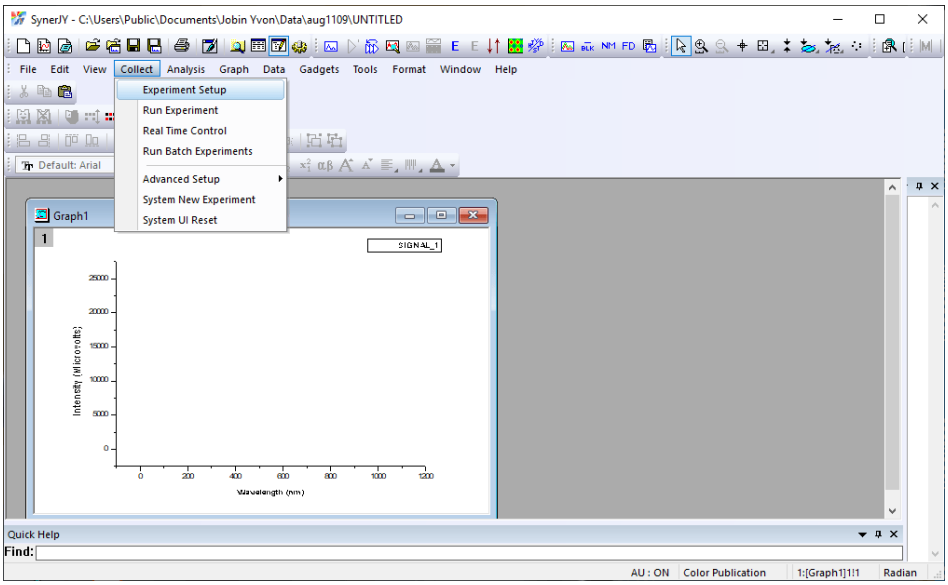



Figure 16.5.5: Choosing Experiment Setup from the Main SynerJY Window. (CC-NC-BY-DUKE CHEM)

- Now, just wait until the system initializes. You will briefly see two windows come and go as the software connects with the monochromator. The first to appear is a **Hardware Configuration** window, and **Triax320PMT** should be highlighted in it.

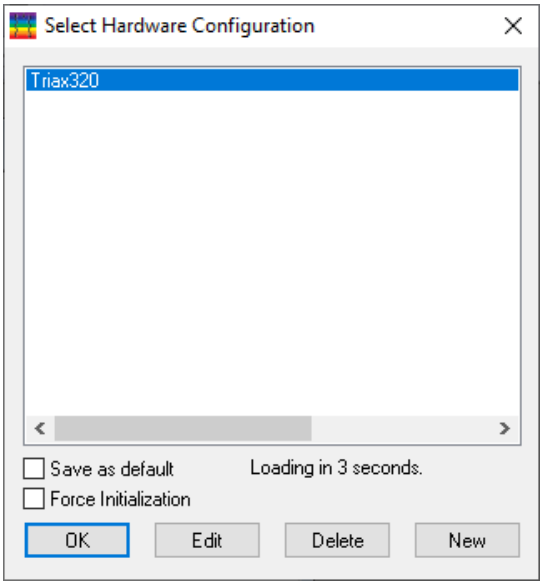



Figure 16.5.6: Hardware Configuration. (CC-NC-BY-DUKE CHEM)

- This window will disappear and be replaced by an **Initialization** Window. The software will initialize the monochromator and PMT and then that window will also disappear.

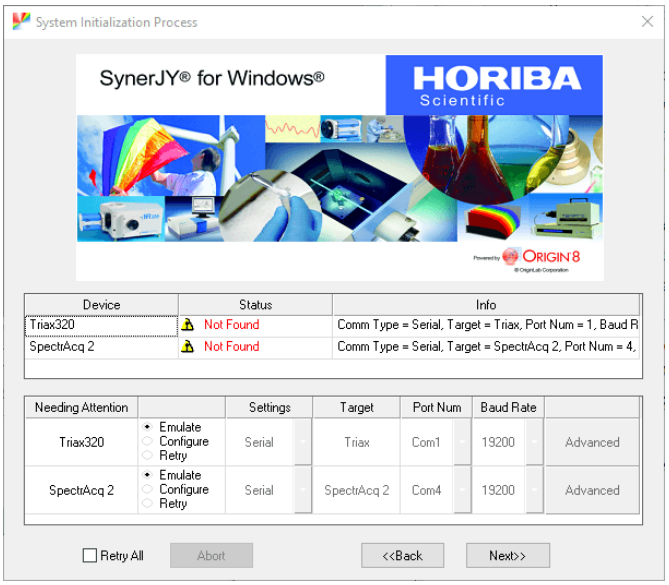



Figure 16.5.7: The Initialization Window. (CC-NC-BY-DUKE CHEM)

- The software will then load the Experiment Setup screen.

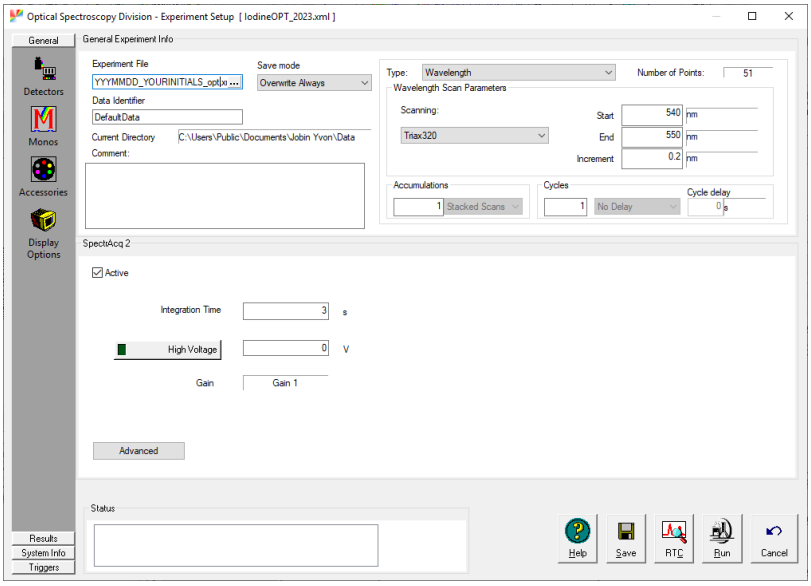
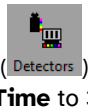
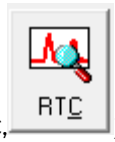



Figure 16.5.8: The Setup Screen. (CC-NC-BY-DUKE CHEM)

7. **Set up the optimization experiment:**
   a. Type a name for your **Experiment File** (use YYYYMMDD_YourInitials_opt).
   b. Press **SAVE**.
   c. Choose a **Start Wavelength of 540 nm** and an **End Wavelength of 550 nm**.
   d. Set the **Increment** to **0.2 nm**.
   e. Make sure **Type** is set to Wavelength, and **Triax320** is selected under **Scanning**.
   f. Click the "Monos" button (

) at the left of the screen and set the **Front_Entrance** and **Front_Exit** Slits each to **0.026 mm**.
   g. Click on the Detectors button (

) button at the left of the window and make sure there is a check in the PMT **Active** box and set the **Integration Time** to 3000 ms (i.e. 3 seconds). Leave the **Gain** at x1.
8. **Turn on the PMT**
   a. Using the buttons on the PMT power supply, apply 900 volts to the PMT. Do this by typing "900" and then pressing the "Enter" button. Then switch the power to "on".

b. On the software, click on the Real Time Control button (RTC, 

).




Figure 16.5.9: Real time controller. (CC-NC-BY-DUKE CHEM)

c. Make sure the Slits and Integration Time are set properly.
d. Change the value in the **Position** box to 543.5 nm.
e. Click on the "Run" button ( 

).
f. Wait a few seconds, then look at the digital readout on the lock-in. You should see less than a tenth of a millivolt signal at this point.
g. Repeat the steps above to change the PMT voltage to 1000 V and watch the signal at the lock-in. Make sure it does not go off scale; decrease the sensitivity if needed.
h. Bring the PMT voltage up to 1100 V, adjusting the lock-in sensitivity to obtain a good signal (several tenths of a mV) without going off scale.
i. Click the "Cancel" button ( 

) to return to the main Experiment screen.

9. **Run the optimization Experiment:** Click on the "Run" button ( 

) to start the short optimization experiment. You will see the spectrum appear in the Display window as the scan progresses. You should see a peak at the pump wavelength. When the scan is complete you may be asked about saving files. To be safe, save all files when asked. Your scan will then appear in the main window of the SynerJY software (Figure 16.5.10).
10. Double Click on the spectrum so that you can edit it. Then select **Pick Peaks** from the **Analysis** menu.

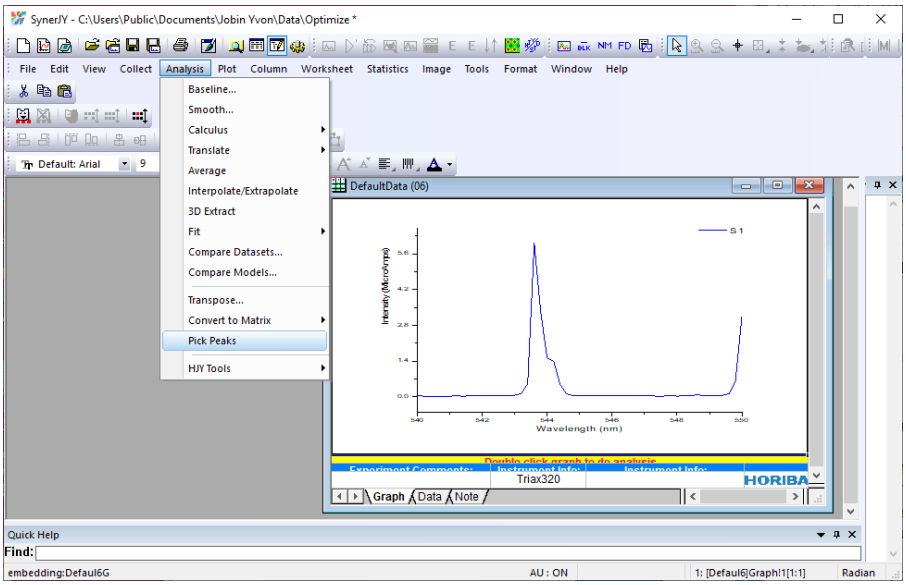



Figure 16.5.10: The Results of the Test Scan. (CC-NC-BY-DUKE CHEM)

a. To begin the peak analysis leave the default settings in the boxes and select **Find Peaks** at the bottom of the **Peak Analyzer** window. Then press **Finish**.

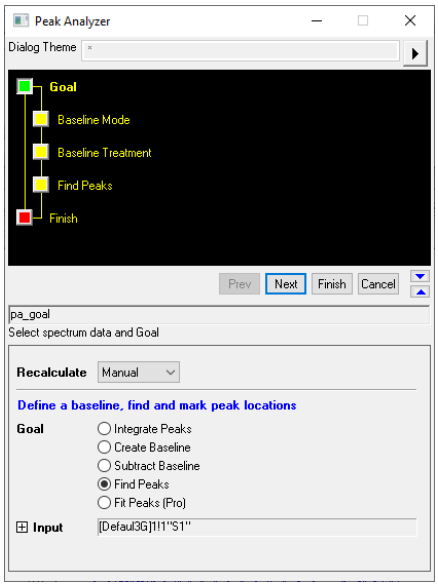



Figure 16.5.11: Copy and Paste Caption here. (Copyright; author via source)

b. If you do not like the results, alter the Height and Width values until you get a good result. In the example shown in Figure 16.5.10 the major peak is found at approx. 543.5 nm, demonstrating that our system is working properly.

11. Do any final optimizing of the signal (check with your TA) and start the run.
12. **Create the Iodine Emission Experiment:**
    a. Make sure the **Increment** is set to 0.2 nm.
    b. Make sure the **Integration Time** is still set at 3000 ms.
    c. Change the **Start** wavelength to 510 nm and **End** wavelength to 800 nm.

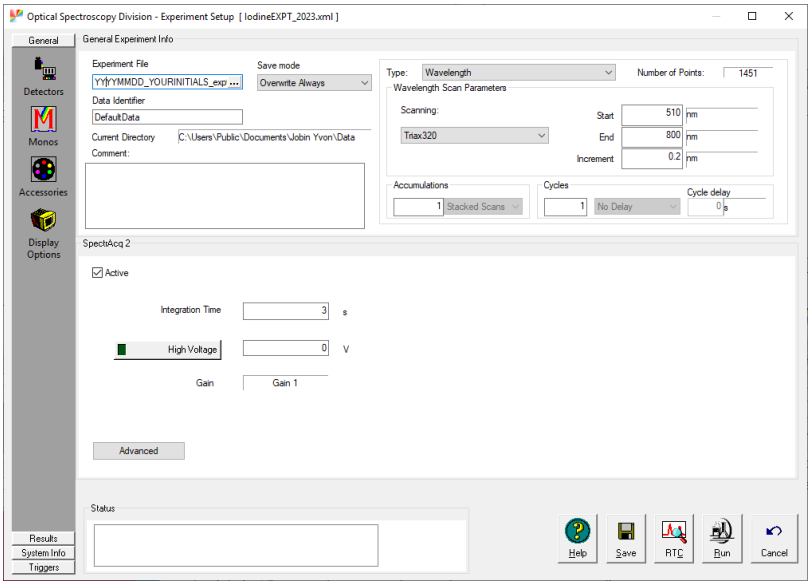
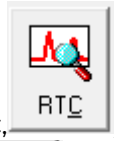
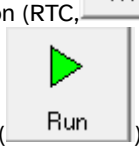



Figure 16.5.12: Setting Up The Sample Run. (CC-NC-BY-DUKE CHEM)

d. Click the Real Time Control button (RTC, 

) to set the monochromator to the start wavelength.

e. Click the **Run** button ONCE only ( 

) and wait a few seconds (this is equivalent to setting the monochromator to the start wavelength and allowing the detector signal to relax).

f. Then click the **Cancel** Button ONCE only ( 

) to return to Setup screen.

g. Click the "Run" button ( 

) from the setup screen to start the full scan.

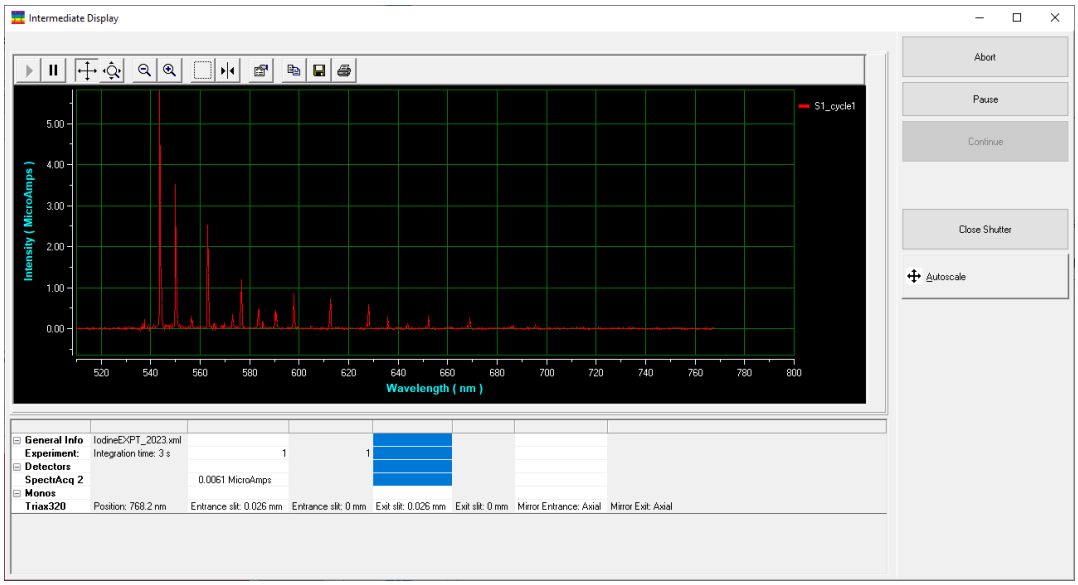



Figure 16.5.13: Data collection. (CC-NC-BY-DUKE CHEM)

h. Watch the data collection for the first 5-10 minutes to be sure everything is running correctly. The total scan will take a at least 1.5 hours. If you leave the room, close the door behind you to be sure that stray light does not get into the experiment.

13. At the end of the scan you may want to rescale the horizontal axis to see the spectrum more clearly.

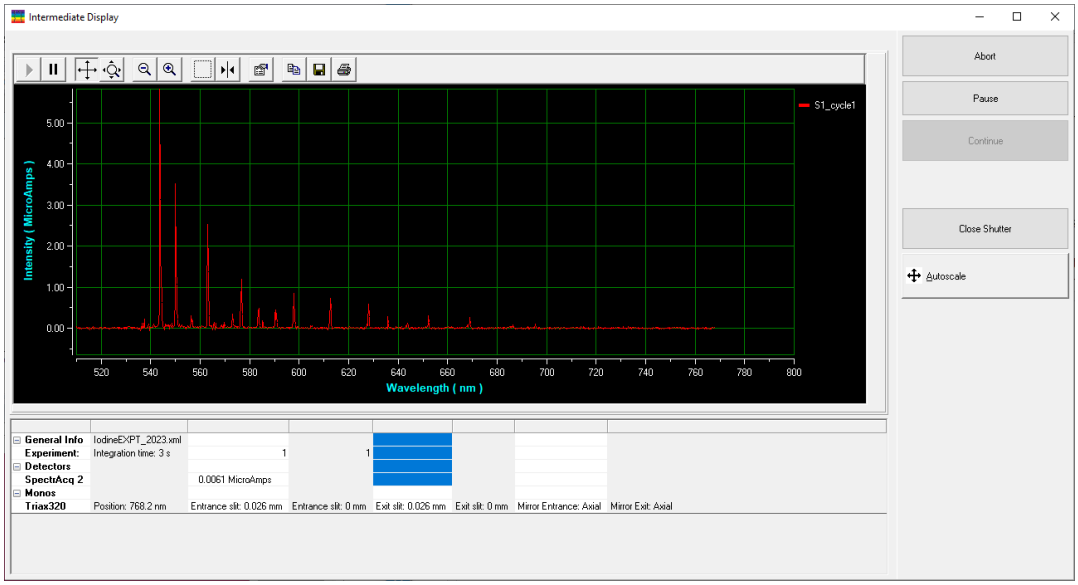



Figure 16.5.14: The FInal Spectrum. (CC-NC-BY-DUKE CHEM)

14. Repeat the Pick Peaks procedure you did earlier on the short scan. Likely you will need to adjust the parameters in the Pick Peaks dialog box to get most or all of the peaks. Below is a suggested set of options:
    a. Goal: **Find Peaks**
    b. Baseline Mode: **Constant, Median**
    c. Baseline Treatment: **Auto subtract baseline**
    d. Find Peaks: **Enable Auto Find, Peak Filtering By Height, Threshhold at ~ 1-2%**
15. When you get a good listing of the peaks look at the bottom of the data window where you will see a list of the files associated with these data (Figure 16.5.15). Click on the Peak_Centers1 worksheet and you will get a table of the peaks found in the spectrum.

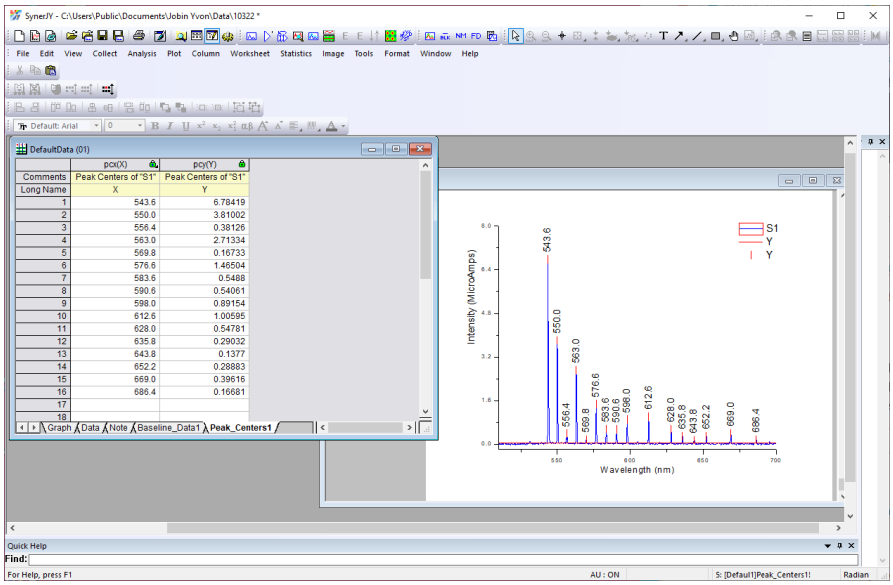



Figure 16.5.15: The Peaks Table. (CC-NC-BY-DUKE CHEM)

You can copy the appropriate data from there to an Excel spreedsheet. You should the save the spreadsheet and any screenshots that you need.

16. **Shutdown:**
    Before you shut down, be sure you have collected all necessary data in your ELN and in excel. Then Send a copy of the ELN to you and your partners.
    a. Turn off the laser using the key.
    b. Turn off the power to the PMT and power off the power supply.
    c. Turn off the power to the Pre-amp Power Supply
    d. Turn off the power to the Lock-in Amplifier.
    e. Turn off the Chopper.
    f. Close the SynerJY software.

# Instructions for Data Analysis

You may consult your instructors and classmates during data analysis, however all work should be your own.

1. Assign at least 19 peaks in the emission spectrum based on the known pump transition. Remember, this is an emission spectrum. Longer wavelengths (lower energy) correspond to transitions from higher ground state vibrations.
    a. Convert the wavelengths of these peaks from nm to wavenumbers.
    b. Create a Birge-Sponer plot (see Equation 5.3.5) by plotting $\Delta G''_{\upsilon}$ vs $(\upsilon'' + 1)$.
2. From the intercept of the Birge-Sponer plot, calculate $\omega''_e$ (using Equation 5.3.5).
3. From the slope of the Birge-Sponer plot, calculate $\chi''_e$ (using Equation 5.3.5).
4. From the Morse Potential (using Equation 5.3.7), calculate $D''_e$.
5. Estimate the uncertainty in the peak positions using the standard deviations from the least squares analysis and calculate the uncertainties in $\omega''_e$, $\chi''_e$ and $D''_e$.
6. For comparison, calculate the value of $D''_e$ using Equation 5.3.9 as follows: From the wavelengths of at least three absorption lines, calculate the corresponding transition energies $\nu_{(\upsilon'',\upsilon')}$ (where $\upsilon'' = 0$) in units of $cm^{-1}$. For these same transitions, calculate $(G_{(\upsilon')} - G_{(0'')})$ using Equation 5.3.4 and your values of $\omega''_e$, $\omega'_e$, $\chi''_e$ and $\chi'_e$. Now use Equation 5.3.8 to calculate the average value of $\nu_{el}$ for the three transitions. Finally, use Equation 5.3.9 and your value of $D'_e$ from Part I to calculate $D''_e$. The value of E(I*) is known to be 76093 $cm^{-1}$ from atomic spectroscopy.[1] Which value of $D''_e$ has the least uncertainty (neglect the error in E(I*))?
7. Calculate the Morse parameter (a") from Equation 5.3.7.
8. To plot the Morse potential wells, you will use the Matlab routine ***morse***. Simply type ***morse*** and follow the screen prompts. Separate ground and excited state Morse potential curves will be plotted using your experimental data, and sent to the printer. For now, both $R''_e$ and $R'_e$ are set at zero. Vibrational quantum levels will be shown for both ground and excited states.
9. The maximum intensity in the absorption spectrum occurs as the excited state vibrational wave functions overlap vertically with the ground state wave functions. A Matlab script, ***overlap***, is used to overlay the two plots and shift the ground and

excited state potential wells such that the center of $v'' = 0$ overlaps with the left edge of the $v' = 25$. At the Matlab prompt type ***overlap*** . The script will animate the overlap of the ground and excited states and the vertical transition. It will also estimate the displacement ($R'_e - R''_e$) (Ångstroms) between the minima of these two potential wells along the R-axis. Save a copy of this graph (or take a screenshot) for your ELN, and record the displacement.

> **Note**
>
> The ground and excited state potential wells are overlaid so that the displacement $R'_e - R''_e$ may be measured. However, this gives a misleading impression of the relative positions (energies) of the two potential wells. Clearly the excited state potential well is at much higher energy than the ground state potential well (see Figure 5.3.3 and note the discontinuity in the V(R) axis). A realistic picture is shown in reference [10]. In the Introduction to Matlab Excercises, you plotted the ground and excited state potential wells for iodine using literature values for $D_e$, a, and $R_e$. You will now repeat this assignment using your results.

10. The functional form of the Morse potential may be represented by the equation

$$V(R) = T_e + D_e \left[1 - e^{-a(R-R_e)}\right]^2 \tag{16.5.1}$$

where $T_e$ is the electronic term energy (the energy at the bottom of the potential well). $T''_e$ and $T'_e$ represent the electronic term energies of the ground and excited states respectively. If we set $T''_e = 0$, then $T'_e = \nu_{el}$. Given that $R''_e = 2.66$ Å (obtained from IR spectroscopy), calculate $R'_e$ using your value of $R'_e - R''_e$.

11. You will now use your values of $T''_e$ (zero), $T'_e$ ( $= \nu_{el}$), $D''_e$, $D'_e$, a", a', $R''_e$ and $R'_e$ to replot the Morse potential wells for the ground and excited states of iodine on the same graph. Return to your Matlab command window, and as instructed, press any key to continue. Enter your calculated $T'_e$. The two Morse potentials will be plotted on one graph and the vibrational quantum levels will be shown for both ground and excited states. Save a copy of this graph (or take a screenshot) for your ELN.
12. Compare all of your results with literature values (See, for example, reference. 1, p. 430-432).

## Discussion Questions

Include discussion of the following in your ELN.

1. Why are the vibrational spacings different in the ground and excited states?
2. Why is the shape of the Morse potential different in the ground and excited states?
3. How is it possible to observe emission peaks at higher energies than the pump energy?

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# 16.6: References and Additional Reading

Duke students can find additional reading materials at the link below, many of which are listed in the references below.

Duke students, click here for additional readings, or find the resources below in the Library (yes, the physical library!)

## References


1. Shoemaker, D.P., Garland, C.W., Nibler, J.W., Experiments in Physical Chemistry, 6th ed., McGraw-Hill, NY, 1996, Chapter XIV, Experiment 40.

2. Silbey, R.J, Alberty, R.A. and. Bewendi, M.G., Physical Chemistry, 4th ed., Wiley, NY, 2005, Chapter 14, Sections 14.1–14.4, 14.8, 14.9.

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# 17: MOLECULAR ELECTRONIC STRUCTURE CALCULATIONS


17.1: Pre-Lab Assignment

17.2: Introduction to Electronic Structure Calculations

17.3: Accessing Spartan

17.4: Exercise 1 - Estimation of the IR Spectrum of HCl, and Comparison of Basis Sets

17.5: Exercise 2 - Molecular Orbitals of Formaldehyde

17.6: Exercise 3 - Modeling Sulfur Dioxide - Comparing the Results of Different Basis Sets and Calculation Models

17.7: Exercise 4 - Modeling the Absorption Spectrum of Cyanine Dyes

17.8: Exercise 5 - Modeling an Intramolecular Rearrangement



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# 17.1: Pre-Lab Assignment

## Pre-Lab Assignment

Complete the general pre-lab assignment for this module. This module is an introduction to computational chemistry and molecular electronic structure calculations using Spartan software. These computational exercises circle back around to some of the "wet lab" modules you completed earlier in the semester.

To help you prepare for this modulewe ask that you do the following:

1. Read the introduction to the lab, and the chapters in your textbook on quantum mechanics and electronic structure theory for molecules.
2. Briefly read the Guidelines for Using Spartan® Software and look over some of the supplemental reading materials provided.

## Planning ahead for your Independent Project

The Spartan exercises will be followed by an independent project in which you can choose to do a computational study.

We ask that you begin to think about your independent project, and we want you to do something you are really interested in! In 310L, you can choose a topic for your independent project, and choose whether you would like to dive into more computational work, or explore other applications of physical chemistry in the peer-reviewed literature. You should begin searching the literature (eg using Web of Science or looking at the Table of Contents for leading Physical Chemistry journals) for physical chemistry topics that interest you. Alternatively, you can think about simple chemical phenomena or reactions that you are interested in and that you can model using Spartan. Come to the laboratory session prepared with a brief written proposal (1 paragraph) on at least two ideas for what you might do for your independent project and be prepared to discuss it with your instructors.

# Introduction

Computers and computational methods have become major tools of chemical research. This comes from the availability of powerful workstations and software packages at affordable prices, the development and implementation of accurate and efficient computational theory, and the insight and user-friendly interface provided by scientific visualization.

In this laboratory exercise, you will use the Spartan® software to explore the calculations of properties of isolated molecules based on a whole range of modeling methods, from empirical molecular mechanics to accurate *ab initio* quantum mechanical methods. You will carefully study the accuracy of each method by comparison with experimental results and with other computational methods. Understanding the limitations of modeling methods is as important as knowing their availability and accuracy. We will learn how such techniques can be used to help solve chemical problems.

There are two parts to the Spartan Exercise:

1. The first part of the exercise is designed to relate to the previous "wet lab" modules of this course.
2. The second part focuses on using computational methods to gain knowledge that is difficult to get from experimental methods; that is to study frontier molecular orbitals and transition state structure in chemical reactions.

> **Note**
>
> This lab is split into 5 separate exercises designed to illustrate the various capabilities of Spartan. The requirements for your lab notebook are stated within each exercise instead of at the end of the chapter. It is recommended that you follow along with the ELN template while completing this lab to ensure that all data is properly recorded.

# Independent Project

This is for *Chemistry 310L students only (301L students don't need to do this)*. After completing the Spartan excecises, you will porpose and complete an independent project - for this project, you are welcome to model your own favorite molecules or reactions. You will need to design this part of the project before you come to the laboratory and learn to ask the right questions with the proper tools. This is an opportunity to explore something that is interesting to you.

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# 17.2: Introduction to Electronic Structure Calculations

Calculation of the electronic structure of a molecule (i.e. the molecular orbitals) can be accomplished by the following steps:

1. **Preparation of the input data**: Within the Born-Oppenheimer approximation, nuclei are held fixed while solving for the *electronic* motion. Before you begin your calculations, you must first define the fixed nuclear positions at which the electronic structure calculation will be performed -- i.e. you must define a molecular geometry. In Spartan®, this is done graphically in much the same way in which you built molecules when you took organic chemistry courses.

   Many of the calculations you undertake here will use a variational approach in which the molecular wavefunction is written as a single Slater determinant of molecular orbitals (MO), where each MO, in turn, is written as a Linear Combination of Atomic Orbitals (LCAOMO). To begin this variational approach, you must obtain a starting "trial wavefunction." In the LCAOMO method, this requires definition of the atomic functions that will be used to construct the MO's. Recall the variational approach to the electronic structure of $H_2$ -- to begin we used a trial LCAOMO wavefunction $\Psi$ written as a linear combination of a 1s atomic orbital on HA ($\Phi$1sA) and a 1s atomic orbital on HB (($\Phi$1sB); i.e., we defined the atomic functions that were used to construct the MO's. In Spartan® you will find a reasonable collection of such sets of atomic functions built into the software, and consequently, selection of an appropriate set of atomic functions is usually achieved by simply choosing from a selection of available methods and basis sets.
2. **Running the calculation:** After building the molecule of interest and selecting the type of calculation to be run, and other relevant parameters, one submits this job for calculation.
3. **Analysis of the results**: This may involve such tasks as viewing electron densities, exploring the bonding or antibonding character of molecular orbitals, animating vibrational modes associated with nuclear motion, viewing energy-minimized structures and determining bond lengths and bond angles, or calculating molecular properties. Most of this analysis is done using the graphical interface available in Spartan® thereby minimizing the need to examine multiple pages of numerical data! Again, Spartan® simplifies the analysis by providing numerous visualizations and menu-driven data displays.

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# 17.3: Accessing Spartan

A network version of Spartan 20 is available from the chemistry server, bohr. Access to Spartan through FastX is the same as access to Matlab, except that you will want to type...

```
01 spartan
```

at the prompt after logging in. Every computer in the physical chemistry lab is already set up with FastX. In addition, you will likely want to have access from your own laptop. Complete instructions for obtaining and configuring FastX, and the Duke VPN (if needed) can be found here.

1. Loading – Spartan® 20




1.1. Click the FastX shortcut icon, FastX on the main screen of any computer in the Advanced Labs. Click on the bohr.chem.duke.edu session. Enter your NetID and password and click Continue. Click on the + at the upper right of the new screen that appears, and click on Xterm. An xterm window should appear. Find your TA or your Instructor if there are problems connecting; it happens sometimes.

2. Type

```
01 spartan
```

This will start the Spartan program and the main screen will appear.

Notice the menus and buttons at the top of the screen.

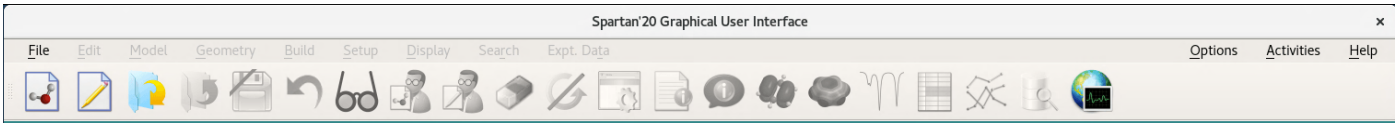



Figure 17.3.1: The Spartan Menu and Button Bar. (CC-NC-BY-DUKE CHEM)

You will use these menus and button to operate Spartan®. Note also the **Help** menu to the right of the menu bar. Among the many useful things included in the Help menu is a summary of mouse commands (within General Operating Features). You will use this summary frequently as you do your work.

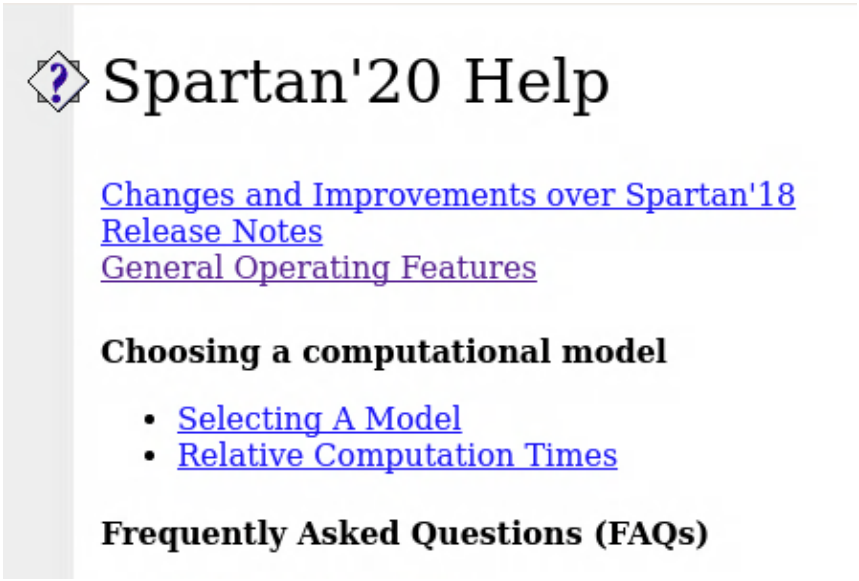



Figure 17.3.2: Spartan Help. (CC-NC-BY-DUKE CHEM)

Once in General Operating Features, scroll down to find the table of mouse functions.

**Using the Mouse**

The following functions are associated with the two-button mouse.

| keyboard | left button[a] | right button[a] |
|---|---|---|
| - | picking, X/Y rotate | X/Y translate |
| **Shift** | range picking, Z rotate | scaling[b] |
| **Control** | multiple picking, global X/Y rotate[b] | global X/Y translate |
| **Control + Shift** | global Z rotate[c] | scaling[b] |
| **Alt** | group picking, bond rotation | bond stretching |
| **Control** ("Build" mode) | fragment X/Y rotate | fragment X/Y translate |
| **Control + Shift** ("Build" mode) | fragment Z rotate | scaling[b] |

a) Left and right buttons together with no modifier keys are used for defining a section box.
b) Scaling is always applied to all open molecules and fragments. The **scroll-wheel** found can also be used for scaling.
c) Global rotations can be either molecule or screen centered. This is controlled by **Global Rotate** in the **Preferences** dialog (**Options** menu).

Mouse/keyboard operations may be broadly separated into two categories: selection (picking) and manipulation (translation/rotation).

**Selection**

Figure 17.3.3: Using the Mouse. (CC-NC-BY-DUKE CHEM)

**Note**

Spartan works best with a 3-button mouse. However it is easy enough to translate the mouse instructions to work equally well with a trackpad.

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# 17.4: Exercise 1 - Estimation of the IR Spectrum of HCl, and Comparison of Basis Sets

**Note**

These Exercises should be completed **individually**. As always, you may work alongside of other students and discuss your results, however each student should open the software on a computer, complete the tasks, and complete the ELN individually. Submit your individual copy of the ELN at the end of this session.

The ELN template is available here (click).

The goal of this first exercise is to compare your experimental FTIR data from the HCl diatomic molecule with computational predictions, and to compare different basis sets.

## Estimation of the IR Spectrum of $H^{35}Cl$ and $H^{37}Cl$

Select New Build from the File from the menu, or click the  button.

1. The right side of the screen is the *model kit*.

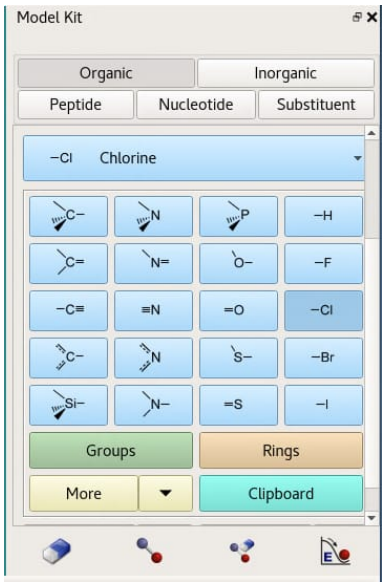



Figure 17.4.1: The Model Kit. (CC-NC-BY-DUKE CHEM)

Notice that you are in the **Organic** area of the model kit. Here you will see several common atom types and their hybridization. You might take a moment now to familiarize yourself with the other screens of the model kit, Inorganic, Substituent, Peptide and Nucleotide.

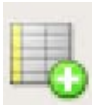
3. From within the Organic area of the model kit, click on the –Cl atom and then double-click somewhere in the working area of the main Spartan screen. You will see a colored line, with the Cl atom at the end. Select Save as from the File menu, or click

the  button. Keep the suggested filename, or give the file a name of your choice. A hydrogen atom is automatically added to your molecule. To see the hydrogen, click the  button to leave the Build Mode and enter the View Mode.

**Note**

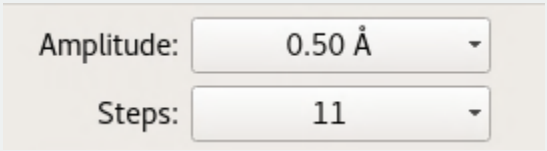
Clicking the  button returns you to the Edit Build Mode.

The exact view of the molecule will depend upon what "model" system you have selected. Use the **Model** menu to change how the molecule looks.

4. Select **Calculations** from the **Setup** menu. Choose **Equilibrium Geometry** at **Ground State** in **Gas,** *with* **Hartree-Fock, 3-21G**. *Total charge* should be **Neutral**, and *Unpaired Electrons* should be **0**. Select *compute*: **IR** (with Current Model). Click on **Submit**. If prompted, save the file (use the same file name). If everything is correct, you will see the "Job "*filename*" has been submitted" box. Click **OK**.
5. After a moment a "Job "filename" completed" box appears on the screen. Click **OK**. Inspect the output of this job using **Display**, **Output**. The **Summary** tab will give you the major results of the calculation. If you expand the **IR** section of the **Summary** you will see the calculated estimate of the frequency of vibration. Record this value in your lab notebook. In the **Output** tab, you will see information about the chosen basis set, the number of steps for geometry optimization, and other information related to the calculation. Close the **Output** dialog box. Then select **Spectra** under the **Display** menu and click on the , and select **IR Calculated**. The calculated spectrum appears on the screen. Click on the  and you will again see the harmonic oscillator frequency of HCl molecule.
6. To animate the vibrational motion, put a check in the box next to the frequency (or click on the peak in the spectrum). If you like, click on the  again and add the Experimental spectrum to the window. How well does the Hartree-Fock calculation reproduce the experimental IR spectrum? To stop the animation, click again on its frequency, or remove the check from the checkbox next to the vibration. Close the spectrum window.

**Note**

If the animated vibration is going too fast, the speed of the animation can be changed in the following way. Click on the  icon at the left of the spectrum display window. You will two editable buttons appear.




To slow down the animation, change the number of steps to a larger value (for example, 30).

Changing the Amplitude will alter the degree of displacement of the nuclei through the course of the vibration.

7. Back in the main window, under the **Geometry** menu choose **Measure Distance**, and find the H-Cl bond length by clicking on the two atoms (or by clicking on the bond between the two atoms). Look to the lower right corner of the screen to see the

bond distance. Record the bond length in your lab manual and compare the result with your experimental and literature data.

Click the  button to close your HCl file.

8. Make a new HCl molecule. Click the  to enter the View Mode. Click once on the chlorine atom to select it. Select **Properties** from the **Display** menu. An Atom Properties Box appears. Change the *Mass Number* from 35 to **37 (for $^{37}$Cl)**. Close the Atom Properties box. Return to the Setup Calculations box and make configure the calculation to be the same HF calculation you did on HCl (do not forget to check the IR option). Click on **Submit**. Save the file under a new name and let the calculation run.
9. Find the harmonic oscillator frequency and the bond length for $H^{37}Cl$. Select **File**, **Close** to close your molecule when you are done.

| **Data for HCl** | Calc. $\nu$ ($cm^{-1}$) | Exp. $\nu$ ($cm^{-1}$) (FTIR) | Cal. Bond Length (Å) | Exp. Bond Length (Å) (FTIR) |
|---|---|---|---|---|
| $H^{35}Cl$ | | | | |
| $H^{37}Cl$ | | | | |

10. Compare your results to those you obtained from the FTIR experiment done earlier in this course (specifically, for $H^{35}Cl$).
11. **Discussion Prompts:**
    What can you conclude about the accuracy of computing bond lengths and vibrational frequencies using this Hartree-Fock calculation?
    Why is the bond length identical for both $H^{35}Cl$ and $H^{37}Cl$?

---

## Comparison of Basis Sets

Try the same calculation with a different basis set (6.31-G* for example), and/or a completely different model (semi-empirical or density functional). Does the accuracy of the results change?

**Note**

This section of your lab notebook should include:

- A table summarizing the results of the $H^{35}Cl/H^{37}Cl$ calculations
- Comparison of computational results to your experimental FTIR data and literature data
- What can you conclude about the accuracy of computing bond lengths and vibrational frequencies using this Hartree-Fock calculation?
- Why is the bond length identical for both HCl and DCl?

(See your ELN template for details)

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# 17.5: Exercise 2 - Molecular Orbitals of Formaldehyde

**Exercise 2 - Molecular Orbitals of Formaldehyde**

This experiment explores the capability of Spartan® to calculate Molecular Orbitals and construct corresponding surfaces. The formaldehyde molecule is used as a model.

1. Click  to start a new file.
2. Build $H_2CO$. Select **Carbonyl** from the **Groups** menu and double-click in the working area. You may want to rotate the molecule on the screen for a better view.

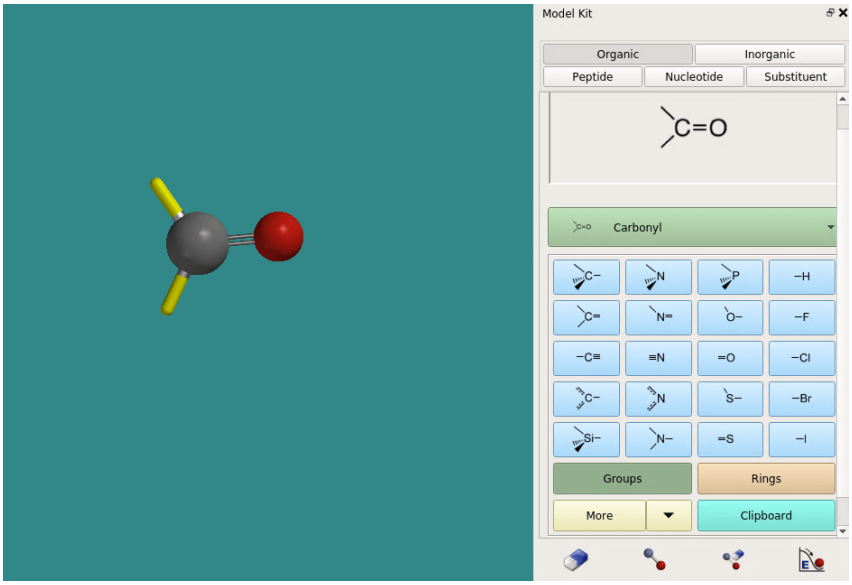



Figure 17.5.1: Building Formaldehyde. (CC-NC-BY-DUKE CHEM)

3. Click the  minimize button (lower right, below Clipboard).
4. Select **Setup, Calculations** from the menu. Choose **Equilibrium Geometry** at **Ground State** in **Gas,** *with* **Hartree-Fock, 6-31G***. *Total charge* should be **Neutral**, and *Unpaired Electrons* should be **0**. Click **OK**.
5. Choose **Submit** from the **Setup** menu. Click on the **OK** button. **Save** the file with the suggested filename, or choose one of your own.
6. Once the calculations have completed, determine the calculated equilibrium values for the C–O and C–H bond lengths, and for the ∠HCH and ∠HCO bond angles, by using **Geometry, Measure Distance/Measure Angle**. Record these values in your lab notebook. Compare your calculated values with literature values.

**Note**

The Computational Chemistry Comparison and Benchmark Database (CCCBDB) at NIST is one suggested place to look for this type of information. Choose an appropriate search string in your favorite web browser. For example: formaldehyde bond lengths and angles NIST. Look for the hit directing you to the CCCBDB site.

| | | | |
|---|---|---|---|
| **$H_2CO$** | C=O length | HCO angle | HCH angle |

| | Calc | Lit | Calc | Lit | Calc | Lit |
|---|---|---|---|---|---|---|
| | | | | | | |
| Reference | | | | | | |

7. Inspect the Output of this job using the  button. Find the **Molecular Orbital Energies** section under the **Summary** tab. Calculate the energy difference between the HOMO and LUMO and record this in your lab notebook.
8. Click the  button to see an abbreviated MO diagram on the left side of the screen. From here you can click on an orbital to view it on the molecule. In this way find and visualize the $\pi$-bonding MO in $H_2CO$. You can change the appearance of the orbital display by changing the **Style** from Solid to Mesh to Transparent, etc. (at the lower right corner of the screen).
9. In the same way, visualize the LUMO surface. How might you describe this molecular orbital?
10. Now visualize the HOMO. How might you describe this one? Take a look at some of the other orbitals and record any other interesting observations (with images) in your lab notebook.

**Note**

Not every MO is shown in the diagram generated by clicking the  button. You can calculate the surface for any desired MO by clicking the  button, and *More Surfaces*. Then, from the *Surface* dropdown menu select **HOMO{-},N** or **LUMO{+},N**, where *N* is how many orbitals above the LUMO or below the HOMO needed to get to the orbital you wish to see. Click on **Apply**, and then **OK**. Put a check mark in the box next to the selected orbital and then return to the Spartan window to see the result.

**Note**

This section of your lab notebook should include:

- A table recording your calculated bond lengths and angles for formaldehyde and a comparison to literature values
- Calculation of the energy difference between the HOMO and the LUMO
- Images and descriptions of the HOMO, LUMO, and any other interesting orbitals of your choice.

(See your ELN template for details)

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# 17.6: Exercise 3 - Modeling Sulfur Dioxide - Comparing the Results of Different Basis Sets and Calculation Models

**Exercise 3 - Modeling Sulfur Dioxide: Comparing the Results of Different Basis Sets and Calculation Models**

This experiment is designed to explore the performance of various basis sets, models of *Ab initio* calculations and *Semi Empirical* calculations, and *Density Functional* calculations. The $SO_2$ molecule is used as a model.

1. Start a New Build.
2. To introduce you to another approach to building a molecule, select the **Inorganic** tab of the builder.
3. Build $SO_2$ as follows: Change the element to sulfur.

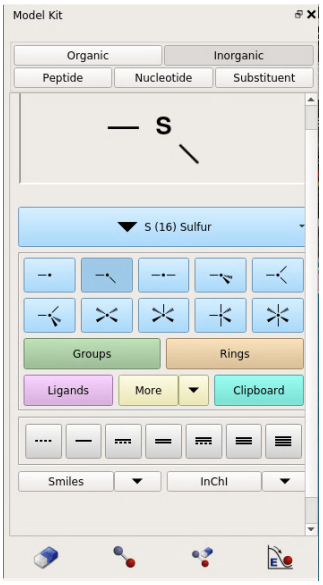
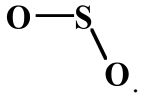



Figure 17.6.1: Selecting the Element Sulfur From the Inorganic Area of the Builder. (CC-NC-BY-DUKE CHEM)

Select  atom hybridization. Double-click in the working area. Rotate the molecule to make all the bonds visible. Select **O** from the periodic table  and Select  atom hybridization. Click at the ends of the bonds to **S** to make



Select double bond  from the Bond Order buttons and double-click on both **S–O** bonds. Be sure they have changed to double bonds.

4. Click the  button to do a quick molecular mechanics minimization of the energy.
5. Select **Setup, Calculations** from the menu. Choose *calculate*: **Equilibrium Geometry** *with* **Hartree-Fock, 6-31G***. *Total charge* should be **Neutral**, and *Unpaired Electrons* should be **0**. Select *compute:* **IR**. Click submit. Save the file when prompted and run the calculation.
6. From the **Summary** section of the **Output** (**Display** menu), record the energy of the molecule in your lab notebook. Record the frequencies of the $SO_2$ vibrations from the **Raman/IR Table** section of the Output Summary in your lab notebook.
7. Go to the **Display Spectra** area and view the calculated IR spectrum as you did for HCl and DCl. Animate the vibrations by

highlighting the different frequencies. Assign frequencies as 'symmetric stretch', 'bend', or 'asymmetric stretch'.
8. Close the spectrum window.
9. Measure and record the **O–S–O** angle and the **S–O** bond length.
10. Return to the calculation setup window and repeat the HF calculation with a 3-21G basis set.
11. Submit the calculation. Record and compare your results for frequencies, bond length, and the angle with the previous calculation.
12. Repeat again using the **STO3G** basis set, the Semi-Empirical theories **PM3**, **RM1**, and **AM1,** and the Density Functional theory $\omega$B97X-D with 6-31G* basis set. It might be a good idea to **Save as** each time to save each calculation in a separate file. Or if not, at least save a new file for each calculation model (HF, Semi-Empirical, Density Functional.

**Note**

If you do not save each calculation under a new filename, the new calculation overwrites the old in the current file.

13. Fill out the table of **Theories** and **Basis sets** for each combination.
14. Compare your results with your experimental (FTIR) data for $SO_2$ (CHEM 310 only), and literature data for frequencies, bond length and bond angle. Which combination of theory and basis set gives the most accurate prediction? Close your molecule.

**Note**

The NIST CCCBDB database is a good source for literature values for the $SO_2$ molecule (click here).

| **Table for $SO_2$** | Theory | Basis set | S–O bond length(Å) | Bond Angle, (°) | $nu1$ | $nu2$ | $nu3$ |
|---|---|---|---|---|---|---|---|
| Ab initio | HF | STO-3G | | | | | |
| | HF | 3-21G | | | | | |
| | HF | 6-31G* | | | | | |
| Semi-empirical | PM3 | N/A | | | | | |
| | RM1 | N/A | | | | | |
| | AM1 | N/A | | | | | |
| Density Functional | $\omega$B97X-D, 6-31G* | | | | | | |
| Your exptl. data | | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Literature data* | | | | | | | |
| * Reference | | | | | | | |

**Note**

This section of your lab notebook should include:

- A table that records, for each basis set:
  - Calculated energy of $SO_2$
  - Frequencies of $SO_2$ oscillations
    - Assign each frequency 'symmetric stretch', 'bend', or 'asymmetric stretch'. You only have to do this for one basis set.
  - S-O bond length
  - O-S-O bond angle
- Comparison of calculated results to experimental (CHEM 310 only) and literature values
- Which combination of theory and basis set gives the most accurate prediction?

(See your ELN template for details)

This page titled 17.6: Exercise 3 - Modeling Sulfur Dioxide - Comparing the Results of Different Basis Sets and Calculation Models is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

# 17.7: Exercise 4 - Modeling the Absorption Spectrum of Cyanine Dyes

This experiment is designed to build and study the series of conjugated dyes used in the UV-Vis experiment earlier in the course. For reference, the substitution number of napthalene is shown in the figure below (from Wikipedia).

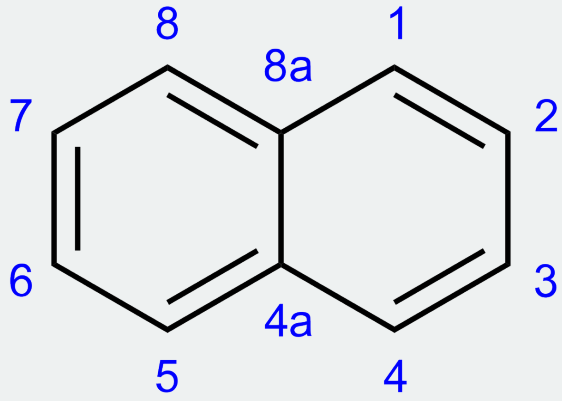
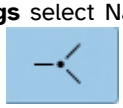



Figure 17.7.1: Numbering of the carbon atoms in naphthalene molecules according to latest (2013) IUPAC rules P-25.3.2.3 and P-25.3.3.1, which is the same as 1979 rule A-22. (By User:Edgar181 - Own work, Public Domain, https://commons.wikimedia.org/w/inde...curid=22671537)

1. The first dye you will build and work with is the 1,1'-diethyl-4,4'-carbocyanine cation. (See Figure 3.2.2 in Experiment 1). Start a new file. Select the **Inorganic** tab of the Builder. Under **Rings** select N**aphthalene**. Click in the workspace to place a naphthalene ring on the screen. Now select the $sp^2$ hybridization  option and check to see that the element in the element selection button is Carbon. Move to the working area and add three $sp^2$ carbons to the 1-position of the naphthylene ring. At this point your structure should look something like this.

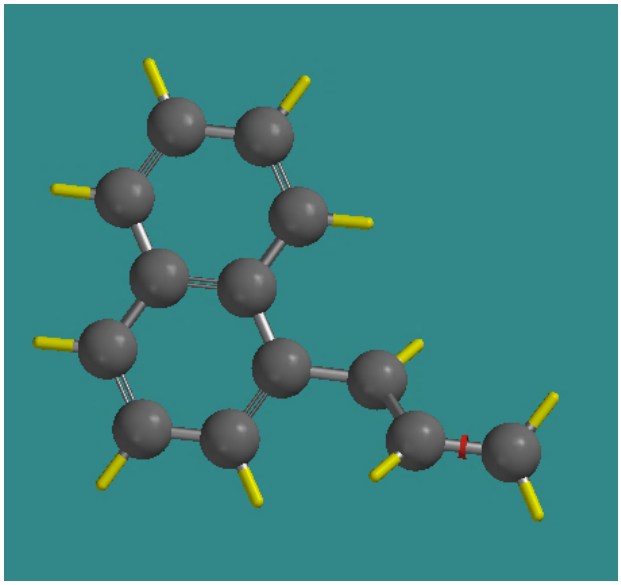
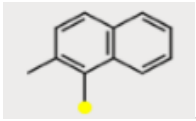


Figure 17.7.1: Adding $sp^2$ Carbons to the Naphthalene Ring. (CC-NC-BY-DUKE CHEM)

Return to the **Naphthalene** selection under **Rings** again. Notice the small yellow circle on the structure in the **Rings** window

. This indicates the “active” valence of the naphthyl group. Make the 1-position of naphthyl active by clicking on the valence in the small structure window. Click on the free valence of the 3$^{rd}$ carbon atom in the working area, to add the second ring to your structure. At this point it might look something like this.

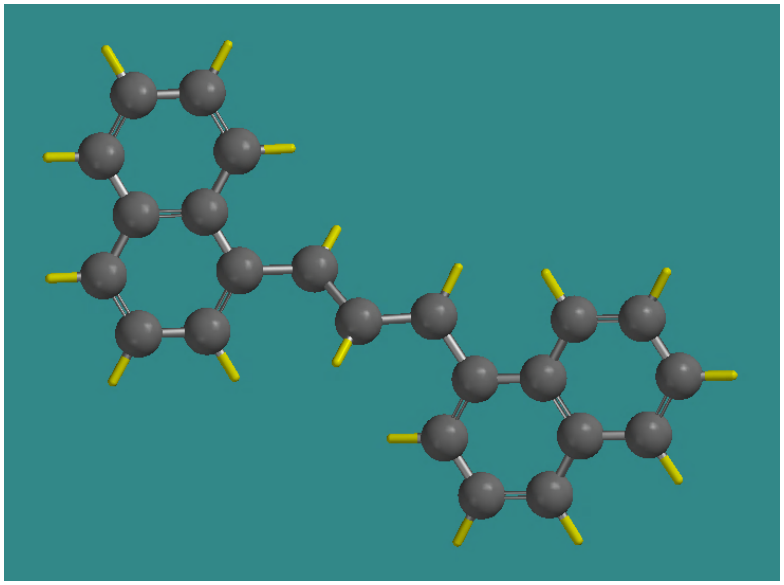


Figure 17.7.2: Adding the Second Naphthalene Ring. (CC-NC-BY-DUKE CHEM)

Now click on the delocalized bond . Double click on each C–C bond connecting the three carbons to each other and to the two rings. Look closely to be sure that all C–C bonds are delocalized.

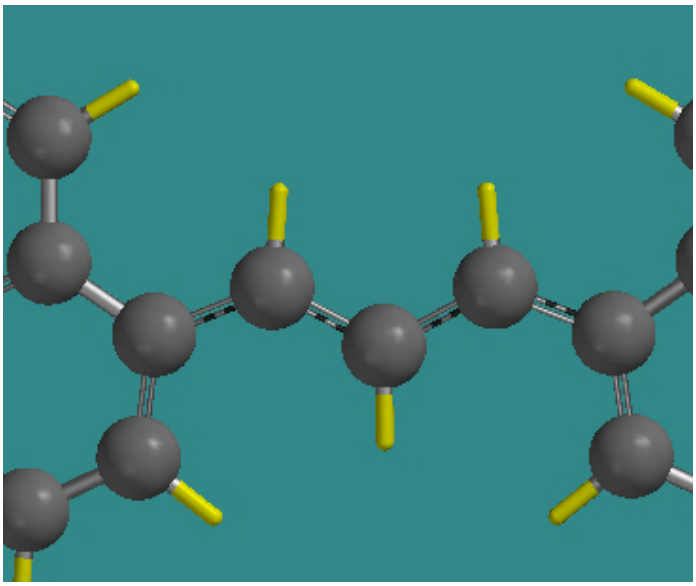


Figure 17.7.3: Changing the Bond Order of the Connecting Carbons. (CC-NC-BY-DUKE CHEM)

Click on the  button to minimize the structure. Chances are good that not all of the connecting carbons between the rings are in the trans- orientation, and that the overall structure is not yet planar. You can rotate around specific bonds to alter the conformation of the molecule. To do this, click on a bond you wish to rotate around. A red arrow appears, wrapping around the bond.

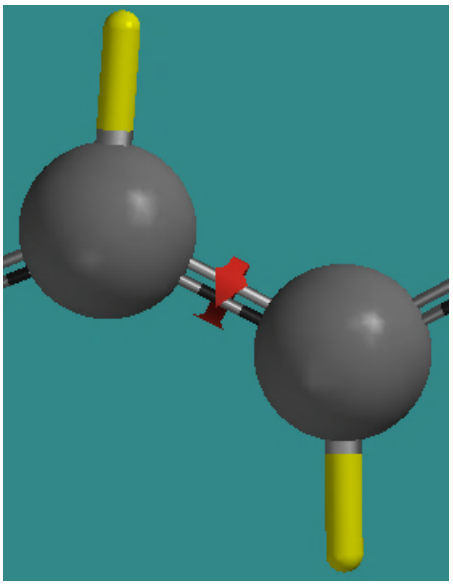


Figure 17.7.4: The Rotate Fragment Arrow. (CC-NC-BY-DUKE CHEM)

Hold down both the control and shift keys and click and drag the left mouse button to rotate a fragment of the molecule around the selected bond. In this way put all of the connecting carbons into the trans-orientation, and position the rings so that they point up and outward away from each other. Click again on the  button to minimize the structure. It should now be planar and look like this.

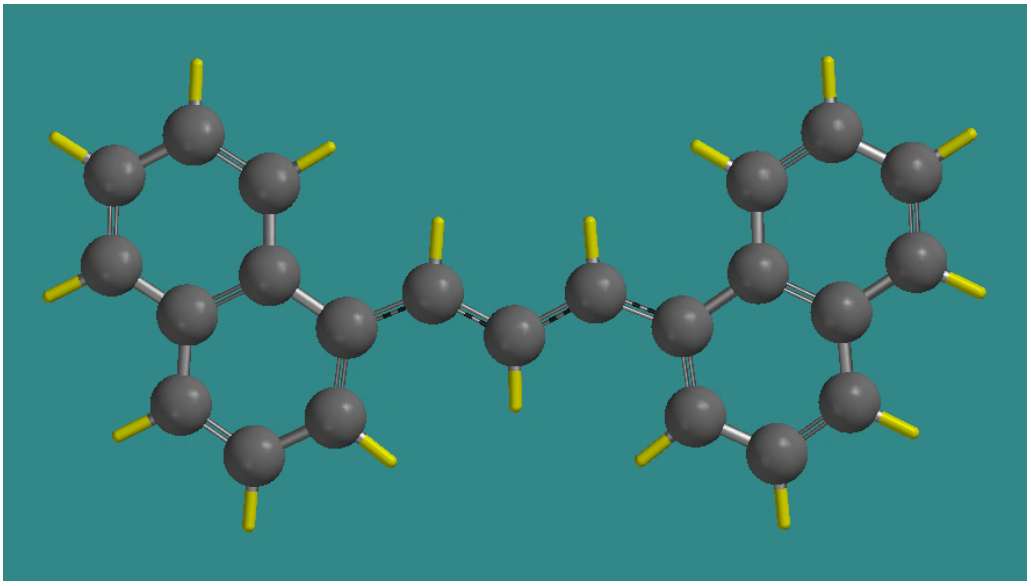


Figure 17.7.5: The Nearly Completed Structure. (CC-NC-BY-DUKE CHEM)

Return to the element section button and choose Nitrogen. Double-click on the carbon atoms of the naphthalene rings that are para- (across from, and in position 4) to the connecting three-carbon chain (look ahead to Figure 17.7.6). The color of the atom should change to blue as the element changes from carbon to nitrogen. Change the element selection button back to Carbon, and change the hybridization to $sp^3$ . Add ethyl groups to the free valence of the nitrogen atoms. **Minimize** the structure using . Check your structure. Is it planar? The final molecule should look something like this (rotated some to show the planar nature).

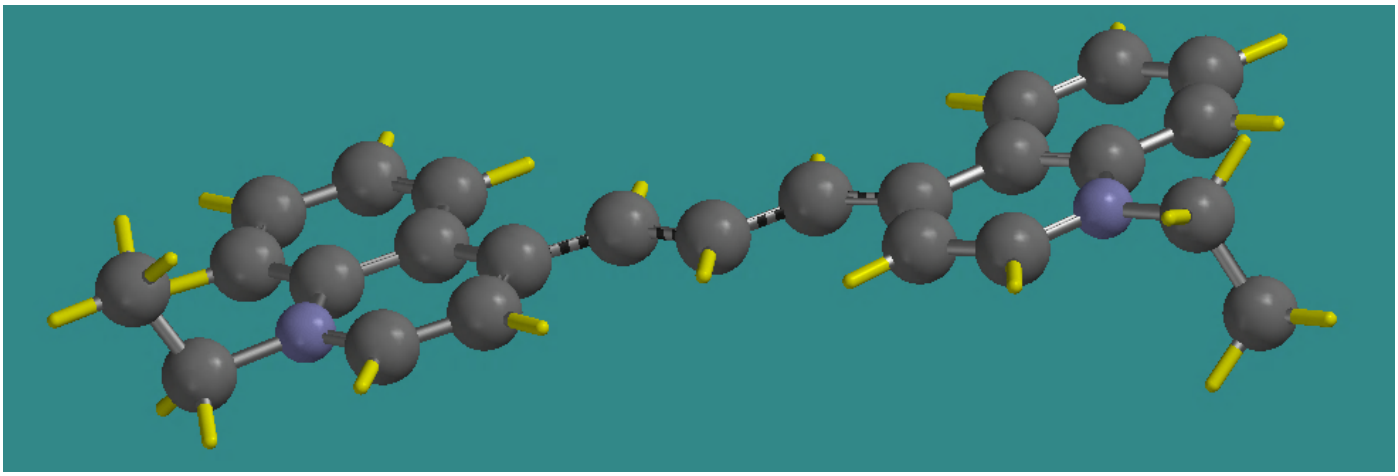


Figure 17.7.6: The Completed Structure. (CC-NC-BY-DUKE CHEM)

Notice in this picture that the ethyl groups are positioned axial to the plane of the rings. **Save** this molecule as dye4.

2. At this point you might see that it take more work to build a larger molecule. It might be prudent, therefore to keep the dye4 file safe, just in case something happens and you need to recall it. To do so, select **Save as** from the **File** menu and save the file as **dye4_MNDO.** Select **Setup, Calculations** from the menu. Choose *calculate*: **Equilibrium Geometry** *at* **Ground State** *in* **Gas** *with* **Semi-Empirical, MNDO**. Set *Total charge* : **Cation**, *Unpaired Electrons*: **0**. Click **Submit**.

3. Once the calculation is finished, inspect the molecule. Did the conformation change? Inspect the **Output** and record the equilibrium geometry **Energy** from the **Summary** section in your lab notebook.

4. In preparation for the next calculation select **Save As** from the **File** menu and name the file **dye4-ci.** Then select **Setup**, **Calculations** again, and change the parameters to, *Calculate*: **Energy** *at* **Ground State** *in* **Gas** *with* **Semi-Empirical, MNDO**. Set *Total charge* : **Cation**, *Unpaired Electrons*: **0**. In the *Options* box: type **CI PRINTLEV=2**. Click **OK**.

*Make sure the above is correctly entered: note Energy instead of Equilibrium Geomentry*

5. **Submit** the calculation.

6. Inspect the **Output** when the calculation is finished. From the **Output** tab, look for the table of **Spin Allowed Singlet Excitations** (immediately below the very long list of Slater Determinants) find the wavelength (in nm) and energy (in eV) of the first transition (it should have a large oscillator strength, OS). Record these values in your lab notebook.

7. Compare your computational results with your experimental and theoretical data generated in the previous "wet lab" dye experiment. Repeat steps 2-6 on dye4 using **AM1** and **PM3** models.

| Dye 4 | E, kcal/mol<br><br>(from the Equilibrium Geometry calculation) | Energy of transition (eV) | $\lambda_{max}$ (nm) |
|---|---|---|---|
| MNDO | | | |
| AM1 | | | |
| PM3 | | | |
| For Comparison: $\lambda_{max}$ from Expt 1 = | | | |

## Things to Think About

- **A Change in Conformation Leads to a Change in Calculated $\lambda_{max}$:** You might have noticed during Exercise 3 with $SO_2$ that with each change in calculation theory (HF, Semi-Empirical, Density Functional) and with each basis set within a given theory, the calculated bond lengths, bond angles, and frequencies of vibration changed. In the same way in this current exercise with the dyes, if you look closely you will see that changing the approximations within the Semi-Empirical calculation (MNDO, PM3, AM1) each lead to slightly different conformations of the molecule. As the result, the predicted value of both the Energy and $\lambda_{max}$ changes.
- **Seeing Trends in the Calculated Results, and that $\lambda_{max}$ Changes with Conformation is Likely More Important than Seeing if the Calculation Gave the "Right" $\lambda_{max}$:** It would be nice if your calculation could give a calculated $\lambda_{max}$ in complete agreement with what you saw for the dye when you did the UV-Vis spectrum in Experiment 1. But thinking about it, there are good reasons why it would not be expected to. For one, your calculation is for a single molecule in the gas phase. In Experiment 1 you measured the spectrum of a large number of molecules in solution in methanol. Indeed, one would expect the results to be different. Does that mean that the calculation is of little value?
- **Thinking about This**: Explain why the actual UV-Vis spectrum of the dye in Experiment 1 had such broad peaks. (Perhaps this understanding, coming from the results of these calculations, is more important than seeing if the calculation gave the "right" $\lambda_{max}$.)

8. Look over the results from Dye 4. Which semi-empirical calculation (MNDO, AM1 or PM3) gave the best result when comparing $\lambda_{max}$ to your Experiment 1 result? Build the other three dyes. Perform that same semi-empirical calculation for each. Determine the energy of the equilibrium geometry, and the energy (in eV) and $\lambda_{max}$ of the spin allowed singlet excitation. Record the results.

| Semi-empirical Calculation did you used | | | | | |
|---|---|---|---|---|---|
| | Name | Equil. Geom. E, (kcal/mol) | Energy of transition (eV) | Calc. $\lambda_{max}$ (nm) | Exptl. $\lambda_{max}$ from Expt. 1 |
| Dye 1 | 1,1'-diethyl-2,2'-cyanine | | | | |
| Dye 2 | 1,1'-diethyl-2,2'-carbocyanine | | | | |
| Dye 3 | 1,1'-diethyl-2,2'-dicarbocyanine | | | | |
| Dye 4 | 1,1'-diethyl-4,4'-carbocyanine | | | | |

9. What can you conclude at the end of this exercise? Do you see the expected trend in $\lambda_{max}$ as a function of the conjugation length of the connecting carbons between the cyanine rings? Does this more sophisticated calculation give more accurate results in terms of predicting $\lambda_{max}$ for the series of dyes as compared to the theoretical, model-based values you calculated in the first dye experiment? Looking only at Dye 4, which you might recall from Experiment 1 did not show the expected increase in $\lambda_{max}$ even though the conjugation length was greater than Dye 3, did the semi-empirical calculation do a better job of accurately predicting the change in $\lambda_{max}$ as you move from Dye 3 to Dye 4?

## Note

This section of your lab notebook should include:

- A table recording, for each dye:
  - Equilibrium geometry energy

    - Energy of the first spin-allowed singlet transition
    - Wavelength of the first spin-allowed singlet transition
- Comparison of computational $\lambda_{max}$ to experimental $\lambda_{max}$ and theoretical $\lambda_{max}$ from the previous dye experiment
- Which semi-empirical calculation gave the most accurate result?
- Do you see the expected trend in $\lambda_{max}$ as a function of the conjugation length of the connecting carbons between the cyanine rings?
- Does this more sophisticated calculation give more accurate results in terms of predicting $\lambda_{max}$ for the series of dyes as compared to the theoretical, model-based values you calculated in the first dye experiment?
- Looking only at Dye 4, which you might recall from Experiment 1 did not show the expected increase in $\lambda_{max}$ even though the conjugation length was greater than Dye 3, did the semi-empirical calculation do a better job of accurately predicting the change in $\lambda_{max}$ as you move from Dye 3 to Dye 4?

(See your ELN template for details)

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# 17.8: Exercise 5 - Modeling an Intramolecular Rearrangement

This exercise is designed to calculate the transition state of the thermal conversion of vinyl alcohol to acetaldehyde using a semi-empirical calculation method. Along the way it will show you how you can model a chemical reaction (in this case an intramolecular rearrangement), and using spreadsheet functionality and graphing to create a reaction profile.

1. Start a new file. Build vinyl alcohol. In the Organic tab, use  to construct the carbon skeleton. Select the  oxygen and click on one of the free valences on the vinyl skeleton. If needed rotate the CO bond into the cis-configuration (i.e., bringing the alcohol hydrogen into position over the C=C double bond). Minimize the structure using .

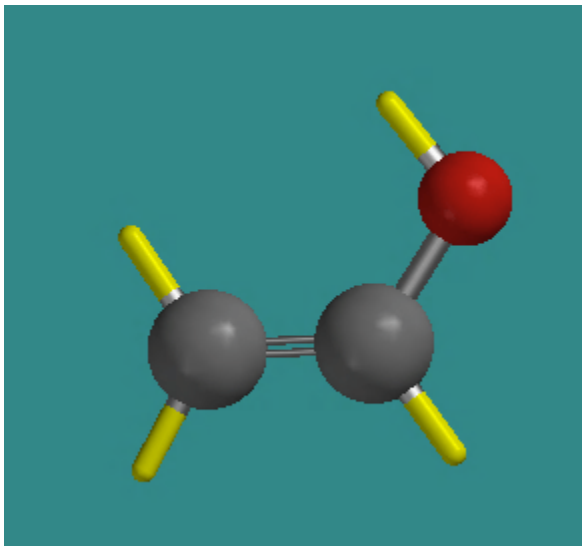


Figure 17.8.1: Vinyl Alcohol. (CC-NC-BY-DUKE CHEM)

2. Setup the following calculation: **Equilibrium Geometry** *from* **Ground State** *in* **Water**, *with* **Semi-Empirical, AM1**. *Total charge*: **Neutral**, *Unpaired Electrons* : **0**. Click **Submit**. Save the file as vinyl alcohol, and let the calculation run
3. When it has finished, go the Summary tab of the Output and record the **Energy** in kJ/mol in your lab notebook.
4. Select **Save As** from the File menu and create a copy of this molecule under the name, **vinyl alcohol_ts**. Select **Guess Transition State** from the **Build** menu.
5. Click on the C=C bond and then the C-O bond. Next, click on the O-H bond and, while holding down the SHIFT key, click on the O-H hydrogen to be transferred and then on the carbon atom to receive this hydrogen. Another electron-pushing arrow should appear along with a faint blue dotted line between the O-H hydrogen and the carbon. It should look like this.

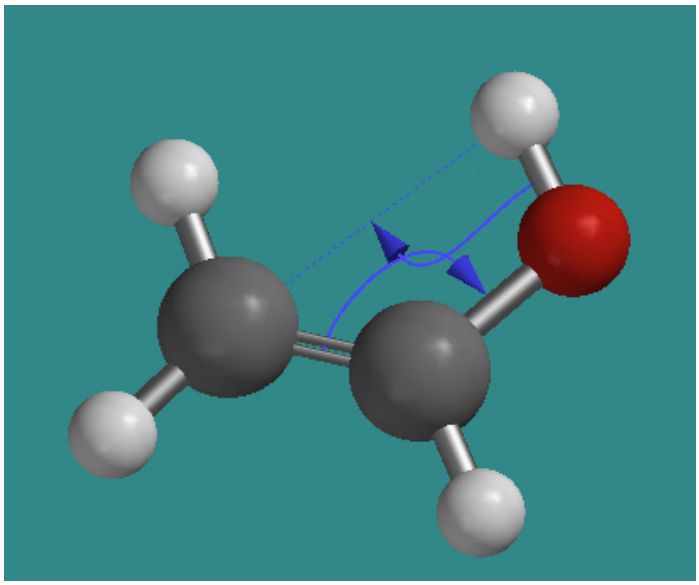


Figure 17.8.2: Building the Transition State Query. (CC-NC-BY-DUKE CHEM)

6. Click on the  button at the lower right of the screen. In a few seconds your initial structure will be replaced by a calculated transition state structure. There should be a name (1_3-H-Shift_ethenol_AM1.ts (Exact)) at the lower right corner of the screen, and the structure should look like this.

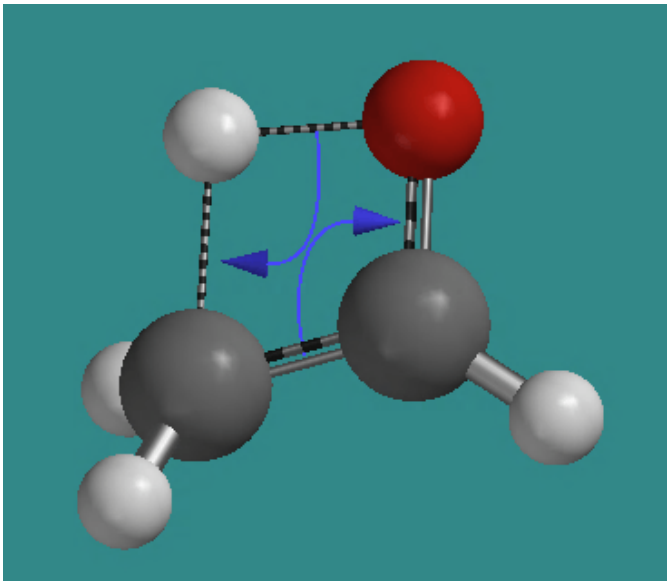
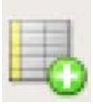


Figure 17.8.3: The Guessed Transition State. (CC-NC-BY-DUKE CHEM)

7. Setup the following calculation: *Calculate* **Transition State Geometry** with **Semi-empirical** *with* **AM1** *in* **Water.** *Charge* should be **Neutral**; *Unpaired Electrons*, **0**; *compute*: **IR. Submit** the job.
8. When it has finished, examine the geometry of the transition state using the **Geometry** functions (bond lengths and angles). Go to **Display, Output** and record the energy of the transition state structure.
9. Select Spectra under the Display menu. Use the  and  to display the calculated IR and frequency table.

Animate the vibrational mode corresponding to the “imaginary” (i) frequency. You might click the  button and change the Steps to 30 to slow down the animation.

## The Imaginary (i) Vibration

The idea is this: By now I am sure you are familiar with a potential energy well showing how the energy of a bond varies as a function of internuclear distance. The minimum of this well represents the equilibrium bond length. Additionally, you know that the tie-lines across this potential well represent vibrational modes of the bond. Now a similar tie line across the potential energy curve of a reaction profile, near where the maximum in the curve represents the transition state of the molecule. We can imagine, and calculate a value for, such a vibrational mode associated with this idea. This calculated "imaginary" vibration is typically denoted with an i, and models the dynamics of the molecule as it traverses over the top of the activation energy barrier through the transition state structure.

Notice in the animation that the C=C double bond lengthens as the hydrogen moves toward the carbon, and that the carbon accepting this hydrogen shifts from $sp^2$ toward $sp^3$ geometry. Notice also that the C-O bond shortens with the hydride shift as it starts to become a C=O bond. And also that the forming carbonyl carbon shows the shift from $sp^3$ to $sp^2$ geometry. That is, this one calculated imaginary vibration shows the structural changes in the transition state and across the top of the activation energy barrier in a reaction profile. Stop the animation and close the Spectrum window.

10. Build acetaldehyde as a **New** file. Set up the same **Equilibrium Geometry** calculation as you did for vinyl alcohol (**Semi-empirical, AM1, Water**). Save the file and **Submit** the calculation. Record the energy as you did for vinyl alcohol and the transition state. Close your molecule.

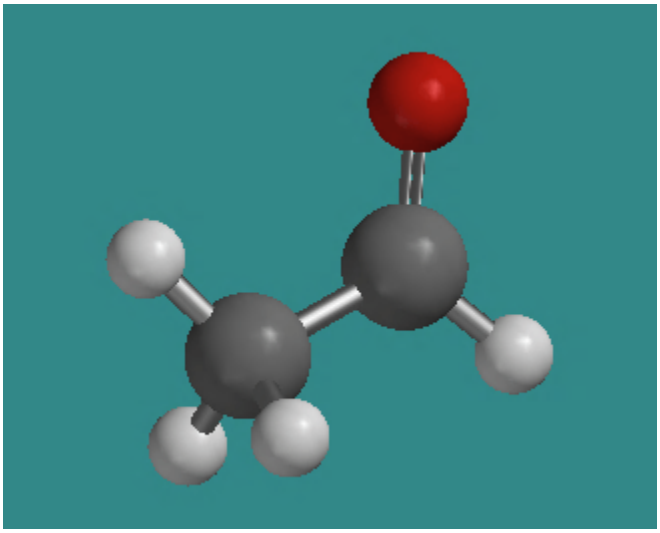


Figure 17.8.4: Acetaldehyde. (CC-NC-BY-DUKE CHEM)

Creating the Reaction Profile:

11. Open your vinyl alcohol molecule made and optimized in steps 4.8.1-4.8.2. From the **File** menu, select **Save-as** and save the file as Reaction Profile. Select **Spreadsheet** from the **Display** menu. A spreadsheet appears on the screen with one entry. This entry is your vinyl alcohol molecule. Double-click on the M001 entry and change the name to Vinyl Alcohol.

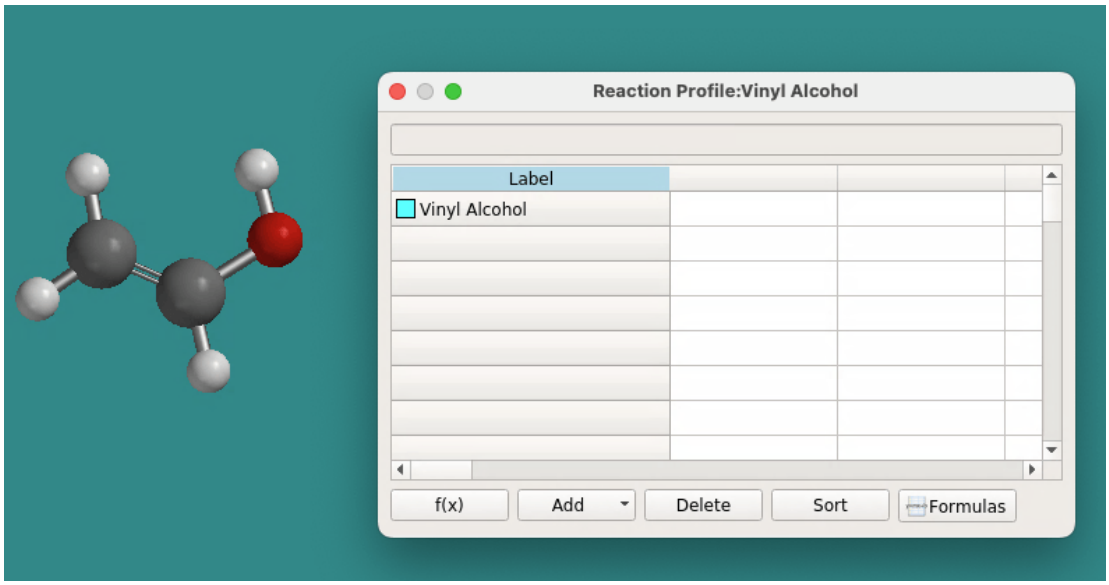



Figure 17.8.5: Adding Molecules to a Spreasheet. (CC-NC-BY-DUKE CHEM)

12. Now open the transition state molecule created and optimized in steps 4.8.4-4.8.7 above. Notice that this molecule opens in its own window (you can see the tabs at the lower left of the Spartan screen). Use **Select All** from the **File** menu to highlight the molecule (or right click on the molecule and select all). Use **Copy** from the **File** menu (or right mouse click – **Copy**) to copy the molecule to the Spartan clipboard. Return to the vinyl alcohol/spreadsheet screen by clicking on its tab. Click once on the cell immediately under the vinyl alcohol entry. Right-click *on that same cell* and paste the transition state into the spreadsheet. Change the name to Transition State.
13. Open and paste your acetaldehyde molecule into the third spreadsheet cell. At this point your spreadsheet will look like this.

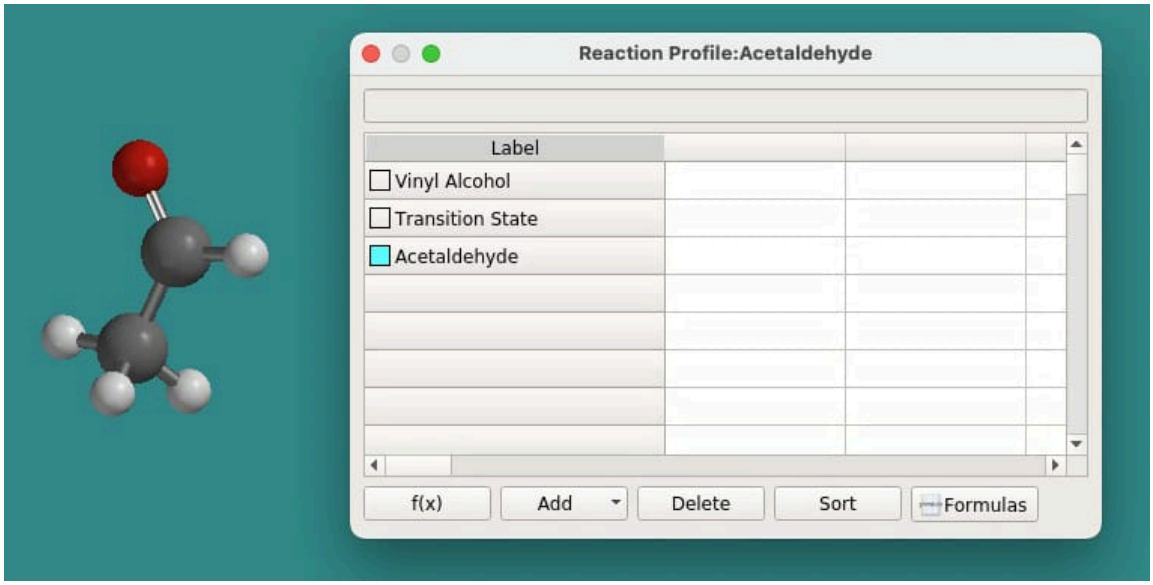



Figure 17.8.6: The Three Molecules in the Spreadsheet. (CC-NC-BY-DUKE CHEM)

14. Open the **Setup Calculations** box for each of the three molecules in the spreadsheet and confirm that the desired calculation is correct for each. If it is not, correct them. It should be Equilibrium Geometry in water, with semi-empirical, AM1 for vinyl alcohol and acetaldehyde; and, Transition State Geometry in water with AM1 for transition state molecule. Click **OK** (not Submit) to close the Setup Calculations box each time.
15. Click the **Add** button in the spreadsheet window. Select **Energy (kJ/mol)** from the list of choices. Click **OK**. You will notice a new Energy column appear in the spreadsheet, with Pending next to each molecule.
16. Return to the **Setup Calculations** box. Click **Submit**. The calculations will run and when complete the spreadsheet will show the aqueous energies for all three entries.

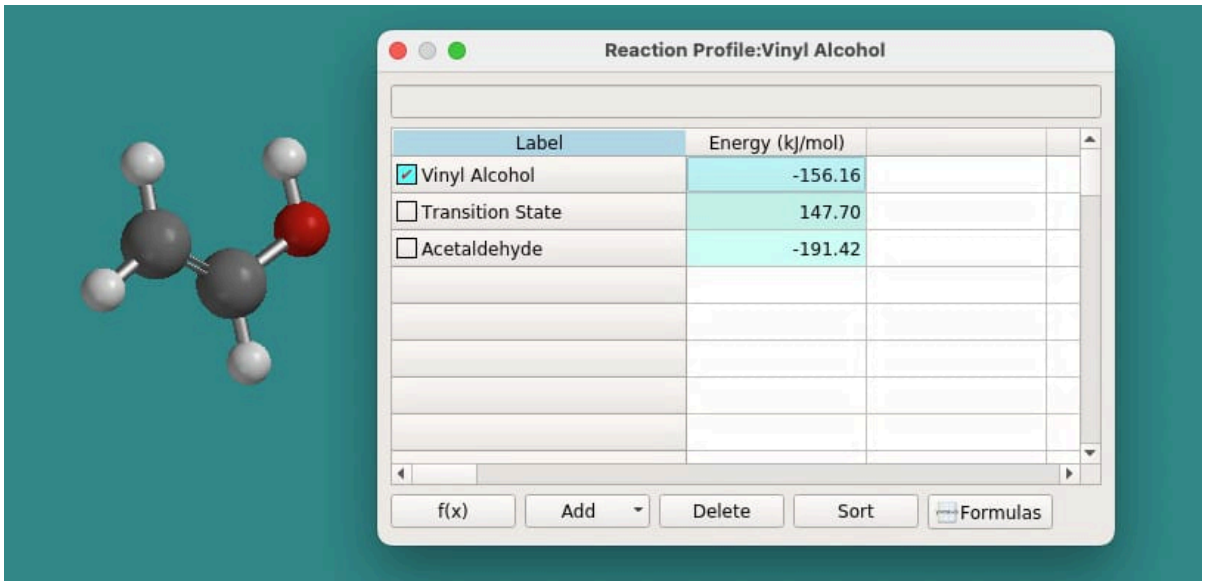
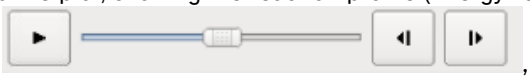



Figure 17.8.7: The Completed Calculations. (CC-NC-BY-DUKE CHEM)

17. Select Plots from the Display menu. Click on the  button and highlight Energy in the window that appears. Click Create. A plot appears in a window to the right of the molecule screen. Click  and select Smooth from the Curve options. Add a Title, and click Done. Click , and the plot, showing the reaction profile (Energy vs molecule) will move to the main screen. You can use the Animation bar, , to step through the profile, showing the structure at each point in the process. Record images of the reaction profile in your lab notebook. Use the energy values from the spreadsheet to calculate the activation energy and $\Delta H$ for the reaction.

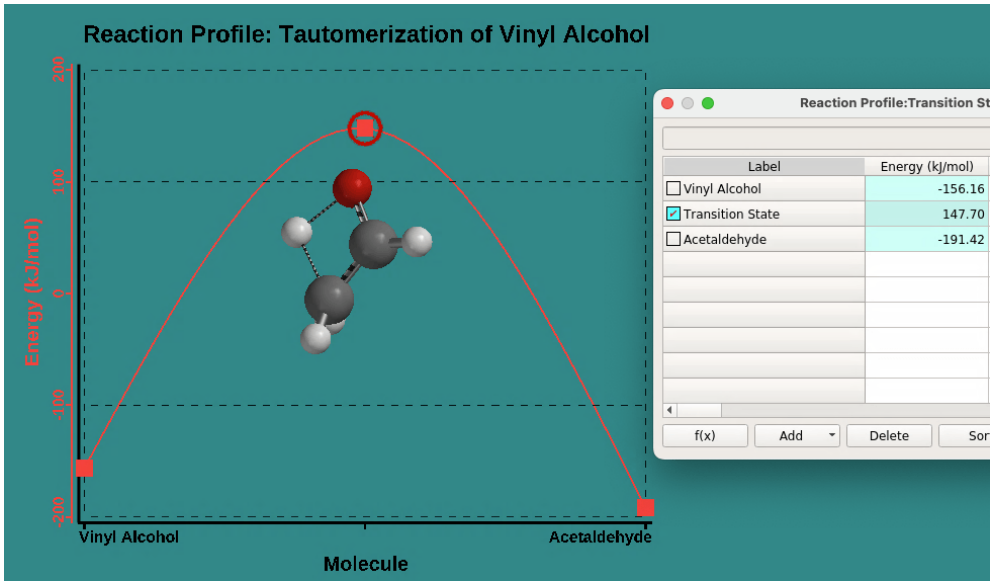



Figure 17.8.8: The Reaction Profile. (CC-NC-BY-DUKE CHEM)

Note

This section of your lab notebook should include:

- The equilibrium geometries energies of the initial, transition, and final states
- Images of all reaction profile plots
- Calculation of the activation energy and $\Delta H$ of the tautomerization reaction

(See your ELN template for details)

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## S

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