CHEM310L - PHYSICAL CHEMISTRY I LAB MANUAL



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CHEM310L

Physical Chemistry Laboratory

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Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Orientation to this course

1.1: Pre-Semester Assignment

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1.6: Lab Performance and Professionalism

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1.1: Pre-Semester Assignment

Please complete the following.

Plan at least three or four hours in the week prior to classes to complete this assignment.

1. Log into Duke's Canvas platform and familiarize yourself with this course's Canvas site.
2. Read the entire orientation module in this manual.
3. Read the Duke Chemistry Safety Manual.
4. Find the syllabus, download it, and read the entire document carefully.
5. Complete the "Orientation Assignment" that is found at the end of the syllabus. Complete the assignment and submit it on Canvas prior to the first day of classes (FDOC).
6. Complete the Matlab Prelab assignment in the next module. It is summarized below:
    a. Download and install MatLab on your personal laptop computer. Duke students can get MatLab for free from Duke OIT.
    b. Complete the MatLab Basic Tutorials to become familiar with basic functions of the MatLab program.

Things to bring to the first lab meeting:

Please bring your working computer with MatLab installed with you to our first meeting.

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1.4: Assignment Details

Pre-Lab Assignments

To prepare for lab, you should do the following:

Wear Protective Clothing: As always, please dress appropriately for a laboratory environment. You must wear close-toes shoes and clothing must cover your body from your upper arms to your knees. You should also have your own pair of protective eyewear, bring them to lab, and wear them the entire time you are in lab. Safety eye wear can be purchased from the Graduate Chemistry Council (GCC). If lab attire is not jiving with your wardrobe, please purchase a lab coat and bring it with you so that you can cover up in lab. No student should be in lab without wearing protective eyewear and appropriate protective clothing.

Prepare by completing the Pre-Lab Assignment: It is absolutely essential that each student be prepared for lab meetings by reading the appropriate module in this manual, and completing the specified pre-laboratory assignments. The pre-laboratory assignments are designed to prepare you to operate efficiently and safely during the experimental module. You will not be allowed to conduct experiments if the pre-lab assignment is not completed before your lab meeting. If there is an extenuating circumstance that prevents your preparation, please inform your instructors as soon as possible.

The pre-lab assignment must be submitted as a single pdf document on Canvas at least 25 minutes before the scheduled lab meeting. Pre-lab assignments should be typ*ed*. If you prefer to write out equations by hand, they should be neat and inserted as an image in the appropriate place (please note that handwritten equations are only accepted for pre-lab assignments and ELNs, *but not for reports*). If you need advice for how to insert equations or images into your documents, please ask for help at least 48 hours before the assignment is due; an in-person (or zoom) meeting is most appropriate for this issue.

Late pre-laboratory work will not be accepted and will receive a score of zero. Your TA will evaluate the work and return it no later than the beginning of your lab section. Your preparedness will also be evaluated by your answers to oral questions pertaining to the laboratory from the TA and other lab instructors. The pre-lab and preparation accounts for 10 points of each experiment requiring a pre-lab.

For every experimental module there is a general pre-lab assignment and a specific pre-lab assignment.

General Pre-Lab Assignment (same for all modules)

Write a brief introduction to the experiment and the experimental plan using the following outline:

I. **Experiment Introduction:** In your own words, briefly describe the underlying theory and explain the principle upon which the experiment is based. Keep it concise; lengthy discussions or derivations of equations are unnecessary.
   a. Background (importance/relevance): A brief description and justification of the importance of the topic, *with references to source material*. What is the topic and why is it interesting and important? This is meant to "hook" the reader so they want to read about the topic.
   b. Theory: A concise paragraph or more describing the general theory for the method/technique used; this section should contain a reference to the appropriate pages of the textbook, or other source material from the literature.
   c. Goals/Purpose: Brief statement of purpose, which should indicate what is analyzed and the technique used. Limit to three to five sentences.

II. **Experimental Plan:** a short summary of the specific things that you would need to know in order to do the experiment without having access to your lab manual, with the understanding that you will always have a TA available to teach you how to use the instrument. The best way to approach this task is to thoroughly read the procedure for the experiment. While reading, take notes on the specifics of the work. What chemicals will you use? If you have to make solutions, what solutions do you need to make and of what concentration? How will you prepare them? What instrument will you use, and what specific instrument settings will you need to input (sometimes you will find this information in the Appendices that discuss the use of the instruments)? How many runs of each sample will you do; and over what wavelength, or temperature, etc. range? You do not need to write down how to use the instrument; we will teach you that. Bottom Line: we want you to write down only that pertinent information about samples, sample preparation, instrument and instrument parameters, numbers of runs, and other things, that you will need to know in order to do your work.

Specific Pre-Lab Assignment

Each module has a pre-lab assignment on the first page of the module. In general, each pre-lab assignment requires you read the entire module and write out the specified pre-lab assignments in your notebook before starting that laboratory work.

Electronic Laboratory Notebooks (ELNs)

Warning: Use cloud storage and backup

As you save your documents and develop systems of organizing your academic life, please learn to use a cloud server to automatically save and back up your work. Duke University supports cloud storage through Box and Microsoft tools. Google tools are also a free option. Proper use of these tools is expected. Please ask Dr. Haas if you need some instruction or recommendations for using these cloud-based tools to avoid loosing your work if/when computer hardware is lost or fails.

While we are aware that there are limited computer labs on campus, you also have access to computers also in the P-chem labs. Please plan to always complete your work 48 hours in advance so that any issues with your personal devices do not interfere with timely submission of assignments.

You will complete each experiment as a group, and there will be a dedicated instructor to answer questions. You will record observations using an electronic laboratory notebook (ELN); an example ELN template will be provided for each experimental module. The ELN will contain a written record of your group's activities during lab. Each student should collect a copy of the group data immediately after the lab meeting. Every P-chem lab computer has internet access, and you may either email data to yourself, save it using OneDrive, Google Drive, or Box, or collect it using a usb drive.

You will make the ELN your own by filling in your own work in the *Background*, *Theory*, and *Purpose* statements (from the pre-lab assignment). Edit these statements as necessary using the pre-lab assignment feedback from your instructor. The data collection should be done in your group. Then, do your own work to complete the questions and data analysis in the ELN. Your completed ELN must be submitted for grading before the end of the lab meeting. Extemtions may be given if extra time is needed to complete the data anaysis outside of the laboratory meeting. The maximum extension is up to the next scheduled meeting (~1 week). The pre-lab assignment accounts for 10 points, and the ELN accounts for 30 points for each experimental module.

Using the electronic laboratory notebook (ELN) template

Templates for each ELN will be provided as a guide to help you understand the minimum expectation for what should be recorded during the laboratory session. You should record all additional information and observations that you think is relevant. One member of the group should create a shared version of the ELN that will be used during the laboratory period, and in which all group members can contribute to the *Observations and Data* section. Then, each group member should make their own copy and complete the individual sections with their own work. ***To guard against the possibility of plagiarism, do not share an electronic copy of any ELN that contains your own work.***

There are three sections to each ELN: The "Observations and Data" section should be edited during lab while your group is working together. **The other sections must be written by you and should be *your own work*.**

Note

Before beginning any electronic laboratory notebook entry, track your changes. This way if you accidentally erase good data it can be retrieved afterwards. SAVE OFTEN when working outside the safety net of cloud-based autosave and backup.

- In Microsoft Word, select **Highlight Changes** from the Track Changes option under the Tools menu.
- In Google Docs, revision history is automatically saved as long as you are connected to the internet.

Pre-Lab section:

(Your own work) This is where you will copy/paste your own pre-lab work.

Observations and Data (Group data collection):

Record all observations and primary data as a group. This should include the actual procedure, instrument used, instrument tolerance (error), instrument settings, any notable observations, and all data collected during the lab period.

This section, in which you will have the same information as the rest of your group members, should contain only the information collected while in the laboratory. It should not contain your evaluation the data/observations in any way (that is the post-experiment work). If data are being collected by hand (handwritten on paper) it should be in clear, easy to read format. This handwritten data should be *immediately* entered into a shared ELN file. For data that are collected by a computer interface to your equipment, note the specific name of the data file in case you have to retrieve the file later! Take screen shots as necessary to capture important data to insert into the ELN. Write observations for each run, including "bad" or aborted runs, in a narrative style and state where the actual data file can be found (including filename) when needed.

Post-Experiment work:

(your own work)

Calculations of results and uncertainties: Unless otherwise instructed all calculations of results and uncertainties should be included as part of the laboratory notebook. In this course doing so will require the typing of a lot of mathematics. Please remember that you always have the option of writing your calculations out neatly on plain paper and scanning it to make a digital image that can be incorporated into an electronic notebook entry. Mathpix is recommended to help you convert equation images to Latex for insertion into typed documents (use the Free & Educational use option!).

Discussion of results: In this section you truly “think in the notebook”. Reflect on what you have done. Write this section in your own words after the observations are completed. Include charts, graphs (see below), tables or rearranged data and your rambling thoughts. Remember this is not a formal report. You want to be neat and complete, not necessarily a literary star. This section need not be long, but it should contain all pertinent information.

Graphs: Often you will generate graphs from your primary data files. They must be represented in this section of the laboratory notebook. It is not difficult to include digital copies of graphs within the electronic laboratory notebook, but you should remember that such images can easily make the file sizes large and thus difficult to work with. Below is a procedure that will work to include copies of your graphs in the notebook while minimizing the overall size of the resulting file. A reliable way to capture graphs/plots to insert into your lab notebook is to use WinSnap for PC (or screenshot on Mac). Each lab computer has WinSnap installed. You can take a screen shot by pressing SHIFT + COMMAND + S on the keyboard. This will allow you to select a region for capture and the image will be saved to the clipboard. Press CONTROL + V to paste. You can also open the WinSnap program from the desktop shortcut instead of using keyboard shortcuts. (SAVE OFTEN!)

Reports

In this course, ELN's that include answers to discussion questions (post-lab questions) are considered "reports" of your work.

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1.6: Lab Performance and Professionalism

A portion of the total available points for this course are allotted to your performance in lab. This includes an expectation for preparation before the lab period, arriving on time, using time effectively, performing the tasks well, contributing to the culture of safety, and helping to maintain a clean and safe environment. Your performance and professionalism in the lab is assessed through **Lab Citizenship points**.

🌟What does it mean to be a "Good Lab Citizen"?

Lab Citizenship refers to more than just following rules. It means self-regulating your behavior in a way that supports a safe, respectful, and productive lab environment—without needing constant reminders from instructors.

Your instructors are here to support your learning, not to act as the "lab police." We expect that you will take ownership of your space, your preparation, and your conduct. This includes not just compliance with safety policies, but also contributing positively to the shared environment, being considerate of others, and acting professionally.

Good Lab citizens:

- Arrive on time and ready to work
- Wear proper lab attire and PPE at all times without reminders
- Turn notifications off on electronic devices used during meetings
- Clean up after themselves and leave shared spaces better than they found them
- Use lab time effectively and help their group stay on track
- Label solutions, handle chemicals safely, and follow disposal protocols
- Respect the physical space, equipment, and people in the lab

When you do these things consistently, it frees your instructors to focus on helping you learn and grow as scientists — not on enforcing rules. Your Lab Citizenship grade score reflects your ability to self-regulate and contribute to a positive lab culture.

Lab Citizenship Checklist

Each Wet Lab session, you can earn 1 Lab Citizenship point by demonstrating professional, safe, and respectful lab conduct. This point is awarded as an “all-or-nothing” score based on the following expectations.

Daily Lab Citizenship Expectations (1 pt)
✔ **Arrived on time and stayed the full session**
✔ **Worked safely and efficiently; used time well***
✔ **Wore appropriate PPE and clothing without reminders**
✔ **Cleaned glassware, workspace, and instruments used**
✔ **Labeled all solutions and disposed of waste properly**
✔ **Maintained a respectful, team-oriented lab environment**

⚠️ Students **will not receive partial credit**—failure to meet any of these expectations may result in 0 points for the day.
*Distraction by electronic devices (messages, social media) during lab time is considered a violation of safety and using time well. You are advised to turn off notifications on electronic devices used during meetings.

Lab Citizenship Penalties

While Lab Citizenship is typically graded on a 1-point-per-session basis, certain behaviors may result in point deductions from your lab report score. These behaviors compromise safety, professionalism, or lab functionality and require stronger consequences.

Repeated or serious infractions will result in direct point deductions from your lab report grade for the corresponding module. The instructional team will notify you if a deduction has been applied and explain why. Some, but not all, examples are shown below:

Infraction	Deduction from Report Score
7—15 minutes late to lab	−5 points
16—20 minutes late to lab	−10 points
More than 20 minutes late	−15 points (not allowed to participate)
Failure to wear safety goggles (after first warning)	−5 points per occurrence
Improper lab clothing (after first warning)	−10 points per occurrence
Working while visibly ill without a face mask	−5 points per occurrence

⚠️ Repeated issues (e.g. forgetting goggles, being late, or poor cleanup) may also trigger **a conversation with the instructional team or department administrators** to resolve concerns and may result in failure of the course.

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CHAPTER OVERVIEW

3: Estimating and Reporting Experimental Error

Learning Objectives

After completing the readings and practice problems recommended in this module, you should be able to:

- Describe and give examples of the following types of error that effect physical measurements, and identify the types of errors that affect precision and those that affect accuracy.
  - Gross / personal error
  - Systematic error
  - Random error
  - Determinate error
  - Indeterminate error
- Describe strategies for optimizing the accuracy of physical measurements and evaluating the precision of physical measurements.
- Identify the sources of random error in a measurement.
- Propagate error using mathematics.
- Report values and their precision in the proper form (applying the rules of significant figures to correctly indicate precision).

3.1: Pre-lab Assignment
3.2: Characterizing Experimental Errors
3.3: Estimating and Reporting Error (Statistics, Propogation, and Rounding)
3.4: Least Squares Linear Regression
3.5: Rejection of Outliers (Q-test)
3.6: Guidelines for Recording and Reporting Data in your ELN
3.7: Homework Problems
3.8: References and Additional Reading

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3.1: Pre-lab Assignment

Pre-lab assignment

In preparation for the lab meeting on Error Analysis, please do the following*:

- Read this entire module
- **Read D.P. Shoemaker, C.W. Garland and J.W. Nibler, Experiments in Physical Chemistry, 6th Ed., McGraw Hill Co. Inc., New York, 1996, Chapter 2.**
- Attempt (does not mean you must complete) all seven problems in the last section of this module; work should be done in a way that you can track your progress and submit your work in the form of a pdf. Submit all attempts in writing 24 hours prior to your scheduled laboratory meeting.

Note that the textbooks referenced in this module are available in the Perkins library, and on Canvas in pdf format (or Duke students click here).
We will meet in a classroom, thus lab attire is not necessary for this session.

*In addition to the general pre-lab assignment (linked below as a reminder), please do the above tasks. **For this particular assignment, an experimental plan is unnecessary**. However, it is good practice to reflect on the purpose of this assignment, so please **do write a background/purpose statement**. You should submit a pdf of your work on Canvas before the deadline (24 hours prior to the lab meeting).

For our overachievers and those who want more, recommended additional reading includes: D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, Analytical Chemistry: An Introduction, 7th Ed., Saunders College Publishing, New York, 2000, Chapters 5-7.

Click here to review the general expectation for Pre-Lab Preparation Assignments.

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3.2: Characterizing Experimental Errors

In this course, you will need to determine the confidence in your results by doing appropriate error analysis. This section and the next are meant to review the types of experimental errors that affect accuracy and precision and to remind you of the simple methods for propagating error.

Errors That Affect Accuracy

Accuracy is how close a measure of central tendency is to its expected value, μ. We express accuracy either as an absolute error, e

$$e = \overline{X} - \mu \tag{3.2.1}$$

or as a percent relative error, %e

$$\%e = \frac{\overline{X} - \mu}{\mu} \times 100 \tag{3.2.2}$$

Although Equation 3.2.1 and Equation 3.2.2 use the mean as the measure of central tendency, we also can use the median.

> The convention for representing a statistical parameter is to use a Roman letter for a value calculated from experimental data, and a Greek letter for its corresponding expected value. For example, the experimentally determined mean is $\overline{X}$ and its underlying expected value is μ. Likewise, the experimental standard deviation is s and the underlying expected value is σ.

We identify as determinate an error that affects the accuracy of an analysis. Each source of a ***determinate error*** has a specific magnitude and sign. Some sources of determinate error are positive and others are negative, and some are larger in magnitude and others are smaller in magnitude. The cumulative effect of these determinate errors is a net positive or negative error in accuracy.

> It is possible, although unlikely, that the positive and negative determinate errors will offset each other, producing a result with no net error in accuracy.

We assign determinate errors into four categories—sampling errors, method errors, measurement errors, and personal errors—each of which we consider in this section.

Sampling Errors

A determinate sampling error occurs when our sampling strategy does not provide a us with a representative sample. For example, if we monitor the environmental quality of a lake by sampling from a single site near a point source of pollution, such as an outlet for industrial effluent, then our results will be misleading. To determine the mass of a U. S. penny, our strategy for selecting pennies must ensure that we do not include pennies from other countries.

> An awareness of potential sampling errors especially is important when we work with heterogeneous materials. Strategies for obtaining representative samples are covered in Chapter 5 of Harvey's Analytical Chemistry text on LibreTexts.

Method Errors

In any analysis the relationship between the signal, S_{total}, and the absolute amount of analyte, n_A, or the analyte's concentration, C_A, is

$$S_{total} = k_A n_A + S_{mb} \tag{3.2.3}$$

$$S_{total} = k_A C_A + S_{mb} \tag{3.2.4}$$

where k_A is the method's sensitivity for the analyte and S_{mb} is the signal from the method blank. A ***method error*** exists when our value for k_A or for S_{mb} is in error. For example, a method in which S_{total} is the mass of a precipitate assumes that k is defined by a pure precipitate of known stoichiometry. If this assumption is not true, then the resulting determination of n_A or C_A is inaccurate.

We can minimize a determinate error in k_A by calibrating the method. A method error due to an interferent in the reagents is minimized by using a proper method blank.

Measurement Errors

The manufacturers of analytical instruments and equipment, such as glassware and balances, usually provide a statement of the item's maximum ***measurement error***, or ***tolerance***. For example, a 10-mL volumetric pipet (Figure 3.2.1) has a tolerance of ±0.02 mL, which means the pipet delivers an actual volume within the range 9.98–10.02 mL at a temperature of 20 °C. Although we express this tolerance as a range, the error is determinate; that is, the pipet's expected volume, μ, is a fixed value within this stated range.



Figure 3.2.1 : Close-up of a 10-mL volumetric pipet showing that it has a tolerance of ±0.02 mL at 20 °C.

Volumetric glassware is categorized into classes based on its relative accuracy. **Class A glassware** is manufactured to comply with tolerances specified by an agency, such as the National Institute of Standards and Technology or the American Society for Testing and Materials. The tolerance level for Class A glassware is small enough that normally we can use it without calibration. The tolerance levels for **Class B glassware** usually are twice that for Class A glassware. In other words, Class B is less accurate. Other types of volumetric glassware, such as beakers and graduated cylinders, are not used to measure volume accurately. Table 3.2.1 provides a summary of typical measurement errors for Class A volumetric glassware. Tolerances for digital pipets and for balances are provided in Table 3.2.2 and Table 3.2.3 .

Tolerance Limits for Class A Volumetric Glassware

Table 3.2.1 : Measurement Errors for **Class A Volumetric Glassware**

Volumetric Pipets		**Volumetric Flasks**		**Burets**	
Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)
1	±0.006	5	±0.02	10	±0.02
2	±0.006	10	±0.02	25	±0.03
5	±0.01	25	±0.03	50	±0.05
10	±0.02	50	±0.05		
20	±0.03	100	±0.08		
25	±0.03	250	±0.12		
50	±0.05	500	±0.20		
100	±0.08	1000	±0.30		
		2000	±0.50		

Tolerance limits for Digital Pipettes

Table 3.2.2 : Measurement Errors for Digital Pipets

Pipet Range	Volume (mL or μL)	Percent Measurement Error
10–100 μL	10	±3.0%
	50	±1.0%
	100	±0.8%
100–1000 μL	100	±3.0%
	500	±1.0%
	1000	±0.6%
1–10 mL	1	±3.0%
	5	±0.8%
	10	±0.6%

The tolerance values for the volumetric glassware in Table 3.2.1 are from the ASTM E288, E542, and E694 standards. The measurement errors for the digital pipets in Table 3.2.2 are from www.eppendorf.com.

Tolerance Limits for Some Common Balances

Table 3.2.3 : Measurement Errors for Selected Balances

Balance	Capacity (g)	Measurement Error
Precisa 160M	160	±1 mg
A & D ER 120M	120	±0.1 mg
Metler H54	160	±0.01 mg

We can minimize a determinate measurement error by calibrating our equipment. Balances are calibrated using a reference weight whose mass we can trace back to the SI standard kilogram. Volumetric glassware and digital pipets are calibrated by determining the mass of water delivered or contained and using the density of water to calculate the actual volume. It is never safe to assume that a calibration does not change during an analysis or over time. One study, for example, found that repeatedly exposing volumetric glassware to higher temperatures during machine washing and oven drying, led to small, but significant changes in the glassware's calibration [Castanheira, I.; Batista, E.; Valente, A.; Dias, G.; Mora, M.; Pinto, L.; Costa, H. S. *Food Control* **2006**, *17*, 719–726]. Many instruments drift out of calibration over time and may require frequent recalibration during an analysis.

Personal Errors

Finally, analytical work is always subject to ***personal error***, examples of which include the ability to see a change in the color of an indicator that signals the endpoint of a titration, biases, such as consistently overestimating or underestimating the value on an instrument's readout scale, failing to calibrate instrumentation, and misinterpreting procedural directions. You can minimize personal errors by taking proper care.

Identifying Determinate Errors

Determinate errors often are difficult to detect. Without knowing the expected value for an analysis, the usual situation in any analysis that matters, we often have nothing to which we can compare our experimental result. Nevertheless, there are strategies we can use to detect determinate errors.

The magnitude of a constant ***determinate error*** is the same for all samples and is more significant when we analyze smaller samples. Analyzing samples of different sizes, therefore, allows us to detect a constant determinate error. For example, consider a quantitative analysis in which we separate the analyte from its matrix and determine its mass. Let's assume the sample is 50.0% w/w analyte. As we see in Table 3.2.4 , the expected amount of analyte in a 0.100 g sample is 0.050 g. If the analysis has a positive

constant determinate error of 0.010 g, then analyzing the sample gives 0.060 g of analyte, or an apparent concentration of 60.0% w/w. As we increase the size of the sample the experimental results become closer to the expected result. An upward or downward trend in a graph of the analyte's experimental concentration versus the sample's mass (Figure 3.2.2) is evidence of a constant determinate error.

Table 3.2.4 : Effect of a Constant Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Constant Error (g)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	0.010	0.060	60.0
0.200	0.100	0.010	0.110	55.0
0.400	0.200	0.010	0.210	52.5
0.800	0.400	0.010	0.410	51.2
1.600	0.800	0.010	0.810	50.6

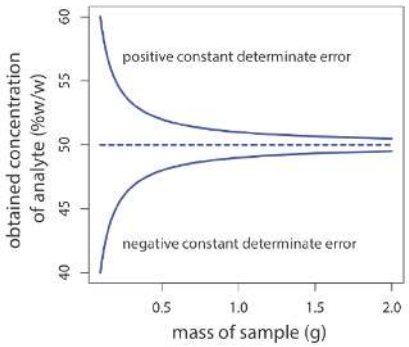


Figure 3.2.2 : Effect of a constant positive determinate error of +0.01 g and a constant negative determinate error of –0.01 g on the determination of an analyte in samples of varying size. The analyte's expected concentration of 50% w/w is shown by the dashed line.

A ***proportional determinate error***, in which the error's magnitude depends on the amount of sample, is more difficult to detect because the result of the analysis is independent of the amount of sample. Table 3.2.5 outlines an example that shows the effect of a positive proportional error of 1.0% on the analysis of a sample that is 50.0% w/w in analyte. Regardless of the sample's size, each analysis gives the same result of 50.5% w/w analyte.

Table 3.2.5 : Effect of a Proportional Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Proportional Error (%)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	1.00	0.0505	50.5
0.200	0.100	1.00	0.101	50.5
0.400	0.200	1.00	0.202	50.5
0.800	0.400	1.00	0.404	50.5
1.600	0.800	1.00	0.808	50.5

One approach for detecting a proportional determinate error is to analyze a standard that contains a known amount of analyte in a matrix similar to our samples. Standards are available from a variety of sources, such as the National Institute of Standards and

Technology (where they are called Standard Reference Materials) or the American Society for Testing and Materials. Table 3.2.6 , for example, lists certified values for several analytes in a standard sample of *Gingko biloba* leaves. Another approach is to compare our analysis to an analysis carried out using an independent analytical method that is known to give accurate results. If the two methods give significantly different results, then a determinate error is the likely cause.

Table 3.2.6 : Certified Concentrations for SRM 3246: *Gingko bilbo* (Leaves)

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
Flavonoids/Ginkgolide B (mass fraction in mg/g)	Qurecetin	2.69 ± 0.31
	Kaempferol	3.02 ± 0.41
	Isorhamnetin	$0.517 \pm 0.0.99$
	Total Aglycones	6.22 ± 0.77
Selected Terpenes (mass fraction in mg/g)	Ginkgolide A	0.57 ± 0.28
	Ginkgolide B	0.470 ± 0.090
	Ginkgolide C	0.59 ± 0.22
	Ginkgolide J	0.18 ± 0.10
	Bilobalide	1.52 ± 0.40
	Total Terpene Lactones	3.3 ± 1.1
Selected Toxic Elements (mass fraction in ng/g)	Cadmium	20.8 ± 1.0
	Lead	995 ± 30
	Mercury	23.08 ± 0.17

> The primary purpose of this Standard Reference Material is to validate analytical methods for determining flavonoids, terpene lactones, and toxic elements in *Ginkgo biloba* or other materials with a similar matrix. Values are from the official Certificate of Analysis available at www.nist.gov.

Constant and proportional determinate errors have distinctly different sources, which we can define in terms of the relationship between the signal and the moles or concentration of analyte (Equation 3.2.3 and Equation 3.2.4). An invalid method blank, S_{mb}, is a constant determinate error as it adds or subtracts the same value to the signal. A poorly calibrated method, which yields an invalid sensitivity for the analyte, k_A, results in a proportional determinate error.

Errors that Affect Precision

Precision is a measure of the spread of individual measurements or results about a central value, which we express as a range, a standard deviation, or a variance. Here we draw a distinction between two types of precision: repeatability and reproducibility. ***Repeatability*** is the precision when a single analyst completes an analysis in a single session using the same solutions, equipment, and instrumentation. ***Reproducibility***, on the other hand, is the precision under any other set of conditions, including between analysts or between laboratory sessions for a single analyst. Since reproducibility includes additional sources of variability, the reproducibility of an analysis cannot be better than its repeatability.

> The ratio of the standard deviation associated with reproducibility to the standard deviation associated with repeatability is called the Horowitz ratio. For a wide variety of analytes in foods, for example, the median Horowtiz ratio is 2.0 with larger

values for fatty acids and for trace elements; see Thompson, M.; Wood, R. “The ‘Horowitz Ratio’–A Study of the Ratio Between Reproducibility and Repeatability in the Analysis of Foodstuffs,” *Anal. Methods*, **2015**, *7*, 375–379.

Errors that affect precision are indeterminate and are characterized by random variations in their magnitude and their direction. Because they are random, positive and negative ***indeterminate errors*** tend to cancel, provided that we make a sufficient number of measurements. In such situations the mean and the median largely are unaffected by the precision of the analysis.

Sources of Indeterminate Error

We can assign indeterminate errors to several sources, including collecting samples, manipulating samples during the analysis, and making measurements. When we collect a sample, for instance, only a small portion of the available material is taken, which increases the chance that small-scale inhomogeneities in the sample will affect repeatability. Individual pennies, for example, may show variations in mass from several sources, including the manufacturing process and the loss of small amounts of metal or the addition of dirt during circulation. These variations are sources of indeterminate sampling errors.

During an analysis there are many opportunities to introduce indeterminate method errors. If our method for determining the mass of a penny includes directions for cleaning them of dirt, then we must be careful to treat each penny in the same way. Cleaning some pennies more vigorously than others might introduce an indeterminate method error.

Finally, all measuring devices are subject to indeterminate measurement errors due to limitations in our ability to read its scale. For example, a buret with scale divisions every 0.1 mL has an inherent indeterminate error of ±0.01–0.03 mL when we estimate the volume to the hundredth of a milliliter (Figure 3.2.3).

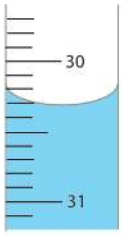


Figure 3.2.3 : Close-up of a buret showing the difficulty in estimating volume. With scale divisions every 0.1 mL it is difficult to read the actual volume to better than ±0.01–0.03 mL.

Evaluating Indeterminate Error

Indeterminate errors associated with our analytical equipment or instrumentation generally are easy to estimate if we measure the standard deviation for several replicate measurements, or if we monitor the signal’s fluctuations over time in the absence of analyte (Figure 3.2.4) and calculate the standard deviation. Other sources of indeterminate error, such as treating samples inconsistently, are more difficult to estimate.

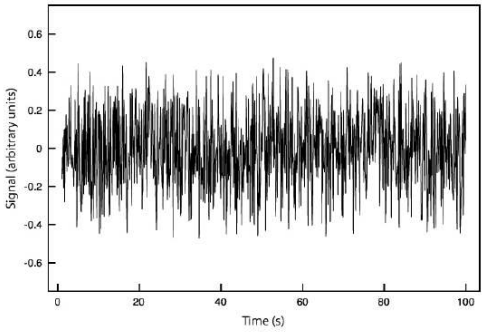


Figure 3.2.4 : Background noise in an instrument showing the random fluctuations in the signal.

Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty [Ellison, S.; Wegscheider, W.; Williams, A. *Anal. Chem.* **1997**, *69*, 607A–613A]. ***Error*** is the difference between a single measurement or result and its expected value. In other words, error

is a measure of ***bias***. As discussed earlier, we divide errors into determinate and indeterminate sources. Although we can find and correct a source of determinate error, the indeterminate portion of the error remains.

Uncertainty expresses the range of possible values for a measurement or result. Note that this definition of uncertainty is not the same as our definition of precision. We calculate precision from our experimental data and use it to estimate the magnitude of indeterminate errors. Uncertainty accounts for all errors—both determinate and indeterminate—that reasonably might affect a measurement or a result. Although we always try to correct determinate errors before we begin an analysis, the correction itself is subject to uncertainty.

Here is an example to help illustrate the difference between precision and uncertainty. Suppose you purchase a 10-mL Class A pipet from a laboratory supply company and use it without any additional calibration. The pipet's tolerance of ±0.02 mL is its uncertainty because your best estimate of its expected volume is 10.00 mL ± 0.02 mL. This uncertainty primarily is determinate. If you use the pipet to dispense several replicate samples of a solution and determine the volume of each sample, the resulting standard deviation is the pipet's precision. Table 3.2.8 shows results for ten such trials, with a mean of 9.992 mL and a standard deviation of ±0.006 mL. This standard deviation is the precision with which we expect to deliver a solution using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ±0.02 mL is worse than its experimentally determined precision of ±0.006 ml. Interestingly, the data in Table 3.2.8 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ±0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty [Kadis, R. *Talanta* **2004**, *64*, 167–173].

Table 3.2.8 : Experimental Results for Volume Dispensed by a 10–mL Class A Transfer Pipet

Replicate	Volume (ml)	Replicate	Volume (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

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3.3: Estimating and Reporting Error (Statistics, Propogation, and Rounding)

In many physical chemistry experiments, the goal is to obtain numerical results by taking measurements and calculating averages or applying theoretical formulas. However, simply producing a number isn't enough – it's essential to evaluate its quality. How accurate is the result? Accuracy indicates the level of uncertainty associated with the measurement. Overstating accuracy without proper justification can be misleading, while understating it can undervalue the result and lead to wasted effort and resources.

This module will deal with two main types of error analyses. You will learn when and how to use each type.

1. **Statistical Analyses** are done when there are multiple replicates of the same measurement(s).
2. **Error Propagation** is done when using measured values to calcuate another numerical value.

A major goal of this module is for you to learn when and how to apply these equations to perform statistical analysis or propagate errors through a function. This skill will be required in nearly every future module in this course.

A summary of useful information and equations is below.

1. Statistical Analyses (on replicate measurements):

Average or mean: The average (or mean) of N measurements on the variable x is:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{3.3.1}$$

Standard deviation (S) is the spread around the mean of several replicate measurements. It has the same units as the measurement and is commonly used to report uncertainty (see Skoog Ch. 6 p 126)

$$S = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \tag{3.3.2}$$

Variance (S^2) is the dispersion between data points. The units are the square of the measured units.

The **Confidence Limits (CL)** are the values that define the confidence interval (which is the bounds about which an experimental value should be located with a given probability). The confidence limit is useful for small sample sizes. A common confidence limit is the 95% confidence limit, and its value is given by the following (see Skoog Ch7 pg 150 and Shoemaker Ch 2 eq 34).

$$CL_{0.95} = t_{0.95}S_m = t_{0.95}\frac{S}{\sqrt{N}} \tag{3.3.3}$$

or more generally

$$CL = \bar{x} \pm \frac{tS}{\sqrt{N}} \tag{3.3.4}$$

where t is the critical t value (from Student's t test) that depends on the degrees of freedom and the given probability. A table of critical t values can be found online. (See also Shoemaker Ch 2, Table 3)

2. Propagation of error (for values determined from a function):

Using partial derivatives

To propagate error to determine the error (Δ) in the value derived from of a function (F), we must propagate error of each part of the function. This is accomplished by taking the square root of the sum of the squares of the partial derivative of the function with respect to each variable (eg partial derivative with respect to x is $\frac{\partial F}{\partial x}$), multiplied by the error in that variable (eg error in x is $\Delta(x)$, and the square of the error is $\Delta^2(x)$. In mathematical form, this is given below (from Shoemaker Ch 2 p 56, eq 54). If you need to brush up on partial derivatives, check out this video (click here). https://youtu.be/SbfRDBmyAMI

$$\Delta^2(F) = \left(\frac{\partial F}{\partial x}\right)^2\Delta^2(x) + \left(\frac{\partial F}{\partial y}\right)^2\Delta^2(y) + \left(\frac{\partial F}{\partial z}\right)^2\Delta^2(z) + \ldots \tag{3.3.5}$$

It is convenient to rearrange this equation as follows to give the error in the value derived from the function:

$$\Delta(F) = \sqrt{\left(\frac{\partial F}{\partial x}\right)^2 \Delta^2(x) + \left(\frac{\partial F}{\partial y}\right)^2 \Delta^2(y) + \left(\frac{\partial F}{\partial z}\right)^2 \Delta^2(z) + \ldots} \tag{3.3.6}$$

Simpler shortcuts:

In some cases, there are shortcuts that allow you to approximate errors without taking the partial derivatives. In the examples below, assume that a, b, c, n are constants and x, y, z are variables with associated errors $\Delta x, \Delta y, \Delta z$:

For functions with only addition and subtraction of values with assiciated error (eg $F = ax \pm by \pm cz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 55)

$$\Delta(F) = \sqrt{a^2\Delta^2(x) + b^2\Delta^2(y) + c^2\Delta^2(z)} \tag{3.3.7}$$

For functions that involve only multiplication and division (eg $F = axyz$ **or** $F = axy/z$ **or** $F = a/xyz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 56)

$$\Delta(F) = F\sqrt{\frac{\Delta^2(x)}{x^2} + \frac{\Delta^2(y)}{y^2} + \frac{\Delta^2(z)}{z^2}} \tag{3.3.8}$$

For functions that involve taking a variable to the power of a constant (eg $F = ax^n$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 57)

$$\Delta(F) = F\sqrt{n^2\frac{\Delta^2(x)}{x^2}} \rightarrow \Delta(F) = Fn\frac{\Delta(x)}{x} \tag{3.3.9}$$

For functions where a variable is an exponent (eg $F = ae^x$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 58)

$$\Delta(F) = \sqrt{a^2e^{2x}\Delta^2(x)} \rightarrow \Delta(F) = F\Delta(x) \tag{3.3.10}$$

For functions taking the logarithm of a variable (eg $F = a\ln(x)$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 59)

$$\Delta(F) = \sqrt{\frac{a^2}{x^2}\Delta^2(x)} \rightarrow \Delta(F) = a\frac{\Delta(x)}{x} \tag{3.3.11}$$

3. Reporting Numeric Results

All numeric results in this course should be reported with explicit statement of uncertainty. The following format is expected:

$$\textbf{Numeric Value } \pm \textbf{Uncertainty} \tag{3.3.12}$$

In your written assignments for this course use the following guidelines when reporting a "final" numeric value. You will be required to use your *best judgement* and to provide a *written justification* of your logic for reporting all final values. More detailed information is found below the guidelines and also in the Shoemaker text.

Guidelines for reporting final numerical values:

- Rules for reporting significant figures should be followed.
- The number of useful decimal places in the uncertainty should match the number of decimal places reported in the value.
- The certainty of a numeric value determined from a function cannot be be more than the certainty of its operands.

A summary of rules for reporting significant Figures (from Shoemaker Ch 2)

The following rules apply only for reporting the *final* value, not for intermediate rounding steps during calculation. In general, do not round values during the calculation process if it can be avoided. However, if you must round prior to comleting a calcaution, then retain *at least one digit more than would be considered "significant"*, and the more the better.

Rules for Rounding Final Values:

Follow the following rules depending on the digit immediately to the right of the place you are rounding. The examples below are rounding to the place underlined, and **the digit immediately to the right is bolded**.

a. Increase the last retained digit by 1 if the nearest dropped digit is more than 5, or if it is 5 followed by any non-zero digits:
   - Examples:
     6.78**9** rounds to 6.79
     54.91**2**3 rounds to 54.9

b. Leave the last retained digit unchanged if the nearest dropped digit is less than 5:
   - Examples:
     2.34**6** rounds to 2.35
     0.21**2**3 rounds to 0.21

c. If the leftmost digit to be dropped is 5 followed by no digits except zero, then increase the last retained digit by 1 if it is odd, and leave it unchanged if it is even:
   - Examples:
     15.32**5** rounds to 15.32
     15.33**5** rounds to 15.34

d. There are times when you should retain an extra digit so that your reported uncertainty is reasonable.

Rules for tracking significant figures for calculated values

Addition: When adding numeric values, the result's precision is limited by the least precise value involved. The number of decimal places in the result should match the fewest decimal places in any component. For example:

$$\begin{array}{r} 15.4 \\ +2.87 \\ +7.621 \\ \hline =25.916 \rightarrow 25.9 \end{array} \tag{3.3.13}$$

Subtraction: When subtracting, the result's precision is limited by the least precise value involved, and the precision of the result will always be less than that of the operands. For example:

$$\begin{array}{r} 289.461 \\ -288.58 \\ \hline 0.881 \rightarrow 0.88 \end{array} \tag{3.3.14}$$

Let's do an analysis to illustrate what this means. In the example above, let's assume an uncertainty of ± 3 in the rightmost digit of each number. Based on this assumption, the least precise operand has uncertainty of ~ 0.01%, while the final reported value has an uncertainty of 3.4%!

When multiplying and dividing: In multiplication and division, the precision of the result is limited by the least precise number involved. The number of significant figures in the result should align with the component having the fewest. ***Note that relative precision isn't solely dependent on the number of significant figures;*** for instance, 99 with two significant figures is approximately as precise as 101 with three. When unsure, do an analysis of the relative uncertainty, and if the uncertinties are approximately equal, use the larger number of significant figures.

Conventions for Reporting and Interpreting Reported Values

1. Numerical values are typically considered uncertain in the last digit by ±3 or more, with perhaps slight uncertainty in the next-to-last digit by up to ±2.
2. If the last digit to be retained is a one or two, an additional digit is retained so that precision is not inappropriately reported due to rounding.

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3.4: Least Squares Linear Regression

Your experimental data will usually be examined in graphic form, which can be more instructive than tabulated data. In any graphic presentation, be sure to plot your independent variable on the abscissa (x-axis) and the dependent variable on the ordinate (y-axis).

If the data are presented in graphic form, the usual procedure is to fit the best curve through the experimental points. As Brownlee[3] puts it,

> "When an investigator observes simultaneously two variables, x and y, usually with good reason he plots the observations on a graph. If there is any sign of an association, he is usually seized with the impulse to fit a line, usually a straight line or, rather infrequently, a parabola or cubic."

When we are "seized with the impulse" to fit a straight line curve the process of curve fitting is called linear regression. We assume that the deviations of the dependent variable y are distributed normally (that is, a Gaussian distribution). This assumption is not required for the determination of the least squares parameters, but it is necessary for construction of confidence intervals or for tests of hypotheses about the parameters. The parameters obtained by least squares under these conditions are unbiased and provide the best estimates of the curve fitting parameters.

Most of the experimental data that you will encounter this semester will have a simple functional form, or can be manipulated in such a way as to assume a simple form. We shall assume here that our data follows a linear relationship. For example, consider a gas that is thought to follow the equation of state

$$\underset{\mathrm{y=a+bx}}{\mathrm{Z} \equiv \frac{\mathrm{PV}}{\mathrm{nRT}} = \mathrm{B_0} + \mathrm{B_1 P}} \tag{3.4.1}$$

Measurements of Z, called the compressibility factor, are made at each of a series of pressures in an effort to determine B_0 andB_0. The least squares approach can be used to determine the slope (b, orB_1) and y-intercept (a, or B_0) which define the best straight line that can be drawn through the data. In simple linear regression analysis, it is assumed that all the error in the measurement lies in the dependent variable (y). This is equivalent to assuming that the precision of the determination of the independent variable (x) is considerable higher than that of y. The measured value of some quantity (y_i) will differ from the value predicted by a linear equation ($y = a + bx$) by an amount r_i called the residual.

$$r_i = y_i - a - bx \tag{3.4.2}$$

The least squares approach identifies the best straight line as the one for which R, the sum of the squares of the residuals, has the smallest value:

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} (y_i - a - bx_i)^2 \tag{3.4.3}$$

The arrows in Figure 4 represent the residuals, and all of them are equally weighted.

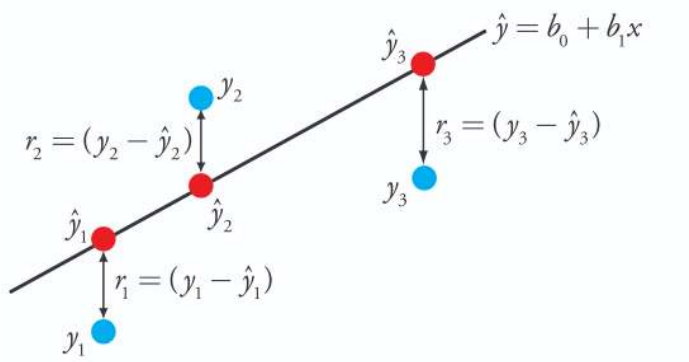


Figure **3.4.1**: Least Squares Linear Regression: *Illustration showing the evaluation of a linear regression in which we assume that all uncertainty is the result of indeterminate errors affecting y. The points in blue, y_i, are the original data and the points in red, $\hat{y}_i$, are the predicted values from the regression equation, $\hat{y} = b_0 + b_1 x$. The smaller the total residual error, the better the fit of the straight-line to the data* (source)

We want to minimize the sum of the squares of the residuals. That is, we want to make *least* the sum of *squares* of residuals, and, thus, the name of the procedure. Since this is a minimization problem, we require that R be as small as possible with respect to a and b by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial a}\right)_b = -2\sum(y_i - a - bx_i) = 0 \tag{3.4.4}$$
$$\left(\frac{\partial R}{\partial b}\right)_a = -2\sum((y_i - a - bx_i)(x_i)) = 0$$

Solving equations 3.4.4 simultaneously, we obtain

$$a = \frac{(\sum x_i^2)(\sum y_i) - (\sum x_i)(\sum x_i y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{3.4.5}$$

$$b = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{3.4.6}$$

While we ultimately want to fit the data to $y_i = a + bx_i$ for a series i of N points, the theoretical development is much easier if we use $y_i = c + b(x_i - \overline{x})$ where obviously a and c are related by $a = c - b\overline{x}$, and where $\overline{x}$ is simply the mean of the x data, $n\overline{x} = \sum_{i=1}^{N} x_i$. This designation of variables is better because "it turns out" that in this approach the parameters b and c are independent, their variances are independent, and the formulas to transform to the parameters a and b are simple. Again, we want to minimize the sum of the squares of the residuals $r_i = y_i - c - b(x_i - \overline{x})$, R.

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} [y_i - (c + b(x_i - \overline{x}))]^2 \tag{3.4.7}$$

Now we require that R be as small as possible with respect to b and c by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial c}\right)_b = -2\sum(y_i - c - b(x_i - \overline{x})) = 0 \tag{3.4.8}$$
$$\left(\frac{\partial R}{\partial b}\right)_c = -2\sum((y_i - c - b(x_i - \overline{x}))(x_i - \overline{x})) = 0$$

These two equations are readily rewritten as

$$\sum y_i = \sum c + \sum b(x_i - \overline{x}) \tag{3.4.9}$$
$$\sum y_i(x_i - \overline{x}) = \sum c(x_i - \overline{x}) + \sum b(x_i - \overline{x})^2$$

which, since $\sum(x_i - \overline{x}) = 0$, simplify to

$$c = \frac{\sum y_i}{N} = -\bar{y}$$
$$b = \frac{\sum y_i (x_i - \bar{x})}{\sum (x_i - \bar{x})^2} \tag{3.4.10}$$

The knowledge of c and b then allows us to determine the parameter, a, $a = c - b\bar{x} = \bar{y} - b\bar{x}$, a particularly simple relation.

The variance and standard deviation of N data points was introduced previously. The appropriate treatment of the parameters c and b in the least squares procedure results in

$$V[c] = \frac{s^2}{N}$$
$$V[b] = \frac{s^2}{\sum (x_i - \bar{x})^2} \tag{3.4.11}$$

where

$$s^2 = \frac{1}{N-2} \sum (y_i - c - b(x_i - \bar{x}))^2 = \frac{1}{N-2} \sum (y_i - a - bx_i)^2 = \frac{R_{min}}{N-2} \tag{3.4.12}$$

Because c and b are independent quantities, it can be shown that

$$V[a] = V[c] + \bar{x}^2 V[b]$$
$$= \frac{s^2}{N} + \bar{x}^2 \frac{s^2}{\sum (x_i - \bar{x})^2} \tag{3.4.13}$$

The standard deviations of a and b, σ_a and σ_b, are then obtained by taking the square roots of V[a] and V[b].

Another statistic that is sometimes used is the *correlation coefficient*, r. It is given by the expression

$$r = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left(N \sum x_i^2 - (\sum x_i)^2\right)\left(N \sum y_i^2 - (\sum y_i)^2\right)}} \tag{3.4.14}$$

When the absolute value of r is close to unity the correlation between the y and x data is good, when it is close to zero the correlation is poor. Because the correlation coefficient is sometimes hard to interpret, it is usually better to work with the standard deviations of the regression parameters, σ_a and σ_b.

Linear regression is a powerful tool that takes the guesswork out of obtaining best fit information. However, like all mathematical tools, it must be used with caution. While the standard deviations and the correlation coefficient give indications of the goodness of the fit, there is no substitute for graphing the data and looking at the result. Since the errors are assumed to be random, the y_i values should be scattered about the best fit straight line in a random fashion. The residuals should likewise be either positive or negative (and sum to zero) without any pattern. If the data show a pattern of curvature, it is possible that the results do not conform to the linear model proposed. A linear regression is *not* valid in this case. You should also be alert to the effects of systematic errors, which may change the slope or the intercept without affecting the linearity of the data.

Linear regression of the type discussed above relies on a number of critical assumptions. Among the most important is that all the uncertainty in each of the y values is the same. If the form of the equation required to provide a linear relationship produces an independent variable that contains a significant uncertainty, the set of conditions that produced the minimum in the residuals of the line may not be the set that actually minimizes the uncertainty in the data. In this case, a "non-linear" least squared technique such as simplex is recommended.

Note

In this course, you can use the MatLab lsq.m script to perform least squares analysis. The equations given above are included in the lsq script.

Weighted Least Squares Analysis

When measurements of the dependent variable incur different uncertainties, a ***weighted*** least squares technique should be used. In this approach, each residual ri is divided by a factor proportional to its uncertainty ε_{y_i}. Then R, the sum of the squares of the residuals, becomes

$$R = \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_{y_i}^2} = \sum_{i=1}^{N} \frac{1}{\varepsilon_{y_i}^2}(y_i - a - bx_i)^2 \tag{3.4.15}$$

Using the same minimization techniques described above, the slope and intercept for weighted least squares become

$$a = \frac{\sum \frac{x_i^2}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2}\right)^2} \tag{3.4.16}$$

$$b = \frac{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2}\right)^2} \tag{3.4.17}$$

Weighted least squares has utility in a number of applications in the physical chemistry laboratory. One common situation arises when a linear equation requires the log of a measured quantity to be the dependent variable. Consider for example, the measurement of vapor pressure. Most pressure sensing devices will provide a constant error in the measurement of P. If the dependent variable to be plotted is lnP, however, its uncertainty is not constant but decreases as P increases. Thus,

$$\varepsilon_{lnP} = \frac{\partial lnP}{\partial P}\varepsilon_P = \frac{\varepsilon_P}{P} \tag{3.4.18}$$

An appropriate weighting factor in this case would be $\varepsilon_{y_i} = \frac{1}{P}$.

When you use Matlab for data analysis this semester, the command **lsq(x,y)** will be used for least squares analysis of x, y data, and the command **wtlsq(x,y)** will be used for weighted least squares analysis. In the latter case, you will be asked for a weighting factor, e. In either case, the program will output the least squares slope, y-intercept, correlation coefficient, standard deviation of the slope, and standard deviation of the intercept.

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3.5: Rejection of Outliers (Q-test)

In a set of collected data, there may be one or more values that deviate markedly from the trend of the others. You should not reject a piece of data that seems suspect until you perform a Q-test. In a set of data of three to ten measurements, the Q-test can be performed on the suspect data point:

$$Q_{exp} \equiv \frac{|\,(\text{ suspected outlier's value }) - (\text{value closest to it })\,|}{(\text{highest value }) - (\text{ lowest value })} \tag{3.5.1}$$

Compare the value of Q_{exp} from the equation above to the critical value of Q_r. If Q_{exp} is greater or equal to Q_r then the suspect value can be rejected. If Q_{exp} is less than Q_r,the value should be retained in the data set.

The following table provides critical values for $Q(\alpha, n)$, where α is the probability of incorrectly rejecting the suspected outlier and n is the number of samples in the data set. There are several versions of the *Q*-Test, each of which calculates a value for Q_{ij} where *i* is the number of suspected outliers on one end of the data set and *j* is the number of suspected outliers on the opposite end of the data set. The critical values for *Q* here are for a single outlier, Q_{10}, where

$$Q_{\text{exp}} = Q_{10} = \frac{|\,(\text{ suspected outlier's value }) - (\text{value closest to it })\,|}{(\text{highest value }) - (\text{ lowest value })}$$

The suspected outlier is rejected if Q_{exp} is greater than $Q(\alpha, n)$. For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's '*Q*' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146.

Table 3.5.1: Critical Values for Dixon's Q-Test

$\frac{\alpha\longrightarrow}{n\downarrow}$	**0.1 (90% confidence limit)**	**0.05 (95% confidence limit)**	**0.04 (96% confidence limit)**	**0.02 (98% confidence limit)**	**0.01 (99% confidence limit)**
3	0.941	0.970	0.976	0.988	0.994
4	0.765	0.829	0.846	0.889	0.926
5	0.642	0.710	0.729	0.780	0.821
6	0.560	0.625	0.644	0.698	0.740
7	0.507	0.568	0.586	0.637	0.680
8	0.468	0.526	0.543	0.590	0.634
9	0.437	0.493	0.510	0.555	0.598
10	0.412	0.466	0.483	0.527	0.568

(see also http://chem-net.blogspot.com/2013/01...atistical.html)

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3.6: Guidelines for Recording and Reporting Data in your ELN

Always consider uncertainty during an experiment, record it in your ELN, and include it in all calculations and reporting. Do not leave the lab until you are sure that you have a valid strategy for determining errors in all final values.

1. **Uncertainty Awareness:**
   Before leaving the lab area, ensure you have a valid strategy for estimating uncertainties in all measured and calculated values.
2. **Estimating Uncertainty During Measurements:**
   - **Equipment Uncertainty**: Record uncertainties provided by equipment or manufacturers (e.g., balance deviation, pipette error). If unavailable, assume uncertainty is ±0.5 of the smallest measurable unit.
   - **Replicates**: For three or more measurements, calculate the standard deviation of the mean.
   - **Function-Based Values**: Perform propagation of error analysis.
   - **Least Squares Fitting**: Use errors from fitted parameters (e.g., slope or intercept) and propagate uncertainty if used in further calculations. Avoid linear regression if data deviates significantly from linearity.
   - **Consult Instructors**: Seek help for unclear sources of uncertainty.
3. **Propagation of Error:**
   Combine individual uncertainties to estimate the overall uncertainty of the final result. Use partial derivatives where necessary, and assume constants (e.g., RR) are error-free.
4. **Reporting Results:**
   - Include propagated uncertainty with each result.
   - Compare results with literature values using percent or absolute error.
   - Ensure significant figures reflect uncertainty and justify their use.
5. **Replicate Measurements:**
   - Report the mean and precision (e.g., standard deviation).
   - Use the Q-test to justify excluding outliers.
6. **Single Measurements:**
   - Estimate and report uncertainty (random or systematic).
   - Compare accuracy to expected values if available.
7. **Least Squares Fitting:**
   - Use weighted or non-weighted regression based on data.
   - Reject outliers only using the Q-test on residuals.
   - Propagate uncertainty from fitted parameters to calculated values.
8. **Qualitative Uncertainty:**
   For variables with no clear quantitative uncertainty, discuss potential sources and their impact on results. Provide reasonable estimates and substantiate with evidence.
9. **Before Leaving the Lab:**
   - Confirm all uncertainties are documented.
   - Check for systematic errors (e.g., calibration issues).
   - Ensure thorough records of measured values and associated uncertainties.

By following these steps, you ensure your experimental results are accurate, reproducible, and clearly reported.

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3.7: Homework Problems

Each practice problem below requires that you correctly apply propagation of errors to report the correct value and its precision (including the error). You should attempt all seven problems prior to our schedule lab meeting on this topic (and submit prior to the meeting on Canvas). This pre-lab assignment will prepare you to participate in the lab meeting by presenting problems on the board, answering questions from your peers, and asking your own questions.

You will submit your work and final answers after the in-lab problem session. Your answers to these problems may be hand-written or typed. However, any submissions that are deemed illegible, unclear, or poorly organized will not be accepted.

> **Note**
>
> (1) We will give you a MatLab template to get you help you in using MatLab for this problem set. However, you may use whatever technology (calculators, software, etc.) you like to aid in working these problems.
>
> (2) It is important to show how your calculations are set-up and, where appropriate, give a sample calculation. Simply giving the final answer is not acceptable.
>
> (3) In reporting all results, you should always round your reported answer to be consistent with your estimated uncertainty. For example: a calculated result of 56.2189 ± 0.0386 would be reported as **56.20 ± 0.04** where 0.04 is the standard deviation, 95% confidence level, or propagated uncertainty.

The seven problems are below. Note that there are Hints that you can click on for each problem.

PROBLEM 1: Statistics

A student makes five independent measurements of each of the linear dimensions of a box. The results are tabulated as follows:

Length (cm)	Width (cm)	Height (cm)
1.010	5.376	2.001
1.015	5.339	2.105
1.013	5.385	1.985
0.999	5.375	1.989
1.009	5.369	2.008

A. Calculate the average values of length, width, and height, and calculate the standard deviation in each of these three quantities. Report the values appropriately, considering the calcuated precision.

B. Calculate the variance of the length, width, and height.

C. Calculate the 95% confidence limits to the measurements of length, width, and height.

D. Calculate the 95% confidence limits to the average volume obtained from the independent measurements of length, width, and height.

Hint

This problems is one where there are five replicate measurements of length, width, and height. That's enough to use some basic statistics to determine our confidence of each measurement. Normally the standard deviation is an appropriate indicator of the data's precision in a case like this where there are multiple measurements. The problem also asks for the variance and the 95% confidence limit. Be sure to report all values in the appropriate number of digits, considering the calculated precision. The equation for variance and for 95% confidence can be found in Section 3.2.

PROBLEM 2: A Simple Case for Propogation of Error

A student weighs a sample using an analytical balance that has an estimated precision of ±0.5 mg. From the data below, calculate the weight of the sample and the range of uncertainty in the net weight.

	Mass (g)
Sample + flask	5.1647 ± 0.0005
Tared flask	2.3712 ± 0.0005

Hint

This is a simple propagation of error problem – any time we add, multiply, divide, or subtract multiple measurements, the final value's error is a propagation (or a combo of) the error associated with each measurement. So, you just need to recognize this fact, and then find the appropriate equation to propagate error in the case when values are subtracted. The appropriate equation is given in Section 3.2 (also on pg 57 of Shoemaker, equation 55...but in the Shoemaker text, you'd need to take the square root of both sides of the equation).

In this case, the function (F) that determines the sample weight is $F = \text{Mass of Sample in Flask} - \text{Mass of empty flask} = x - y$

Apply Equation 3.2.7 where $a, b = 1$ (and thus can be ignored), and the uncertainty in the measurements are $\Delta x = \Delta y = 0.0005\ g$. Specifically for this case, the uncertainty is:

$$\Delta F = \sqrt{(0.0005)^2 + (0.0005)^2} \tag{3.7.1}$$

PROBLEM 3: Statistics and Rejection of Discordant Data

An investigator measures the photon emission in the reaction

$$Na^+ + O^- \rightarrow Na^* + O \xrightarrow{h\nu} Na + O$$

in which the emitted photon (at 589 nm) is counted by means of a photomultiplier. Here are some typical "run" data

Run #	**Signal + Background (counts/sec)**	**Background (counts/sec)**
1	1500	1000
2	1200	1250
3	1375	1100
4	1425	900
5	1280	1200
6	1490	1363

Evaluate the data using statistical methods only and calculate:

A. The average signal value.

B. The standard deviation and variance in the average signal value.

C. The 95% confidence limits to the average signal value.

D. Using the Q test, determine whether the results from any one run can be rejected as discordant data at the 90% confidence level

Hint

This is a noisy data set where the signal is just barely detectable. The problem explicitly asks for calculation of variance (variance is just the square of standard deviation), 95% confidence limit (see problem 1), and application of the Q-test to determine whether any of the data points should be rejected. The Q-test is described in Section 3.3.1.

PROBLEM 4: Least Squares Analysis and Rejection of Discordant Data

A. Fit a straight line:

$$y = a + bx$$

to the following set of data points by the linear least-squares method

x 26 30 44 50 62 68 74
y 92 85 78 81 54 51 40

and calculate the coefficients a and b using the Equations (3.4.5) and (3.4.6) from Section 3.4.

B. Plot the x,y data and the least-squares line, and submit this with your report.

C. Calculate the standard deviation of the coefficients, a and b using Equations (3.4.11), (3.4.12) and (3.4.13) from from Section 3.4 (note that the lsq script does this automatically for you, and you are welcome to use it!).

D. Calculate the correlation coefficient, using equation (3.4.14) from Section 3.4. What is the significance of the sign of r?

E. Apply the Q-test to the y-residuals (see Equation (3.4.2) from Section 3.4), to determine whether there is a statistical basis for rejection of any of the data points as an outlier, (I) at the 96% confidence level (II) at the 90% confidence level.

F. If a data point is rejected, repeat the regression analysis (steps A-D) using the remaining data.

G. Comment quantitatively on the effect of data removal on the regression analysis.

Hint

You will need to plot the x,y data and then perform a linear fit. You are explicitly instructed to determine the standard deviation of the slope and y-intercept of the least squares fit linear function. There are three ways I know to determine these values: (1) Excel, using the "LINEST" array function. (2) MatLab, using the lsq custom script or the Statistics and Machine Learning Toolkit (3) Logger pro does it automatically with linear fitting. The LSQ script is recomended.

Hints for individual parts:

- A,B) - just plot the data and best fit line and get the equation.
- C, D) use lsq (Matlab)
- E) Following the linear regression analysis, perform a Q-test at two different confidence intervals - 96% and 90%. For this, you will need the critical Q-values for these two confidence limits (see Section 3.4.1).

PROBLEM 5: Error Propagation

In a chemistry lab, students obtain the following data and are asked to find the molecular weight (M) of methanol using PV = nRT. Determine the uncertainty in the result using a propagation of error treatment.

	Pressure (methanol)	Temperature	mass (methanol)
Trial 1	72.5 ± 0.5 mmHg	295.10 ± 0.05 K	0.1331 ± 0.0002 g
Trial 2	72.0 ± 0.5 mmHg	295.05 ± 0.05 K	0.1329 ± 0.0002 g

The volume (V) in both trials was 1.05678 liter, with no uncertainty given. You must decide on the uncertainty in V. If necessary, perform appropriate conversions of the units for each quantity, including R, so that the final value of M is reported in the correct units.

Hint

This is a propagation of error problem, where we are multiplying and dividing individual measurements to find the value of interest. In this case, it is the determination of the molecular weight (which I'm going to represent as MW) of methanol from the mass of methanol, pressure, temperature, and volume measurements.

So, first…how would we do this?

$$MW = \frac{\text{mass of methanol in grams}}{\text{moles methanol}} = \frac{m}{n} \tag{3.7.2}$$

The mass of methanol was measured in the experiment, and the number of moles can be determined from $PV = nRT$. The calculation involves multiplication and division to determine $n = \frac{PV}{RT}$, and then involves division again to determine \ (MW=\dfrac{m}/{n}.

We can substitute into the equation for MW and get everything into one combined equation:

$$MW = \frac{m}{n} = m\frac{PV}{RT} = mRTPV \tag{3.7.3}$$

Once you recognize that it is simply a propagation of errors problem in which the factors are multiplied and divided, you can determine the error in the molecular weight value using Equation 3.2.8.

The errors in P, T, and m are explicitly given. The error in V is not explicitly given, but we can assume that the error is indicated in the number of digits given in the volume measurement. The volume given is 1.0567**8** liters or 1,056.7**8** mL - so we assume we are uncertain in the last digit (the 8) by roughly half a digit…. to +/- 0.00005 L or +/- 0.05 mL.

Note: Pay attention to units. Depending on which units you choose for R, unit conversion may be necessary.

PROBLEM 6: Error Propagation

The rate constant for the reaction

$$2DI \rightarrow D_2 + I_2$$

is measured at two temperatures with the given estimated uncertainties:

$k_{660} = (1.2 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $660 \pm 2K$

$k_{660} = (1.8 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $720 \pm 2K$

A. Calculate the activation energy E_{act} for the reaction using

$$ln\left(\frac{k_2}{k_1}\right) = -\frac{E_{act}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

B. Assuming the above equation is a correct expression for E_{act}, what is the uncertainty in E_{act}?

Hint

The calculation of E_{act} using the given data is relatively straightforward. The error in the value of E_{act} is a propagation of the uncertainty of the two k values and two T values. The function is complicated enough that it should be addressed using partial derivatives (Equation 3.2.6). There is no one simple shortcut in this case, but if the function is broken down into simpler functions, then error can be determined in a step-wise fashion using the shortcuts.

PROBLEM 7: Error Propagation

In the method of Clement and Desormes, the heat capacity ratio of an ideal gas is determined from the manometrically determined values of P_1, the gas pressure at temperature T_1; P_2, the gas pressure immediately after a reversible adiabatic expansion when the

temperature is T_2; and, P_3, the gas pressure after the gas has warmed back up to temperature T_1. The equation used to calculate the heat capacity ratio is

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{C_V}{R}+1}{\frac{C_V}{R}}$$

where

$$\frac{C_V}{R} = \frac{P_2\left[1-\left(\frac{P_3}{P_1}\right)\right]}{P_3-P_2}$$

Calculate the uncertainty in the heat capacity ratio γ, given the following data:
P_1 = 763.1 ± 0.2 mmHg
P_2 = 757.0 ± 0.1 mmHg
P_3 = 758.7 ± 0.2 mmHg

Hint

> This is propogation of error problem where the error in the value of γ is a propagation of the uncertainty of the three P measurements. The calcaution of γ involves a complex function for which no short cuts are available. I recomend using partial derivatives to arrive at a proper estimation of error in the heat capacity ratio. *Some students have broken the function into separate parts and used shortcuts for each, and have arrived at a reasonable estimation of error…though I find this to be more work than doing it using partial derivatives).*

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3.8: References and Additional Reading

1. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th Edition, McGraw-Hill, New York, NY, 1996, pp 27-89.

2. Bettelheim, F. A., Experimental Physical Chemistry, W.B. Saunders Co., Philadelphia, 1971, Chapter 2.

3. Brownlee, K. A., Statistical Theory and Methodology in Science and Engineering, 2nd Edition, John Wiley and Sons, Inc., New York, New York, 1965, pp 334-338.

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CHAPTER OVERVIEW

4: Absorption Spectrum of Conjugated Dyes

You will measure the absorption spectra of a series of conjugated dyes and then use two theoretical models, the Particle-In-A-Box Approximation and, later, the Hückel Molecular Orbital Approximation to explain the observed spectra.

The general approach to this experiment is adapted from D. P. Shoemaker, C. W. Garland, and J. W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996, p378. The experiment has been revised to suit our laboratory environment.

- 4.1: Prelaboratory Assignment
- 4.2: Introduction
- 4.3: Procedure for Collecting Absorption Spectra and Applying the PIB model
- 4.4: Hückel Calculations Using Hulis (Part II)
- 4.5: Instructions for using the UV-Vis Spectrophotometers
- 4.6: References and Additional Reading
- 4.7: TA Notes

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4.1: Prelaboratory Assignment

In addition to the general pre-lab assignment, please complete the specific tasks listed below. Your assignment must be submitted on Canvas before the deadline.

Pre-Lab assignment for Absorption Spectra of Conjugated Dyes

1. **Find structures and literature values for λ_{max} for the four dyes to be studied in this experiment.** This information is readily available on the Sigma-Aldrich web site (http://www.sigmaaldrich.com) by searching for the name of each dye. Enter a copy of each dye structure and its λ_{max} value(s) in the ELN. If more than one λ_{max} value is listed, record all of them in your notebook. Cite your sources.
   - **Dye #1**: 1,1'-diethyl-2,2'-cyanine iodide
   - **Dye #2**: 1,1'-diethyl-2,2'-carbocyanine chloride
   - **Dye #3**: 1,1'-diethyl-2,2'-dicarbocyanine iodide
   - **Dye #4**: 1,1'-diethyl-4-4'-carbocyanine iodide

   Some additional resources for more precise λ_{max} values are:
   - Hamer, F.M., *A Comparison of the Absorption Spectra of Some Typical Symmetrical Cyanine Dyes*, Proceedings of the Royal Society of London, Series A, 154 (883), 1936, pps. 703-723 (doi: 10.1098/rspa.1936.0078)
   - And/or find other sources for these values by searching for the dye names in Web of Science.
2. **Use your knowledge of HOMO and LUMO to answer the questions below.**
   a. Give a definition of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).
   b. How are HOMO and LUMO related to UV-Vis absorption spectroscopy, specifically in the context of the λ_{max} values of these dyes?
   c. How does the HOMO-LUMO energy gap change as the length of a conjugated π system increases? (consider your knowledge from organic chemistry)
3. Examine the structure of each dye (specifically the length of the conjugated chain between the N atoms). What trend do you expect in the λ_{max} values of this series of dyes? Is your hypothesis consistent with the literature values?
4. Read one of the following (Duke students click here):
   - Change, R., Physical Chemistry for the Chemical Sciences, University Science Books, CA, 2014 (Section 10.9)
   - Chang, R., Physical Chemistry for the Chemical and Biological Sciences, University Science Books, CA, 2000 (Section 14.8)

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4.2: Introduction

Definition: Conjugation

A conjugated π system is one that contains alternating single and double or triple bonds along a chain of carbon atoms. The most common type of conjugation is alternating double and single bonds. A simple example is the butadiene molecule. $H_2C{=}CH{-}CH{=}CH_2$

The Particle-In-A-Box approximation

Electrons in the π-electron system of a conjugated aromatic compound are not restricted to specific nuclei but are free to move throughout the system. In a linear conjugated system the potential energy of the electrons will vary along the chain, being lowest near the nuclei and highest between them. To a first approximation, however, it can be assumed that the potential energy of the electrons is constant along the length of the chain and increases to infinity one bond distance beyond the end atoms of the chain. The electrons may be visualized as being contained in a one-dimensional potential well, of length ℓ, and occupying orbitals of different energy within the well. The wave functions representing the orbitals and the energy levels of the orbitals can be obtained by solving the Schrödinger equation for this system.

For a one-dimensional system the Schrödinger equation takes the form

$$\frac{\partial^2 \psi_{(x)}}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi_{(x)} = 0 \tag{4.2.1}$$

where $\psi_{(x)}$ are wavefunctions that satisfy the equation (eigenfunctions), E is the energy of the particle of mass m, V is the potential energy, and h is Planck's constant.

The potential energy, V, is a constant within the well of length ℓ, where $\psi_{(x)}$ must vanish for $x \leq 0$ and $x \geq \ell$ and $V = \infty$. This allows us to conveniently set V equal to zero in the region $0 \leq x \geq \ell$ when deriving solutions of the equation. The equation then reduces to

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2 \psi_{(x)}}{\partial x^2} = E\psi_{(x)} \tag{4.2.2}$$

Solutions of this equation are $\psi_{(x)} = A \cdot \sin\left(\frac{n\pi x}{\ell}\right)$, where A is a constant and n = 1,2,3,... etc.

Verification that this wave function is indeed a solution of the Schrödinger equation may be obtained by substitution into the left- and right-hand sides of the above equation.

$$\begin{aligned}\text{Left-hand side} &= \frac{-h^2}{8\pi^2 m}\left(\frac{-n^2\pi^2}{\ell^2}\right) A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ &= \frac{-h^2}{8m\ell^2} A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ \text{Right-hand side} &= EA \cdot \sin\left(\frac{n\pi x}{\ell}\right)\end{aligned}$$

The function $\psi_{(x)}$ is a solution of the Schrödinger equation when the energy E of the system has the values $E = \frac{n^2 h^2}{8m\ell^2}$. The allowed energy levels are depicted diagrammatically below.

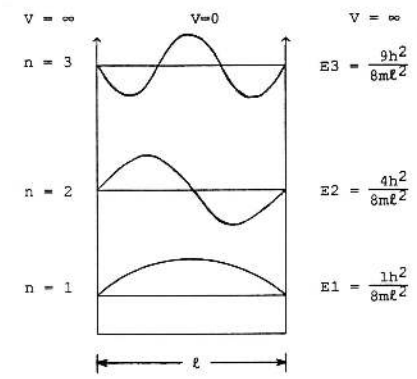


Figure **4.2.1**: The Particle-in-a-Box Model.

The ground state configuration for the conjugated system of a molecule is derived by allocating two electrons to each of the energy levels in accord with the Pauli exclusion principle. Thus, a molecule with Nπ electrons will have the N/2 lowest levels filled and all the higher levels empty. When the molecule absorbs UV-vis light, the energy absorbed is from an electron in the HOMO (where n = N/2) becoming excited to the LUMO where n = (N/2) + 1. The energy change, ΔE, for this transition is

$$\begin{aligned}\Delta E &= E_{\left(\frac{N}{2}+1\right)} - E_{\left(\frac{N}{2}\right)} \\ &= \frac{\left[\left(\frac{N}{2}\right)+1\right]^2 h^2}{8m\ell^2} - \frac{\left(\frac{N}{2}\right)^2 h^2}{8m\ell^2} \\ &= \frac{(N+1)\,h^2}{8m\ell^2}\end{aligned}$$

Since $\Delta E = h\nu = \frac{hc}{\lambda}$ where c is the speed of light and λ is the wavelength, then

$$\lambda = \frac{8mc}{h}\frac{\ell^2}{(N+1)} \tag{4.2.3}$$

Thus if ℓ is known, this relation can be used to calculate the wavelength maximum of the band representing the transition from the ground state to the first excited state in a π-electron system.

PIB model for cyanine dyes:

This Particle-in-th-Box model can be applied to carbocyanine dyes which may be represented, for example, by the resonance forms shown below for the 1,1'- diethyl-4,4'-carbocyanine (cryptocyanine) cation.

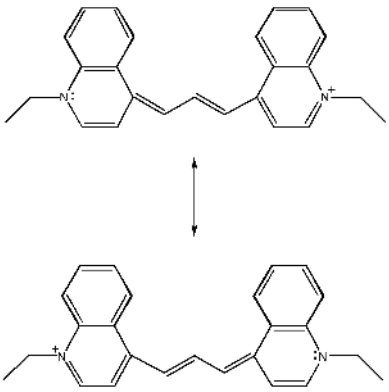


Figure **4.2.2**: The *1,1'-Diethyl-4,4'-carbocyanine (cryptocyanine) cation.* (CC-NC-BY-DUKE CHEM)

The π-electrons in the molecule are regarded as a collection of "free" electrons (independent particles) confined to a box, whose wavefunctions are the square-well functions. Once again, these electrons are distributed among the wavefunctions and energy levels according to Pauli principles, so that the absorption of energy (light) according to this model will follow equation 4.2.3. To

apply the model to the absorbance λ of a specific molecule we need to determine N (number of \pi electrons) and ℓ (length of the conjugated chain).

Number of π electrons in cyanine dyes (N): In the chain between the two nitrogen atoms, each carbon atom contributes one π electron. The π system also includes a total of three additional electrons contributed from the N atoms. Two of these electrons are contributed from the neutral N, while one is contributed from the cationic nitrogen (assuming the resonance structures shown in Figure **4.2.2**). If we denote the number of carbon atoms in the polymethine chain (between the two nitrogen atoms) by p, then N, the number of π-electrons, is p + 3.

$$N = p + 3 \tag{4.2.4}$$

Where N is the number of π electrons in the system, and p is the number of carbon atoms between the nitrogen atoms.

Approximation of ℓ in cyanine dyes: The total length of the potential well is taken to be the length of the shortest carbon chain between the nitrogen atoms *plus one bond length at each end*. Assuming that the length of one bond is $1.39x10^{-8}$ cm, an approximation for \(\ell]) is

$$\ell = (p + 3)a \tag{4.2.5}$$

where $a = 1.39x10^{-8}$ cm is the mean distance between atoms in the chain.

PIB model for Cyanine Dyes: Substituting 4.2.4 for N and 4.2.5 for ℓ in equation 4.2.3 yields:

$$\lambda = \frac{8mca^2}{h}\frac{(P+3)^2}{P+4} \tag{4.2.6}$$

If polarizable groups are present at the ends of the chain, then the potential energy of the π-electrons in the chain does not rise so steeply at the ends. This results in lengthening of the box length, ℓ, which can be incorporated into equation 4.2.6 through the addition of a new "lengthening" parameter, γ, resulting in

$$\lambda = \frac{8mca^2}{h}\frac{(P+3+\gamma)^2}{P+4} \tag{4.2.7}$$

where γ should be a constant for a series of dyes of a given type and should lie between 0 and 2. If such a series is studied experimentally, the empirical parameter γ may be adjusted to achieve the best fit to the data.

The Hückel Molecular Orbital (HMO) model

The molecular orbital (MO) energy level diagrams of a conjugated π- system can be constructed using a set of approximations suggested by Erich Hückel. The Hückel Molecular Orbital (HMO) method is not traditionally approached as an ab-initio quantum calculation (from theory alone), but is usually used as an empirical method (includes experimental data) for doing quantum calculations. This means that some number of adjustable parameters appear in the theory, and these parameters are determined by comparison with experiment (such as the electronic spectra of dye molecules). If the theory is successful, it can be used to predict the spectra and properties of other conjugated systems once the values of the adjustable parameters have been set for some set of reference compounds.

The Hückel model assumes that a π-molecular orbital, Ψ, delocalized over n atoms can be written as a linear combination of n atomic orbitals (LCAO) ϕ_i

$$\Psi = \sum_i c_i \phi_i \tag{4.2.8}$$

where the ϕ_i's are the atomic p_z orbitals on the atoms i (z is perpendicular to the molecular plane). The corresponding one-electron π density at atom i is given by

$$\rho_{i\pi} = c_i^2 \tag{4.2.9}$$

The energy E and the coefficients c_i for the ground state are determined by use of the *variation principle*, which says that one should choose the coefficients such that

$$E = \frac{\int \Psi H \Psi d\tau}{\Psi^2 d\tau} = minimum \tag{4.2.10}$$

Here the Hamiltonian, H, is an effective one-electron energy operator whose explicit form need not be specified in the empirical HMO approach. The variation principle ensures that the lowest-energy state is as close as possible to the true energy, and the coefficients are obtained from the minimization relations

$$\frac{\partial E}{\partial c_i} = 0; \quad i = 1 \ldots n \tag{4.2.11}$$

This results in n equations of the form

$$\begin{array}{cccc} c_1 (H_{11} - S_{11}E) + & c_2 (H_{12} - S_{12}E) + & \ldots & c_n (H_{1n} - S_{1n}E) = 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ c_1 (H_{n1} - S_{n1}E) + & c_2 (H_{n2} - S_{n2}E) + & \ldots & c_n (H_{nn} - S_{nn}E) = 0 \end{array} \tag{4.2.12}$$

In these equations, $H_{ii} = \int \phi_i H \phi_i d\tau \equiv \alpha_i$, called the ***Coulomb integral***, is the energy of an electron in a 2p orbital on atom i, while $H_{ij} = \int \phi_i H \phi_j d\tau \equiv \beta_{ij}$, the *resonance* or ***bond integral***, represents the interaction energy of two atomic orbitals on atoms i and j. Both α_i and β_{ij} are negative energy quantities. $S_{ij} = \int \phi_i \phi_j d\tau$ is the overlap integral, which, in the simplest approximation, is taken to be 1 if i = j, and 0 otherwise. For a π system involving only carbon atoms, $\alpha_i \equiv \alpha$ and Equations 4.2.12 take the form

$$\begin{array}{cccc} c_1 (\alpha - E) + & c_2 \beta_{12} + & \ldots & c_n \beta_{1n} = 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ c_1 \beta_{n1} + & c_2 \beta_{n2} + & \ldots & c_n (\alpha - E) = 0 \end{array} \tag{4.2.13}$$

These equations have a nontrivial solution only if the corresponding ***secular determinant*** vanishes:

$$\begin{vmatrix} \alpha - E & \beta_{12} & \ldots & \beta_{1n} \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \beta_{n1} & \beta_{n2} & \ldots & \alpha - E \end{vmatrix} = 0 \tag{4.2.14}$$

The HMO method makes several simplifying assumptions. The first of these are as follows:

1. The π-orbitals are considered separately from the σ-orbitals. The σ-orbitals only enter indirectly in so far as they determine the geometry of the molecule.
2. Treat all the carbon atoms as identical. This means that all the Coulomb integrals (α) are equal.

The next stage is to express the π-orbitals as LCAOs of the C2p-orbitals, ϕ. In ethene (CH_2=CH_2) we would write

$$\Psi = c_A (\phi_A) + c_B (\phi_B) \tag{4.2.15}$$

and in butadiene ($\mathbf{H_2C{=}CH{-}CH{=}CH_2}$)

$$\Psi = c_A (\phi_A) + c_B (\phi_B) + c_C (\phi_C) + c_D (\phi_D) \tag{4.2.16}$$

The optimum coefficients and energies are found by the variation principle. This involves solving the secular determinant, equation (Appendix B.7), which for ethene would be

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{4.2.17}$$

and its roots are $E = \alpha \pm \beta$. The state with energy $\alpha + \beta$ corresponds to the bonding combination (β is negative) and $\alpha - \beta$ corresponds to the antibonding combination, Figure 4.2.1.



Figure 4.2.1: The Hückel Molecular Orbital Energy Levels of Ethene. Two electrons occupy the lower π-*orbital.* (CC-NC-BY-DUKE CHEM)

Each carbon atom supplies one electron to the π-system and the bonding orbital is occupied by an electron pair. The π-electronic energy of ethene is therefore $2\alpha + 2\beta$. The excited state of the molecule, when an electron is excited into the π^*-orbital, lies about 2β above the ground state.

In the case of butadiene, the approximations result in the determinant

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{4.2.18}$$

This expands into the quadratic equation

$$x^4 - 3x^2 + 1 = 0; \quad x = \frac{(\alpha - E)}{\beta} \tag{4.2.19}$$

with roots x^2 = 2.62, 0.38. Therefore, the energies of the four LCAO-MOs are

$$E = \alpha \pm 1.62\beta \quad and \quad E = \alpha \pm 0.62\beta \tag{4.2.20}$$

as shown in Figure 4.2.2. There are four electrons to accommodate, and so the ground state configuration is $1\pi^2 2\pi^2$.



Figure 4.2.2: The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π-orbitals. The four p-electrons (one supplied by each carbon atom) occupy the two lower (\pi \)-orbitals. Note that the orbitals are delocalized. (CC-NC-BY-DUKE CHEM)

An important point emerges when we calculate the total π-electron binding energy in butadiene and compare it with what we find in ethene. In ethene the total energy is $2(\alpha + \beta) = (2\alpha + 2\beta)$; in butadiene it is $2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = (4\alpha + 4.48\beta)$. Therefore, the energy of the butadiene molecule lies lower by $(4\alpha + 4.48\beta) - 2(2\alpha + 2\beta) = 0.48\beta$ (roughly –36 kJ mol^{-1}) than the sum of two π-bonds. This extra stabilization of a conjugated system is called the ***delocalization energy.***

To obtain the wavefunction for a given energy state, E_j, one substitutes E = E_j into Equation 4.2.13 and solves for the jth set of coefficients c_{j1}, c_{j2}, ..., c_{jn}. This process actually gives only ratios of coefficients; to determine numerical values, we add the

normalization condition

$$\int \Psi_j^2 d\tau = \sum_i c_{ij}^2 = 1 \tag{4.2.21}$$

The four Hückel molecular orbitals for 1,3-butadiene are

$$\begin{aligned} \Psi_1 &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\ \Psi_2 &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 \\ \Psi_3 &= 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 \\ \Psi_4 &= 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4 \end{aligned} \tag{4.2.22}$$

In addition to π-electron energies and wavefunctions, the HMO approach also allows one to calculate several other quantities of chemical interest, such as electron densities, bond orders and free valence.

Heteroatoms

Heteroatoms (X) may be incorporated in the HMO method by appropriate changes in the empirical α and β parameters associated with each atom and bond. A common example would be the inclusion of the π-electron contribution from the nitrogen atom in pyridine. These changes are incorporated in units of the standard α_0 and β_0, usually of benzene, by use of the definitions

$$\alpha_X = \alpha_0 + h_X\beta_0 \tag{4.2.23}$$

$$\beta_{CX} = k_{CX}\beta_0 \tag{4.2.24}$$

Calculations involving such changes can be made by solving the secular equations. Unfortunately there remains considerable controversy concerning the specific values to be used for the h and k-parameters of various heteroatoms. Part of the problem is that there are several variations of MO theory and each will yield somewhat different parameter values with a given application.

We should distinguish, for example, the nitrogen in pyridine from a pyridinium nitrogen. In the former case, the heteroatom contributes two electrons to the π-system; in the latter case it contributes one. In the second part of the analysis of your experimental data, you will use a "canned" HMO computer program to determine the energy levels and molecular orbitals of the π-states of the dye molecules (as a function of β). By comparison of these results with your experimental data, you will determine an empirical value for β. Note that this program incorporates values for the heteroatom parameters h and k. You will need only to specify the location and type (e.g., pyridine-type nitrogen) of each heteroatom in the molecule to be studied.

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4.3: Procedure for Collecting Absorption Spectra and Applying the PIB model

The ELN Template that can be used by your group during data collection for this part of the experiment is here: Dyes ELN Template

Please review the guidance on ELN templates.

This template is provided as a guide so that you know what data and information should be kept in a notebook. You may keep your notebook in any way you'd like, but it must be submitted in the form that is legible and can be submitted as a pdf on Gradescope.

Materials

- **Equipment:**
  - UV/Vis spectrometer (you will use either an Agilent Cary 60 Spectrometer or an Agilent Cary 100 Spectrometer)
  - Cuvettes (you will use glass cuvettes, which are optically transparent to visible (but not to UV) light)
- **Reagents:**
  - Reagent grade methyl alcohol (methanol)
  - Stock solutions of four polymethine dyes dissolved in methanol (solutions are approximately 10^{-4} M):
    - 1,1'-diethyl-2,2'-cyanine iodide
    - 1,1'-diethyl-2,2'-carbocyanine chloride (also known as pinacyanol chloride)
    - 1,1'-diethyl-2,2'- dicarbocyanine iodide
    - 1,1'-diethyl-4,4'-carbocyanine iodide (also known as cryptocyanine)

Note

The cyanine dyes used in this experiment are toxic irritants. Solutions of these dyes in methanol must be handled wearing gloves at all times. Perform all dilutions in a fume hood. Read the safety data sheets for these dyes (http://www.sigmaaldrich.com) prior to the lab.

Procedure

Determine Experimental λ_{max} from Absorption Spectra:

1. Perform instrument diagnostics tests using the Validate program. (See Operation Instructions for Agilent Cary Spectrophotometers)
2. Fill four standard glass cuvettes approximately 4/5 full with methanol (about 2.5 - 3 mL). Then add 3-15 drops of one dye to each cuvette. Add enough dye that you can see a light color for each solution.
3. Use the UV-vis to record the spectrum of each dye. If needed, adjust the solution concentration of one or more of the dye samples until the peak maximum absorbance reading is approximately 0.2 to 1.0 absorbance units.
4. Annotate the resulting overlay display of all four dyes, noting which dye is associated with each trace and the associated λ_{max} value.

Use Particle in the Box model to calculate theoretical λ_{max}

1. Determine γ for the series of homologous dyes.

   Use the Matlab script called ***dye_v3*** to determine the "best" value of γ This script will prompt you for information about the four dyes, and the experimentally measured values of λ_{max}. It will solve the particle in a box equation for λ, separately for each dye, over the range of γ from 0.00 to 2.00 in steps of 0.01. It will sum the absolute deviation between the calculated λ and your experimentally measured λ_{max} for each value of γ, for each dye. It will output the one value of γ that produces the smallest summed deviation over the series of the four dyes. That is, the script will calculate the value of gamma which gives the best fit

between peak wavelengths calculated using the free electron model and peak wavelengths measured experimentally. To use this script, start up a Matlab session and type the dye_v3 command:

```
dye_v3
```

Then simply enter the information as prompted by the script.

2. Use the output value of γ to calculate a value for λ_{max} for each of the four dyes using the equation

$$\lambda = \frac{8mca^2}{h}\frac{(p+3+\gamma)^2}{p+4} \tag{4.3.1}$$

(Remember that the value of the average bond length of a carbon-carbon bond, a, is 1.39 x 10^{-8} cm the mass of the electron, m, is 9.1 x 10^{-31} kg.)

Thinking about the Data

Be sure to address all of the following in your ELN.

1. **What is the experimental maximum wavelength for each dye solution?**
   Carefully examine all spectra (absorbance versus λ) and determine the wavelength of maximum absorbance (λ_{max}), for each dye. Enter your data with appropriate certainty in a data table in your ELN.
2. **What is the uncertainty in your experimental peak wavelength determinations?**
   Estimate error in each assignment of (λ_{max}) considering both the instrument tolerance indicated by the validation procedure (the wavelength accuracy test) and the data interval that was used during data collection.
3. **How do your results compare to literature values?**
   Compare your experimental results for λ_{max} with literature values for λ_{max} that you found as part of the pre-lab assignment.[10-12,14]
4. **What is the energy of electronic transition (absorption)?**
   For each dye, calculate the energy (eV and kJ/mol) of the *experimentally* observed λ_{max}.
5. **Determine γ for the series of homologous dyes.**
   Record the calculated value of γ in your ELN.
6. Calculate the **absolute error** between your experimental (from the spectrum) values and the literature values. Calculate both the absolute error and the percent deviation between your experimental (from the spectrum) and your calculated theoretical (Particle-in-a-box Model) λ_{max} results and record them in your notebook.
7. Tabulate your data in the format shown below.

		WAVELENGTH (nm)					
Dye #	Name of Data file	λ_{max} Literature*	λ_{max} Experimental		λ_{max} Particle in a Box		
			Value (nm)	Absolute Error (nm)	Value (nm)	Absolute Error (nm)	% Error
1			±				
2			±				
3			±				
4			±				
* reference for your literature values goes here							

8. Use the table above as the basis for a discussion of your results as follows:

a. Compare your experimental λ_{max} values (from your spectra) with literature λ_{max} values. In your discussion, include a comparison of these λ_{max} values in the context of their absolute errors (the absolute error between your experimental result and the literature) and how that compares to the uncertainty (± value) of the measured and reported λ_{max} values.

b. Compare the results of the Particle in the Box (PIB) model calculations of λ_{max} to the values derived from experiment.

- As part of this comparison, discuss the agreement of computational to measured values in terms of the absolute error between computational and experimental values.
- Also describe the relationship between λ_{max} and p for the measured λ_{max} values, and compare this trend with that of the computational results.

c. Discuss how well the dyes fit into the trend described in part 8b. If they do not all fit the trend identified for a homologous series, explain why in the context of the PIB model and the structure of each dye.

d. How is the PIB model useful and what might be done to improve the results?

9. Calculate the wavelength (in nm) and minimum energy (eV) of the molecule 1,3,5,7-octatetrene ($CH_2{=}CHCH{=}CHCH{=}CHCH{=}CH_2$) using the particle-in-a-box model. What color does the molecule absorb from white light? What color does it then appear to the eye?

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4.4: Hückel Calculations Using Hulis (Part II)

The ELN template for this part of the experiment is here: ELN01_2_Huckle2022.docx

Huckle Calculation Tasks

Perform the tasks listed here using the instructions for using Hulis that are given below.

1. Perform Huckle Molecular Orbital (HMO) calculations for each of the four dyes. In the HMO analysis, omit the ethyl groups since they are not part of the conjugated network. Save a screen-shot image of the entire program window showing the structure and the orbital diagram before moving on to the next one.
2. Calculate the energy difference, ΔE, between the HOMO and LUMO levels (in terms of β) for each dye.
3. Plot the experimentally observed ΔE's (kJ/mol) (from UV-vis in Part I, plot as y or ordinate) vs the calcuated HMO ΔE's (abscissa or x).
   a. From the least-squares slope of the resultant line, determine a semiempirical value for β (β is the spectroscopic exchange integral). Report the uncertainty in β.
   b. Compare your derived value of β with the accepted range for this constant (a.k.a spectroscopic exchange integral), which is – 250 to – 350 kJ/mole.[9]
4. Use your value of β to calculate the energy difference, ΔE, between the HOMO and LUMO levels in units of kJ/mol and eV for each dye. Using these energies, calculate the wavelength (nm) at which you would expect to observe this HOMO → LUMO transition for each dye, using the HMO model.
5. Calculate the percent error between your calculated HMO results your experimental values. Tabulate your data in the format shown below.

	WAVELENGTH (nm)						
Dye #	λ_{max} Literature*	λ_{max} Experimental		λ_{max} Particle-in-box		λ_{max} HMO	
		Value (nm)	Absolute Error (nm)	Value (nm)	% Error (from exp.)	Value (nm)	% Error (from exp.)
		±					
		±					
		±					
		±					

* reference for your literature values goes here

6. Use this table as the basis for discussion of your results. Which theoretical model gives the best fit to the experimental data, and why? Are the results for each dye equally satisfactory? If your answer is no, explain why you think this is so. How are these models useful and what might be done to improve the results?
7. Calculate the wavelength (nm) and minimum excitation energy (eV) of the molecule CH2=CHCH=CHCH=CHCH=CH2 using the HMO model program. In calculation use your value of β to convert to electron volts. What color does the molecule absorb from white light? What color does it then appear?

Instructions For Using The Program "Hulis" ver. 3.0.x

Note

Hulis is a Java applet. Java must be installed to run the applet. You are welcome to run it from your own laptop if Java is installed. But for your convenience in the event that you do not want Java on your computer, the program is available on all of the lab computers.

Hulis and Java can be downloaded here: Huckel Theory and HuLis

1. Double-click on the Hulis icon to Start the Program
2. Running the Program:
   The main screen shows a molecule builder. Highlight **Build** on the left side of the screen if it is not already highlighted when the program starts.

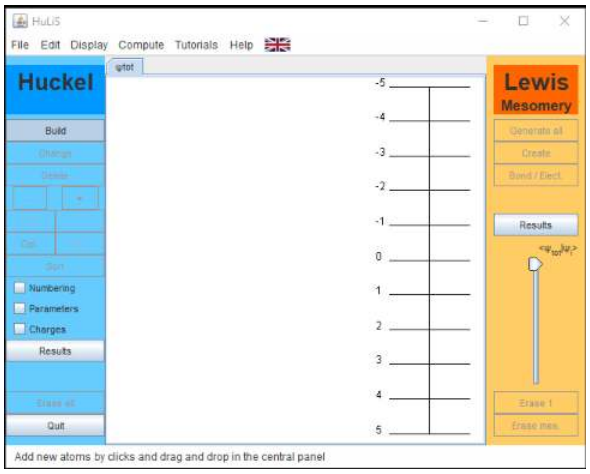


Figure 4.4.1: The Hulis Main Screen. (CC-NC-BY-DUKE CHEM)

   To build a molecule, for example, Dye 1, begin by clicking anywhere in the blank window in the center of the screen. A CH_3 group should appear. Click on one of the available hydrogens to add a conjugated carbon to your molecule. As you add carbons to form the first ring, you will see the orbital diagram for the molecule appear in the right-hand panel of the program.



   You can follow the electron count from this pane of the program window. After putting 6 carbons to form the ring, you will need to form a bond between the two open and adjacent carbons. To do this, simply click on one of the open carbons and drag a bond over to the adjacent open carbon. The hydrogens will disappear and a delocalized C-C bond will form.



3. Continue adding carbon atoms as appropriate to form the template molecule. When you are done your structure will look like this:

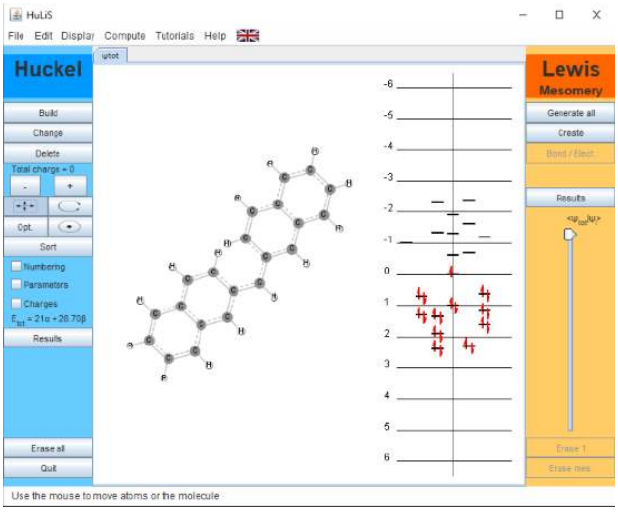


Figure **4.4.2**: Dye 1. Note that for the purposes of a Hückel calculation the ethyl groups are omitted (CC-NC-BY-DUKE CHEM)

> **Note**
>
> You can rescale the display on the screen using Zoom out from the Display menu. You can also move, rotate, and center the molecule in the display window with the appropriate control buttons in the left-hand (blue colored) pane of the program window. In the image above the Move button is currently highlighted.

4. You now need to change two of the carbon atoms to nitrogen to complete the structure. Click on the Change button in the left-hand pane, and then double-click on the appropriate carbon in your structure. A Change Atom box appears. Select =NR to change this to the pyridinium group. Check to be sure the value in the Hx box = 0.51. Click on OK. Now change the other carbon to a nitrogen in the same way, but this time select the –NR2 option. Be Sure the value in the Hx box = 1.37. Click OK. Finally, make the molecule a cation by clickingh the + in the left-hand pane to increase the Total charge to 1. You final molecule will look as shown below.



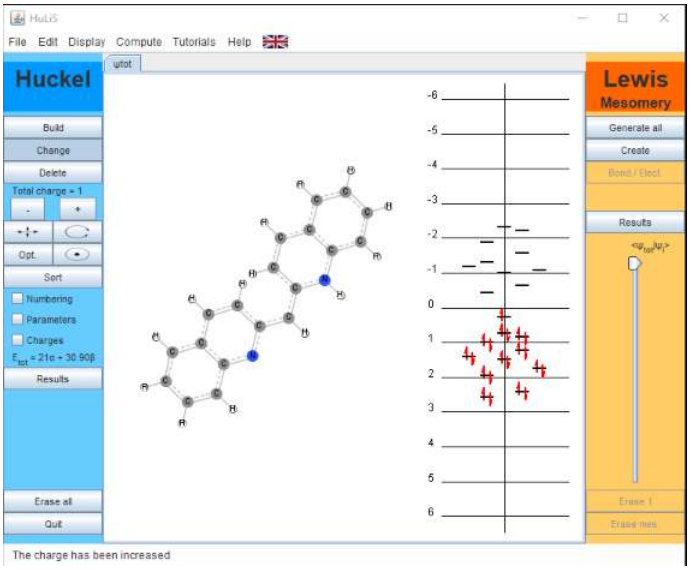
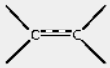


Figure **4.4.3**: 1,1'-Diethyl-2,2'-Cyanine Iodide. The ethyl groups are omitted to simplify the calculations. (CC-NC-BY-DUKE CHEM)

Looking at the orbital diagram in the right-hand (orange) pane of the program screen you will see the occupied and unoccupied orbitals, as calculated by the simple Hückel approximation. You can see that the 21 pi-electrons in the molecule occupy the first 11 pi-orbitals; the HOMO to LUMO transition occurs between the 11th and 12th pi-orbital.

5. Click on the Results button, and a Results window appears with significant information about the Hückel calculation. Please note the following things:

   a. As you scan down the Hamiltonian matrix check to see that the Coulomb and Exchange integrals for heteroatoms and carbon-to-heteroatom bonds are as shown in the table below. If you need to see how your atoms are numbered in your structure to make it easier to find them in the Result table, put a check in the Numbering box in the left hand pane of the program window.

Atom	Bond		Number of p-Electrons	Coulomb Integral	Exchange Integral
C			1	0.00	1.00
N		Pyridine	2	1.37	0.89
N		Pyridinium	1	0.51	1.02

   b. In the Orbitals section of the Results box count over the appropriate number of orbitals (11 in the case of Dye 1), and record the results for the HOMO and LUMO in this molecule.

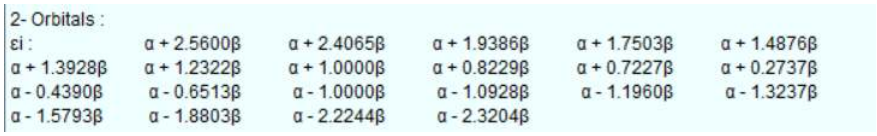


Figure 4.4.4: Orbital Energies for Dye 1. (CC-NC-BY-DUKE CHEM)

Notice that in this case the energy of the HOMO is $\alpha + 0.2737\beta$; and, the energy of the LUMO is $\alpha - 0.4390\beta$.

> **Note**
>
> **NOTE**: you can change the number of digits in the display from **Preferences**, under the **File** menu.

Close the Results Box.

   c. To get a visual representation of the pi-molecular orbitals generated in the Hückel program, simply click on one of the orbitals in the right-hand pane of the program window. The orbital will appear on top of the molecule in the main screen. The image below is of the HOMO.

   You can turn off the orbital display from your molecule by clicking below the orbitals in the right-hand pane of the program window. Save a screen-shot image of the entire program window showing the structure and the orbital diagram.

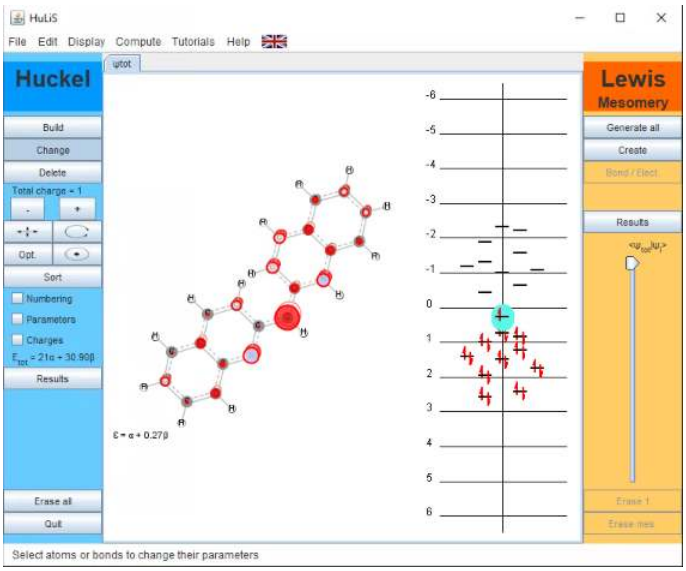


Figure 4.4.5: The Highest Occupied Molecular Orbital in Dye 1. (CC-NC-BY-DUKE CHEM)

This page titled 4.4: Hückel Calculations Using Hulis (Part II) is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

4.5: Instructions for using the UV-Vis Spectrophotometers

Below are the instructions for using the Agilent Cary Series UV-Visible spectrophotometer in the Absorption Spectrum of Conjugated Dyes experiment.

There are two sample holders in the instrument. The Sample is placed in the front holder. A Reference cuvette can be placed in the back holder or the back holder can be left empty (no cuvette).

Start-up:

At the begriming of the lab period, check to confirm that the UV-vis is switched "on". There are several UV-vis instruments in the Duke Chemistry undergraduate learning spaces. Be sure you discuss which instrument you will use with your instructor.

- The **Cary 100** instruments have tungsten and deuterium lamps that must be warmed up for approximately 1 hour prior to use for best results. However, since we are only doing qualitative analysis, it is sufficient for this experiment to warm them up for only a couple of minutes.
- The **Cary 60** instrument has a xenon flash lamp, which does not require warm up.

How to turn on the Cary 100: 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.

How to turn on the Cary 60: The Cary 60 should not be turned off. But, if it is off, check that the cell holders are empty and press the power button on the instrument.

Validating the Wavelength Accuracy of the UV-Vis Spectrometer

1. Open the Validation Software by clicking the  icon from the Windows main screen. After a few moments the software 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 in the upper center turns green, the system is ready. You will see absorbance in the upper left and wavelength in the upper right.

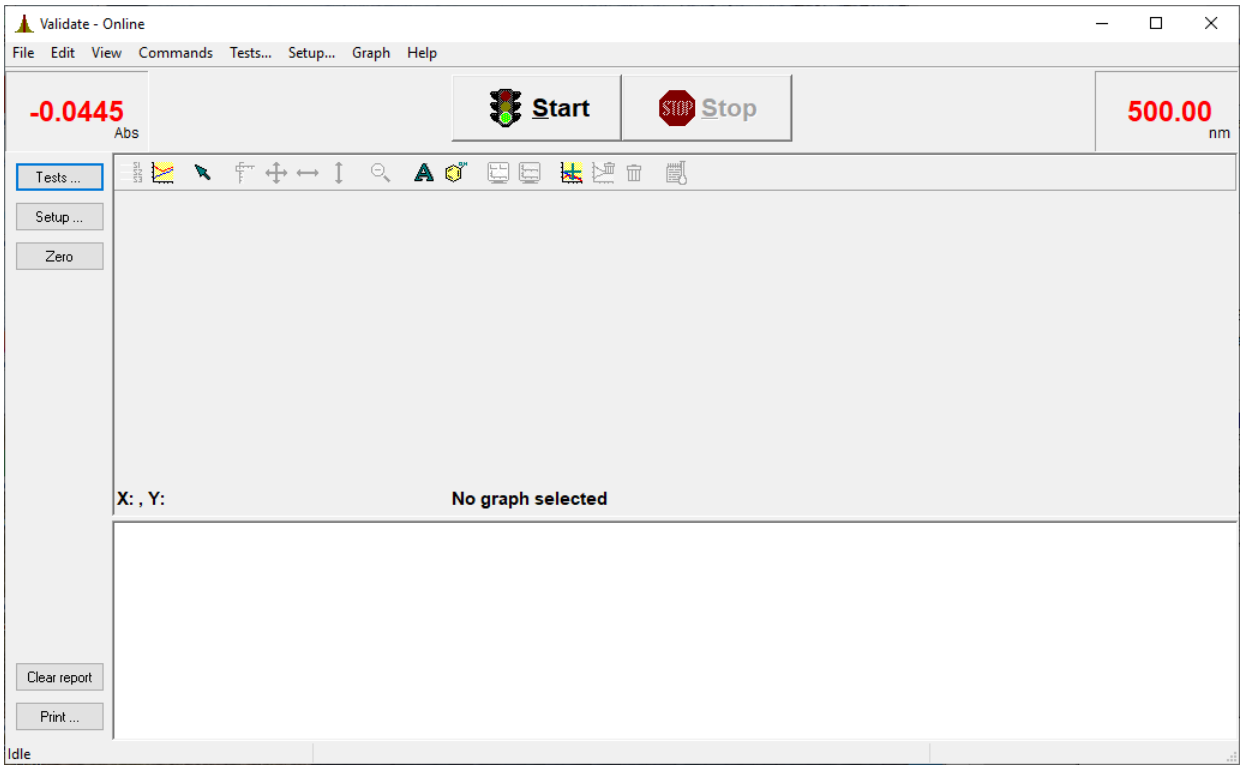


Figure **4.5.1**: The Validate Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the Tests ... button and select Instrument Performance Tests. While you could run all of the tests listed, the one that is required is the Wavelength Accuracy test. Depending on whether you are using a Cary 100 or a Cary 60, this test with use either the D2 or Xe lamp. Be sure to note which instrument you are using and which lamp is used for the wavelenght validation. Using the button, you can remove all tests from the list except for the Wavelength Accuracy. The screen should look as shown here.

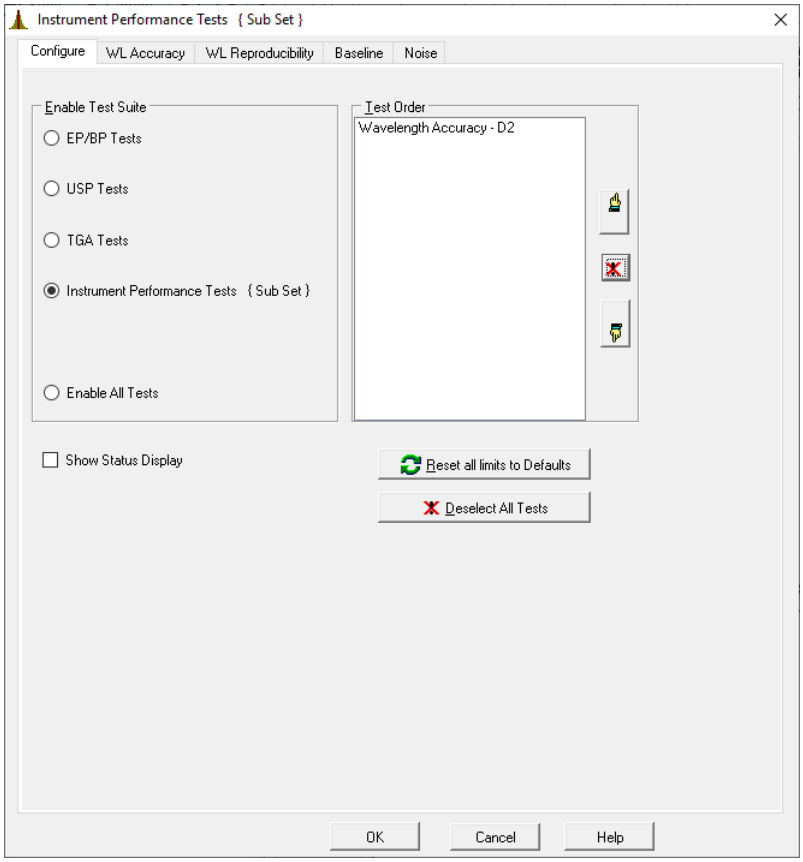


Figure **4.5.2**: Selecting the Wavelength accuracy test. (CC-NC-BY-DUKE CHEM)

3. Click the Setup ... button and, when the setup screen appears, place your names in the Name line; and, the name of the test in the comments box. In the Options section select Auto Print, Results and Graph. Data Form and Company Logo should not be checked. % Page Height set at 50 is fine.
4. Click OK to return to the main screen.
5. Check the sample compartment to be sure that there are no samples in the instrument and that there is nothing blacking the light path. Gently close the sample compartment.
6. Click Start to begin wavelength accuracy test. As the test proceeds the emission spectrum from the lamp will be displayed. At the conclusion of the test, a report will be generated on the screen. **Include these data in your laboratory report**. Check to be sure that the difference between the expected and observed peak positions is one the order of $\pm 0.2 - 0.4$ nm. If it is greater than that, consult your TA or your Instructor before proceeding further.

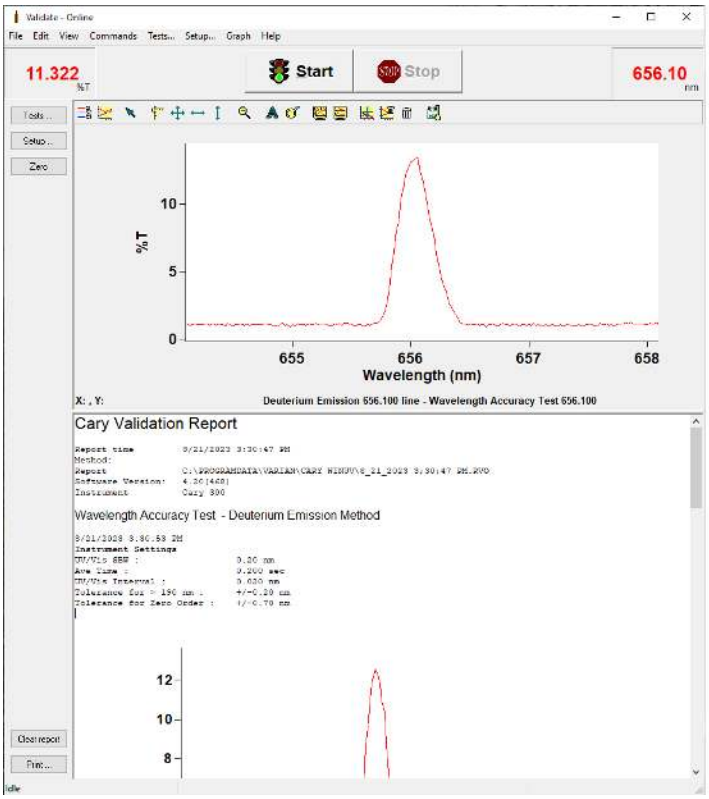


Figure **4.5.3**: Results of the a Wavelength Accuracy Test using the Deuterium lamp emission on a Cary 100 series spectrophotometer. (CC-NC-BY-DUKE CHEM)

7. Exit the Validation software and return to the Windows Desktop.

Absorption Spectrum of Conjugated Dyes

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.

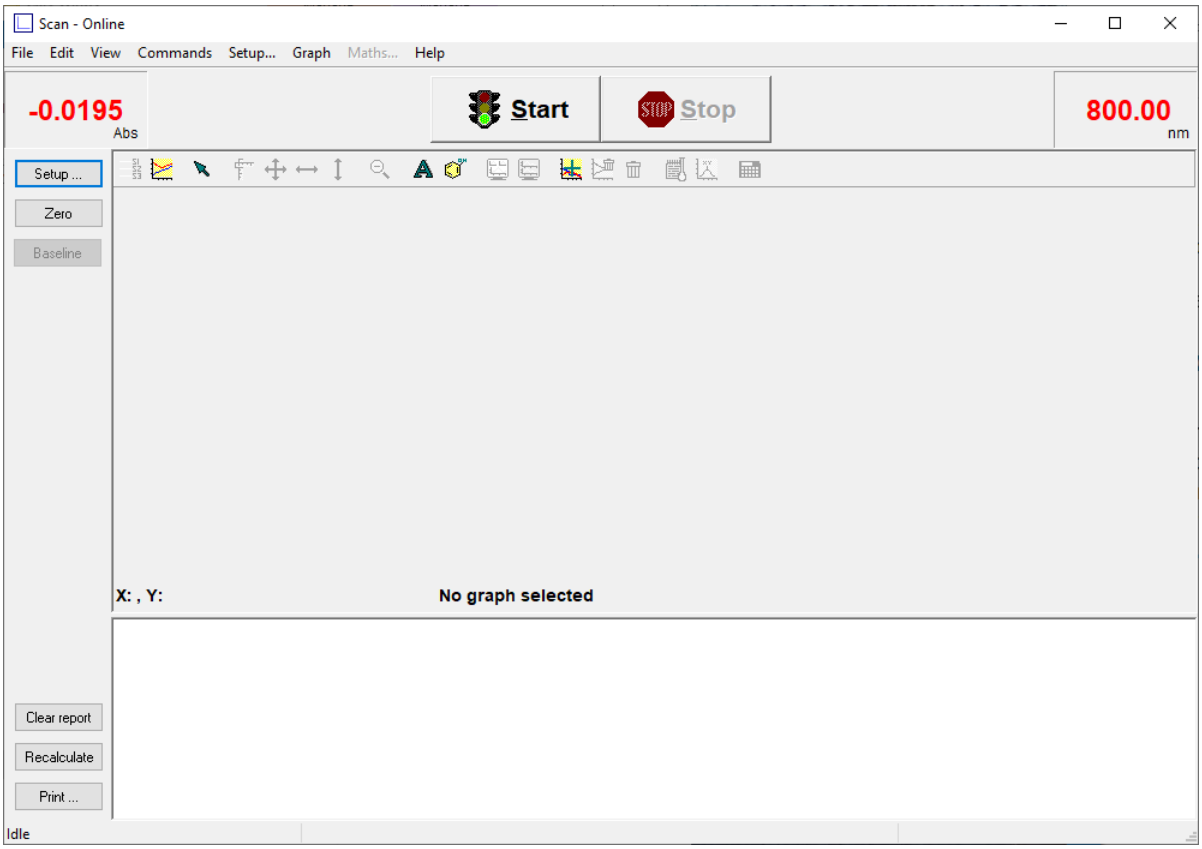


Figure 4.5.4: The Scan Module Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the Setup ... button and wait for the setup screen to appear. Select, first, the Cary tab to begin setting parameters for your sample runs. Under X-mode, the Mode should be set to nanometers and your scan range from 750 nm to 400 nm. Under Y-mode, the Mode should be set to absorbance and the range from (-)0.05 to 1.0. The Ave time should be 0.1 seconds and the Data interval should be set to 1 nm. This will yield a Scan Rate of 600 nm/min.

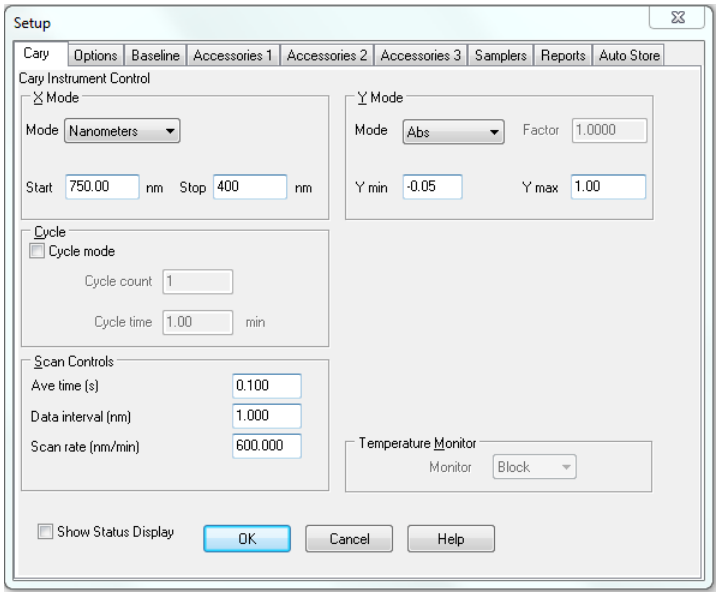


Figure 4.5.5: The Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

3. Select the Options tab on the setup screen and set the Spectral Band Width (SBW) to 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 Overlay Data.

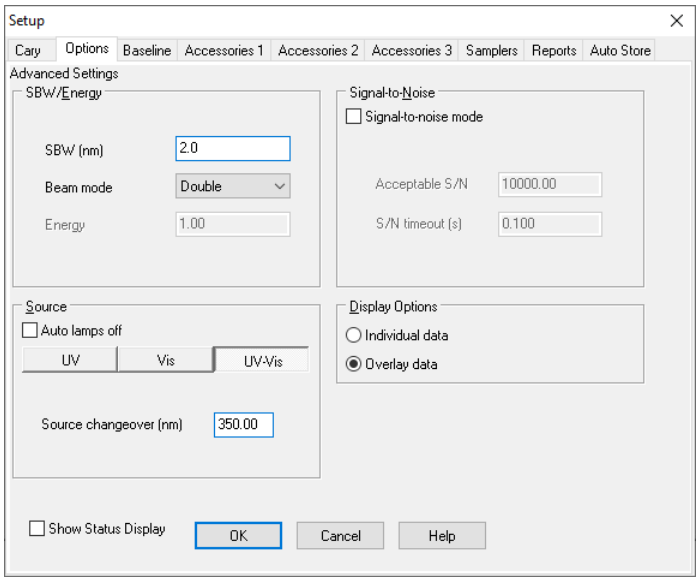


Figure **4.5.6**: The Options Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

4. Finally, select the Reports tab.
   - Put your names in the Name box and the title of the experiment in the Comment box.
   - In the Options box, check Data Form, Graph and Focused trace. Do not check Auto print, or Parameters. Select All Traces. And % Page Height set at 50 is fine.
   - Under Peak Table, put a check in All peaks.
   - Be sure the Include XY pairs table is not checked.
   - Click the Peak Information button, and set the Threshold to 0.200. Put Peaks in the Peak Type box.
   - Click OK to close the Peak information box, and OK again to return to the main screen.

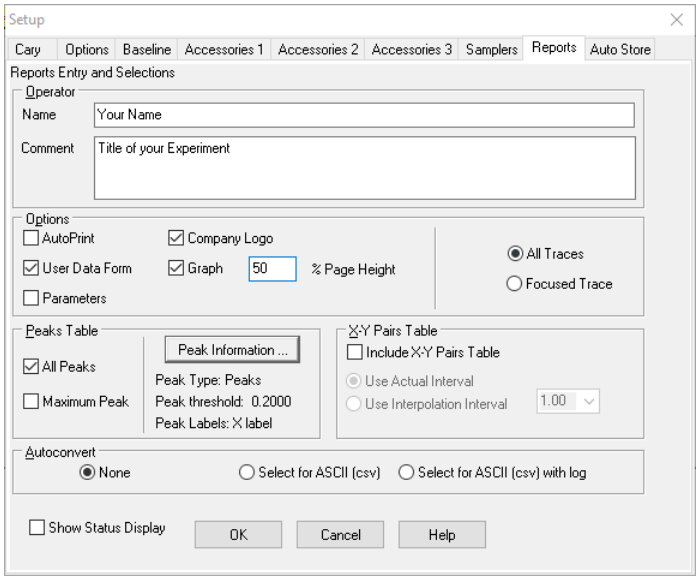


Figure **4.5.7**: The Reports Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

5. Place your first sample in the sample compartment and if you are using a reference cuvette, put your reference in the reference compartment and close the cover.
6. Click Start to begin the run.
7. You will be prompted for a filename. Since you will be running four samples, give the file a general name, for example Dyes with the date (many sample spectra can be stored in a single file).
8. You will then be prompted for a sample name. Place the name of the sample (Dye 1, 2, 3, or 4) in this box.

9. As each run proceeds you will see the spectrum generated in real time on the screen. Make sure the maximum absorbance of each sample is between approximately 0.2 and 1.0; adjust the dye concentration to get the proper absorbance.
10. At the conclusion of each run, place the next sample in the sample compartment and initiate the new scan.

> **Note**
>
> If you didn't select Overlay Data, or if you want to add or remove traces from the overlaid runs on the screen, click the  button at the upper left of the main screen. Select files to add or to remove by checking or removing cheks from available traces shown in the list. Then click OK. Your changes will be made to the main screen.

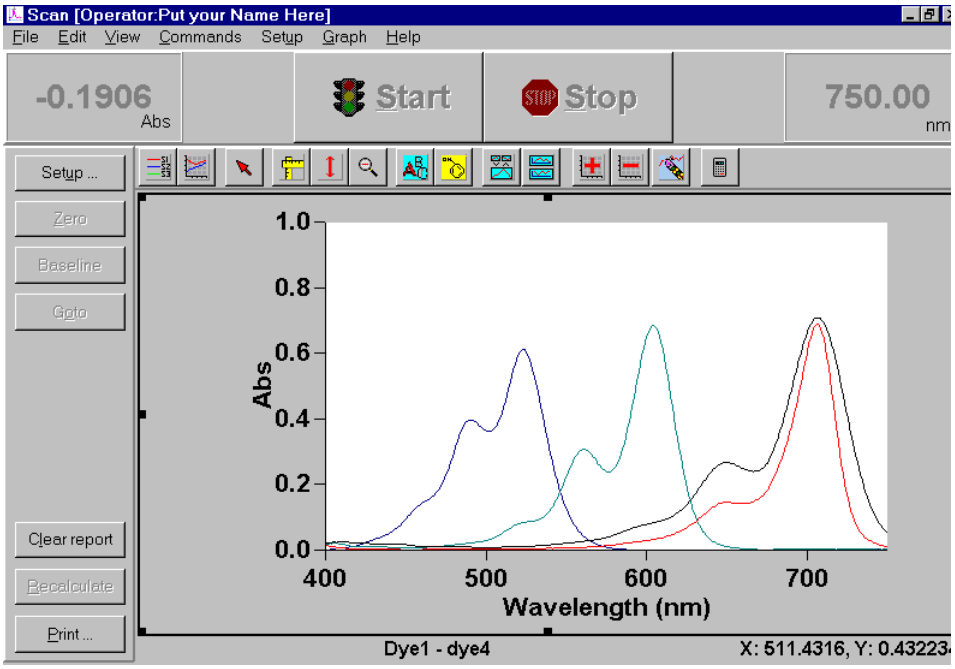


Figure **4.5.8**: The Absorption Spectra of the Dyes. (CC-NC-BY-DUKE CHEM)

This page titled 4.5: Instructions for using the UV-Vis Spectrophotometers is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

4.6: 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. Castellan, G. W., Physical Chemistry, Addison-Wesley, Reading, Mass., 1972, Chapters 19-22.

2. Barrow, G. Physical Chemistry, 3rd ed., McGraw-Hill, New York, NY, 1973, Chapters 3 and 12.

3. Shoemaker, D. P., Garland, C. W., and Nibler, J. W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, NY, 1996, Chapter XIV, Experiment 34.

4. Farrell, T.T., J. Chem. Ed., **1985**, 62, 351.

5. Olsson, L.F., J. Chem. Ed., **1986**, 63, 756.

6. Kuhn, H., J. Chem. Phys., **1949**, 17, 1198.

7. Herzfeld, K.F.; Sklar, A. L. Rev. Mod. Phys., **1942**, 14, 294.

8. Silbey, R. J., Alberty, R.A., and Bawendi, M.G., Physical Chemistry, 4th ed., Wiley, NY, 2005, Chapter 9, Section 9.6; Chapter 11, Section 11.7.

9. Cotton, F.A., "Chemical Applications of Group Theory", Wiley, New York, 1971, Section 7.1 and pp. 366-367.

10. Suzuki, H., "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, 1967, Chapter 17, p. 374.

11. Aldrich Catalog, Aldrich Chemical Company, Inc., 1992., found in FFSC 1113 or online.

12. Venkataraman, K., "The Chemistry of Synthetic Dyes", Academic Press, Inc., NY, 1952, Volume II, Chapter XXXVIII, p. 1155.

13. Streitwieser, A., "Molecular Orbital Theory for Organic Chemists", John Wiley & Sons, Inc., NY, 1967, Chapter 2.

14. Okawara, M., Kitao, T., Hirashima, T., and Matsuoka, M., Physical Sciences Data 35: Organic Colorants, Kodansha, Tokyo; Elsevier, Amsterdam-Oxford- New York-Tokyo, 1988, pp. 318-321.

15. Taubmann, G., J. Chem. Ed., **1992**, 69, 96.

16. Atkins, P.W. Physical Chemistry, 5th ed., W. H. Freeman, NY, 1994, Sections 12.1, 14.9, or, 6th ed., W. H. Freeman, NY, 1997, Sections 12.1, 14.9.

17. Engel, T., Drobney, G and Reid, P., Physical Chemistry for the Life Sciences, Pearson Prentice Hall, NJ, 2008 (Section 14.3).

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4.7: TA Notes

This page is directed toward laboratory teaching assistants, but is deliberately left open for students to read.

TA Notes

After completion of this module students will be able to:

- Use online resources to find expected values for λ_{max} for the dyes
- Follow instructions to operate a UV-visible spectrophotometer
- Apply chemical theories (particle in a box) to explain experimental observations
- Use programing skills and computational software (MatLab) to analyze data
- Practice recording observations in an electronic laboratory notebook (ELN)
- Apply knowledge of chemical theories and data to describe and discuss results

Pre-Semester Preparations

Do the following during the TA training week(s)

1. Check that the materials listed below are available and sufficient for all students to use them. All items are in the prep room on the shelves and in the refrigerator/freezer.
   If they are running low, please create more or inform the instructor. Each group of 3-4 students will need the following:

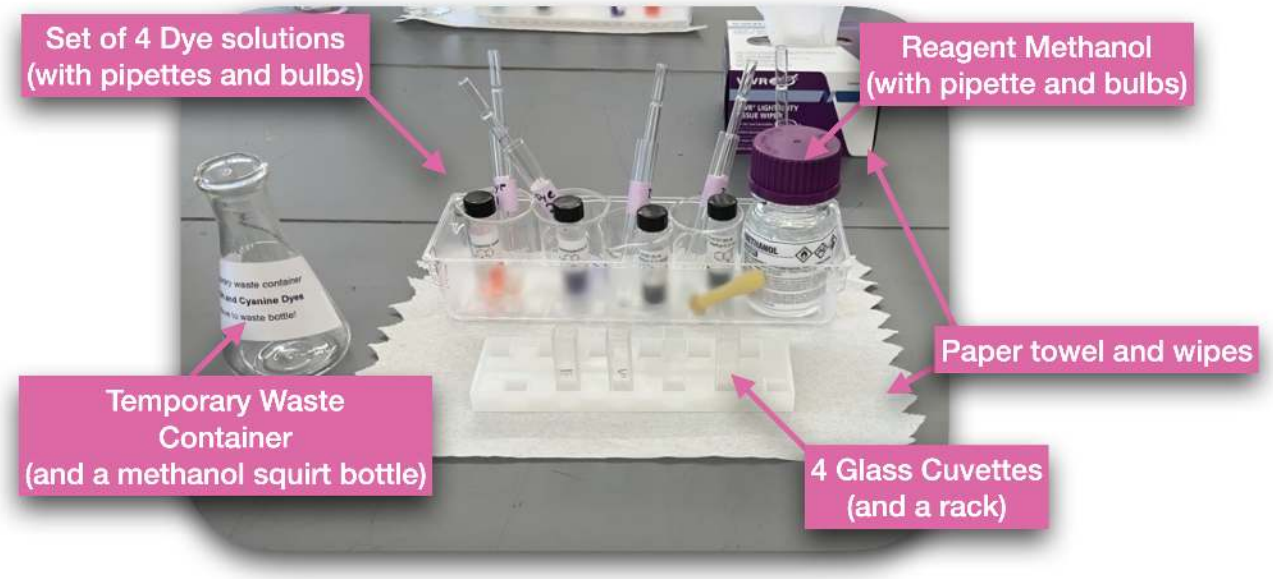


Figure 4.7.1: The materials needed to complete this experiment are shown in this picture. (Kathryn Haas; CC-BY-NC-SA)

   - **Set of 4 Dye solutions**: One set of the dye solutions
   - **Methanol reagent**: One small bottle of reagent methanol for diluting the dye solutions.
   - **At least five glass Pasteur pipettes:** one for "clean" methanol, and one for each dye solution.
   - **Bulbs**: at least three bulbs to be used by multiple students preparing solutions.
   - **Set of 4 glass cuvettes:** One cuvette for each dye solution
   - **Cuvette rack:** One is required, two racks is ideal.
     **Teach students to always keep cuvettes in a rack or instrument cell holder, never directly on the bench.
   - **Methanol wash bottles**: Be sure that there is one full methanol wash bottle available for each group. This is for rinsing cuvettes.
   - **Lab wipes** (ie Kimwipes) for wiping cuvettes.

- **Paper towel mat** to catch spills. Additional paper towels are at sink areas.

2. Complete instrument training with Dr. Haas.
3. Perform the entire experiment as if you were a student.
4. Write and submit a report as if you were a student.
5. Practice grading your and your partner's report using the grading rubric.

Pre-Lab Preparations

When you are on TA duty, arrive at least 20-30 minutes early to prepare and ready the materials listed above for students. Most of the set-up can be done ahead of time, but dye solutions should be kept cold when not in use.

- Take dye solutions out of freezer and place them at student stations.
- Check that dye solution colors are as expected (see Figure **4.7.2**).
  - **Dye #1**: 1,1'-diethyl-2,2'-cyanine iodide is **pinkish-orange.**
  - **Dye #2**: 1,1'-diethyl-2,2'-carbocyanine chloride is bright **blue** (not purple at all!)
  - **Dye #3**: 1,1'-diethyl-2,2'-dicarbocyanine iodide is dark **turquoise**.
  - **Dye #4**: 1,1'-diethyl-4-4'-carbocyanine iodide is **dark blue** (not yellow/green/brown color)
- At the UV-vis instrument and computer:
  - Turn on the UV-vis if you'd like to allow it to warm up.
  - Create a file folder for that day's section in the course directory on the computer hard drive.
  - Put the most recent version of the ELN on the UV-vis computer you will use.



Figure **4.7.2**: Check that the dye solutions are not degraded by comparing their colors to this figure or to the dye stocks that are always stored in the freezer. (Kathryn Haas; CC-BY-NC-SA)

Helping your students

During the laboratory session, you are expected to be present and available for the entire 4.5 hours. Your job is to help students to complete the experiment safely and successfully, while upholding expectations and academic standards for the students.

In this particular laboratory session, please provide guidance and instruction on the following:

- **Creating the solutions for analysis**: Students will put a few drops of the concentrated dye solutions into the cuvette and dilute with methanol. Please have an idea of what the solutions should "look like" (ie how dark/concentrated the should they be so that students can collect usable spectra). And, please make sure students are filling their cuvette about 3/4 full (not too full that it spills in the spectrometer, but full enough so that the light beam goes through the solution).
- **Using the spectrometer**: Be ready to step in if the students ask for help while validating the instrument and taking the spectrum. Be able to answer questions like "do I need to put a blank cuvette in the back"? "Do I need to take a baseline"? "Why does my spectrum look all noisy at Abs = 3? "Why do we need glass cuvettes - can I use quartz?"
- **Annotating spectra:** Show students how to add their wavelengths and label the Dyes on the spectrum through the annotation tool.

- **Saving data:** Please direct students to the folder in the course directory and instruct them to save their data to that folder using the format "YYYMMDD_filename_comments"
- **Filling out their ELN:** Be aware of what information the students should put in their ELN and guide them appropraitely. If they are moving on to the next step without recording the data, please remind them to do so. But, please let students do it themselves.
- **Taking turns:** Please help students to take turns controlling the instrument. Each student should be allowed to collect and annotate at least one spectrum.
- **Using the custom "dye" script in MatLab:** Be familiar with the script and how it is used, and guide students through the steps as necessary.

Encourage students to proceed through the data analysis and complete the ELN prior to leaving the lab. Remember, your role is as their coach - help encourage them to get their work done now while help is available so they do not feel overwhelmed later. If they need to take a bathroom or snack break, encourage them to do so before returning to the classroom room to complete the exercise.

Shut down/ clean up

Unless there is an unforeseen issue, your students should be finished with the lab work before 5 pm. They are to leave the room in clean condition prior to leaving lab and returning to the conference room.

- Remind students to clean up before returning to the classroom. Students should do the following:
  - Clean cuvettes with rinse methanol three times and leave the cleaned cuvettes in the rack.
  - Empty the temporary waste container into the primary waste container labeled for this experiment. Rinse the flask into the primary waste using rinse methanol.
  - Return the temporary waste container to the bench
- TAs should do the following shut down tasks before returning to the classroom:
  - Encourage students to continue their work in the classroom until their ELN is complete.
  - Turn off the UV-vis.
  - Return the dye solutions to the freezer.
  - If you are the last section of experiment, return all materials to their storage location in the prep room.
  - Be sure that the primary waste container is capped.
  - Remind students to clean up.
- Remind students to sign out with the time they leave and get your signature.
- Check the TA checklist for additional items to be completed.

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CHAPTER OVERVIEW

5: Molecular Spectroscopy of Iodine

5.1: Prelaboratory Assignment
5.2: Introduction
5.3: Potential Energy Curves
5.4: Experimental Part I - Absorption Spectrum of Iodine Vapor
5.5: Experimental Part II - Emission Spectrum of Iodine Vapor
5.6: References and Additional Reading

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5.1: 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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5.2: Introduction

This module uses a simple homodiatomic molecule, $\mathbf{I_2}$, 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 $\mathbf{I_2}$.

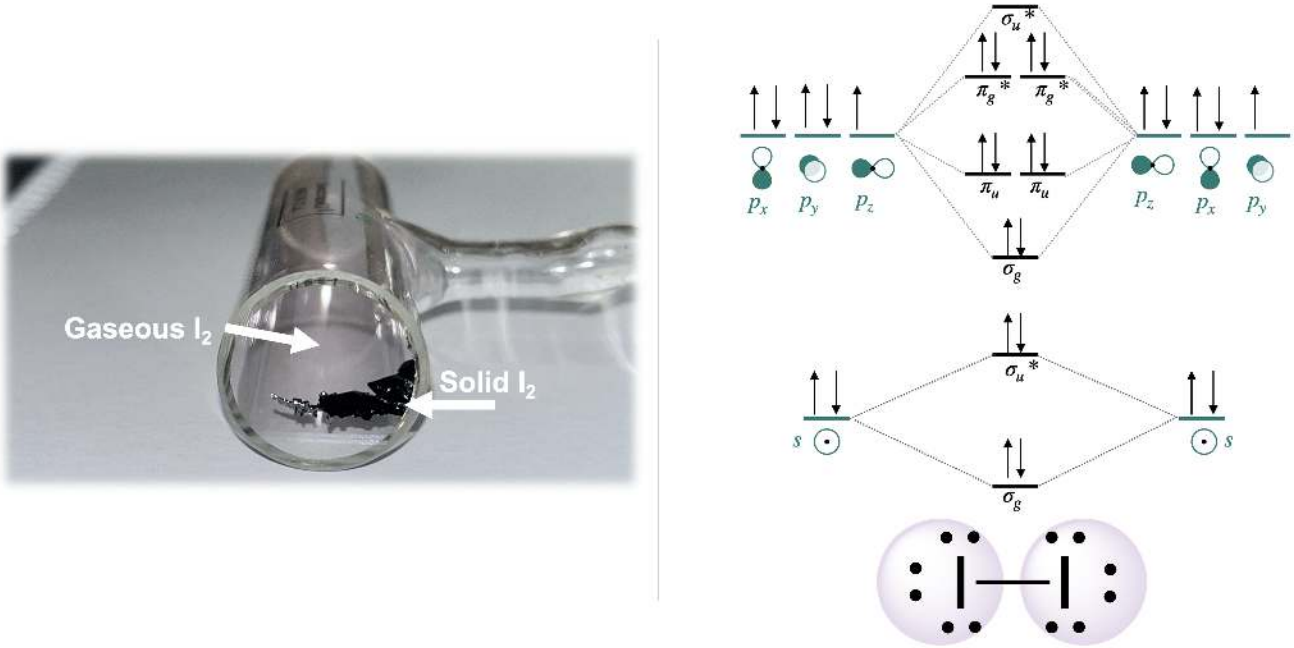


Figure 5.2.1: Left; A spectroscopic cell containing $\mathbf{I_2}$. Right; A Lewis dot structure and an approximate valence molecular orbital diagram for $\mathbf{I_2}$ (CC-BY-NC-SA; Kathryn Haas)

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 $\mathbf{I_2}$ 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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5.3: 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

$$V(R) = \frac{1}{2}k(R - R_e)^2 \tag{5.3.1}$$

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.

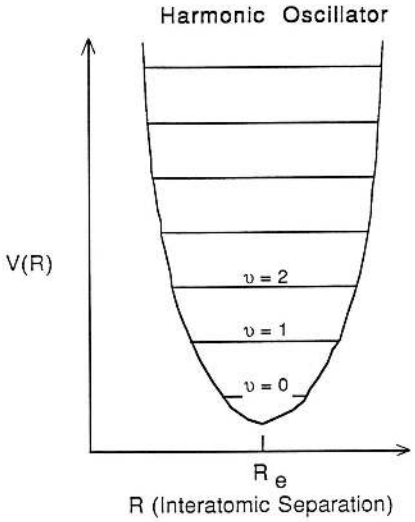


Figure 5.3.1: The potential energy V(R) and vibrational energy levels for a harmonic oscillator. (CC-NC-BY_DUKE CHEM)

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_υ increases linearly with the vibrational quantum number υ according to the equation

$$E_\upsilon = h\nu\left(\upsilon + \frac{1}{2}\right) \tag{5.3.2}$$

where h is Planck's constant and ν is the vibrational frequency. The vibrational frequency ν is related to the force constant k and the reduced mass μ through the relation

$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{k}{\mu}\right)} \tag{5.3.3}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ 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 ∞. 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.

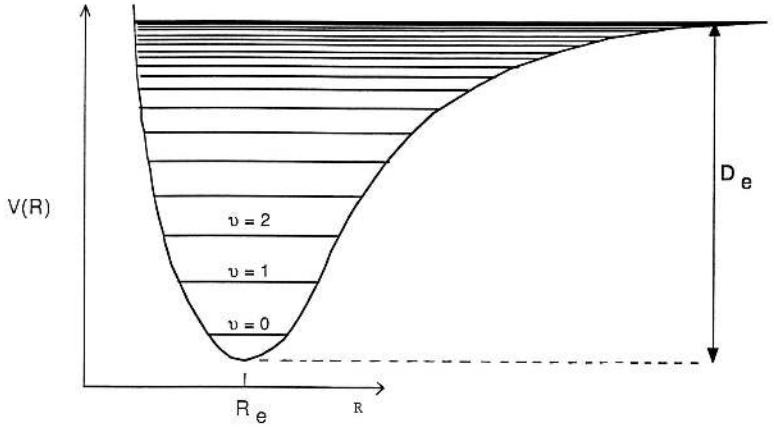


Figure 5.3.2: A typical Morse potential for a diatomic molecule. (CC-NC-BY-DUKE CHEM)

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 $v+\frac{1}{2}$

$$G_v = \omega_e\left(v+\frac{1}{2}\right) - \omega_e\chi_e\left(v+\frac{1}{2}\right)^2 + \ldots \tag{5.3.4}$$

where G_v is the energy of quantum level v in cm^{-1}, ω_e is the "harmonic frequency" of the oscillator in cm^{-1}, and χ_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

$$\Delta G_{(v)} = \left|G_{(v+1)} - G_{(v)}\right| = \omega_e - 2\omega_e\chi_e\,(v+1) \tag{5.3.5}$$

By measuring G_v for a given state, and plotting the change in vibrational energy spacing $\Delta G_{(v)}$ with respect to $v+1$, both ω_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 ω_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_v 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

$$V(R) = D_e\left[1 - e^{-a(R-R_e)}\right]^2 \tag{5.3.6}$$

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

$$a = \sqrt{\frac{8\pi^2 c\mu\omega_e\chi_e}{h}} \tag{5.3.7}$$

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

Thus, for this potential, the constants, a, and D_e can be determined from a measurement of ω_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 ∞ (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

$$\nu_{(v'',v')} = \nu_{el} + G_{(v')} - G_{(v'')} \tag{5.3.8}$$

where ν_{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 ν_{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

$$D_e'' = \nu_{el} + D_e' - E(I^*) \tag{5.3.9}$$

This can be seen in Figure 5.3.3.

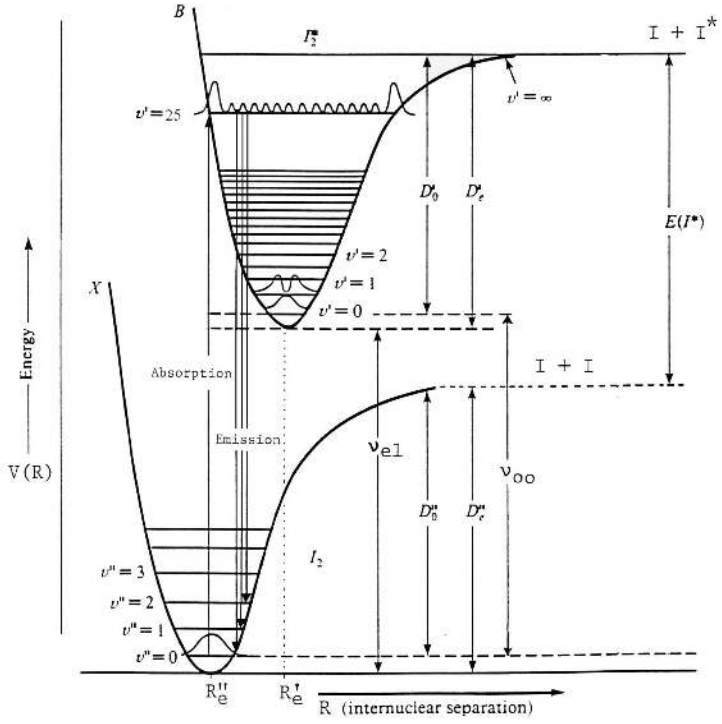


Figure **5.3.3**: Schematic representation of the ground (X) and excited (B) states of iodine. Various electronic transitions are indicated by arrows. (CC-NC-BY-DUKE CHEM)

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 ω'_e and χ'_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 ω''_e, χ''_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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5.4: 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

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.

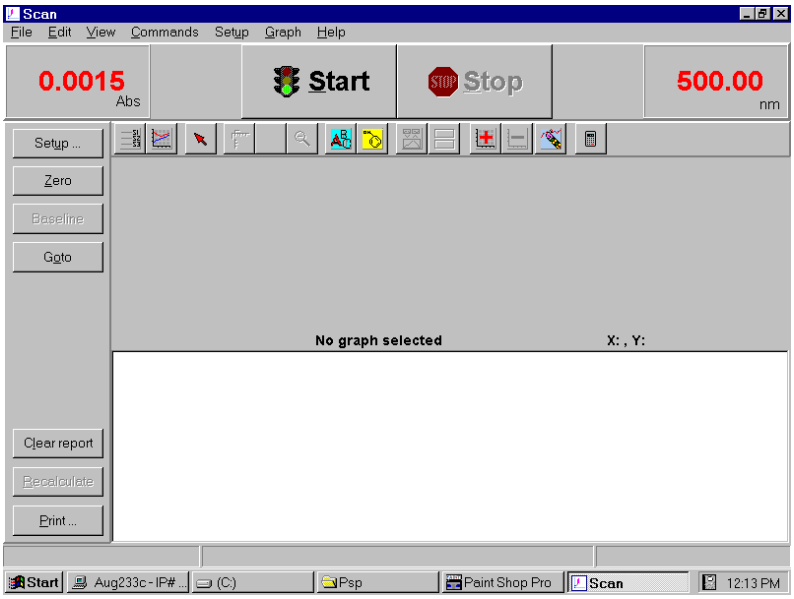


Figure **5.4.4**: The Scan Module Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the Setup ... 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.

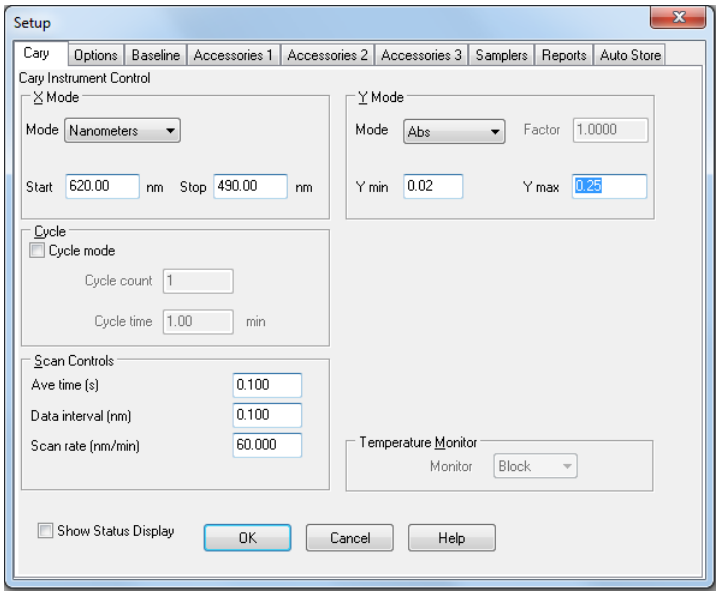


Figure **5.4.5**: The Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

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.

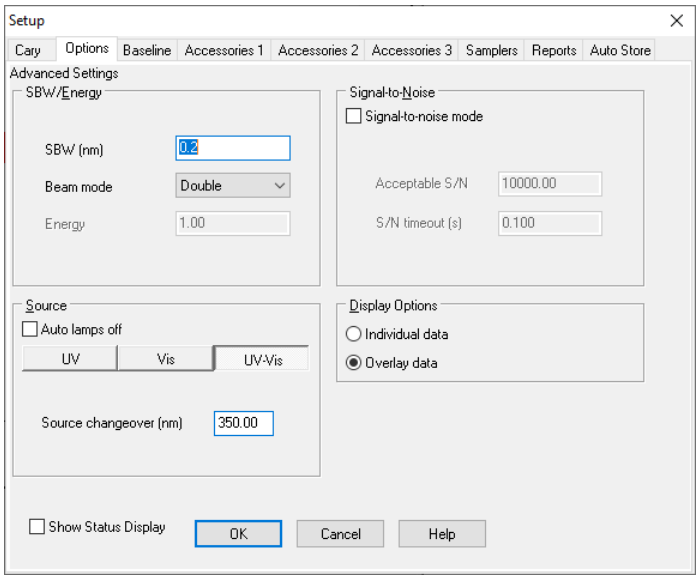


Figure **5.4.6**: The Options Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

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.

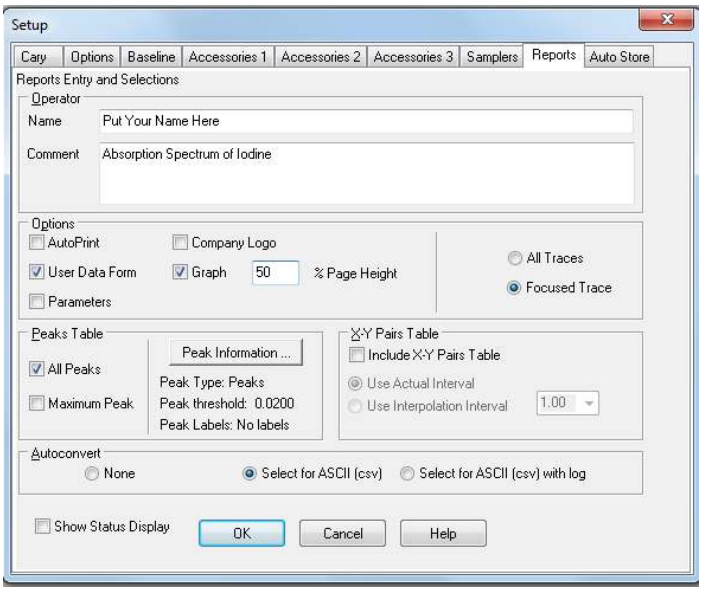


Figure **5.4.7**: The Reports Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

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 Start 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.

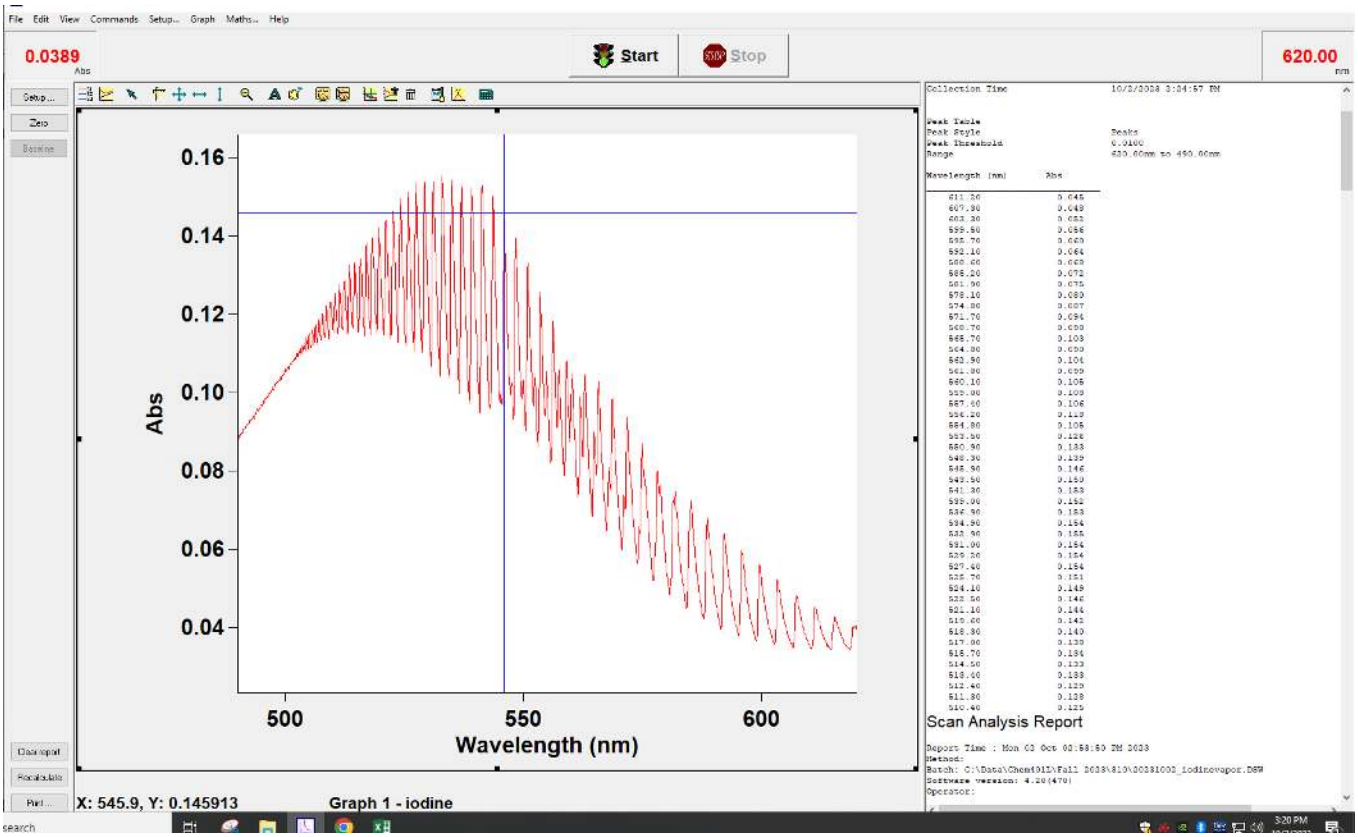


Figure **5.4.8**: The Absorption Spectrum of Iodine Vapor. (CC-NC-BY-DUKE CHEM)

6. At the conclusion of the run, find the $v'' = 0 \ \ to \ \ v' = 25$ 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 ω'_e using Equation 5.3.5.
5. From the slope calculate χ'_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 ω'_e, χ'_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 ν_{00} (the energy of the transition from $v'' = 0$ to $v' = 0$ is notated by the symbol ν_{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 χ''_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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5.5: 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 ($\mathbf{I_2}$) will be put under high vacuum to vaporize the $\mathbf{I_2}$ 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 5.5.1: 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.

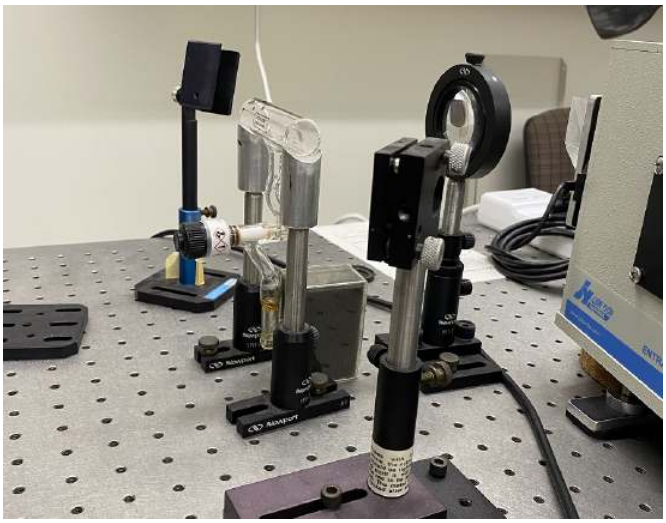


Figure 5.5.2: A sample cell is positioned on the sample cell holder in the path of the laser. The valve on the sample chamber is positioned toward the laser and away from the detector, as shown. (CC-BY-SA; Kathryn Haas, Duke Chem)

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.

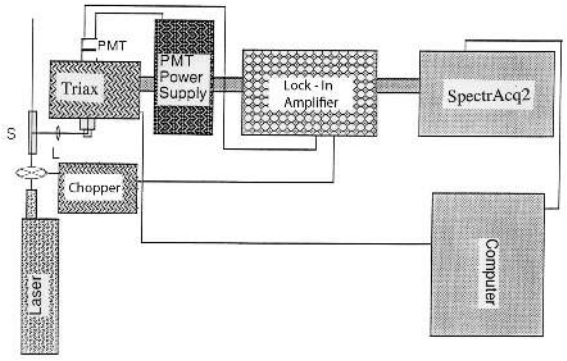


Figure 5.5.1: Instrumentation used for Laser Fluorescence Experiments. (CC-NC-BY-DUKE CHEM)

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

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.

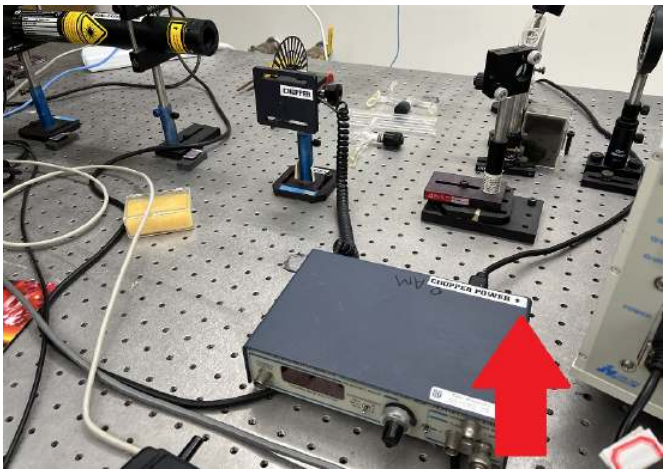


Figure **5.5.3**: The chopper and its power supply are labeled. Turn on the chopper using the switch on the back side of the power supply. (CC-BY-SA; Kathryn Haas, Duke Chem)

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.

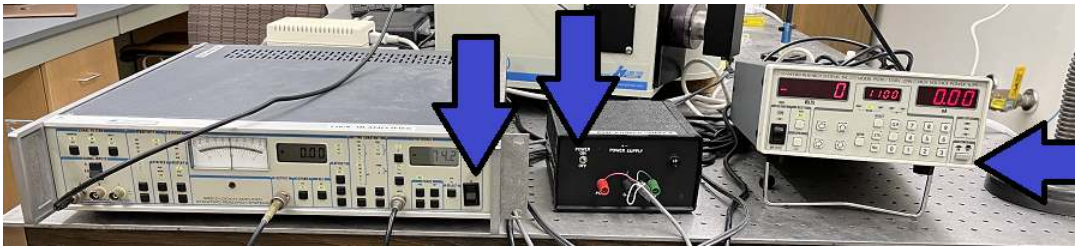


Figure **5.5.4**: **a) The Pre-Amp power supply** is the black box in the center of the picture; it is turned off using the silver toggle switch. **b) the Lock-in Amplifier** is the box on the left of the photo; it is powered on using the black toggle switch at the bottom right of the control panel. **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**.

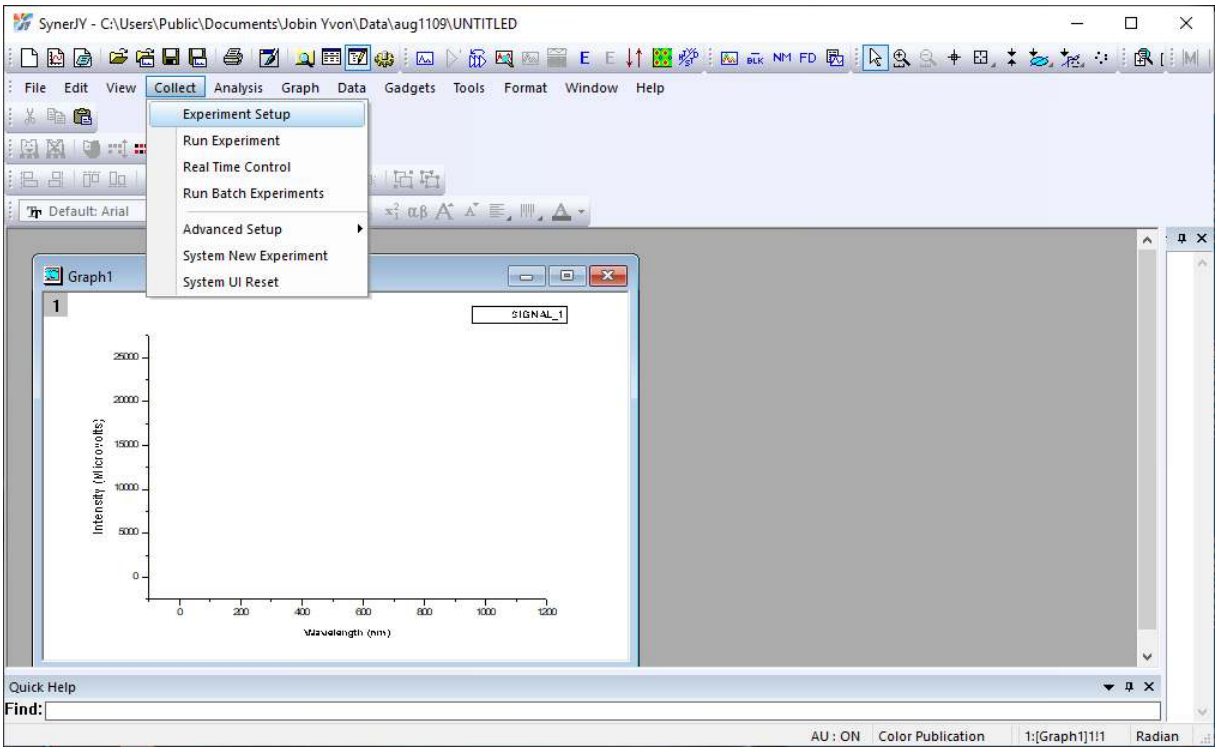


Figure 5.5.5: Choosing Experiment Setup from the Main SynerJY Window. (CC-NC-BY-DUKE CHEM)

- 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.

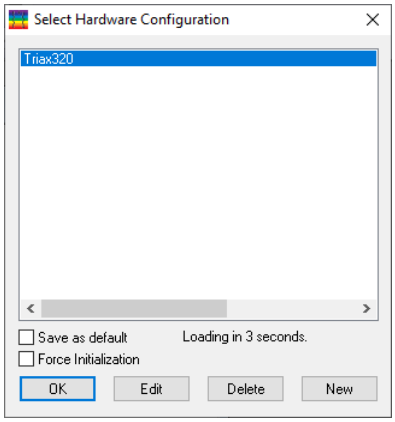


Figure 5.5.6: Hardware Configuration. (CC-NC-BY-DUKE CHEM)

- 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 **5.5.7**: The Initialization Window. (CC-NC-BY-DUKE CHEM)

- The software will then load the Experiment Setup screen.

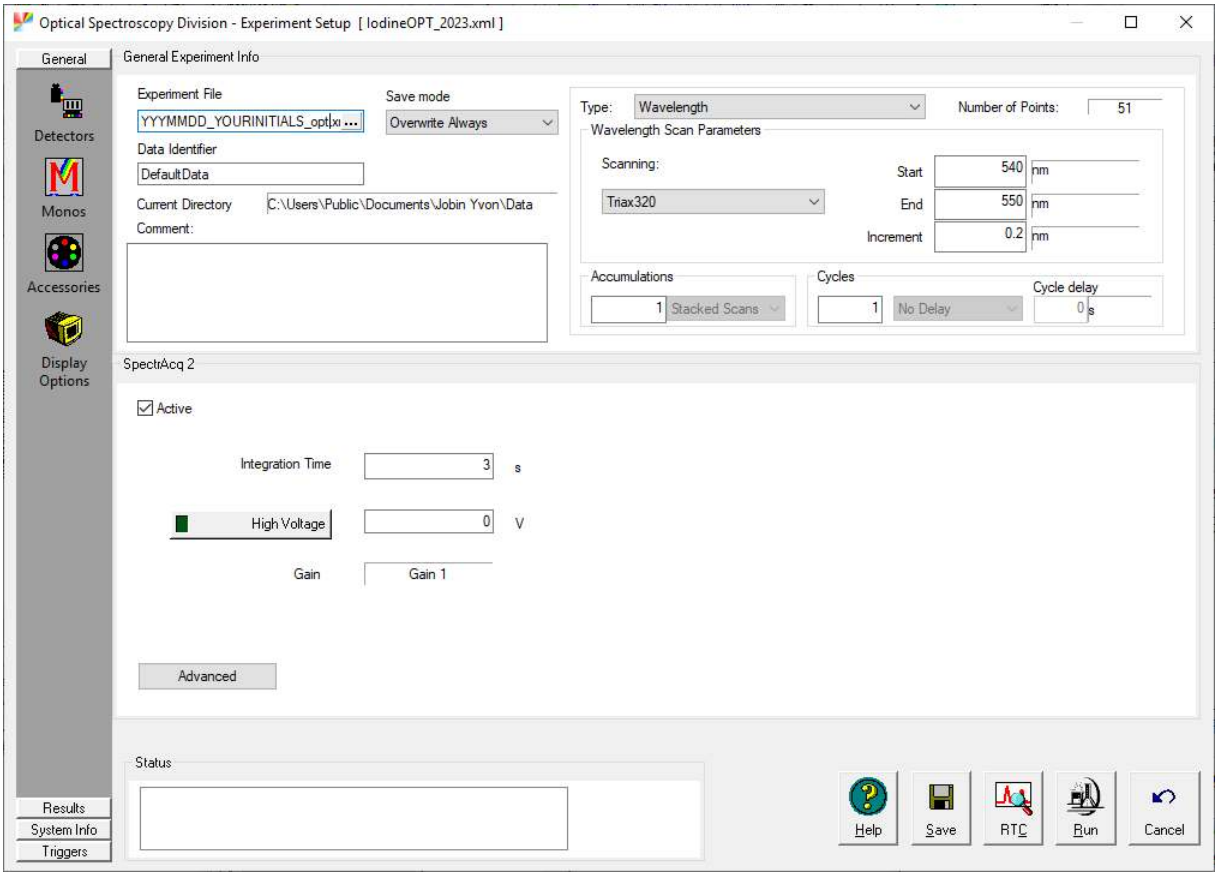


Figure **5.5.8**: The Setup Screen. (CC-NC-BY-DUKE CHEM)

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, ).

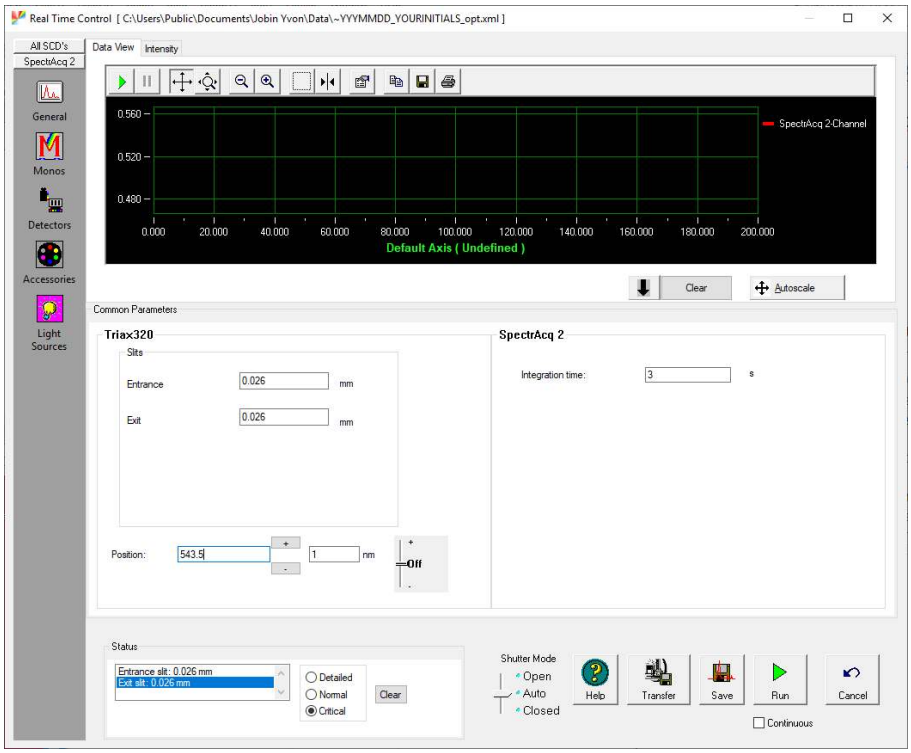


Figure **5.5.9**: Real time controller. (CC-NC-BY-DUKE CHEM)

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 5.5.10).
10. Double Click on the spectrum so that you can edit it. Then select **Pick Peaks** from the **Analysis** menu.

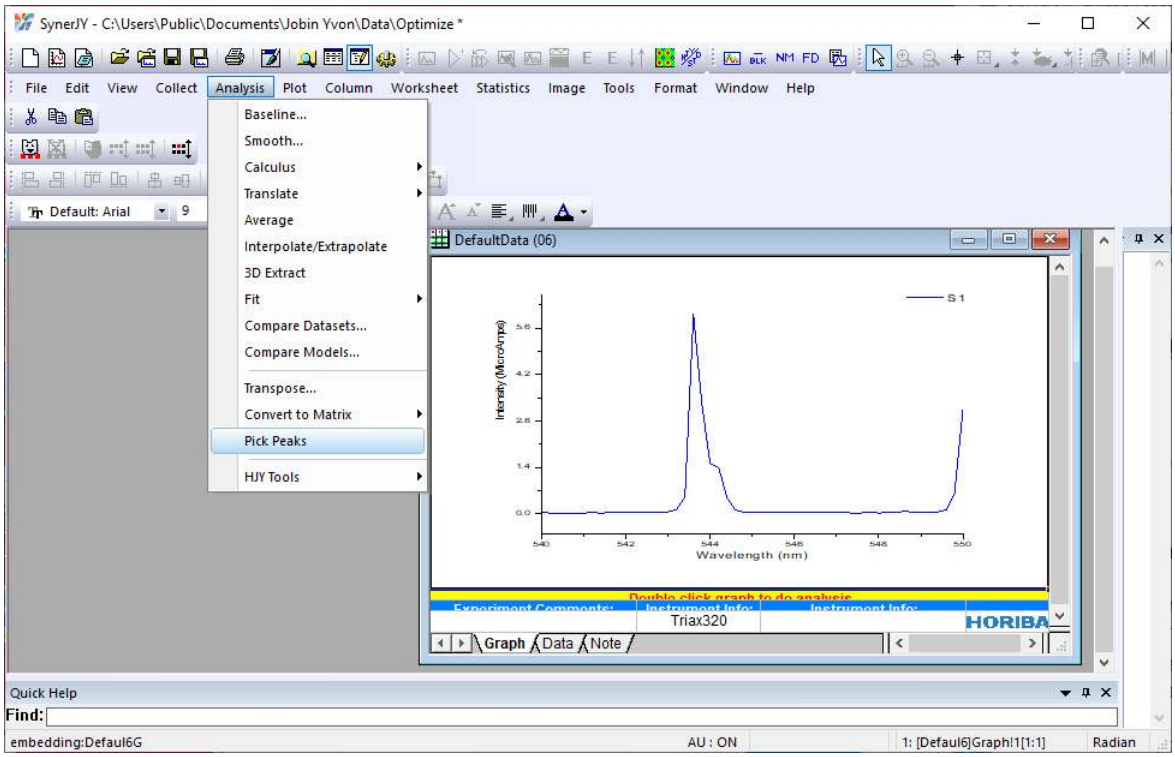


Figure 5.5.10: The Results of the Test Scan. (CC-NC-BY-DUKE CHEM)

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**.

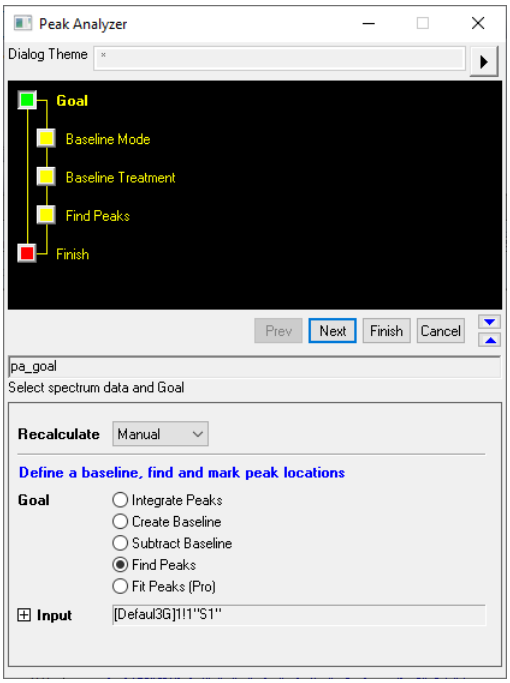


Figure **5.5.11**: Copy and Paste Caption here. (Copyright; author via source)

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 **5.5.10** 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.

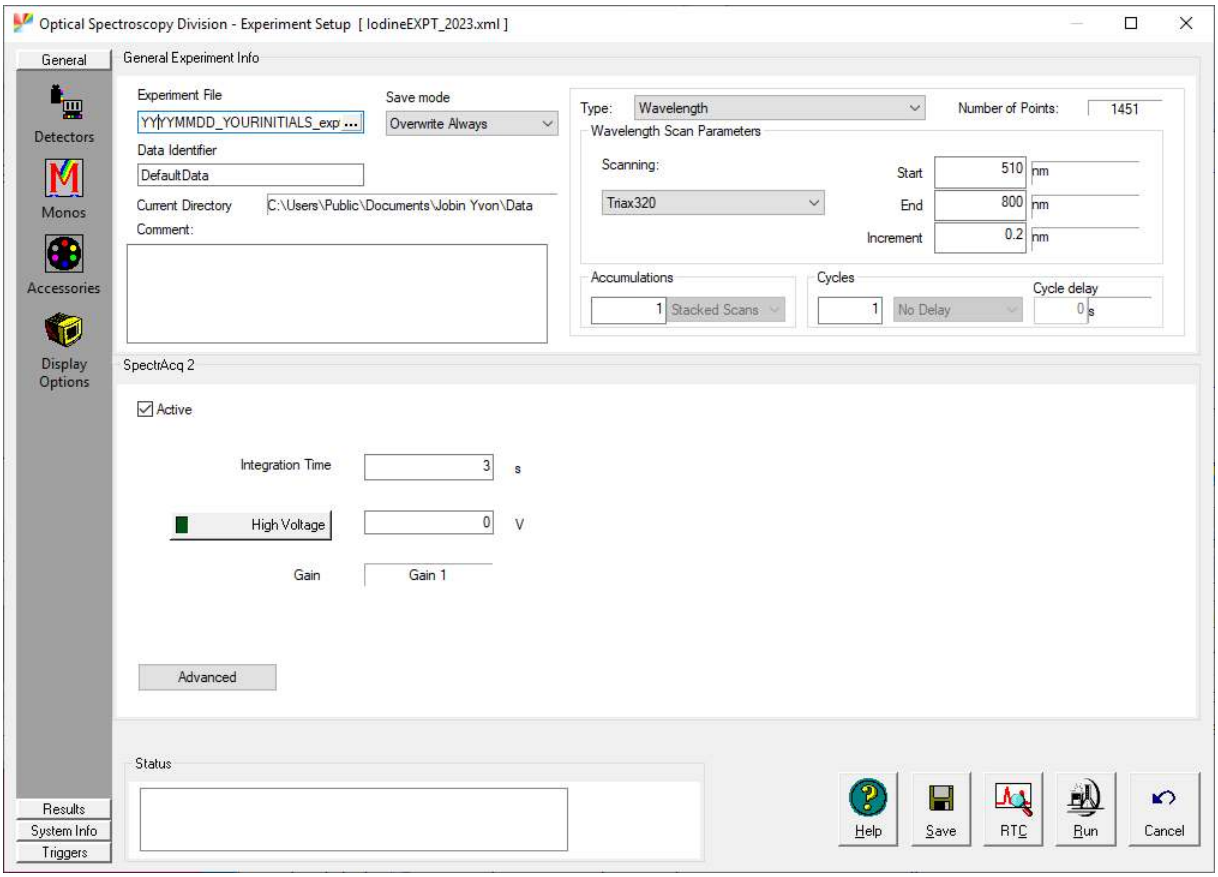


Figure **5.5.12**: Setting Up The Sample Run. (CC-NC-BY-DUKE CHEM)

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.

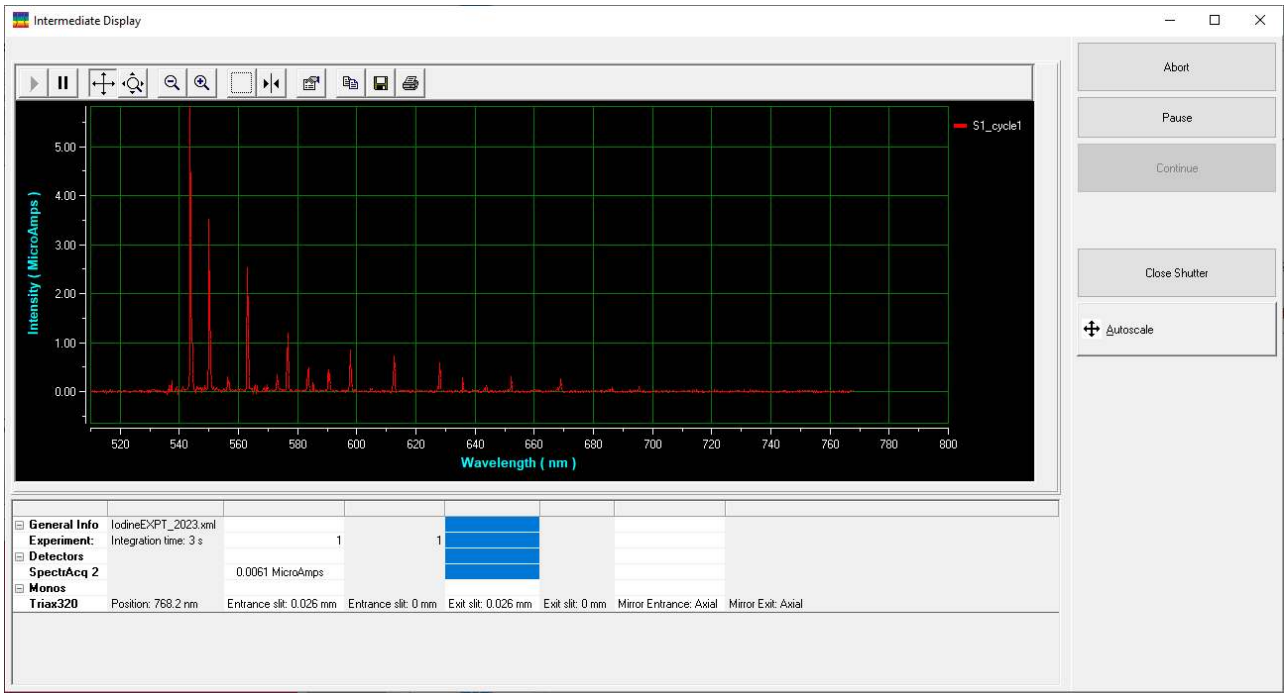


Figure **5.5.13**: Data collection. (CC-NC-BY-DUKE CHEM)

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.

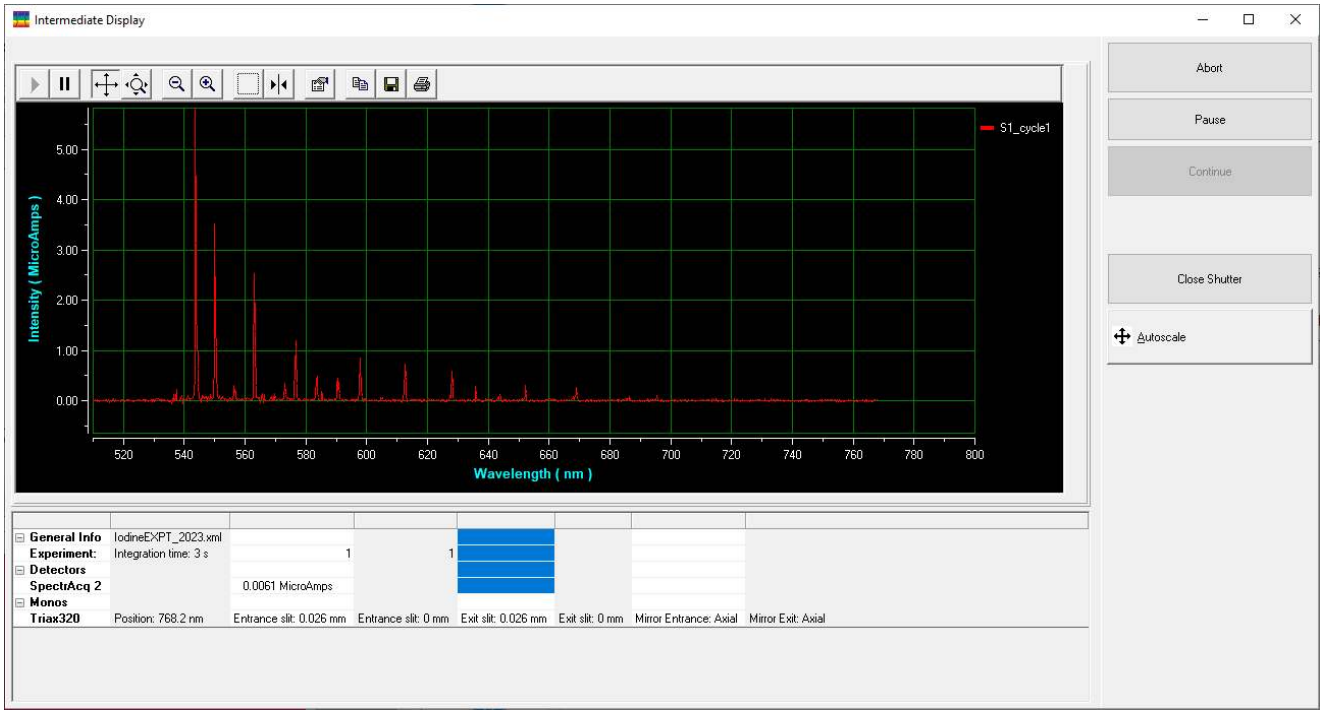


Figure **5.5.14**: The FInal Spectrum. (CC-NC-BY-DUKE CHEM)

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:

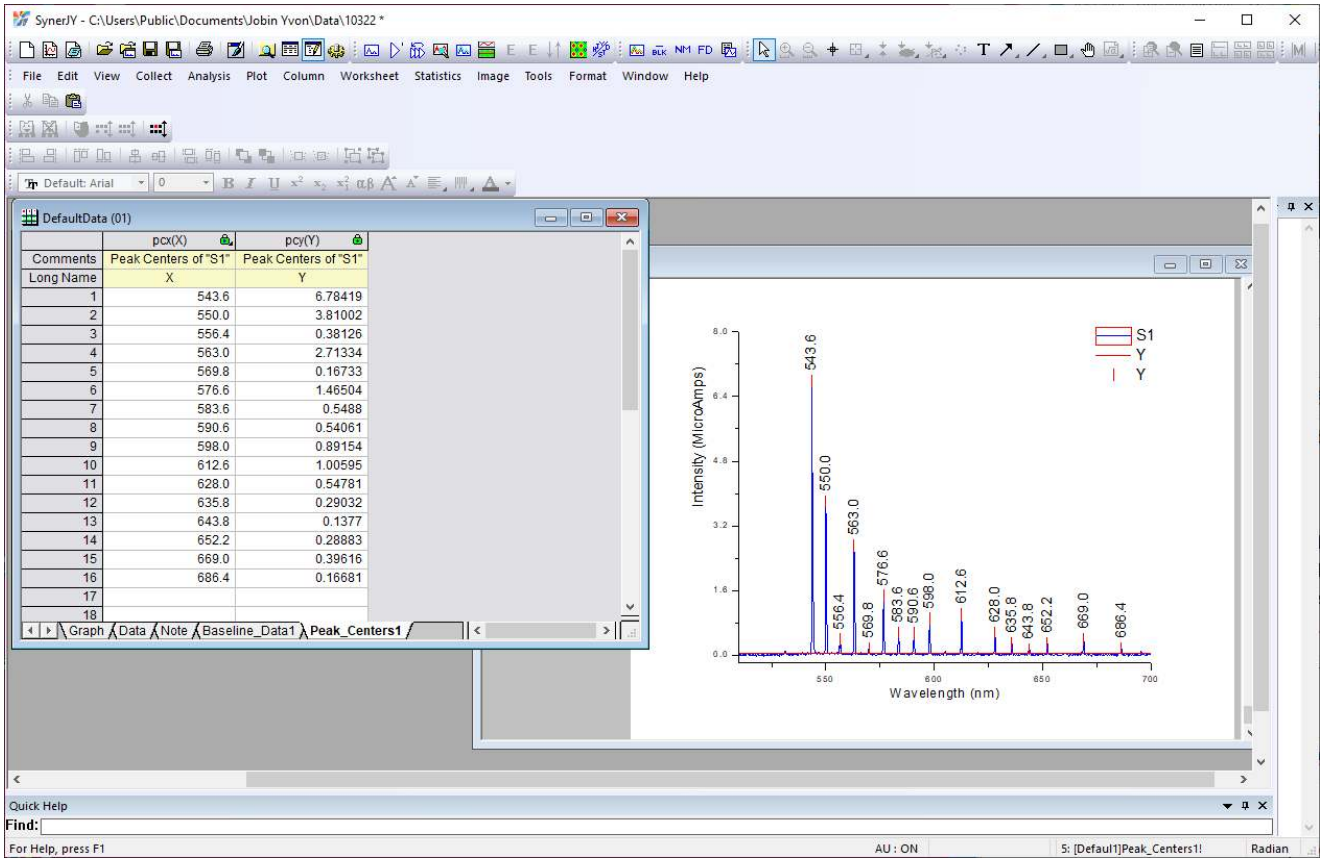
    a. Goal: **Find Peaks**

    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 **5.5.15**). Click on the Peak_Centers1 worksheet and you will get a table of the peaks found in the spectrum.



	pcx(X)	pcy(Y)
Comments	Peak Centers of "S1"	Peak Centers of "S1"
Long Name	X	Y
1	543.6	6.78419
2	550.0	3.81002
3	556.4	0.38126
4	563.0	2.71334
5	569.8	0.16733
6	576.6	1.46504
7	583.6	0.5488
8	590.6	0.54061
9	598.0	0.89154
10	612.6	1.00595
11	628.0	0.54781
12	635.8	0.29032
13	643.8	0.1377
14	652.2	0.28883
15	669.0	0.39616
16	686.4	0.16681
17		
18		

Figure **5.5.15**: 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 $\Delta G''_v$ vs $(v'' + 1)$.
2. From the intercept of the Birge-Sponer plot, calculate ω''_e (using Equation 5.3.5).
3. From the slope of the Birge-Sponer plot, calculate χ''_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 ω_e'', χ_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 $\nu_{(v'',v')}$ (where $v'' = 0$) in units of cm^{-1}. For these same transitions, calculate $(G_{(v')} - G_{(0'')})$ using Equation 5.3.4 and your values of ω_e'', ω_e', χ_e'' and χ_e'. Now use Equation 5.3.8 to calculate the average value of ν_{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 7603 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

$$V(R) = T_e + D_e\left[1 - e^{-a(R-R_e)}\right]^2 \tag{5.5.1}$$

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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5.6: 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.

3. Steinfeld, J.I., *J. Chem. Educ.*, **1965**, 42, 85.

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CHAPTER OVERVIEW

6: Rotation-Vibration Spectrum of HCl

6.1: Pre-lab Assignment

6.2: Background on Rotovibrational Spectroscopy

6.2.1: The Electromagnetic Spectrum and Molecular Transitions

6.2.2: Rotational Transitions Accompany Vibrational Transitions

6.2.3: Transition Intensities

6.2.4: The Pure Rotational Spectrum has Unequal Spacings

6.2.5: Anharmonicity and Vibrational Overtones

6.3: Experimental and Instructions

6.4: References

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6.1: Pre-lab Assignment

Learning Objectives

- Develop an energy level diagram and relate that diagram to rotational-vibrational spectra.
- Identify, describe, and interpret the molecular constants that can be extracted from gas-phase IR spectra.
- Discover the impact of spectral resolution on precision of molecular constants derived from the spectral data.
- Use data to evaluate and refine quantum mechanical models.

In addition to the "general" prelab work expected for all experiments in the course (Introduction and Experimental Plan as described in the Orientation Module), please complete the following and submit the work prior to the lab meeting.

Note

Read this entire manual and complete the following written assignment (to be turned in with the usual pre-lab assignment):

1. Consider the types of molecular motions and their energies:
   a. What types of motion can gas-phase molecules exhibit?
   b. In general, what type of motion allows molecules to absorb infrared radiation?
2. The frequency of electromagnetic radiation is often reported in units of wavenumbers (cm^{-1}). Consider the equation $E = \frac{hc}{\lambda}$ and to determine whether wavenumbers (use units as your guide) are directly or inversely proportional to energy.
3. Consider a hypothetical diatomic gas with a typical harmonic frequency of 2000 cm^{-1}.
   a. Draw the energy level diagram corresponding to the vibrational energy levels for this molecule (assume harmonic oscillator).
   b. To which region of the electromagnetic spectrum do transitions between these energy levels belong?
   c. A sample of this diatomic gas is placed in a spectrometer capable of measuring absorbance in the range 1000 – 5000 cm^{-1}. Predict the appearance of the spectrum (intensity of absorbance vs. frequency). Put frequency (in cm^{-1}) on the x-axis and intensity of absorbance on the y-axis. Draw the spectrum and explain you reasoning.
   d. Go back to the energy level diagram you drew in 3A. Add an arrow to your energy level diagram from 3A to represent each transition drawn in your spectrum in 3C.
4. Show which equations you would use to find: B_e; α_e; $\tilde{\nu}_o$.

Adapted from Beck, Jordan P., and Diane M. Miller. “Encouraging Student Engagement by Using a POGIL Framework for a Gas-Phase IR Physical Chemistry Laboratory Experiment.” *Journal of Chemical Education* 99, no. 12 (December 13, 2022): 4079–84. https://doi.org/10.1021/acs.jchemed.2c00314.

Additional reading: (available in the library, Duke students click here)

- Part l. Instrumentation, *Journal of Chemical Education*, **1986,** *63* (1), A5. (This is a description of how the Michaelson Interferometer is applied in FTIR spectroscopy. See also the video lined below.)
- Shoemaker, D.P., Garland, C.W., and Nibler, J.W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, New York, 1996, Chapter XIV, **Experiment 37**.
- McQuarrie, D.A. and Simon, J.D. "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Sections 13.2-13.4, 18.4-18.5); Atkins, P., Physical Chemistry, 5th ed., sections 16.8 – 16.11
- Silbey, R.J., Alberty, R. A. Bawendi, M.G., Physical Chemistry, 4th ed., Sections 13.4, 13.6 and 13.7, for a discussion of rotation-vibration spectroscopy of diatomic molecules.

Helpful videos

Dr. Welsher's P-Chem lectures are on YouTube!

In addition, the videos below provide a nice introduction and demonstration of the theory and techniques you will use.

Introduction to the Michaelson Interferometer in FTIR



Introduction to rotovibrational spectroscopy



Filling a gas cell



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SECTION OVERVIEW

6.2: Background on Rotovibrational Spectroscopy

A note from your instructors

We are working to replace the commercial textbooks used in this course. While we're still working on it, we are providing the following sections (which are still under construction). The section on transition intensities is the only section that was part of the original manual for this course, and is not covered in the Shoemaker textbook.

6.2.1: The Electromagnetic Spectrum and Molecular Transitions

6.2.2: Rotational Transitions Accompany Vibrational Transitions

6.2.3: Transition Intensities

6.2.4: The Pure Rotational Spectrum has Unequal Spacings

6.2.5: Anharmonicity and Vibrational Overtones

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6.2.1: The Electromagnetic Spectrum and Molecular Transitions

Electromagnetic radiation, or light, exhibits dual behavior as both waves and particles. Wave properties, such as refraction, best explain phenomena like light passing through different mediums. Conversely, particle behavior provides a more accurate description in certain scenarios, like absorption and emission. The nature of electromagnetic radiation remains unclear, with wave and particle models coexisting since the development of quantum mechanics in the early 20th century. Despite this ambiguity, these dual models effectively characterize electromagnetic radiation.

It consists of oscillating electric and magnetic fields that travel through space at a constant velocity. In a vacuum, the speed of light (c) is $2.99792 \times 10^8 \frac{m}{s}$. When passing through a medium other than a vacuum, its velocity (v) is slightly less than c, with the difference being <0.1%. For practical purposes, the speed of light is often approximated as $3.00 \times 10^8 \frac{m}{s}$. The oscillations in the electric and magnetic fields are perpendicular to each other and the wave's propagation direction. An model of plane-polarized electromagnetic radiation, featuring a single oscillating electric field and a single oscillating magnetic field, is illustrated in Figure 6.2.1.1.

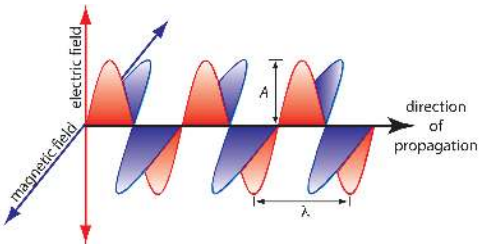


Figure 6.2.1.1: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, *A*, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{6.2.1.1}$$

where A_t is the magnitude of the electric field at time t, A_t is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{6.2.1.2}$$

where A_m is the magnetic field's maximum amplitude.

Units of energy

The **wavelength**, λ, is defined as the distance between successive maxima (Figure 6.2.1.1). The relationship between wavelength (in m) and frequency (in s^{-1} or Hz) is given below. Wavelength is usually expressed in nanometers (1 nm = 10^{-9} m) for ultraviolet and visible light, and in microns (1 μm = 10^{-6} m) for infrared light.

$$\lambda = \frac{c}{\nu} \tag{6.2.1.3}$$

Wavelength is a unit used often by chemists, especially in UV-vis spectroscopy. Because it is inversely related to energy (ie smaller wavelengths are higher energy), many scientists prefer units that are directly proportional to energy. An alternate unit, the **wavenumber**, $\tilde{\nu}$, is used frequently, especially in infrared spectroscopy. In general it seems to be the preferred unit of physicist due to its direct correlation to energy. It is useful to know how to convert between these two commonly-used units. The unit $\tilde{\nu}$ is simply the reciprocal of wavelength.

$$\tilde{\nu} = \frac{1}{\lambda} \tag{6.2.1.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Keeping symbols straight

Heads up! The word "frequency" refers to cycles per unit time, but can also be measured in a length scale. Frequency measured in cycles per seconds (s^{-1} can be expressed in the metric base unit Hertz, and can have the symbol f or ν. When it is expressed in a length scale, like wavenumbers (cm^{-1}), it has the symbol $\tilde{\nu}$.

- When converting units from ν (in s^{-1}) to λ, use the speed of light to convert between time and length scales as in 6.2.1.3.
- When converting from $\tilde{\nu}$ to λ, use 6.2.1.4 and convert metric units as necessary.

Regions of the Spectrum and Types of Transitions

Electromagnetic radiation spans a wide range of frequencies and wavelengths, prompting the division of this spectrum into distinct regions for convenience, known as the **electromagnetic spectrum** (Figure **6.2.1.2**). These divisions are based on the atomic or molecular transitions responsible for the absorption or emission of photons. It's important to note that the boundaries between these regions are not fixed, allowing for potential overlap between different spectral regions.

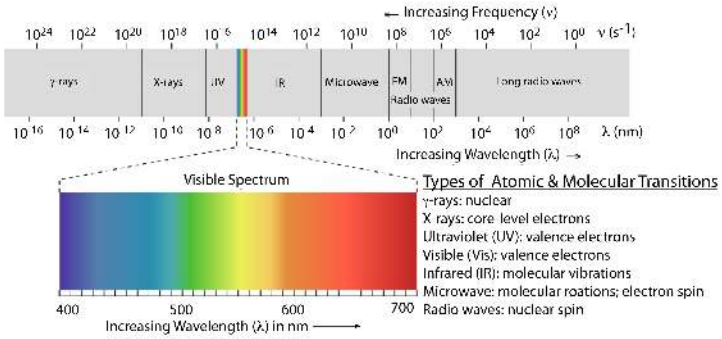


Figure **6.2.1.2**: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Given the energy levels of molecules and their corresponding wavelengths, we can determine the frequency within the electromagnetic spectrum regions using the equation:

$$\Delta E = E_u - E_l = h$$

Here, h represents the energy change between the upper (u) and lower (l) states.

The frequencies of molecular transitions fall within specific ranges. These ranges are listed in the table below in order of increasing energies.

Table **6.2.1.1**: Each type of molecular motion and its corresponding region of the electromagnetic spectrum. Ranges are approximate.

Wavelengths	Frequency (cm^{-1})	Frequency (s^{-1})	Region	Transitions
1 mm - 1 m	~ 0.01	10^8 - 10^{11}	microwave	rotational transitions of large polyatomic molecules
~100 μm	~10	10^{12}	far infrared	rotational transitions of small molecules
~ 10 μm	~100 - 5000	~ 10^{13}	infrared	vibrational transitions
~700 - 400 nm	~ 14,000 - 25,000	~10^{14}	visible and ultraviolet	electronic transitions

Absorption and Emission

In absorption spectroscopy a photon is absorbed by an atom or molecule, which undergoes a transition from a lower-energy state to a higher-energy, or excited state (Figure 6.2.1.3). The type of transition depends on the photon's energy (see table above). Absorbing electromagnetic radiation can cause transitisions (excitations) in the rotational, vibrational, or electronic states depending on the energy of the photon. Likewise, relaxation of the molecule back to a lower-energy rotational, vibrational, or electronic state can result in emission of a photon (Figure 6.2.1.3).

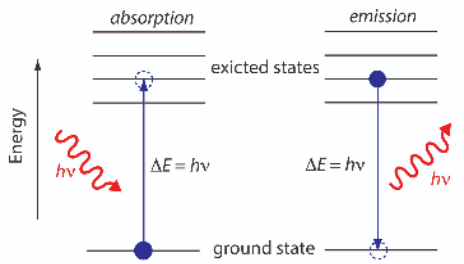


Figure 6.2.1.3: Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule. When a photon of energy hν strikes the atom or molecule, absorption may occur if the difference in energy, ΔE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hν, equals the difference in energy, ΔE, between the two states.

When it absorbs electromagnetic radiation the number of photons passing through a sample decreases. The measurement of this decrease in photons, which we call **absorbance**, is a useful analytical signal. Note that each of the energy levels in Figure 6.2.1.3 has a well-defined value because they are *quantized*. Absorption occurs only when the photon's energy, *h*ν, matches the difference in energy, Δ*E*, between two energy levels. A plot of absorbance as a function of the photon's energy is called an **absorbance spectrum**. Figure 6.2.1.4, for example, shows the visible absorbance spectrum of cranberry juice.

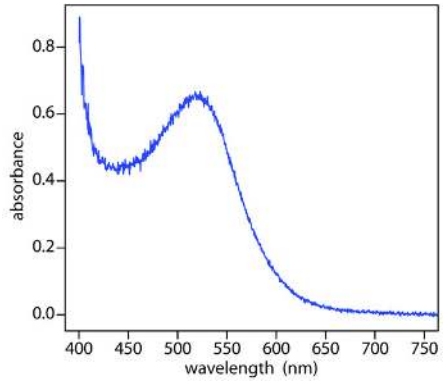


Figure 6.2.1.4). Visible absorbance spectrum of cranberry juice. As a result, the juice appears red.

When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we call **emission** (Figure 6.2.1.4). There are several ways in which an atom or molecule may end up in an excited state, including thermal energy, absorption of a photon, or by a chemical reaction. Emission following the absorption of a photon is also called **photoluminescence**, and that following a chemical reaction is called **chemiluminescence**. A typical emission spectrum is shown in Figure 6.2.1.5.

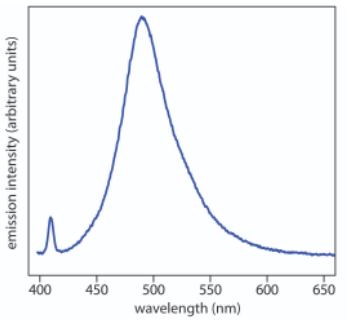


Figure **6.2.1.5**: Photoluminescence spectrum of the dye coumarin 343, which is incorporated in a reverse micelle suspended in cyclohexanol. The dye's absorbance spectrum (not shown) has a broad peak around 400 nm. The sharp peak at 409 nm is from the laser source used to excite coumarin 343. The broad band centered at approximately 500 nm is the dye's emission band. Because the dye absorbs blue light, a solution of coumarin 343 appears yellow in the absence of photoluminescence. Its photoluminescent emission is blue-green. Source: data from Bridget Gourley, Department of Chemistry & Biochemistry, DePauw University).

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6.2.2: Rotational Transitions Accompany Vibrational Transitions

The infrared region (IR) of the electromagnetic spectrum is of interest to chemists because it corresponds to the energy of the vibrational modes of molecules (specifically the region between 4000 to 400 cm^{-1}). When the frequency of infrared radiation matches the vibrational frequency of a molecule, the molecule can become vibrationally excited by transitioning from the vibrational ground state to a vibrational excited state.In the case of diatomic molecules, like HCl, there is only one vibrational mode. Thus, we might expect one vibrational absorption band in the IR spectrum.

However, in the gas phase IR spectrum of HCl, there is a complex pattern of bands (see Figure **6.2.2.1**). The structure that is observed in the IR spectrum of HCl was one of the early pieces of evidence supporting quantum mechanics and the idea that molecular states (like vibrational and rotational states) are quantized. The person who first measured a high-resolution spectrum like the one shown in Figure **6.2.2.1**, and who used this spectrum experimental confirmation of the Franck–Condon principle, was a **Elmer Imes** (click here for Wikipedia - unfortunately, we couldn't find a public domain photo of him, but google his name and you'll find him!). Imes is best known for his collaboration with James Franck in 1926, where they conducted experiments on molecular spectra (like Figure **6.2.2.1**) and provided experimental confirmation of the Franck–Condon principle. This principle relates to the intensity distribution of vibrational transitions in molecular spectra. Imes was the first African American in the 20th century to gain a Ph.D., and he became a physics professor at Fisk University. Elmer Imes's work, along with that of his contemporaries, laid the foundation for our understanding of molecular structures and behaviors, particularly in the realm of rotational-vibrational spectroscopy. His contributions have had a lasting impact on the study of molecular physics and spectroscopy. You will follow in his footsteps during this module!

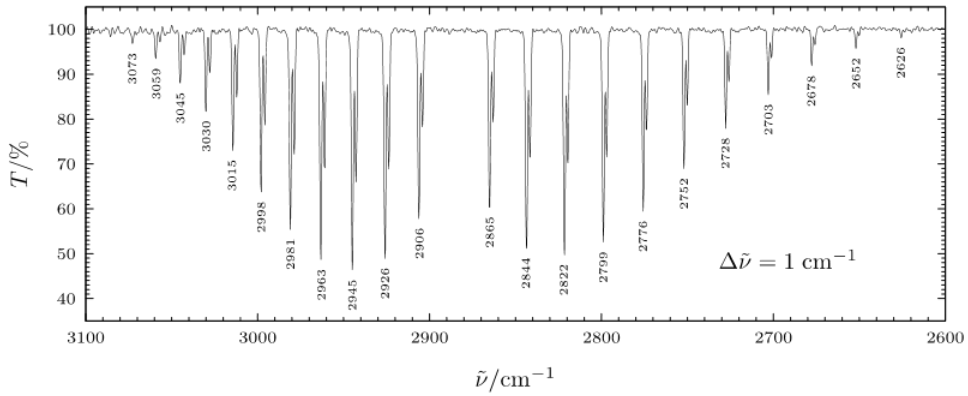


Figure **6.2.2.1**. Gas phase FTIR spectrum of HCl. In this view, the data is plotted in a similar fashion as you may have seen in organic chemistry courses. The intensity is shown as % transmission on the Y axis and wavenumbers on the X axis. The X axis is plotted from high to low wavenumber. Figure used with permission from Wikipedia.

While every peak on the spectrum shown in Figure **6.2.2.1** represents a transition from the ground vibrational state to the first vibrational excited state, each represents a unique transition from one rotational state of the ground vibrational state to a different rotational state of the vibrational exited state. This coupling of rotational and vibrational states that appears in the IR spectrum in Figure **6.2.2.1** illustrates the quantized nature of molecular motions.

Models of Molecular Motion

To explain the spectrum shown above, we start by considering all the possible molecular motions and useing simple models to describe them

VIBRATIONAL motions and the HARMONIC OSCILLATOR model

The HCl molecule vibrates along the bond axis. We can treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete energies given by

$$E(v) = h\nu\left(v + \frac{1}{2}\right) \text{ or } \tilde{E}(v) = \tilde{\nu}\left(v + \frac{1}{2}\right) \tag{6.2.2.1}$$

Where υ is the vibrational quantum number and can have integer values 0, 1, 2, 3...etc., and ν or $\tilde{\nu}$ is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} \tag{6.2.2.2}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{6.2.2.3}$$

At room temperature, nearly 100% of the molecules are in their ground vibrational state $\upsilon = 0$ according to the Boltzman distribution. By convention, the ground vibrational state is indicated by a double prime (") while the exited state is indicated by a single prime (').

- **Ground state: $\upsilon'' = 0$, nearly homogeneous population in the ground state at room temp.**
- **First excited state: $\upsilon' = 1$**

At room temperature, the lowest energy vibrational state $\upsilon = 0$ is populated, so $\upsilon'' = 0$. Thus, the only reasonable transition is from $\upsilon'' = 0$ to $\upsilon' = 1$, and $\Delta\upsilon = +1$.

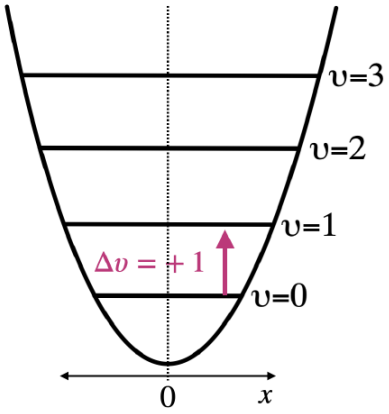


Figure **6.2.2.2**: The potential energy (U) well of an 'ideal' harmonic oscillator. The well is defined by the function $U = \frac{1}{2}kx^2$, where k is the force constant and x is the displacement from equilibrium bond length. The vibrational quantum numbers (υ) are indicated for the first three vibrational energy levels. The transition between $\upsilon = 0$ to $\upsilon = 1$ is indicated by the magenta arrow. (Kathryn Haas; CC-BY-SA)

The harmonic oscillation is a useful approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of the energy levels, all transitions would occur at the **same** frequency (i.e. you'd get a single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

"Real" bond vibrations are anharmonic

The vibrational energy levels of a real molecule are not evenly spaced and are more like that shown in the illustration in Figure **6.2.2.3**, where the energies are more closely spaced as υ increases. However, the harmonic oscillator is a reasonable approximation at $\upsilon = 0$ and $\upsilon = 1$.

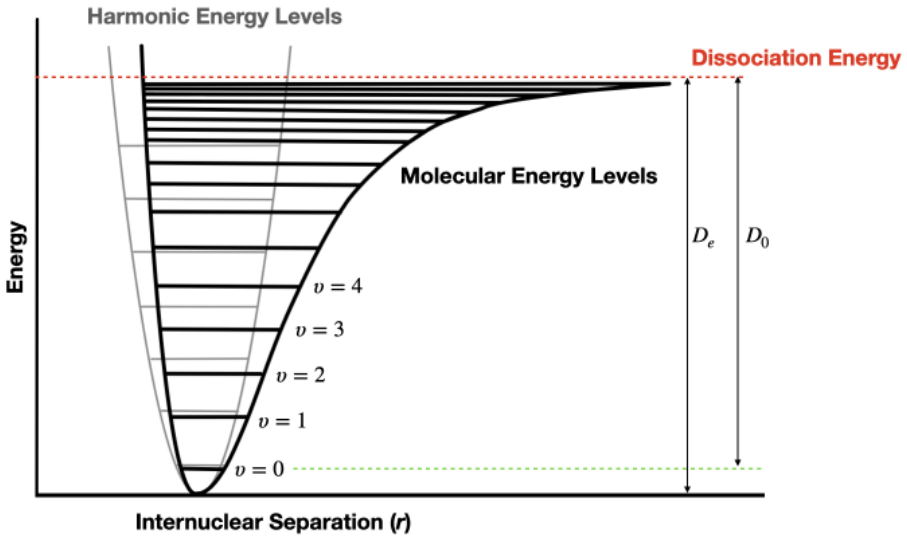


Figure **6.2.2.3**: Illustration of vibrational energy levels predicted by the harmonic oscillator model and those of a real diatomic molecule. (Kathryn Haas; CC-BY-SA)

ROTATIONAL motions and the the RIGID ROTOR model

The HCl molecule also has rotational motions. We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \tag{6.2.2.4}$$

In which J is the rotational quantum number with integer values 0, 1, 2, 3...etc., and I is the moment of inertia, given by

$$I = \mu r^2 \tag{6.2.2.5}$$

where μ is the reduced mass (Equation 6.2.2.3) and r is the equilibrium bond length.

Experimentally, frequencies of light are measured (in units of cm^{-1}), so it is convinient to use these units in our expressions. The frequency can be divided by hc to give energy in units of wavenumbers. The expression for the rotational energy levels expressed in wavenumbers is $\tilde{E}_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 cI} J(J+1) = \tilde{B}J(J+1)$. And, we can simplify the expression by defining the rotational constant $\tilde{B}$ as

$$\tilde{B} = \frac{h}{8\pi^2 Ic} \tag{6.2.2.6}$$

This gives the allowed energies of rotation, in wavenumbers, as

$$\tilde{E}_J = \tilde{B}J(J+1) \tag{6.2.2.7}$$

> Tip: It is important to note in which units you are working. The frequencies and rotational constants can have different units (eg Hz or wavenumbers). To keep track, we are using the tilde $\tilde{X}$ to indicate wavenumber units, but some texts don't do this - they always represent the rotational constant as B, whether in frequency or wavenumbers. Just be sure you are paying attention and are using consistent units in your calcaulations.

Just as in the notations for vibrational states, the convention for notating rotational ground state is by a double prime (") while the exited state is indicated by a single prime ('). The lowest-energy rotational state is $J'' = 0$. Rotational energy levels are very close in energy (much closer than vibrational energy levels), and so at temperatures close to room temperature, there is enough energy so

that higher-energy states are populated (e.g. $J'' = 1, 2, 3...$ are also populated). The statistical probability of each rotational state being populated can be calculated using the Boltzmann distribution.

- **Ground state: J''; at room temperature there is heterogeneous population of the rotational states.**
- **Excited state: J'; upon excitation we can also expect a heterogenous population of excited states.**

The rotational energy states are closer in energy than vibrational energy states. And, real molecules undergo rotationas and vibrations simultaneously. Thus, one way to show the rotational energy levels is to superimpose them on a diagram of the harmonic oscillator vibrational energy levels, as is illustrated in Figure **6.2.2.3**.

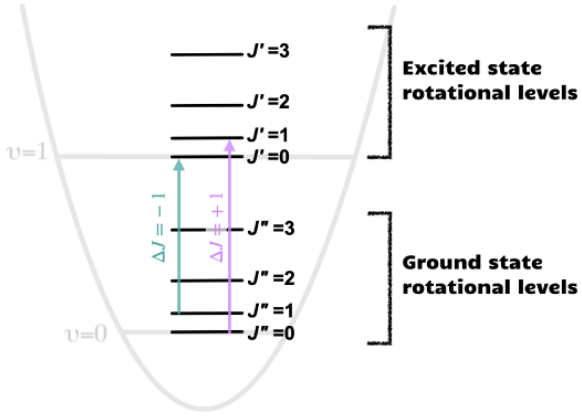


Figure **6.2.2.3**: The rotational states are shown superimposed in the vibrational states. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels. All ground state rotational states are indicated by J'' in purple, and rotational states of the excited state are indicated by J' in orange. A transition with $\Delta J = +1$ is indicated by the arrow on the left. A transition with $\Delta J = -1$ is indicated by the arrow on the right. (Kathryn Haas; CC-BY-SA)

Combining rotational and vibrational models

Real molecules are rotating and vibrating simultaneously, and the rotational and vibrational states are coupled. We could express the energies of these motions (in wavenumbers) as a simple combination of rotational and vibrational motions:

$$\tilde{E}_{v,J} = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}_v J(J+1) \tag{6.2.2.8}$$

However, this approximation ignores the fact that the rotational motions affect the centrifugal stretching of a bond, and thus the bond length and vibrational motions are afected by rotational motion. Vice versa, a vibrational excitation would increase the equilibrium bond length (r_e), and would affect the Moment of Inertia (I). A more complete representation of the energies of roto-vibrational states is expressed as a term value, $T(v, J)$, is given below. $T(v, J)$ in Equation **6.2.2.9** combines factors from rotational (rigid rotor) and vibrational (harmonic oscillator) energies, as well as factors that account for anharmonicity, centrifugal stretching, and the interactions between rotational and vibrational motions.

$$T(v,J) = \frac{E(v,J)}{hc} = \tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\nu}_e x_e\left(v+\frac{1}{2}\right)^2 + B_e J(J+1) \\ - D_e J^2(J+1)^2 - \alpha_e\left(v+\frac{1}{2}\right)J(J+1) \tag{6.2.2.9}$$

where c is the speed of light, $\tilde{\nu}$ is the frequency in cm-1, v is the vibrational quantum number, J is the rotational quantum number, and r_e is the internuclear separation. This expression takes into account the following:

- Anharmonicity with the term $-\tilde{\nu}x_e\left(v+\frac{1}{2}\right)^2$, where $\tilde{\nu}x$ is the anharmonicity parameter in cm^{-1}.
- Centrifugal stretching with the term $-DJ^2(J+1)^2$, where D is a constant.
- The interaction between rotational and vibrational motions with the term $-\alpha\left(v+\frac{1}{2}\right)J(J+1)$ where α is the rotovibrational coupling constant that accounts for interactions between rotational and vibrational motions.

We can simply this through approximation of the harmonic oscillator by assuming that the the harmonic oscillator is good enough for the case where the vibrational transitions are occurring almost exclusively between the two lowest-energy vibrational states: $v'' = 0$ and $v' = 1$. This gives a reasonable approximation that we can use as a model for rotational and vibrational motions of a diatomic:

Approximate allowed energies of roto-vibrational states:

$$\tilde{E}_{v,J} = \tilde{\nu}\left(v + \frac{1}{2}\right) + \tilde{B}J(J+1) - \tilde{D}[J(J+1)]^2 - \tilde{\alpha}\left(v + \frac{1}{2}\right)J(J+1) \tag{6.2.2.10}$$

- $\tilde{E}$ is the energy
- $\tilde{\nu}$ is the vibrational frequency in cm^{-1}
- v is the vibrational quantum number
- J is the rotational quantum number
- $\tilde{B}$ is the rotational constant
- $\tilde{D}$ is a constant related to centrifugal stretching
- $\tilde{\alpha}$ is the rotovibrational coupling constant in cm^{-1}

Selection Rules for vibrational and rotational transitions on diatomic molecules

- **Vibrational Transition Selection Rules**: The vibrational quantum number can change by 1: $\Delta v = \pm 1$. However, normally we can assume energy can only go upwards because of the nearly homogeneous population of $v'' = 0$ near room temperature.
- **Rotational Transition Selection Rules**: The rotational quantum number can change by 1: $\Delta J = \pm 1$. Since at room temperature, $J'' = 0, 1, 2..$. (several different rotational states are populated), transitions to higher and lower-energy rotational states are possible.

The P, Q, and R Branches

These selection rules mean that transitions with ΔJ or Δv equal to 0, 2, 3...etc are not allowed. The fact that the transition $\Delta J = 0$ is forbidden means that a purely vibrational excitation (with no accompanying rotational transition) is not observed in the case of diatomic molecules. The rotational selection rule gives rise to distinct "branches" of the gas phase IR spectrum for diatomics like HCl; They are named using letters P, Q, R in order of increasing energy and corresponding to $\Delta J = -1, 0, +1$, respectively. Due to the unequal spacing of rotational energy levels, each transition requires a different energy.

At the highest energies are the transitions of the R-branch (when $\Delta J = +1$) and at the lowest energies are the transitions of the P-branch ($\Delta J = -1$). Between the P and R branches is the Q branch ($\Delta J = 0$). The Q branch is absent in the gas phase IR spectrum of HCl because $\Delta J = 0$ is forbidden; thus it appears as a gap in the spectrum . Figure 6.2.2.4 illustrates allowed transitions on the energy diagram .

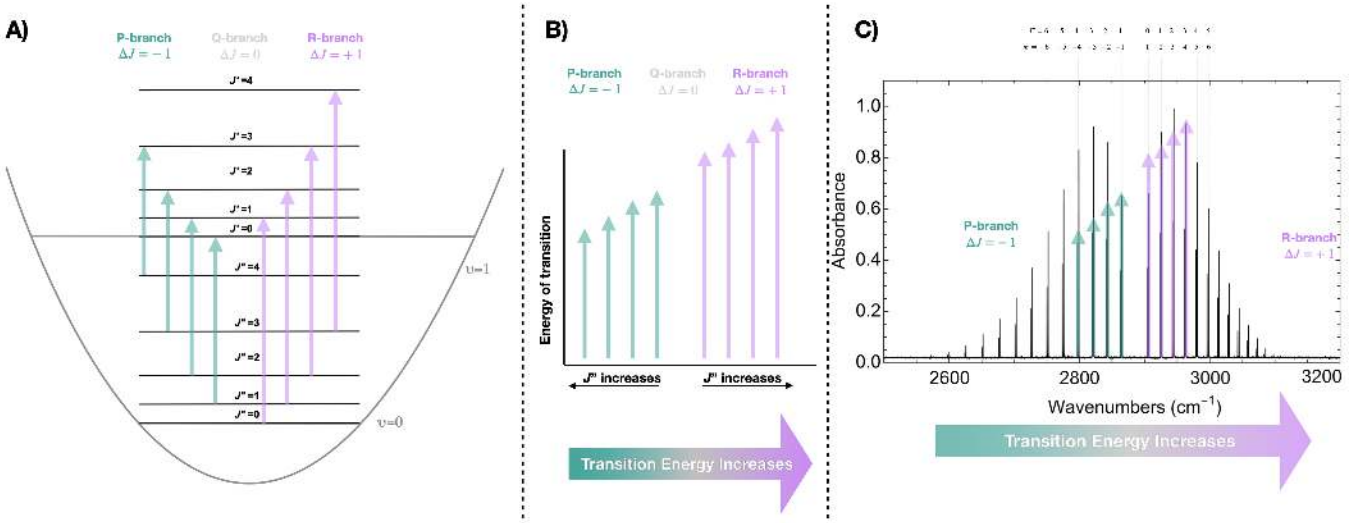


Figure 6.2.2.4: Allowed Rotation-Vibration Transitions are indicated using vertical arrows. The vibrational energy states are indicated with *upsilon* and rotational energy levels indicated by J. **A)** The rotational energy levels (J) are superimposed on the vibrational energy levels of the ground state (v'') and first vibrational excited state (v'). **B)** Illustration of the relative energy for transitions of P and R branches. Because of unequal spacing between the rotational energy levels, the individual transitions differ in energy. In **panel A**, arrows increase in magnitude from left to right. To illustrate this, each arrow from **panel A** is placed with tails aligned in **panel B** so their relative magnitudes are obvious. The magnitude of the energy transition is qualitatively indicated by the length of the arrow. C) The P and R branches, the m values, and the arrows from Panels A and B are annotated on the FTIR spectrum of HCl (taken at 0.1 cm^{-1} resolution). (Kathryn Haas; CC-BY-SA)

Frequencies of P, Q, and R Branches

The frequency of a rotovibrational transition is the difference in energy (in cm^{-1}) of the excited state and ground state: $T(v', J') - T(v'', J'')$. Thus the frequencies of vibrational transition from $v = 0 \rightarrow 1$ can be calculated from the Equation 6.2.2.9. The calculation is simplified by dropping D_e out of the equation, since D_e (the centrifugal distortion constant) is usually very small. Simplified equations for calculations of the frequencies of each peak in the R and P branches are given below.

R Branch frequencies

For peaks of the R-branch, where allowed J values are $J'' = 0, 1, 2, \ldots$ and $J' = 1, 2, 3\ldots$, and $\Delta J = +1$, the vibrational frequency for a given J'' is:

$$\tilde{\nu}_R = \tilde{\nu}_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)\, J'' - \alpha_e J''^2 \tag{6.2.2.11}$$

Q Branch (the forbidden frequency)

$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e x_e \tag{6.2.2.12}$$

*this is the forbidden transition (because $\Delta J = 0$ is forbidden). This is the frequency of the forbidden "vibration-only" transition, and it appears as a gap in the spectrum.

P Branch frequencies

For peaks of the P branch, where allowed J values are $J'' = 1, 2, 3, \ldots$ and $J' = 0, 1, 2\ldots$, and $\Delta J = -1$, the vibrational frequency for a given J'' is:

$$\tilde{\nu}_P = \tilde{\nu}_0 - (2B_e - 2\alpha_e)\, J'' - \alpha_e J''^2 \tag{6.2.2.13}$$

General equation for all frequencies

We can write a more general equation for the frequencies by defining a new value m, where $m = -J''$ for P branch, and $m = J'' + 1$ for R branch:

$$\tilde{\nu}(m) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 \tag{6.2.2.14}$$

Trends in peak spacing ($\Delta\tilde{\nu}$)

Consider a scenario where the interactions between vibrational and rotational motions is negligible, and thus α_e is small. In this scenario, the equations above (equations 6.2.2.11 and 6.2.2.13) would yield a linearly relationship between J'' and $\tilde{\nu}$. In this imaginary scenario, we would expect a spectrum with equally-spaced lines in the P and R branches, where the separation between the lines is $2B_e$ (in other words $\Delta\tilde{\nu} = 2B_e$).

However, in a real diatomic like HCl, there is significant interaction between vibrational and rotational motions, and α_e is significant. The result is a non-linear relationship between J' and $\tilde{\nu}$, where the spacing of the R branch decreases as J'' increases (R branch lines become more closely spaced), and the spacing in the P branch becomes larger as J'' increases (P branch lines become are farther apart).

R Branch peaks become more closely spaced

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{6.2.2.15}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$+(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{6.2.2.16}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$–(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

References

1. McQuarrie, Donald A. Quantum Chemistry. New York: University Science Books, 2007.

Contributors and Attributions

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- Kathryn Haas

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6.2.3: Transition Intensities

Transition Intensities

The relative intensity of the P- and R-branch lines depends on the thermal distribution of rotational states; more specifically, they depend on the population of the J'' states. The intensity of a spectral line depends not only on the transition probability (selection rules) and the frequency ν (energy of radiation), but also on the number of molecules in any initial state. Since most infrared (IR) spectra are observed under conditions of thermal equilibrium, we need only consider the distribution of the molecules over the different quantum states in thermal equilibrium.

According to the Boltzmann equation, the number of molecules dN_E that have a classical vibrational energy between E and $E + dE$ is proportional to $e^{-\frac{E}{k_B T}} dE$, where k_B is Boltzmann's constant and T is the absolute temperature. In quantum theory, only discrete values, $E_{(\nu)}$, are possible for the vibrational energy. The number of molecules in each of the vibrational states is then proportional to the Boltzmann factor $e^{-\frac{E_{(\nu)}}{k_b T}}$. The zero-point energy can be left out, since to add this to the exponent would only result in a multiplication factor that would be the same for all the vibrational levels (including the zero level).

The thermal distribution of the rotational levels (unlike that of the vibrational levels) is not simply given by the Boltzmann factor. We must account for the fact that, according to quantum theory, each state of an atomic system with total angular momentum J consists of 2J+1 energy levels which are degenerate in the absence of an external field; that is, the state has a (2J+1)-fold degeneracy. The number of molecules N_J in the rotational level J of the lowest vibrational state at the temperature T is thus proportional to

$$N_J \propto (2J+1)\, e^{-\frac{F_{(J)} hc}{k_B T}} \tag{6.2.3.1}$$

where $F_{(J)}$ is the rotational term value (equal to $\frac{E_{(J)}}{hc}$). For sufficiently large T or small rotational constant B, the population of the J^{th} rotational level, for N molecules, is given by the following equation [see p. 125 in reference (3)]

$$N_J = N \frac{hcB}{kT} (2J+1)\, e^{-\frac{BJ(J+1)hc}{kT}} \tag{6.2.3.2}$$

Since the factor 2J+1 increases linearly with J, the number of molecules in the different rotational levels goes through a maximum before decreasing with the rotational quantum number. It can be shown[3] that this maximum lies at

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2} \tag{6.2.3.3}$$

This expression clearly shows that J_{max} increases with decreasing B and increasing T. It should be noted that the number of molecules in the lowest rotational level, J = 0, is not zero. With increasing temperature, the band extends over a wider frequency range and the intensity maxima of the two rotational branches move outward and at the same time become flatter.

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 5.2.3.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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6.2.4: The Pure Rotational Spectrum has Unequal Spacings

Vibrational energy which is a consequence of the oscillations/ vibrations of the nuclei along inter nuclear axis, is possible only when the distance between the nuclei is not fixed/ rigid; that means the separation between the two nuclei is flexible/ elastic (non-rigid rotator). Consequently, centrifugal force, when the molecule is rotating, tends to fly the reduced mass μ away from the axis of rotation. To keep the mass rotating about the axis, there must be some restoring force to counter balance the centrifugal force. The work done to supply this force is stored as potential energy. Therefore, unlike the case of rigid rotator, total energy of rotation in a molecule comprises of kinetic and the potential energy corresponding to centrifugal force of rotation.

Let r_e is the distance between the nuclei when the separation is taken to be rigid and r_c under the action of the centrifugal force. According to Hook's law, restoring force is proportional to change in internuclear distance $(r_c - r_e)$, or $= k(r_c - r_e)$ which in turn, will be equal to the centrifugal force.

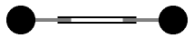


Figure 6.2.4.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{6.2.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{6.2.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{6.2.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 6.2.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{6.2.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{6.2.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 6.2.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1 + \Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{6.2.4.6}$$

$$= \frac{L^2(1 - 2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{6.2.4.7}$$

using

$$(1 + \Delta r/r_e)^{-2} \approx (1 - 2\Delta r/r_e) \tag{6.2.4.8}$$

$$E_r = \frac{L^2}{2\mu {r_e}^2} - \frac{L^4}{k\mu^2 {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{6.2.4.9}$$

$$= \frac{L^2}{2\mu {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2 {r_e}^6} \tag{6.2.4.10}$$

$$= \frac{\hbar^2\, J(J+1)}{2\mu {r_e}^2} - \frac{\hbar^4\, J^2(J+1)^2}{2k\mu^2 {r_e}^6} \tag{6.2.4.11}$$

Use of Equation 6.2.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\sqrt{J(J+1)} \tag{6.2.4.12}$$

has been made to obtain relation in Equation 6.2.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{6.2.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{6.2.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{6.2.4.15}$$

First term in the Equation 6.2.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 6.2.4.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 6.2.4.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 6.2.4.2.

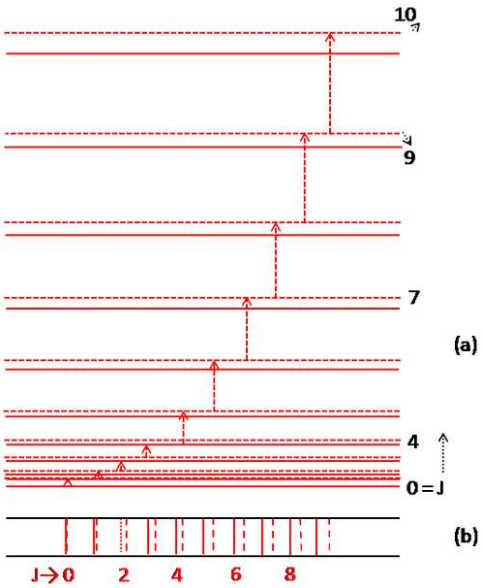


Figure 6.2.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational

lines decreases with increase in J , as shown in the Figure **6.2.4.2**. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4 \ \ cm^{-1}$ and $D \sim 0.0004\, cm^{-1}$. Usually, D is ignored in the calculations. Figure **6.2.4.2** exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors and Attributions

- 202.141.40.218/wiki/index.php...r_Spectroscopy

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6.2.5: Anharmonicity and Vibrational Overtones

Although the harmonic oscillator proves useful for modeling lower energy levels, like $v = 0, 1$, it fails at higher numbers of v. It not only fails to properly model atomic bonds and dissociations, but also is unable to match spectra showing additional lines that are not accounted for in the harmonic oscillator model.

6.2.5.1: Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to a transition of $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure **6.2.5.1**). For example, the parabolic potential of the Harmonic Oscillator approximation means that the vibrations can hold any amount of energy and bonds can stretch to any length, while in real molecules if the atoms are too far apart the bond will dissociate.

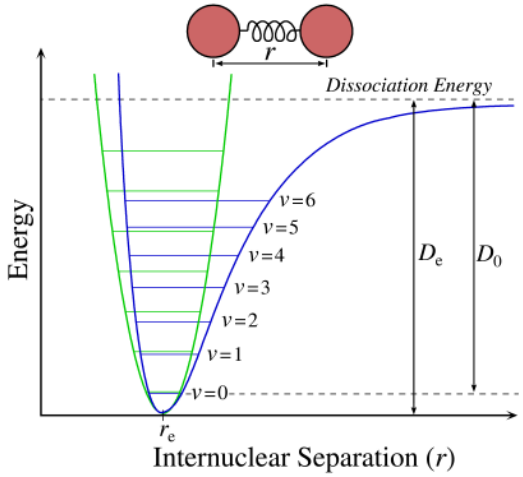


Figure **6.2.5.1** : Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure **6.2.5.1** , the harmonic oscillator potential well (in green) only roughly fits over the more accurate anharmonic oscillator well (in blue). The blue curve accounts for dissociation at large R values, which the green curve does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \tag{6.2.5.1}$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant, ignoring the absolute energy term($V(R_e)$) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 6.2.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{6.2.5.2}$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

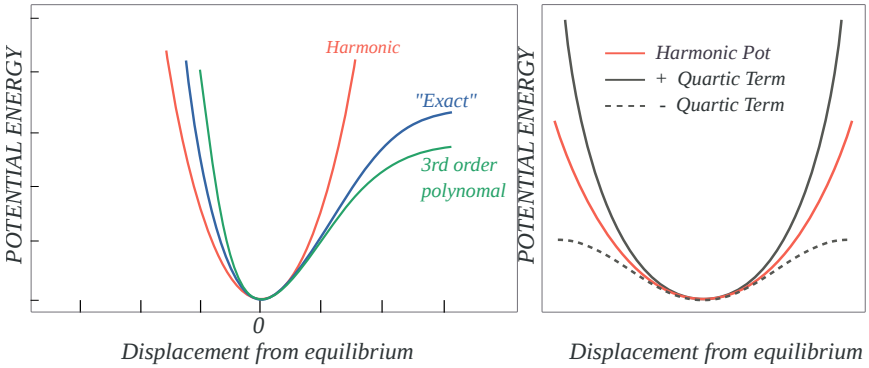


Figure 6.2.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right)$$

When the cubic term in the expansion (Equation 6.2.5.2) is included, and the Schrödinger equation is solved using perturbation theory this gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although E_v technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 6.2.5.1.

6.2.5.2: Overtones

The Harmonic Oscillator approximation predicts that there will be only one line in the spectrum of a diatomic molecule, while experimental data shows there is in fact one dominant line--**the fundamental**--and other weaker lines. How can we account for these extra lines?

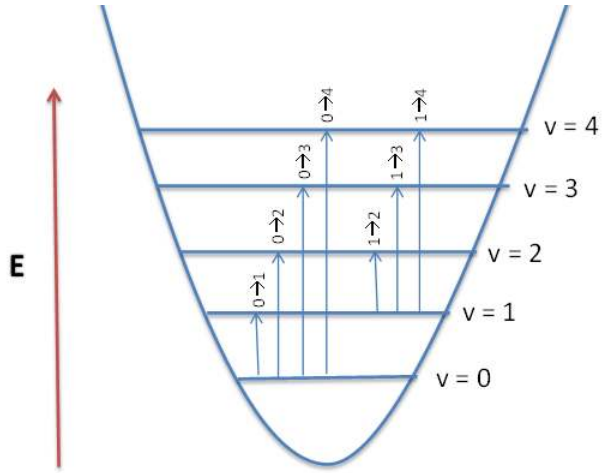


Figure **6.2.5.3** : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n > 1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 0 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

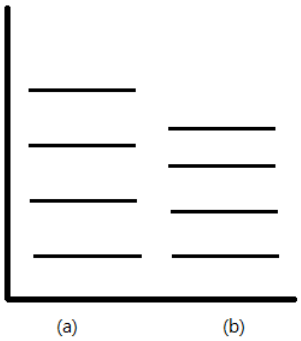


Figure **6.2.5.4** : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure **6.2.5.4**. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \textbf{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic **HCl** in the gas phase:

Table **6.2.5.1** : HCl vibrational spectrum.

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table **6.2.5.1** that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

? Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi_e}$.

? Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

6.2.5.3: References

1. Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry; Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry, 5th Edition (Nakamoto, Kazuo)
2. Lyle McAfee Journal of Chemical Education 2000 77 (9), 1122
3. Stuart, Barbara. *Infrared Spectroscopy: Fundamentals and Applications.* Wiley, 2004. Print.

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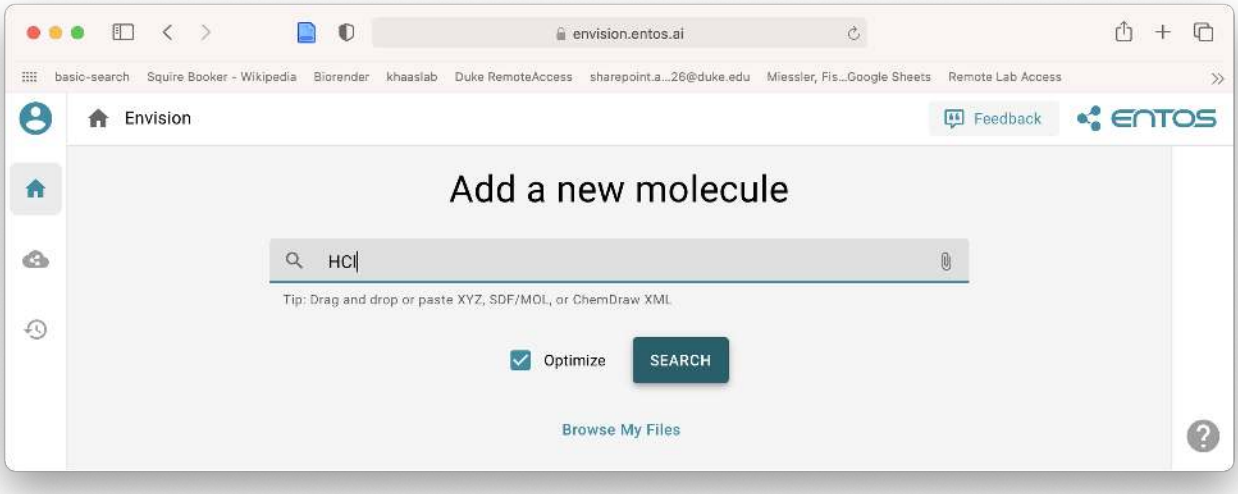
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6.3: Experimental and Instructions

> **Note**
>
> The ELN and other files for this experiment are here: Shared Files for Duke Students

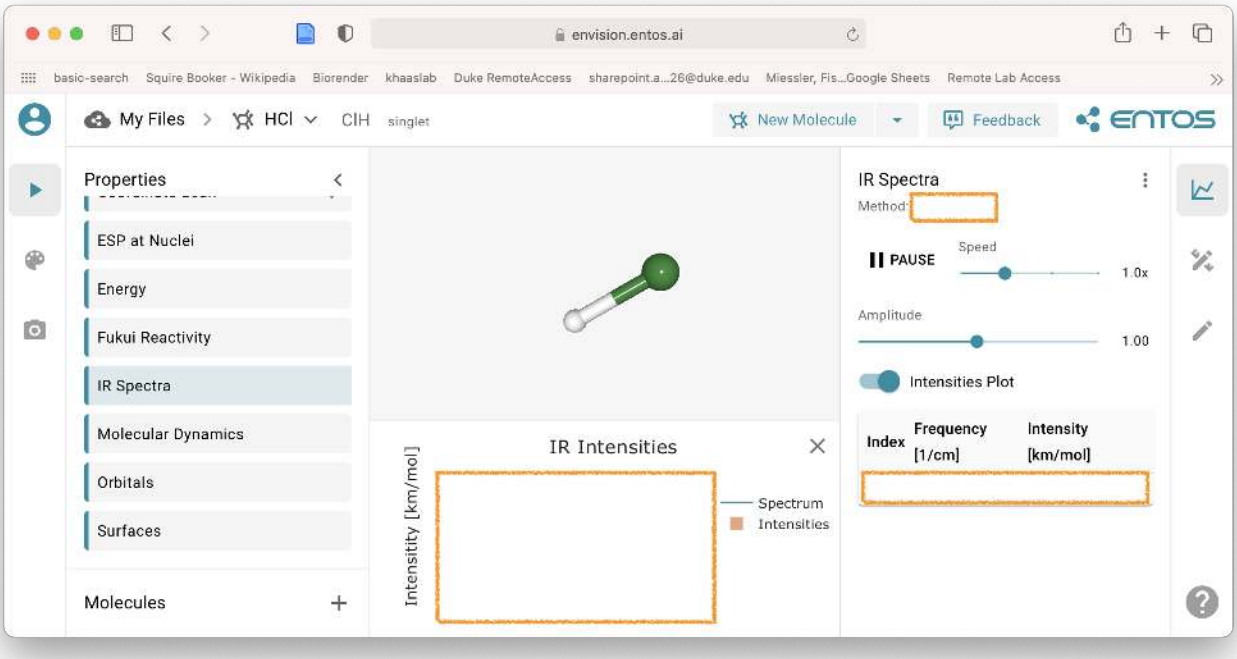
Part 1A: Computational prediction of vibrational frequency

On your computer's internet browser, please navigate to Entos Envision (https://envision.entos.ai), a free online computational platform. Use your duke email address to register a new account or log into your account. Type "HCl" in the text entry box and press "search".



The molecular structure of hydrochloric acid (HCl) is already calculated and available in Entos's database. Capture a snapshot of the HCl model.

From the lefthand menu, choose "IR Spectra". Record the calculation basis set (listed as "method"), the Frequency of vibration (and units), and a snapshot of the simulated IR spectrum. Comment on whether the simulated spectrum matches your prediction from the pre-lab assignment.



Next, measure the calculated bond length. To do this, click on "Energy" on the lefthand menu, then go to the righthand icon menu and choose the "Measure Bond Lengths and Angles option ( ). Then click on each atom of the bond and note the measured bond length.

Part IB: Preparation of sample and collection of FTIR spectrum

Preparation of Gas Sample Cell

- Gaseous HCl will be introduced into an IR gas cell.
- Hydrogen chloride is a **colorless, pungent, and corrosive gases** that fume in air. Contact will cause **burns to the skin, severe burns to the eyes and burns to the respiratory system if inhaled.** A vacuum line will be used to transfer the gases from their high-pressure containers to an evacuated IR cell.
- When not in use the IR gas cell must be stored in the desiccator. The cell is constructed of a glass body with KBr windows at each end. Ensure that the salt windows are kept free of moisture at all times. Please do not touch these windows.

Vacuum-Line Start-Up

Most of the following will 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 below 30 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 and fill with liquid N_2 from the 4L dewar such that the N_2 trap is submerged in liquid N_2
10. Check the level of N_2 as the experiment progresses. Refill if necessary to ensure the trap remains cold.
11. Check to ensure the pressure at the end of the main manifold is below 30 mtorr before proceeding.

Transferring HCl to gas cell

1. Remove gas cell from the desiccator and attach to the middlemost section of the working manifold shown below in Figure **6.3.1**.

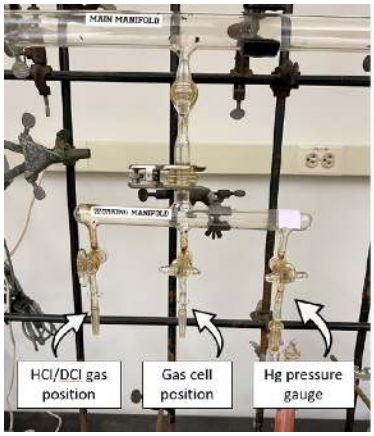


Figure **6.3.1**: Vacuum line set-up: working manifold and main manifold

2. Evacuate the back of the gas cell and introduce a vacuum to the interior of the cell.
3. Remove cell from manifold, bring it to the FTIR instrument, and take a background spectrum (see "Obtaining an FTIR Spectrum using the Nicolet iS50" below).
4. Replace the gas cell onto the working manifold and open it to vacuum.
5. Connect the pressurized HCl cannister to the working manifold via a vacuum-rated line. This line should contain its own needle valve that may be closed to separate the cannister from the rest of the working manifold. Introduce a vacuum to the line and to the pocket between this needle valve and the main valve on the cannister. The HCl cannister should remain closed at this time. Close the needle valve once this pocket has been evacuated.
6. Close the working manifold off from the main manifold.
7. Introduce a small amount of HCl gas to the pocket between the cannister and the needle valve by turning the cannister's main valve 180 degrees open briefly, and returning 180 degrees to close the cannister once more.
8. After ensuring the HCl cannister is closed, open the needle valve to release HCl into the working manifold. Use the mercury pressure gauge on the working manifold to monitor this process.
    - If the pressure rises such that it threatens to expel mercury from the pressure gauge, open the working manifold to the main manifold to release pressure.
9. Slowly release HCl from the working manifold using the valve to the main manifold until the pressure in the gas cell reaches 10 mmHg.
10. Close the gas cell off from the working manifold and open the working manifold to the main line to release any excess HCl from the rest of the system. (Remember to include the pocket between the needle valve and the HCl cannister!)
11. Record the FTIR spectrum using "Obtaining an FTIR Spectrum using the Nicolet iS50" below.
12. Once all data has been collected, return the gas cell to the working manifold and safely evacuate all remaining HCl.
13. Close and remove the evacuated gas cell and return it to the desiccator.

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 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.

Obtaining an FTIR Spectrum using the Nicolet iS50

You will use a Nicolet iS50 FT-IR Fourier Transform Infrared (FTIR) Spectrometer to collect FTIR spectra. Below are instructions for its use.

Note on Collecting Data

This is a single-beam instrument, as so you'll collect a background spectrum first, then subtract that background from the spectrum of your sample.

- Begin by recording a background interferogram of the evacuated gas cell. A fast Fourier transform (FFT) will be applied to obtain the background transmittance spectrum.
- Next, introduce your gas sample into the same gas cell and record a new interferogram. The software will perform FFT analysis on this interferogram to obtain the transmittance spectrum of your sample. To calculate the sample's transmittance spectrum, this spectrum is then ratioed against the single beam background spectrum. Finally, the absorbance spectrum of your sample will be calculated and displayed.

Setup the Experiment and Collect a Background Spectrum

1. Check the sample holder in the spectrometer to make sure there is nothing blocking the path of the infrared beam.
2. Mount the evacuated gas cell on the gas cell holder.
3. Close the cover and allow the sample compartment to be purged with dry, CO_2-free air for at 5 minutes, noting the time so that the purge time is reasonably accurate. While the chamber is purged, set up the software.
4. The Omnic software may already be loaded. If not, load it by clicking the 

icon on the Windows desktop. As the software loads you will see a blue light turn on at the top front right side of the instrument.



Figure **6.3.1**: The Omnic Button Bar. (CC-NC-BY-DUKE CHEM)

5. Click the **Experiment Setup** from the toolbar (Figure **6.3.1**), and go to the **Collect** tab (Figure **6.3.2**). Enter the appropriate settings. The settings for your first scan are below:
    - No of scans: **8 scans**
    - Resolution: **8 cm^{-1}**
    - Final Format: **Absorbance**
    - Background Handling: Collect background after **200 minutes**. (This is the time that the background is considered useful and after this time you will need to collect a new background spectrum)

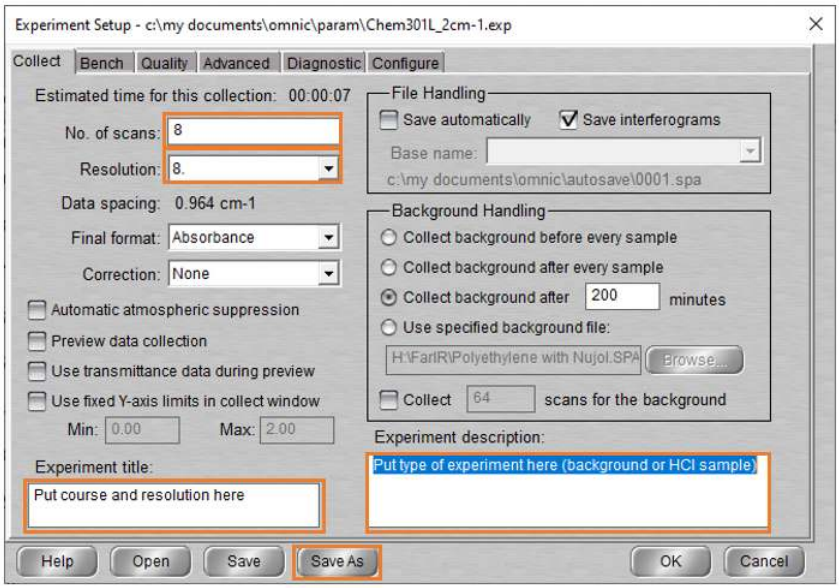


Figure **6.3.2**: The Collect Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

- Click on the **Bench** tab (Figure **6.3.3**)and wait for the interferogram to appear. The **Max** signal should be around 4.5. Click **OK**.

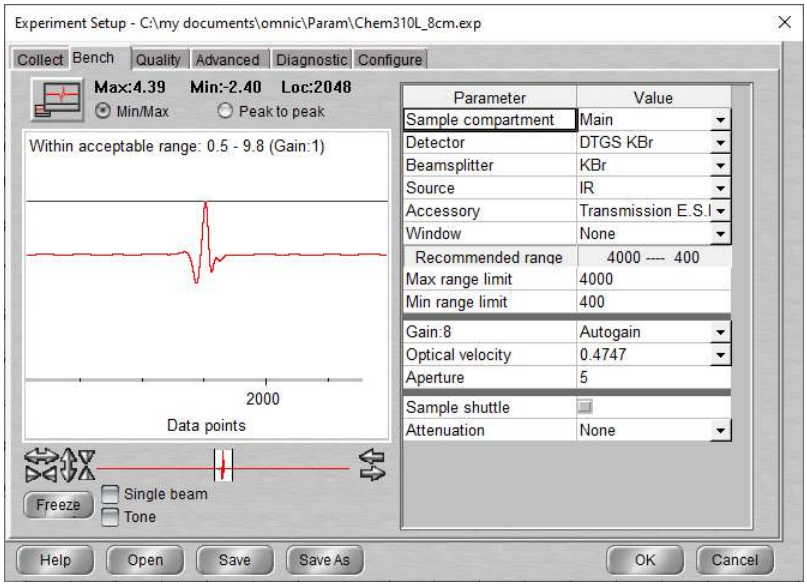


Figure **6.3.3**: The Bench Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

6. Select **Collect Background** from the **Collect** menu (or with the **Col Bkg** button, see Figure **6.3.1**).
   - Click **OK** when you see the **Confirmation** box. It will take about 4 minutes for the background scan to complete. Part way through, the background scan will be displayed on the main software screen.
   - Once complete, **add the spectrum to the window** when prompted.
   - Note the presence of water vapor, CO_2, and the polymer coating on the in the spectrum (Figure **6.3.4**). This arises from the atmosphere surrounding the cell (Remember: you gas cell is evacuated at this point).
   - Capture a figure of the background for your ELN using **Edit→ Copy** or using the Snipping Tool software.
   - Save your background data file:
   - Go to **File → Save as**. Save the file in your course data folder using the file name format **8cm_background_DDMMYYYY_initials**.

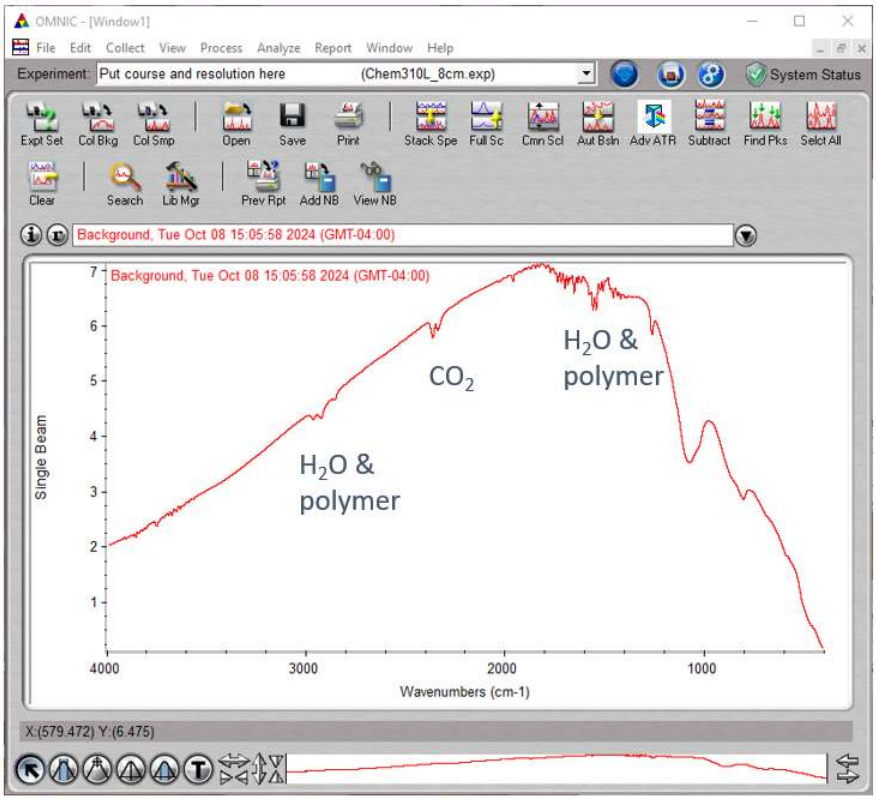


Figure **6.3.4**: A Typical Background Spectrum collected at 8 cm^{-1} resolution. (CC-NC-BY-DUKE CHEM)

Collect Sample Spectrum

7. Remove the evacuated gas cell from the sample compartment. Under the guidance of your TA, introduce about 1 cm Hg pressure of HCl gas into the cell. You must be careful to avoid the introduction of air into the cell. Replace the gas cell on the sample holder, and close the door of the sample compartment. Allow the sample compartment to purge for the same time as in the background spectrum.
8. Select **Collect Sample** from the **Collect** menu (or use the **Col Smp** button). You can enter a title or leave the default date/time when prompted. Click **OK**, and **OK** again in the Confirmation box to start the run.
9. When the scan is complete, add the scan to the window and you will see both sample and background displayed.
10. **Save** the spectrum data file (**File → Save as**). Use the data file format **HCl_8cm_YYYYMMDD_initials**
11. **Save the spectrum again** using **Save as** and choose the **.csv file format.** (You need this one for data fitting!)

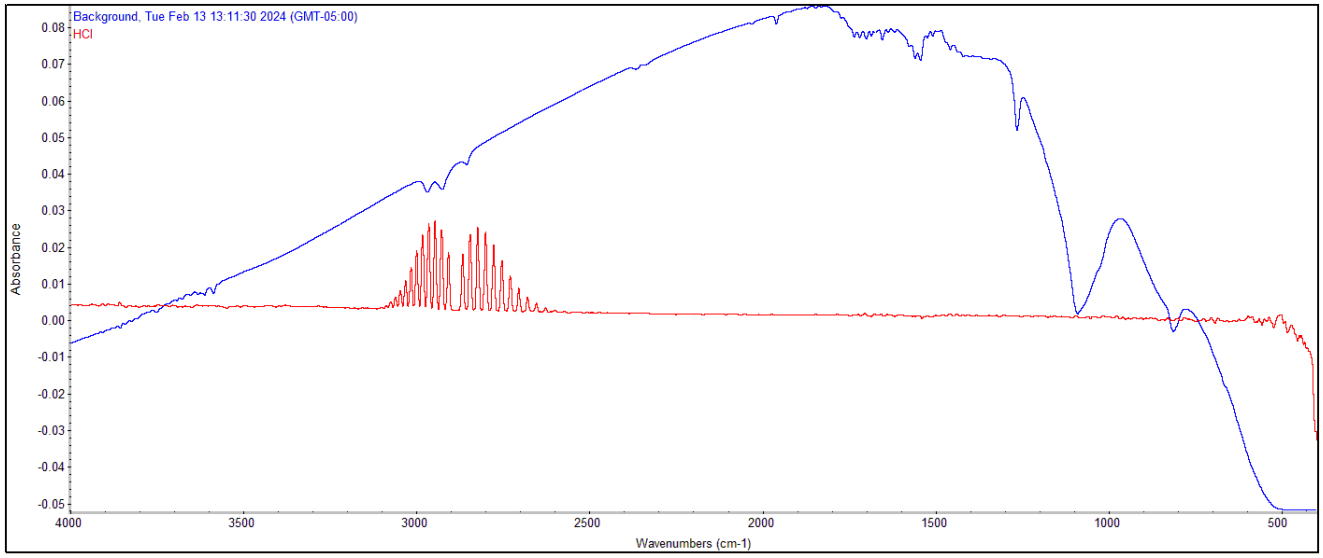


Figure **6.3.5**: Overlaid Background and HCl FTIR Spectrum at 8 cm $^{-1}$ resolution. (CC-NC-BY-DUKE CHEM)

12. Click on the **background** scan to make it the active scan (red) and select **Hide Spectra** from the **View** menu to remove the background spectrum from view.

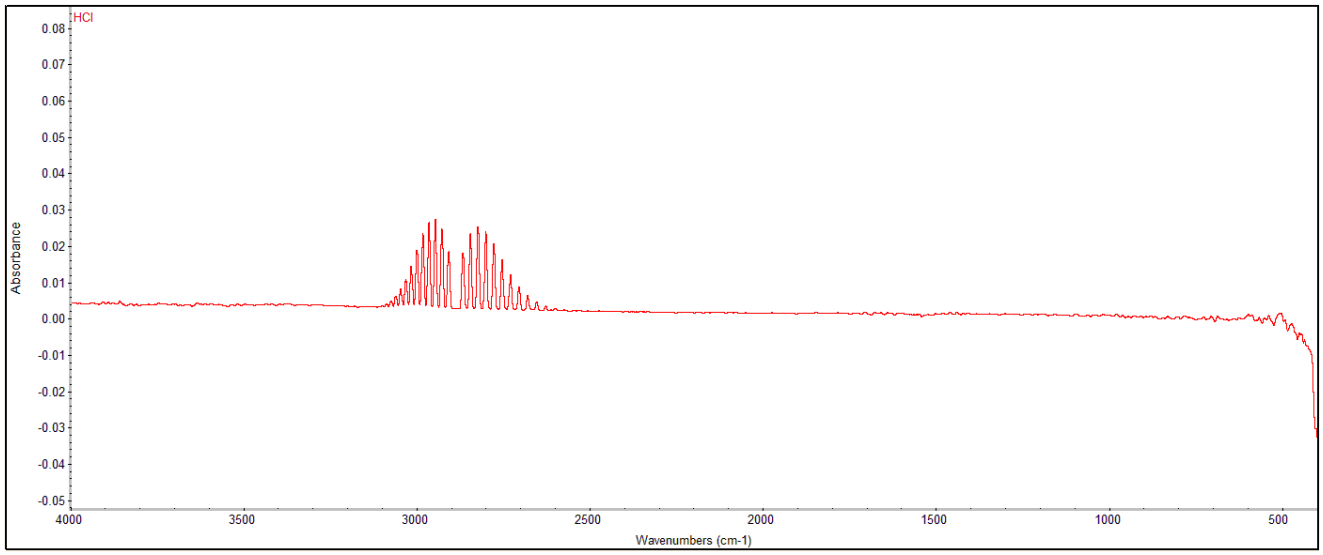


Figure **6.3.6**: The Sample Spectrum (background is hidden). (CC-NC-BY-DUKE CHEM)

13. Zoom in on the region around the HCl peaks **6.3.7**. You can do this using the left mouse button to click, drag a box around, and click again to zoom in on a specific region. You can also use the zooming tools at the bottom of the window.

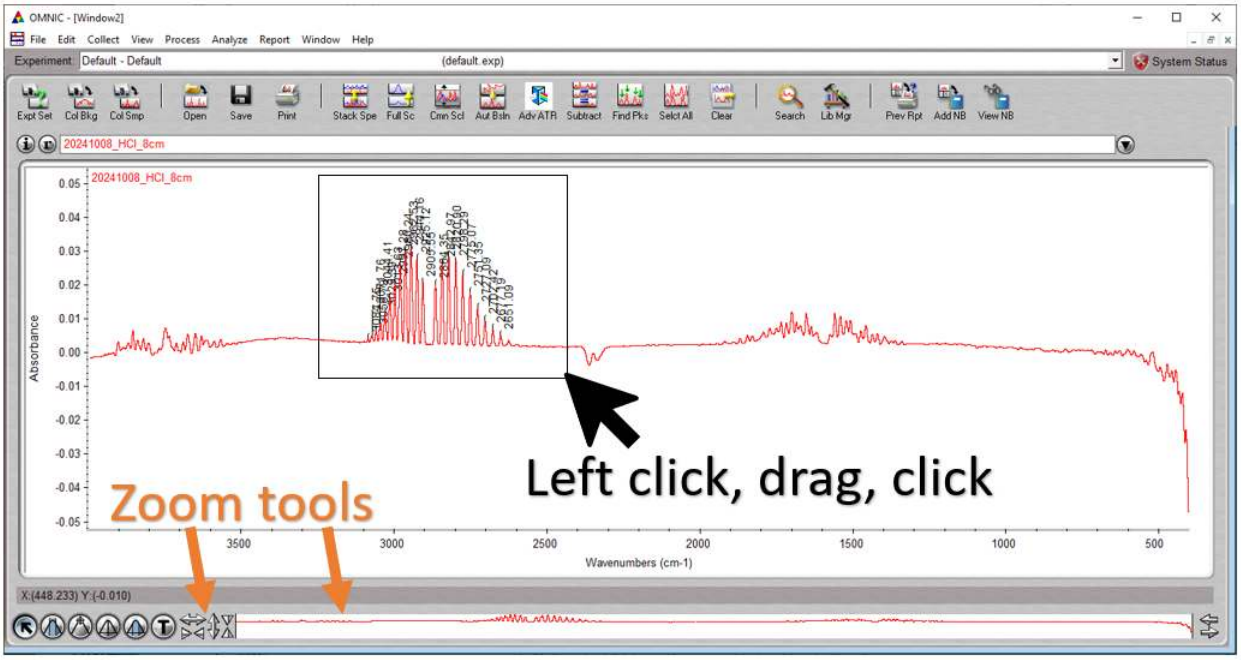


Figure **6.3.7**: Enlarging the peaks region. (CC-NC-BY-DUKE CHEM)

14. Select **Find Peaks** from the **Analyze** menu or click the 

button (Figure **6.3.8**. Move the horizontal threshold bar down so that it captures as many of the peaks as possible without getting into the noise at the baseline (see Figure **6.3.8** below). You can also adjust the **sensitivity** slider at the left of the screen to fine tune the peak selection. When you have a good selection of peaks, do the following:
    - Capture an enlarged view that contains all of the peaks and peak labels, put this in your ELN.
    - Click the **Clipboard** button to put the peaks table into the Windows Clipboard.
    - Open Excel and paste the clipboard into a spreadsheet (Ctr1 + V).
    - Save the **spreadsheet containing the peaks** in your data folder.
    - Make sure you've saved a screenshot (as already instructed) and that you have saved the excel file containing the list of peaks. Find these files on the computer and open them to be sure you have them and the contain the expected information.
    - Click **Replace** at the top right of the screen to bring you back to the active window.

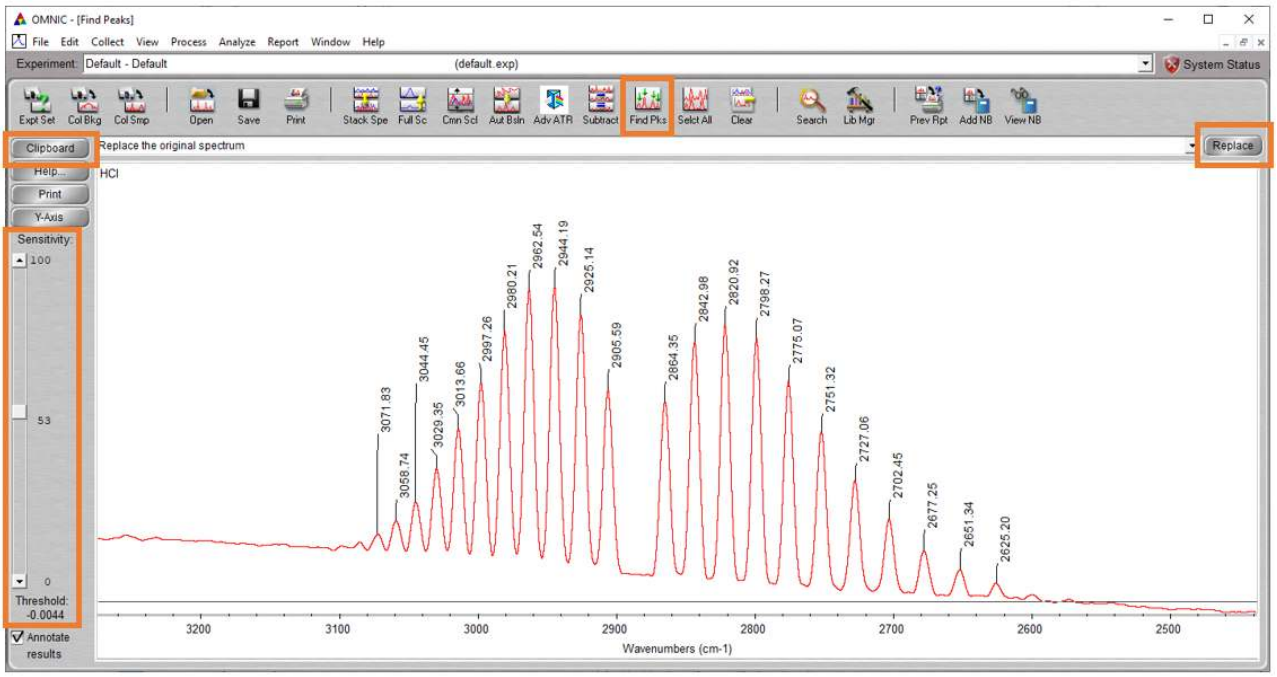


Figure 6.3.8: The find peaks result shown in enlarged view for an HCl spectrum taken at 8 cm resolution. Peaks are labeled using the Find Peaks option. A list of found peaks can be copied to the clipboard using the Clipboard button at the top left of the window while "Find Peaks" is active. (CC-NC-BY-DUKE CHEM)

15. If you wish to record the spectrum of a new sample, repeat steps above (repeat background collection if you are collecting data at a different resolution!).

Shutdown the Instrument and Store the Gas Cell

7. Simply **CLOSE THE OMICS SOFTWARE!**
   When you are done with the instrument and all of your work is saved, close the software. You will notice the blue light on the instrument turn off as the instrument goes into standby mode.
8. Remove your sample from the sample compartment and **close the cover**.
9. Re-evacuate the gas cell to remove your sample and store the evacuated cell (with stopcocks closed) in the desiccator.

Data Analysis for HCl FTIR spectrum for Part I

After collecting your first spectrum, please email your results to yourself, your group, and your instructors. Then assemble your group and begin group discussion and analysis of the data. The files linked at the top of this page will guide you to analyze the spectrum, derive mathematical models to fit the data, and calculate molecular parameters from the fits. (links copied here for convenience: Shared Files for Duke Students). Your instructors will be on hand to help guide you if you get stuck.

Part II: How does instrument resolution effect the certainty of derived parameters?

In Part II, you will collect the same spectrum of HCl at different instrument resolutions to determine how instrument resolution affects the error in your results. If you are finished with part I early, you may be able to collect this data in the first lab period. Otherwise, data collection for Part II will happen in the second week of this module.

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6.4: References

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CHAPTER OVERVIEW

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7.5: Exercise 2 - Molecular Orbitals of Formaldehyde

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

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

7.8: Exercise 5 - Modeling an Intramolecular Rearrangement

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7.1: 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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7.2: 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 Ψ written as a linear combination of a 1s atomic orbital on HA (Φ1sA) and a 1s atomic orbital on HB ((Φ1sB); 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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7.3: 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...

```
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,  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

```
spartan
```

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

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

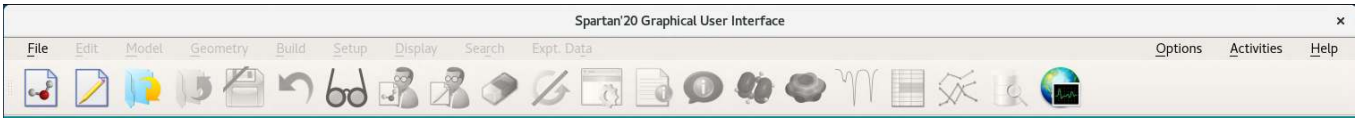


Figure 7.3.1: The Spartan Menu and Button Bar. (CC-NC-BY-DUKE CHEM)

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.

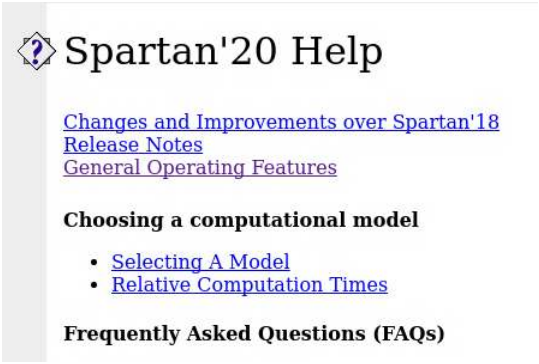


Figure 7.3.2: Spartan Help. (CC-NC-BY-DUKE CHEM)

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 **7.3.3**: 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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7.4: 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*.

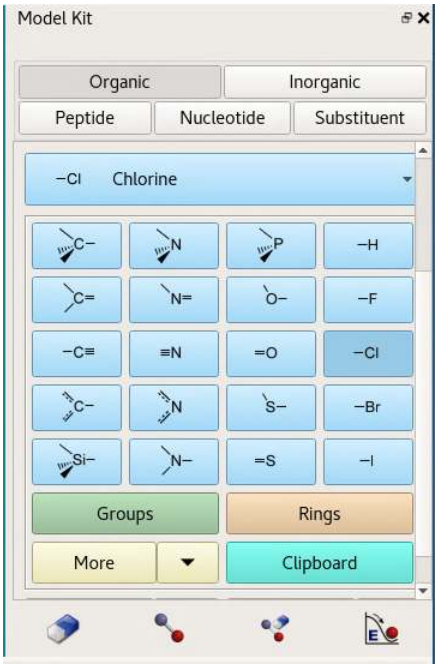


Figure **7.4.1**: The Model Kit. (CC-NC-BY-DUKE CHEM)

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

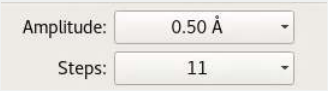
Clicking the  button returns you to the Edit Build Mode.

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. ν (cm^{-1})	Exp. ν (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)

This page titled 7.4: Exercise 1 - Estimation of the IR Spectrum of HCl, and Comparison of Basis Sets is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

7.5: 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.

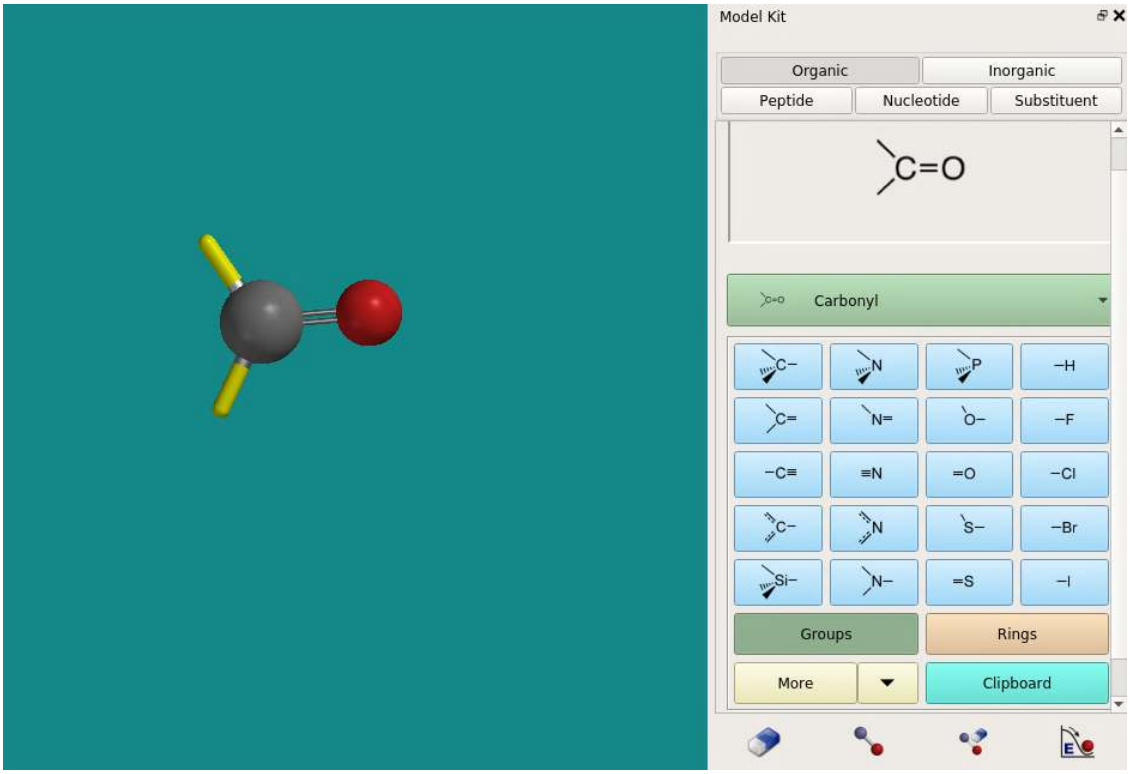


Figure **7.5.1**: Building Formaldehyde. (CC-NC-BY-DUKE CHEM)

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.

	C=O length		HCO angle		HCH angle	
H_2CO	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 π-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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7.6: 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.

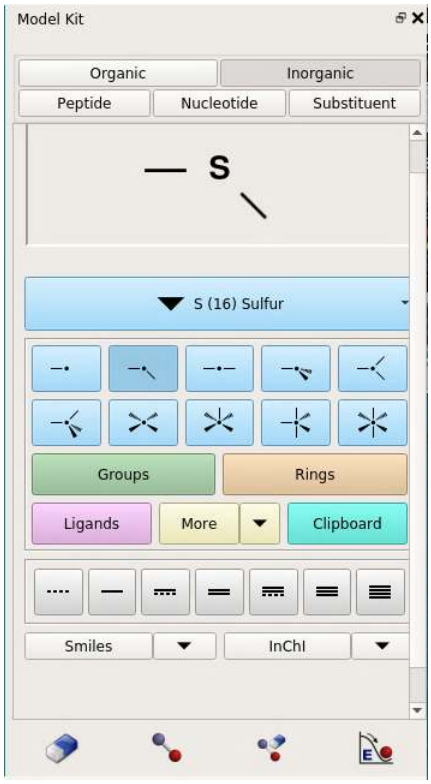


Figure 7.6.1: Selecting the Element Sulfur From the Inorganic Area of the Builder. (CC-NC-BY-DUKE CHEM)

Select atom hybridization. Double-click in the working area. Rotate the molecule to make all the bonds visible. Select **O** from the periodic table O (8) Oxygen and Select atom hybridization. Click at the ends of the bonds to **S** to make O—S(O).

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 ωB97X-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, (˚)	*nu*1	*nu*2	*nu*3
Ab initio	HF	STO-3G					
	HF	3-21G					
	HF	6-31G*					
Semi-empirical	PM3	N/A					
	RM1	N/A					
	AM1	N/A					
Density Functional	ωB97X-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)

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7.7: 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).

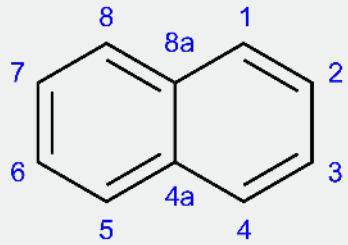


Figure **7.7.1**: Numbering of the carbon atoms in naphthalene molecules according to latest (2013) IUPAC rules P-25.3.2.3 and P-25.3.3.1, which is the same as 1979 rule A-22. (By User:Edgar181 - Own work, Public Domain, https://commons.wikimedia.org/w/inde...curid=22671537)

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.

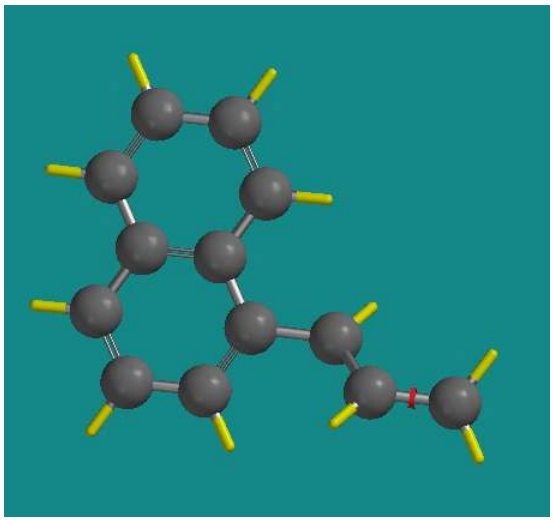
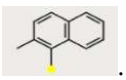


Figure **7.7.1**: Adding sp^2 Carbons to the Naphthalene Ring. (CC-NC-BY-DUKE CHEM)

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 3rd carbon atom in the working area, to add the second ring to your structure. At this point it might look something like this.

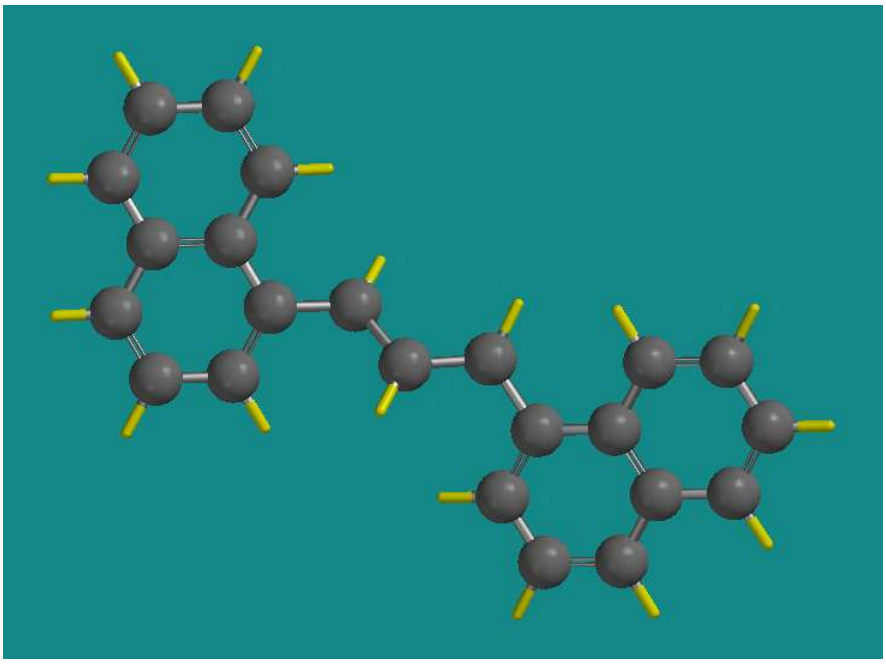


Figure 7.7.2: Adding the Second Naphthalene Ring. (CC-NC-BY-DUKE CHEM)

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.

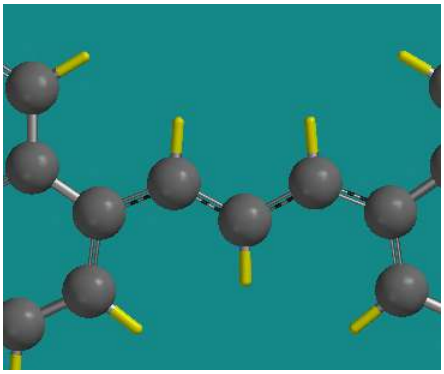


Figure 7.7.3: Changing the Bond Order of the Connecting Carbons. (CC-NC-BY-DUKE CHEM)

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.

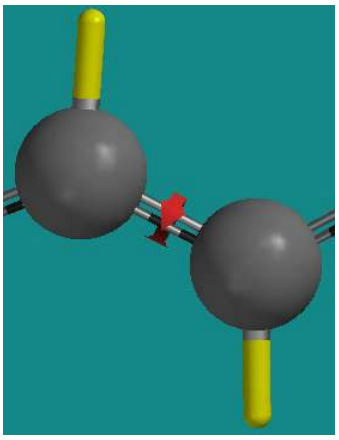


Figure **7.7.4**: The Rotate Fragment Arrow. (CC-NC-BY-DUKE CHEM)

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.

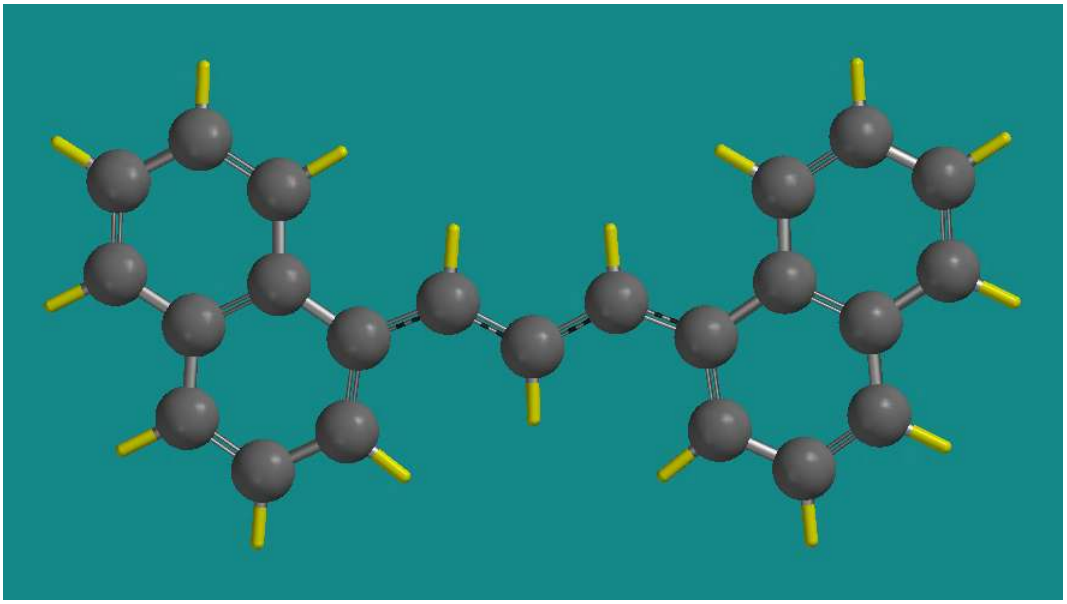


Figure **7.7.5**: The Nearly Completed Structure. (CC-NC-BY-DUKE CHEM)

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 **7.7.6**). 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).

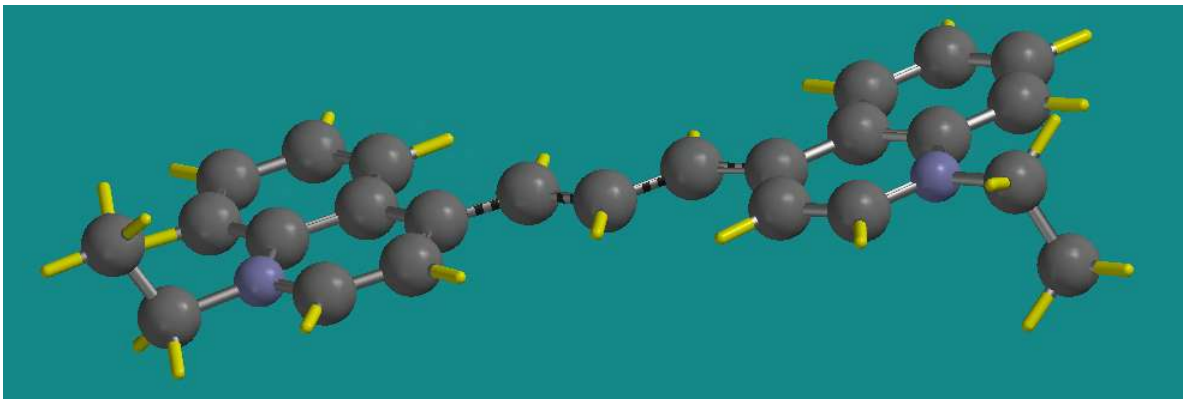


Figure **7.7.6**: The Completed Structure. (CC-NC-BY-DUKE CHEM)

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.

E, kcal/mol (from the Equilibrium Geometry calculation)	
Dye4	Energy of transition (eV)	λ_{max} (nm)
M		

N D O	
A M 1	
P M 3	
For Comparison: λ_{max} from Expt 1 =	

Things to Think About

- **A Change in Conformation Leads to a Change in Calculated λ_{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 λ_{max} changes.
- **Seeing Trends in the Calculated Results, and that λ_{max} Changes with Conformation is Likely More Important than Seeing if the Calculation Gave the "Right" λ_{max}:** It would be nice if your calculation could give a calculated λ_{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" λ_{max}.)

8. Look over the results from Dye 4. Which semi-empirical calculation (MNDO, AM1 or PM3) gave the best result when comparing λ_{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 λ_{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. λ_{max} (nm)	Exptl. λ_{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 λ_{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 λ_{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 λ_{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 λ_{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 λ_{max} to experimental λ_{max} and theoretical λ_{max} from the previous dye experiment
- Which semi-empirical calculation gave the most accurate result?
- Do you see the expected trend in λ_{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 λ_{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 λ_{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 λ_{max} as you move from Dye 3 to Dye 4?

(See your ELN template for details)

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7.8: 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  .

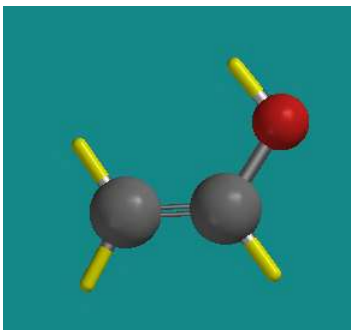


Figure **7.8.1**: Vinyl Alcohol. (CC-NC-BY-DUKE CHEM)

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.

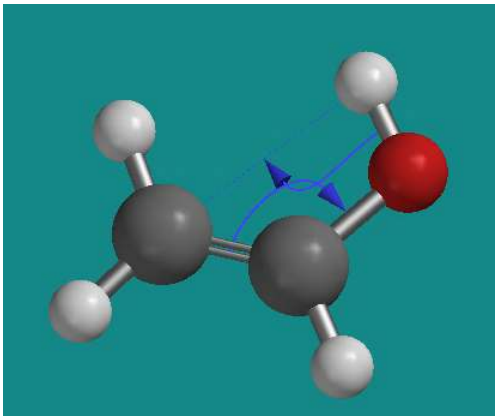


Figure **7.8.2**: Building the Transition State Query. (CC-NC-BY-DUKE CHEM)

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.

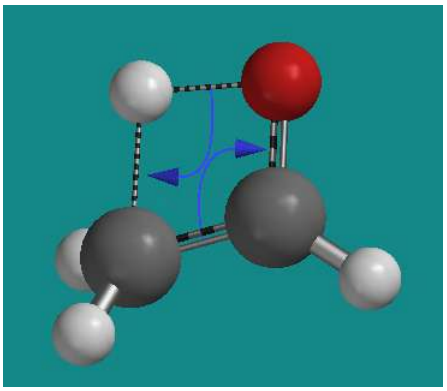


Figure **7.8.3**: The Guessed Transition State. (CC-NC-BY-DUKE CHEM)

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.

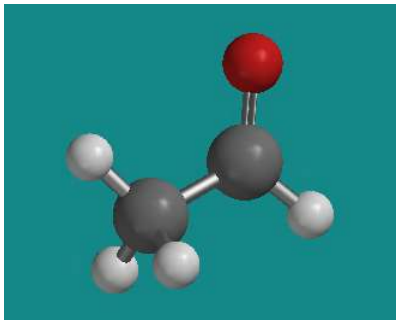


Figure **7.8.4**: Acetaldehyde. (CC-NC-BY-DUKE CHEM)

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.

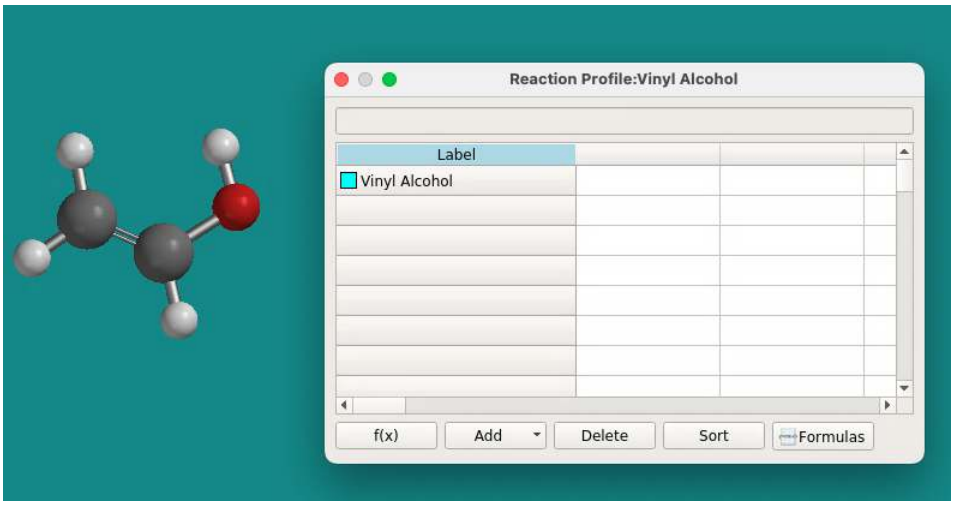


Figure 7.8.5: Adding Molecules to a Spreasheet. (CC-NC-BY-DUKE CHEM)

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.

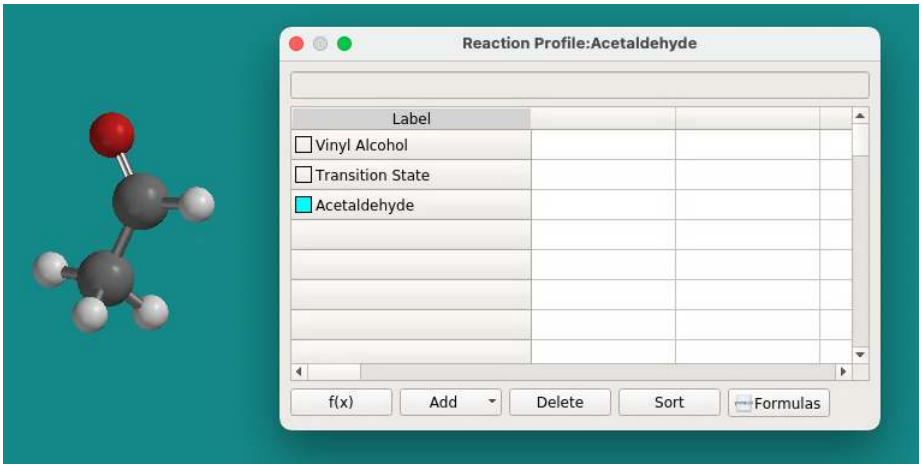


Figure 7.8.6: The Three Molecules in the Spreadsheet. (CC-NC-BY-DUKE CHEM)

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.

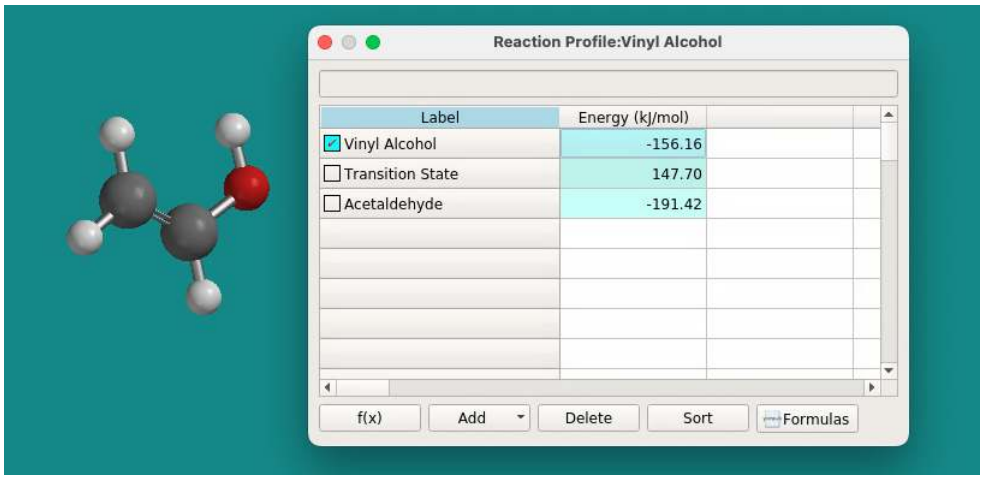


Figure 7.8.7: The Completed Calculations. (CC-NC-BY-DUKE CHEM)

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 ΔH for the reaction.

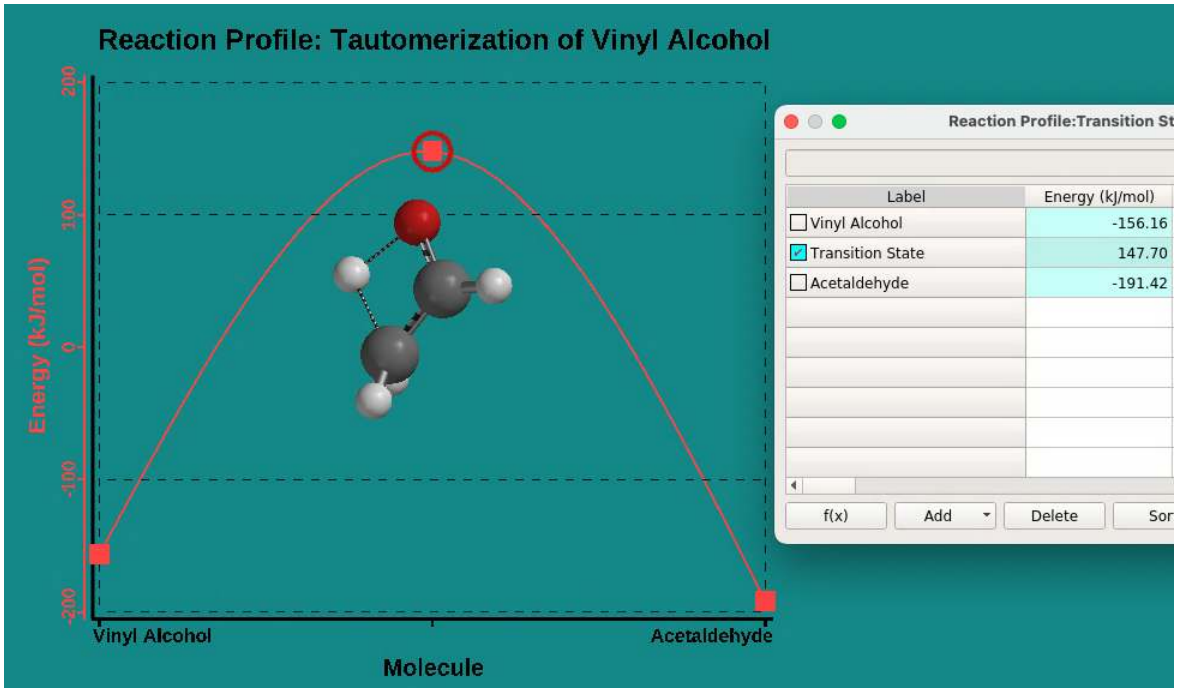


Figure 7.8.8: The Reaction Profile. (CC-NC-BY-DUKE CHEM)

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 ΔH of the tautomerization reaction

(See your ELN template for details)

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CHAPTER OVERVIEW

8: Independent Project

8.1: Pre-Lab and Introduction

8.2: Literature

8.3: Computational

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8.1: Pre-Lab and Introduction

Pre-meeting assignment for Independent Project

Prior to the first scheduled meeting for the Independent Project, do the following:

- Complete the Electronic Structure Calcuations from the previous module.
- Read this entire module.
- Submit two ideas for a project topic to Canvas. Your two proposals can be for either two computational project ideas, two literature project ideas, or one of each. These do not need to be the project you end up with, but you do need to start thinking about what questions you want to ask and answer.

This project is only assigned to students in CHEM310L (not CHEM301L). Its time to see how physical chemistry can be applied to a topic that really interests you.

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. You should prepar 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.

You will choose a topic, study it using computation or literature, and present your work to your classmates. Please prepare two proposals for this project and discuss them with your instructors.

Objectives of the Independent Project:

1. To apply what you're learned in class and lab to learn more about computation and/or a cutting edge research application!
2. To teach your classmates about a cool new topic in physical chemistry!
3. To practice communicating technical scientific topics through an oral presentation.

Project options

You may choose from one of the following options for your independent project:

1. Literature Project: Read a research article and present it as an application of physical chemistry.
2. Computational Project: Design a mini research project using electronic structure calculations, and present your results and conclusions.

Final Presentation

Your learning during this project will be demonstrated through a short in-class presentation. You will present the findings of your project to the class in a 7-minute presentation on the scheduled presentation day (see syllabus schedule). You will be graded on the information you present and your ability to answer any questions from your peers. If you have questions about format, ask us!

Peer Review

During the presentations, you will peer review your classmates. You will be assessed on your critical review of other students' works, and your feedback will be shared with those students anonymously. However, your review will not determine other student's grades.

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8.2: Literature

One option for your independent project is to explore a topic from class (lab or lecture) that intrigues you and find its application in modern chemical literature. This option would allow you to familiarize yourself with prominent physical chemistry journals, search chemical literature, and apply class concepts to real world applications.

This will involve looking at physical chemistry journals, choosing an article, reading the article critically, and summarizing the contents for your peers. The article you choose must a **full research article** (not a communication or a review article) and has been published recently (in the last **5 years**) in a reputable **physical chemistry journal**.

Find an article:

Start by seeing what's out there. Find the table of contents for a journal that focuses on physical chemistry or find the most popular articles for the last 12 months from one of the ACS journals. Links for some of the Journals of Physical Chemistry from ACS are linked below.

- Journal of Physical Chemistry A
  - Current Issue (https://pubs.acs.org/toc/jpcafh/current)
  - Top articels (https://pubs.acs.org/action/showMost...nalCode=jpcafh)
- Journal of Physical Chemistry B
  - Current Issue (https://pubs.acs.org/toc/jpcbfk/current)
  - Top articles (https://pubs.acs.org/action/showMost...nalCode=jpcbfk)
- Journal of Physical Chemistry C
  - Current Issue (https://pubs.acs.org/toc/jpccck/current)
  - Top articles (https://pubs.acs.org/action/showMost...nalCode=jpccck)
- The Journal of Physical Chemistry Letters
  - Current Issue (https://pubs.acs.org/toc/jpclcd/current)
  - Top articels (https://pubs.acs.org/action/showMost...nalCode=jpclcd)

With one of the lists, do the following.

1. Spend 10 minutes to scan the titles and abstracts of the articles in the latest issue(s).
   a. What subdisciplines or applications of physical chemistry do you notice?
   b. Are there any applications that surprise you?
   c. Is there anything that piques your interest?
2. Look at the synopsis figure that accompanies each title.
   1. Do the figures change your assignment of subdiscipline?
   2. Do the figures change your interest in reading the article?
3. Choose one paper that you would be interesting in learning more about and examine the abstract more closely. Decide if you want to actually read this paper. If not, move on to another, check out the Journal's ASAP articles, or go to a different journal to find something that is interesting to you. Alternatively, you can check out the list of top articles read for a specific year (eg: Top articles for 2021 are here: https://axial.acs.org/2022/01/20/mos...articles-2021/)

Structure your presentation

You will present the published research as if you were a researcher in the group of authors. You do not need to present the entire paper with all of its data. Select one or more of the most important points (the most important pieces of data, and conclusions drawn from them) from the paper and let that be the topic of your presentation.

In structuring your presentation:

1. Start is with the **question** the authors sought to answer. Give enough background about the question so that your audience can understand why the question is interesting or important.

2. Describe the **methods** used to answer the question. You do not need to cover each method in depth, but give your audience enough information that they can understand the meaning of the data you present.
3. Describe the **results**. As with the methods, help your audience understand what each piece of data means, but be concise.
4. Describe what **conclusions** were made from these results. Your audience should be able to understand how the results add up to the **conclusion** that were drawn.
5. Finally, you can bring up any limitations, changes you would make to the study, outstanding questions, and new directions.

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8.3: Computational

First, gain familiarity with electronic structure calculations in the previous module!

If you have lingering questions from a class or from your individual research that might be addressed using electronic structure calcuations, you can try to do so in this project! Once the Electronic Structure Calculations module is complete, you will have an understanding of the software's capabilities. Talk to your instructors about ideas or submit a proposal on Gradescope.

Examples of previous student's projects:

- Using Spartan to model tautomers of fluorescein to determine if absorption spectra would differ.
- Modeling a reaction mechanism to determine the energy of a transition state which would help explain confusing experimental results.
- Looking at the relative energies of ozone formation and ozone's reaction with oxygen and ozone depleting molecules.

Structure your presentation

One way you could structure your presentation is as follows.

1. Start with the **question** you sought to answer. Give enough background about the question so that your audience can understand why the question is interesting or important.
2. Describe the **methods** you used to answer the question.
3. Describe your **results**.
4. Describe the **conclusions** you make from the results. Your audience should be able to understand how your results add up to the **conclusion** you have drawn.
5. Finally, you can bring up any limitations, changes you would make to the study, outstanding questions, and new directions.

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9: Under Construction

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9.2: FTIR spectrum of HCl

Later in this semester, you will use a Fourier Transform Infrared (FT-IR) Spectrometer to investigate the coupling between the vibrational and rotational motions of a diatomic molecule, using hydrogen chloride (HCl) as the example. The FT-IR spectrum of HCl gas is a classic demonstration of quantum behavior. The diatomic, HCl, has only one IR-active vibrational mode. Yet, a close look at its IR spectrum shows interesting structure that can only be explained by quantization and coupling of the molecule's rotations to the vibrational motions.

This activity will help you get acquainted with MatLab, and it will also serve as a template for how you can approach data analysis later this semester. So, after you complete this, save your work and plan to use it again later!

> Be sure that the supporting files provided by our instructors are in your MatLab working directory. Using MatLab, open the "FTIR_StudentGuide.mlx" live script file, and follow the instructions in the document.

Below is an FT-IR spectrum of HCl gas (Figure **9.2.1**). Since chlorine has two naturally-abundant isotopes, ^{35}Cl and ^{37}Cl, the spectrum is actually the spectrum of $H^{35}Cl$ and $H^{37}Cl$. The taller set of peaks is from $H^{35}Cl$, while the shorter set of peaks is from $H^{37}Cl$.

FT-IR Spectrum of a mixture of HCl^{35} and HCl^{37}

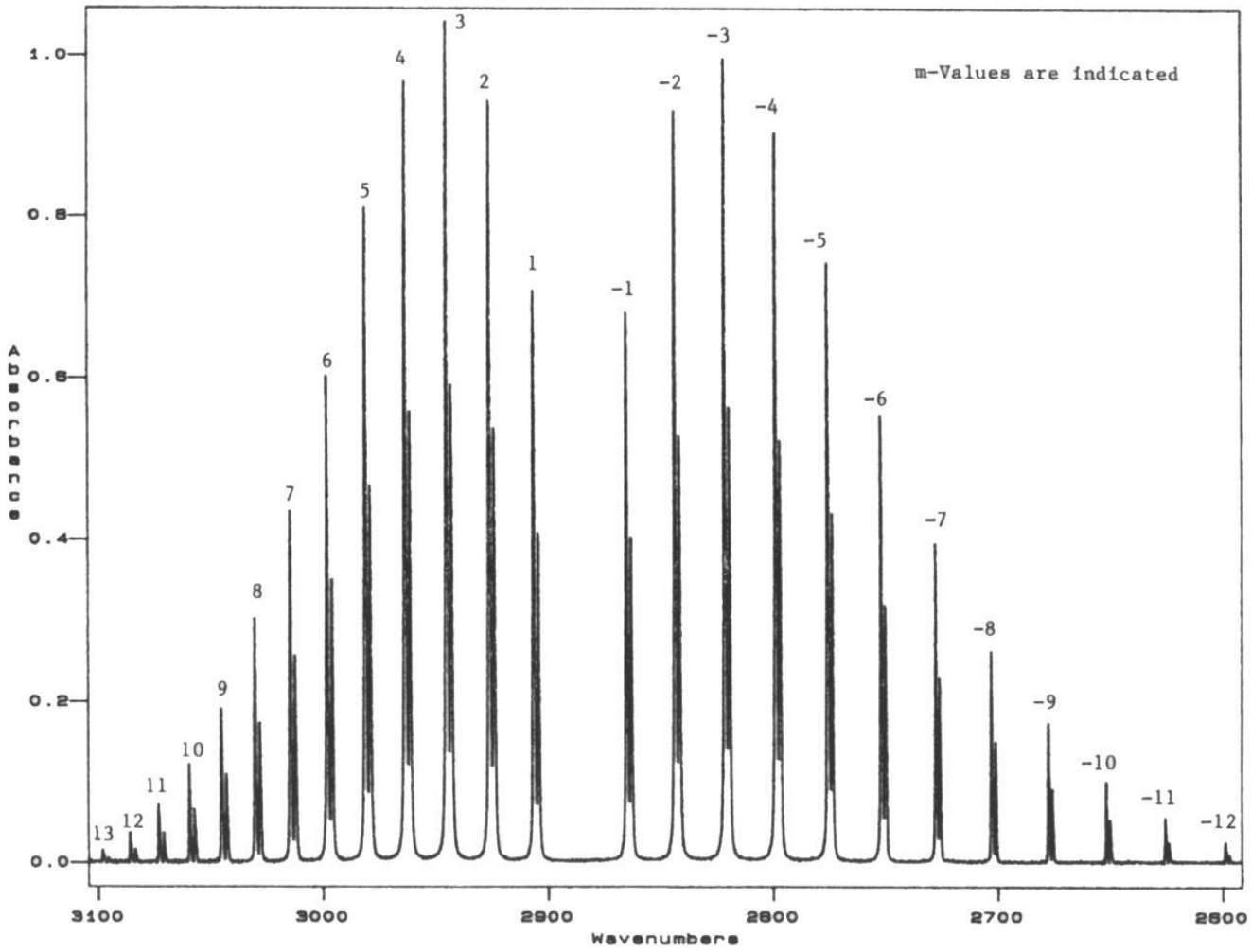


Figure **9.2.1**: FTIR Spectrum of HCl. (CC-NC-BY; DUKE CHEM)

Table of Peak Energies in wavenumbers:

Table **9.2.1** : $\tilde{\nu}_{(m)}(cm^{-1})$ for HCl from m = 4 to -4

$\tilde{\nu}_{(m)}(cm^{-1})$	m	isotope HCl^{35} or HCl^{37}
2963.01		
2960.84		
2944.57		
2942.52		
2925.65		
2923.48		
2906.00		
2903.95		
2864.78		
2862.85		
2843.33		
2841.40		
2821.27		
2819.34		
2798.61		
2796.80		

1. Determine from Figure **9.2.1** which peaks arise from $H^{35}Cl$ and which peaks arise from $H^{37}Cl$ and give each pair of peaks an appropriate m value.
2. Enter the peak positions $\tilde{\nu}_{(m)}$ for $H^{35}Cl$ and $H^{37}Cl$ as two separate vectors into Matlab.
3. Create a corresponding vector of m values from +4 to –4.
4. For each isotope, use Matlab to calculate the separation between adjacent peaks $\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)}$.

> **Note**
>
> $\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0

5. For each isotope, $H^{35}Cl$ and $H^{37}Cl$, do a separate plot of $\Delta\tilde{\nu}_{(m)}(cm^{-1})$ (y-axis) versus m (x-axis) with each data point indicated by a small circle.

> **Note**
>
> When plotting an x-y graph, the vectors x and y must be the same length. If $\Delta\tilde{\nu}_{(m)}$ cannot be calculated for a particular m value (see step (4)), then that value of m must be deleted from the vector of m values.

6. Perform a linear least-squares regression analysis and determine the slope, y-intercept, and standard deviation in the slope and intercept.
7. Create a final plot for each isotope, $H^{35}Cl$ and $H^{37}Cl$, that includes the raw data and the least-squares fitting.

Save your work!

When you have completed the steps above and have created a final plot, it is a good idea to get feedback from your instructors to confirm that you have successfully created a "full-credit" plot. Then, please export your work, inlcuding the final plot, as a pdf file and move to the next section.

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9.3: Part I - Data Analysis

Data Analysis for HCl/DCl FTIR spectra

Note

This is one of the more laborious data analyses you will do this semester. Let's minimize the number of repetitive tasks to save you some time. The following shortcuts are recommended:

- **Collaborate with a partner on steps 1-3 (allowed in this specific case only)**:You may collaborate with your lab partners in steps 1-3 below. One student should work up the data (steps 1-3 ONLY) for $H^{35}Cl$ and $H^{37}Cl$, and the second student should do the same analysis for $D^{35}Cl$ and $D^{37}Cl$. You should then share your graphs of $\Delta\tilde{\nu}_{(m)}$ versus m and the values determined for the slopes and y-intercepts of these plots. Each student should do one complete analysis (either HCl or DCl) alone, and the other analysis can be the work of a partner. However, you are responsible for all work that is in your ELN, so be sure your partner's work is correct. *Steps 4 and onward should be completed individually, as usual.
- **Calculate errors for one isotope only**: The propagation of errors that you calculate for one isotope should similar (perhaps not identical, but close enough) as for another isotope. Save time by propagating errors carefully for (B_e, α_e, $\tilde{\nu}_o$, Ie, re, and k for one isotope, then use those errors as an approximation for the errors for analogous values for other isotopes.
- **Use what you know!** Do you remember that MatLab Introduction module way back in the beginning of this course? It was a long time ago, but it was a template for data analysis in this module! Go back and use what you already know, and what you already created as a template, for this data analysis.

Collaborate with a partner

1. Label each peak in your spectra as "P" or "R" and its J-value as: P(1), P(2),..., R(O), R(1),... etc., as shown in Figure 2 on page 399 of Shoemaker, Garland and Nibler. (**Note:** Spectra recorded using your iS50 FTIR spectrometer are plotted with the wavenumber (abscissa) decreasing from left to right.)
2. For each of the four isotopic combinations ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$), make a table of the m values and the corresponding peak frequencies $\tilde{\nu}_{(m)}$. For each isotopic combination, calculate the separation between adjacent peaks.

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} \tag{9.3.1}$$

Note

$\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0. Therefore m = –1 must be deleted from the vector of m values.

3. Plot the differences between adjacent absorption frequencies (i.e., $\Delta\tilde{\nu}_{(m)}$ versus m. Then perform a linear least squares fit of the data with the understanding that

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} = (2B_e - 3\alpha_e) - 2\alpha_e m \tag{9.3.2}$$

Use the standard deviations of the slope and intercept in your error analysis (Q14).

Work on your own

4. **Compute B_e and α_e** for each isotope from the intercept ($2B_e - 3\alpha_e$) and the slope $-2\alpha_e$ of each best fit line (Equation 9.3.2).
5. **Calculate the frequency of the forbidden transition $\tilde{\nu}_o$** using your calculated values of B_e and α_e. To do this, use equation 9 in expt 37 of Shoemaker, Garland and Nibler. The equation is $\tilde{\nu}_m = \tilde{\nu}_o + (2B_e - 2\alpha_e)m - \alpha_e m^2$. Calculate $\tilde{\nu}_o$ from several of the lines with low m values. Calculate the average value, and standard deviation, of $\tilde{\nu}_o$.

> **Note**
>
> You will get the best results by using only the lines closest to the center (e.g., m = ±1, ±2).

6. **Create a table** of $\tilde{\nu}_o$, B_e, and α_e for the four isotopic combinations The units should be cm^{-1}.
7. **Calculate the moment of inertia (I_e), and the internuclear distance (a.k.a. equilibrium bond length, r_e)** for all four isotopic combinations.
8. **Calculate the harmonic oscillator force constant, k**, for each isotopic combination from your calculated values of $\tilde{\nu}_o$. In doing so you will need to assume that $\tilde{\nu}_o$ and the harmonic oscillator frequency $\tilde{\nu}_e$ are the same, thus ignoring the effects of anharmonicity (see the formulas and discussion on pages 400 and 401 of Shoemaker, Garland and Nibbler).
9. **Compare your values of r_e and k with those reported in the literature.** Why are these values independent of isotopic substitution?
10. **Determine the isotope effects:** Compute the ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for ^{35}Cl and ^{37}Cl in the case of HCl, and again in the case of DCl. Compare these with the predicted values given by Eqs. (11) and (13) on page 400 of Shoemaker, Garland and Nibbler.
11. From the results in 10, above, **explain why is the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl?** That is, when looking at your FTIR spectrum, the ^{35}Cl/^{37}Cl line separation is significantly greater in the DCl case then when compared to the HCl case. A descriptive answer is a good start, but your experimental observations should also be supported with a calculation that justifies the experimental observation.
12. Apply the Boltzmann distribution to explain observed band intensities in terms of the populations of the ground-state levels (see section 4.2). Again, a descriptive answer is a good start, but it should be supported with calculated results. You might create a spreadsheet to do these calculations. Does a calculation based on the Boltzmann population of rotational states match what you see experimentally in terms of which rotational lines show the greatest intensity?
13. From the mean line intensities for at least 10 features (for example five or more lines from the HCl spectrum and five or more from the DCl spectrum for a total of at least 10), determine the relative abundance of the two Cl isotopes. Estimate the weighted average atomic mass of Cl (that you might see on a periodic table for example) assuming that ^{35}Cl and ^{37}Cl have masses of 34.968 and 36.956 amu, respectively. Compare your result with the reported atomic mass of Cl.
14. For <u>one</u> isotope only, calculate the estimated uncertainty in each of the parameters determined for this experiment (B_e, α_e, $\tilde{\nu}_o$, I_e, r_e, and k). (Another table would be helpful)
15. Why is it important to purge the sample compartment of the FTIR spectrometer for both the background and sample runs? Why is it important to purge both background and sample for the same amount of time?

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9.4: Part I - References

1. Moore, W.J., Physical Chemistry, 4th ed., Prentice-Hall, Englewood Cliffs, New Jersey, 1972, pp. 767-770; or Pauling, L.; Wilson, E.B. Introduction to Quantum Mechanics, McGraw-Hill, New York, 1935.

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9.5: Part II - Data Analysis

4.7.1. Assign the fundamental bands of SO_2 as: symmetric stretch, $\tilde{\nu}_1$; bend, $\tilde{\nu}_2$; asymmetric stretch, $\tilde{\nu}_3$; and, report their frequencies. Compare your value with those reported in the literature.

4.7.2. Then assign any other bands, comparing the observed frequencies with those calculated from combinations of the fundamental values $\tilde{\nu}_1$, $\tilde{\nu}_2$, $\tilde{\nu}_3$.

4.7.3. Calculate k_1 and $\frac{k_\delta}{\ell^2}$ from Equations (1) and (3) (on page 385 of Shoemaker, Garland and Nibler) using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$. Check the valence-force model by calculating both sides of Eq. (2) (also on p. 385 of Shoemaker) and comparing them. Again, compare your results with literature values.

Note

When finding literature values for the force constants of SO_2, you will likely notice that different notations are used. It may be difficult to find the k_1 and $\frac{k_\delta}{\ell^2}$ notation used in Shoemaker, Garland and Nibler (and as such in this manual). For example, Kivelson[8] reports these same vales as f_d; and, $\frac{f_a}{d^2}$ and reports the values in units of $\frac{dynes}{cm}$ rather than $\frac{N}{m}$. Be prepared to convert.

4.7.4 Using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_1$, calculate $\tilde{C}_{v(vib)}$ at 298 K and at 500 K from Eq. (8) on page 386 of Shoemaker, Garland and Nibler.

4.7.5 At these same temperatures, calculate $\tilde{C}_v$ from the expression

$$\tilde{C}_v = 3R + \tilde{C}_{v(vib)} \tag{9.5.1}$$

and compare your results with the following $\tilde{C}_v$ values (obtained from directly measured values of $\tilde{C}_p$ and the expression

$$\tilde{C}_v = \tilde{C}_p - R \tag{9.5.2}$$

$\tilde{C}_v$ = 30.5 J K^{-1} mol^{-1} at 298 K and 37.7 J K^{-1} mol^{-1} at 500 K.

4.7.6 Calculate the uncertainty of each result you report in this experiment.

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9.6: Part II - References

1. Herzberg, G. Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, Princeton, New Jersey, **1945**, pps. 168-172, 251-269, 285.

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9.7: Emission Spectrum of Iodine Vapor

This semester, you use a laser spectrometer to investigate the Molecular Spectroscopy of Iodine Vapor. In this assignment you will plot the electronic potential energy curves (Morse potentials) for the iodine molecule. A discussion of the terms used in this assignment can be found in your textbook (D. A. McQuarrie, and J. D. Simon "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Chapter 13, Section 13.1-13.7.

The functional form of the ground and excited state Morse potential wells for iodine molecule I_2 are given by the expression

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

where V(R) is the potential energy of the system (y-axis), R is the interatomic separation (x-axis) between the iodine atoms, and T_e, and D_e, a and R_e are constants. Literature values for these constants are given below.

Constant	Ground State	Excited State
T_e	0 (cm^1) (arbitrarily set)	15730 (cm^1)
D_e	12244 (cm^1)	4112 (cm^1)
a	1.87 $\left(\mathring{A}\right)^{-1}$	2.00 $\left(\mathring{A}\right)^{-1}$
R_e	2.67 $(\mathring{A})$	2.97 $(\mathring{A})$

1. Generate a vector R that varies between 2 and 6 Å, in increments of 0.01 Å.
2. For both ground and excited states, calculate V(R) for each value of R using the above expression and the constants from the table. **NOTE:** These constants should be used in the units given above. No conversions are necessary.
3. On the same graph, plot V(R) (y-axis) versus R (x-axis), for both ground and excited states. Rescale the axes using the following axis scales:
   - V(R): 0 – 22500 cm^{-1}
   - R: 2 – 6 Å
4. Assemble a pdf document that contains both this assignment and the FTIR assignment into one pdf document and submit your work on Gradescope.

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9.8: Practice using a custom script

Install a custom script

The custom scripts (files with .m extension) and binary files (files with .mat extension) for this course are available here (click to go to OneDrive) using your Duke NetID. If you are using the Chemistry Department *bohr* server to access Matlab, the scripts are already installed for you.

If you are using your own computer, the scripts and binary files should be added to the correct folder on your computer. Follow the instructions in this video to install the lsq script, which performs least squares analysis.



Practice using a custom script and a binary file

This is an exercise to give you some practice in using Matlab to analyze data provided in a binary file, and plot the results using a custom script for least squares analysis. Before you start, make sure the custom files lsq.m and expt-1.mat are in your working MatLab directory (see video above). The binary file "expt-1" simply contains pre-defined 80 x 1 vector matrixes "x" and "y". This is just to save you the hassle of typing in the values for each vector.

> One way to work through this activity is to open the "Practice_LiveScript_XXX.mlx" file, and simply follow the instructions within the Live Script document.

Follow the steps below (there is a video below to walk you through these steps):

1. Open the MatLab program and be sure that you are working in the directory containing the lsq script and expt-1 binary file.
2. Type the following: **load expt-1**
   Your workspace now contains two variables, x and y which obey the following relation:

$$y = Ae^{-Cx} \tag{9.8.1}$$

3. Plot y (ordinate) versus x (abscissa). Using Matlab, recalculate your data in linear form (ln y versus x) and plot the result. Using least squares analysis of the linearized data, calculate the values of A and C and report the standard deviation in these values. Using your calculated values of A and C, use Matlab to draw (a) the least-squares fitted line through your linear plot and (b) the best fit curve through your exponential plot. (NOTE: data should appear as points using the symbol 'o' and least squares fitted lines should be solid lines.)

> **Expectation for a full-credit plot:**
>
> - Data is plotted in scatter format.
> - Axes are correctly labeled, with correct units.

- When appropriate, a curve fit to the data is shown
  - equation of the line is shown on the plot, but not obscuring the data
  - uncertainty in slope and intercept provided
  - correlation coefficient (R) provided
- Approrpate units are given for every value and every axis label.
- Plot is centered on graph.
- Text is easily readable (usually this means it is large enough to read easily.

4. You should show the plots described in (3) together with the values of A and C to your instructor. Each graph should have a title, and the x- and y-axes should be labeled.



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SECTION OVERVIEW

9.9: Matlab Practice (In Class Activity)

> **Note**
>
> Before attempting these exercises, please make sure you have access to a working copy of the MatLab software and you have the custom scripts and binary files installed in the MatLab directory. If you are using FastX to access MatLab on campus, these files are already installed for you on the server. Otherwise, you should install MatLab and the custom files on your computer before proceeding.

The practice exercises in this module are meant to be completed during the scheduled meeting. The Matlab practice exercises are are designed to help you become literate in MatLab programing language and the MatLab GUI's so that you can accomplish the data analysis in this course. MatLab is the preferred tool for data analysis for the modules later in this lab semester.

Both of the activities below can be completed during the first laboratory meeting; collaboration among students is welcome, though each of you should complete the activity and submit your own work. Your work should be inspected by your teaching assistant (TA) before you submit the assignments and leave for the day. If your TA determines that you have done the activities correctly, you will receive full credit for this assignment.

9.9.1: The Basics

9.9.2: Practice with LiveScript

9.9.3: MatLab for Data Analysis In This Course

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9.9.1: The Basics

Originally Created by Lindsay Pederson, Fall 2022 | Modified by Kathryn Haas each semester since.

Caution

This exercise may be an uncomfortable experience if you haven't completed the basic MATLAB tutorials that were part of your pre-lab assignment. If you are feeling lost during this activity, please go back to the basic MATLAB tutorials to get comfortable with the basic commands and practice working with matrices before returing to this exercise.

MatLab General Layout

Open the MatLab program to begin. If the layout of your MatLab window looks different than the arrangement illustrated below, you can switch to the default layout using the "Layout" button in the Home Tab toolbar (see below). Choose "Default Layout" from the "Layout" drop down menu. If the layout still seems different than what is shown it might be because you have a Script or LiveScript file open in your MatLab program.

Compare your MatLab window to what is shown below. Read the figure below and familiarize yourself with the panels of the MatLab window. Then follow the instructions.

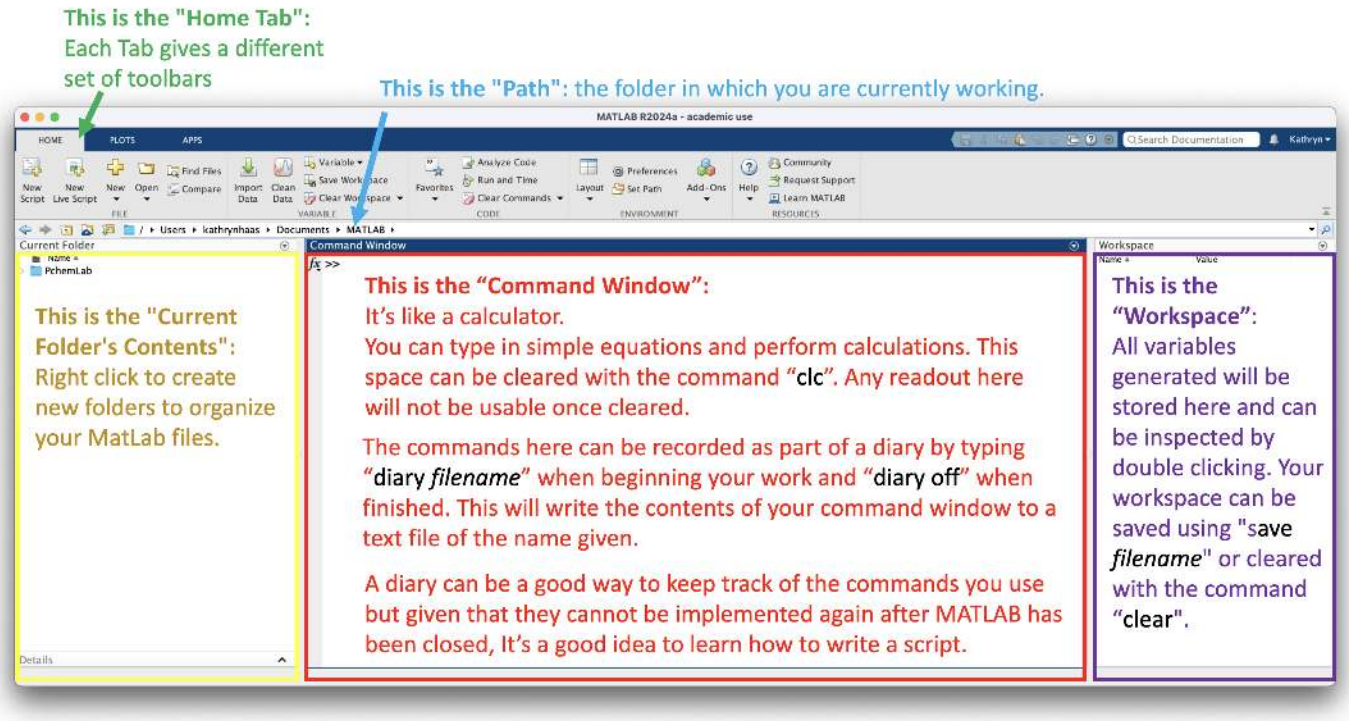


Figure 9.9.1.1: The default layout of the MatLab window (as of version R2024a). The tabs above the top toolar give access to different toolbar options. The file path is shown under the top toolar and indicates the current working folder. The Current folder's contents is shown in the pannel on the left. The center window is the Command Window, which functions like a calcuator. Type commands into the command window, save the work in the command window using the "diary filename" command to start saving and "diary off" when finished. All variables enterend in the Command Window will be populated in the Workspace, shown in the panel on the right. The Workspace can be saved using the "save filename" command or by using the "save workspace" button in the Home Tab toolbar. The workspace can be cleared using the "clear" command. (CC-NC-BY-SA; Kathryn Haas)

Practice with the Command Window

Find the command window in MATLAB. The command window is like a calculator. You can type simple equations here to perform calculations. The command window can be cleared by the command:

```
clc
```

All work is lost after the space is cleared.

The commands entered in the command window can be recorded in a text file (a diary). To record a diary, use the command "diary filename" at the beginning of your work:

```
diary filename
```

And then then at the end of the work:

```
diary off
```

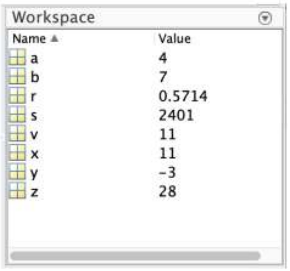
The diary file is a good way to keep track of commands, but the work cannot be implemented again from the diary file, so it has limited utility. **Script** and **Live Script** files are a much more useful way to record your work. **First, let's practice using the command window:**

Using the command window, begin a diary file with the name "practice_diary". Then do the following:

1. Clear the workspace by typing the clear command.
2. Create a variable *b* and set it equal to 7
3. Create a variable *a* and set it equal to 4
4. Add *a* and *b* and assign the result as *x*
5. Subtract *a* and *b* and assign the result as y
6. Multiply *a* and *b* and assign the result as *z*
7. Divide *a* by *b* and assign the result as r
8. Find *b* to the power of *a* and assign the result as s
9. Use the up arrow key to go back to the the command from step 4. Edit the command to assign it as *v* istead of *x* and end the command a semicolon; What does the semicolon do?
10. End the diary
11. Clear the command window with clc

The workspace

Notice that your workspace now contains all variables you defined. The workspace should look like this:



You can save the variables in the workspace as a binary ".mat file" with the command:

```
save filename
```

Use the command window to save your workspace using the file name "practice_workspace.mat". Notice the new file shows up in the **Current Folder Window**.

Now, clear the workspace with the clear command.

```
clear
```

Just for practice, use the load command to load the file you just saved and inspect the workspace:

```
load filename
```

Clear the workspace again before moving to the next section.

? Discussion Questions9.9.1.1

1. Where was the practice_diary file saved and what extension does it have? How would you submit a file like this to Gradescope?
2. When mathematical operations are performed in the command window, how are they defined in the workspace? What happens to the previous value in the workspace when you enter a new operation? (eq, try a + b , then a^b)
3. What does a semicolon at the end of a command do?
4. What does a percentage sign at the beginning of a line do?

Practice with Script Files

The Command Window is convenient for quick operations that you don't want to save. But it has some big limitations. For example, even if you do save the diary, you can't re-run any of the commands automatically. A better way to save your work is by entering it in a Script File.

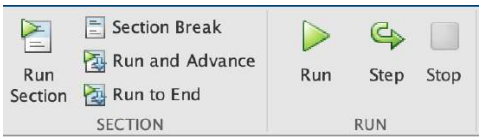
One way to start a new script is to go to the Home Tab and select **New**, then **Script**. Instead, let's use the command line to start a new script called "reference_script.m". Type the following into the command window:

```
edit reference_script.m
```

This will create a new script file. The new file should appear in the Current Folder window and it will open as a new tab in the Editor Window.

Find the Editor Window. In the Editor window, type the following:

```
%% Editor Exercises %%
% single percent sign indicates a text line
% double %% percent (only) indicates a section break.
% you can run each section of the editor by pressing the Run Section button.
% you can run the entire editor by pressing the Run button
```

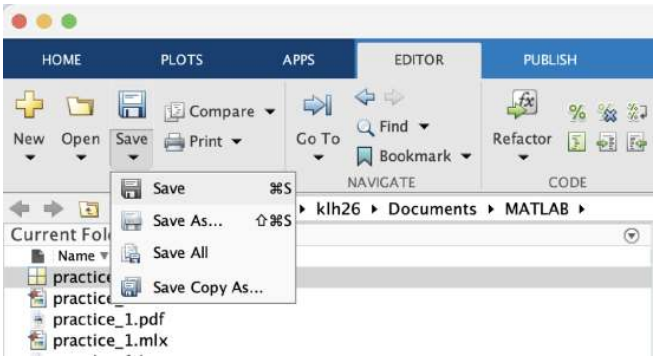



```
%%
%Type this into the new script in the Editor
b = 7
a = 4
% then hit run.
```

Notice what happens in the command window and in the workspace.

```
% again, type these examples of simple operations into the editor
x = a+b
y = a-b
z = a*b
r = a/b
s = b^a
% hit run and look at the command window
% then clear the command window and clear the workspace
% then add semicolons to the end of the lines and hit run again
```

Now that we see how the editor works, let's save the contents of the editor window as "reference_script.m". Go to the Editor tab and choose save.



At the end of the script that you just saved, add the following. Then run each section to see what happens. You can view any variables by typing their name in the command window.

```
%%
%% Building a reference sheet %%
a = 7;
b = 4;

%%
%Simple matrix - you can use spaces or commas to separate entries%
l = [1 2 3];
%%
%multiple rows - separated by semicolons%
m = [1;2;3];
%%
%matrices can have expressions in them%
n = [a+b, a-b, a*b];
%%
%transpose matrices with an apostrophe%
N = n';
%%
%multiply matrices
L = l*m;
M = m.*N;
```

```
%works the same with division
%%
%Create a matrix with regularly spaced intervals - defaults to one if not
%otherwise specified%
e = [1:16];
E = [1:0.5:16];
%%
%To reference specific elements of a matrix, call the matrix and then add
%coordinates (row, column) or just one number if it's a vector%
e7 = e(7);
m2 = m(2);
%%
%delete specific elements of a matrix
h = [1 2 3;4 5 6;7 8 9];
h(2) = [];
%check value of h in workspace
%%
%How to plot stuff
%you can just say "plot" but to intentionally keep track of figures it's a
%good idea to invoke figures by number
x = [1 2 3 4 5];
y = x.^2;
z = y./2;
figure(1)
hold on
plot(x,y)
plot(x,z,"o")
hold off
A = [1, 5, 0, 20];
axis(A)
xlabel('x')
ylabel('x^2')
title('Example')
%you can get help for any function you want to use (ex: plot()) by searching
%in the "Search Documentation" box at the top right of the screen
```

Save your files. Then clear the workspace and command windows before proceeding to the next section.

? Discussion Questions9.9.1.2

1. What is the purpose of the period in the following statement? What happens if the period is removed?

```
M = m.*N;
```

2. How can you delete the value 0.4 in the following matrix?

```
mat1 = [0.1 0.2 0.3 0.4 0.5 0.9 1.0];
```

3. What does the "o" specification do in the code below:

```
plot(x,z,"o")
```

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9.9.2: Practice with LiveScript

Install a custom script

The custom scripts (files with .m extension) and binary files (files with .mat extension) for this course are available here (click to go to GoogleDrive) using your Google account. If you are using the Chemistry Department *bohr* server to access Matlab, the scripts are already installed for you.

If you are using your own computer, the scripts and binary files should be added to the correct folder on your computer. Follow the instructions in this video to install the lsq script, which performs least squares analysis.



Practice using a custom script and a binary file

This is an exercise to give you some practice in using Matlab to analyze data provided in a binary file, and plot the results using a custom script for least squares analysis. Before you start, make sure the custom files lsq.m and expt-1.mat are in your working MatLab directory (see video above). The binary file "expt-1" simply contains pre-defined 80 x 1 vector matrixes "x" and "y". This is just to save you the hassle of typing in the values for each vector.

> Open the "Practice_LiveScript_XXX.mlx" file, and simply follow the instructions within the Live Script document.

The file linked above will walk you through the following steps to create a "final" plot.

1. Open the MatLab program and be sure that you are working in the directory containing the lsq script and expt-1 binary file.
2. Type the following: **load expt-1**
   Your workspace now contains two variables, x and y which obey the following relation:

$$y = Ae^{-Cx} \tag{9.9.2.1}$$

3. Plot y (ordinate) versus x (abscissa). Using Matlab, recalculate your data in linear form (ln y versus x) and plot the result. Using least squares analysis of the linearized data, calculate the values of A and C and report the standard deviation in these values. Using your calculated values of A and C, use Matlab to draw (a) the least-squares fitted line through your linear plot and (b) the best fit curve through your exponential plot. (NOTE: data should appear as points using the symbol 'o' and least squares fitted lines should be solid lines.)

> **Expectation for a "final" full-credit plot in this course:**
>
> - Data is plotted in scatter format.
> - Axes are correctly labeled, with correct units.
> - When appropriate, a curve fit to the data is shown
>   - equation of the line is shown on the plot, but not obscuring the data

    - uncertainty in slope and intercept provided
    - correlation coefficient (R) provided
  - Approrpate units are given for every value and every axis label.
  - Plot is centered on graph.
  - Text is easily readable (usually this means it is large enough to read easily.

4. You should show the plots described in (3) together with the values of A and C to your instructor. Each graph should have a title, and the x- and y-axes should be labeled.

This is an old video of this activity (before LiveScript files were developed.)



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9.9.3: MatLab for Data Analysis In This Course

MatLab is the preferred tool for data analysis in this course. That means that we will provide MatLab templates for your data analysis in each module and we can provide some basic support for your computational work if you use MatLab. However, if you have a favorite tool that is not MatLab, you are welcome to use it instead from now on, but please know that your instructional team may not be able to offer technical support for other computational programs.

We provide the MatLab Live Script files that can support your work in the modules this semester. Let's take a close look at the one for your "Error Analysis" problem set (your next assignment, in Module 3).

With any time remaining in the class meeting, or with your time out of class, access the MatLab files for this course and find the "Treatment of Error folder". From this folder, open the file called "Error_StudentGuide_date.mlx" and follow the instructions within to begin completing your next assignment. Also proceed to the next module (Module 3) in this manual to view the pre-lab assignment for your next meeting.

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SECTION OVERVIEW

9.10: The Treatment of Experimental Error

Learning Objectives

After completing the readings and practice problems recommended in this module, you should be able to:

- Describe and give examples of the following types of error that effect physical measurements, and identify the types of errors that affect precision and those that affect accuracy.
  - Gross / personal error
  - Systematic error
  - Random error
  - Determinate error
  - Indeterminate error
- Describe strategies for optimizing the accuracy of physical measurements and evaluating the precision of physical measurements.
- Identify the sources of random error in a measurement.
- Propagate error using mathematics.
- Report values and their precision in the proper form (applying the rules of significant figures to correctly indicate precision).

9.10.1: Characterizing Experimental Errors

9.10.2: Estimating and Reporting Error (Statistics, Propogation, and Rounding)

9.10.3: Least Squares Linear Regression

9.10.4: Rejection of Outliers (Q-test)

9.10.5: Guidelines for Recording and Reporting Data in your ELN

9.10.6: References and Additional Reading

9.10.7: Pre-lab Assignment

9.10.8: Learning Objectives, Important Info

9.10.9: Characterizing Experimental Errors

9.10.10: Propagation of Uncertainty

9.10.11: Least Squares Linear Regression

- 9.10.11.1: Rejection of Discordant Data
- 9.10.11.2: Weighted Least Squares Analysis
- 9.10.11.3: References

9.10.12: Homework Problems

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9.10.1: Characterizing Experimental Errors

In this course, you will need to determine the confidence in your results by doing appropriate error analysis. This section and the next are meant to review the types of experimental errors that affect accuracy and precision and to remind you of the simple methods for propagating error.

Errors That Affect Accuracy

Accuracy is how close a measure of central tendency is to its expected value, μ. We express accuracy either as an absolute error, e

$$e = \overline{X} - \mu \tag{9.10.1.1}$$

or as a percent relative error, %e

$$\%e = \frac{\overline{X} - \mu}{\mu} \times 100 \tag{9.10.1.2}$$

Although Equation 9.10.1.1 and Equation 9.10.1.2 use the mean as the measure of central tendency, we also can use the median.

> The convention for representing a statistical parameter is to use a Roman letter for a value calculated from experimental data, and a Greek letter for its corresponding expected value. For example, the experimentally determined mean is $\overline{X}$ and its underlying expected value is μ. Likewise, the experimental standard deviation is s and the underlying expected value is σ.

We identify as determinate an error that affects the accuracy of an analysis. Each source of a ***determinate error*** has a specific magnitude and sign. Some sources of determinate error are positive and others are negative, and some are larger in magnitude and others are smaller in magnitude. The cumulative effect of these determinate errors is a net positive or negative error in accuracy.

> It is possible, although unlikely, that the positive and negative determinate errors will offset each other, producing a result with no net error in accuracy.

We assign determinate errors into four categories—sampling errors, method errors, measurement errors, and personal errors—each of which we consider in this section.

Sampling Errors

A determinate sampling error occurs when our sampling strategy does not provide a us with a representative sample. For example, if we monitor the environmental quality of a lake by sampling from a single site near a point source of pollution, such as an outlet for industrial effluent, then our results will be misleading. To determine the mass of a U. S. penny, our strategy for selecting pennies must ensure that we do not include pennies from other countries.

> An awareness of potential sampling errors especially is important when we work with heterogeneous materials. Strategies for obtaining representative samples are covered in Chapter 5 of Harvey's Analytical Chemistry text on LibreTexts.

Method Errors

In any analysis the relationship between the signal, S_{total}, and the absolute amount of analyte, n_A, or the analyte's concentration, C_A, is

$$S_{total} = k_A n_A + S_{mb} \tag{9.10.1.3}$$

$$S_{total} = k_A C_A + S_{mb} \tag{9.10.1.4}$$

where k_A is the method's sensitivity for the analyte and S_{mb} is the signal from the method blank. A ***method error*** exists when our value for k_A or for S_{mb} is in error. For example, a method in which S_{total} is the mass of a precipitate assumes that k is defined by a pure precipitate of known stoichiometry. If this assumption is not true, then the resulting determination of n_A or C_A is inaccurate.

We can minimize a determinate error in k_A by calibrating the method. A method error due to an interferent in the reagents is minimized by using a proper method blank.

Measurement Errors

The manufacturers of analytical instruments and equipment, such as glassware and balances, usually provide a statement of the item's maximum ***measurement error***, or ***tolerance***. For example, a 10-mL volumetric pipet (Figure 3.2.1) has a tolerance of ±0.02 mL, which means the pipet delivers an actual volume within the range 9.98–10.02 mL at a temperature of 20 °C. Although we express this tolerance as a range, the error is determinate; that is, the pipet's expected volume, μ, is a fixed value within this stated range.



Figure 3.2.1 : Close-up of a 10-mL volumetric pipet showing that it has a tolerance of ±0.02 mL at 20 °C.

Volumetric glassware is categorized into classes based on its relative accuracy. **Class A glassware** is manufactured to comply with tolerances specified by an agency, such as the National Institute of Standards and Technology or the American Society for Testing and Materials. The tolerance level for Class A glassware is small enough that normally we can use it without calibration. The tolerance levels for **Class B glassware** usually are twice that for Class A glassware. In other words, Class B is less accurate. Other types of volumetric glassware, such as beakers and graduated cylinders, are not used to measure volume accurately. Table 3.2.1 provides a summary of typical measurement errors for Class A volumetric glassware. Tolerances for digital pipets and for balances are provided in Table 3.2.2 and Table 3.2.3 .

Tolerance Limits for Class A Volumetric Glassware

Table 3.2.1 : Measurement Errors for **Class A Volumetric Glassware**

Volumetric Pipets		**Volumetric Flasks**		**Burets**	
Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)
1	±0.006	5	±0.02	10	±0.02
2	±0.006	10	±0.02	25	±0.03
5	±0.01	25	±0.03	50	±0.05
10	±0.02	50	±0.05		
20	±0.03	100	±0.08		
25	±0.03	250	±0.12		
50	±0.05	500	±0.20		
100	±0.08	1000	±0.30		
		2000	±0.50		

Tolerance limits for Digital Pipettes

Table 3.2.2 : Measurement Errors for Digital Pipets

Pipet Range	Volume (mL or μL)	Percent Measurement Error
10–100 μL	10	±3.0%
	50	±1.0%
	100	±0.8%
100–1000 μL	100	±3.0%
	500	±1.0%
	1000	±0.6%
1–10 mL	1	±3.0%
	5	±0.8%
	10	±0.6%

The tolerance values for the volumetric glassware in Table 3.2.1 are from the ASTM E288, E542, and E694 standards. The measurement errors for the digital pipets in Table 3.2.2 are from www.eppendorf.com.

Tolerance Limits for Some Common Balances

Table 3.2.3 : Measurement Errors for Selected Balances

Balance	Capacity (g)	Measurement Error
Precisa 160M	160	±1 mg
A & D ER 120M	120	±0.1 mg
Metler H54	160	±0.01 mg

We can minimize a determinate measurement error by calibrating our equipment. Balances are calibrated using a reference weight whose mass we can trace back to the SI standard kilogram. Volumetric glassware and digital pipets are calibrated by determining the mass of water delivered or contained and using the density of water to calculate the actual volume. It is never safe to assume that a calibration does not change during an analysis or over time. One study, for example, found that repeatedly exposing volumetric glassware to higher temperatures during machine washing and oven drying, led to small, but significant changes in the glassware's calibration [Castanheira, I.; Batista, E.; Valente, A.; Dias, G.; Mora, M.; Pinto, L.; Costa, H. S. *Food Control* **2006**, *17*, 719–726]. Many instruments drift out of calibration over time and may require frequent recalibration during an analysis.

Personal Errors

Finally, analytical work is always subject to ***personal error***, examples of which include the ability to see a change in the color of an indicator that signals the endpoint of a titration, biases, such as consistently overestimating or underestimating the value on an instrument's readout scale, failing to calibrate instrumentation, and misinterpreting procedural directions. You can minimize personal errors by taking proper care.

Identifying Determinate Errors

Determinate errors often are difficult to detect. Without knowing the expected value for an analysis, the usual situation in any analysis that matters, we often have nothing to which we can compare our experimental result. Nevertheless, there are strategies we can use to detect determinate errors.

The magnitude of a constant ***determinate error*** is the same for all samples and is more significant when we analyze smaller samples. Analyzing samples of different sizes, therefore, allows us to detect a constant determinate error. For example, consider a quantitative analysis in which we separate the analyte from its matrix and determine its mass. Let's assume the sample is 50.0% w/w analyte. As we see in Table 3.2.4 , the expected amount of analyte in a 0.100 g sample is 0.050 g. If the analysis has a positive

constant determinate error of 0.010 g, then analyzing the sample gives 0.060 g of analyte, or an apparent concentration of 60.0% w/w. As we increase the size of the sample the experimental results become closer to the expected result. An upward or downward trend in a graph of the analyte's experimental concentration versus the sample's mass (Figure 3.2.2) is evidence of a constant determinate error.

Table 3.2.4 : Effect of a Constant Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Constant Error (g)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	0.010	0.060	60.0
0.200	0.100	0.010	0.110	55.0
0.400	0.200	0.010	0.210	52.5
0.800	0.400	0.010	0.410	51.2
1.600	0.800	0.010	0.810	50.6

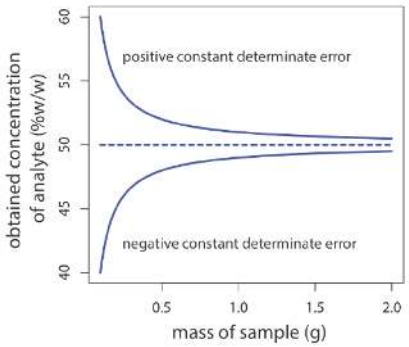


Figure 3.2.2 : Effect of a constant positive determinate error of +0.01 g and a constant negative determinate error of –0.01 g on the determination of an analyte in samples of varying size. The analyte's expected concentration of 50% w/w is shown by the dashed line.

A ***proportional determinate error***, in which the error's magnitude depends on the amount of sample, is more difficult to detect because the result of the analysis is independent of the amount of sample. Table 3.2.5 outlines an example that shows the effect of a positive proportional error of 1.0% on the analysis of a sample that is 50.0% w/w in analyte. Regardless of the sample's size, each analysis gives the same result of 50.5% w/w analyte.

Table 3.2.5 : Effect of a Proportional Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Proportional Error (%)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	1.00	0.0505	50.5
0.200	0.100	1.00	0.101	50.5
0.400	0.200	1.00	0.202	50.5
0.800	0.400	1.00	0.404	50.5
1.600	0.800	1.00	0.808	50.5

One approach for detecting a proportional determinate error is to analyze a standard that contains a known amount of analyte in a matrix similar to our samples. Standards are available from a variety of sources, such as the National Institute of Standards and

Technology (where they are called Standard Reference Materials) or the American Society for Testing and Materials. Table 3.2.6 , for example, lists certified values for several analytes in a standard sample of *Gingko biloba* leaves. Another approach is to compare our analysis to an analysis carried out using an independent analytical method that is known to give accurate results. If the two methods give significantly different results, then a determinate error is the likely cause.

Table 3.2.6 : Certified Concentrations for SRM 3246: *Gingko bilbo* (Leaves)

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
Flavonoids/Ginkgolide B (mass fraction in mg/g)	Qurecetin	2.69 ± 0.31
	Kaempferol	3.02 ± 0.41
	Isorhamnetin	$0.517 \pm 0.0.99$
	Total Aglycones	6.22 ± 0.77
Selected Terpenes (mass fraction in mg/g)	Ginkgolide A	0.57 ± 0.28
	Ginkgolide B	0.470 ± 0.090
	Ginkgolide C	0.59 ± 0.22
	Ginkgolide J	0.18 ± 0.10
	Bilobalide	1.52 ± 0.40
	Total Terpene Lactones	3.3 ± 1.1
Selected Toxic Elements (mass fraction in ng/g)	Cadmium	20.8 ± 1.0
	Lead	995 ± 30
	Mercury	23.08 ± 0.17

> The primary purpose of this Standard Reference Material is to validate analytical methods for determining flavonoids, terpene lactones, and toxic elements in *Ginkgo biloba* or other materials with a similar matrix. Values are from the official Certificate of Analysis available at www.nist.gov.

Constant and proportional determinate errors have distinctly different sources, which we can define in terms of the relationship between the signal and the moles or concentration of analyte (Equation 9.10.1.3 and Equation 9.10.1.4). An invalid method blank, S_{mb}, is a constant determinate error as it adds or subtracts the same value to the signal. A poorly calibrated method, which yields an invalid sensitivity for the analyte, k_A, results in a proportional determinate error.

Errors that Affect Precision

Precision is a measure of the spread of individual measurements or results about a central value, which we express as a range, a standard deviation, or a variance. Here we draw a distinction between two types of precision: repeatability and reproducibility. ***Repeatability*** is the precision when a single analyst completes an analysis in a single session using the same solutions, equipment, and instrumentation. ***Reproducibility***, on the other hand, is the precision under any other set of conditions, including between analysts or between laboratory sessions for a single analyst. Since reproducibility includes additional sources of variability, the reproducibility of an analysis cannot be better than its repeatability.

> The ratio of the standard deviation associated with reproducibility to the standard deviation associated with repeatability is called the Horowitz ratio. For a wide variety of analytes in foods, for example, the median Horowtiz ratio is 2.0 with larger

values for fatty acids and for trace elements; see Thompson, M.; Wood, R. “The ‘Horowitz Ratio’–A Study of the Ratio Between Reproducibility and Repeatability in the Analysis of Foodstuffs,” *Anal. Methods*, **2015**, *7*, 375–379.

Errors that affect precision are indeterminate and are characterized by random variations in their magnitude and their direction. Because they are random, positive and negative ***indeterminate errors*** tend to cancel, provided that we make a sufficient number of measurements. In such situations the mean and the median largely are unaffected by the precision of the analysis.

Sources of Indeterminate Error

We can assign indeterminate errors to several sources, including collecting samples, manipulating samples during the analysis, and making measurements. When we collect a sample, for instance, only a small portion of the available material is taken, which increases the chance that small-scale inhomogeneities in the sample will affect repeatability. Individual pennies, for example, may show variations in mass from several sources, including the manufacturing process and the loss of small amounts of metal or the addition of dirt during circulation. These variations are sources of indeterminate sampling errors.

During an analysis there are many opportunities to introduce indeterminate method errors. If our method for determining the mass of a penny includes directions for cleaning them of dirt, then we must be careful to treat each penny in the same way. Cleaning some pennies more vigorously than others might introduce an indeterminate method error.

Finally, all measuring devices are subject to indeterminate measurement errors due to limitations in our ability to read its scale. For example, a buret with scale divisions every 0.1 mL has an inherent indeterminate error of ±0.01–0.03 mL when we estimate the volume to the hundredth of a milliliter (Figure 3.2.3).

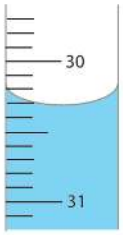


Figure 3.2.3 : Close-up of a buret showing the difficulty in estimating volume. With scale divisions every 0.1 mL it is difficult to read the actual volume to better than ±0.01–0.03 mL.

Evaluating Indeterminate Error

Indeterminate errors associated with our analytical equipment or instrumentation generally are easy to estimate if we measure the standard deviation for several replicate measurements, or if we monitor the signal’s fluctuations over time in the absence of analyte (Figure 3.2.4) and calculate the standard deviation. Other sources of indeterminate error, such as treating samples inconsistently, are more difficult to estimate.

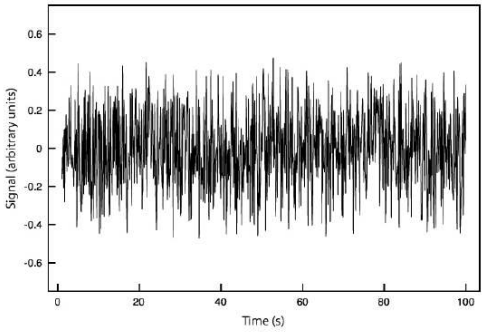


Figure 3.2.4 : Background noise in an instrument showing the random fluctuations in the signal.

Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty [Ellison, S.; Wegscheider, W.; Williams, A. *Anal. Chem.* **1997**, *69*, 607A–613A]. ***Error*** is the difference between a single measurement or result and its expected value. In other words, error

is a measure of ***bias***. As discussed earlier, we divide errors into determinate and indeterminate sources. Although we can find and correct a source of determinate error, the indeterminate portion of the error remains.

Uncertainty expresses the range of possible values for a measurement or result. Note that this definition of uncertainty is not the same as our definition of precision. We calculate precision from our experimental data and use it to estimate the magnitude of indeterminate errors. Uncertainty accounts for all errors—both determinate and indeterminate—that reasonably might affect a measurement or a result. Although we always try to correct determinate errors before we begin an analysis, the correction itself is subject to uncertainty.

Here is an example to help illustrate the difference between precision and uncertainty. Suppose you purchase a 10-mL Class A pipet from a laboratory supply company and use it without any additional calibration. The pipet's tolerance of ±0.02 mL is its uncertainty because your best estimate of its expected volume is 10.00 mL ± 0.02 mL. This uncertainty primarily is determinate. If you use the pipet to dispense several replicate samples of a solution and determine the volume of each sample, the resulting standard deviation is the pipet's precision. Table 3.2.8 shows results for ten such trials, with a mean of 9.992 mL and a standard deviation of ±0.006 mL. This standard deviation is the precision with which we expect to deliver a solution using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ±0.02 mL is worse than its experimentally determined precision of ±0.006 ml. Interestingly, the data in Table 3.2.8 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ±0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty [Kadis, R. *Talanta* **2004**, *64*, 167–173].

Table 3.2.8 : Experimental Results for Volume Dispensed by a 10–mL Class A Transfer Pipet

Replicate	Volume (ml)	Replicate	Volume (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

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9.10.2: Estimating and Reporting Error (Statistics, Propogation, and Rounding)

In many physical chemistry experiments, the goal is to obtain numerical results by taking measurements and calculating averages or applying theoretical formulas. However, simply producing a number isn't enough – it's essential to evaluate its quality. How accurate is the result? Accuracy indicates the level of uncertainty associated with the measurement. Overstating accuracy without proper justification can be misleading, while understating it can undervalue the result and lead to wasted effort and resources.

This module will deal with two main types of error analyses. You will learn when and how to use each type.

1. **Statistical Analyses** are done when there are multiple replicates of the same measurement(s).
2. **Error Propagation** is done when using measured values to calcuate another numerical value.

A major goal of this module is for you to learn when and how to apply these equations to perform statistical analysis or propagate errors through a function. This skill will be required in nearly every future module in this course.

A summary of useful information and equations is below.

1. Statistical Analyses (on replicate measurements):

Average or mean: The average (or mean) of N measurements on the variable x is:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{9.10.2.1}$$

Standard deviation (S) is the spread around the mean of several replicate measurements. It has the same units as the measurement and is commonly used to report uncertainty (see Skoog Ch. 6 p 126)

$$S = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \tag{9.10.2.2}$$

Variance (S^2) is the dispersion between data points. The units are the square of the measured units.

The **Confidence Limits (CL)** are the values that define the confidence interval (which is the bounds about which an experimental value should be located with a given probability). The confidence limit is useful for small sample sizes. A common confidence limit is the 95% confidence limit, and its value is given by the following (see Skoog Ch7 pg 150 and Shoemaker Ch 2 eq 34).

$$CL_{0.95} = t_{0.95}S_m = t_{0.95}\frac{S}{\sqrt{N}} \tag{9.10.2.3}$$

or more generally

$$CL = \bar{x} \pm \frac{tS}{\sqrt{N}} \tag{9.10.2.4}$$

where t is the critical t value (from Student's t test) that depends on the degrees of freedom and the given probability. A table of critical t values can be found online. (See also Shoemaker Ch 2, Table 3)

2. Propagation of error (for values determined from a function):

Using partial derivatives

To propagate error to determine the error (Δ) in the value derived from of a function (F), we must propagate error of each part of the function. This is accomplished by taking the square root of the sum of the squares of the partial derivative of the function with respect to each variable (eg partial derivative with respect to x is $\frac{\partial F}{\partial x}$), multiplied by the error in that variable (eg error in x is $\Delta(x)$, and the square of the error is $\Delta^2(x)$. In mathematical form, this is given below (from Shoemaker Ch 2 p 56, eq 54). If you need to brush up on partial derivatives, check out this video (click here). https://youtu.be/SbfRDBmyAMI

$$\Delta^2(F) = \left(\frac{\partial F}{\partial x}\right)^2\Delta^2(x) + \left(\frac{\partial F}{\partial y}\right)^2\Delta^2(y) + \left(\frac{\partial F}{\partial z}\right)^2\Delta^2(z) + \ldots \tag{9.10.2.5}$$

It is convenient to rearrange this equation as follows to give the error in the value derived from the function:

$$\Delta(F) = \sqrt{\left(\frac{\partial F}{\partial x}\right)^2 \Delta^2(x) + \left(\frac{\partial F}{\partial y}\right)^2 \Delta^2(y) + \left(\frac{\partial F}{\partial z}\right)^2 \Delta^2(z) + \ldots} \tag{9.10.2.6}$$

Simpler shortcuts:

In some cases, there are shortcuts that allow you to approximate errors without taking the partial derivatives. In the examples below, assume that a, b, c, n are constants and x, y, z are variables with associated errors $\Delta x, \Delta y, \Delta z$:

For functions with only addition and subtraction of values with assiciated error (eg $F = ax \pm by \pm cz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 55)

$$\Delta(F) = \sqrt{a^2\Delta^2(x) + b^2\Delta^2(y) + c^2\Delta^2(z)} \tag{9.10.2.7}$$

For functions that involve only multiplication and division (eg $F = axyz$ **or** $F = axy/z$ **or** $F = a/xyz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 56)

$$\Delta(F) = F\sqrt{\frac{\Delta^2(x)}{x^2} + \frac{\Delta^2(y)}{y^2} + \frac{\Delta^2(z)}{z^2}} \tag{9.10.2.8}$$

For functions that involve taking a variable to the power of a constant (eg $F = ax^n$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 57)

$$\Delta(F) = F\sqrt{n^2\frac{\Delta^2(x)}{x^2}} \rightarrow \Delta(F) = Fn\frac{\Delta(x)}{x} \tag{9.10.2.9}$$

For functions where a variable is an exponent (eg $F = ae^x$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 58)

$$\Delta(F) = \sqrt{a^2e^{2x}\Delta^2(x)} \rightarrow \Delta(F) = F\Delta(x) \tag{9.10.2.10}$$

For functions taking the logarithm of a variable (eg $F = a\ln(x)$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 59)

$$\Delta(F) = \sqrt{\frac{a^2}{x^2}\Delta^2(x)} \rightarrow \Delta(F) = a\frac{\Delta(x)}{x} \tag{9.10.2.11}$$

3. Reporting Numeric Results

All numeric results in this course should be reported with explicit statement of uncertainty. The following format is expected:

$$\textbf{Numeric Value } \pm \textbf{Uncertainty} \tag{9.10.2.12}$$

In your written assignments for this course use the following guidelines when reporting a "final" numeric value. You will be required to use your *best judgement* and to provide a *written justification* of your logic for reporting all final values. More detailed information is found below the guidelines and also in the Shoemaker text.

Guidelines for reporting final numerical values:

- Rules for reporting significant figures should be followed.
- The number of useful decimal places in the uncertainty should match the number of decimal places reported in the value.
- The certainty of a numeric value determined from a function cannot be be more than the certainty of its operands.

A summary of rules for reporting significant Figures (from Shoemaker Ch 2)

The following rules apply only for reporting the *final* value, not for intermediate rounding steps during calculation. In general, do not round values during the calculation process if it can be avoided. However, if you must round prior to comleting a calcaution, then retain *at least one digit more than would be considered "significant"*, and the more the better.

Rules for Rounding Final Values:

Follow the following rules depending on the digit immediately to the right of the place you are rounding. The examples below are rounding to the place underlined, and **the digit immediately to the right is bolded**.

a. Increase the last retained digit by 1 if the nearest dropped digit is more than 5, or if it is 5 followed by any non-zero digits:
   - Examples:
     6.78**9** rounds to 6.79
     54.91**2**3 rounds to 54.9

b. Leave the last retained digit unchanged if the nearest dropped digit is less than 5:
   - Examples:
     2.34**6** rounds to 2.35
     0.212**3** rounds to 0.21

c. If the leftmost digit to be dropped is 5 followed by no digits except zero, then increase the last retained digit by 1 if it is odd, and leave it unchanged if it is even:
   - Examples:
     15.32**5** rounds to 15.32
     15.33**5** rounds to 15.34

d. There are times when you should retain an extra digit so that your reported uncertainty is reasonable.

Rules for tracking significant figures for calculated values

Addition: When adding numeric values, the result's precision is limited by the least precise value involved. The number of decimal places in the result should match the fewest decimal places in any component. For example:

$$\begin{array}{r} 15.4 \\ +2.87 \\ +7.621 \\ \hline =25.916 \rightarrow 25.9 \end{array} \tag{9.10.2.13}$$

Subtraction: When subtracting, the result's precision is limited by the least precise value involved, and the precision of the result will always be less than that of the operands. For example:

$$\begin{array}{r} 289.461 \\ -288.58 \\ \hline 0.881 \rightarrow 0.88 \end{array} \tag{9.10.2.14}$$

Let's do an analysis to illustrate what this means. In the example above, let's assume an uncertainty of ± 3 in the rightmost digit of each number. Based on this assumption, the least precise operand has uncertainty of ~ 0.01%, while the final reported value has an uncertainty of 3.4%!

When multiplying and dividing: In multiplication and division, the precision of the result is limited by the least precise number involved. The number of significant figures in the result should align with the component having the fewest. ***Note that relative precision isn't solely dependent on the number of significant figures;*** for instance, 99 with two significant figures is approximately as precise as 101 with three. When unsure, do an analysis of the relative uncertainty, and if the uncertinties are approximately equal, use the larger number of significant figures.

Conventions for Reporting and Interpreting Reported Values

1. Numerical values are typically considered uncertain in the last digit by ±3 or more, with perhaps slight uncertainty in the next-to-last digit by up to ±2.
2. If the last digit to be retained is a one or two, an additional digit is retained so that precision is not inappropriately reported due to rounding.

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9.10.3: Least Squares Linear Regression

Your experimental data will usually be examined in graphic form, which can be more instructive than tabulated data. In any graphic presentation, be sure to plot your independent variable on the abscissa (x-axis) and the dependent variable on the ordinate (y-axis).

If the data are presented in graphic form, the usual procedure is to fit the best curve through the experimental points. As Brownlee[3] puts it,

> "When an investigator observes simultaneously two variables, x and y, usually with good reason he plots the observations on a graph. If there is any sign of an association, he is usually seized with the impulse to fit a line, usually a straight line or, rather infrequently, a parabola or cubic."

When we are "seized with the impulse" to fit a straight line curve the process of curve fitting is called linear regression. We assume that the deviations of the dependent variable y are distributed normally (that is, a Gaussian distribution). This assumption is not required for the determination of the least squares parameters, but it is necessary for construction of confidence intervals or for tests of hypotheses about the parameters. The parameters obtained by least squares under these conditions are unbiased and provide the best estimates of the curve fitting parameters.

Most of the experimental data that you will encounter this semester will have a simple functional form, or can be manipulated in such a way as to assume a simple form. We shall assume here that our data follows a linear relationship. For example, consider a gas that is thought to follow the equation of state

$$\underset{y = a + bx}{Z \equiv \frac{PV}{nRT} = B_0 + B_1 P} \tag{9.10.3.1}$$

Measurements of Z, called the compressibility factor, are made at each of a series of pressures in an effort to determine B_0 andB_0. The least squares approach can be used to determine the slope (b, orB_1) and y-intercept (a, or B_0) which define the best straight line that can be drawn through the data. In simple linear regression analysis, it is assumed that all the error in the measurement lies in the dependent variable (y). This is equivalent to assuming that the precision of the determination of the independent variable (x) is considerable higher than that of y. The measured value of some quantity (y_i) will differ from the value predicted by a linear equation ($y = a + bx$) by an amount r_i called the residual.

$$r_i = y_i - a - bx \tag{9.10.3.2}$$

The least squares approach identifies the best straight line as the one for which R, the sum of the squares of the residuals, has the smallest value:

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} (y_i - a - bx_i)^2 \tag{9.10.3.3}$$

The arrows in Figure 4 represent the residuals, and all of them are equally weighted.

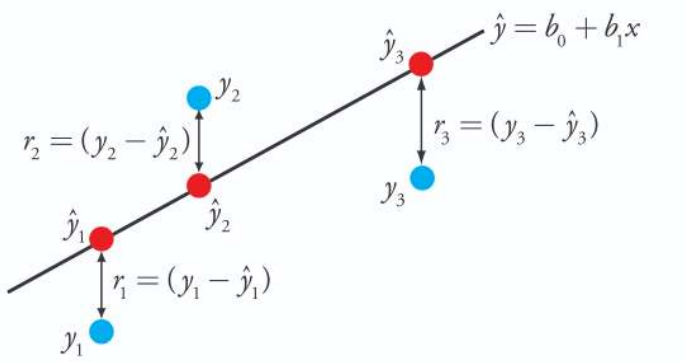


Figure **9.10.3.1**: Least Squares Linear Regression: *Illustration showing the evaluation of a linear regression in which we assume that all uncertainty is the result of indeterminate errors affecting y. The points in blue, y_i, are the original data and the points in red, $\hat{y}_i$, are the predicted values from the regression equation, $\hat{y} = b_0 + b_1 x$. The smaller the total residual error, the better the fit of the straight-line to the data* (source)

We want to minimize the sum of the squares of the residuals. That is, we want to make *least* the sum of *squares* of residuals, and, thus, the name of the procedure. Since this is a minimization problem, we require that R be as small as possible with respect to a and b by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial a}\right)_b = -2\sum(y_i - a - bx_i) = 0 \tag{9.10.3.4}$$
$$\left(\frac{\partial R}{\partial b}\right)_a = -2\sum((y_i - a - bx_i)(x_i)) = 0$$

Solving equations 9.10.3.4 simultaneously, we obtain

$$a = \frac{(\sum x_i^2)(\sum y_i) - (\sum x_i)(\sum x_i y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{9.10.3.5}$$

$$b = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{9.10.3.6}$$

While we ultimately want to fit the data to $y_i = a + bx_i$ for a series i of N points, the theoretical development is much easier if we use $y_i = c + b(x_i - \overline{x})$ where obviously a and c are related by $a = c - b\overline{x}$, and where $\overline{x}$ is simply the mean of the x data, $n\overline{x} = \sum_{i=1}^{N} x_i$. This designation of variables is better because "it turns out" that in this approach the parameters b and c are independent, their variances are independent, and the formulas to transform to the parameters a and b are simple. Again, we want to minimize the sum of the squares of the residuals $r_i = y_i - c - b(x_i - \overline{x})$, R.

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} [y_i - (c + b(x_i - \overline{x}))]^2 \tag{9.10.3.7}$$

Now we require that R be as small as possible with respect to b and c by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial c}\right)_b = -2\sum(y_i - c - b(x_i - \overline{x})) = 0 \tag{9.10.3.8}$$
$$\left(\frac{\partial R}{\partial b}\right)_c = -2\sum((y_i - c - b(x_i - \overline{x}))(x_i - \overline{x})) = 0$$

These two equations are readily rewritten as

$$\sum y_i = \sum c + \sum b(x_i - \overline{x}) \tag{9.10.3.9}$$
$$\sum y_i (x_i - \overline{x}) = \sum c(x_i - \overline{x}) + \sum b(x_i - \overline{x})^2$$

which, since $\sum(x_i - \overline{x}) = 0$, simplify to

$$c = \frac{\sum y_i}{N} = -\bar{y} \qquad (9.10.3.10)$$
$$b = \frac{\sum y_i (x_i - \bar{x})}{\sum (x_i - \bar{x})^2}$$

The knowledge of c and b then allows us to determine the parameter, a, $a = c - b\bar{x} = \bar{y} - b\bar{x}$, a particularly simple relation.

The variance and standard deviation of N data points was introduced previously. The appropriate treatment of the parameters c and b in the least squares procedure results in

$$V[c] = \frac{s^2}{N} \qquad (9.10.3.11)$$
$$V[b] = \frac{s^2}{\sum (x_i - \bar{x})^2}$$

where

$$s^2 = \frac{1}{N-2} \sum (y_i - c - b(x_i - \bar{x}))^2 = \frac{1}{N-2} \sum (y_i - a - bx_i)^2 = \frac{R_{min}}{N-2} \qquad (9.10.3.12)$$

Because c and b are independent quantities, it can be shown that

$$V[a] = V[c] + \bar{x}^2 V[b] \qquad (9.10.3.13)$$
$$= \frac{s^2}{N} + \bar{x}^2 \frac{s^2}{\sum (x_i - \bar{x})^2}$$

The standard deviations of a and b, σ_a and σ_b, are then obtained by taking the square roots of V[a] and V[b].

Another statistic that is sometimes used is the *correlation coefficient*, r. It is given by the expression

$$r = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left(N \sum x_i^2 - (\sum x_i)^2\right)\left(N \sum y_i^2 - (\sum y_i)^2\right)}} \qquad (9.10.3.14)$$

When the absolute value of r is close to unity the correlation between the y and x data is good, when it is close to zero the correlation is poor. Because the correlation coefficient is sometimes hard to interpret, it is usually better to work with the standard deviations of the regression parameters, σ_a and σ_b.

Linear regression is a powerful tool that takes the guesswork out of obtaining best fit information. However, like all mathematical tools, it must be used with caution. While the standard deviations and the correlation coefficient give indications of the goodness of the fit, there is no substitute for graphing the data and looking at the result. Since the errors are assumed to be random, the y_i values should be scattered about the best fit straight line in a random fashion. The residuals should likewise be either positive or negative (and sum to zero) without any pattern. If the data show a pattern of curvature, it is possible that the results do not conform to the linear model proposed. A linear regression is *not* valid in this case. You should also be alert to the effects of systematic errors, which may change the slope or the intercept without affecting the linearity of the data.

Linear regression of the type discussed above relies on a number of critical assumptions. Among the most important is that all the uncertainty in each of the y values is the same. If the form of the equation required to provide a linear relationship produces an independent variable that contains a significant uncertainty, the set of conditions that produced the minimum in the residuals of the line may not be the set that actually minimizes the uncertainty in the data. In this case, a "non-linear" least squared technique such as simplex is recommended.

Note

In this course, you can use the MatLab lsq.m script to perform least squares analysis. The equations given above are included in the lsq script.

Weighted Least Squares Analysis

When measurements of the dependent variable incur different uncertainties, a ***weighted*** least squares technique should be used. In this approach, each residual ri is divided by a factor proportional to its uncertainty ε_{y_i}. Then R, the sum of the squares of the residuals, becomes

$$R = \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_{y_i}^2} = \sum_{i=1}^{N} \frac{1}{\varepsilon_{y_i}^2}(y_i - a - bx_i)^2 \tag{9.10.3.15}$$

Using the same minimization techniques described above, the slope and intercept for weighted least squares become

$$a = \frac{\sum \frac{x_i^2}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2}\right)^2} \tag{9.10.3.16}$$

$$b = \frac{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2}\right)^2} \tag{9.10.3.17}$$

Weighted least squares has utility in a number of applications in the physical chemistry laboratory. One common situation arises when a linear equation requires the log of a measured quantity to be the dependent variable. Consider for example, the measurement of vapor pressure. Most pressure sensing devices will provide a constant error in the measurement of P. If the dependent variable to be plotted is lnP, however, its uncertainty is not constant but decreases as P increases. Thus,

$$\varepsilon_{lnP} = \frac{\partial lnP}{\partial P}\varepsilon_P = \frac{\varepsilon_P}{P} \tag{9.10.3.18}$$

An appropriate weighting factor in this case would be $\varepsilon_{y_i} = \frac{1}{P}$.

When you use Matlab for data analysis this semester, the command **lsq(x,y)** will be used for least squares analysis of x, y data, and the command **wtlsq(x,y)** will be used for weighted least squares analysis. In the latter case, you will be asked for a weighting factor, e. In either case, the program will output the least squares slope, y-intercept, correlation coefficient, standard deviation of the slope, and standard deviation of the intercept.

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9.10.4: Rejection of Outliers (Q-test)

In a set of collected data, there may be one or more values that deviate markedly from the trend of the others. You should not reject a piece of data that seems suspect until you perform a Q-test. In a set of data of three to ten measurements, the Q-test can be performed on the suspect data point:

$$Q_{exp} \equiv \frac{|\,(\text{ suspected outlier's value }) - (\text{value closest to it})\,|}{(\text{highest value}) - (\text{ lowest value })} \tag{9.10.4.1}$$

Compare the value of Q_{exp} from the equation above to the critical value of Q_r. If Q_{exp} is greater or equal to Q_r then the suspect value can be rejected. If Q_{exp} is less than Q_r,the value should be retained in the data set.

The following table provides critical values for $Q(\alpha, n)$, where α is the probability of incorrectly rejecting the suspected outlier and n is the number of samples in the data set. There are several versions of the *Q*-Test, each of which calculates a value for Q_{ij} where *i* is the number of suspected outliers on one end of the data set and *j* is the number of suspected outliers on the opposite end of the data set. The critical values for *Q* here are for a single outlier, Q_{10}, where

$$Q_{\text{exp}} = Q_{10} = \frac{|\,(\text{ suspected outlier's value }) - (\text{value closest to it})\,|}{(\text{highest value}) - (\text{ lowest value })}$$

The suspected outlier is rejected if Q_{exp} is greater than $Q(\alpha, n)$. For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's '*Q*' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146.

Table 9.10.4.1: Critical Values for Dixon's Q-Test

$\frac{\alpha\longrightarrow}{n\downarrow}$	**0.1 (90% confidence limit)**	**0.05 (95% confidence limit)**	**0.04 (96% confidence limit)**	**0.02 (98% confidence limit)**	**0.01 (99% confidence limit)**
3	0.941	0.970	0.976	0.988	0.994
4	0.765	0.829	0.846	0.889	0.926
5	0.642	0.710	0.729	0.780	0.821
6	0.560	0.625	0.644	0.698	0.740
7	0.507	0.568	0.586	0.637	0.680
8	0.468	0.526	0.543	0.590	0.634
9	0.437	0.493	0.510	0.555	0.598
10	0.412	0.466	0.483	0.527	0.568

(see also http://chem-net.blogspot.com/2013/01...atistical.html)

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- **35.5: Critical Values for Dixon's Q-Test** by David Harvey is licensed CC BY-NC-SA 4.0.

9.10.5: Guidelines for Recording and Reporting Data in your ELN

Always consider uncertainty during an experiment, record it in your ELN, and include it in all calculations and reporting. Do not leave the lab until you are sure that you have a valid strategy for determining errors in all final values.

1. **Uncertainty Awareness:**
   Before leaving the lab area, ensure you have a valid strategy for estimating uncertainties in all measured and calculated values.
2. **Estimating Uncertainty During Measurements:**
   - **Equipment Uncertainty**: Record uncertainties provided by equipment or manufacturers (e.g., balance deviation, pipette error). If unavailable, assume uncertainty is ±0.5 of the smallest measurable unit.
   - **Replicates**: For three or more measurements, calculate the standard deviation of the mean.
   - **Function-Based Values**: Perform propagation of error analysis.
   - **Least Squares Fitting**: Use errors from fitted parameters (e.g., slope or intercept) and propagate uncertainty if used in further calculations. Avoid linear regression if data deviates significantly from linearity.
   - **Consult Instructors**: Seek help for unclear sources of uncertainty.
3. **Propagation of Error:**
   Combine individual uncertainties to estimate the overall uncertainty of the final result. Use partial derivatives where necessary, and assume constants (e.g., RR) are error-free.
4. **Reporting Results:**
   - Include propagated uncertainty with each result.
   - Compare results with literature values using percent or absolute error.
   - Ensure significant figures reflect uncertainty and justify their use.
5. **Replicate Measurements:**
   - Report the mean and precision (e.g., standard deviation).
   - Use the Q-test to justify excluding outliers.
6. **Single Measurements:**
   - Estimate and report uncertainty (random or systematic).
   - Compare accuracy to expected values if available.
7. **Least Squares Fitting:**
   - Use weighted or non-weighted regression based on data.
   - Reject outliers only using the Q-test on residuals.
   - Propagate uncertainty from fitted parameters to calculated values.
8. **Qualitative Uncertainty:**
   For variables with no clear quantitative uncertainty, discuss potential sources and their impact on results. Provide reasonable estimates and substantiate with evidence.
9. **Before Leaving the Lab:**
   - Confirm all uncertainties are documented.
   - Check for systematic errors (e.g., calibration issues).
   - Ensure thorough records of measured values and associated uncertainties.

By following these steps, you ensure your experimental results are accurate, reproducible, and clearly reported.

This page titled 9.10.5: Guidelines for Recording and Reporting Data in your ELN is shared under a not declared license and was authored, remixed, and/or curated by Kathryn Haas.

9.10.6: References and Additional Reading

1. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th Edition, McGraw-Hill, New York, NY, 1996, pp 27-89.

2. Bettelheim, F. A., Experimental Physical Chemistry, W.B. Saunders Co., Philadelphia, 1971, Chapter 2.

3. Brownlee, K. A., Statistical Theory and Methodology in Science and Engineering, 2nd Edition, John Wiley and Sons, Inc., New York, New York, 1965, pp 334-338.

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9.10.7: Pre-lab Assignment

Pre-lab assignment

In preparation for the lab meeting on Error Analysis, please do the following*:

- Read this entire module
- **Read D.P. Shoemaker, C.W. Garland and J.W. Nibler, Experiments in Physical Chemistry, 6th Ed., McGraw Hill Co. Inc., New York, 1996, Chapter 2.**
- Attempt (does not mean you must complete) all seven problems in the last section of this module; work should be done in a way that you can track your progress and submit your work in the form of a pdf. Submit all attempts in writing 24 hours prior to your scheduled laboratory meeting.

Note that the textbooks referenced in this module are available in the Perkins library, and on Canvas in pdf format (or Duke students click here).
We will meet in a classroom, thus lab attire is not necessary for this session.

*In addition to the general pre-lab assignment (linked below as a reminder), please do the above tasks. **For this particular assignment, an experimental plan is unnecessary**. However, it is good practice to reflect on the purpose of this assignment, so please **do write a background/purpose statement**. You should submit a pdf of your work on Canvas before the deadline (24 hours prior to the lab meeting).

For our overachievers and those who want more, recommended additional reading includes: D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, Analytical Chemistry: An Introduction, 7th Ed., Saunders College Publishing, New York, 2000, Chapters 5-7.

Click here to review the general expectation for Pre-Lab Preparation Assignments.

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9.10.8: Learning Objectives, Important Info

In many physical chemistry experiments, the goal is to obtain numerical results by taking measurements and calculating averages or applying theoretical formulas. However, simply producing a number isn't enough – it's essential to evaluate its quality. How accurate is the result? Accuracy indicates the level of uncertainty associated with the measurement. Overstating accuracy without proper justification can be misleading, while understating it can undervalue the result and lead to wasted effort and resources.

> This module will deal with two main types of error analyses. You will learn when and how to use each type.
>
> 1. **Statistical Analyses** are done when there are multiple replicates of the same measurement(s).
> 2. **Error Propagation** is done when using measured values to calcuate another numerical value.
>
> A major goal of this module is for you to learn when and how to apply these equations to perform statistical analysis or propagate errors through a function. This skill will be required in nearly every future module in this course.

A summary of useful information and equations is below.

1. Statistical Analyses (on replicate measurements):

Average or mean: The average (or mean) of N measurements on the variable x is:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{9.10.8.1}$$

Standard deviation (S) is the spread around the mean of several replicate measurements. It has the same units as the measurement and is commonly used to report uncertainty (see Skoog Ch. 6 p 126)

$$S = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \tag{9.10.8.2}$$

Variance (S^2) is the dispersion between data points. The units are the square of the measured units.

The **Confidence Limits (CL)** are the values that define the confidence interval (which is the bounds about which an experimental value should be located with a given probability). The confidence limit is useful for small sample sizes. A common confidence limit is the 95% confidence limit, and its value is given by the following (see Skoog Ch7 pg 150 and Shoemaker Ch 2 eq 34).

$$CL_{0.95} = t_{0.95}S_m = t_{0.95}\frac{S}{\sqrt{N}} \tag{9.10.8.3}$$

or more generally

$$CL = \bar{x} \pm \frac{tS}{\sqrt{N}} \tag{9.10.8.4}$$

where t is the critical t value (from Student's t test) that depends on the degrees of freedom and the given probability. A table of critical t values can be found online. (See also Shoemaker Ch 2, Table 3)

2. Propagation of error (for values determined from a function):

Using partial derivatives

To propagate error to determine the error (Δ) in the value derived from of a function (F), we must propagate error of each part of the function. This is accomplished by taking the square root of the sum of the squares of the partial derivative of the function with respect to each variable (eg partial derivative with respect to x is $\frac{\partial F}{\partial x}$), multiplied by the error in that variable (eg error in x is $\Delta(x)$, and the square of the error is $\Delta^2(x)$. In mathematical form, this is given below (from Shoemaker Ch 2 p 56, eq 54). If you need to brush up on partial derivatives, check out this video (click here). https://youtu.be/SbfRDBmyAMI

$$\Delta^2(F) = \left(\frac{\partial F}{\partial x}\right)^2\Delta^2(x) + \left(\frac{\partial F}{\partial y}\right)^2\Delta^2(y) + \left(\frac{\partial F}{\partial z}\right)^2\Delta^2(z) + \ldots \tag{9.10.8.5}$$

It is convenient to rearrange this equation as follows to give the error in the value derived from the function:

$$\Delta(F) = \sqrt{\left(\frac{\partial F}{\partial x}\right)^2 \Delta^2(x) + \left(\frac{\partial F}{\partial y}\right)^2 \Delta^2(y) + \left(\frac{\partial F}{\partial z}\right)^2 \Delta^2(z) + \ldots} \tag{9.10.8.6}$$

Simpler shortcuts:

In some cases, there are shortcuts that allow you to approximate errors without taking the partial derivatives. In the examples below, assume that a, b, c, n are constants and x, y, z are variables with associated errors $\Delta x, \Delta y, \Delta z$:

For functions with only addition and subtraction of values with assiciated error (eg $F = ax \pm by \pm cz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 55)

$$\Delta(F) = \sqrt{a^2\Delta^2(x) + b^2\Delta^2(y) + c^2\Delta^2(z)} \tag{9.10.8.7}$$

For functions that involve only multiplication and division (eg $F = axyz$ **or** $F = axy/z$ **or** $F = a/xyz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 56)

$$\Delta(F) = F\sqrt{\frac{\Delta^2(x)}{x^2} + \frac{\Delta^2(y)}{y^2} + \frac{\Delta^2(z)}{z^2}} \tag{9.10.8.8}$$

For functions that involve taking a variable to the power of a constant (eg $F = ax^n$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 57)

$$\Delta(F) = F\sqrt{n^2\frac{\Delta^2(x)}{x^2}} \rightarrow \Delta(F) = Fn\frac{\Delta(x)}{x} \tag{9.10.8.9}$$

For functions where a variable is an exponent (eg $F = ae^x$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 58)

$$\Delta(F) = \sqrt{a^2e^{2x}\Delta^2(x)} \rightarrow \Delta(F) = F\Delta(x) \tag{9.10.8.10}$$

For functions taking the logarithm of a variable (eg $F = a\ln(x)$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 59)

$$\Delta(F) = \sqrt{\frac{a^2}{x^2}\Delta^2(x)} \rightarrow \Delta(F) = a\frac{\Delta(x)}{x} \tag{9.10.8.11}$$

3. Reporting Numeric Results

All numeric results in this course should be reported with explicit statement of uncertainty. The following format is expected:

$$\textbf{Numeric Value } \pm \textbf{Uncertainty} \tag{9.10.8.12}$$

In your written assignments for this course use the following guidelines when reporting a "final" numeric value. You will be required to use your *best judgement* and to provide a *written justification* of your logic for reporting all final values. More detailed information is found below the guidelines and also in the Shoemaker text.

Guidelines for reporting final numerical values:

- Rules for reporting significant figures should be followed.
- The number of useful decimal places in the uncertainty should match the number of decimal places reported in the value.
- The certainty of a numeric value determined from a function cannot be be more than the certainty of its operands.

A summary of rules for reporting significant Figures (from Shoemaker Ch 2)

The following rules apply only for reporting the *final* value, not for intermediate rounding steps during calculation. In general, do not round values during the calculation process if it can be avoided. However, if you must round prior to comleting a calcaution, then retain *at least one digit more than would be considered "significant"*, and the more the better.

Rules for Rounding Final Values:

Follow the following rules depending on the digit immediately to the right of the place you are rounding. The examples below are rounding to the place underlined, and **the digit immediately to the right is bolded**.

a. Increase the last retained digit by 1 if the nearest dropped digit is more than 5, or if it is 5 followed by any non-zero digits:
   - Examples:
     6.78**9** rounds to 6.79
     54.9**1**23 rounds to 54.9
b. Leave the last retained digit unchanged if the nearest dropped digit is less than 5:
   - Examples:
     2.34**6** rounds to 2.35
     0.21**2**3 rounds to 0.21
c. If the leftmost digit to be dropped is 5 followed by no digits except zero, then increase the last retained digit by 1 if it is odd, and leave it unchanged if it is even:
   - Examples:
     15.32**5** rounds to 15.32
     15.33**5** rounds to 15.34
d. There are times when you should retain an extra digit so that your reported uncertainty is reasonable.

Rules for tracking significant figures for calculated values

Addition: When adding numeric values, the result's precision is limited by the least precise value involved. The number of decimal places in the result should match the fewest decimal places in any component. For example:

$$\begin{array}{r} 15.4 \\ +2.87 \\ +7.621 \\ \hline =25.916 \rightarrow 25.9 \end{array} \tag{9.10.8.13}$$

Subtraction: When subtracting, the result's precision is limited by the least precise value involved, and the precision of the result will always be less than that of the operands. For example:

$$\begin{array}{r} 289.461 \\ -288.58 \\ \hline 0.881 \rightarrow 0.88 \end{array} \tag{9.10.8.14}$$

Let's do an analysis to illustrate what this means. In the example above, let's assume an uncertainty of ± 3 in the rightmost digit of each number. Based on this assumption, the least precise operand has uncertainty of ~ 0.01%, while the final reported value has an uncertainty of 3.4%!

When multiplying and dividing: In multiplication and division, the precision of the result is limited by the least precise number involved. The number of significant figures in the result should align with the component having the fewest. ***Note that relative precision isn't solely dependent on the number of significant figures;*** for instance, 99 with two significant figures is approximately as precise as 101 with three. When unsure, do an analysis of the relative uncertainty, and if the uncertinties are approximately equal, use the larger number of significant figures.

Conventions for Reporting and Interpreting Reported Values

1. Numerical values are typically considered uncertain in the last digit by ±3 or more, with perhaps slight uncertainty in the next-to-last digit by up to ±2.
2. If the last digit to be retained is a one or two, an additional digit is retained so that precision is not inappropriately reported due to rounding.

Guidelines

1. **Before you leave the lab, remember to do the following**:
   (a) Make note of the uncertainties in each of the physical quantities you measure. Follow the suggestions in step (2) below. Consult your TA concerning systematic errors that may arise from instrumental calibration and measurements.
   (b) Be aware of the consequences of systematic errors, such as starting the clock too late in one of the kinetics experiments.
2. **Some rules of thumb on estimation of uncertainties in mass, volume, pressure and temperature measurements**
   (a) Find and record the uncertainties associated with your equipment and instrumentation. This information is often listed right on the device, or is easily obtained from the manufactures statement of equipment specifications. In the rare event that such information is not available, you may assume that single experimentally measured values are uncertain in the last digit by at least ± 0.5 of the smallest unit or measurable digit. For example, if a digital voltmeter reads 5.432 V, and no other information is available, the uncertainty may be estimated to be ± 0.005 V.
   (b) The uncertainty of our analytical balances is either ± 0.0001 g or ± 0.0002 g, You can often find it stated on the individual balance and associated with the letter d (for deviation). For example, the label might say d=0.1 mg.
   (c) The position of the liquid level in a burette or a graduated 1 mL Mohr pipet can be estimated to ± 0.05 mL (half of the smallest unit measurable). Initial and final readings must be made, however, so that the probable error in the volume measured will be,

$$\sqrt{(0.05)^2 + (0.05)^2} = 0.07 \qquad (9.10.8.15)$$

   A similar analysis can be applied to pressure determination by measurement of mercury levels in a U-tube manometer.
   (d) For non-graduated volumetric pipets, the error limits can be found right on the pipet itself, or in the " Comparison of Class A and B Volumetric Glassware" link, found in the External Links section of your Sakai site or from other resources readily available online. You might also look in the Baxter Scientific catalog found in the lab. This catalog is a useful source for tolerances and error limits of thermometers, balances, pipets, burets, volumetric flasks and graduated cylinders.
3. **In the case of Replicate or Single Measurements**
   (a) If you make a series of replicate measurements of the same quantity, you should report the mean of that quantity together with its precision (standard deviation, variance or 95% confidence limits) calculated by statistical analysis. Unless otherwise requested in the lab manual, use the standard deviation as a measure of precision. If the accepted value of the quantity has been reported in the literature, you might also report the percent error or absolute error as a measure of the accuracy of your measurement(s). If you feel that one of the replicate measurements should be rejected, use the Q-test to justify your decision.
   (b) If you make a single measurement of a quantity, give your best estimate of the uncertainty in that measurement, whether random or systematic. If appropriate (see 2.2.3(a) above), you should also report the accuracy of that measurement. The suggestions given in Step (2.2.2) may help. Consult your TA if in doubt.
4. **Graphical Analysis**
   (a) If you use graphical analysis to determine the value of any quantity, you must make a decision whether or not to use a weighted least squares regression analysis. In most cases, a non-weighted analysis (using the command lsq in Matlab) will suffice. If you perform a weighted least squares analysis, you will have to decide on what weighting factor, e, to use. If the data deviate systematically from linearity, a linear regression analysis is meaningless, and should **not** be performed.
   (b) Outliers may be rejected only on the basis of a Q-test performed on the residuals.
   (c) The standard deviation may be used as a measure of the uncertainty in the slope and intercept calculated by linear least squares regression.
   (d) In most cases, you will use the values of the slope and/or y-intercept to calculate a physical quantity. In either case, you must perform a propagation of error treatment to determine the uncertainty in that physical quantity.
5. **Propagation of Error**
   Whether or not you perform a graphic analysis, you will use experimentally determined variables to calculate one or more physical quantities. In each case you must estimate the uncertainty in each measured variable and then propagate that uncertainty through to the final result. In a few simple cases you may take advantage of Equations (55) - (59) (Shoemaker et. al., 1996). Usually however, you will use Equation (54) (Shoemaker et. al., 1996), and take partial derivatives to calculate the probable propagated error. Physical constants, such as the gas constant, R, may be assumed to be error free.

6. **Reporting the Final Numerical Result(s) in your Notebooks and Reports**
   (a) Each numerical result should be reported together with the associated uncertainty, which is usually the probable propagated error. In addition, and where possible, you should report the accuracy of your result by comparison with literature values and calculation of the absolute error.
   (b) In reporting your results, ensure that the use of significant figures is appropriate to the uncertainty in those results. Use the conventions for significant figures and for rounding off data described earlier in this text.
7. **Discuss Qualitative Uncertainties in your Notebooks and Reports**
   In some cases, it may be difficult to quantitatively estimate the uncertainty in an experimental variable. In this instance, you may be asked to provide a qualitative discussion of the sources of uncertainty in the experiment. This discussion should be as thorough as possible. You should include "reasonable" estimates of the uncertainties in measured parameters together with a discussion of how these uncertainties will affect the final result. Any estimates of uncertainty should be substantiated by hard facts!!

And finally, if you read nothing else .....

1. Estimate the uncertainty in each experimentally determined variable. Usually this involves one or more of the following:

(a) Calculate the standard deviation of a quantity determined from the mean of a series of replicate measurements.

(b) Find and record the uncertainties associated with your equipment and instrumentation. This information is often listed right on the device, or is easily obtained from the manufactures statement of equipment specifications. In the rare event that such information is not available, you may assume that single experimentally measured values are uncertain in the last digit by at least ± 0.5 of the smallest unit or measurable digit. For example, if a digital voltmeter reads 5.432 V, and no other information is available, the uncertainty may be estimated to be ± 0.005 V.

(c) Perform a simple propagation of error analysis (usually equation (54) (Shoemaker et. al., 1996)) if a quantity (e.g., volume, pressure) is determined from a difference of two or more readings.

(d) Extraction of a Physical Quantity from Graphical Analysis: Calculation of the standard deviation of the slope (or intercept) is followed by a propagation of error treatment of the functional form of that slope (or intercept) to give the uncertainty in the physical quantity to be extracted. If the data deviate systematically from linearity, a linear regression analysis is meaningless and should not be performed.

(e) If the source or estimation of uncertainty seems more obscure, -- **CONSULT YOUR TA BEFORE YOU LEAVE THE LAB.**

2. Once you have determined the uncertainties associated with each individual measurement, perform a propagation of error treatment to estimate their combined effect on the uncertainty of the physical quantity of interest. Use equation (54) or some combination of equations (55) - (59) (Shoemaker et. al., 1996). Physical constants such as the Gas Constant, R, may be assumed to be error free.

3. Report your final result(s), the probable propagated error associated with that result, and the percent error or absolute error if appropriate literature values are available.

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9.10.9: Characterizing Experimental Errors

In this course, you will need to determine the confidence in your results by doing appropriate error analysis. This section and the next are meant to review the types of experimental errors that affect accuracy and precision and to remind you of the simple methods for propagating error.

Errors That Affect Accuracy

Accuracy is how close a measure of central tendency is to its expected value, μ. We express accuracy either as an absolute error, e

$$e = \overline{X} - \mu \tag{9.10.9.1}$$

or as a percent relative error, %e

$$\%e = \frac{\overline{X} - \mu}{\mu} \times 100 \tag{9.10.9.2}$$

Although Equation 9.10.9.1 and Equation 9.10.9.2 use the mean as the measure of central tendency, we also can use the median.

> The convention for representing a statistical parameter is to use a Roman letter for a value calculated from experimental data, and a Greek letter for its corresponding expected value. For example, the experimentally determined mean is $\overline{X}$ and its underlying expected value is μ. Likewise, the experimental standard deviation is s and the underlying expected value is σ.

We identify as determinate an error that affects the accuracy of an analysis. Each source of a ***determinate error*** has a specific magnitude and sign. Some sources of determinate error are positive and others are negative, and some are larger in magnitude and others are smaller in magnitude. The cumulative effect of these determinate errors is a net positive or negative error in accuracy.

> It is possible, although unlikely, that the positive and negative determinate errors will offset each other, producing a result with no net error in accuracy.

We assign determinate errors into four categories—sampling errors, method errors, measurement errors, and personal errors—each of which we consider in this section.

Sampling Errors

A determinate sampling error occurs when our sampling strategy does not provide a us with a representative sample. For example, if we monitor the environmental quality of a lake by sampling from a single site near a point source of pollution, such as an outlet for industrial effluent, then our results will be misleading. To determine the mass of a U. S. penny, our strategy for selecting pennies must ensure that we do not include pennies from other countries.

> An awareness of potential sampling errors especially is important when we work with heterogeneous materials. Strategies for obtaining representative samples are covered in Chapter 5 of Harvey's Analytical Chemistry text on LibreTexts.

Method Errors

In any analysis the relationship between the signal, S_{total}, and the absolute amount of analyte, n_A, or the analyte's concentration, C_A, is

$$S_{total} = k_A n_A + S_{mb} \tag{9.10.9.3}$$

$$S_{total} = k_A C_A + S_{mb} \tag{9.10.9.4}$$

where k_A is the method's sensitivity for the analyte and S_{mb} is the signal from the method blank. A ***method error*** exists when our value for k_A or for S_{mb} is in error. For example, a method in which S_{total} is the mass of a precipitate assumes that k is defined by a pure precipitate of known stoichiometry. If this assumption is not true, then the resulting determination of n_A or C_A is inaccurate.

We can minimize a determinate error in k_A by calibrating the method. A method error due to an interferent in the reagents is minimized by using a proper method blank.

Measurement Errors

The manufacturers of analytical instruments and equipment, such as glassware and balances, usually provide a statement of the item's maximum ***measurement error***, or ***tolerance***. For example, a 10-mL volumetric pipet (Figure 9.10.9.1) has a tolerance of ±0.02 mL, which means the pipet delivers an actual volume within the range 9.98–10.02 mL at a temperature of 20 °C. Although we express this tolerance as a range, the error is determinate; that is, the pipet's expected volume, μ, is a fixed value within this stated range.



Figure 9.10.9.1 : Close-up of a 10-mL volumetric pipet showing that it has a tolerance of ±0.02 mL at 20 °C.

Volumetric glassware is categorized into classes based on its relative accuracy. **Class A glassware** is manufactured to comply with tolerances specified by an agency, such as the National Institute of Standards and Technology or the American Society for Testing and Materials. The tolerance level for Class A glassware is small enough that normally we can use it without calibration. The tolerance levels for **Class B glassware** usually are twice that for Class A glassware. In other words, Class B is less accurate. Other types of volumetric glassware, such as beakers and graduated cylinders, are not used to measure volume accurately. Table 9.10.9.1 provides a summary of typical measurement errors for Class A volumetric glassware. Tolerances for digital pipets and for balances are provided in Table 9.10.9.2 and Table 9.10.9.3 .

Tolerance Limits for Class A Volumetric Glassware

Table 9.10.9.1 : Measurement Errors for **Class A Volumetric Glassware**

Volumetric Pipets		**Volumetric Flasks**		**Burets**	
Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)
1	±0.006	5	±0.02	10	±0.02
2	±0.006	10	±0.02	25	±0.03
5	±0.01	25	±0.03	50	±0.05
10	±0.02	50	±0.05		
20	±0.03	100	±0.08		
25	±0.03	250	±0.12		
50	±0.05	500	±0.20		
100	±0.08	1000	±0.30		
		2000	±0.50		

Tolerance limits for Digital Pipettes

Table 9.10.9.2 : Measurement Errors for Digital Pipets

Pipet Range	Volume (mL or μL)	Percent Measurement Error
10–100 μL	10	±3.0%
	50	±1.0%
	100	±0.8%
100–1000 μL	100	±3.0%
	500	±1.0%
	1000	±0.6%
1–10 mL	1	±3.0%
	5	±0.8%
	10	±0.6%

The tolerance values for the volumetric glassware in Table 9.10.9.1 are from the ASTM E288, E542, and E694 standards. The measurement errors for the digital pipets in Table 9.10.9.2 are from www.eppendorf.com.

Tolerance Limits for Some Common Balances

Table 9.10.9.3 : Measurement Errors for Selected Balances

Balance	Capacity (g)	Measurement Error
Precisa 160M	160	±1 mg
A & D ER 120M	120	±0.1 mg
Metler H54	160	±0.01 mg

We can minimize a determinate measurement error by calibrating our equipment. Balances are calibrated using a reference weight whose mass we can trace back to the SI standard kilogram. Volumetric glassware and digital pipets are calibrated by determining the mass of water delivered or contained and using the density of water to calculate the actual volume. It is never safe to assume that a calibration does not change during an analysis or over time. One study, for example, found that repeatedly exposing volumetric glassware to higher temperatures during machine washing and oven drying, led to small, but significant changes in the glassware's calibration [Castanheira, I.; Batista, E.; Valente, A.; Dias, G.; Mora, M.; Pinto, L.; Costa, H. S. *Food Control* **2006**, *17*, 719–726]. Many instruments drift out of calibration over time and may require frequent recalibration during an analysis.

Personal Errors

Finally, analytical work is always subject to ***personal error***, examples of which include the ability to see a change in the color of an indicator that signals the endpoint of a titration, biases, such as consistently overestimating or underestimating the value on an instrument's readout scale, failing to calibrate instrumentation, and misinterpreting procedural directions. You can minimize personal errors by taking proper care.

Identifying Determinate Errors

Determinate errors often are difficult to detect. Without knowing the expected value for an analysis, the usual situation in any analysis that matters, we often have nothing to which we can compare our experimental result. Nevertheless, there are strategies we can use to detect determinate errors.

The magnitude of a constant ***determinate error*** is the same for all samples and is more significant when we analyze smaller samples. Analyzing samples of different sizes, therefore, allows us to detect a constant determinate error. For example, consider a quantitative analysis in which we separate the analyte from its matrix and determine its mass. Let's assume the sample is 50.0% w/w analyte. As we see in Table 9.10.9.4 , the expected amount of analyte in a 0.100 g sample is 0.050 g. If the analysis has a

positive constant determinate error of 0.010 g, then analyzing the sample gives 0.060 g of analyte, or an apparent concentration of 60.0% w/w. As we increase the size of the sample the experimental results become closer to the expected result. An upward or downward trend in a graph of the analyte's experimental concentration versus the sample's mass (Figure 9.10.9.2) is evidence of a constant determinate error.

Table 9.10.9.4 : Effect of a Constant Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Constant Error (g)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	0.010	0.060	60.0
0.200	0.100	0.010	0.110	55.0
0.400	0.200	0.010	0.210	52.5
0.800	0.400	0.010	0.410	51.2
1.600	0.800	0.010	0.810	50.6

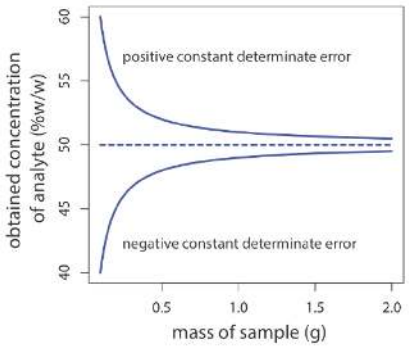


Figure 9.10.9.2 : Effect of a constant positive determinate error of +0.01 g and a constant negative determinate error of –0.01 g on the determination of an analyte in samples of varying size. The analyte's expected concentration of 50% w/w is shown by the dashed line.

A ***proportional determinate error***, in which the error's magnitude depends on the amount of sample, is more difficult to detect because the result of the analysis is independent of the amount of sample. Table 9.10.9.5 outlines an example that shows the effect of a positive proportional error of 1.0% on the analysis of a sample that is 50.0% w/w in analyte. Regardless of the sample's size, each analysis gives the same result of 50.5% w/w analyte.

Table 9.10.9.5 : Effect of a Proportional Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Proportional Error (%)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	1.00	0.0505	50.5
0.200	0.100	1.00	0.101	50.5
0.400	0.200	1.00	0.202	50.5
0.800	0.400	1.00	0.404	50.5
1.600	0.800	1.00	0.808	50.5

One approach for detecting a proportional determinate error is to analyze a standard that contains a known amount of analyte in a matrix similar to our samples. Standards are available from a variety of sources, such as the National Institute of Standards and

Technology (where they are called Standard Reference Materials) or the American Society for Testing and Materials. Table 9.10.9.6 , for example, lists certified values for several analytes in a standard sample of *Gingko biloba* leaves. Another approach is to compare our analysis to an analysis carried out using an independent analytical method that is known to give accurate results. If the two methods give significantly different results, then a determinate error is the likely cause.

Table 9.10.9.6 : Certified Concentrations for SRM 3246: *Gingko bilbo* (Leaves)

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
Flavonoids/Ginkgolide B (mass fraction in mg/g)	Qurecetin	2.69 ± 0.31
	Kaempferol	3.02 ± 0.41
	Isorhamnetin	$0.517 \pm 0.0.99$
	Total Aglycones	6.22 ± 0.77
Selected Terpenes (mass fraction in mg/g)	Ginkgolide A	0.57 ± 0.28
	Ginkgolide B	0.470 ± 0.090
	Ginkgolide C	0.59 ± 0.22
	Ginkgolide J	0.18 ± 0.10
	Bilobalide	1.52 ± 0.40
	Total Terpene Lactones	3.3 ± 1.1
Selected Toxic Elements (mass fraction in ng/g)	Cadmium	20.8 ± 1.0
	Lead	995 ± 30
	Mercury	23.08 ± 0.17

> The primary purpose of this Standard Reference Material is to validate analytical methods for determining flavonoids, terpene lactones, and toxic elements in *Ginkgo biloba* or other materials with a similar matrix. Values are from the official Certificate of Analysis available at www.nist.gov.

Constant and proportional determinate errors have distinctly different sources, which we can define in terms of the relationship between the signal and the moles or concentration of analyte (Equation 9.10.9.3 and Equation 9.10.9.4). An invalid method blank, S_{mb}, is a constant determinate error as it adds or subtracts the same value to the signal. A poorly calibrated method, which yields an invalid sensitivity for the analyte, k_A, results in a proportional determinate error.

Errors that Affect Precision

Precision is a measure of the spread of individual measurements or results about a central value, which we express as a range, a standard deviation, or a variance. Here we draw a distinction between two types of precision: repeatability and reproducibility. ***Repeatability*** is the precision when a single analyst completes an analysis in a single session using the same solutions, equipment, and instrumentation. ***Reproducibility***, on the other hand, is the precision under any other set of conditions, including between analysts or between laboratory sessions for a single analyst. Since reproducibility includes additional sources of variability, the reproducibility of an analysis cannot be better than its repeatability.

> The ratio of the standard deviation associated with reproducibility to the standard deviation associated with repeatability is called the Horowitz ratio. For a wide variety of analytes in foods, for example, the median Horowtiz ratio is 2.0 with larger

values for fatty acids and for trace elements; see Thompson, M.; Wood, R. “The ‘Horowitz Ratio’–A Study of the Ratio Between Reproducibility and Repeatability in the Analysis of Foodstuffs,” *Anal. Methods*, **2015**, *7*, 375–379.

Errors that affect precision are indeterminate and are characterized by random variations in their magnitude and their direction. Because they are random, positive and negative ***indeterminate errors*** tend to cancel, provided that we make a sufficient number of measurements. In such situations the mean and the median largely are unaffected by the precision of the analysis.

Sources of Indeterminate Error

We can assign indeterminate errors to several sources, including collecting samples, manipulating samples during the analysis, and making measurements. When we collect a sample, for instance, only a small portion of the available material is taken, which increases the chance that small-scale inhomogeneities in the sample will affect repeatability. Individual pennies, for example, may show variations in mass from several sources, including the manufacturing process and the loss of small amounts of metal or the addition of dirt during circulation. These variations are sources of indeterminate sampling errors.

During an analysis there are many opportunities to introduce indeterminate method errors. If our method for determining the mass of a penny includes directions for cleaning them of dirt, then we must be careful to treat each penny in the same way. Cleaning some pennies more vigorously than others might introduce an indeterminate method error.

Finally, all measuring devices are subject to indeterminate measurement errors due to limitations in our ability to read its scale. For example, a buret with scale divisions every 0.1 mL has an inherent indeterminate error of ±0.01–0.03 mL when we estimate the volume to the hundredth of a milliliter (Figure 9.10.9.3).

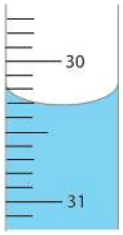


Figure 9.10.9.3 : Close-up of a buret showing the difficulty in estimating volume. With scale divisions every 0.1 mL it is difficult to read the actual volume to better than ±0.01–0.03 mL.

Evaluating Indeterminate Error

Indeterminate errors associated with our analytical equipment or instrumentation generally are easy to estimate if we measure the standard deviation for several replicate measurements, or if we monitor the signal’s fluctuations over time in the absence of analyte (Figure 9.10.9.4) and calculate the standard deviation. Other sources of indeterminate error, such as treating samples inconsistently, are more difficult to estimate.

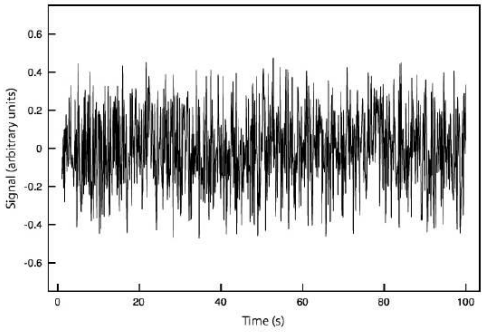


Figure 9.10.9.4 : Background noise in an instrument showing the random fluctuations in the signal.

Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty [Ellison, S.; Wegscheider, W.; Williams, A. *Anal. Chem.* **1997**, *69*, 607A–613A]. ***Error*** is the difference between a single measurement or result and its expected value. In other words, error

is a measure of ***bias***. As discussed earlier, we divide errors into determinate and indeterminate sources. Although we can find and correct a source of determinate error, the indeterminate portion of the error remains.

Uncertainty expresses the range of possible values for a measurement or result. Note that this definition of uncertainty is not the same as our definition of precision. We calculate precision from our experimental data and use it to estimate the magnitude of indeterminate errors. Uncertainty accounts for all errors—both determinate and indeterminate—that reasonably might affect a measurement or a result. Although we always try to correct determinate errors before we begin an analysis, the correction itself is subject to uncertainty.

Here is an example to help illustrate the difference between precision and uncertainty. Suppose you purchase a 10-mL Class A pipet from a laboratory supply company and use it without any additional calibration. The pipet's tolerance of ±0.02 mL is its uncertainty because your best estimate of its expected volume is 10.00 mL ± 0.02 mL. This uncertainty primarily is determinate. If you use the pipet to dispense several replicate samples of a solution and determine the volume of each sample, the resulting standard deviation is the pipet's precision. Table 9.10.9.8 shows results for ten such trials, with a mean of 9.992 mL and a standard deviation of ±0.006 mL. This standard deviation is the precision with which we expect to deliver a solution using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ±0.02 mL is worse than its experimentally determined precision of ±0.006 ml. Interestingly, the data in Table 9.10.9.8 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ±0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty [Kadis, R. *Talanta* **2004**, *64*, 167–173].

Table 9.10.9.8 : Experimental Results for Volume Dispensed by a 10–mL Class A Transfer Pipet

Replicate	Volume (ml)	Replicate	Volume (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

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9.10.10: Propagation of Uncertainty

Suppose we dispense 20 mL of a reagent using the Class A 10-mL pipet whose calibration information is given in the Table in the previous section. If the volume and uncertainty for one use of the pipet is 9.992 ± 0.006 mL, what is the volume and uncertainty if we use the pipet twice?

As a first guess, we might simply add together the volume and the maximum uncertainty for each delivery; thus

$$(9.992\text{ mL} + 9.992\text{ mL}) \pm (0.006\text{ mL} + 0.006\text{ mL}) = 19.984 \pm 0.012\text{ mL}$$

It is easy to appreciate that combining uncertainties in this way overestimates the total uncertainty. Adding the uncertainty for the first delivery to that of the second delivery assumes that with each use the indeterminate error is in the same direction and is as large as possible. At the other extreme, we might assume that the uncertainty for one delivery is positive and the other is negative. If we subtract the maximum uncertainties for each delivery,

$$(9.992\text{ mL} + 9.992\text{ mL}) \pm (0.006\text{ mL} - 0.006\text{ mL}) = 19.984 \pm 0.000\text{ mL}$$

we clearly underestimate the total uncertainty.

So what is the total uncertainty? From the discussion above, we reasonably expect that the total uncertainty is greater than ±0.000 mL and that it is less than ±0.012 mL. To estimate the uncertainty we use a mathematical technique known as the propagation of uncertainty. Our treatment of the propagation of uncertainty is based on a few simple rules.

A Few Symbols

A ***propagation of uncertainty*** allows us to estimate the uncertainty in a result from the uncertainties in the measurements used to calculate that result. For the equations in this section we represent the result with the symbol R, and we represent the measurements with the symbols A, B, and C. The corresponding uncertainties are u_R, u_A, u_B, and u_C. We can define the uncertainties for A, B, and C using standard deviations, ranges, or tolerances (or any other measure of uncertainty), as long as we use the same form for all measurements.

> The requirement that we express each uncertainty in the same way is a critically important point. Suppose you have a range for one measurement, such as a pipet's tolerance, and standard deviations for the other measurements. All is not lost. There are ways to convert a range to an estimate of the standard deviation. See Appendix 2 of Harvey's Analytical Chemistry Text for more details.

Uncertainty When Adding or Subtracting

When we add or subtract measurements we propagate their absolute uncertainties. For example, if the result is given by the equation

$$R = A + B - C$$

the the absolute uncertainty in R is

$$u_R = \sqrt{u_A^2 + u_B^2 + u_C^2} \tag{9.10.10.1}$$

Example 9.10.10.1

If we dispense 20 mL using a 10-mL Class A pipet, what is the total volume dispensed and what is the uncertainty in this volume? First, complete the calculation using the manufacturer's tolerance of 10.00 mL±0.02 mL, and then using the calibration data from the Table 1.3.8 in the previous section.

Solution

To calculate the total volume we add the volumes for each use of the pipet. When using the manufacturer's values, the total volume is

$$V = 10.00\ \text{mL} + 10.00\ \text{mL} = 20.00\ \text{mL}$$

and when using the calibration data, the total volume is

$$V = 9.992\ \text{mL} + 9.992\ \text{mL} = 19.984\ \text{mL}$$

Using the pipet's tolerance as an estimate of its uncertainty gives the uncertainty in the total volume as

$$u_R = (0.02)^2 + (0.02)^2 = 0.028\ \text{mL} = 0.028\ \text{mL}$$

and using the standard deviation for the data in Table 1.3.8 gives an uncertainty of

$$u_R = (0.006)^2 + (0.006)^2 = 0.0085\ \text{mL}$$

Rounding the volumes to four significant figures gives 20.00 mL ± 0.03 mL when we use the tolerance values, and 19.98 ± 0.01 mL when we use the calibration data.

Uncertainty When Multiplying or Dividing

When we multiple or divide measurements we propagate their relative uncertainties. For example, if the result is given by the equation

$$R = \frac{A \times B}{C}$$

then the relative uncertainty in R is

$$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2 + \left(\frac{u_C}{C}\right)^2} \tag{9.10.10.2}$$

Example 9.10.10.2

The quantity of charge, Q, in coulombs that passes through an electrical circuit is

$$Q = i \times t$$

where i is the current in amperes and t is the time in seconds. When a current of 0.15 A ± 0.01 A passes through the circuit for 120 s ± 1 s, what is the total charge and its uncertainty?

Solution

The total charge is

$$Q = (0.15\ \text{A}) \times (120\ \text{s}) = 18\ \text{C}$$

Since charge is the product of current and time, the relative uncertainty in the charge is

$$u_R = \sqrt{\left(\frac{0.01}{0.15}\right)^2 + \left(\frac{1}{120}\right)^2} = 0.0672$$

and the charge's absolute uncertainty is

$$u_R = R \times 0.0672 = (18\ \text{C}) \times (0.0672) = 1.2\ \text{C}$$

Thus, we report the total charge as 18 C ± 1 C.

Uncertainty for Mixed Operations

Many chemical calculations involve a combination of adding and subtracting, and of multiply and dividing. As shown in the following example, we can calculate the uncertainty by separately treating each operation using Equation 9.10.10.1 and Equation 9.10.10.2 as needed.

Example 9.10.10.3

For a concentration technique, the relationship between the signal and the an analyte's concentration is

$$S_{total} = k_A C_A + S_{mb}$$

What is the analyte's concentration, C_A, and its uncertainty if S_{total} is 24.37 ± 0.02, S_{mb} is 0.96 ± 0.02, and k_A is $\mathbf{0.186 \pm 0.003\ ppm^{-1}}$?

Solution

Rearranging the equation and solving for C_A

$$C_A = \frac{S_{total} - S_{mb}}{k_A} = \frac{24.37 - 0.96}{0.186\ \text{ppm}^{-1}} = \frac{23.41}{0.186\ \text{ppm}^{-1}} = 125.9\ \text{ppm}$$

gives the analyte's concentration as 126 ppm. To estimate the uncertainty in C_A, we first use Equation 9.10.10.1 to determine the uncertainty for the numerator.

$$u_R = \sqrt{(0.02)^2 + (0.02)^2} = 0.028$$

The numerator, therefore, is 23.41 ± 0.028. To complete the calculation we use Equation 9.10.10.2 to estimate the relative uncertainty in C_A.

$$\frac{u_R}{R} = \sqrt{\left(\frac{0.028}{23.41}\right)^2 + \left(\frac{0.003}{0.186}\right)^2} = 0.0162$$

The absolute uncertainty in the analyte's concentration is

$$u_R = (125.9\ \text{ppm}) \times (0.0162) = 2.0\ \text{ppm}$$

Thus, we report the analyte's concentration as 126 ppm ± 2 ppm.

? Exercise 9.10.10.1

To prepare a standard solution of Cu^{2+} you obtain a piece of copper from a spool of wire. The spool's initial weight is 74.2991 g and its final weight is 73.3216 g. You place the sample of wire in a 500-mL volumetric flask, dissolve it in 10 mL of HNO_3, and dilute to volume. Next, you pipet a 1 mL portion to a 250-mL volumetric flask and dilute to volume. What is the final concentration of Cu^{2+} in mg/L, and its uncertainty? Assume that the uncertainty in the balance is ±0.1 mg and that you are using Class A glassware.

Answer

The first step is to determine the concentration of Cu^{2+} in the final solution. The mass of copper is

$$74.2991\ \text{g} - 73.3216\ \text{g} = 0.9775\ \text{g Cu}$$

The 10 mL of HNO_3 used to dissolve the copper does not factor into our calculation. The concentration of Cu^{2+} is

$$\frac{0.9775\ \text{g Cu}}{0.5000\ \text{L}} \times \frac{1.000\ \text{mL}}{250.0\ \text{mL}} \times \frac{1000\ \text{mg}}{\text{g}} = 7.820\ \text{mg Cu}^{2+}\text{/L}$$

Having found the concentration of Cu^{2+}, we continue with the propagation of uncertainty. The absolute uncertainty in the mass of Cu wire is

$$u_{\text{g Cu}} = \sqrt{(0.0001)^2 + (0.0001)^2} = 0.00014\ \text{g}$$

The relative uncertainty in the concentration of Cu^{2+} is

$$\frac{u_{\text{mg/L}}}{7.820\ \text{mg/L}} = \sqrt{\left(\frac{0.00014}{0.9775}\right)^2 + \left(\frac{0.20}{500.0}\right)^2 + \left(\frac{0.006}{1.000}\right)^2 + \left(\frac{0.12}{250.0}\right)^2} = 0.00603$$

Solving for $u_{\text{mg/L}}$ gives the uncertainty as 0.0472. The concentration and uncertainty for Cu^{2+} is 7.820 mg/L ± 0.047 mg/L.

Uncertainty for Other Mathematical Functions

Many other mathematical operations are common in analytical chemistry, including the use of powers, roots, and logarithms. Table 9.10.10.1 provides equations for propagating uncertainty for some of these function where *A* and *B* are independent measurements and where *k* is a constant whose value has no uncertainty.

Table 9.10.10.1 : Propagation of Uncertainty for Selected Mathematical Functions

Function	u_R	Function	u_R
$R = kA$	$u_R = ku_A$	$R = \ln(A)$	$u_R = \frac{u_A}{A}$
$R = A + B$	$u_R = \sqrt{u_A^2 + u_B^2}$	$R = \log(A)$	$u_R = 0.4343 \times \frac{u_A}{A}$
$R = A - B$	$u_R = \sqrt{u_A^2 + u_B^2}$	$R = e^A$	$\frac{u_R}{R} = u_A$
$R = A \times B$	$u_R = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2}$	$R = 10^A$	$\frac{u_R}{R} = 2.303 \times u_A$
$R = \frac{A}{B}$	$u_R = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2}$	$R = A^k$	$\frac{u_R}{R} = k \times \frac{u_A}{A}$

Example 9.10.10.4

If the pH of a solution is 3.72 with an absolute uncertainty of ±0.03, what is the $[H^+]$ and its uncertainty?

Solution

The concentration of H^+ is

$$[H^+] = 10^{-pH} = 10^{-3.72} = 1.91 \times 10^{-4}\ M$$

or 1.9×10^{-4} M to two significant figures. From Table 9.10.10.1 the relative uncertainty in $[H^+]$ is

$$\frac{u_R}{R} = 2.303 \times u_A = 2.303 \times 0.03 = 0.069$$

The uncertainty in the concentration, therefore, is

$$(1.91 \times 10^{-4}\ M) \times (0.069) = 1.3 \times 10^{-5}\ M$$

We report the $[H^+]$ as $1.9(\pm 0.1) \times 10^{-4}$ M, which is equivalent to $1.9 \times 10^{-4}\ M\ \pm 0.1 \times 10^{-4}\ M$.

Exercise 9.10.10.2

A solution of copper ions is blue because it absorbs yellow and orange light. Absorbance, *A*, is defined as

$$A = -\log T = -\log\left(\frac{P}{P_o}\right)$$

where, *T* is the transmittance, P_o is the power of radiation as emitted from the light source and *P* is its power after it passes through the solution. What is the absorbance if P_o is 3.80×10^2 and *P* is 1.50×10^2? If the uncertainty in measuring P_o and *P* is 15, what is the uncertainty in the absorbance?

Answer

The first step is to calculate the absorbance, which is

$$A = -\log T = -\log \frac{P}{P_o} = -\log \frac{1.50 \times 10^2}{3.80 \times 10^2} = 0.4037 \approx 0.404$$

Having found the absorbance, we continue with the propagation of uncertainty. First, we find the uncertainty for the ratio P/P_o, which is the transmittance, T.

$$\frac{u_T}{T} = \sqrt{\left(\frac{15}{3.80 \times 10^2}\right)^2 + \left(\frac{15}{1.50 \times 10^2}\right)^2} = 0.1075$$

Finally, from Table 9.10.10.1 the uncertainty in the absorbance is

$$u_A = 0.4343 \times \frac{u_T}{T} = (0.4343) \times (0.1075) = 4.669 \times 10^{-2}$$

The absorbance and uncertainty is 0.40 ± 0.05 absorbance units.

Is Calculating Uncertainty Actually Useful?

Given the effort it takes to calculate uncertainty, it is worth asking whether such calculations are useful. The short answer is, yes. Let's consider three examples of how we can use a propagation of uncertainty to help guide the development of an analytical method.

One reason to complete a propagation of uncertainty is that we can compare our estimate of the uncertainty to that obtained experimentally. For example, to determine the mass of a penny we measure its mass twice—once to tare the balance at 0.000 g and once to measure the penny's mass. If the uncertainty in each measurement of mass is ±0.001 g, then we estimate the total uncertainty in the penny's mass as

$$u_R = \sqrt{(0.001)^2 + (0.001)^2} = 0.0014 \text{ g}$$

If we measure a single penny's mass several times and obtain a standard deviation of ±0.050 g, then we have evidence that the measurement process is out of control. Knowing this, we can identify and correct the problem.

We also can use a propagation of uncertainty to help us decide how to improve an analytical method's uncertainty. In Example 9.10.10.3 , for instance, we calculated an analyte's concentration as 126 ppm ± 2 ppm, which is a percent uncertainty of 1.6%. Suppose we want to decrease the percent uncertainty to no more than 0.8%. How might we accomplish this? Looking back at the calculation, we see that the concentration's relative uncertainty is determined by the relative uncertainty in the measured signal (corrected for the reagent blank)

$$\frac{0.028}{23.41} = 0.0012 \text{ or } 0.12\%$$

and the relative uncertainty in the method's sensitivity, k_A,

$$\frac{0.003 \text{ ppm}^{-1}}{0.186 \text{ ppm}^{-1}} = 0.016 \text{ or } 1.6\%$$

Of these two terms, the uncertainty in the method's sensitivity dominates the overall uncertainty. Improving the signal's uncertainty will not improve the overall uncertainty of the analysis. To achieve an overall uncertainty of 0.8% we must improve the uncertainty in k_A to ±0.0015 ppm^{-1}.

? Exercise 9.10.10.3

Verify that an uncertainty of ±0.0015 ppm^{-1} for k_A is the correct result.

Answer

An uncertainty of 0.8% is a relative uncertainty in the concentration of 0.008; thus, letting u be the uncertainty in k_A

$$0.008 = \sqrt{\left(\frac{0.028}{23.41}\right)^2 + \left(\frac{u}{0.186}\right)^2}$$

Squaring both sides of the equation gives

$$6.4 \times 10^{-5} = \left(\frac{0.028}{23.41}\right)^2 + \left(\frac{u}{0.186}\right)^2$$

Solving for the uncertainty in k_A gives its value as $\mathbf{1.47 \times 10^{-3}}$ or ±0.0015 ppm^{-1}.

Finally, we can use a propagation of uncertainty to determine which of several procedures provides the smallest uncertainty. When we dilute a stock solution usually there are several combinations of volumetric glassware that will give the same final concentration. For instance, we can dilute a stock solution by a factor of 10 using a 10-mL pipet and a 100-mL volumetric flask, or using a 25-mL pipet and a 250-mL volumetric flask. We also can accomplish the same dilution in two steps using a 50-mL pipet and 100-mL volumetric flask for the first dilution, and a 10-mL pipet and a 50-mL volumetric flask for the second dilution. The overall uncertainty in the final concentration—and, therefore, the best option for the dilution—depends on the uncertainty of the volumetric pipets and volumetric flasks. As shown in the following example, we can use the tolerance values for volumetric glassware to determine the optimum dilution strategy [Lam, R. B.; Isenhour, T. L. *Anal. Chem.* **1980**, *52*, 1158–1161].

Example 9.10.10.5 :

Which of the following methods for preparing a 0.0010 M solution from a 1.0 M stock solution provides the smallest overall uncertainty?

(a) A one-step dilution that uses a 1-mL pipet and a 1000-mL volumetric flask.

(b) A two-step dilution that uses a 20-mL pipet and a 1000-mL volumetric flask for the first dilution, and a 25-mL pipet and a 500-mL volumetric flask for the second dilution.

Solution

The dilution calculations for case (a) and case (b) are

$$\text{case (a): } 1.0 \text{ M} \times \frac{1.000 \text{ mL}}{1000.0 \text{ mL}} = 0.0010 \text{ M}$$

$$\text{case (b): } 1.0 \text{ M} \times \frac{20.00 \text{ mL}}{1000.0 \text{ mL}} \times \frac{25.00 \text{ mL}}{500.0 \text{mL}} = 0.0010 \text{ M}$$

Using tolerance values from Table 2.1.3.1, the relative uncertainty for case (a) is

$$u_R = \sqrt{\left(\frac{0.006}{1.000}\right)^2 + \left(\frac{0.3}{1000.0}\right)^2} = 0.006$$

and for case (b) the relative uncertainty is

$$u_R = \sqrt{\left(\frac{0.03}{20.00}\right)^2 + \left(\frac{0.3}{1000}\right)^2 + \left(\frac{0.03}{25.00}\right)^2 + \left(\frac{0.2}{500.0}\right)^2} = 0.002$$

Since the relative uncertainty for case (b) is less than that for case (a), the two-step dilution provides the smallest overall uncertainty. Of course we must balance the smaller uncertainty for case (b) against the increased opportunity for introducing a determinate error when making two dilutions instead of just one dilution, as in case (a).

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9.10.11: Least Squares Linear Regression

Your experimental data will usually be examined in graphic form, which can be more instructive than tabulated data. In any graphic presentation, be sure to plot your independent variable on the abscissa (x-axis) and the dependent variable on the ordinate (y-axis).

If the data are presented in graphic form, the usual procedure is to fit the best curve through the experimental points. As Brownlee[3] puts it,

> "When an investigator observes simultaneously two variables, x and y, usually with good reason he plots the observations on a graph. If there is any sign of an association, he is usually seized with the impulse to fit a line, usually a straight line or, rather infrequently, a parabola or cubic."

When we are "seized with the impulse" to fit a straight line curve the process of curve fitting is called linear regression. We assume that the deviations of the dependent variable y are distributed normally (that is, a Gaussian distribution). This assumption is not required for the determination of the least squares parameters, but it is necessary for construction of confidence intervals or for tests of hypotheses about the parameters. The parameters obtained by least squares under these conditions are unbiased and provide the best estimates of the curve fitting parameters.

Most of the experimental data that you will encounter this semester will have a simple functional form, or can be manipulated in such a way as to assume a simple form. We shall assume here that our data follows a linear relationship. For example, consider a gas that is thought to follow the equation of state

$$\underset{y = a + bx}{Z \equiv \frac{PV}{nRT} = B_0 + B_1 P} \tag{9.10.11.1}$$

Measurements of Z, called the compressibility factor, are made at each of a series of pressures in an effort to determine B_0 andB_0. The least squares approach can be used to determine the slope (b, orB_1) and y-intercept (a, or B_0) which define the best straight line that can be drawn through the data. In simple linear regression analysis, it is assumed that all the error in the measurement lies in the dependent variable (y). This is equivalent to assuming that the precision of the determination of the independent variable (x) is considerable higher than that of y. The measured value of some quantity (y_i) will differ from the value predicted by a linear equation ($y = a + bx$) by an amount r_i called the residual.

$$r_i = y_i - a - bx \tag{9.10.11.2}$$

The least squares approach identifies the best straight line as the one for which R, the sum of the squares of the residuals, has the smallest value:

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} (y_i - a - bx_i)^2 \tag{9.10.11.3}$$

The arrows in Figure 4 represent the residuals, and all of them are equally weighted.

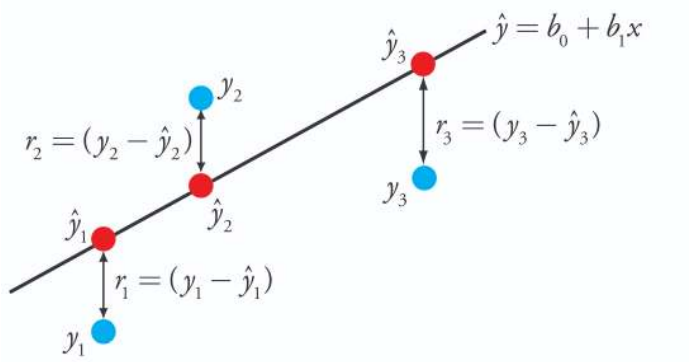


Figure **9.10.11.1**: Least Squares Linear Regression: *Illustration showing the evaluation of a linear regression in which we assume that all uncertainty is the result of indeterminate errors affecting y. The points in blue, y_i, are the original data and the points in red, $\hat{y}_i$, are the predicted values from the regression equation, $\hat{y} = b_0 + b_1 x$. The smaller the total residual error, the better the fit of the straight-line to the data* (source)

We want to minimize the sum of the squares of the residuals. That is, we want to make *least* the sum of *squares* of residuals, and, thus, the name of the procedure. Since this is a minimization problem, we require that R be as small as possible with respect to a and b by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial a}\right)_b = -2\sum(y_i - a - bx_i) = 0 \tag{9.10.11.4}$$
$$\left(\frac{\partial R}{\partial b}\right)_a = -2\sum((y_i - a - bx_i)(x_i)) = 0$$

Solving equations 9.10.11.4 simultaneously, we obtain

$$a = \frac{(\sum x_i^2)(\sum y_i) - (\sum x_i)(\sum x_i y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{9.10.11.5}$$

$$b = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{9.10.11.6}$$

While we ultimately want to fit the data to $y_i = a + bx_i$ for a series i of N points, the theoretical development is much easier if we use $y_i = c + b(x_i - \overline{x})$ where obviously a and c are related by $a = c - b\overline{x}$, and where $\overline{x}$ is simply the mean of the x data, $n\overline{x} = \sum_{i=1}^{N} x_i$. This designation of variables is better because "it turns out" that in this approach the parameters b and c are independent, their variances are independent, and the formulas to transform to the parameters a and b are simple. Again, we want to minimize the sum of the squares of the residuals $r_i = y_i - c - b(x_i - \overline{x})$, R.

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} [y_i - (c + b(x_i - \overline{x}))]^2 \tag{9.10.11.7}$$

Now we require that R be as small as possible with respect to b and c by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial c}\right)_b = -2\sum(y_i - c - b(x_i - \overline{x})) = 0 \tag{9.10.11.8}$$
$$\left(\frac{\partial R}{\partial b}\right)_c = -2\sum((y_i - c - b(x_i - \overline{x}))(x_i - \overline{x})) = 0$$

These two equations are readily rewritten as

$$\sum y_i = \sum c + \sum b(x_i - \overline{x}) \tag{9.10.11.9}$$
$$\sum y_i(x_i - \overline{x}) = \sum c(x_i - \overline{x}) + \sum b(x_i - \overline{x})^2$$

which, since $\sum(x_i - \overline{x}) = 0$, simplify to

$$c = \frac{\sum y_i}{N} = -\bar{y} \qquad (9.10.11.10)$$
$$b = \frac{\sum y_i (x_i - \bar{x})}{\sum (x_i - \bar{x})^2}$$

The knowledge of c and b then allows us to determine the parameter, a, $a = c - b\bar{x} = \bar{y} - b\bar{x}$, a particularly simple relation.

The variance and standard deviation of N data points was introduced previously. The appropriate treatment of the parameters c and b in the least squares procedure results in

$$V[c] = \frac{s^2}{N} \qquad (9.10.11.11)$$
$$V[b] = \frac{s^2}{\sum (x_i - \bar{x})^2}$$

where

$$s^2 = \frac{1}{N-2} \sum (y_i - c - b(x_i - \bar{x}))^2 \qquad (9.10.11.12)$$
$$= \frac{1}{N-2} \sum (y_i - a - bx_i)^2 = \frac{R_{min}}{N-2}$$

Because c and b are independent quantities, it can be shown that

$$V[a] = V[c] + \bar{x}^2 V[b] \qquad (9.10.11.13)$$
$$= \frac{s^2}{N} + \bar{x}^2 \frac{s^2}{\sum (x_i - \bar{x})^2}$$

The standard deviations of a and b, σ_a and σ_b, are then obtained by taking the square roots of V[a] and V[b].

Another statistic that is sometimes used is the *correlation coefficient*, r. It is given by the expression

$$r = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left(N \sum x_i^2 - (\sum x_i)^2\right)\left(N \sum y_i^2 - (\sum y_i)^2\right)}} \qquad (9.10.11.14)$$

When the absolute value of r is close to unity the correlation between the y and x data is good, when it is close to zero the correlation is poor. Because the correlation coefficient is sometimes hard to interpret, it is usually better to work with the standard deviations of the regression parameters, σ_a and σ_b.

Linear regression is a powerful tool that takes the guesswork out of obtaining best fit information. However, like all mathematical tools, it must be used with caution. While the standard deviations and the correlation coefficient give indications of the goodness of the fit, there is no substitute for graphing the data and looking at the result. Since the errors are assumed to be random, the y_i values should be scattered about the best fit straight line in a random fashion. The residuals should likewise be either positive or negative (and sum to zero) without any pattern. If the data show a pattern of curvature, it is possible that the results do not conform to the linear model proposed. A linear regression is *not* valid in this case. You should also be alert to the effects of systematic errors, which may change the slope or the intercept without affecting the linearity of the data.

Linear regression of the type discussed above relies on a number of critical assumptions. Among the most important is that all the uncertainty in each of the y values is the same. If the form of the equation required to provide a linear relationship produces an independent variable that contains a significant uncertainty, the set of conditions that produced the minimum in the residuals of the line may not be the set that actually minimizes the uncertainty in the data. In this case, a "non-linear" least squared technique such as simplex is recommended.

Note

In this course, you can use the MatLab lsq.m script to perform least squares analysis. The equations given above are included in the lsq script.

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9.10.11.1: Rejection of Discordant Data

In a set of collected data, there may be one or more values that deviate markedly from the trend of the others. You should not reject a piece of data that seems suspect until you perform a Q-test. In a set of data of three to ten measurements, the Q-test can be performed on the suspect data point:

$$Q_{exp} \equiv \frac{|\,(\text{suspected outlier's value}) - (\text{value closest to it})\,|}{(\text{highest value}) - (\text{lowest value})} \tag{9.10.11.1.1}$$

Compare the value of Q_{exp} from the equation above to the critical value of Q_r. If Q_{exp} is greater or equal to Q_r then the suspect value can be rejected. If Q_{exp} is less than Q_r,the value should be retained in the data set.

The following table provides critical values for $Q(\alpha, n)$, where α is the probability of incorrectly rejecting the suspected outlier and n is the number of samples in the data set. There are several versions of the *Q*-Test, each of which calculates a value for Q_{ij} where *i* is the number of suspected outliers on one end of the data set and *j* is the number of suspected outliers on the opposite end of the data set. The critical values for *Q* here are for a single outlier, Q_{10}, where

$$Q_{\text{exp}} = Q_{10} = \frac{|\,(\text{suspected outlier's value}) - (\text{value closest to it})\,|}{(\text{highest value}) - (\text{lowest value})}$$

The suspected outlier is rejected if Q_{exp} is greater than $Q(\alpha, n)$. For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's '*Q*' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146.

Table 9.10.11.1.1: Critical Values for Dixon's Q-Test

$\frac{\alpha\longrightarrow}{n\downarrow}$	**0.1 (90% confidence limit)**	**0.05 (95% confidence limit)**	**0.04 (96% confidence limit)**	**0.02 (98% confidence limit)**	**0.01 (99% confidence limit)**
3	0.941	0.970	0.976	0.988	0.994
4	0.765	0.829	0.846	0.889	0.926
5	0.642	0.710	0.729	0.780	0.821
6	0.560	0.625	0.644	0.698	0.740
7	0.507	0.568	0.586	0.637	0.680
8	0.468	0.526	0.543	0.590	0.634
9	0.437	0.493	0.510	0.555	0.598
10	0.412	0.466	0.483	0.527	0.568

(see also http://chem-net.blogspot.com/2013/01...atistical.html)

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9.10.11.2: Weighted Least Squares Analysis

When measurements of the dependent variable incur different uncertainties, a ***weighted*** least squares technique should be used. In this approach, each residual ri is divided by a factor proportional to its uncertainty ε_{y_i}. Then R, the sum of the squares of the residuals, becomes

$$R = \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_{y_i}^2} = \sum_{i=1}^{N} \frac{1}{\varepsilon_{y_i}^2}(y_i - a - bx_i)^2 \tag{9.10.11.2.1}$$

Using the same minimization techniques described above, the slope and intercept for weighted least squares become

$$a = \frac{\sum \frac{x_i^2}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2}\right)^2} \tag{9.10.11.2.2}$$

$$b = \frac{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2}\right)^2} \tag{9.10.11.2.3}$$

Weighted least squares has utility in a number of applications in the physical chemistry laboratory. One common situation arises when a linear equation requires the log of a measured quantity to be the dependent variable. Consider for example, the measurement of vapor pressure. Most pressure sensing devices will provide a constant error in the measurement of P. If the dependent variable to be plotted is lnP, however, its uncertainty is not constant but decreases as P increases. Thus,

$$\varepsilon_{lnP} = \frac{\partial lnP}{\partial P}\varepsilon_P = \frac{\varepsilon_P}{P} \tag{9.10.11.2.4}$$

An appropriate weighting factor in this case would be $\varepsilon_{y_i} = \frac{1}{P}$.

When you use Matlab for data analysis this semester, the command **lsq(x,y)** will be used for least squares analysis of x, y data, and the command **wtlsq(x,y)** will be used for weighted least squares analysis. In the latter case, you will be asked for a weighting factor, e. In either case, the program will output the least squares slope, y-intercept, correlation coefficient, standard deviation of the slope, and standard deviation of the intercept.

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9.10.11.3: References

1. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th Edition, McGraw-Hill, New York, NY, 1996, pp 27-89.

2. Bettelheim, F. A., Experimental Physical Chemistry, W.B. Saunders Co., Philadelphia, 1971, Chapter 2.

3. Brownlee, K. A., Statistical Theory and Methodology in Science and Engineering, 2nd Edition, John Wiley and Sons, Inc., New York, New York, 1965, pp 334-338.

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9.10.12: Homework Problems

Each practice problem below requires that you correctly apply propagation of errors to report the correct value and its precision (including the error). You should attempt all seven problems prior to our schedule lab meeting on this topic (and submit prior to the meeting on Canvas). This pre-lab assignment will prepare you to participate in the lab meeting by presenting problems on the board, answering questions from your peers, and asking your own questions.

You will submit your work and final answers after the in-lab problem session. Your answers to these problems may be hand-written or typed. However, any submissions that are deemed illegible, unclear, or poorly organized will not be accepted.

> **Note**
>
> (1) We will give you a MatLab template to get you help you in using MatLab for this problem set. However, you may use whatever technology (calculators, software, etc.) you like to aid in working these problems.
>
> (2) It is important to show how your calculations are set-up and, where appropriate, give a sample calculation. Simply giving the final answer is not acceptable.
>
> (3) In reporting all results, you should always round your reported answer to be consistent with your estimated uncertainty. For example: a calculated result of 56.2189 ± 0.0386 would be reported as **56.20 ± 0.04** where 0.04 is the standard deviation, 95% confidence level, or propagated uncertainty.

The seven problems are below. Note that there are Hints that you can click on for each problem.

PROBLEM 1: Statistics

A student makes five independent measurements of each of the linear dimensions of a box. The results are tabulated as follows:

Length (cm)	Width (cm)	Height (cm)
1.010	5.376	2.001
1.015	5.339	2.105
1.013	5.385	1.985
0.999	5.375	1.989
1.009	5.369	2.008

A. Calculate the average values of length, width, and height, and calculate the standard deviation in each of these three quantities. Report the values appropriately, considering the calcuated precision.

B. Calculate the variance of the length, width, and height.

C. Calculate the 95% confidence limits to the measurements of length, width, and height.

D. Calculate the 95% confidence limits to the average volume obtained from the independent measurements of length, width, and height.

Hint

> This problems is one where there are five replicate measurements of length, width, and height. That's enough to use some basic statistics to determine our confidence of each measurement. Normally the standard deviation is an appropriate indicator of the data's precision in a case like this where there are multiple measurements. The problem also asks for the variance and the 95% confidence limit. Be sure to report all values in the appropriate number of digits, considering the calculated precision. The equation for variance and for 95% confidence can be found in Section 3.2.

PROBLEM 2: A Simple Case for Propogation of Error

A student weighs a sample using an analytical balance that has an estimated precision of ±0.5 mg. From the data below, calculate the weight of the sample and the range of uncertainty in the net weight.

	Mass (g)
Sample + flask	5.1647 ± 0.0005
Tared flask	2.3712 ± 0.0005

Hint

This is a simple propagation of error problem – any time we add, multiply, divide, or subtract multiple measurements, the final value's error is a propagation (or a combo of) the error associated with each measurement. So, you just need to recognize this fact, and then find the appropriate equation to propagate error in the case when values are subtracted. The appropriate equation is given in Section 3.2 (also on pg 57 of Shoemaker, equation 55...but in the Shoemaker text, you'd need to take the square root of both sides of the equation).

In this case, the function (F) that determines the sample weight is $F = \text{Mass of Sample in Flask} - \text{Mass of empty flask} = x - y$

Apply Equation 3.2.7 where $a, b = 1$ (and thus can be ignored), and the uncertainty in the measurements are $\Delta x = \Delta y = 0.0005\ g$. Specifically for this case, the uncertainty is:

$$\Delta F = \sqrt{(0.0005)^2 + (0.0005)^2} \tag{9.10.12.1}$$

PROBLEM 3: Statistics and Rejection of Discordant Data

An investigator measures the photon emission in the reaction

$$Na^+ + O^- \rightarrow Na^* + O \xrightarrow{h\nu} Na + O$$

in which the emitted photon (at 589 nm) is counted by means of a photomultiplier. Here are some typical "run" data

Run #	**Signal + Background (counts/sec)**	**Background (counts/sec)**
1	1500	1000
2	1200	1250
3	1375	1100
4	1425	900
5	1280	1200
6	1490	1363

Evaluate the data using statistical methods only and calculate:

A. The average signal value.

B. The standard deviation and variance in the average signal value.

C. The 95% confidence limits to the average signal value.

D. Using the Q test, determine whether the results from any one run can be rejected as discordant data at the 90% confidence level

Hint

This is a noisy data set where the signal is just barely detectable. The problem explicitly asks for calculation of variance (variance is just the square of standard deviation), 95% confidence limit (see problem 1), and application of the Q-test to determine whether any of the data points should be rejected. The Q-test is described in Section 3.3.1.

PROBLEM 4: Least Squares Analysis and Rejection of Discordant Data

A. Fit a straight line:

$$y = a + bx$$

to the following set of data points by the linear least-squares method

x 26 30 44 50 62 68 74
y 92 85 78 81 54 51 40

and calculate the coefficients a and b using the Equations (3.4.5) and (3.4.6) from Section 3.4.

B. Plot the x,y data and the least-squares line, and submit this with your report.

C. Calculate the standard deviation of the coefficients, a and b using Equations (3.4.11), (3.4.12) and (3.4.13) from from Section 3.4 (note that the lsq script does this automatically for you, and you are welcome to use it!).

D. Calculate the correlation coefficient, using equation (3.4.14) from Section 3.4. What is the significance of the sign of r?

E. Apply the Q-test to the y-residuals (see Equation (3.4.2) from Section 3.4), to determine whether there is a statistical basis for rejection of any of the data points as an outlier, (I) at the 96% confidence level (II) at the 90% confidence level.

F. If a data point is rejected, repeat the regression analysis (steps A-D) using the remaining data.

G. Comment quantitatively on the effect of data removal on the regression analysis.

Hint

You will need to plot the x,y data and then perform a linear fit. You are explicitly instructed to determine the standard deviation of the slope and y-intercept of the least squares fit linear function. There are three ways I know to determine these values: (1) Excel, using the "LINEST" array function. (2) MatLab, using the lsq custom script or the Statistics and Machine Learning Toolkit (3) Logger pro does it automatically with linear fitting. The LSQ script is recomended.

Hints for individual parts:

- A,B) - just plot the data and best fit line and get the equation.
- C, D) use lsq (Matlab)
- E) Following the linear regression analysis, perform a Q-test at two different confidence intervals - 96% and 90%. For this, you will need the critical Q-values for these two confidence limits (see Section 3.4.1).

PROBLEM 5: Error Propagation

In a chemistry lab, students obtain the following data and are asked to find the molecular weight (M) of methanol using PV = nRT. Determine the uncertainty in the result using a propagation of error treatment.

	Pressure (methanol)	Temperature	mass (methanol)
Trial 1	72.5 ± 0.5 mmHg	295.10 ± 0.05 K	0.1331 ± 0.0002 g
Trial 2	72.0 ± 0.5 mmHg	295.05 ± 0.05 K	0.1329 ± 0.0002 g

The volume (V) in both trials was 1.05678 liter, with no uncertainty given. You must decide on the uncertainty in V. If necessary, perform appropriate conversions of the units for each quantity, including R, so that the final value of M is reported in the correct units.

Hint

This is a propagation of error problem, where we are multiplying and dividing individual measurements to find the value of interest. In this case, it is the determination of the molecular weight (which I'm going to represent as MW) of methanol from the mass of methanol, pressure, temperature, and volume measurements.

So, first…how would we do this?

$$MW = \frac{\text{mass of methanol in grams}}{\text{moles methanol}} = \frac{m}{n} \tag{9.10.12.2}$$

The mass of methanol was measured in the experiment, and the number of moles can be determined from $PV = nRT$. The calculation involves multiplication and division to determine $n = \frac{PV}{RT}$, and then involves division again to determine \ (MW=\dfrac{m}/{n}.

We can substitute into the equation for MW and get everything into one combined equation:

$$MW = \frac{m}{n} = m\frac{PV}{RT} = mRTPV \tag{9.10.12.3}$$

Once you recognize that it is simply a propagation of errors problem in which the factors are multiplied and divided, you can determine the error in the molecular weight value using Equation 3.2.8.

The errors in P, T, and m are explicitly given. The error in V is not explicitly given, but we can assume that the error is indicated in the number of digits given in the volume measurement. The volume given is 1.0567**8** liters or 1,056.7**8** mL - so we assume we are uncertain in the last digit (the 8) by roughly half a digit…. to +/- 0.00005 L or +/- 0.05 mL.

Note: Pay attention to units. Depending on which units you choose for R, unit conversion may be necessary.

PROBLEM 6: Error Propagation

The rate constant for the reaction

$$2DI \rightarrow D_2 + I_2$$

is measured at two temperatures with the given estimated uncertainties:

$k_{660} = (1.2 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $660 \pm 2K$

$k_{660} = (1.8 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $720 \pm 2K$

A. Calculate the activation energy E_{act} for the reaction using

$$ln\left(\frac{k_2}{k_1}\right) = -\frac{E_{act}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

B. Assuming the above equation is a correct expression for E_{act}, what is the uncertainty in E_{act}?

Hint

The calculation of E_{act} using the given data is relatively straightforward. The error in the value of E_{act} is a propagation of the uncertainty of the two k values and two T values. The function is complicated enough that it should be addressed using partial derivatives (Equation 3.2.6). There is no one simple shortcut in this case, but if the function is broken down into simpler functions, then error can be determined in a step-wise fashion using the shortcuts.

PROBLEM 7: Error Propagation

In the method of Clement and Desormes, the heat capacity ratio of an ideal gas is determined from the manometrically determined values of P_1, the gas pressure at temperature T_1; P_2, the gas pressure immediately after a reversible adiabatic expansion when the

temperature is T_2; and, P_3, the gas pressure after the gas has warmed back up to temperature T_1. The equation used to calculate the heat capacity ratio is

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{C_V}{R}+1}{\frac{C_V}{R}}$$

where

$$\frac{C_V}{R} = \frac{P_2\left[1-\left(\frac{P_3}{P_1}\right)\right]}{P_3-P_2}$$

Calculate the uncertainty in the heat capacity ratio γ, given the following data:
P_1 = 763.1 ± 0.2 mmHg
P_2 = 757.0 ± 0.1 mmHg
P_3 = 758.7 ± 0.2 mmHg

Hint

> This is propogation of error problem where the error in the value of γ is a propagation of the uncertainty of the three P measurements. The calcaution of γ involves a complex function for which no short cuts are available. I recomend using partial derivatives to arrive at a proper estimation of error in the heat capacity ratio. *Some students have broken the function into separate parts and used shortcuts for each, and have arrived at a reasonable estimation of error…though I find this to be more work than doing it using partial derivatives).*

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SECTION OVERVIEW

9.11: Rotation-Vibration Spectrum of HCl AND DCl; Vibrational Spectrum of SO2

Part I. The general approach to this experiment is adapted from Shoemaker, D.P., Garland, C.W. and Nibler, J.W., Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996. In preparation for this experiment please read Experiment 37 in Shoemaker, Garland and Nibler beginning on page 397. You will want to read and understand the theory section including the subsections involving selection rules and isotope effects. In addition to this information the following section on transition intensities is offered.

Part II. The general approach to this experiment is adapted from D. P. Shoemaker, C. W. Garland, and J. W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996. In preparation for this experiment please read Experiment 35 in Shoemaker, Garland and Nibler beginning on page 383. You will want to read and understand the theory section including the subsections on the valence-force model and the vibrational partition function.

9.11.1: Data Analysis

9.11.2: Prelaboratory Exercise

9.11.3: Transition Intensities

9.11.4: Part I - FTIR spectrum of a mixture of HCl and DCl gas

9.11.5: Part II - FTIR spectrum of SO2

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9.11.1: Data Analysis

Data Analysis for HCl/DCl FTIR spectra

> **Note**
>
> This is one of the more laborious data analyses you will do this semester. Let's minimize the number of repetitive tasks to save you some time. The following shortcuts are recommended:
>
> - **Collaborate with a partner on steps 1-3 (allowed in this specific case only)**:You may collaborate with your lab partners in steps 1-3 below. One student should work up the data (steps 1-3 ONLY) for $H^{35}Cl$ and $H^{37}Cl$, and the second student should do the same analysis for $D^{35}Cl$ and $D^{37}Cl$. You should then share your graphs of $\Delta\tilde{\nu}_{(m)}$ versus m and the values determined for the slopes and y-intercepts of these plots. Each student should do one complete analysis (either HCl or DCl) alone, and the other analysis can be the work of a partner. However, you are responsible for all work that is in your ELN, so be sure your partner's work is correct. *Steps 4 and onward should be completed individually, as usual.
> - **Calculate errors for one isotope only**: The propagation of errors that you calculate for one isotope should similar (perhaps not identical, but close enough) as for another isotope. Save time by propagating errors carefully for (B_e, α_e, $\tilde{\nu}_o$, Ie, re, and k for one isotope, then use those errors as an approximation for the errors for analogous values for other isotopes.
> - **Use what you know!** Do you remember that MatLab Introduction module way back in the beginning of this course? It was a long time ago, but it was a template for data analysis in this module! Go back and use what you already know, and what you already created as a template, for this data analysis.

Collaborate with a partner

1. Label each peak in your spectra as "P" or "R" and its J-value as: P(1), P(2),..., R(O), R(1),... etc., as shown in Figure 2 on page 399 of Shoemaker, Garland and Nibler. (**Note:** Spectra recorded using your iS50 FTIR spectrometer are plotted with the wavenumber (abscissa) decreasing from left to right.)
2. For each of the four isotopic combinations ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$), make a table of the m values and the corresponding peak frequencies $\tilde{\nu}_{(m)}$. For each isotopic combination, calculate the separation between adjacent peaks.

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} \tag{9.11.1.1}$$

> **Note**
>
> $\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0. Therefore m = –1 must be deleted from the vector of m values.

3. Plot the differences between adjacent absorption frequencies (i.e., $\Delta\tilde{\nu}_{(m)}$ versus m. Then perform a linear least squares fit of the data with the understanding that

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} = (2B_e - 3\alpha_e) - 2\alpha_e m \tag{9.11.1.2}$$

   Use the standard deviations of the slope and intercept in your error analysis (Q14).

Work on your own

4. **Compute B_e and α_e** for each isotope from the intercept $(2B_e - 3\alpha_e)$ and the slope $-2\alpha_e$ of each best fit line (Equation 9.11.1.2).
5. **Calculate the frequency of the forbidden transition $\tilde{\nu}_o$** using your calculated values of B_e and α_e. To do this, use equation 9 in expt 37 of Shoemaker, Garland and Nibler. The equation is $\tilde{\nu}_m = \tilde{\nu}_o + (2B_e - 2\alpha_e)m - \alpha_e m^2$. Calculate $\tilde{\nu}_o$ from several of the lines with low m values. Calculate the average value, and standard deviation, of $\tilde{\nu}_o$.

> **Note**
>
> You will get the best results by using only the lines closest to the center (e.g., m = ±1, ±2).

6. **Create a table** of $\tilde{\nu}_o$, B_e, and α_e for the four isotopic combinations The units should be cm^{-1}.
7. **Calculate the moment of inertia (I_e), and the internuclear distance (a.k.a. equilibrium bond length, r_e)** for all four isotopic combinations.
8. **Calculate the harmonic oscillator force constant, k**, for each isotopic combination from your calculated values of $\tilde{\nu}_o$. In doing so you will need to assume that $\tilde{\nu}_o$ and the harmonic oscillator frequency $\tilde{\nu}_e$ are the same, thus ignoring the effects of anharmonicity (see the formulas and discussion on pages 400 and 401 of Shoemaker, Garland and Nibbler).
9. **Compare your values of r_e and k with those reported in the literature.** Why are these values independent of isotopic substitution?
10. **Determine the isotope effects:** Compute the ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for ^{35}Cl and ^{37}Cl in the case of HCl, and again in the case of DCl. Compare these with the predicted values given by Eqs. (11) and (13) on page 400 of Shoemaker, Garland and Nibbler.
11. From the results in 10, above, **explain why is the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl?** That is, when looking at your FTIR spectrum, the ^{35}Cl/^{37}Cl line separation is significantly greater in the DCl case then when compared to the HCl case. A descriptive answer is a good start, but your experimental observations should also be supported with a calculation that justifies the experimental observation.
12. Apply the Boltzmann distribution to explain observed band intensities in terms of the populations of the ground-state levels (see the section on Transition Intensities in this manual). Again, a descriptive answer is a good start, but it should be supported with calculated results. You might create a spreadsheet to do these calculations. Does a calculation based on the Boltzmann population of rotational states match what you see experimentally in terms of which rotational lines show the greatest intensity?
13. From the mean line intensities for at least 10 features (for example five or more lines from the HCl spectrum and five or more from the DCl spectrum for a total of at least 10), determine the relative abundance of the two Cl isotopes. Estimate the weighted average atomic mass of Cl (that you might see on a periodic table for example) assuming that ^{35}Cl and ^{37}Cl have masses of 34.968 and 36.965 amu, respectively. Compare your result with the reported atomic mass of Cl.
14. For <u>one</u> isotope only, calculate the estimated uncertainty in each of the parameters determined for this experiment (B_e, α_e, $\tilde{\nu}_o$, I_e, r_e, and k). (Another table would be helpful)
15. Why is it important to purge the sample compartment of the FTIR spectrometer for both the background and sample runs? Why is it important to purge both background and sample for the same amount of time?

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9.11.2: Prelaboratory Exercise

Important note

Students in CHEM301L will only complete Part I of this module ($\mathbf{HCl/DCl}$) and its related assignments.

Students in CHEM310L will complete all of this module, including both Part I ($\mathbf{HCl/DCl}$) and part II ($\mathbf{SO_2}$).

Reading assignment

This experiment involves many calculations; advanced knowledge of what you will have to do will be very helpful. In preparation for this experiment please read Experiment 37 in Shoemaker, Garland and Nibler beginning on page 397. You will want to read and understand the theory section including the subsections involving selection rules and isotope effects. In addition to this information read this module (not that there are two parts, and what you do depends on your course number). Additional references below are strongly recommended.

- Part l. Instrumentation, *Journal of Chemical Education*, **1986,** *63* (1), A5.
- Shoemaker, D.P., Garland, C.W., and Nibler, J.W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, New York, 1996, Chapter XIV, Experiments 35 and 37.
- McQuarrie, D.A. and Simon, J.D. "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Sections 13.2-13.4, 18.4-18.5); Atkins, P., Physical Chemistry, 5th ed., sections 16.8 – 16.11; and, Silbey, R.J., Alberty, R. A.
- Bawendi, M.G., Physical Chemistry, 4th ed., Sections 13.4, 13.6 and 13.7, for a discussion of rotation-vibration spectroscopy of diatomic molecules.

Written assignment

In addition to the usual prelab work expected for all experiments in the course (Introduction and Experimental Plan), please complete the following and submit the work prior to the lab meeting.

For Part 1 (CHEM310L and 301L), show which equations you would use to find: B_e; α_e; $\tilde{\nu}_o$; k; $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$; and $\frac{B_e^*}{B_e}$

For Part 2 (CHEM310L only), show which equations you would use to determine: k_1; $\frac{k_\delta}{l^2}$; $\tilde{C}_v(vib)$

Helpful videos

These videos provide a nice introduction and demonstration of the theory and techniques you will use.

Introduction to rotovibrational spectroscopy



Filling a gas cell



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9.11.3: Transition Intensities

Transition Intensities

The intensity of a spectral line depends not only on the transition probability and the frequency ν but also on the number of molecules in the initial state. Thus for a theoretical prediction of intensities, a knowledge of the numbers of molecules in the various initial states is necessary, in addition to a knowledge of the transition probabilities. Since most infrared (IR) spectra are observed under conditions of thermal equilibrium, we need only consider the distribution of the molecules over the different quantum states in thermal equilibrium.

According to the Boltzmann equation, the number of molecules dN_E that have a classical vibrational energy between E and $E + dE$ is proportional to $e^{-\frac{E}{k_B T}} dE$, where k_B is Boltzmann's constant and T is the absolute temperature. In quantum theory, only discrete values, $E_{(\nu)}$, are possible for the vibrational energy. The number of molecules in each of the vibrational states is then proportional to the Boltzmann factor $e^{-\frac{E_{(\nu)}}{k_b T}}$. The zero-point energy can be left out, since to add this to the exponent would only result in a multiplication factor that would be the same for all the vibrational levels (including the zero level).

The thermal distribution of the rotational levels (unlike that of the vibrational levels) is not simply given by the Boltzmann factor. We must account for the fact that, according to quantum theory, each state of an atomic system with total angular momentum J consists of 2J+1 energy levels which are degenerate in the absence of an external field; that is, the state has a (2J+1)-fold degeneracy. The number of molecules N_J in the rotational level J of the lowest vibrational state at the temperature T is thus proportional to

$$N_J \propto (2J+1)\, e^{-\frac{F_{(J)} hc}{k_B T}} \tag{9.11.3.1}$$

where $F_{(J)}$ is the rotational term value (equal to $\frac{E_{(J)}}{hc}$). For sufficiently large T or small rotational constant B, the population of the J^{th} rotational level, for N molecules, is given by the following equation [see p. 125 in reference (3)]

$$N_J = N \frac{hcB}{kT} (2J+1)\, e^{-\frac{B_J (J+1) hc}{kT}} \tag{9.11.3.2}$$

Since the factor 2J+1 increases linearly with J, the number of molecules in the different rotational levels goes through a maximum before decreasing with the rotational quantum number. It can be shown[3] that this maximum lies at

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2} \tag{9.11.3.3}$$

This expression clearly shows that J_{max} increases with decreasing B and increasing T. It should be noted that the number of molecules in the lowest rotational level, J = 0, is not zero. With increasing temperature, the band extends over a wider frequency range and the intensity maxima of the two rotational branches move outward and at the same time become flatter.

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9.11.4: Part I - FTIR spectrum of a mixture of HCl and DCl gas

Note

The ELN for this entire experiment is here: ELN03_FTIR2022.docx

In preparation for this experiment, read your textbook (McQuarrie, D.A. and Simon, J.D. "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Sections 13.2-13.4, 18.4-18.5); Atkins, P., Physical Chemistry, 5th ed., sections 16.8 – 16.11; and, Silbey, R.J., Alberty, R. A. and Bawendi, M.G., Physical Chemistry, 4th ed., Sections 13.4, 13.6 and 13.7, for a discussion of rotation-vibration spectroscopy of diatomic molecules. Each pair of students may share some of the data analysis as described in Section 4.3.3.

Preparation of Gas Sample Cell

- A mixture of HCl and DCl will be introduced into an IR gas cell. Note that because natural chlorine is a mixture of two isotopes ^{35}Cl and ^{37}Cl (in a ratio of 3 to 1), this sample is a mixture of four different gases, each with a distinct spectrum.
- Hydrogen chloride and deuterium chloride are **colorless, pungent, and corrosive gases** that fume in air. Contact will cause **burns to the skin, severe burns to the eyes and burns to the respiratory system if inhaled**. A vacuum line will be used to transfer the gases from their high-pressure containers to an evacuated IR cell.
- When not in use the IR gas cell must be stored in the desiccator. The cell is constructed of a glass body with KBr windows at each end. Ensure that the salt windows are kept free of moisture at all times. Please do not touch these windows.

Vacuum-Line Start-Up

Most of the following will 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 below 30 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 and fill with liquid N_2 from the 4L dewar such that the N_2 trap is submerged in liquid N_2
10. Check the level of N_2 as the experiment progresses. Refill if necessary to ensure the trap remains cold.
11. Check to ensure the pressure at the end of the main manifold is below 30 mtorr before proceeding.

Transferring HCl and DCl to gas cell

1. Remove gas cell from the desiccator and attach to the middlemost section of the working manifold shown below in Figure 9.11.4.1.

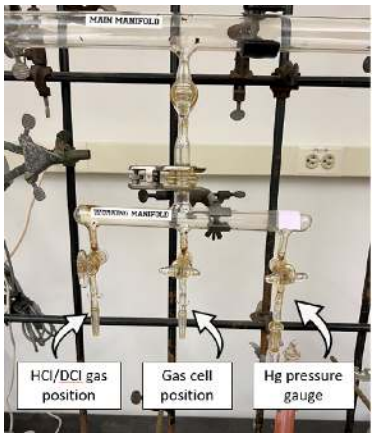


Figure **9.11.4.1**: Vacuum line set-up: working manifold and main manifold

2. Evacuate the back of the gas cell and introduce a vacuum to the interior of the cell.
3. Remove cell from manifold, bring it to the FTIR instrument, and take a background spectrum (see "Obtaining an FTIR Spectrum using the Nicolet iS50" below).
4. Replace the gas cell onto the working manifold and open it to vacuum.
5. Connect the pressurized HCl cannister to the working manifold via a vacuum-rated line. This line should contain its own needle valve that may be closed to separate the cannister from the rest of the working manifold. Introduce a vacuum to the line and to the pocket between this needle valve and the main valve on the cannister. The HCl cannister should remain closed at this time. Close the needle valve once this pocket has been evacuated.
6. Close the working manifold off from the main manifold.
7. Introduce a small amount of HCl gas to the pocket between the cannister and the needle valve by turning the cannister's main valve 180 degrees open briefly, and returning 180 degrees to close the cannister once more.
8. After ensuring the HCl cannister is closed, open the needle valve to release HCl into the working manifold. Use the mercury pressure gauge on the working manifold to monitor this process.
    - If the pressure rises such that it threatens to expel mercury from the pressure gauge, open the working manifold to the main manifold to release pressure.
9. Slowly release HCl from the working manifold using the valve to the main manifold until the pressure in the gas cell reaches 10 mmHg.
10. Close the gas cell off from the working manifold and open the working manifold to the main line to release any excess HCl from the rest of the system. (Remember to include the pocket between the needle valve and the HCl cannister!)
11. Repeat steps 5-10 using DCl gas to introduce an additional 10 mmHg DCl into the gas cell such that the final contents of the cell are 10 mmHg HCl and 10 mmHg DCl. (What pressure DCl needs to be introduced to the working manifold for this to happen? *Hint: it's not 10 mmHg.*)
12. Record HCl/DCl spectrum using "Obtaining an FTIR Spectrum using the Nicolet iS50" below.
13. Once all data has been collected, return the gas cell to the working manifold and safely evacuate all remaining HCl/DCl.
14. Close and remove the evacuated gas cell and return it to the desiccator.

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.

Obtaining an FTIR Spectrum using the Nicolet iS50

You will use a Nicolet iS50 FT-IR Fourier Transform Infrared (FTIR) Spectrometer to collect FTIR spectra. Below are instructions for its use.

1. Check the sample holder in the spectrometer to make sure there is nothing blocking the path of the infrared beam. Close the cover of the instrument.
2. The Omnic software may already be loaded. If not, load it by clicking the 

icon on the Windows desktop. As the software loads you will a blue light appear on the right side of the instrument and the main window with the menu items and button bar.



Figure 9.11.4.1: The Omnic Button Bar. (CC-NC-BY-DUKE CHEM)

Note on Collecting Data

This is a single beam instrument. You must first record a background interferogram of the evacuated gas cell. A fast Fourier transform (FFT) will then be performed to give background transmittance spectrum. You will then introduce your gas sample into the SAME gas cell and record a new interferogram. FFT analysis of this interferogram will give a single beam *transmittance* spectrum of your sample. This spectrum is then ratioed against the single beam background spectrum to give the transmittance spectrum of your sample. Finally the absorbance spectrum of your sample is calculated and displayed.

3. Open the sample compartment of the FTIR spectrometer and mount the evacuated gas cell on the gas cell holder. Close the cover and allow the sample compartment to be purged with dry, CO_2-free air for at 5 minutes, noting the time so that the purge time is reasonably accurate.
4. Check the **Experiment Setup** from the **Collect** menu. It should be set to run 8 scans at 0.125 Cm^{-1} resolution. You should be working in Absorbance format and a background scan should be "good" for 200 minutes.

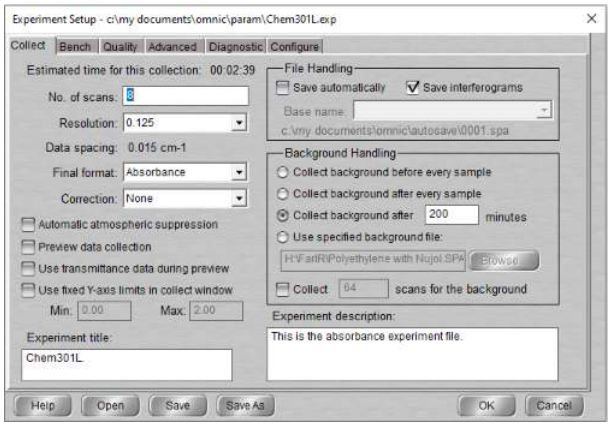


Figure 9.11.4.2: The Collect Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

Click on the **Bench** tab and wait for the interferogram to appear. The **Max** signal should be around 4.5. Click **OK**.

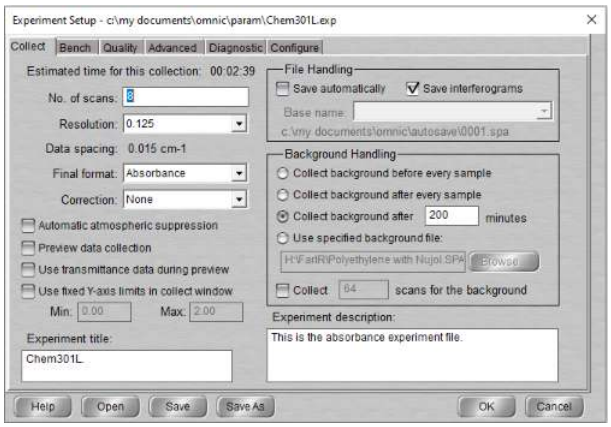


Figure **9.11.4.3**: The Bench Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

5. Select **Collect Background** from the **Collect** menu (or with the **Col Bkg** button). Click **OK** when you see the **Confirmation** box. It will take about 4 minutes for the background scan to complete. Part way through, the background scan will be displayed on the main software screen. Once complete, add the spectrum to the window when prompted. Note the presence of water vapor and CO_2 in the spectrum. This arises from the atmosphere surrounding the cell (Remember: you gas cell is evacuated at this point). Keep a copy of the background both as a file (**File → Save as**), and take a screen shot for your ELN.

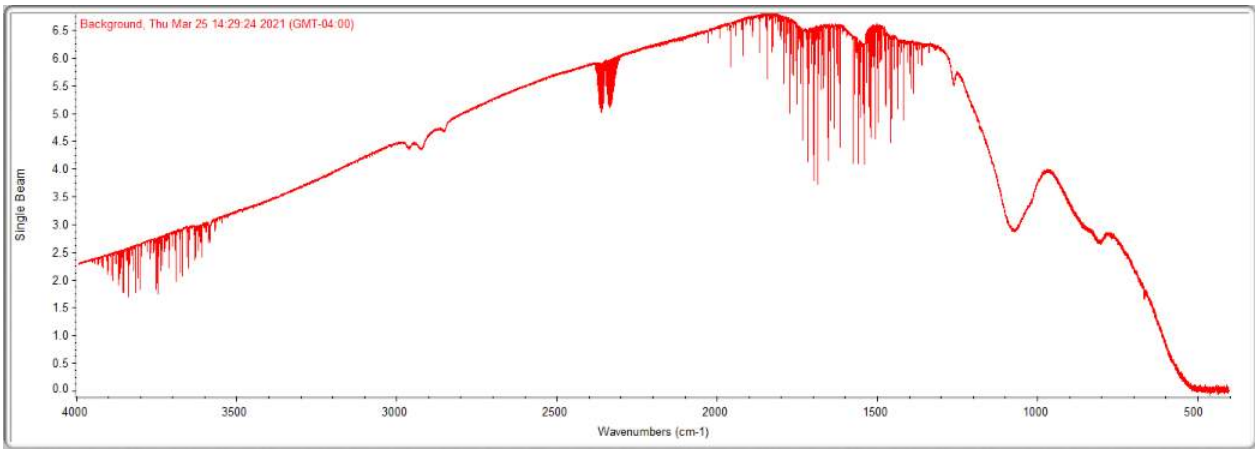


Figure **9.11.4.4**: A Typical Background Spectrum. (CC-NC-BY-DUKE CHEM)

6. Remove the evacuated gas cell from the sample compartment. Under the guidance of your TA, introduce first 1 cm Hg pressure of DCl gas followed by about 0.8 cm Hg pressure of HCl gas into the cell. You must be careful to avoid the introduction of air into the cell. Replace the gas cell on the sample holder, and close the door of the sample compartment. Allow the sample compartment to purge for the same time as in the background spectrum.
7. Select **Collect Sample** from the **Collect** menu (or use the **Col Smp** button). You can enter a title or leave the default date/time when prompted. Click **OK**, and **OK** again in the Confirmation box to start the run.
8. When the scan is complete, add the scan to the window and you will see both sample and background displayed. **Save** the data file (**File → Save as**).

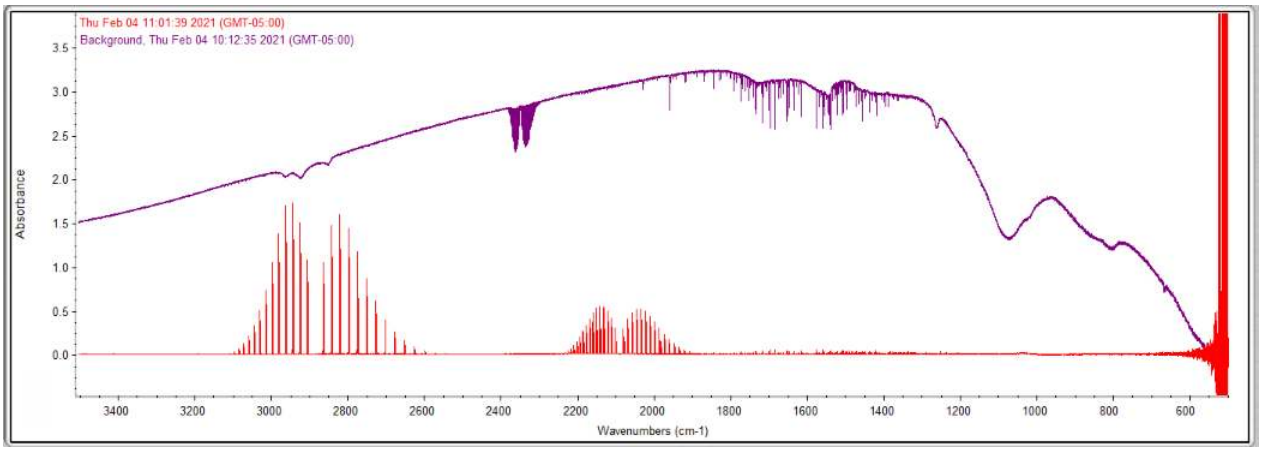


Figure **9.11.4.5**: Sample and Background Together. (CC-NC-BY-DUKE CHEM)

Click on the background scan and select **Hide Spectra** from the **View** menu to remove the background spectrum from view.

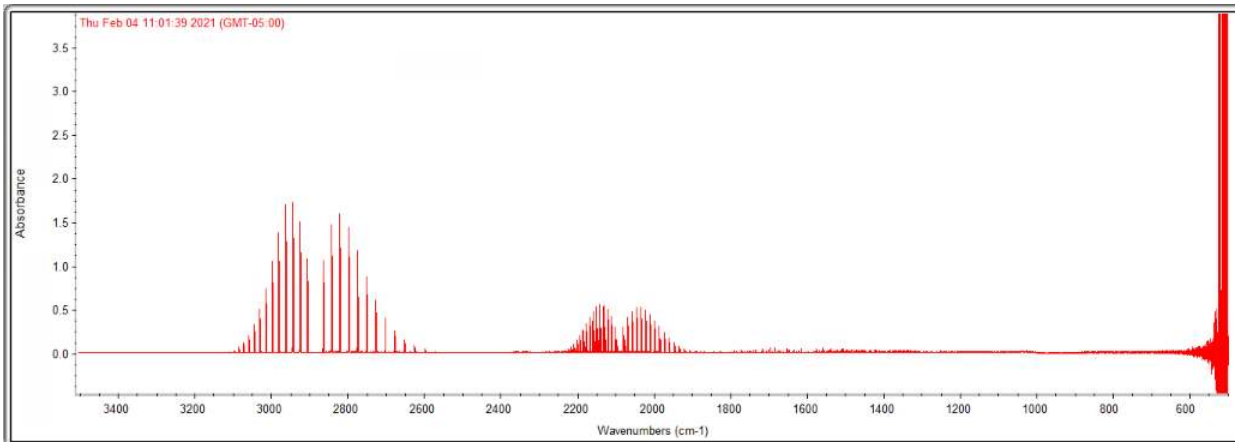


Figure **9.11.4.6**: The Sample Spectrum. (CC-NC-BY-DUKE CHEM)

9. You will see two (or three) sets of peaks in the region 3200-1800 cm–1. Which of these is the spectrum of HCl and which the spectrum of DCl? Explain your reasoning. In your report, explain the origin of the third set of peaks (if observed). Click and drag a box around the $H^{35}Cl/H^{37}Cl$ absorption and double-click in the box to expand the scale so that the spectrum of fills the screen.

10. Select **Find Peaks** from the **Analyze** menu or click the 

button. Move the horizontal threshold bar down so that it captures as many of the peaks as possible without getting into the noise at the baseline (see Figure 4.3.7 below). You can also adjust the **sensitivity** slider at the left of the screen to fine tune the peak selection. When you have a good selection of peaks, click the **Clipboard** button to put the peaks table into the Windows Clipboard. Open Excel and paste the clipboard into a spreadsheet. Save the spreadsheet along with a screenshot of the peak positions overlaid onto the speactum as seen in Figure 4.3.7.

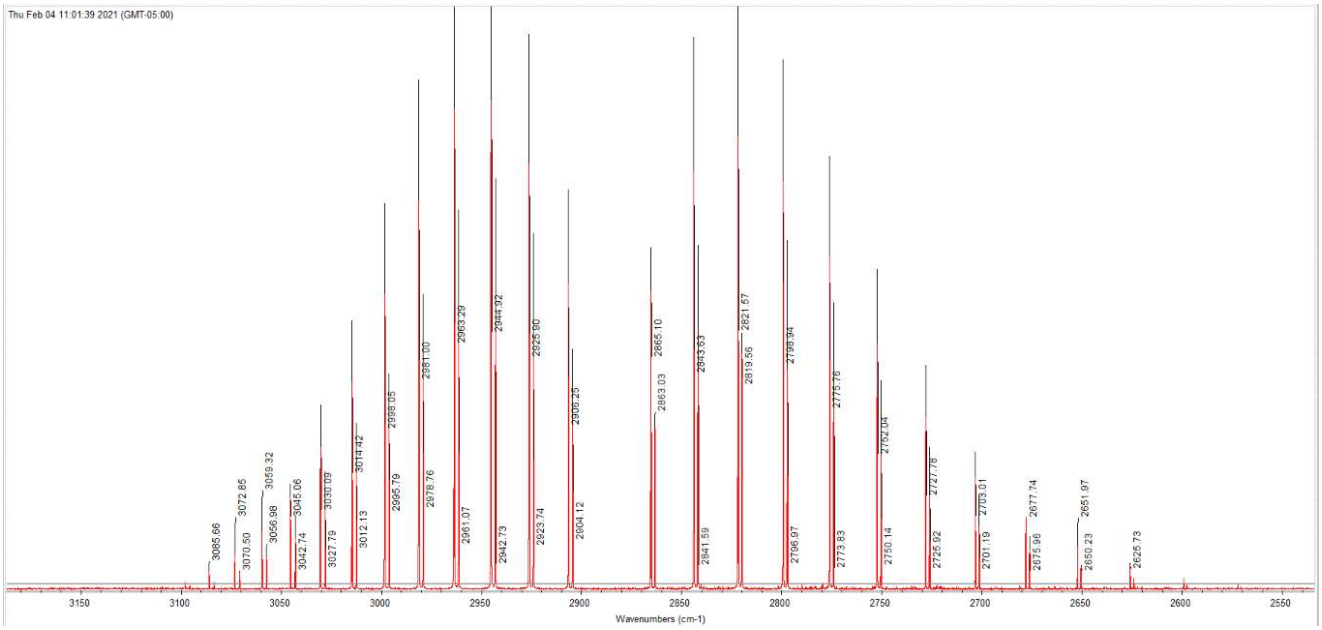


Figure **9.11.4.7**: the Find Peaks Function. (CC-NC-BY-DUKE CHEM)

11. Click Replace at the top right of the screen to bring you back to the active window. Click and drag the white selection window over to the DCl spectrum.



Figure **9.11.4.8**: The Selection Window. (CC-NC-BY-DUKE CHEM)

Re-scale the DCl spectrum in the window and repeat the peak-finding steps being sure to add the resultant peaks table to your Excel spreadsheet.

12. Save screen shots of the spectra and the report for your ELN.
13. If you wish to record the spectrum of a new sample, say of SO_2 in Part 2 of this experiment, repeat steps (4.3.2.6)-(4.3.2.12).
14. When you are done with the instrument and all of your work is saved, close the software. You will notice the blue light on the instrument turn off as the instrument goes into standby mode.
15. Remove your sample from the sample compartment and **close the cover**.
16. Re-evacuate the gas cell to remove your sample and store the evacuated cell (with stopcocks closed) in the desiccator.

Data Analysis for HCl/DCl FTIR spectra

Note

This is probably the most intense data analyses you will conduct this semester. Let's minimize the number of repetitive tasks to save you some time. The following shortcuts are recommended:

- **Collaborate with a partner on steps 1-3 (allowed in this specific case only)**:You may collaborate with your lab partners in steps 1-3 below. One student should work up the data (steps 1-3 ONLY) for $H^{35}Cl$ and $H^{37}Cl$, and the second student should do the same analysis for $D^{35}Cl$ and $D^{37}Cl$. You should then share your graphs of $\Delta\tilde{\nu}_{(m)}$ versus m and the values determined for the slopes and y-intercepts of these plots. Each student should do one complete analysis (either HCl or DCl) alone, and the other analysis can be the work of a partner. However, you are responsible for all work that is in your ELN, so be sure your partner's work is correct. *Steps 4 and onward should be completed individually, as usual.
- **Calculate errors for one isotope only**: The propagation of errors that you calculate for one isotope should similar (perhaps not identical, but close enough) as for another isotope. Save time by propagating errors carefully for (B_e, α_e, $\tilde{\nu}_o$, Ie, re, and k for one isotope, then use those errors as an approximation for the errors for analogous values for other isotopes.

- **Use what you know!** Do you remember that MatLab Introduction module way back in the beginning of this course? It was a long time ago, but it was a template for data analysis in this module! Go back and use what you already know, and what you already created as a template, for this data analysis.

Collaborate with a partner

1. Label each peak in your spectra as "P" or "R" and its J-value as: P(1), P(2),..., R(O), R(1),... etc., as shown in Figure 2 on page 399 of Shoemaker, Garland and Nibler. (**Note:** Spectra recorded using your iS50 FTIR spectrometer are plotted with the wavenumber (abscissa) decreasing from left to right.)
2. For each of the four isotopic combinations ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$), make a table of the m values and the corresponding peak frequencies $\tilde{\nu}_{(m)}$. For each isotopic combination, calculate the separation between adjacent peaks.

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} \tag{9.11.4.1}$$

> **Note**
>
> $\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0. Therefore m = –1 must be deleted from the vector of m values.

3. Plot the differences between adjacent absorption frequencies (i.e., $\Delta\tilde{\nu}_{(m)}$ versus m. Then perform a linear least squares fit of the data with the understanding that

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} = (2B_e - 3\alpha_e) - 2\alpha_e m \tag{9.11.4.2}$$

   Use the standard deviations of the slope and intercept in your error analysis (Q14).

Work on your own

4. **Compute B_e and α_e** for each isotope from the intercept $(2B_e - 3\alpha_e)$ and the slope $-2\alpha_e$ of each best fit line (Equation 9.11.4.2).
5. **Calculate the frequency of the forbidden transition $\tilde{\nu}_o$** using your calculated values of B_e and α_e. To do this, use equation 9 in expt 37 of Shoemaker, Garland and Nibler. The equation is $\tilde{\nu}_m = \tilde{\nu}_o + (2B_e - 2\alpha_e)m - \alpha_e m^2$. Calculate $\tilde{\nu}_o$ from several of the lines with low m values. Calculate the average value, and standard deviation, of $\tilde{\nu}_o$.

> **Note**
>
> You will get the best results by using only the lines closest to the center (e.g., m = ±1, ±2).

6. **Create a table** of $\tilde{\nu}_o$, B_e, and α_e for the four isotopic combinations The units should be cm^{-1}.
7. **Calculate the moment of inertia (I_e), and the internuclear distance (a.k.a. equilibrium bond length, r_e)** for all four isotopic combinations.
8. **Calculate the harmonic oscillator force constant, k**, for each isotopic combination from your calculated values of $\tilde{\nu}_o$. In doing so you will need to assume that $\tilde{\nu}_o$ and the harmonic oscillator frequency $\tilde{\nu}_e$ are the same, thus ignoring the effects of anharmonicity (see the formulas and discussion on pages 400 and 401 of Shoemaker, Garland and Nibbler).
9. **Compare your values of r_e and k with those reported in the literature.** Why are these values independent of isotopic substitution?
10. **Determine the isotope effects:** Compute the ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for ^{35}Cl and ^{37}Cl in the case of HCl, and again in the case of DCl. Compare these with the predicted values given by Eqs. (11) and (13) on page 400 of Shoemaker, Garland and Nibbler.
11. From the results in 10, above, **explain why is the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl?** That is, when looking at your FTIR spectrum, the $^{35}Cl/^{37}Cl$ line separation is significantly greater in the DCl case then when compared to the HCl case. A descriptive answer is a good start, but your experimental observations should also be supported with a calculation that justifies the experimental observation.
12. Apply the Boltzmann distribution to explain observed band intensities in terms of the populations of the ground-state levels (see section 4.2). Again, a descriptive answer is a good start, but it should be supported with calculated results. You might create a spreadsheet to do these calculations. Does a calculation based on the Boltzmann population of rotational states match what you see experimentally in terms of which rotational lines show the greatest intensity?

13. From the mean line intensities for at least 10 features (for example five or more lines from the HCl spectrum and five or more from the DCl spectrum for a total of at least 10), determine the relative abundance of the two Cl isotopes. Estimate the weighted average atomic mass of Cl (that you might see on a periodic table for example) assuming that ^{35}Cl and ^{37}Cl have masses of 34.968 and 36.956 amu, respectively. Compare your result with the reported atomic mass of Cl.
14. For one isotope only, calculate the estimated uncertainty in each of the parameters determined for this experiment (B_e, α_e, $\tilde{\nu}_o$, I_e, r_e, and k). (Another table would be helpful)
15. Why is it important to purge the sample compartment of the FTIR spectrometer for both the background and sample runs? Why is it important to purge both background and sample for the same amount of time?

References and further Reading for Part I

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9.11.5: Part II - FTIR spectrum of SO2

Reminder

The general approach to Part II of this experiment is adapted from D. P. Shoemaker, C. W. Garland, and J. W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996. In preparation for this experiment please read Experiment 35 in Shoemaker, Garland and Nibler beginning on page 383. You will want to read and understand the theory section including the subsections on the valence-force model and the vibrational partition function.

Prepare the sample of SO_2

A vacuum line will be used to evacuate the IR gas cell of HCl/DCl gas. Then transfer the toxic SO_2 gas from its high-pressure containers to the evacuated IR cell. The cell should be loaded with $\mathbf{SO_2}$ to a pressure of $\mathbf{0.5 - 1.0}$ cm Hg. Use assistance from your TA and use the protocols and precautions described earlier as a guide.

Note

You will use a pressure of SO_2 less than or equal to 1 cm Hg. If the pressure of SO_2 in the gas cell is much higher, you will not be able to observe the fine structure on the most intense fundamental frequency. If the gas pressure is too low, you may not be able to observe the weak combination bands. Depending on your skill with transferring known pressures of gases on the vacuum line, you may find it easier to record the spectrum using two different gas pressures so that all the features of the spectrum are well resolved.

Collect the FTIR spectrum of SO_2

Use the protocols and precautions described earlier as a guide.

1. Record an FTIR absorbance spectrum of $\mathbf{SO_2}$ at 0.125 cm^{-1} resolution, and under the same conditions used for the HCl/DCl sample, and ratio against the background spectrum of the evacuated cell.
2. Plot the absorbance spectrum over the range $\mathbf{4000 - 400\ cm^{-1}}$ (or a range suggested by your TA). Determine the frequency of each band seen in the spectrum. Inspect the data carefully and identify combination bands and overtone bands that are visible in the spectrum.
3. Use the Omnic **Annotation Tool** (look to the bottom of the spectrum window for the Ⓣ button) to label the center position of each fundamental band and of any overtone or combination bands you observe.
    - You use this tool by clicking on the Ⓣ button, position the cursor (now with an associated T) at the point you want to measure.
    - Then click and drag a line up (maybe up and over).
    - When you click again the wavelength at that position on the spectrum will be added as an annotation to the spectrum (see picture).
    - If you want to delete an annotation, drag a box around the annotation (the actual wavelength added to the screen) and select **Delete Annotation** from the **Edit** menu.

    Note

    Notice that in determining the frequency of vibration in you are estimating the center of the feature by eye and hand, rather than having the Omnic software determine the peak position. To get an estimate of the uncertainty of your determination, do between three and five repeated trials of estimating the frequency and find the mean and standard deviation.

    Notice also that because we are using both an instrument and a gas cell with KBr windows, we will not be able to see the bending mode clearly or completely as the KBr starts to absorb strongly in that region of the spectrum. You should, however, see enough of the bending mode to get a crude estimate of its frequency. Get help from your TA, and comment in your ELN why this frequency may show greater deviation from expected values than the others.

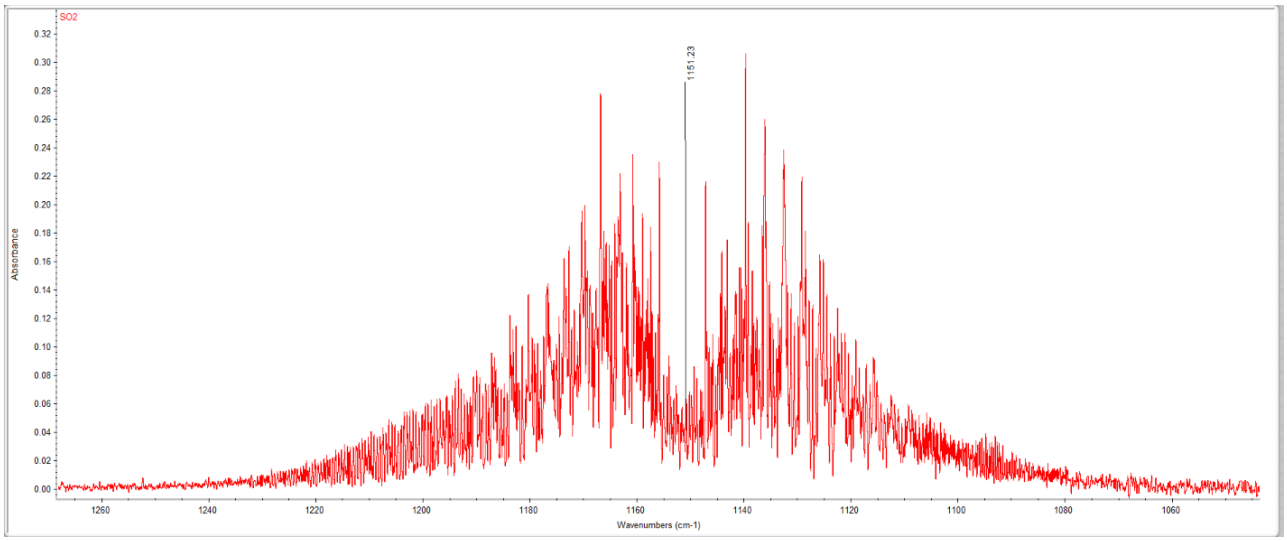


Figure **9.11.5.1**: The Symmetric Stretch of $SO_{2(g)}$. (CC-NC-BY-DUKE CHEM)

Clean up/ Shut down

Please use the vacuum line to evacuate the gas cell and store the evacuated cell in the desiccator. Please work under supervision of your instructor to shut down the gas line using the protocols and precautions described earlier as a guide.

Treatment and Analysis of Data

1. Assign the fundamental bands of SO_2 as: symmetric stretch, $\tilde{\nu}_1$; bend, $\tilde{\nu}_2$; asymmetric stretch, $\tilde{\nu}_3$; and, report their frequencies. Compare your value with those reported in the literature.
2. Then assign any other bands, comparing the observed frequencies with those calculated from combinations of the fundamental values $\tilde{\nu}_1$, $\tilde{\nu}_2$, $\tilde{\nu}_3$.
3. Calculate k_1 and $\frac{k_\delta}{l^2}$ from Equations (1) and (3) (on page 385 of Shoemaker, Garland and Nibler) using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$. Check the valence-force model by calculating both sides of Eq. (2) (also on p. 385 of Shoemaker) and comparing them. Again, compare your results with literature values.

> **Note**
>
> When finding literature values for the force constants of SO_2, you will likely notice that different notations are used. It may be difficult to find the k_1 and $\frac{k_\delta}{l^2}$ notation used in Shoemaker, Garland and Nibler (and as such in this manual). For example, Kivelson[8] reports these same vales as f_d; and, $\frac{f_a}{d^2}$ and reports the values in units of $\frac{dynes}{cm}$ rather than $\frac{N}{m}$. Be prepared to convert.

4. Using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_1$, calculate $\tilde{C}_{v(vib)}$ at 298 K and at 500 K from Eq. (8) on page 386 of Shoemaker, Garland and Nibler.
5. At these same temperatures, calculate $\tilde{C}_v$ from the expression

$$\tilde{C}_v = 3R + \tilde{C}_{v(vib)} \tag{9.11.5.1}$$

and compare your results with the following $\tilde{C}_v$ values (obtained from directly measured values of $\tilde{C}_p$ and the expression

$$\tilde{C}_v = \tilde{C}_p - R \tag{9.11.5.2}$$

$\tilde{C}_v$ = 30.5 J K^{-1} mol^{-1} at 298 K and 37.7 J K^{-1} mol^{-1} at 500 K.

6. Calculate the uncertainty of <u>each</u> result you report in this experiment.

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