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A General Chemistry Experiment to Predict and Measure Functional-Group Stretching Frequencies

Scott P. Sibley,* Esther J. Gibbs, and Pamela L. Crum

Department of Chemistry, Goucher College, Baltimore, MD 21204-2794, ssibley@goucher.edu

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Abstract: An experiment suitable for first-year students is reported. In this activity, students use a molecular modeling program to compute infrared spectra for a series of molecules. From the data obtained, students generate a group frequency chart and use it to identify unknowns. This provides students with an introduction to vibrational spectroscopy and the use of molecular modeling.

Introduction

The use of molecular modeling software to visualize molecules and to calculate molecular properties is now commonplace. Infrared and Raman spectra can also be investigated using commercial software packages. While students in first-semester chemistry commonly get exposure to UV/visible spectrophotometry, it is much less common for them to obtain and analyze IR spectra. In this laboratory, students investigate the absorption of electromagnetic radiation (EMR) in the infrared region of the spectrum. CAChe [1] molecular modeling software from Fujitsu is used to draw molecules containing various functional groups and to predict their IR spectra. Students then derive a correlation table from their computed results.

After obtaining an experimental spectrum of an unknown, students identify the unknown from five choices, based on the functional group stretches observed. This laboratory allows students to understand the relationship between an absorption spectrum and the types of atoms and bonds in a molecule.

Student Prelaboratory Preparation and Background

This activity can be implemented as a one-week or two-week laboratory experiment. At Goucher, students have performed an earlier activity on molecular structures and on the use of the molecular modeling program CAChe to draw molecules and calculate minimum-energy structures. A copy of this laboratory exercise is available. They have also done an experiment using UV/visible spectroscopy and absorption of electromagnetic radiation. As a result of this student background, this exercise can be done in a single three-hour laboratory period.

This laboratory experiment is used with little or no prelaboratory lecture. Students are expected to have read the experiment before arriving in the laboratory. For this experiment, the reading gives students a refresher on absorption of light, energy–wavelength relationships, transitions, and the regions of the electromagnetic spectrum. In addition, it is possible to have students use commercial software (IR Tutor) in conjunction with this exercise to provide more background information on IR spectroscopy.

Students are introduced to the concept of using infrared (IR) spectroscopy to learn about the structure of molecules. Use is made of the fact that atoms bonded together move relative to each other, vibrating like balls bound together by springs. The vibrations of the bonds can be increased by absorption of EMR of the appropriate energy. Both stretching and bending motions are introduced, using CO_2 and its motions as examples. In drawings presented to the students, springs are used to represent bonds, and motions are shown using arrows. Given the symmetric stretch and a bend for CO_2, students are asked to come up with another possible motion. The asymmetric stretch is often identified.

Functional groups have been introduced in previous weeks, and these are at the heart of the experiment. Different combinations of bonded atoms (e.g., $-OH$, $-NH_2$, etc.) or types of chemical bonds (e.g. C–C, C=C) in a molecule absorb different wavelengths of IR light. Light of only the proper wavelength is absorbed. Because of this, IR spectroscopy can be used to identify the presence of a given type of chemical bond in molecules. This laboratory focuses on the group frequency region, because the fingerprint region involves complex combinations of stretches and bends. In order to give students more background on IR vibrations, the instructor can give more information on vibrational energies. The energy for exciting a vibration for two bonded atoms in a diatomic molecule is approximated by $E = (h/2\pi)\sqrt{k/\mu}$, where k is the force constant (related to the strength of the bond) and μ is the effective mass, given by $m_1 m_2/(m_1 + m_2)$, where m_1 and m_2 are the masses of the atoms. This information can be used to help students discuss the different frequencies that they observe in the laboratory.

Experimental

Part 1: Computation. In this exercise, students work in groups of two or three for one laboratory period. The group first uses the CAChe computer modeling software to draw and save the molecule 2-butanone. Students are provided with condensed molecular structures for all molecules to be drawn, though they could be assigned to use internet resources to look up the structures. After obtaining the energy-minimized structure, students then calculate IR transitions for 2-butanone using the MOPAC PM3/CI FORCE semi empirical computational routine, which was found to give better results than the faster molecular mechanics methods. Density

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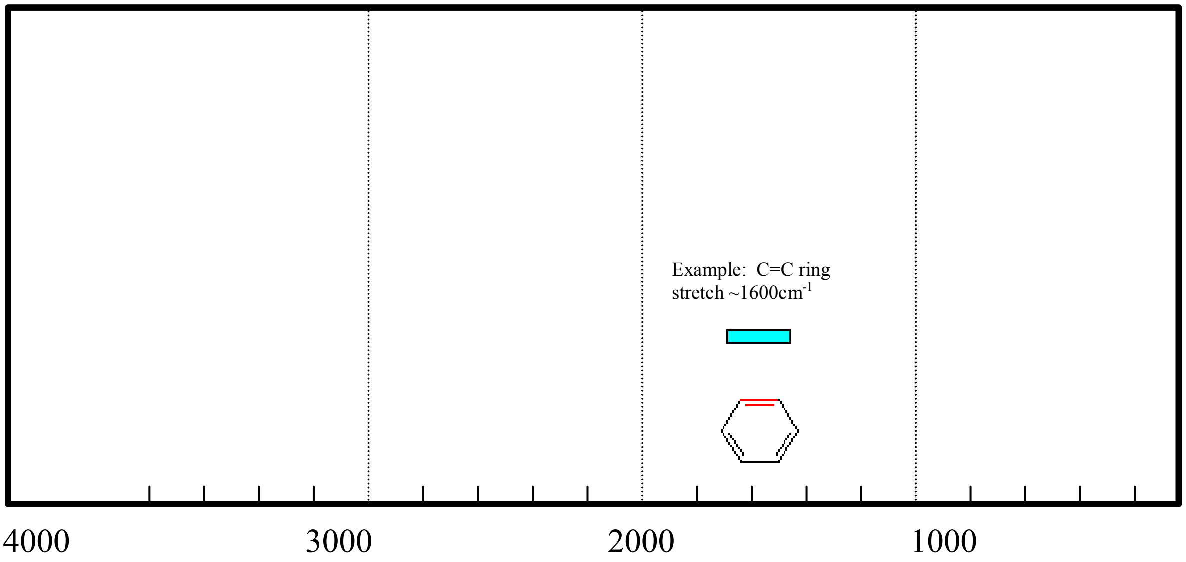

Figure 1. Template for student group frequency correlation chart.

functional methods could be used, though the calculations were found to take substantially longer time using them. The computation time and the complexity of the spectrum are related to the size of the molecule, thus small molecules were chosen for this experiment. After obtaining the predicted infrared absorption spectrum, students display both the molecule and the spectrum on the screen using the windows "tile" function. When a particular transition is selected on the spectrum, the atomic motions giving rise to that transition are shown. It may be helpful and sometimes necessary to rotate the molecule to clearly see the direction of the arrow(s). If students have difficulty seeing the arrows, it can be helpful to switch from a ball-and-stick to a line drawing. For 2-butanone, students quickly identify the C–H stretching region at approximately 3000cm^{-1} and the carbonyl stretch which is seen here at ~1900cm^{-1}. The frequencies calculated by computational methods are typically a bit higher than experimental values, and it is common to use a scaling factor to bring the calculated values into better agreement with experimental data [2]. In this experiment, the predicted frequencies are also a bit high, and students are informed that their calculated values are typically up to 200cm^{-1} high; however, the functional groups chosen for this experiment have vibrational frequencies that are sufficiently different such that analysis is relatively straightforward even for beginning chemistry students without the need for the complication of scaling factors. If the instructor wishes, students can multiply their calculated values by approximately 0.92 to get better agreement with experiment for this exercise.

Peak intensities are also predicted, and these can be recorded in the laboratory notebook. Intensities are not necessary for identification of the unknowns, though they can be useful. Students observe that most calculated transitions below 1500cm^{-1} are due to combinations, so they include only stretches at energies higher than this in their chart. The students are encouraged, however, to explore the motions corresponding to peaks in the fingerprint region.

Noting the frequencies, students begin to generate a correlation table. They are given the C=C stretch (listed as approximately 1600 cm^{-1}) already on the table as an example. After entering the region for the C=O and C–H stretch for 2-butanone, students perform the same calculation for butyronitrile and methanol. The students again see the C–H stretch at 3000cm^{-1} as well as the C≡N and O–H stretches, respectively.

The finished chart should include stretches for C=O, O–H, C–H, C≡N, and C=C. This "correlation chart" generated by the students is then used to identify the functional groups in unknowns from the IR spectra they measure experimentally (Figure 1).

Part 1: Unknowns. Safety: before arriving to laboratory, students should look up appropriate material safety data sheets for safety concerns related to the unknowns toluene, butyraldehyde, hexane, acetonitrile, and ethanol that are used in the experiment**.** If students are to prepare samples, they must wear goggles and aprons and handle chemicals with gloves in a hood, following appropriate safety procedures.

Other molecules, such as butane, isopropanol, malononitrile, o-xylene, or others, could also be used as unknowns, taking into account any safety concerns. It is important for the instructor to run calculations on all molecules before using them, to make sure that the predicted spectra will match satisfactorily with experimental results. Student groups should be given more than one unknown. Students can obtain the actual IR spectrum with help from the instructor, using an FTIR spectrometer. Because all of the unknowns for this laboratory are liquids, spectra can be conveniently obtained by placing a drop between sodium chloride plates. If a spectrometer is unavailable, *or to ensure complete safety*, students can search for spectra online or can use collected volumes of spectra. It should be noted that CAChe predicts gas-phase spectra. For alcohols, the experimental O–H frequency is substantially lower than predicted, due to hydrogen bonding in the liquid phase. This can be a starting point for discussion, if the students have been exposed to the concepts of intermolecular forces. Alternatively, to give improved agreement with calculated O–H frequencies, a spectrum of the vapor can be simply obtained by using an IR gas cell. Based on the spectra obtained and the correlation chart made previously, students choose from a list which molecules they think the unknowns are, explaining their

Table 1. Comparison of Approximate Calculated and Experimental Values

Vibration	Calculated Energy (cm^{-1})	Vibration	Experimental Energy (cm^{-1})
C–H (e.g. butanone)	3090	C–H	~3000
C=O (butanone)	1900	C=O (butyraldehyde)	1730
C≡N (butyronitrile)	2290	C≡N (acetonitrile)	2250
O–H (methanol)	3880	O–H (ethanol, gas)	3600
C=C (toluene)	1600 (given)	C=C (toluene)	1605

reasoning in detail. While identification of most of the unknowns relies on a characteristic stretching peak other than C-H stretches, hexane is identified by the absence of other high-energy features. If students are unsure, they can run a calculation on their unknown molecules using CAChe to get predicted spectra and compare them to the actual experimental data.

Because the peak energies are very different for different functional groups, students in general have had little trouble identifying most or all of the unknowns. Comparison of approximate calculated and experimental values is shown in Table 1.

Additional Concepts

Aside from identification of the unknowns, the experiment provides opportunity to explore related concepts. For example, students are asked to decide which occur at higher energy, stretches or bending motions. Also, the effect of bond strength on frequency is noted. Peaks for C–C stretches occur below 1200 cm^{-1}, while C=C stretches occur at higher energy. Using CAChe, students draw the molecule ethene and minimize the structure. They measure the C=C distance, and then do the same for the C–C bond in ethane. Students are asked to comment on the correlation of bond length to the energy of the vibrations. Finally, this is the first experience that most general chemistry students have had using the units of wavenumbers. Converting between various units and comparing IR energies to those seen in previous UV/visible experiments allows students to become more familiar with the magnitudes of energies for transitions. Students are asked to calculate the energy in joules (J) for the carbonyl bond-stretching transition and compare this value to the energy of blue light, which is used for electronic transitions.

Summary

Infrared absorption spectra are calculated for a series of small molecules containing various functional groups, using the CAChe software package. After generating a correlation chart students use the information about functional group stretches to identify unknown molecules. The activity provides exposure to computational methods, and provides an effective way to introduce the concepts of infrared spectroscopy at the introductory level.

Instructor Notes. It is important that students are given explicit instructions for use of the molecular modeling program. This experiment was performed using CAChe Worksystem version 4.4. Later versions may require slight adjustments of the instructions. Before running the IR spectral calculation, students should make sure to get the approximate molecular geometry for the molecule using the “beautify” function, and should save the molecule to the hard drive (not to the floppy drive). For the laboratory work to work as desired on our computers, the calculation settings were modified. If desired, this can be saved as a new procedure, such as CACHE LAB, that will be visible in the pull-down window. When modifying the procedure steps, both the operations, MOPAC-PM3_CIGND_GeoPRE and MOPAC-PM3_CIGND_Force should be modified. For MOPAC-PM3_CIGND_GeoPRE, the optimizations tab should have “Cartesian coordinates” and “maintain coordinates” selected, and the properties tab should have keyword GEO-OK. For MOPAC-PM3_CIGND_Force the properties tab should have LET typed in as a keyword, and “Cartesian coordinates” should be selected. These settings were found to work reliably.

Another common problem encountered when doing the experiment is that students close the Calculation Manager (CalcMgr) window, which is necessary for CAChe to run properly. If this window is closed, an error message will be given when trying to run the calculation, saying that the server is disconnected in which case the program must be restarted.

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Supporting Materials. The laboratory handouts for students on the Introduction to Molecular Modeling and the Introduction to Infrared (IR) Spectroscopy laboratory are available in the one compressed ZIP file (s00897020576b.zip) available at http://dx.doi.org/10.1007/s00897020576b.

References and Notes

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