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ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · JULY 2004

Impact Factor: 1.11 · DOI: 10.1021/ed081p1196

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Modeling Stretching Modes of Common Organic Molecules with the Quantum Mechanical Harmonic Oscillator

An Undergraduate Vibrational Spectroscopy Laboratory Exercise



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Over the past few decades, techniques and theories for understanding chemical phenomena have become more and more focused on molecular-scale phenomena. As a result, undergraduate physical chemistry curricula must change to recognize the need for basic coverage of quantum mechanics, bonding theory, and spectroscopy. At the second-year undergraduate level, physical chemistry material must often be presented at a conceptual or semiquantitative level to non-physical chemistry majors, such that students with limited mathematical background are able to learn about the significance of key areas such as quantum mechanics in chemistry. In this context, there is a need for practical, lab-based exercises that illustrate the principles associated with these areas without the use of complex and expensive equipment.

We have developed an introductory undergraduate physical organic chemistry exercise that introduces the harmonic oscillator's use in vibrational spectroscopy. The original idea is based on a simple demonstration of the influence of reduced mass and bond order on the observed wavenumber for various bond stretching modes (1). The exercise has run successfully for several years in our second-year undergraduate physical chemistry course. Students have obtained consistently excellent results and have been impressed with the way in which a series of seemingly disparate observations can be accounted for with a very simple model having only one adjustable parameter. With a refined value for the effective single-bond force constant, most stretching mode wavenumber values can be estimated to within about $\pm 10\%$ with a simple calculation. It is clearly demonstrated that the reason the stretching modes (and other vibrational modes by inference) appear at different wavenumber values within the IR spectral range is principally the result of variations in the mass of the nuclei involved in the motion, and variations in the force constant, as reflected through the bond order.

We have found that students are unfamiliar with the concept of modeling and model construction, which often forms the basis for the first steps in developing a full scientific theory. One of the significant pedagogical strengths of this exercise is therefore the introduction to the idea of the modeling of physical and chemical phenomena. Basic modeling concepts such as model design, implementation, and refinement are reinforced in this exercise.

Procedures

IR Spectra

Students develop a simple model for the prediction of the wavenumbers of the infrared absorptions associated with the vibrational stretching modes of single, double, and triple bonds from covalently bound molecules composed of C, H,

O, and N (CHON molecules). Spectroscopic data are obtained by running IR spectra of a selection of commonly available organic liquids (acetone, acetonitrile, butanamine, cyclohexene, and propanol) chosen for their low cost, relatively simple spectra, and variety in terms of types of stretching modes present. Samples are prepared by placing a few drops of the neat liquid on a NaCl plate (25-mm diameter \times 4-mm thick). A second plate is placed on top of the first to generate a thin layer of the neat liquid between the two plates. The IR spectrum of each sample is recorded using a standard FTIR spectrometer at 4-cm^{-1} resolution.

Students are asked to identify the absorptions associated with each type of stretching mode with reference to a table of vibrational group frequencies found in most books on qualitative spectroscopy (1, 2). The chosen molecules ensure that students will have data available for the following stretching modes: C–H (sp^2 and sp^3), C=C, O–H, N–H, $\text{C}\equiv\text{N}$, C=O, and C–O. Students are asked to determine which modes should be present, given the particular functional groups present.¹ Where more than one absorption is associated with stretching modes due to coupled pairs or higher-order sets of essentially equivalent bonds, students are instructed to record the average wavenumber value for the set. Once identified in the spectra, the wavenumber of each absorption peak is determined and the full spectrum printed with the wavenumber markers present.

Analysis and Modeling

The analysis and modeling exercise begins with the student calculating the force constant that would be predicted by the quantum-mechanical harmonic oscillator (QMHO) model. Each stretching vibration in the molecule is assumed to be associated with a diatomic molecule composed of the two atoms that are involved in the stretching mode in question. Using the reduced mass of the appropriate model diatomic molecule and the observed vibrational mode wavenumber for the mode in question, the force constant is determined using,

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (1)$$

where c is the speed of light in cm s^{-1} , k is the force constant in N m^{-1} , and μ is the reduced mass of a single molecule in kg. Students are then asked to assume a linear relationship between bond order and force constant and to convert all effective force constants into effective single-bond force constants, dividing by two all the calculated force constants for stretching modes involving double bonds and by three those

for triple bonds. Using these values as a guide, students estimate a trial value for k_{eff} , the effective single-bond force constant for a typical CHON molecule. Students are told that the value they choose should be of the order of 10^2 N m^{-1} .

The effective single-bond force constant is then used in conjunction with the following equation,

$$\bar{\nu}_{\text{pred}} = \frac{1}{2\pi c} \sqrt{\frac{\alpha k_{\text{eff}}}{\mu}} \quad (2)$$

where α is the order of the bond in question, to generate predicted vibrational wavenumbers for all the observed modes for which data have been recorded. This is done by inputting the values of α , k_{eff} , and μ for the pseudodiatomic molecule representing the stretching mode in question, and calculating a predicted wavenumber, $\bar{\nu}_{\text{pred}}$. A plot of $\bar{\nu}_{\text{pred}}$ versus $\bar{\nu}_{\text{obs}}$ is then generated and linear regression is performed.

To introduce the idea of model refinement, students adjust the value of k_{eff} , either by trial-and-error, by averaging the effective single-bond force constants from their data set, or by making direct use of the value of the regression line's slope. The slope of the regression line will have a value of 1.00 with the best value of k_{eff} . Therefore, students may use the closeness of their slope to this ideal value as their optimization criterion. Such optimization of k_{eff} ultimately results in determination of the best effective single-bond force constant, k_{opt} , for the model with the data set used.² As a test application of their model, students are asked to conclude the exercise by using the model to predict the wavenumber position of the absorptions expected for the stretching modes associated with several other types of functional groups, some of which belong to molecules not in the CHON family.

Discussion and Results

Through this exercise, students learn that the major causes for the variation in the position of IR spectroscopic absorptions due to stretching modes are (i) changes in the mass of the nuclei involved in the vibration and (ii) changes in the order of the bond involved. Students also learn how to apply spreadsheets to repetitive calculations and are introduced to the basic ideas behind development of a simple model. Students learn how to record infrared spectra of simple organic liquids as thin films. The equation for the QMHO is introduced, along with the idea of the crude relationship between the force constant and bond order. The idea that different vibrational modes for polyatomic molecules have categorical distinctions is reinforced.

The experiment helps students learn about the concept of modeling through direct, hands-on use and optimization of a simple model. Student manipulation of the oscillator mass and force constant of a molecule effectively teaches and reinforces the importance of these properties in vibrational spectroscopy. Through prediction and comparison of the wavenumber position of various types of stretching vibrational modes, students appreciate the limitations of this model.

Figure 1 gives typical student data demonstrating the relationship between the wavenumber calculated using the

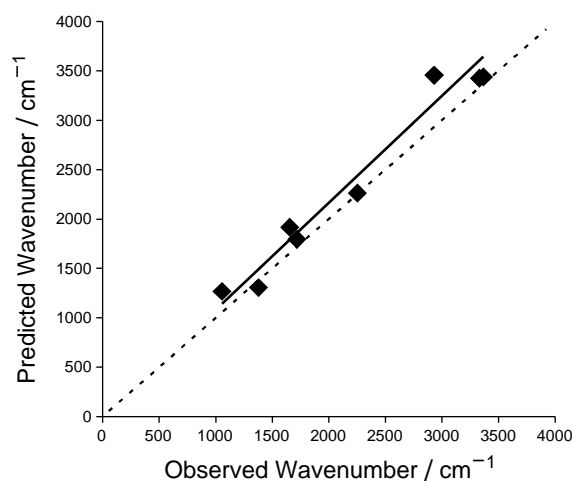


Figure 1. Plot of calculated ($k_{\text{eff}} = 650 \text{ N m}^{-1}$) versus observed wavenumber for typical student data, with regression line. Dotted line represents ideal case.

Table 1. Typical Results for Stretching Mode Absorption Predictions for Normal Modes Associated with Functional Groups Not Included in the Experimental Data Set

| Mode | Observed Wavenumber/ cm^{-1} | Bond Order | Predicted Wavenumber/ cm^{-1} (% error) ^a |
|--------------------------------|--|------------|--|
| $\text{R}_2\text{C}=\text{S}$ | 1200 | 2 | 1471 (22%) |
| $\text{R}_2\text{C}=\text{NR}$ | 1660 | 2 | 1709 (3.0%) |
| $\text{R}_3\text{P}=\text{O}$ | 1150 | 2 | 1337 (16%) |
| $\text{R}_2\text{S}=\text{O}$ | 1050 | 2 | 1330 (27%) |
| $\text{RN}=\text{O}$ | 1550 | 2 | 1590 (2.6%) |
| $\text{RS}-\text{H}$ | 2565 | 1 | 3119 (22%) |
| $\text{R}_3\text{Si}-\text{H}$ | 2200 | 1 | 3126 (42%) |
| $\text{R}_3\text{C}-\text{F}$ | 1000 | 1 | 1133 (13%) |
| $\text{R}_3\text{C}-\text{Cl}$ | 700 | 1 | 1026 (47%) |
| $\text{R}_3\text{C}-\text{Br}$ | 550 | 1 | 951 (73%) |

^aWavenumber predicted using $k_{\text{opt}} = 556 \text{ N m}^{-1}$.

model ($k_{\text{eff}} = 650 \text{ N m}^{-1}$, arbitrary initial guess) with respect to the experimental stretching mode absorption wavenumber. The solid line is the linear regression fit, for which the slope is 1.0813 and the correlation coefficient $R^2 = 0.9541$, with the regression line restricted to pass through the origin. When fully optimized, the model yields a slope of 1.00, representing a 1:1 relationship between predicted and observed wavenumber, on average. Typical regression coefficients are $R^2 > 0.9$ when no gross errors are present.

An optimization procedure exploiting the slope of the regression line is outlined in the Supplemental Material,^W and generates a value of $k_{\text{opt}} = 556 \text{ N m}^{-1}$ using the same data as in Figure 1. Typical student predictions for various stretching vibrational mode types using k_{opt} are given in Table 1, with the corresponding group frequency values given.

Equipment and Chemicals

- Students require a standard FTIR spectrometer with NaCl plates and holder for thin film samples.
- A standard fume hood may be needed for sample preparation.
- Disposable pipets may be used for sample preparation.
- Plates may be cleaned with lint-free disposable tissues.
- Approximately one milliliter of each of acetone, acetonitrile, butanamine, cyclohexene, and propanol is required per student.

Hazards

Owing to the small volume and relatively innocuous nature of the chemicals used, there are no significant hazards in this experiment, beyond those that are typically encountered in the manipulation of small volumes of organic solvents.

^WSupplemental Material

Instructions for the students and detailed notes for the instructor are available in this issue of *JCE Online*.

Notes

1. This part of the exercise offers a useful reinforcement of qualitative spectroscopic principles that may have already been covered in an organic chemistry course.

2. Methods for optimization are presented in the Supplemental Materials.^W

Literature Cited

1. Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. *Introduction to Spectroscopy: A Guide for Students of Organic Chemistry*; Saunders: Philadelphia, 1979; p 21.
2. See for example Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991.