1 / VOL. 1, NO. 6
THE CHEMICAL EDUCATOR
© 1996 SPRINGER-VERLAG NEW YORK, INC.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
10.1007/s00897970069a

Laboratories and Demonstrations

Vibrational Spectroscopy: An Integrated Experiment

B. A. DEGRAFF*, T. C. DEVORE, and **DEBORAH SAUDER**[1]
Department of Chemistry
James Madison University
Harrisonburg, VA. 22807
[1] Department of Chemistry and Physics
Hood College, Frederick, MD 21701
degrafba@jmu.edu

An integrated experiment on vibrational spectroscopy is presented. The experiment utilizes the ir and Raman spectra of a series of halomethanes to illustrate a number of techniques and concepts. Application of symmetry concepts, the uncoupled oscillator approximation, and molecular modeling are all employed to interpret the experimental data obtained. The experiment uses readily available apparatus and commercial software. Details for the assembly of a low cost Raman spectrometer are also provided.

It is now possible to provide an integrated experiment spanning a number of concepts and techniques…

Introduction

Vibrational spectroscopy has been presented in the undergraduate physical chemistry laboratory for several decades. Infrared (IR) laboratory experiments that explore some

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

aspects of the spectra of diatomic molecules [1–10], triatomic molecules [11–22], and larger molecules [23–30] appear regularly in the literature. Raman experiments have appeared far less frequently [31–41]. With the development of lasers and improved detection technologies, interest in, and applications of, Raman spectroscopy have exploded. In addition to its traditional use for structure elucidation, Raman spectroscopy is now the technique of choice for many remote sensing and time-resolved applications [42]. However, the conventional wisdom is that the expense associated with research-grade Raman spectrometers makes this experiment too expensive for the undergraduate teaching laboratory. As demonstrated by recent articles, however, simple Raman experiments are now accessible at modest cost.

Symmetry combined with group theory forms a powerful technique for qualitatively predicting the spectral activity of the normal modes of vibration. Although projection operators can be used to generate representations of the atomic motion [43], it is often difficult for students to visualize the relative atomic motions. Modern molecular modeling software can help. Several software packages include vibrational calculation routines, and presentation software that dramatically animates the normal modes of vibration. Combining these techniques with standard IR and Raman experiments can greatly increase student understanding of the normal modes of vibration.

This experiment combines symmetry and group theory, molecular modeling, and group frequencies (uncoupled oscillator model) with modern infrared and Raman spectroscopy to investigate the vibrational spectra of a series of halomethanes. The student is introduced to the basics of vibrational spectroscopy through software animation. This allows visualization of normal modes, degeneracy, stretches and bends, and dipole moment changes. Actual IR and Raman spectra of the series are then obtained. Students quickly note that not all frequencies appear in both types of spectra. At this point they use symmetry and group theory to predict the number of normal modes expected to appear in the IR and Raman spectrum of each molecule. Molecular modeling, using varying levels of sophistication, is then used to predict the spectrum of each molecule. This gives the student a chance to discover the strengths (and some of the pitfalls) of each of these methods. The software also allows visualization of the atomic vibrations. Finally, students compare the predicted and measured frequencies and also explore a simple application of the uncoupled oscillator model to understand the basis of group frequencies which they have seen previously in organic laboratory. This experiment

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

should be equally useful in a traditional physical chemistry laboratory course, an upper level integrated laboratory, or even in an instrumental analysis course.

Prelab Exercises

To assist in visualizing vibrations more complex than those encountered with diatomics, students work through an exercise based on a simple and inexpensive software package, Vibrational Modes.[1] This program can provide an excellent, although limited, animated introduction to vibrational spectroscopy for students at almost any level. It allows the student to observe the vibrational modes for a fixed number of "triatomic" (*vide infra*) molecules. The user can assign any number of quanta to one or more of the normal modes of vibration and create an on-screen trace of the atomic motions that result. The program easily provides for isotopic substitution and clearly shows the effects of deuterium-for-hydrogen exchange on both the frequency and the extent of motion. It is also simple to change the equilibrium bond lengths and/or bond angles, and to include zero-point motion. The program will list the frequencies and the force constants for any molecule in its files.

Vibrational Modes is user-friendly and self-explanatory. Its chief limitations are that it contains only triatomic species (CH_3CH_2I is treated as triatomic) and it considers only harmonic forces. The program is *not* set up as a tutorial and it will require a set of instructor-generated questions for the student to "get the point" [44]. It is, however, an excellent resource for introducing normal modes, degeneracy, and visualizing stretches and bends, and understanding vibrational dipole-moment changes.

Acquisition of Spectra

Materials

The usual series consists of CCl_4, $CHCl_3$, $CDCl_3$, $CFCl_3$, CH_2Cl_2, and CD_2Cl_2. All are commercially available in high-purity form. *Caution: These compounds should be handled with adequate protection and ventilation.* For the Raman spectra, the liquids are transferred to 5-mm NMR tubes, degassed, and the tube sealed. Samples prepared in this fashion will last indefinitely. For the IR spectra, a 10-cm gas-phase cell is filled with

---

[1] Vibrational Modes is available (Mac OS®) from Physics Academic Software. ISBN: 1-56396-087-7. URL: http://pinet.aip.org/pas/vibmode.html.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

vapor using a simple vacuum line. Both the Raman and IR spectra can be obtained in a three-hour laboratory period.

Infrared Spectra

Virtually any working infrared instrument will do, including older dispersive units. No resolution of rotational structure is involved and most bands are easily seen. We have used both a Nicolet Magna 750 FTIR and a Midac M2000 with similar results. Typical spectra were obtained from 4000 to 400 cm^{-1} with 1-cm^{-1} or 4-cm^{-1} resolution respectively. The sample pressure in the cell was adjusted by trial and error. The intensity of the weaker bands may be enhanced by increasing the pressure of the sample in the cell.

Raman Spectroscopy

All the components of our setup, except our sample holder, are commercially available. A block diagram for our apparatus is shown in Figure 1. We have obtained Raman spectra of excellent quality from a number of neat liquids and concentrated aqueous solutions using any of the configurations discussed below. The system will also serve well as a fluorimeter, and we have carried out a number of such experiments with both organic and inorganic fluorophores. The setup consists of a laser excitation source, sample compartment, scanning monochromator, and a detection system based on a lock-in amplifier. We briefly discuss each of the elements below, but wish to emphasize that all combinations of modules possible have been tested and all yield suitable spectra.[2]

A variety of different lasers have been used; all with acquisition costs below eight thousand dollars. Specifically, we have used a He:Cd laser at 442 nm (15 mW) and at 325 nm (8 mW) with equal success. Our workhorse is a Nd:YAG laser which is frequency doubled (λ = 532 nm) and Q-switched. It provides about 200 mW average power (2.5 kHz) at 532 nm. We have used both the 488-nm (15 mW) and 514-nm (30 mW) lines of an air-cooled Ar^+ ion laser with good results. An OEM diode-pumped Nd:YAG laser with 15 mW CW proved quite adequate and provides the lowest cost entry-level system. Alas, a 10 mW He:Ne laser did not provide acceptable spectra with any of the configurations tested.

---

[2] Further details, drawings, and a list of vendors are available from the authors.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

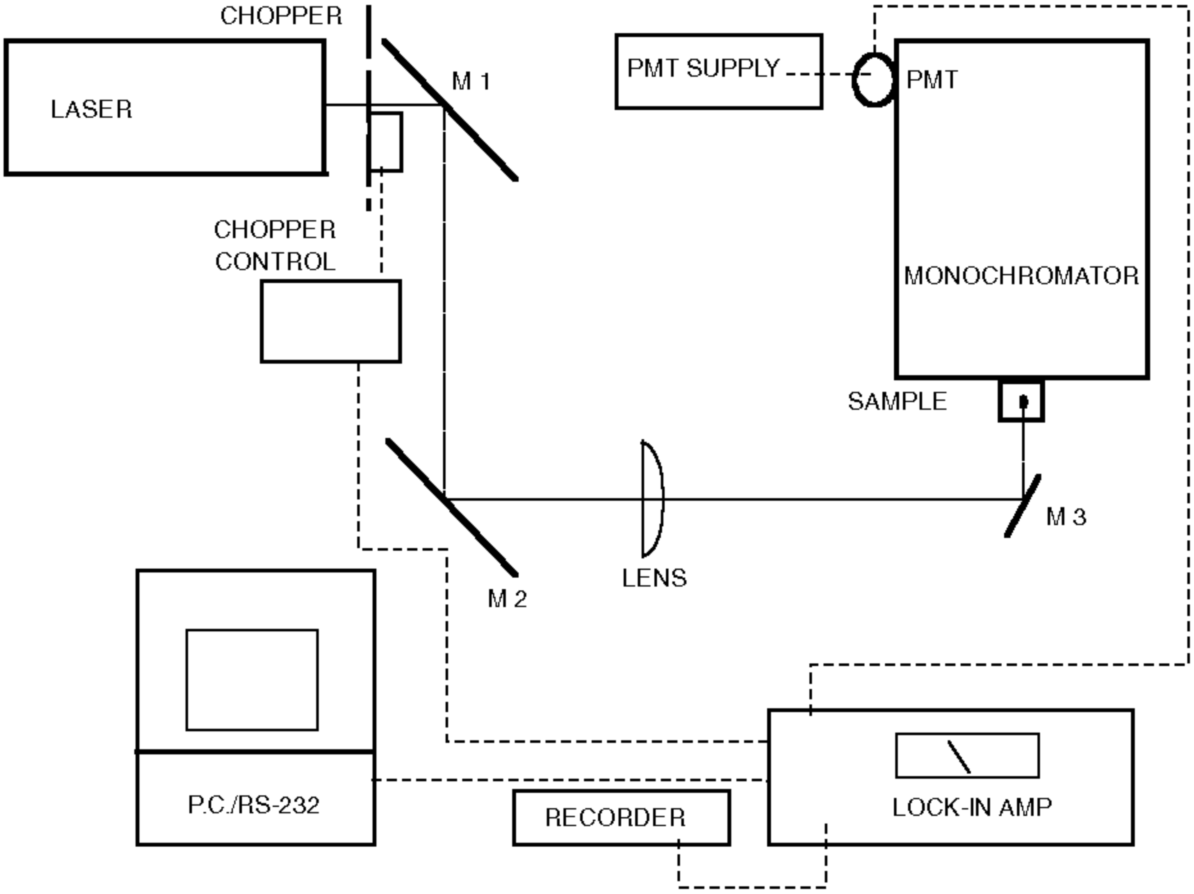

FIGURE 1. SCHEMATIC DIAGRAM OF RAMAN APPARATUS.

The samples are permanently sealed in standard 5-mm flat-bottom NMR tubes. The sample tubes are held in an aluminum block sample holder of local design which is mounted on the faceplate of the monochromator over the entrance slit. The laser beam enters the sample from below and the Raman scattered light is observed at 90°. A short-focal-length lens is placed in the laser beam so that the beam is brought to a focus (beam waist) in the sample at about the center of the slit. The sample holder has a removable back-plate for sample viewing. Without the back-plate one can see the laser beam path and adjust the lens and other components so that the “line of emission light” is collinear with the entrance slit of the monochromator by using a tube filled with a dilute solution of rhodamine 6G dye. Using this simple approach, we have observed signal increases of a factor of 10 over an unfocused/nonaligned beam. Finally, to collect as much of the Raman scattered light as possible, provision is made to mount a short piece of (Pyrex) borosilicate glass rod on the exit slit of the sample holder between the sample holder and

ISSN 1430-4171
http://journals.springer-ny.com/chedr

S 1430-4171 (97)06069-X

the entrance slit of the monochromator. The rod serves as a cylindrical lens and, properly chosen, can enhance the signal-to-noise ratio by more than a factor of two.

For the samples discussed in this article and a wide variety of neat liquids and concentrated solutions, we have found a good quality 0.25-meter scanning monochromator with adjustable slits to be quite adequate. Initially, all our spectra were taken on a very old (20 years) 0.5-meter Czerny–Turner scanning monochromator. This produced excellent spectra, including the anti-Stokes lines of the halomethanes discussed here. Although we have switched to a newer 0.25-meter stepper-motor-driven unit with a computer interface, we wish to emphasize that older units can obtain all the spectra shown. Currently, holographic notch filters are available for most laser lines used. They are expensive, but can significantly reduce interference from Rayleigh scattered laser light when a single monochromator is used. However, their use is *not* recommended for this experiment. A number of the Raman lines of interest lie too close to the excitation line to use the notch filter, which typically blocks to 400 cm^{-1} to the red of the laser line. For the systems used in this experiment, we have had no trouble in detecting the fundamentals to within 200 cm^{-1} of the exciting line. A typical slit width was 150 μ.

The assembly uses a standard ambient-temperature photomultiplier tube (PMT). While we have routinely used an R928 PMT, a much less expensive R372 also served quite well for this experiment. Load resistors from 75 kΩ to 1 MΩ were used and in no case was dark current the limiting problem. A signal-to-noise ratio greater than ten was used as the criterion for acceptable spectra. Clearly, use of a cooled PMT or charge-coupled detector would allow detection of weaker signals, but the configuration described here is more than adequate.

We use a medium-grade (ca. $3000) lock-in amplifier with either a commercial or a home-built chopper. For our routine configuration, the Q-switch frequency of the laser and the reference frequency for the lock-in amplifier are taken from a common source and no chopper is required. For CW lasers, we strongly recommend a lock-in amplifier, but our tests show that suitable spectra can be obtained by simply driving a strip-chart recorder with the PMT output (DC coupled). This latter and minimal configuration, when combined with the OEM diode-pumped Nd:YAG laser, provides entry-level access to Raman spectroscopy for less than ten thousand dollars. The spectra shown in Figure 2 were taken using the lock-in amplifier interfaced to a minimal PC (Q-switched,

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

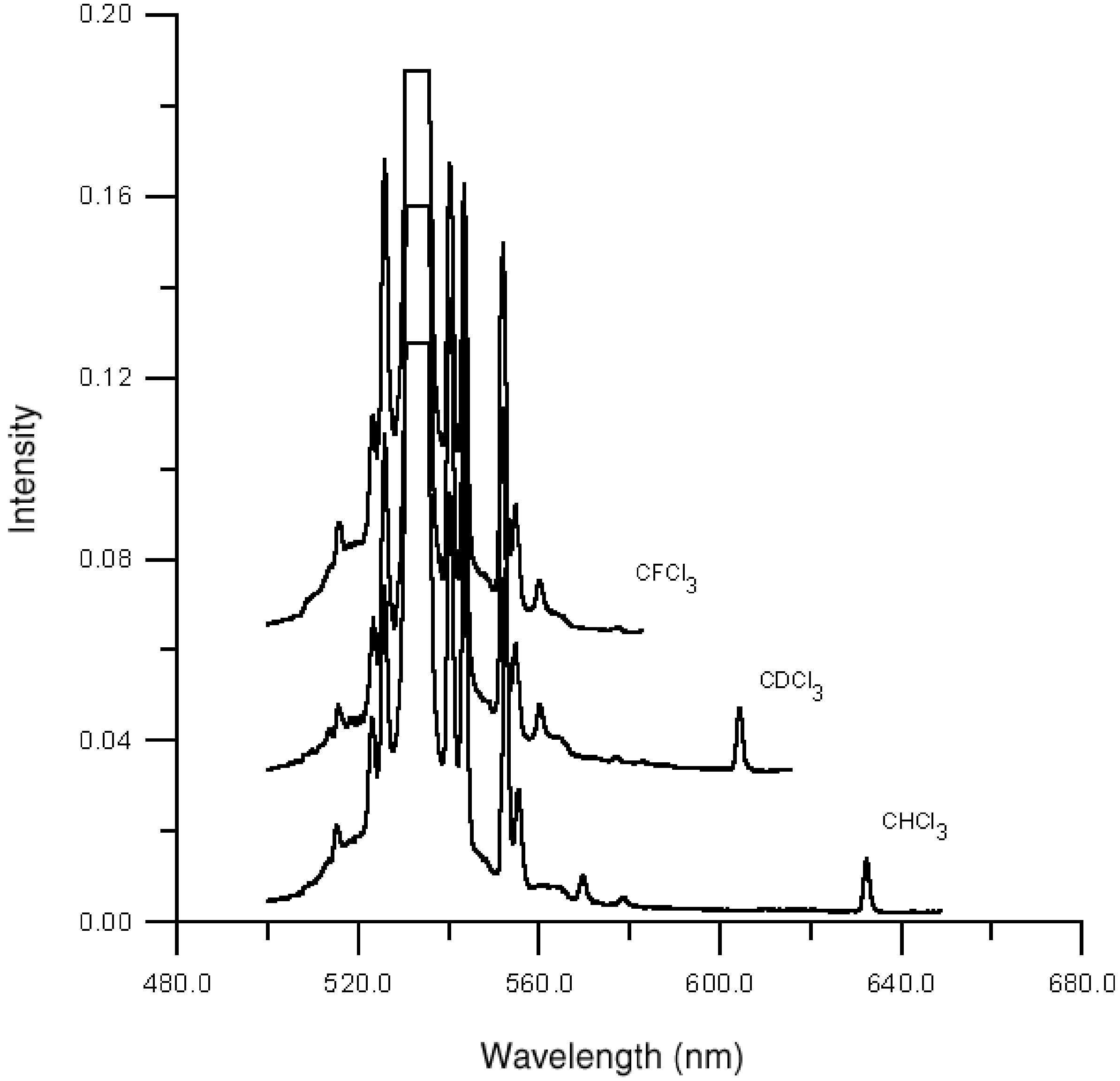

FIGURE 2. RAMAN SPECTRA.

doubled Nd:YAG as excitation). Our experiment is controlled through a Microsoft QuickBasic® program and the ASCII data files obtained were manipulated by commercial plotting software (GRAPHER, Golden Software). However, for several years we simply output the signal from the lock-in amplifier to a strip-chart recorder with the use of manually imposed calibration marks. Students routinely achieved a

THE CHEMICAL EDUCATOR

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

precision of about 0.5 nm. This was sufficient to position all of the Raman peaks to within 4% of their literature values. All fundamentals were clearly visible and resolved.

Our take-home message is simply this. At this writing, the cost of the least expensive commercial Raman instrument is still more than thirty-thousand dollars. By using low-cost commercial modules, departments with only modest resources can provide their students with hands-on exposure to one of the most important and rapidly growing techniques in vibrational spectroscopy for about one-third of this cost. A wide variety of components can be used, including older units that are still serviceable. Using this approach, one can go well beyond demonstrating Raman with the classic CCl_4 spectrum and illustrate a number of basic concepts in vibrational spectroscopy.

Results

The Raman spectra of $CHCl_3$, $CDCl_3$, and $CFCl_3$ obtained using the described Raman apparatus are presented in Figure 2. The $CFCl_3$ spectrum is included to allow the students to explore the uncoupled oscillator approximation. The infrared spectra obtained for CCl_4, $CHCl_3$, $CDCl_3$, $CFCl_3$ and CH_2Cl_2 are presented in Figure 3. The spectra clearly show the increase in the number of IR bands as the symmetry is lowered. Unfortunately, the full IR spectrum of the halomethanes can not be obtained with KBr optics, so a comparison of the stretching regions is more appropriate here. The differences in intensity of the symmetry types can be noted and the complimentary nature of the two methods is obvious.

After obtaining a set of IR and Raman spectra for the series of halomethanes, the students are confronted with some major differences in the number of peaks seen for a particular compound. We then review symmetry and group theory to see if we can explain the results with these concepts.

Symmetry and Group Theory

Symmetry is a powerful method for predicting the number of degeneracies and the spectral activities for the normal modes of vibration. The procedure used has been presented in a text on symmetry and group theory [43], in chemical education journals [28, 45], and in some physical chemistry textbooks [46, 47]. Briefly, all possible motions of the molecule are described by $3N$ displacement vectors (where N is the number of atoms in the molecule; three vectors for each atom). The symmetry of these

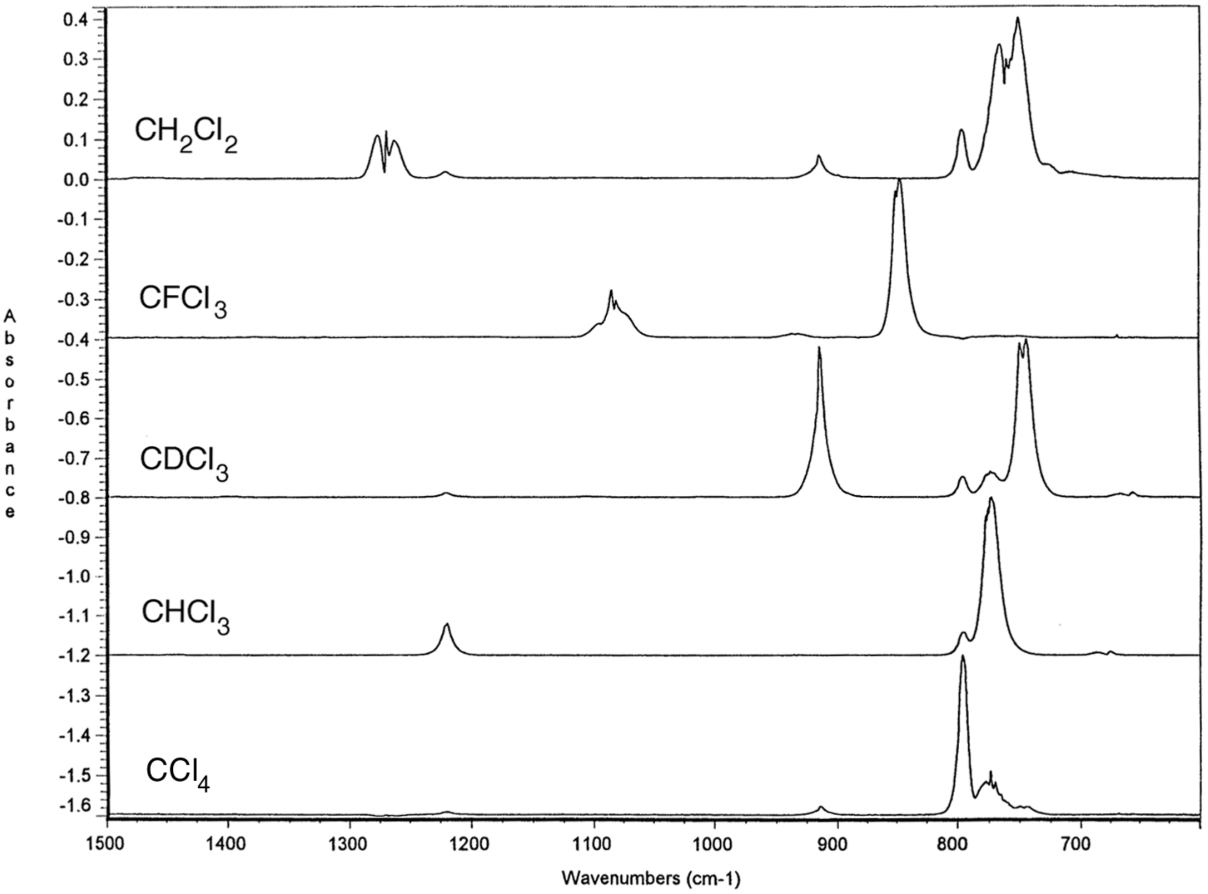

FIGURE 3. IR SPECTRA.

motions can be established from the character of the displacement matrix spanned by these displacement vectors. The character is determined by examining the motion of each displacement vector under each symmetry operation. One adds +1 to the character for each vector that does not change position under the operation, 0 is added for each vector that is changed into some other displacement vector, and –1 is added for each vector that changes sign during the operation. The reducible representation thus generated is resolved into its component irreducible representations and the translations and rotations are subtracted to give the symmetry types for the normal modes of vibration. The normal modes that transform like the translation vectors (x, y, z) are infrared active. Those that transform like the polarizability tensors (xy, xz, yx, x^2, y^2, or z^2) are Raman active. Projection operators can be used to determine the types of molecular motions expected for each normal mode.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

The molecules presented here belong to one of three point groups T_d, C_{3v}, or C_{2v}. The normal modes of vibration for five-atom molecules with T_d symmetry have been presented [28, 45–47]. The nine normal modes of vibration produce four fundamental frequencies: one singly degenerate mode of A_1 symmetry, one doubly degenerate mode of E symmetry, and two triply degenerate modes of T_2 symmetry. The two modes of T_2 symmetry are infrared active; all four modes are Raman active. The A_1 mode and one of the T_2 modes correspond to bond stretching motions, while the E mode and the other T_2 modes primarily result from changes in the bond angles [28, 45]. Similar calculations for the C_{3v} and C_{2v} cases give results which are summarized below.

Five-atom molecules with C_{3v} symmetry have six fundamental vibrations: three singly degenerate modes of A_1 symmetry and three doubly degenerate modes of E symmetry. All six bands are both infrared and Raman active. Two of the A_1 modes and one of the E modes correspond to bond-stretching motions in the molecule. It is also possible to limit the discussion to the stretching modes. These modes can be easily symmetry-classified by using one vector oriented along each chemical bond as the basis set and treating these displacements in the usual manner.

Five-atom molecules with C_{2v} symmetry have nine singly degenerate fundamental vibrations: four modes of A_1 symmetry, one mode of A_2 symmetry, two modes of B_1 symmetry, and two modes of B_2 symmetry. The A_2 mode is infrared inactive; all modes are Raman active.

Molecular Modeling

With the increasing availability of computer systems and low-cost modeling software, the financial barrier to including computer simulations as an integral part of the chemistry curriculum is disappearing. Five different programs that span both the cost and the sophistication range of available software were reviewed for this study. This list is not intended to be all-inclusive, but it does give an overview of the options that are currently available and the results presented are intended to provide individual instructors with baseline information that can be used in structuring pre- and postlab activities. While all have some limitations, all five do a wonderful job of animating the normal modes of molecular vibrations.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

Vibrational Modes (*vide supra*)

IR Tutor

IR Tutor[3] is a self-contained tutorial that begins with an entertaining cartoon of Galileo's discovery of the electromagnetic spectrum and extends to a cartoon presentation of the quantum mechanical oscillator that is perfectly suited for beginning organic students. Other sections discuss the operations of a traditional IR absorption spectrometer and of an FTIR spectrometer. It is possible to access the spectral section directly and bypass the historical information.

IR Tutor is intended for use in the organic curriculum and considers IR spectroscopy from the standpoint of characteristic functional-group frequencies. It allows students to simultaneously see both the actual IR spectrum and the vibrational motions corresponding to these peaks. The program is set up to run as a tutorial and requires minimal instructor input for students to see the importance of characteristic frequencies as an identification tool for organic chemists. The connection to high-resolution spectra of diatomic molecules is harder to make since the program library only includes a fixed set of organic molecules.

AniMol

AniMol[4] uses the results of ab initio calculations (stored in a database) to illustrate the normal modes of vibration. It has a larger library than either of the previous programs and shows the vibrational analysis at two different levels of computational sophistication. This program allows the user to observe excitation of two normal modes simultaneously or to observe a single excitation in different molecules. As with IR Tutor, it is possible to view a vibrational spectrum, highlight a peak, and see the motion responsible for the absorption. One nice feature of the program is that the observation angle can be changed to allow the student to view the molecular motion from several angles. This makes it easier to identify the differences between the symmetric and the asymmetric stretches, for example. Unfortunately, no molecules of T_d symmetry are

---

[3] IR Tutor is a trademark of The Perkin-Elmer Corporation. URLs: http://www.cc.columbia.edu/~nkd2/irtutor/irtutor.html and http://www.perkin-elmer.com:80/ft-ir/ftirsft3.html.

[4] AniMol (for Windows) is available from Innovative Software. URL: http://members.aol.com/isoftware/animol32/animol32/htm.

available in the standard library and students may be confused by the use of scaling factors to correct the calculated vibrational frequencies to more closely match those observed experimentally.

HyperChem™

HyperChem[5] is a substantial step up in both cost and features. It allows the students to do semiempirical and small-basis-set ab initio calculations on any molecule . Among other things, the vibrational frequencies and the IR intensity expected for each mode can be determined from these calculations. In contrast to the less expensive programs, HyperChem presents the spectrum as a two-level display. The upper level shows all of the vibrational frequencies while the lower level shows the expected IR spectrum. This feature allows the instructor to very nicely correlate the IR and Raman spectra to different normal modes of motion. Clicking on a frequency produces the animation of the corresponding molecular vibration. HyperChem allows rotation of the molecule to observe animations of normal-mode vibrations from any angle. Unfortunately, the vibrational animation must be restarted each time the observation angle is changed, which may frustrate the less patient students.

The students can learn to build molecules easily and they seem to enjoy using this program, but there are some potential pitfalls. HyperChem does not impose symmetry constraints and the energy-minimized structures calculated for high symmetry molecules are often asymmetric enough to split the degeneracies of the normal modes. (This was particularly true for chlorine-containing molecules calculated using PM3 with the “steepest descent” or “Polak–Ribierie” minimization algorithms.) While easily corrected, this clearly can be a trap for the student. The HyperChem numbering convention for the normal modes (low to high) is opposite the standard convention used by Herzberg [48] and others. The limitations of the methods available mean that the quantitative agreement between the calculated frequencies and the measured frequencies will be off by approximately 10% and the “better calculations” do not necessarily give better results. There was no provision for isotopes in our version of HyperChem. Given the hype surrounding the proliferation of molecular modeling packages and the all-too-common tendency of some students to believe anything that comes from a computer, a

---

[5] HyperChem is available from Hypercube Inc. URL: http//www.hyper.com.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

careful comparison between these calculations and experiment should be quite instructive for the student. Literature values for the fundamentals are readily obtained from primary sources, which is a good exercise in searching the literature [49, 50].

Spartan™

The most sophisticated program used here was Spartan[6] (v4.0), which was run on a Silicon Graphics Indigo™ workstation. Despite the dramatically higher cost of the hardware, there are real advantages to using Spartan over HyperChem. Spartan on the workstation is fast enough to do ab initio calculations up to the HF-6-311G* level (ca. 90 min for CCl_4). The vibrational visualization features are definitely a step above the others. It is possible to excite one mode in each of any number of molecules simultaneously, and to move and rotate the molecules during animation. However, a side-by-side display of $CHCl_3$ and $CDCl_3$ did not produce any observable effect on either the extent or frequency of the animation of any of the vibrational modes. The frequencies calculated are listed with their symmetry assignments, but cannot be displayed as IR or Raman spectra.

Calculations with the semiempirical methods are identical to those from HyperChem; which is not surprising considering that both programs use the same parameter sets. The calculated frequencies using ab initio basis sets are no more accurate than those calculated using the much faster semiempirical methods. Wavefunction has recently introduced similar software packages that run on a Power Macintosh®[7] and under Microsoft Windows®. We have not, however, used either of these versions.

The results obtained for some typical calculations are presented in Table 1. The semiempirical calculations were done with HyperChem and the ab initio calculations were done using Spartan, but the calculations, up to the STO-3G level, could have been done using either package.

Simple Calculations and the Uncoupled Oscillator Approximation

Most students do not make the connection between the analysis of the classic gas-phase

---

[6] Spartan is a trademark of Wavefunction, Inc. URL: http://www.wavefun.com/.

[7] Power Macintosh is a registered trademark of Apple Computer, Inc.

TABLE 1. A Comparison of the Calculated Vibrational Frequencies and Bondlengths Calculated to the Values Reported in the Literature and Those Measured in This Experiment.

CCl_4 (T_d Symmetry)

Method	ν_1*	ν_2	ν_3	ν_4	$r_{C\text{-}Cl}$*
PM3	458	195	670	284	1.747
AM1	556	228	850	343	1.760
MNDO	551	191	999	298	1.782
HF-STO-3G	520	225	1034	328	1.818
HF-6-31G	503	244	903	349	1.767
lit.value	458	218	776	314	1.760
IR (obsd)	----	----	795	----	-----
Raman (obsd)	465	215	781	311	

$CHCl_3$ (C_{3v} Symmetry)

Method	ν_1*	ν_2	ν_3	ν_4	ν_5	ν_6	$r_{C\text{-}H}$*	$r_{C\text{-}Cl}$*
PM3	2965	636.5	346	1146	662	240	1.112	1.753
AM1	3002	699.1	414	1119	861	281	1.117	1.748
MNDO	3270	753.6	371	1197	980	238	1.105	1.782
HF-STO-3G	3635	763.6	399	1419	1015	274	1.099	1.808
HF-6-31G	3412	732.2	403	1404	875	289	1.071	1.763
lit. value	3034	680	363	1220	774	261	1.10	1.76
IR obsd	3033	678	----	1219	773	----	----	----
Raman. (obsd)	3030	672	358	1215	768	256		

$CFCl_3$ (C_{3v} Symmetry)

Method	ν_1*	ν_2	ν_3	ν_4	ν_5	ν_6	$r_{C\text{-}F}$*	$r_{C\text{-}Cl}$*
PM3	1436	528	307	692	388	211	1.349	1.779
AM1	1372	604	364	828	418	248	1.376	1.786
MNDO	1582	642	329	971	426	216	1.327	1.807
HF-STO-3G	1397	508	365	1023	365	290	1.352	1.827

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

TABLE 1. A Comparison of the Calculated Vibrational Frequencies and Bondlengths Calculated to the Values Reported in the Literature and Those Measured in This Experiment (cont.).

$CFCl_3$ (C_{3v} Symmetry) (cont.)

HF-6-31G	1270	585	385	967	438	272	1.322	1.758
lit. value	1085	535.3	349.5	847	398	241	1.33	1.76
IR (obsd)	1084	536	-----	846	----	----	----	----
Raman (obsd)	1090	529	343	842	391	235		

CH_2Cl_2 (C_{2v} Symmetry)

Method	ν_1*	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
PM3	3077	1353	887	273	1090	3033	660	1218	669
AM1	3078	1327	864	313	1057	3037	874	1218	771
MNDO	3292	1390	902	270	1099	3313	968	1303	835
STO-3G	3603	1717	858	308	1349	3740	1007	1498	1010
HF-6-31G	3308	1601	773	312	1305	3393	990	1433	841
lit. value	2999	1467	717	282	1153	3040	898	1268	758
IR (obsd)	2997	1466	716	-----	-----	-----	898	1268	759
Raman (obsd)	2992	458	712	279	1148	3036	-----	----	753

*All frequencies in given cm^{-1}, bond lenghts (r) given in angstroms.

HCl spectrum and the low-resolution, functional group IR analysis with which they are so familiar from the organic laboratory. The uncoupled oscillator approximation, which is the basis of functional group analysis, is almost never presented in either organic or physical chemistry courses. Indeed, only one discussion of it has appeared in the chemical education literature [51].

Briefly, under appropriate circumstances the stretching motions of polyatomic molecules can be treated as a collection of diatomic motions. This works best when the atomic masses of the diatomic pair are greatly different [1–10], or when there is no common

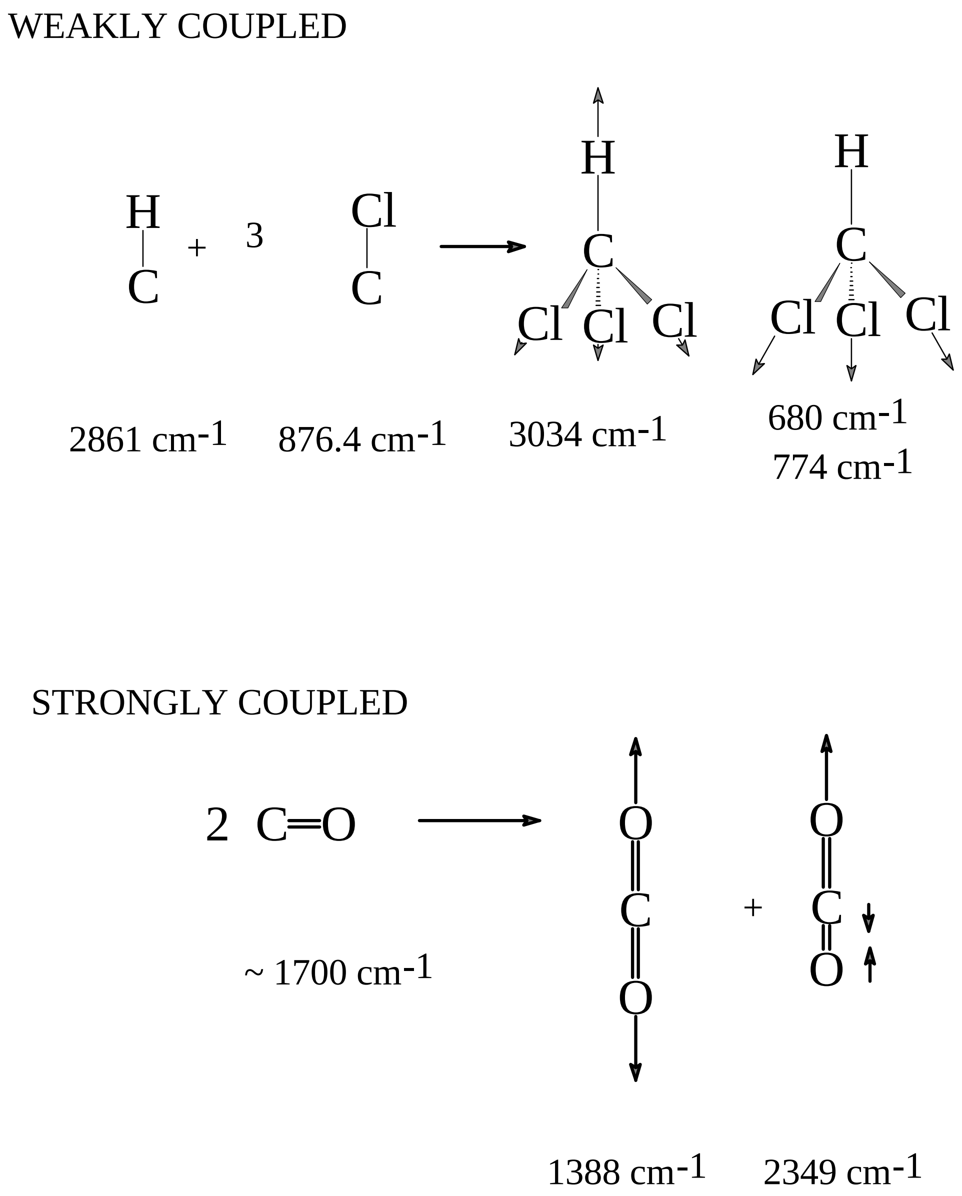

FIGURE 4. INDEPENDENT OSCILLATORS.

atom [11–22]. Even a common atom is not fatal if the motions for the two “diatomic” components are not coincident.

For example, the $CHCl_3$ molecule can be thought of as one C–H and three C–Cl diatomics (see Figure 4). Here the masses of the two atoms involved in both diatomics are quite different (C–H and C–Cl), but the carbon atom is common to both and some coupling of the motions is expected. Since the C–Cl stretches are at ca. 106° to each other and to the C–H motion, the coupling is small. The C–Cl splitting gives a symmetric and an asymmetric stretch which occur at similar frequencies. An extreme case of coupling due to a common atom occurs in CO_2, where the approximation that it is two CO units fails badly. The stretching modes in CO_2 are split by over 1200 cm^{-1}. Neither fundamental frequency is very close to the value of ca. 1700 cm^{-1} that is usually expected for the double-bonded C=O (Figure 4). For interested students, there are extended discussions of which “groups” have frequencies for which the independent oscillator model works, and which group frequencies are sensitive to their neighbors [52]. Finally, an interesting application of the uncoupled oscillator approach is available [53].

The students explore the uncoupled oscillator concept further when they analyze the spectra of $CHCl_3$, $CDCl_3$, and $CFCl_3$. Here they focus on the C–H, C–D, and C–F oscillators. Because of the 106^o angle between the C–X (X = H, D, F) and the C–Cl oscillators, we might expect the coupling to be small and the independent oscillator approximation to work well. To show that the two motions are largely independent, the students estimate the expected frequency of the C–D and C–F stretch based on the observed force constant for the C–H stretch using a diatomic approximation. An interesting question then arises as to whether the diatomic model should be (Cl_3 C)–X or simply C–X. Using the experimental value for the C–H stretch, students calculate the expected C–D stretch using both C–D and Cl_3C–D oscillator approximations. They are surprised to find that the former gives a much better value than the latter. The same type of calculation is done for the C–F stretch, extrapolating from C–H. Again, the results are much better with the C–F oscillator approximation. Calculated and observed values are shown in Table 2. Students are then asked to explain any difference between their calculated and observed values. Many students realize that the force constants for C–H and C–F are not the same, and one can provide an interesting problem by asking the students to devise a means of correcting for this.

Conclusion

The take-home message is simply this: It is now possible to provide an integrated experiment spanning a number of concepts and techniques of vibrational spectroscopy using relatively low-cost hardware and software. Combining techniques such as IR

TABLE 2. Estimation of Vibrational Frequency Using Uncoupled Oscillator Model For The Test Molecules: H-CCl_3, D-CCl_3, and F-CCl_3.

Molecule	$DCCl_3$	$FCCl_3$
ν calculated with X-CCl_3	2151 cm^{-1}	746 cm^{-1}
ν calculated with X-C	2223 cm^{-1}	1746 cm^{-1}
ν observed	2256 cm^{-1}	1090 cm^{-1}

Calculations done taking $\nu = 1/2\pi[k/\mu]^{1/2}$ (where k is the force constant and μ is the reduced mass), ν(C-H) = 3030 cm^{-1}, and correcting for the change in μ of the oscillator. No change in k is required for D-CCl_3, but the force constant, k, for F-CCl_3 is clearly different.

spectroscopy, Raman spectroscopy, and molecular modeling helps the student grasp the synergism between experiment and theory.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the generous support of the National Science Foundation, Division of Undergraduate Education, which through its ILI and UFE programs made this work possible.

REFERENCES

1. Wilson, K. W. “Student Experiments in Infrared Spectroscopy” *J. Chem. Educ.* **1953**, *30*, 340.
2. Stafford, F. E.; Holt, C. W.; Paulson, G. L.; “Vibration–rotation Spectrum of HCl: A Physical Chemistry Experiment” *J. Chem. Educ.* **1963,** *40*, 245.
3. Roberts, B. “The HCl Vibrational Rotational Spectrum” *J. Chem. Educ.* **1966**, *43*, 357.
4. Richards, L. W. “The Infrared Spectra of Four Isotopes in HCl: A Molecular Structure Experiment” *J. Chem. Educ.* **1966**, *43*, 552.
5. Buettner, G. R. “An Easy DCl(g) Prep for the HCl(g)–DCl(g) IR Experiment” *J. Chem. Educ.* **1985**, *62*, 524.
6. Armanious, M.; Shoja, M. “Analysis of Near-IR Spectrum of HCl Molecule using Apple II” *J. Chem. Educ.* **1986**, *63*, 71.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

7. Fry, A. J. “A Convenient Synthesis of DCl and HCl-^{36}Cl” *J. Chem. Educ.* **1987**, *64*, 366.

8. Pu, Q. “Simulation of the Infrared Spectrum of HCl” *J. Chem Educ.* **1990**, *67,* 1034.

9. Ganapathisubramanian, N. “Vibrational–Rotational Spectroscopy: Simultaneous Generation of HCl, DCl, HBr, and DBr” *J. Chem. Educ.* **1993**, *70,* 1035.

10. George, W. O.; Griffiths, I. W.; Minty, B.; Lewis, Rh. “Enhancement of the Rotation–Vibration Bands of HCl” *J. Chem. Educ.* **1994**, *71,* 621.

11. Guillory, W. A. “The Infrared Spectra of Gases at 300 K and of Frozen Films at 77 K: A Physical Chemistry Experiment” *J. Chem. Educ.* **1969**, *46,* 681.

12. Ford, T. A. “Determination of the Vibrational Constants of some Diatomic Molecules: A Combined Infrared Spectroscopic and Quantum Chemical Third Year Chemistry Project” *J. Chem. Educ.* **1979**, *56,* 57.

13. Garcia, J. M. G. “Molecular Parameters of Diatomic Molecules: A Programmable Calculator Program” *J. Chem. Educ.* **1981**, *58,* 610.

14. Henderson, G.; Ko, C.-S.; Huang, T.-C. “ Infrared Emission Spectrum of the Hydroxyl Radical: A Novel Experiment in Molecular Spectroscopy” *J. Chem. Educ.* **1982**, *59,* 683.

15. Castaño, F.; de Juan, J.; Martinez, E. “The Calculation of Potential Energy Curves of Diatomic Molecules: the RKR Method” *J. Chem. Educ.* **1983**, *60,* 91.

16. Lucas, J. M.; Mota, F.; Novoa, J. J. “Theoretical Study of the Vibrational–Rotational Spectra of Diatomic Molecules: A Quantum Chemistry Experiment” *J. Chem. Educ.* **1986**, *63,* 919.

17. Prais, Michael G. “Analysis of the Vibrational–Rotational Spectrum of Diatomic Molecules” *J. Chem. Educ.* **1986**, *63,* 747.

18. Goodfriend, P. L. “Diatomic Vibrations Revisited” *J. Chem. Educ.* **1987**, *64*, 753.

19. Rieck, D. F.; Kundell, F. A.; Clements, P. J. “The Generation of Heteronuclear Diatomic Gases for Determination of Rotational Spectra: A Variation of a Classic Physical Chemistry Experiment” *J. Chem. Educ.* **1989**, *66,* 682.

20. Bozlee, B. J.; Luther, J. H.; Buraczewski, M. “The Infrared Overtone Intensity of a Simple Diatomic: Nitric Oxide” *J. Chem. Educ.* **1992**, *69,* 370.

21. Schor, H. H. R.; Teixeira, E. L. “The Fundamental Rotational–Vibrational Band of CO and NO: Teaching the Theory of Diatomic Molecules” *J. Chem. Educ.* **1994**, *71,* 771.

22. Mina-Camilde, N.; Manzanares I., C.; Caballero, J. F. “Molecular Constants of Carbon Monoxide at v = 0, 1, 2, and 3” *J. Chem. Educ.* **1996**, *73,* 804.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97)06069-X

23. Richards, L. W. “The Infrared Spectra of C_2H_2 and C_2D_2: An Experiment on Molecular Structure and Symmetry” *J. Chem. Educ.* **1966**, *43,* 644.

24. Mendelsohn, R.; Monse, E. U. “Vibrational Spectroscopy of CS_2: A Physical Chemistry Experiment” *J. Chem. Educ.* **1981**, *58,* 582.

25. Boehm, G.; Dwyer, M. “Infrared Spectrum of Methanol: A First-Year Student Experiment” *J. Chem. Educ.* **1981**, *58,* 809.

26. Herman, H.; Lievin, J. “Acetylene: From Intensity Alteration in Spectra to Ortho Para Molecules” *J. Chem. Educ.* **1982**, *59,* 17.

27. McNaught, I. J. “Structural Parameters of Methyl Iodide by Infrared Spectroscopy” *J. Chem. Educ.* **1982**, *59,* 879.

28. DeVore, T. C.; Gallaher, T. D. “Infrared Spectroscopy of Spherical Top (T_d) Molecules: A Physical Chemistry Experiment” *J. Chem. Educ.* **1983**, *60,* 522.

29. Dierenfeldt, K. E. “Isotope Ratio, Oscillator Strength, and Band Positions from CO_2 IR Spectra” *J. Chem. Educ.* **1995**, *72,* 281.

30. David, C. W. “IR Vibration–Rotation Spectra of the Ammonia Molecule” *J. Chem. Educ.* **1996**, *73,* 46.

31. Bulkin, B. J. “Topics in Chemical Instrumentation. XLVIII. Raman Spectroscopy—Part One” *J. Chem. Educ.* **1969**, *46,* A781.

32. Bulkin, B. J. “Topics in Chemical Instrumentation. XLVIII. Raman Spectroscopy—Part Two” *J. Chem. Educ.* **1969**, *46,* A859.

33. DeHaan, F. P.; Thibeault, J. C.; Ottesen, D. K. “ Raman Spectra of ZXY_3 compounds: A Dry-Lab Spectral Analysis Experiment” *J. Chem. Educ.* **1974**, *51*, 263.

34. Hoskins, L. C. “Pure Rotational Raman Spectroscopy of Diatomic Molecules” *J. Chem. Educ.* **1975**, *52,* 568.

35. Hoskins, L. C. “Pure Rotational Raman Spectroscopy: A Dry-Lab Experiment” *J. Chem. Educ.* **1977**, *54,* 642.

36. Strommen, D. P.; Nakamoto, K. “ Resonance Raman Spectroscopy” *J. Chem. Educ.* **1977**, *54*, 47.

37. Shaw, C. F. III “Resonance Fluorescence and Resonance Raman Spectroscopy of Bromine and Iodine Vapor” *J. Chem. Educ.* **1981**, *58,* 343.

38. Hoskins, L. C. “Resonance Raman Spectroscopy of β-Carotene and Lycopene: A Physical Chemistry Experiment” *J. Chem. Educ.* **1984**, *61,* 460.

ISSN 1430-4171
THE CHEMICAL EDUCATOR
http://journals.springer-ny.com/chedr

S 1430-4171 (97)06069-X

39. Galloway, D. B.; Ciolkowski, E. L.; Dallinger, R. F., “Raman Spectroscopy for the Undergraduate Physical and Analytical Laboratories” *J. Chem Educ.* **1992**, *69,* 79.

40. O’Brien, L. C.; Kubicek, R. L.; O’Brien, J. J. “ Laser Raman Spectroscopy of Diamond” *J. Chem. Educ.* **1994**, *71,* 759.

41. Fitzwater, D. A.; Thomasson, K. A.; Glinski, R. J. “A Modular Raman Spectroscopy System Using a Helium–Neon Laser That is Also Suited for Emission Spectrophotometry Experiments” *J. Chem. Educ.* **1995**, *72,* 187.

42. Eckbreth, A. C. In *Laser Diagnostics for Combustion Temperature and Species;* Gupta, A. K.; Lilley, D. G., Eds.; Abacus: Cambridge, MA, 1988.

43. Cotton, F. A. *Chemical Applications of Group Theory,* 2nd ed.; Wiley-Interscience: New York, 1971.

44. A set of suitable exercises for this software, along with a complete experimental write-up and other related materials, are available from the authors at no cost.

45. Condren, S. M.; “Group Theory Calculations of Molecular Vibrations Using Spreadsheets” *J. Chem. Educ.* **1994**, *71,* 486.

46. Noggle, J. H. *Physical Chemistry,* 3rd ed.; Harper Collins: New York, 1996.

47. Atkins, P. W. *Physical Chemistry,* 5th ed.; Freeman: New York, 1994.

48. Herzberg, G. Infrared and Raman Spectra of Polyatomic Molecules; Van Nostrand: Princeton, 1945.

49. Palma, F. E.; Piotrowski, E. A.; Sundaram, S.; Cleveland, F. F. “Substituted Methanes. Part XXXIV. Raman and Infrared Spectral Data and Calculated Thermodynamic Properties for CH_2Cl_2, $CHDCl_2$, and CD_2Cl_2” *J. Mol. Spec.* **1964**, *13,* 119 and references therein .

50. Ngai, L. H.; Mann, R. H. “A Transferable Urey–Bradley Force Field and the Assignments of Some Mixed Halomethanes” *J. Mol. Spec.,* **1971**, *38,* 322.

51. Dows, D. A. “On the Origin of Characteristic Group Frequencies in Infrared Spectra” *J. Chem. Educ.* **1958**, *35,* 629.

52. Weissberger, A. *Technique of Organic Chemistry, Vol IX;* Interscience: New York, 1956.

53. Pacansky, J.; Calder, V. “Matrix-Isolation Spectra of H_2S and D_2S: An Example of the Application of the Uncoupled Oscillator Approximation” *J. Chem. Phys.* **1970**, *53,* 4519.