An Inexpensive Laser Raman Spectrometer Based on CCD Detection

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Abstract: We describe an inexpensive modular Raman spectrometer system that can be assembled from commercial components for under $5000. Three typical applications are presented: a demonstration of a vibrational isotope effect, a Raman polarization experiment, and a resonance Raman experiment. This spectrometer system should make it easier to include the important topic of Raman spectroscopy in the undergraduate physical and analytical chemistry laboratory curricula.

Introduction

Raman spectroscopy, a companion technique to infrared spectroscopy, is capable of giving detailed information about molecular structure and quantitative analysis. Various types of Raman spectroscopy have been used for many years to investigate a wide variety of questions, ranging from the molecular changes involved in color vision [1, 2] to the molecular structures of inorganic complexes in solution [3]. In addition, Raman spectroscopy is broadly used as an analytical technique that is complementary to infrared spectroscopy. Here, applications in environmental monitoring, quality control, and biochemistry have been prominent. Unlike infrared spectroscopy, Raman spectroscopy provides information about totally symmetric molecular vibrations. In addition, Raman spectroscopy allows one to obtain vibrational spectra of substances in aqueous solution. This second property makes Raman spectroscopy an especially valuable tool for biophysical chemists. Most undergraduate instrumental and physical chemistry textbooks contain detailed discussions of Raman spectroscopy [3–6]. It is an important topic both because of its broad applicability in chemical analysis and because it can provide fundamental molecular parameters, such as molecular shapes and vibrational frequencies. Further analysis of Raman spectra allows students to obtain information about force constants, which can be compared to predictive theories of chemical bonding. The bond-strength information available from Raman spectroscopy allows for pedagogically valuable opportunities to include computational chemistry in the undergraduate curriculum [7–9].

Despite its importance, Raman spectroscopy is absent from many undergraduate teaching laboratories, most likely because of the expense and effort required to obtain a sufficiently sensitive Raman device; however, several authors recently have reported low-cost, modular, custom-made Raman instruments and described Raman-based laboratory exercises that are suitable for undergraduate physical chemistry or analytical chemistry students [8, 10–12]. Two of these units can be built for under $14,000 [8, 12]. Most of these low-cost modular units are based on low-power lasers, monochromators, and PMT detection. Another approach that further decreases cost and increases ease of use, portability, and robustness involves replacing the monochromator-PMT module with a charge-coupled device (CCD) detector [12, 13, 14]. In fact, some commercial Raman spectrometers are based on CCD technology (for example, Ocean Optics and Boston Advanced Technologies, Inc.).

In this article, we describe a low-cost modular Raman apparatus based on CCD detection that can be assembled from commercial components for under $5000. This apparatus makes use of an Ocean Optics S2000/PC1000 spectrometer (www.oceanoptics.com) configured and marketed for routine absorbance measurements. It is sensitive enough to record Raman spectra of neat organic liquids, aqueous salt solutions, and efficient resonant Raman scattering species in less than a minute. The modular design allows for flexibility and is pedagogically valuable because students can see and work with the various components of the apparatus. In fact, the design is simple enough that undergraduate students should be able to assemble the system and collect the desired spectra given a reasonable amount of time (three-to-five hours, depending on the skills of the students and the number of spectra taken).

Experimental Details

The experimental layout is shown in Figure 1. The beam from a 532-nm linearly polarized laser is passed directly into the sample without focusing. To observe polarization effects, a half-wave plate is placed between the laser and the sample to rotate the polarization of the beam. One can often obtain half-wave plates from surplus equipment at a fraction of their new cost (for example from MWK Laser Products [15]). In order to measure depolarization ratios quantitatively, a polarization analyzer must be placed between the sample and the fiber optic. Samples are held in a standard 1-cm glass fluorimeter cell and scattered light is collected at a 90° angle from the laser beam path. A notch filter is placed between the sample cell and

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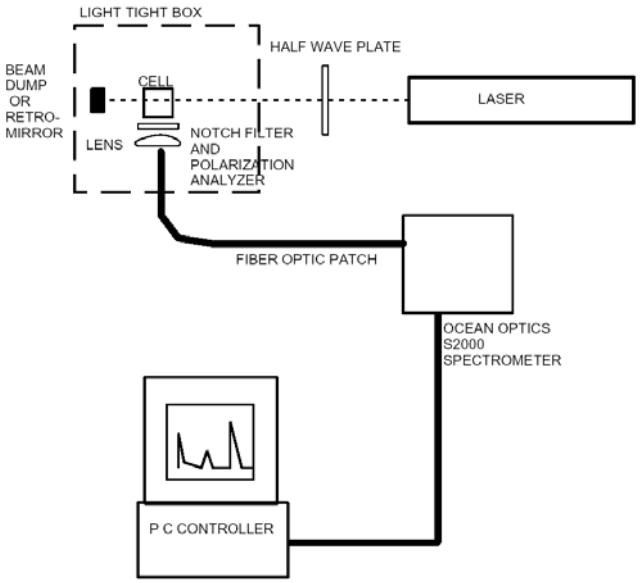

Figure 1. Raman apparatus schematic (top view).

the fiber optic coupling to reduce the Rayleigh scattered 532-nm excitation light, thus minimizing pixel bleeding. The notch filter manufacturer, Kaiser Optical Systems [16] claims a 2-nm bandpass width for their notch filters. This corresponds to ~70 cm^{-1} at the 532-nm Nd/YAG line; however, the wavelength of the notch is rather angle-dependent and in practice we find that we cannot observe Raman peaks less than 150 cm^{-1} from the exciting line. (It should be noted that the samples discussed in this work have large enough Raman shifts that Raman peaks can be observed even without the interference filter.) A collecting lens (Ocean Optics model 74-UV) focuses the scattered light into the fiber optic patch. The fiber optic patch to the spectrometer has a 400-μm diameter (Ocean Optics model P400-1-VIS/NIR). A box surrounds the sample, filter, lens, and fiber optic cable end in order to prevent room light from reaching the detector. The other end of the fiber optic cable is connected to the spectrometer (Ocean Optics S2000/PC2000), which contains a 50-μm slit and a 600-groove- per-mm grating with a blaze wavelength of 400 nm and a vendor-estimated efficiency of ~30%. The multipin electronics cable from the spectrometer leads to an AD converter card (Ocean Optics model ADC500/PC1000) in a 90-MHz Pentium PC. Ocean Optics software (OOIBase 32) is used to collect and process the data. The Ocean Optics spectrometer, AD converter card, and software were purchased for approximately $2000. Fiber optic patch cords from Ocean Optics are ~$150 for a 2-m length. The collecting lens costs $159.

The entire unit is constructed on an 8-in-by-8-in aluminum breadboard from Thor Labs [17]. When one combines the breadboard with the small optical rails, lens holders, and other mounting hardware available from the same vendor, a wide range of suitable configurations are possible that include additional collection and retro mirrors, filters, and polarizing optics.

Very satisfactory spectra of neat organic liquids, saturated aqueous solutions of oxyanion salts, and an efficient resonance Raman scattering molecule (β-carotene) were obtained with the continuous wave (CW) 532-nm output of an inexpensive (under $2000) 10-mW doubled Nd/YAG laser (Power Technology model LDCU3/4899) [18]. In the case of the aqueous salt solutions, respectable spectra can be obtained with ~1 M concentrations; however, a saturated solution is easily prepared and improves the signal-to-noise ratio. Improved signal to noise is obtained when a 50-mW Nd/YAG (JDS Uniphase model 4301-050) [19] or a 40-mW Ar^+ ion laser is used; however, these lasers are significantly more expensive. Both of the Nd/YAG sources are diode-pumped and intercavity-doubled with polarized output. Both are small and portable. We also tried an inexpensive pulsed (Q-switched, 2-mW average power, 1-KHz repetition rate) Nd/YAG laser, but we could not obtain Raman spectra with this source, presumably because of the low power and small duty cycle.

The Ocean Optics spectrometer software allows integration times to be varied from 1 ms to 65 s; for most samples, integration times of between 15 and 60 s were required. Because of the relative weakness of the Raman signal in comparison to pixel noise, a dark spectrum (with laser light blocked) must be subtracted from the overall signal. The Ocean Optics software explicitly allows for dark spectrum subtraction. The dark spectrum must be collected using the same integration time as the spectrum. Spectra were not corrected for any wavelength variation in the response of the CCD detector; therefore, the relative intensities of peaks are not quantitative. The spectral window, however, is relatively small and the wavelength variation in pixel sensitivity should be modest. Raman scattering intensities were collected as unitless channel counts.

The apparatus in Figure 1 was successfully lined up by undergraduate students using the 10-mW Nd/YAG as a source and neat chloroform as the sample. An even more efficient way to optimize the system is to place a fluorescent sample in the cuvette and to maximize the magnitude of this signal before replacing the fluorophore with a scattering substance. The spectra shown in Figures 2 and 3 were obtained by students. The samples were neat chloroform, neat deuterated chloroform, and a saturated solution of $NaClO_4$.

Because of the intense interest in Resonance Raman Spectroscopy (RRS) of biological samples, we also obtained a RRS spectrum of β-carotene, a classic, efficient RRS scattering molecule. The spectrum in Figure 4 was collected using a 90° collection geometry. The concentration of β-carotene is critical and our best results were with solutions with 0.4 < Abs at 532 nm < 0.8. The exact concentrations of these solutions were unknown because eluted material from a chromatography column was used directly in the experiment. The concentrations can be estimated from the known molar extinction coefficient [20] and are in the μM range. We also obtained satisfactory spectra using a front-face collection geometry in which the light collected is back-scattered light from the front face of the cell with the detector positioned about 15° from the exciting laser beam. For this configuration the solution was typically Abs ~2.5 in β-carotene. The front-face collection method is useful for very opaque, turbid, or highly absorbing materials.

Commercially available β-carotene is readily available and relatively inexpensive; however, it does contain impurities, one of which is luminescent and must be removed before attempting the resonance Raman experiment. This can easily be done using a short column of either alumina or silica gel with CH_2Cl_2 as the eluant. We purified the β-carotene on neutral alumina using CH_2Cl_2 as the eluant. It was also purified using flash chromatography with silica gel as the support and CH_2Cl_2 as the eluant. Both columns were ~12 cm in length and the separation was completed in less than 90 minutes. We did not determine the identity of the luminescent impurity.

Results and Discussion

Figures 2, 3, and 4 show the results of isotopic substitution, polarization, and resonance Raman experiments, respectively. These spectra were all taken using the 532-nm output of the doubled 10-mW Nd/YAG as the incident light and 45-to-60-s integration times.

Figure 2 shows the Raman spectra of chloroform and deuterated chloroform. In chloroform the small peak at 3019 cm^{-1} has been assigned to the C–H stretching vibration [21]. Figure 2 illustrates the isotope effect in this vibrational mode when hydrogen is replaced by deuterium. The heavier isotope lowers the frequency of the C–H stretching vibration, which is well-described by the diatomic approximation [9]. The small Raman peak that appears just below 1205 cm^{-1} in the chloroform spectrum is attributed to the ν_4 asymmetric-

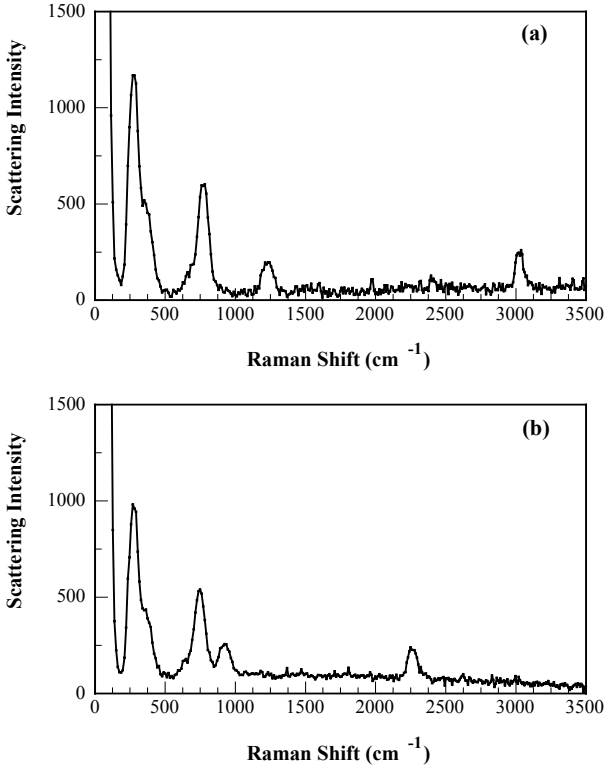

Figure 2. Raman spectra of neat chloroform (a) and deuterated chloroform (b).

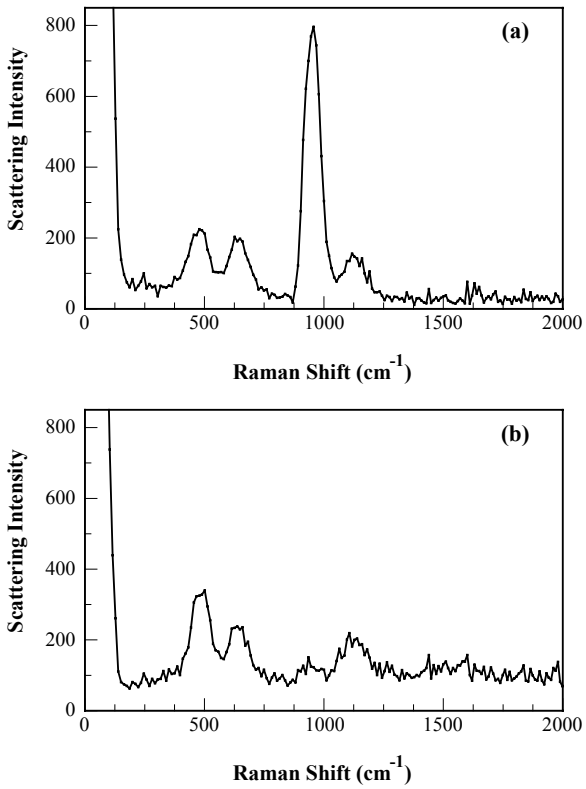

Figure 3. Raman spectra of a saturated solution of $NaClO_4$ with (a) vertically and (b) horizontally polarized light impinged on the sample.

stretching vibration [21]. This vibrational mode involves motion of the hydrogen atom and its vibrational frequency is also decreased as the result of deuterium substitution, as shown in Figure 2.

Raman spectroscopy allows one to distinguish totally symmetric vibrations from other vibrations via measurement of the depolarization ratio for individual Raman peaks. A totally symmetric mode will only radiate light of the same polarization as the excitation laser. This effect is well described in various texts and is often shown for the case of the totally symmetric stretching mode of CCl_4 [5]. Several alternatives to CCl_4 exist for demonstrating this effect. In Figure 3 we show the effect for the totally symmetric ν_1 mode of the ClO_4^- ion. The figure shows the spectra obtained using both vertically polarized and horizontally polarized light. The large ν_1 peak near 1000 cm^{-1} cannot be observed when the beam is horizontally polarized. The very small amount of scattered light observed at this wavelength in our horizontally polarized spectrum results from imperfect polarization of the laser beam.

In addition to the experiments above, we examined neat CCl_4 and concentrated solutions of a number of metal oxyanion salts. Satisfactory Raman spectra were obtained and the peak positions were in agreement with published values. We also examined polarization effects for these samples. All of the molecules we investigated had tetrahedral structure. In every case the Raman peak corresponding to the totally symmetric vibration disappeared when horizontal polarization was used.

Lastly, we demonstrated the possibility of performing resonance Raman experiments with this system. Figure 4 shows the resonance Raman spectrum of β-carotene in chloroform. Also shown on the same plot is the regular Raman spectrum of chloroform taken under identical conditions as the β-carotene. This shows rather nicely the remarkable enhancement due to the resonance effect, as the β-carotene is at μM concentration and chloroform is ~12 M. For Figure 4 we deliberately added a very small amount of the unknown luminescent impurity obtained directly from the chromatography column so that its emission envelope is clearly visible. The 1155-cm^{-1} and 1525-cm^{-1} bands of β-carotene can easily be seen above this emission envelope. If one has access to an Ar^+ laser, then one can examine the change in the A term as suggested by Hoskins [6]. We were, however, unsuccessful with the 10-mW Nd/YAG source in obtaining quality resonance Raman from $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline) in 1 M Na_2SO_4 as suggested in [22, 23]. Suitable spectra for this system could be obtained with the 488-nm and 514-nm lines of a 40-mW Ar^+ laser and also with a 50-mW Nd/YAG. Thus, when selecting chemical systems, one must be aware of the large differences in resonance Raman scattering efficiencies.

The Ocean Optics spectrometer used in this study is normally employed for solution absorbance and luminescence studies; therefore, it is configured to provide a large spectral window (~600 nm) at the expense of resolution. We evaluated our effective resolution using a mercury discharge lamp and found the operational resolution to be <2 nm in the visible. This corresponds to <70 cm^{-1} resolution near the 532-nm exciting line. While we clearly did not have baseline resolution of all Raman peaks, there was no problem with peak location and the resulting values for Raman frequency shifts were quite acceptable.

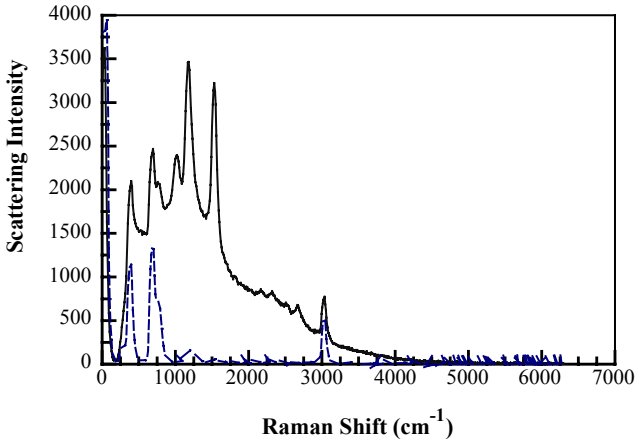

Figure 4. Solid line: Resonance Raman spectrum of β-carotene in chloroform. The emission envelope of a fluorescent impurity is visible underneath the spectrum. Dashed line: Nonresonant Raman spectrum of neat chloroform taken under the same conditions.

Several improvements on the setup are easily made. First, the slit used for our spectrometer is 50-µm by ~1000 µm. Thus a 1-mm fiber optic patch could be substituted for our 400-µm patch and would effectively double the signal with no loss of resolution. Second, our spectrometer uses a 600 g-per-mm grating, but both 1200 and 1800 g per mm are available from Ocean Optics and would increase wavelength resolution. The tradeoff is that this would narrow the available spectral window, but for a dedicated Raman unit this would be a beneficial tradeoff. We deliberately did not focus the laser beam in the sample. While focusing should increase the Raman signal, it does make alignment and collection more difficult. We wanted to demonstrate that satisfactory Raman spectra could be obtained using relatively low laser powers without the need for tight alignment. Clearly, for samples that are less efficient scatterers, focusing the laser beam should improve the signal-to-noise ratio. Finally, one can use front-face collection to enhance the Raman signal. This again requires careful alignment and could be tedious for inexperienced students setting up the apparatus.

Conclusions

An inexpensive modular Raman spectrometer can be assembled using a commercially available spectrometer containing a CCD detector. This spectrometer is capable of producing Raman spectra of neat liquids, concentrated solutions of oxyanion salts, and resonance Raman scatterers using laser excitation with powers as low as 10 mW. (Higher laser powers will allow for observation of spectra from solutions with lower concentrations or less efficient resonance Raman scatterers.) Because the CCD detector multiplexes the Raman spectrum, spectra can be obtained in a shorter amount of time than is needed with a scanning monochromator, allowing students more time to investigate polarization effects. We have demonstrated that this apparatus can be used to demonstrate isotope and polarization effects. This system will make it possible to perform a host of Raman spectroscopy experiments in an undergraduate setting.

Safety. Appropriate laser safety goggles should be worn when lining up the apparatus and when inserting the samples in the beam. Some of the organic liquids traditionally used for Raman spectroscopy ($CHCl_3$, CCl_4, for example) are toxic and some are known or suspected carcinogens. Wear gloves and use stoppered cuvettes when using these substances.

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