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Low-Cost Raman Spectroscopy using a Violet Diode Laser

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Abstract: New generations of diode lasers that emit violet light make possible the assembly of a low-cost Raman spectrometer for use in the student laboratory. Because Raman scattering intensity is inversely proportional to the fourth power of the wavelength of the incident radiation, the use of these violet lasers has advantages over their longer-wavelength counterparts. The higher scattering efficiencies permit the use of a relatively inexpensive PC-based spectrometer (e.g., an Ocean Optics spectrometer) for wavelength analysis of the scattered radiation. Combined with a notch filter and several lenses, the violet diode laser and spectrometer permit the construction of an instrument at a total cost of around $6500, including the PC-based spectrometer. This cost will decrease dramatically in the near future as violet diode lasers are commercialized for data storage applications. Performance of the instrument is demonstrated on carbon tetrachloride, water, and benzene. These experiments show Stokes radiation bands in agreement with published data. While the use of the notch filter and limited resolution of the spectrometer obscure some bands, the instrument serves to illustrate fundamental principles of Raman spectroscopy appropriate for physical and analytical chemistry teaching laboratories.

Introduction

Raman spectroscopy is an important technique in analytical and physical chemistry and is complementary to infrared spectroscopy in that it provides similar kinds of information about a molecule (i.e., functional groups and structure), but also information for molecules that are not infrared active or are in aqueous solution. In principle, the technique is simple to perform. A light beam is shot at a sample, and the scattered light is energy analyzed. A great majority of the light is scattered elastically without change in energy; this is referred to as Rayleigh scattering. A relatively small number (ca. 1 out of every 10^7) [1] of the photons lose energy due to interaction with the sample. The photons that lose energy by inducing vibrations give rise to a set of lines to the lower-energy side of the intense Rayleigh scattering peak. These transitions are referred to as Stokes lines. It is also possible for the molecules in excited vibrational states to give their energy to the impinging photons. These transitions lead to higher energies than the Rayleigh scattered photons and to anti-Stokes lines. Because the relative populations at room temperature of the excited vibrational states are significantly smaller than that of the ground state, the anti-Stokes lines are generally weaker than the Stokes lines. Every substance has a unique set of allowed vibrational energies, and Raman spectroscopy can be used not only to identify an unknown sample but can also provide information about bond lengths, strengths, and angles. While the selection rule for detecting infrared spectroscopy is that the vibration must lead to a changing dipole moment, the selection rule for Raman spectroscopy is related to the polarizability of the molecule [1, 2]. It should be noted that while the above discussion concerns vibrations of molecules, rotational and electronic energy levels may also be studied [2], although this is a much less common application of the technique.

Raman experiments for the student physical chemistry laboratory have been described [3, 4]. Historically, the main problem in implementing Raman spectroscopy is cost. The technique traditionally requires a grating monochromator, photomultiplier-tube detector, and an intense monochromatic light source. Lasers of at least moderate power are the only practical radiation sources. In a low-cost approach, several teachers have described “dry-lab” experiments in which the student interprets reference spectra [5–7], but these lack the “hands-on” aspect of performing an actual experiment. To address this issue, Lorigan, et al [8] developed a cost-effective Raman experiment for the classroom using a helium/neon gas laser and a PC-based spectrometer consisting of an array of charge-coupled device (CCD) detectors. Furthermore, DeGraff and colleagues [9] assembled an inexpensive laser Raman spectrometer by combining a PC-based spectrometer with a 10-mW, 532-nm frequency-doubled Nd:Yag laser. Vickers et al. [10] have also used a CCD-based spectrometer with a very high-power (500 mW) 785-nm near-infrared diode laser.

Because Raman scattering intensity depends inversely on the incident radiation wavelength raised to the fourth power [3], using a shorter wavelength laser could potentially reduce the need for high radiant power. Continuous-wave gas lasers operating in the violet spectral region (e.g., 400 nm) can be purchased but are costly. A more convenient light source for a classroom Raman spectrometer is a diode laser. Diode lasers are solid-state devices producing highly polarized, though uncollimated radiation. Violet diode lasers have recently become available, and their cost should plummet in the next few years as they are mass-produced for future generations of DVD players. This commercialization is driven by the fact that data storage capacity is diffraction-limited, and higher data densities can be achieved if shorter wavelengths are used. Red diode lasers (635 nm) are presently used for this purpose and can be purchased for as little as $20, including driver circuitry; it is anticipated that violet lasers could eventually approach this cost.

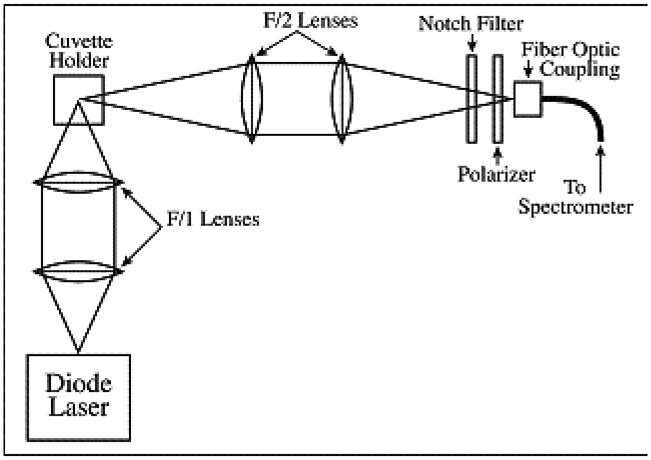


Figure 1. Schematic of the Raman spectrometer consisting of a 402-nm diode laser, four biconvex lenses, a 405-nm notch filter, a linear polarizer, and a cuvette holder. The diode-laser controller and Ocean Optics USB2000 spectrometer are not shown for clarity.

Whitten and colleagues [11, 12] recently demonstrated several chemical education experiments with violet diode lasers, and this paper extends these efforts to Raman spectroscopy. In the present work, a diode laser-based Raman spectrometer has been assembled from a violet diode laser and components available in most college-level physical chemistry laboratories. The instrument has been used to measure Raman spectra of carbon tetrachloride, water, and benzene. Because diode lasers emit highly polarized light, they also facilitate measuring the depolarization ratios of the various Stokes bands, and this is demonstrated using a single linear polarizer.

Instrument Description

The instrument consists of just a few components assembled on a standard optical bench as shown in Figure 1. These components and approximate costs are a 402 nm, 30 mW diode laser (Nichia NDHV310APBE2, $1500), a diode laser controller (ThorLabs LDC500, $1000), a thermoelectrically cooled diode laser mount (ThorLabs TCLDM9, $500), and a thermoelectric temperature controller (ThorLabs TEC2000, $1000). Thermoelectric cooling is optional but is recommended to extend the life of the laser; it could be replaced with an efficient heat sink, saving about $1500. The instrument also includes four 50.8-mm diameter lenses of two different focal lengths (Thorlabs LB1723-A and LB1630-A), a homemade cuvette holder, a quartz cuvette, a low-cost interference optical notch filter centered at 405 nm (Semrock NF01-405U-25, $895), a linear polarization filter (Edmund Industrial Optics F47-216, $100), and an Ocean Optics spectrometer with fiber-optic input (Ocean Optics USB2000, $1500 with educational discounts). The Ocean Optics spectrometer is UV-enhanced and equipped with a 300-mm diameter fiber, 600-line/mm grating blazed at 300 nm and 25-mm slit. This combination of components gives an optical resolution [13] of about 1.33 nm FWHM (full width at half maximum) at 400 nm. This is an equivalent resolution of 83 cm^{-1}. Note that the exact wavelength of the diode laser may vary with lot number, even for the same part number, and the user should confirm that it will fall within the operating range of the 405-nm notch filter. Associated optical mounts available from vendors such as ThorLabs are also required.

Resolution could be improved somewhat, at the sacrifice of sensitivity, with the use of a smaller slit and/or a finer grating. Slits down to 5 mm and gratings up to 1800 lines/mm are available. Note that the grating blaze wavelength must match the laser wavelength closely if these finer gratings are used. If a 10-mm slit and 1800-lines/mm grating is used in the USB2000, the resolution could be improved to 0.30 nm FWHM, which is an equivalent resolution of 19 cm^{-1} at 400 nm. In this case, the 300-mm optical fiber should be replaced with a 600-mm fiber to compensate somewhat for the loss in sensitivity. These higher performance options would raise the cost of the instrument by ca. $2,000. Ocean Optics also offers several higher-resolution spectrometers (e.g., HR2000 or HR4000), but at a significant price increase, which, in our opinion, defeats the low-cost objective.

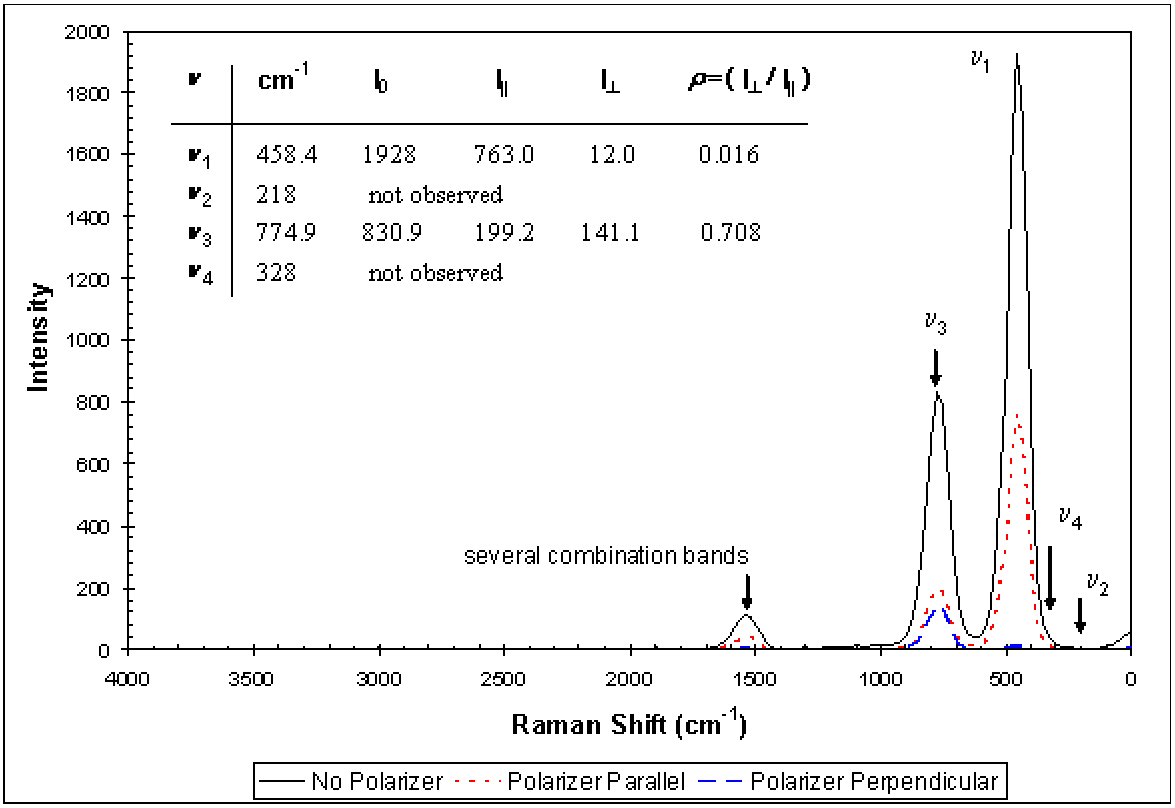
The optics on the laser side of the cuvette holder match the *F* number of the diode laser (approximately *F*/1), collimate the laser beam, and then focus the light onto the sample in the cuvette holder. The intensity of the beam at the cuvette holder is approximately 1W/cm^2. The two *F*/2 lenses on the spectrometer side of the cuvette collimate the 90°-scattered light, match the *F* number of the fiber (~*F*/2.2), then focus it onto the end of the optical fiber of the spectrometer. The optical notch filter is placed in the optical path and greatly reduces the amount of Rayleigh scattered light entering the spectrometer. The laser, the cuvette, and the optical fiber lie at the focal points of their respective lenses. The distance between lenses is not critical because the light is collimated in those regions. We use an interlens distance of about three inches.

When making depolarization-ratio measurements, the linear polarizer is inserted into the optical path. The diode laser is oriented so as to produce plane-polarized light in the vertical direction. When the polarizer is rotated to a vertical orientation, the polarization of the detected radiation is considered “parallel.” When the polarizer is rotated to the horizontal, it is considered “perpendicular.” A measurement is made with both polarization settings, and the data are compared. When not making a depolarization ratio measurement, the polarizer is removed to maximize light intensity. To reduce stray light, the entire optical bench is draped with a black rubberized opaque fabric sheet (Thorlabs, BK5).

The Ocean Optics USB2000 spectrometer used to detect the Raman scattering uses a 2048-pixel CCD-detector array. The CCD array behaves much like photographic film in that the array integrates incident photons over time. Thus, the longer the exposure, the more faint the light which can be detected. Because Raman scattering is very faint, the integration time is set for about 5 s with averaging set for 10 exposures; a single measurement takes about 50 s.

Experimental

With the instrument configured as described, a quartz cuvette containing the sample is placed in the cuvette holder. The OOIBase32 software (supplied by Ocean Optics and included with the spectrometer) produces standard UV/Vis spectral data as intensity versus wavelength in nanometers. The data are then imported into a spreadsheet program (e.g., Excel) and post-processed into the traditional form of a Raman spectrograph (i.e., Stokes-band intensity versus wave-number difference from the Rayleigh peak).



ν	cm^{-1}	I_0	$I_\parallel$	$I_\perp$	$\rho=(I_\perp/I_\parallel)$
ν_1	458.4	1928	763.0	12.0	0.016
ν_2	218	not observed			
ν_3	774.9	830.9	199.2	141.1	0.708
ν_4	328	not observed			

Figure 2. Measured Raman spectrum of CCl4 showing two of the four fundamental Stokes bands at 458 and 775 cm^{-1}. Note that one peak, normally observed at 218 cm^{-1}, is obscured by absorption of the notch filter. Another peak, normally observed at ca. 328 cm^{-1}, is not resolved. The peak observed at 1533 cm^{-1} is composed of combinations of all four of the fundamental bands [15].

Figure 2 shows a representative measured Raman spectrum for CCl_4. The positions of the Stokes bands closely match those from published sources [14, 15]. Although CCl_4 has four fundamental Raman bands, only two (n_1 and n_3) are observed in our experiment. One band (n_2) cannot be observed due to absorption by the notch filter. The other band (n_4) is not resolved. The band observed at 1533 cm^{-1} is probably a combination of the four fundamental bands, that is, $2n_3$, $(2n_1 + 2n_4)$ and $(n_1 + n_3 + n_4)$. Note the band identification nomenclature is from Herzberg; other authors use different schemes.

The depolarization ratio can be used to determine whether or not a Raman transition is symmetric. Symmetric vibrations tend to preserve the polarization of the incident light while asymmetric ones tend to scramble it. In this type of measurement, a linear polarizer is placed in front of the optical fiber of the spectrometer. A depolarization measurement is the ratio of the peak intensity of a particular Stokes band when the polarizer is rotated perpendicular to the laser light divided by the peak intensity when the polarizer is parallel to the polarized laser light. The depolarization ratio, r, indicates whether the scattered light's polarization has been preserved or destroyed. Theoretical values of this ratio are 0.25 for preservation of polarization and 0.75 for complete depolarization [15]; however, experimental results often do not match these values due to factors that include impurities in the sample, imperfect polarization of the light source, and imperfections in the optical components. As a result, we have found that a more practical rule of thumb is to assume the polarization is preserved for $r < 1/2$ and destroyed for $r > 1/2$.

It can be seen from Figure 2 that n_1 remains polarized, while band n_3 is de-polarized; this is consistent with the theoretical description [15] of CCl_4. If the polarization is destroyed by the scattering process, the vibrational mode responsible for the scattering is not symmetrical. If the polarization is conserved, the vibrational mode is symmetrical. Thus, the n_1 band corresponds to the fully symmetric stretching of the CCl_4 molecule, and the n_3 band corresponds to an asymmetric mode.

When the depolarization ratio measurement is combined with the Stokes band frequency (i.e., energy) and group theory, the structure of small molecules and bond force constants (both for stretching and bending) can be determined; however, a higher resolution instrument is likely required for these types of studies.

Figure 3 shows the results of a measurement performed with HPLC-grade water in a quartz cuvette. Three Stokes bands corresponding to the three fundamental Raman vibrational modes for the water molecule [15] are observed. The bands assigned to n_1 (3259 cm^{-1}) and n_3 (3422 cm^{-1}) are strong, but they are only 163 cm^{-1} apart. Such a separation should be resolved by our instrument with an 83 cm^{-1} resolution, but, due to hydrogen bonding in water, all the Raman bands are broadened considerably [16, 17]. Thus, these lines simply cannot be resolved, regardless of resolution.

Beyond the line broadening effects of hydrogen bonding, some researchers [17] have argued that these two bands (n_1 and n_3) are actually composed of multiple overlapping bands. Clearly, the simple model based solely upon symmetry is inadequate to explain the band structure of water; however, the overall spectrum closely matches spectra from published sources [14–17].

To investigate a larger molecule, one that does not have a Raman band near the Rayleigh peak, and one that does not exhibit hydrogen-bonding effects, anhydrous benzene was examined. ACS grade (99%) benzene was dried overnight using size 3A molecular sieves and filtered with a 2-mm polyethylene filter and syringe. Figure 4 shows the resulting Raman spectrum.

All fundamental Raman bands, except for the weakest (n_3), can be clearly seen and correspond to known spectra [14, 18]. Note that the bands corresponding to the symmetric vibrations, n_1 (symmetric C–H

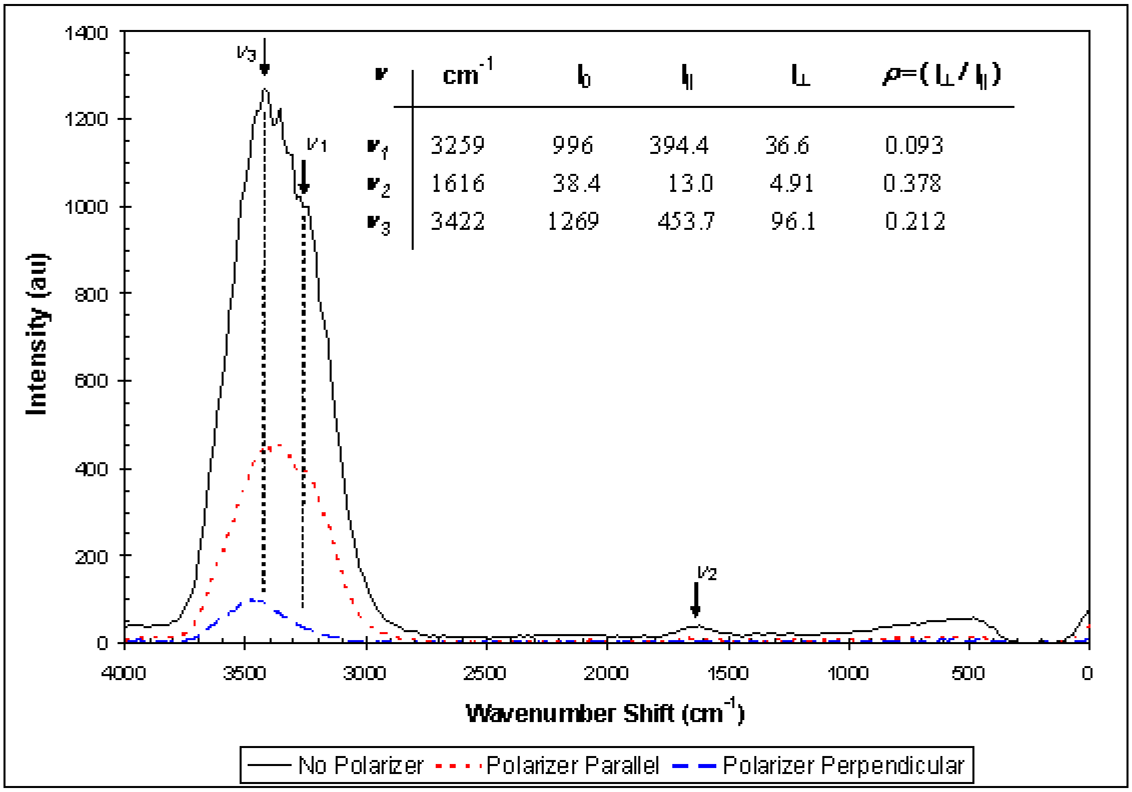


Figure 3. Measured Raman spectrum of water. The (normally very weak) Stokes band at 1616 cm^{-1} can just barely be detected. Bands n_1 and n_3 are assigned based upon ref. 15.

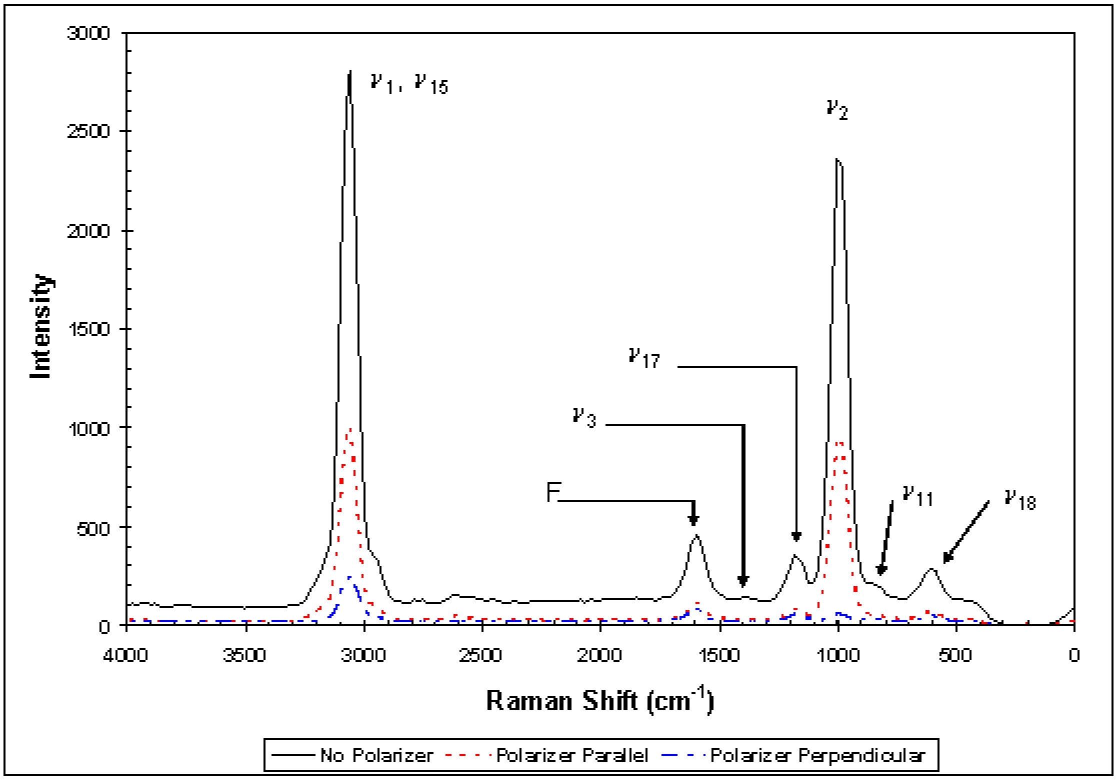


Figure 4. Measured Raman spectrum of benzene. The seven active Raman bands and the Fermi resonance [18] band (labeled F, 1597 cm^{-1}) are observed. The bands labeled n_1 (3059 cm^{-1}, r = 0.247) and n_2 (991cm^{-1}, r = 0.067) are from symmetric vibrations as indicated by their low depolarization ratios. The n_{15} band is also symmetric but lies too close to n_1 to be resolved. The n_3 (1350 cm^{-1}) and n_{11} (850 cm^{-1}) bands are only just discernable above the baseline. The bands labeled n_{17} (1183 cm^{-1}, r = 0.713) and n_{18} (607 cm^{-1}, r = 0.715) are due to asymmetric vibrational modes. The band labeling is consistent with that in ref. 15.

stretch) and n_2 (ring-breathing), can clearly be determined as such via measurement of the depolarization ratios. All other modes are asymmetric and, therefore, largely depolarize the incident radiation, resulting in roughly equal attenuation regardless of polarizer orientation.

As discussed previously, several authors have demonstrated the use of other color lasers with PC-based spectrometers. It is difficult to compare the relative performance of the instruments because different optical configurations and experimental conditions have been used. A shorter wavelength (l) laser, such as the one used in the present work, may offer some advantages because of the l^{-4} wavelength dependence of scattering intensity. DeGraff and colleagues [9] investigated the use of several lasers in addition to the 532-nm laser with which most of their measurements were acquired; however, a violet diode laser such as the one used in the present work was not evaluated, most likely because these types of lasers and 405-nm notch filters were not commonly available at the time of that investigation. An indication that the violet diode laser gives somewhat better (or at least similar performance) compared to longer wavelengths sources, such as the 532-nm laser used in reference 9, is that integration times of between 15 and 60 s were used in that work. In the present studies, an integration time of 5 s was used (although 10 scans were acquired and averaged by the computer).

It is clear that a variety of low-cost lasers will perform satisfactorily for classroom Raman spectroscopy experiments. The choice ultimately depends on cost and availability. The inevitable commercialization of violet diode lasers for data storage purposes should eventually drive their costs down below that of other low-cost lasers and make them most attractive for Raman spectroscopy.

Conclusion

A low-cost, diode-laser-based Raman spectrometer for the classroom has been demonstrated. The instrument does not have the performance of a research-grade instrument, but it can be used to extract Stokes bands for compounds such as carbon tetrachloride, water, or benzene and make depolarization ratio measurements. The open architecture of the spectrometer gives the student greater insight into Raman spectrometry than can be achieved in "dry laboratory" exercises. The low cost and simplicity of construction of the instrument offers a practical alternative for the demonstration of Raman spectroscopy in the classroom. The cost of violet diode lasers is expected to drop dramatically in the near future, and it should be possible for any college or high school laboratory with a PC-based spectrometer to demonstrate Raman spectroscopy.

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