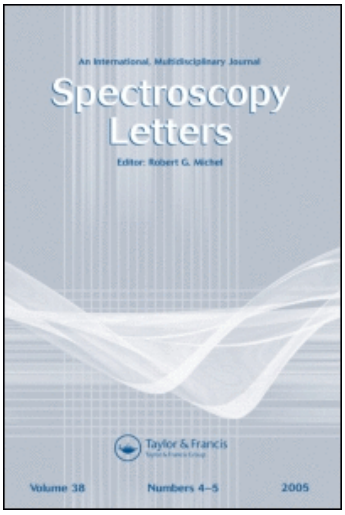

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Hudspeth, Evan D. , Cleveland, Danielle , Batchler, Kathleen L. , Nguyen, Phuong A. , Feaser, Tracey L. , Quattrochi, Lauren E. , Morenz, Jesse , Balram, Shrimati A. , Michel, Robert G. , Zhou, Jack X. and Lombardi, Daniel(2006) 'Teaching Raman Spectroscopy in Both the Undergraduate Classroom and the Laboratory with a Portable Raman Instrument', Spectroscopy Letters, 39: 1, 99 — 115
To link to this Article: DOI: 10.1080/00387010500434297
URL: http://dx.doi.org/10.1080/00387010500434297

Spectroscopy Letters, 39: 99–115, 2006

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010500434297

Teaching Raman Spectroscopy in Both the Undergraduate Classroom and the Laboratory with a Portable Raman Instrument

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Abstract: We have evaluated a small portable Raman instrument on loan from B&W Tek, Inc., and have determined that it can successfully be used in the classroom both as a visual aid for teaching the fundamentals of Raman spectroscopy and for a variety of undergraduate experiments as a normal component of an instrumental analysis class. Having portable Raman instrumentation would allow the instructor to demonstrate the principles of Raman spectroscopy, as well as the concepts of calibration curves, blank subtraction, detection limits, and regression analysis. Both qualitative and quantitative types of experiments were done for solid Tylenol tablets, aqueous solutions of isopropyl alcohol, dimethyl sulfoxide, methanol, and ethanol, and gaseous CO_2 and N_2O_4. Additionally, surface-enhanced resonance Raman spectra of Rhodamine 6G were obtained using a chloride ion–activated silver colloid. Spectra from the B&W Tek, Inc., instrument were comparable to literature Raman spectra.

Keywords: Calibration curve, portable Raman instrumentation, qualitative and quantitative analysis, teaching Raman spectroscopy, undergraduate experiments

Received 8 March 2005, Accepted 11 April 2005

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INTRODUCTION

Over the past decade, new technology, including sensitive low-noise CCD detectors, stable, high-power, solid-state diode lasers, efficient holographic notch filters, and fiber-coupled, filtered probes,[1–6] has vastly improved Raman spectroscopic instrumentation. These advances have allowed once expensive and laboratory-bound instruments to become low-cost, compact, portable, and rugged instruments that can be used for on-site, *in situ*, real-time monitoring to obtain both qualitative and quantitative analyses of a variety of samples. We have evaluated a small portable Raman instrument on loan from B&W Tek, Inc., to determine its suitability for an assortment of undergraduate experiments that we would like to have as a normal component of our instrumental analysis class. Portable Raman instrumentation in the classroom would provide an excellent visual aid for students and allow the instructor not only to demonstrate many principles of Raman spectroscopy and instrumentation, but also to illustrate the concepts of calibration curves, blank subtraction, detection limits, and regression analysis. These concepts are well established in undergraduate textbooks on analytical chemistry.[7–9] In order to explore the feasibility of a set of student experiments to be used in our analytical chemistry laboratory, analyses were conducted on solid Tylenol tablets, aqueous solutions of isopropyl alcohol, dimethyl sulfoxide, methanol, and ethanol, and gaseous CO_2 and N_2O_4. Additionally, surface-enhanced resonance Raman spectra (SERRS) of Rhodamine 6G were obtained using a chloride-ion-activated silver colloid.[10–13]

INSTRUCTION

The integration of portable instrumentation into the curriculum has the potential to allow an instructor to effectively teach the various principles of Raman spectroscopy including the history, theory, and instrumentation, as well to as visually demonstrate the collection and interpretation of Raman spectra in real-time. Until recently, the cost of Raman instrumentation had precluded the use of Raman spectroscopy in undergraduate classrooms and laboratories. However, several publications have shown an increase in the effort to introduce inexpensive, modular Raman instrumentation to the classroom.[14–18]

Mechanisms and History of Raman Scattering

The mechanism and basic energy transition diagrams for Raman scattering have been covered at length in various undergraduate analytical chemistry and instrumental analysis texts.[1,19,20] Briefly, an instantaneous exchange of

energy between a monochromatic light source and a molecule occurs, causing polarization of the Raman active molecule, resulting in two different types of photon scattering. The first type, Rayleigh scattering, constitutes the majority of all photon scattering. Here, the emitted photon is elastically scattered by the molecule, the incident light retains its original frequency, and no shift in wavelength from the incident photon is observed. The second type, Raman scattering, is caused by inelastic scattering of photons by the molecule, and this results in the production of a different wavelength from the incident light. Two types of energy shifts, Stokes and anti-Stokes, are possible, and these are related to the vibrational energy spacing in the extant electronic state of the molecule. The Stokes shifted light, which tends to be stronger than the anti-Stokes shifted light, was used in the current paper. Here, the incident photon deposits energy into the oscillations of the molecule, resulting in a lower photon energy, and therefore a lower frequency, being scattered. In the case of anti-Stokes scattering, the incident photon instantaneously extracts energy from the oscillations of a molecule, resulting in scattering of higher frequency light by the molecule. Because anti-Stokes scattering requires the molecule to begin in a vibrationally excited state, this type of scattering is statistically less likely than Stokes scattering. Multiple vibrational levels are involved in the initial energy exchange, resulting in multiple Stokes-shifted lines, and matching anti-Stokes shifted lines. The energy differences between the Rayleigh and Raman scattered frequencies correspond to allowed quantized bond vibrations, and therefore the wavenumbers of the Stokes and anti-Stokes shifts are direct measures of the vibrational energies of the molecule.

Indian scientist C. V. Raman first observed the Raman effect in 1928, and he was awarded the 1931 Nobel Prize in physics for his systematic exploration of the phenomenon.[1] Although research into this phenomenon continued, progress was severely hampered because the Raman-scattered light was a factor of 10^8 less intense than the Rayleigh-scattered light and was therefore very difficult to detect. However, this difficulty was considerably reduced with the introduction of intense laser light in the 1960s, because the resulting Raman-scattered light became more intense and easier to detect.

Resonance Raman spectroscopy (RRS), surface-enhanced Raman spectroscopy (SERS), and the hybrid surface-enhanced resonance Raman spectroscopy (SERRS) were developed in the 1970s, with the advent of the tunable laser, to further enhance the inherently weak Raman signal. RRS is achieved when the excitation wavelength is at or near the electronic absorption maximum of the analyte.[1] The Raman signal of a substance can be enhanced by a factor of 10^2 to 10^6 by RRS. However, the major obstacle for the RRS technique is that the Raman spectrum can be obscured by fluorescence of the analyte. SERS was first observed when Raman spectroscopy was used to analyze pyridine on the surface of a silver electrode.[21] It was found that an enhancement in the Raman signal of the pyridine occurred when the silver electrode was roughened. Although the mechanism of this

enhancement is not yet fully understood, the combination of the excitation of surface plasmons and an electromagnetic attraction between substrate and analyte are thought to be responsible. Further studies have obtained SERS spectra of molecules adsorbed onto various forms of metal surfaces including transition metal electrodes,[22,23] colloidal metal solutions,[10,24] metal island arrays,[25,26] and nanoparticle-coated filter paper.[27,28] The Raman signal of an analyte can be enhanced by a factor of 10^3 to 10^6 using SERS.[1] The introduction of SERRS combined the enhancement benefits of the use of metal surfaces in SERS with the use of resonant light in RRS to achieve larger Raman signals with reduced fluorescence interference. Interaction of the resonant incident light with the metal species is thought to provide an efficient pathway for rapid nonradiative decay, which mitigates the fluorescence pathway for deactivation of a resonantly excited molecule. In this way, the benefits of SERS are compounded by the enhancements lent by the use of resonant light (RRS) with little interference from fluorescence of the analyte.

A Raman spectrum is obtained by measuring the intensity of the scattered photons as a function of the frequency difference between the incident and scattered photons. These shifts in wavelength are effectively independent of the incident photon wavelength, because they are measured as differences, therefore, the spectra serve as "fingerprints" for the particular molecular species present. Subsequently, Raman spectroscopy can be used for both qualitative identification and quantitative determination, as well as for acquisition of structural and vibrational information on the molecule of interest.[2] Although comprehensive Raman band assignment is beyond the scope of this paper, an approach to band assignment might usefully be included in the instruction at this point.

Instrumentation

After the mechanisms, history, and various incarnations of Raman spectroscopy have been introduced, the instructor can then display and discuss the components that make up a typical portable Raman instrument, as shown in Fig. 1. Recent technological and engineering advances have improved the efficiency, durability, and availability of modular Raman instrumentation components, and continued miniaturization trends support the portability of these components for use in on-site and process applications. Improved components include high-sensitivity, low-noise, thermoelectrically (TE) cooled, red-sensitive linear-array charge-coupled device (CCD) detectors; stable, solid-state, high-power, red-emitting diode lasers; efficient holographic notch filters; high-throughput imaging spectrographs; and fiber-coupled, filtered probe-heads.[3] Here all of the hardware and software used for experimentation were generously on loan from B&W Tek, Inc., and the experimental arrangement is shown in Fig. 1. A BWT-40-OEM diode

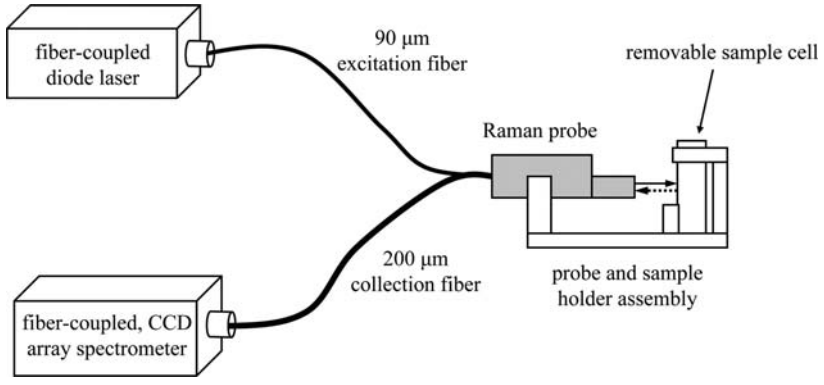

Figure 1. The experimental arrangement for acquiring Raman spectra with modular equipment. Incident radiation from a fiber-coupled 532-nm diode laser, represented by the solid arrow, is delivered to a Raman probe-head via a 90-μm excitation fiberoptic for sample irradiation. Raman scattered light from the sample, represented by the dashed arrow, is collected by the probe-head and delivered to the linear array CCD spectrometer through a 200-μm collection fiber.

pumped solid-state green laser (B&W Tek, Inc., Newark, DE, USA) provided 40 mW output power at 1.8 A and 532 nm to the sample through a 90-μm-diameter, 1.5-m-long excitation fiberoptic cable connected to an RPB-532 Raman Probe (InPhotonics, Inc., Norwood, MA, USA). The probe and standard sample cells were held in place by a lab-constructed probe and sample cell holder designed to provide reproducibility of sample cell placement and light source positioning. The Raman scattered light was then transmitted through a 200 μm-diameter, 1.5 m-long collection fiberoptic cable to the BTC110E miniature TE-cooled, fiber-coupled, 2048-element linear silicon array CCD spectrometer (B&W Tek, Inc.). This spectrometer had a 5 V DC power input at less than 1.2 A, and an operating temperature range from 0°C to 40°C. Spectrometer to computer communication was provided by an RS-232 cable, via the BW-Spec software, which was included on CD for use with a Microsoft Windows–based computer.

One of the instructional highlights of the B&W Tek portable Raman instrumentation is the ability to demonstrate and explain the use of fiberoptic cables and probe-heads. Besides making instruments more compact and rugged, these two particular advances have allowed for monitoring and analysis at distances of more than 100 m from the analyte of interest.[1,4] Both incident radiation, and the Raman scattered light, can be transmitted using fiberoptics with little or no loss via total internal reflection.[4] An internal diagram of the probe, Fig. 2, shows a bandpass filter to ensure the monochromaticity of the excitation beam, and a long-pass filter to reject the Rayleigh and anti-Stokes scattering before transmission through the collection fiber to the spectrometer.

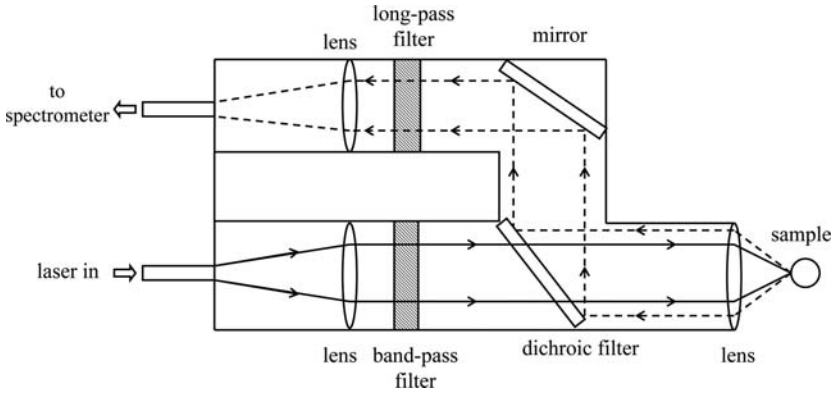

Figure 2. Layout of the InPhotonics, Inc., Raman probe-head assembly including lenses, filters, mirrors, and sample position. The solid arrows indicate the path of incident laser light, and the dashed lines indicate the path of any resultant Raman-scattered light.

EXPERIMENTAL AND DATA ANALYSIS

The ability to conduct experiments in the classroom using compact and portable instrumentation allows the instructor to illustrate the concepts of calibration curves, blank subtraction, detection limit measurements, and regression analysis. In the current paper, both qualitative molecular identification experiments and quantitative experiments are demonstrated. Here, preliminary experiments were conducted on solid Tylenol tablets, aqueous solutions of isopropyl alcohol, dimethyl sulfoxide, methanol, and ethanol, and gaseous CO_2 and N_2O_4. Additionally, surface-enhanced resonance Raman (SERRS) spectra of Rhodamine 6G were obtained using a chloride-activated silver colloid.[10–13]

For all experiments, a sample blank was recorded and automatically subtracted from the Raman signal of the analyte using the BW-Spec software. It should be noted that the raw spectral data provided by the spectrometer can be displayed in either wavelength (nm) or wavenumber (cm^{-1}), but this output has not been subtracted from the excitation wavelength to display the Raman shift. However, the BW-Spec software is conveniently capable of exporting the spectra to an external spreadsheet for further manipulation and analysis. Here, Microsoft Excel was used to determine the Raman shift. This would be a good time to indicate to students that units of cm^{-1} are directly proportional to energy and therefore proportional to the vibrational energy of a molecule.

Solid Samples

A representative Raman spectrum of a solid Tylenol tablet is shown in Fig. 3. The transparent outer coating of the tablet did not appear to interfere with the

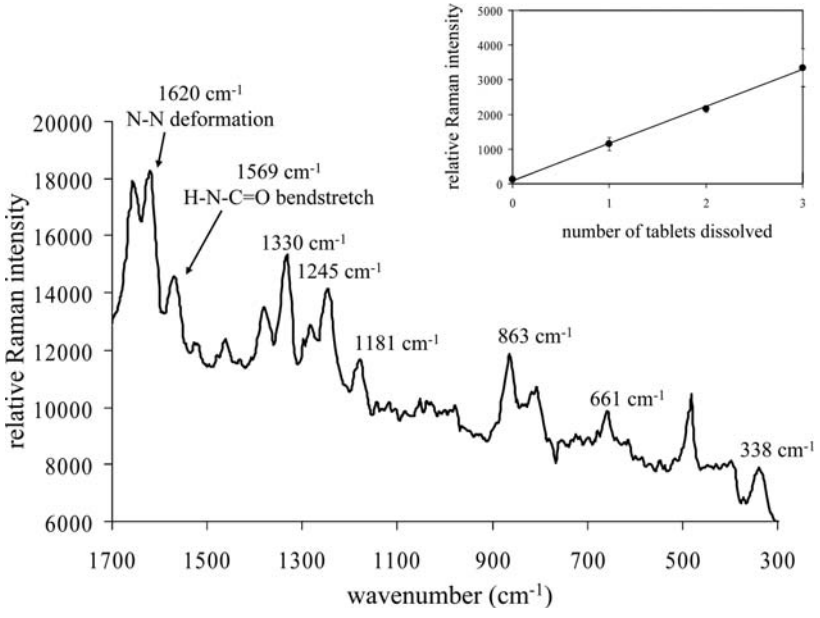

Figure 3. Raman spectrum of a solid Tylenol tablet. Labeled Raman shift values were compared to known literature values for acetaminophen. The inset shows a calibration curve for 0–3 tablets of Tylenol partially dissolved in 5% hydrochloric acid.

Raman signal when using a relatively short integration time of 10-s. An almost identical spectrum (not shown) was obtained using a 40-s integration time by first crushing the tablet into a powder before placing it into the sample cell. The spectrum and labeled peaks were compared to literature values for acetaminophen.[29,30] The inset of Fig. 3 demonstrates that a calibration curve for 0–3 Tylenol tablets partially dissolved in 20 mL hydrochloric acid (5% v/v), to mimic stomach contents, can be created. A spatula and vigorous stirring were used to break up the tablets until each solution had a milky-white appearance with small particles of the tablets suspended in the solution. Each solution was scanned three times with a 40-s integration time, and for each solution, the Raman signal intensity was recorded at $1657\,cm^{-1}$. Using these data, Excel, and procedures explained in undergraduate analytical textbooks,[7–9] a best fit line was determined. The limit of detection was found to be 0.1 tablets.

Aqueous Solutions of Organic Liquids

Similarly, Raman spectra and aqueous calibration curves were obtained for solutions of dimethyl sulfoxide (DMSO), isopropyl alcohol, methanol, and

Table 1. Raman spectroscopy of aqueous solutions of organic liquids

Analyte	Spectrometer integration time (s)	Raman shift used for calibration (cm^{-1})	Limit of detection (% v/v)	References
Dimethyl sulfoxide	20	1045	0.2	[29,31,32]
Isopropyl alcohol	40	2881	0.2	[29,33]
Methanol	40	2863	1.3	[29,35]
Ethanol	20	2856	0.5	[29,34]

ethanol. Aqueous calibration curves were created using the mean intensity of a prominent Raman shift in each spectrum. Detection limits for each analyte were also determined. Experimental details for each analyte are given in Table 1, and an example of a spectrum and calibration curve obtained for DMSO is presented in Fig. 4. The linearity of each calibration curve was found to be dependent on the integration time chosen for the analyte of interest. Initially, a 40-s integration time was used for each calibration standard, but both DMSO and ethanol solutions with concentrations above 70% v/v were found to saturate the CCD. This was resolved by shortening

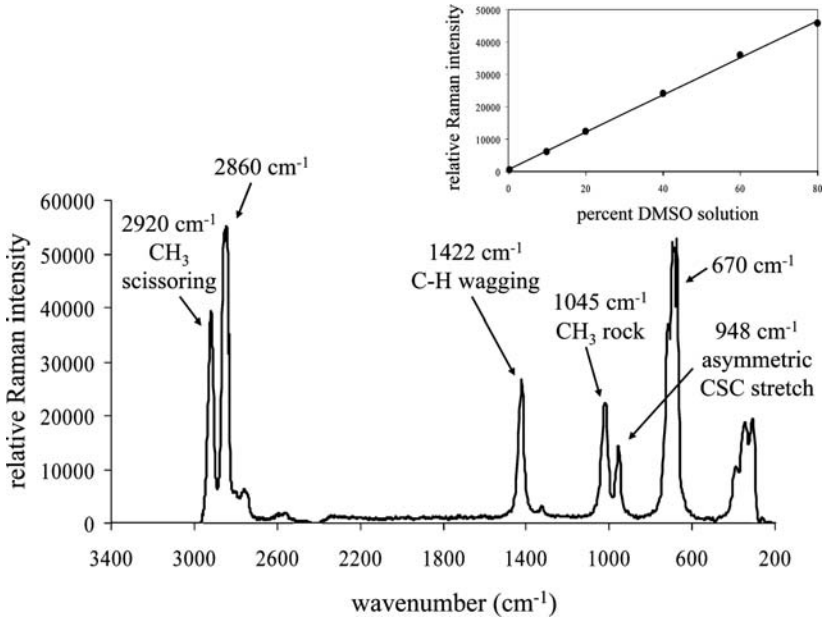

Figure 4. Raman spectrum of dimethyl sulfoxide. The inset shows a calibration curve of aqueous solutions ranging in concentration from 0% to 80% dimethyl sulfoxide by volume.

the integration time to 20-s for these two analytes. The observed and labeled Raman shifts for each analyte were found to be comparable to literature values.[29,31–35] The range and limit of detection for each analyte was in agreement with typical analyte concentrations in Raman spectroscopy.[35–37]

As previously mentioned, a laboratory-constructed probe and sample cell holder was used to improve the reproducibility of the placement of the sample cell and positioning of the light source. Random errors were studied using variance analysis, which has been covered at length in undergraduate analytical textbooks.[7,8,38] An examination of the standard deviation of the signal among multiple aliquots of a particular lab sample represents the portion of the total variance that can be ascribed to sample heterogeneity. This was accomplished by obtaining multiple scans of the same solution and represents imprecision due to instrumental errors. The remainder of the total variance, or the standard deviation in the signal among single aliquots from multiple lab samples of the same concentration, can be attributed to irreproducibility in solution preparation. Here, three calibration solutions of each concentration were prepared to measure this portion of the total variance. It was determined that approximately 8% of the total variance was of instrumental origin, while 92% of the imprecision was due to irreproducibility in the replicates, probably as a result of human error during the preparation of the calibration standards.

Students will appreciate the diverse potential of Raman spectroscopy when analyzing the above four aqueous organic solutions, and additional experiments could supplement their understanding of the instrument components, analytical concepts, and real-world applications possible with the portable Raman instrument. For example, students could determine the concentrations of two or more organic components in an unknown solution, as done by Vickers et al. for mixtures of toluene and cyclohexane.[15] Additionally, students could use the results of the calibration curve for ethanol in the current paper to determine the concentration of ethanol in various alcoholic beverages, as done by Sanford et al.[37] Although Raman band assignment is beyond the scope of this paper, the instructor may find it useful to discuss assignment principles or band origins. For example, students could correlate the molecular structure and functional groups of each organic liquid with the presence or absence of Raman bands in each corresponding spectrum.

Gas-Phase Analytes

The gas-phase equilibrium between NO_2 and N_2O_4 was chosen for its significance to environmental concerns, as the brownish-colored NO_2 is a primary ingredient of smog. At standard temperature and pressure, the two gases are at equilibrium, with the colorless gas N_2O_4 disassociating to form NO_2 molecules. It is well-known that gas-phase analytes are inherently more difficult to detect with spectroscopic instruments, because the molecules of

interest in the gas-phase are less compressed and therefore more dilute than in the liquid and solid phases. Additionally, Dyer and Hendra have suggested that it is difficult to detect gas-phase NO_2/N_2O_4 using UV-visible excitation due to the fluorescence of NO_2.[39] At this point, the instructor may find it appropriate to explain how near-infrared lasers have been used successfully with Raman instrumentation to decrease fluorescence of analytes, as discussed in greater detail in Refs.[1–5]. For this experiment, a standard gas-phase sample cell with a 5-cm pathlength was used and held in place using a clamp. A 30-s integration time was found to give the best results. Shorter integration times failed to generate detectable peaks, whereas greater integration times resulted in fluorescence interference that effectively drowned out the peaks of interest. A 30-s scan of the evacuated gas cell was used as a blank. The gas cell was then filled with NO_2/N_2O_4 from a stock cylinder until the familiar brownish color was clearly visible in the cell, at which point the cell was quickly stoppered. The Raman spectrum, Fig. 5, was compared and matched to the spectrum and prominent peaks discussed in Ref.[39]. This experiment demonstrated that both gases are present in the sample cell and are detectable using the B&W Tek, Inc., instrument with a visible 532-nm laser.

Carbon dioxide was chosen as a second gas-phase analyte due to the familiarity of students with the gas in the environment, biological life cycles, and common commercial uses. Here, a 50-s integration time was found to give the

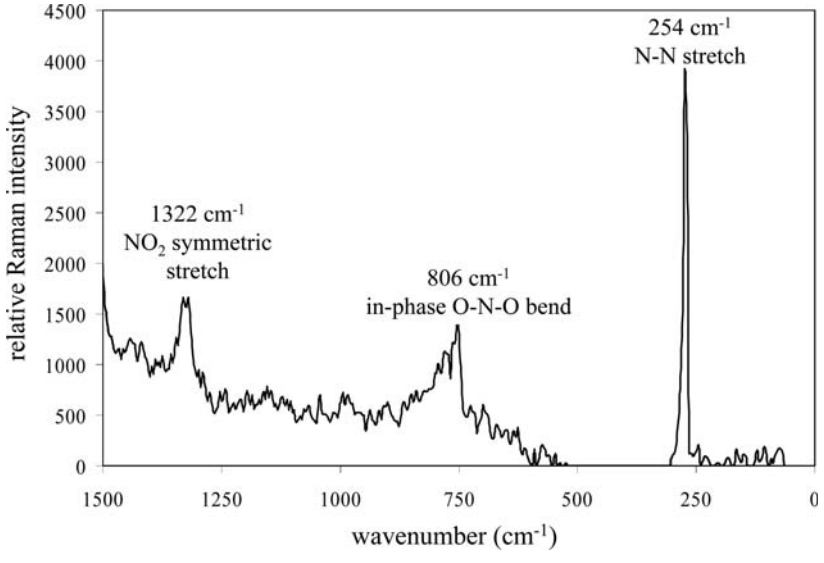

Figure 5. Raman spectrum of the gas-phase equilibrium between NO_2 and N_2O_4. Labeled Raman shift values were compared with known literature values for a mixture containing both gases.

best results. As previously described, an evacuated gas cell was used for the dark scan. Then, small pieces of dry ice were placed in the bottom of the gas sample cell. The gas cell was positioned so that the laser beam was approximately 1 cm above the solid dry ice. The cell was stoppered to allow the concentration of carbon dioxide to increase, and a 50-s scan was taken. As soon as each scan was complete, the stopper was removed to release the buildup of pressure in the sample cell. The Raman spectrum of gas-phase CO_2 (not shown) was matched to the spectra and characteristic peaks obtained and discussed in Ref.[40].

Surface-Enhanced Resonance Raman Spectroscopy

An excellent candidate for the demonstration of the SERRS and RRS techniques is Rhodamine 6G (R6G). This cationic dye is associated with a chloride ion and has its absorption maximum at 524-nm, which makes it suitable for RRS with a 532-nm laser.[12] The silver colloid used in these experiments was prepared by the standard citrate reduction method described by Lee and Meisel.[10] The colloid was carefully stored out of the light and prepared freshly each week.[10,11]

Growth of the SERRS Signal as a Function of Time

A SERRS signal was observed for R6G once the dye had adsorbed to active sites on the silver particles suspended in the colloid. In the current paper, the required active sites on the silver particles were created by the interaction between the silver and an activating chloride anion,[13] which was delivered by the addition of 0.6 mL of a 1×10^{-2} M aqueous solution of NaCl to the silver colloid prior to adding the analyte. This colloid-anion mixture was allowed to activate for 5 min before addition of a 10 μL aliquot of a 3×10^{-8} M solution of R6G. Once the R6G was added, the adsorption of the dye molecule to the active sites of the colloid was tracked by monitoring the growth of the SERRS signal size as a function of time, and the results are shown in Fig. 6. Here, a 10-s integration time was used, and scans of the R6G complex were obtained 1, 5, 10, and 60 min after the addition of the dye to the activated colloid. The sample cell was taken out of the laser beam in between scans to minimize photolability of the R6G-Ag complex.[13] Previously, this growth process had been found to require more than 1 hr to allow complete adsorption of the dye to the activated silver particles,[13] and the results in the current paper support that observation. By copying each spectrum from the BW-SPEC program to the clipboard and pasting it into Microsoft Power-Point, or similar software, a movie depicting the growth of the SERRS signal as a function of time could be made. An alternate presentation, also pedagogically useful, would be an overlay of time intervals of the spectra, as done in Fig. 6, to demonstrate the evolution of the SERRS signal.

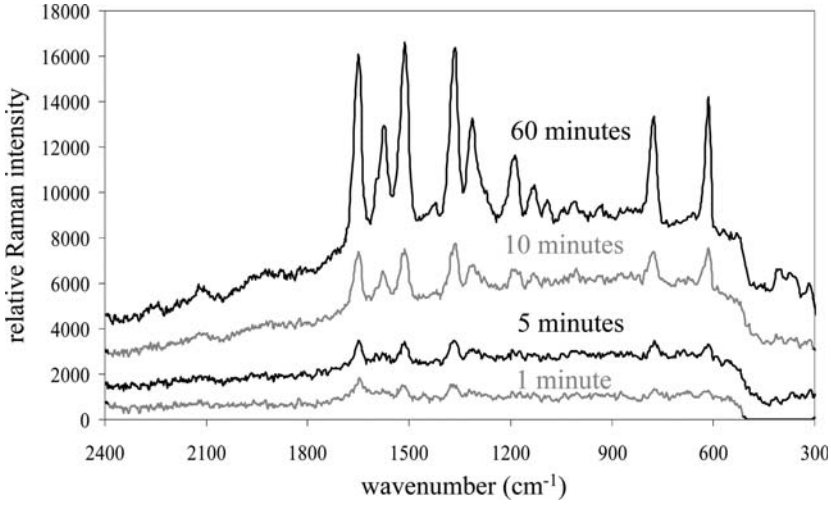

Figure 6. Evolution in time of the surface-enhanced resonance Raman spectrum of 10^{-8} M Rhodamine 6G. Spectra were taken 1, 5, 10, and 60 min after addition of 10^{-8} M Rhodamine 6G to the chloride-ion-activated silver colloid.

Comparison of RRS and SERRS

In order to observe the enhancement provided by the SERRS technique compared with the RRS technique, an RRS spectrum of a 3×10^{-8} M aqueous solution of R6G was first obtained using a 10-s integration time. As shown in Fig. 7, the RRS spectrum was completely obscured by a broad fluorescence peak across the entire detection range. A SERRS spectrum of R6G was then obtained using the same 10-s integration period. As previously described, the colloid-chloride-R6G mixture was allowed to sit for 1 hr to allow the R6G to fully adsorb onto the activated silver particles. The observed SERRS spectrum, Fig. 7, and peaks in the boxed area were compared and matched to peaks discussed in the literature for R6G.[11,13,41] The extent of the quenching of fluorescence provided by the addition of silver particles is evident upon comparison of the RRS and SERRS spectra in Fig. 7. This indicates that SERRS can be a very powerful technique for detection of suitable trace analytes.

Effect of the Concentration of the Activating Agent on SERRS Signals

The enhancement of the SERRS signal for R6G has been shown to be dependent on the amount of activating chloride ions present in the sample.[12,42] It has been postulated that the presence of the anion assists in the generation of electrostatic interaction for binding between R6G and the silver particles, possibly through induced aggregation of the colloid, or that

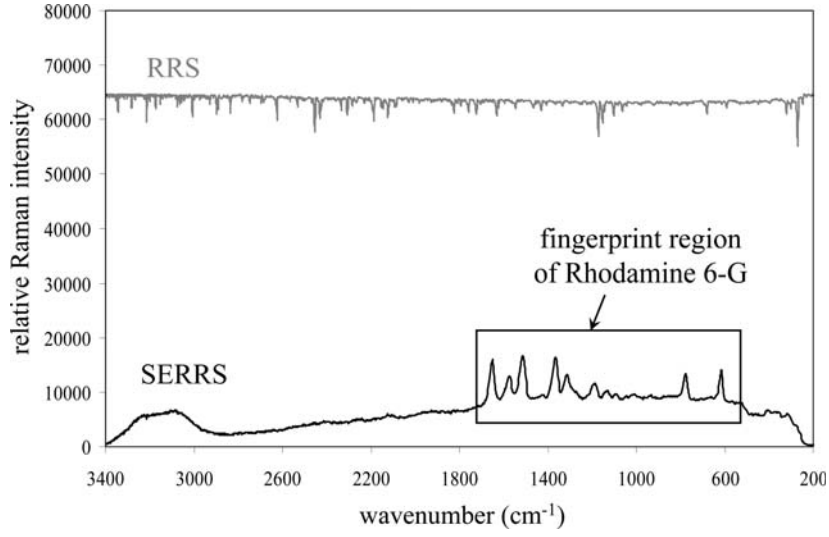

Figure 7. Comparison of signals from resonance Raman and surface-enhanced resonance Raman spectroscopic techniques for 10^{-8} M Rhodamine 6G. See text for details.

it contributes to overall enhancement through increased charge transfer.[42] Here, the concentration of the aqueous NaCl activating solution was varied and produced the results shown in Fig. 8. As previously described, following the addition of each concentration of chloride, the anion-colloid-dye mixture was allowed to sit for 1 hr to allow the adsorption process to

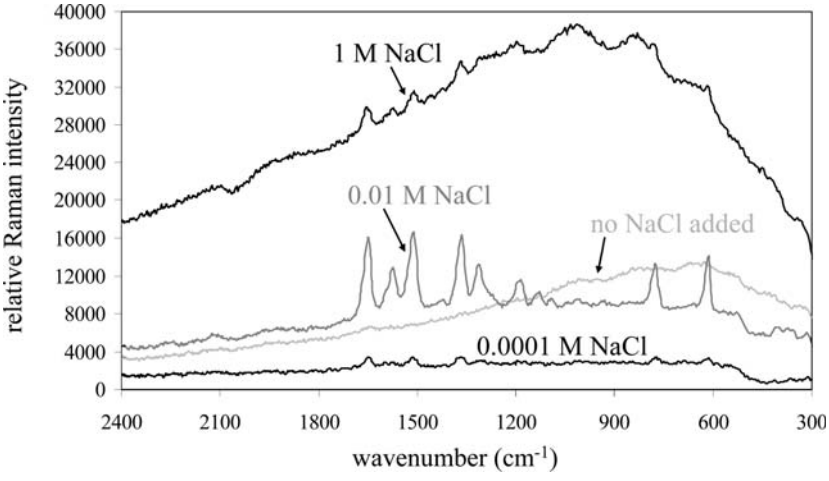

Figure 8. Effect of the concentration of the chloride ion on the surface-enhanced resonance Raman spectrum of 10^{-8} M Rhodamine 6G. See text for details.

fully occur, and the same 10-s integration time was used for these experiments. In the first trial, no aqueous NaCl was added to the sample cell. Although the fluorescence present in the RRS spectrum, Fig. 7, was considerably reduced, the well-defined peaks of the 0.01 M chloride-ion-activated SERRS signal, previously shown in Fig. 6 and overlaid in Fig. 8, were absent when the silver colloid was not treated with activating agent. In another experiment, a 10-μL aliquot of 1×10^{-4} M aqueous solution of NaCl was used. The result, shown in Fig. 8, was similar to the spectrum with no chloride ions added; however, small R6G peaks were evident. A chloride ion deficiency is thought to reduce the number of active sites available for interaction with the R6G molecules, and consequently, the signal enhancement provided by SERRS was severely reduced under these conditions. For the final experiment, a 1 M aqueous solution of NaCl was used to determine the effect of using excess activating agent, and these results are also shown in Fig. 8. Here, while the fluorescence was again reduced in comparison with the RRS spectrum (Fig. 7), and the Raman peaks were slightly more defined than those obtained under chloride-deficient conditions, the Raman peaks were not as intense as when the ideal chloride concentration (1×10^{-2} M NaCl) was used. Li et al. obtained similar results, noting that after reaching a maximum SERS signal enhancement, a chloride ion quenching effect occurred.[12] The authors postulated that the precipitation of silver chloride from solution had decreased the SERS signal intensity at increased chloride concentrations.

CONCLUSION

Portable Raman instrument components, including fiberoptic cables, probeheads, miniature diodes, and TE-cooled CCDs, are relatively inexpensive and allow Raman spectroscopy to be introduced easily into the undergraduate classroom and laboratory. An abundance of pedagogical research suggests that students learn better and retain knowledge longer when provided with visual aids or models. Ormrod suggested that the supplementation of verbal explanations with visual aids should work to promote more effective long-term memory storage and retrieval.[43] As demonstrated in the "instruction" section of this paper, this type of portable Raman instrumentation allows the instructor to not only discuss but also to easily demonstrate the fundamentals of Raman spectroscopy, which may in turn allow students to better comprehend and retain the material.

The spectra and experiments detailed in the "Experimental and Data Analysis" section of this paper could be completed over several typical undergraduate laboratory periods and have excellent pedagogical value in the illustration of concepts of Raman spectroscopy, analytical chemistry, and modern instrumentation. The qualitative and quantitative experiments described in the current paper provide students with the opportunity to

detect solid-, liquid-, and gas-phase analytes in various matrices. Students would also learn concepts of calibration curves, blank subtraction, detection limit measurements, and regression analysis from these experiments. A basic SERRS experiment is provided to demonstrate enhancement of the Raman signal by use of a chloride-activated silver colloid and to give the students a broader perspective of the experiments feasible with a portable Raman instrument. Further, each experiment presented here could easily be incorporated into more comprehensive experiments recently demonstrated in several articles using similar Raman instruments.[15,37,40] For instance, the thought that portable Raman instrumentation could be coupled with liquid chromatographic techniques[44] to enhance the specificity of detection is attractive for educational purposes.

ACKNOWLEDGMENTS

Thanks are due to the National Science Foundation's program for Research Experience for Undergraduates, at the University of Connecticut, which supported one of us (K.L.B.). In addition, thanks are due to B&W Tek, Inc., for the loan of the spectrometer, Raman probe-head (In Photonics, Inc.), and diode laser. We thank Pedro Cid-Aguero for helpful discussions and for the loan of equipment to conduct the gas-phase Raman experiments. We gratefully acknowledge the craftsmanship of machinist Dave Osier, at the University of Connecticut, for his expertise in crafting the probe and sample cell holder.

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