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Raman Spectroscopy with Helium–Neon Laser Excitation and Charge-Coupled Device Detection

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Abstract: Raman spectroscopy with He–Ne laser excitation and charge-coupled device (CCD) detection has been demonstrated for liquid pyridine and solid anthracene samples. The high quantum efficiency and essentially noiseless operation of the CCD make it ideal for use with low-intensity lasers such as the He–Ne laser. The possible utility of this experimental scheme as an alternative to Fourier transform Raman spectroscopy is discussed.

Two recent articles in this journal have reported the use of Nd:YAG near-IR laser excitation at 1064 nm with either Fourier transform[1] or conventional scanning[2] detection of Raman scattering. These approaches are powerful means of obtaining Raman spectra on samples difficult to study with common blue or green visible wavelength excitation owing to fluorescence or photodecomposition of the sample. Near-IR excitation is not likely to cause significant electronic excitation in most materials that would result in fluorescence or photodecomposition. Thus, previously difficult-to-analyze materials such as polymers and biological materials are readily amendable to study with these approaches.

However, there are disadvantages that accrue to the use of these techniques. Nd:YAG lasers are more expensive than the more conventional visible wavelength lasers (e.g., Ar^+), and the beam is not visible to the human eye, making alignment of the beam for sampling more difficult. Moreover, in cases where interferometric approaches are used, near-IR detectors (e.g., Ge or InGaAs) must be used which are noisier than conventional photodetectors in the visible region. Additionally, total rejection of the Rayleigh line remains difficult, causing a significant degradation of the ideally predicted S/N advantage of FT methods and making access to the low-frequency region extremely difficult.

One possible alternative to these methods involving Nd:YAG laser excitation might be the use of long-wavelength excitation in the far-visible/near-IR region (<1000 nm) of the spectrum from dye lasers or possibly even diode lasers with high sensitivity detection in more conventional Raman sampling arrangements. This approach would still allow the fluorescence problem encountered in the majority of difficult samples to be minimized by judicious choice of excitation wavelength. Moreover, the multiplex advantage of the FT method could still be realized if multichannel detectors were used.

Until recently, no such multichannel detector existed with the requisite sensitivity in this region of the spectrum. Intensified photodiode arrays have poor responsivity in the far-visible region of the spectrum. A possible alternative to the use of intensified photodiode arrays is the charge-coupled device (CCD) detector. These devices have only recently been introduced into analytical spectroscopy applications,[3-8] but appear to have great potential in spectroscopy because of their high sensitivity, wide spectral responsivity, and large dynamic range.

A CCD is a light-sensitive device based on MOS technology. During exposure to light, charge accumulates at each light-sensitive pixel in a two-dimensional array in proportion to the intensity of light striking the detector. The characteristics of these detectors for spectroscopy have been reviewed in detail elsewhere.[3-7] Of importance to the work reported here is the high quantum efficiencies of these devices in the far-visible/near-IR region of the spectrum (<1000 nm) and extremely low noise. Figure 1 shows the quantum efficiency of the CCD used in this work as a function of wavelength. For wavelengths between ca. 500 and 800 nm, the quantum efficiency is greater than 30%, maximizing at 43% at 750 nm. At wavelengths greater than 800 nm, the quantum efficiency drops but remains of measurable values for wavelengths up to 1000 nm. Thus, these detectors have very good responsivity in the far-visible/near-IR region of the spectrum.

This report details experiments designed to address the potential utility of this approach. A small He–Ne laser was chosen as the excitation source to demonstrate the concept. However, because of the availability of dyes in this region of the spectrum, almost any wavelength for excitation could, in principle, be accessed.

Experimental Section

Raman spectra were acquired with a system consisting of a Spex Model 1403 double monochromator with 1800 grooves/mm holographic gratings. A photomultiplier tube (RCA C31034A) was used as a detector for spectra acquired with Ar^+ laser excitation. A Thomson-CSF TH7882CDA CCD consisting of 384 columns by 576 rows of pixels, each 23 μm on a side, was used for spectra acquired with He–Ne laser excitation. This CCD contains 221 184 light-sensitive elements on this two-dimensional array. The CCD was coupled to a side exit port on the monochromator accessible with a swing-away mirror. The CCD was oriented with its long axis (576 rows) along the slit axis of the spectrometer and the short axis (384 columns) along the dispersion axis as shown in Figure 2. Although the spectral bandwidth that can be sampled in this arrangement is smaller than that measured if the CCD is rotated by 90°, the presence of a charge trap in the CCD dictates this arrangement for spectral integrity of the response to be maintained. The effects of orientation of this CCD on the spectral response are discussed in more detail elsewhere.[9] The CCD was housed in a Model CH210 camera head from Photometrics, Ltd. (Tucson, AZ) which allows operation at ca. −110 °C. The electronics and data system associated with reading out the signal from the CCD and generating the spectral images were also from Photometrics, Ltd. Further details of the experimental setup will be presented in a forthcoming publication.[9]

Spectra acquired with the CCD were obtained with 10 mW of He–Ne laser excitation at the sample. Spectra acquired with the PMT were obtained with ca. 150 mW of Ar^+ laser excitation at 514.5 nm.

Pyridine was from Burdick & Jackson Laboratories, Inc. and used as received. Anthracene was from Fisher and also used as received.

Results and Discussion

One disadvantage to the use of multichannel detectors in the far-visible region of the spectrum is that the bandwidth of the spectrometer is considerably less than in the visible region of the spectrum owing to the increase in dispersion at longer wavelengths.

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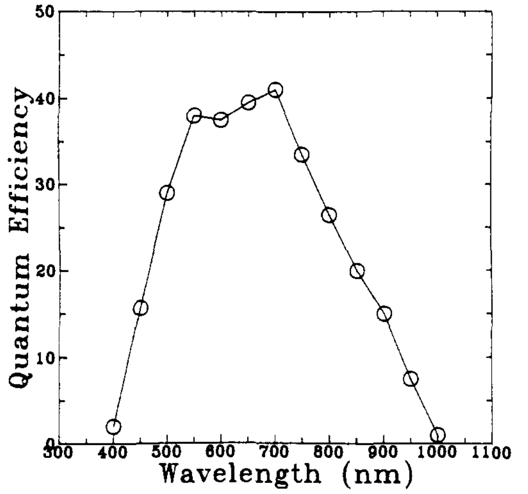

Figure 1. Quantum efficiency of Thomson-CSF 7882 CCD.

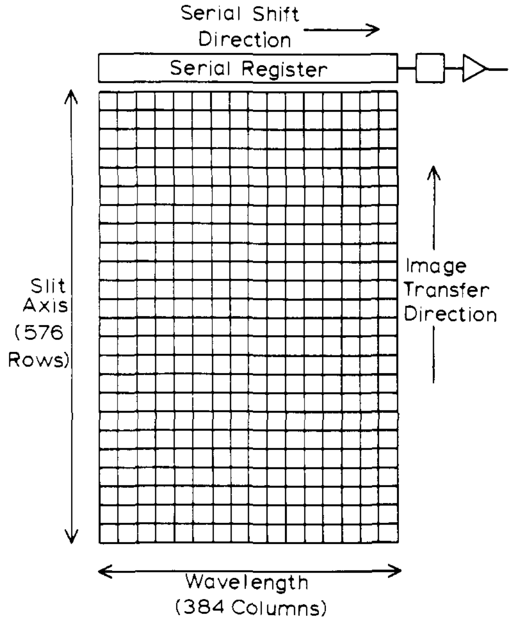

Figure 2. Schematic of the orientation of the Thompson CCD.

This fact decreases the magnitude of Fellgett's advantage relative to that which would be achieved by these detectors in the visible region of the spectrum. The reciprocal linear dispersion of the double monochromator with 1800 grooves/mm gratings used here was estimated to be ca. 5.6 cm^{-1}/mm with 632.8-nm excitation using the 760- and 790-cm^{-1} bands of a standard CCl_4 sample as compared to ca. 10 cm^{-1}/mm with 514.5-nm excitation. Thus, only ca. 50 cm^{-1} of the spectra could be observed at one time with this arrangement. Assuming a resolution increment to be 1 cm^{-1}, Fellgett's advantage for the CCD decreases from a factor of 9.4 at 514.5 nm to 7.0 at 632.8 nm. The spectra reported here were obtained in 50-cm^{-1} sections and "glued" together to give the spectral response.

The spectral bandwidth could, in principle, be increased through the use of coarser gratings. For example, based on spectral bandpass information on the double monochromator used in this work, gratings with 600 grooves/mm would provide a reciprocal linear dispersion of greater than 6 cm^{-1}/mm for wavelengths less than ca. 850 nm. Thus, sections of spectra that could be obtained with this arrangement would be greater than 50 cm^{-1} for excitation well into the far-visible region of the spectrum. The utility of this approach for far-visible excitation will be investigated in this laboratory shortly.

The quality of spectra that can be acquired with a CCD detector and low-power He-Ne laser excitation is demonstrated by the spectrum of liquid pyridine shown in Figure 3. This spectrum was obtained with only 10 mW of laser power in the frequency regions containing the strong ring breathing modes at 991 and 1030 cm^{-1} and the C-H stretching mode at 3059 cm^{-1}. Each portion of the spectrum was acquired in a total of 5 min, 2.5 min for each 50-cm^{-1} interval.

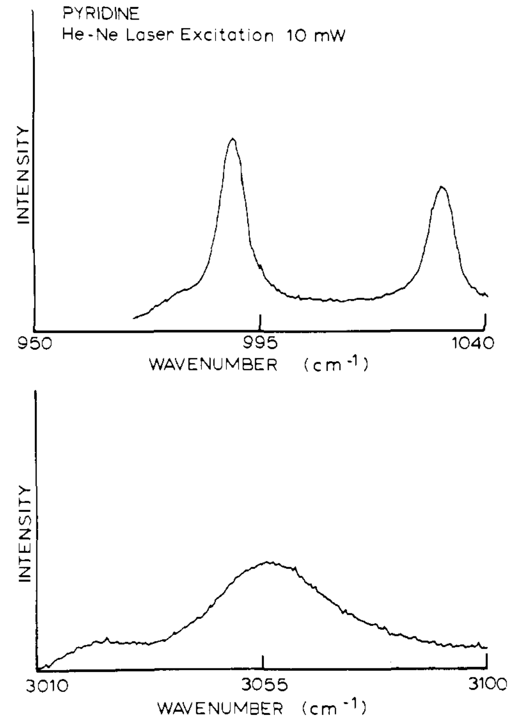

Figure 3. Raman spectrum of pyridine: 632.8-nm excitation, 10-mW power, 5-min integration time.

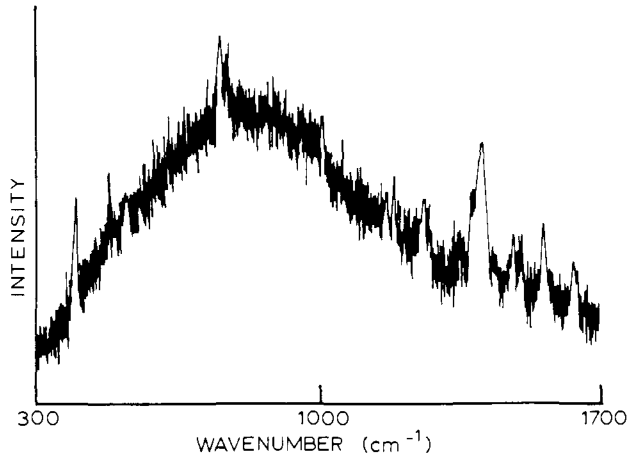

Figure 4. Raman spectrum of anthracene: 514.5-nm excitation, 150-mW power.

The S/N ratio of ca. 60 observed with this very low laser power is excellent and suggests that this approach may, in fact, be a viable alternative to the FT-Raman methods that have recently been popularized.[1,10,11] Careful consideration of the sensitivity and noise properties of these CCD detectors suggests that dye laser excitation in the far-visible or near-IR regions with CCD detection should, in theory, provide spectra of better quality than could be obtained using either PMT detection in a normal scanning arrangement or near-IR detection (e.g., Ge or InGaAs) in a FT arrangement. The basis for this superiority, at least for wavelengths less than or equal to ca. 1000 nm, lies in the high sensitivity and extremely low detector noise of the CCD (ca. 6 photoelectrons

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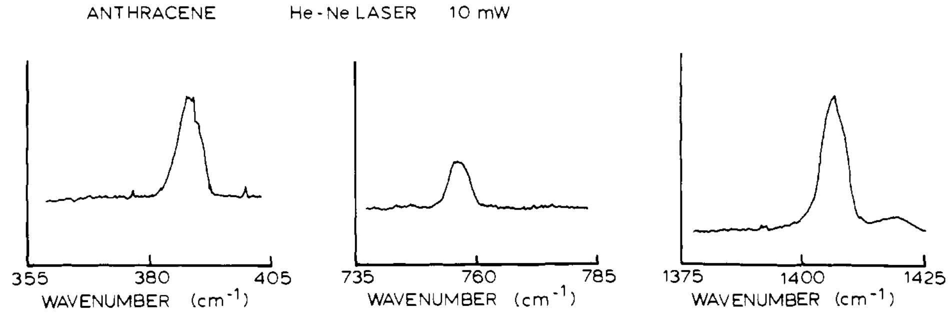

Figure 5. Raman spectrum of anthracene: 632.8-nm excitation, 10-mW power, 1-min integration time.

RMS equivalent readout noise, negligible dark current for short integration times) which provide a shot-noise limited operating environment.

A common figure of merit used to compare detector quality of IR detectors is the noise-equivalent power (NEP). This value represents the amount of light in watts (W) that must impinge on the detector in order to generate an output with a signal-to-noise ratio of unity at a given bandpass. Obviously, the smaller the value of the NEP, the better the detector. Assuming a bandwidth of 1 Hz, the PMT used in this work has a NEP of ca. 3.7×10^{-16} W/Hz$^{1/2}$ at 632.8 nm, the excitation wavelength used for these studies. Ge and InGaAs detectors used in near-IR FT-Raman experiments have NEP values on the order of 1×10^{-15} to 8×10^{-15} W/Hz$^{1/2}$, presumably at the wavelength of maximum response. These values are still larger than required for operation in a shot-noise limited environment. Thus, all FT–Raman experiments are currently performed under detector-noise limited conditions which makes the use of interferometric approaches advantageous.

For comparison, the NEP for a CCD can be evaluated using equations presented by Denton and co-workers[3] for photon flux needed for a particular S/N. It is important to note that, because the CCD is an integrating detector, the NEP can be improved by integrating the signals for longer and longer periods. This gain cannot be realized with nonintegrating detectors. At 632.8 nm where the quantum efficiency is ca. 39%, the NEP of the Thomson CCD is ca. 3.5×10^{-20} W/Hz$^{1/2}$ for a 2.5-min experiment. This integration time is similar to that used to acquire the spectrum in Figure 3. The NEP of the CCD under these conditions is ca. four orders of magnitude better than the PMT at this wavelength. For a 1-s experiment at this wavelength, the NEP only increases to 5.4×10^{-18} W/Hz$^{1/2}$. At 1050 nm where the quantum efficiency of the CCD is very low (ca. 2%), its extremely low noise characteristics still give it lower NEP values than the near-IR detectors used in FT–Raman. For example, for a 2.5-min experiment at 1050 nm, the NEP of the Thomson CCD is ca. 4.1×10^{-19} W/Hz$^{1/2}$. For a 1-s experiment, the NEP increases to 6.2×10^{-17} W/Hz$^{1/2}$, a value still two orders of magnitude better than Ge or InGaAs detectors. Thus, when used with dye laser excitation in the far-visible/near-IR regions of the spectrum, these detectors should allow spectra of comparable or better quality than those obtained with FT–Raman approaches to be obtained.

To demonstrate the utility of this approach in discriminating against fluorescence, a sample of technical grade anthracene was studied. This material usually contains impurities whose fluorescence interferes with the acquisition of the Raman spectrum with visible wavelength excitation in the blue or green regions of the spectrum. For this region, this material has been a popular one to demonstrate the power of FT–Raman methods.[1,11]

A Raman spectrum of the powdered anthracene sample contained in melting point capillary excited with 514.5-nm Ar$^+$ laser radiation is shown in Figure 4 for the frequency region between 300 and 1700 cm^{-1}. Obviously, the anthracene vibrational bands are difficult to see over the noisy fluorescence background. Figure 5 shows three regions of the Raman spectrum acquired with 10 mW of He–Ne laser excitation and CCD detection. Each portion of the spectrum was acquired in only 1 min. The S/N ratio of the anthracene peaks is very good and no evidence of fluorescence in this spectrum is observed.

In summary, the use of high-sensitivity CCD detection for Raman spectroscopy with He–Ne laser excitation has been demonstrated. The results contained in this report suggest that Raman spectroscopy with CCD detection and long-wavelength excitation may provide an alternate approach to the use of FT–Raman methods for many difficult-to-analyze samples. Further work is continuing in this laboratory to investigate the utility of these methods and will be reported at a later date.

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Registry No. Pyridine, 110-86-1; anthracene, 120-12-7.