

Multichannel Fourier Transform Raman Spectroscopy: Combining the Advantages of CCDs with Interferometry

JUN ZHAO and RICHARD L. McCREERY*

Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210

A common-path (Sagnac) interferometer combined with a charge-coupled device (CCD) was evaluated for Raman spectroscopy in the near-infrared region. A spatial interferogram of the scattered light was projected onto the face of the CCD, and a Fourier transform of the intensity vs. pixel data yielded a Raman spectrum. This multichannel Fourier transform (MCFT) technique retains several advantages of FT spectroscopy, including high throughput, excellent frequency precision, and wide spectral coverage, while also retaining the multichannel, shot-noise-limited operation of the CCD. The signal-to-noise ratio (SNR) for the MCFT system was comparable to that for a dispersive spectrometer for the same laser power and integration time, and its frequency and intensity stability were excellent. Resolution is dictated by the number of CCD pixels, and was 25 cm^{-1} for the initial MCFT system. In addition to stability, a possibly important feature of the MCFT spectrometer is its large $A\Omega$ product (*etendue*), which results in a signal which is independent of laser beam diameter over the range of $60\text{ }\mu\text{m}$ to 1.3 mm .

Index Headings: Raman spectroscopy; CCDs; Interferometry; Multichannel spectroscopy; FT-Raman.

INTRODUCTION

The introduction of FT-Raman in 1986 stimulated rapid growth in Raman applications, mainly because of the reduced fluorescence interference of many samples excited by near-infrared lasers.¹⁻⁶ FT-Raman also benefits from advantages inherent to interferometry: high collection efficiency due to the absence of slits, excellent wavelength precision, easily variable resolution and spectral coverage, and an active history of hardware and software development for FT-IR applications. Unfortunately, FT-Raman as currently implemented has restrictions on the signal-to-noise ratio (SNR) which are fundamental. Detectors for the 1- to $2\text{-}\mu\text{m}$ wavelengths of interest are noisy, so the SNR is limited by detector noise rather than signal shot noise. Even with a perfect (i.e., noiseless) detector, FT-Raman would suffer from a multiplex disadvantage, because the shot noise from all multiplexed wavelengths monitored by the detector would be detected simultaneously. The result is an SNR comparable to that for a single-channel dispersive system with equal mea-

surement time. So an FT-Raman spectrometer consisting of a Michelson interferometer and noiseless detector would lose the multiplex advantage but retain high wavelength precision and high throughput.

Dispersive Raman spectrometers with low-noise multichannel charge-coupled device (CCD) detectors avoid the limitation imposed by detector noise and maintain the multichannel advantage of array detectors.⁷⁻¹² The sensitivity of silicon-based CCDs extends to $1.1\text{ }\mu\text{m}$, permitting laser operation at $\sim 800\text{ nm}$, thus avoiding much of the fluorescence associated with visible excitation. Although dispersive CCD Raman spectrometers can yield much higher SNR than FT-Raman or scanning systems, they have some inherent limitations. The small CCD pixel width (typically $25\text{ }\mu\text{m}$) requires a small entrance slit and corresponding small collection efficiency, and increasing efficiency by increasing slit width degrades resolution. In addition, dispersive systems cannot easily vary spectral coverage, and always face a resolution vs. spectral coverage trade-off. With a finite number of pixels along the wavelength axis, one must sacrifice resolution to cover a wider spectral range. The wavelength precision of a dispersive system is not generally as good as that of an interferometer, because of backlash and thermal drift of mechanical components and alignment.

For a large number of Raman samples, the spectroscopist would like to combine the precision and throughput of FT-Raman with the low-noise and multichannel characteristics of CCDs. Sweedler et al.^{13,14} reported such a device for emission spectroscopy, and one report of a related device used for Raman scattering has appeared.¹⁵ Although a variety of optical arrangements have been reported,^{16,17} they share the common approach of generating an interferogram across the face of an array detector. An example is the "common-path" or "Sagnac" interferometer shown in Fig. 1. There is no moving mirror, but a pathlength difference between the two beams leaving the beamsplitter generates the interferogram. As noted by Okamoto et al.,¹⁶ the entrance aperture size does not affect resolution, leading to potentially high throughput. Fourier transformation of the interferogram leads to an intensity vs. wavenumber plot, which is easily presented as a Raman spectrum. Takahashi et al.¹⁵ dubbed

Received 4 January 1996; accepted 8 April 1996.

* Author to whom correspondence should be sent.

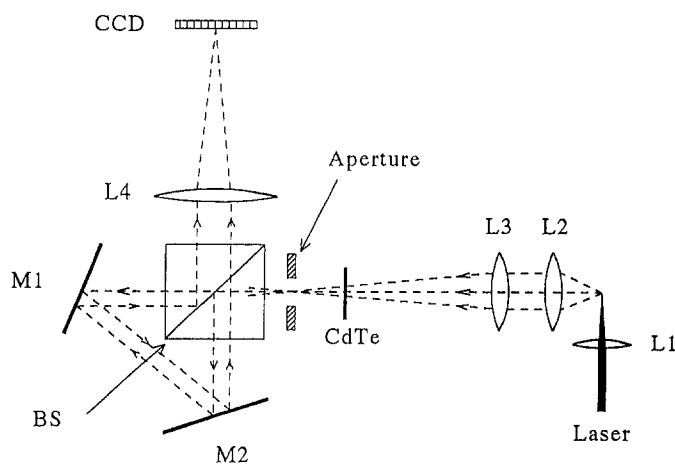


FIG. 1. Optical diagram of the common-path multichannel Fourier transform interferometer. **BS** is a cube beamsplitter, **L4** is a 470-mm-focal-length Fourier lens. **L1** (FL=50 mm) and **L2** (FL = 320 mm) improve the collection of the interferometer (about $f/10$ to about $f/1.3$).

the combination of an interferometer and CCD “multi-channel Fourier transform spectroscopy” or MCFT.

The current report explores the suitability of the common-path interferometer for Raman spectroscopy, with particular attention to wavelength precision, SNR, resolution, and practical advantages.

THEORY

The common-path interferometer has been analyzed by several groups,^{13–17} and the results are summarized here. The resolution increases as the path difference (2α) increases, up to a limit imposed by the Nyquist criterion. For an interferogram collected by an N channel linear array, the Nyquist frequency $\sigma_{\max}$ (in cm^{-1}) is given by Eq. 1, and the resolution is given by Eq. 2.^{13,16}

$$\sigma_{\max} = \frac{F}{2d\alpha} \quad (1)$$

$$\Delta\sigma = \frac{2\sigma_{\max}}{N} \quad (2)$$

where $\Delta\sigma$ is the best resolution achievable; F is the focal length of **L4** (see Fig. 1); d is the pixel width; α is the spatial separation of the two virtual images of the sample;[†] and N is the number of illuminated CCD channels.

For Raman spectroscopy with an 830-nm laser, $\sigma_{\max}$ can be set to the laser frequency or less, and $\Delta\sigma$ will be 24 cm^{-1} . Fourier transformation of the interferogram will yield a spectrum from 0 cm^{-1} to the Nyquist limit of $12,048 \text{ cm}^{-1}$, although the CCD is sensitive only to energies above 9090 cm^{-1} (1100 nm). Aliasing of wavelengths below 830 nm is possible, but these are of interest only for anti-Stokes Raman experiments. To avoid the possibility of aliasing, a CdTe absorption filter eliminated wavelengths below 850 nm, including the elastically scattered laser light.¹⁸

The sensitivity of the spectrometer depends on the

etendue ($A\Omega$ product) of the interferometer/CCD combination.^{5,7,11} The f /number of the system is determined by the focal length of lens **L4**, the interferometer optics, and the size of the beamsplitter and CCD (total area, not pixel size). Although the system shown in Fig. 1 has a relatively high f /number ($\sim f/10$), the collection aperture is very large ($\sim 11 \text{ mm}$) in comparison to a slit or CCD pixel. Even after we take beamsplitter losses into account, the $A\Omega$ product of the instrument depicted in Fig. 1 is much larger than a conventional dispersive system with a CCD. Since the 11-mm aperture is impractically large to fill directly with Raman scattered light, lens **L2** and **L3** in Fig. 1 were used to reduce the aperture to 1.5 mm and the collection angle to $f/1.3$.

EXPERIMENTAL

The optical apparatus is shown schematically in Fig. 1. The 830-nm light coming from a Ti:sapphire laser was focused onto the sample by lens **L1** [focal length (FL) = 50 mm]. The scattered light was collimated by lens **L2** (FL = 50 mm), and then focused by lens **L3** (FL = 320 mm) to form a magnified image of the sample at the entrance aperture. The aperture was 11 mm in diameter. A 3-mm-thick CdTe absorption filter was placed before the aperture to eliminate wavelengths below 850 nm.¹⁸ The common-path interferometer was composed of a beamsplitter (**BS**) and two mirrors (**M1** and **M2**). The common-path interferometer has been discussed elsewhere,^{13–17} but the **BS**, **M1**, and **M2** form a pair of identical virtual images at two points behind **M2**, which then interfere while illuminating the CCD. A CCD detector (EEV 15-11, deep depletion, 1024 channels) was placed at the focal plane of a Fourier lens **L4** (FL = 470 mm, $f/8$) to generate sharp fringes. The fringe spacing was controlled by adjusting the position and angle of **M2**.

The dispersive spectrometer used for comparison was an ISA 640 spectrograph and EEV CCD 05-10 (1152 channel) detector with $f/5.5$ collection. The laser illuminated the sample at 90° relative to the collection axis, with the beam parallel to the slit image. The beam diameter was varied as described below, by defocussing the laser with a translation stage.

RESULTS

Figure 2, trace **a**, is the raw interferogram for naphthalene illuminated by 135 mW of 832-nm laser light. The CCD was positioned to monitor the centerburst and half of the symmetric interferogram. The amplitude and dc level decrease away from the centerburst is apparently due to the uneven angular distribution of scattered intensity. Fourier transformation with no preprocessing yields the upper trace of Fig. 3. The spectrum covers the entire Raman shift range from about -100 cm^{-1} on the anti-Stokes side (determined by the Nyquist limit) to the dc frequency component at $\sim 13,000 \text{ cm}^{-1}$ on the Stokes side. In this case, the laser, anti-Stokes Raman, and Stokes Raman up to about 350 cm^{-1} are absorbed by the CdTe filter, and Raman shifts above about 2400 cm^{-1} are beyond the red cutoff of the CCD quantum efficiency curve. Spectrum 3a is an expansion of the upper trace in Fig. 3 over the useful range of 300 to 1800 cm^{-1} , still without any preprocessing. Interferogram 2b was ob-

[†] Equation 2 was derived from equations 2 and 3 of Ref. 13. However, α should be defined as the spatial separation of the two virtual images of the sample, which is related, but not equal, to the displacement defined in Ref. 13.

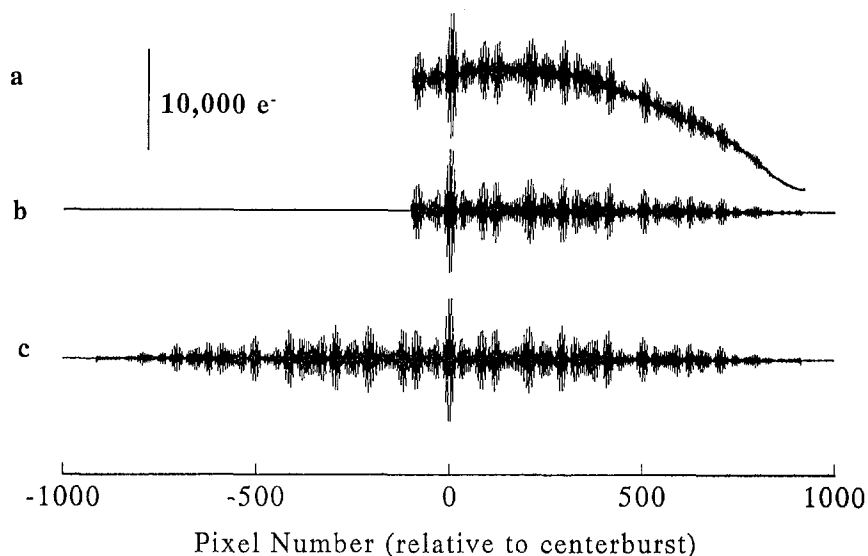


FIG. 2. Interferogram of a naphthalene pellet. (a) Raw interferogram from a 1024-channel detector, 135 mW laser power at sample, integrated for 5 s. (b) The interferogram from *a* after removal of low-frequency components and zero-filling to yield 2000 points. (c) After removal of the points left of the centerburst and reflection of the right half of the interferogram from *b*.

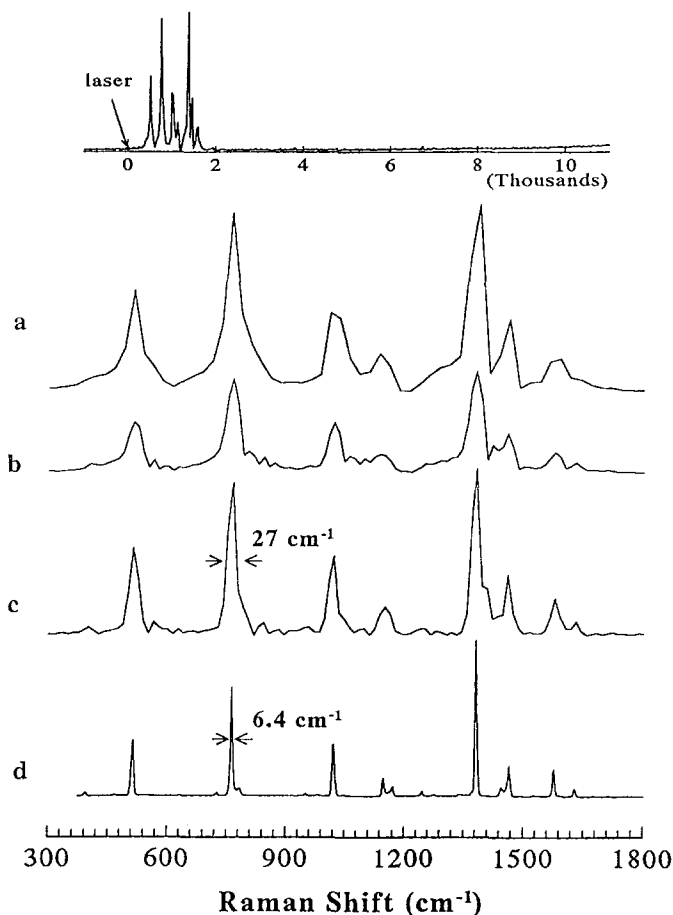


FIG. 3. Upper trace: raw FT of interferogram in Fig. 2a, plotted over entire Raman shift range. (a) Expansion of upper trace over 300–1800-cm⁻¹ range. (b) FT of Fig. 2b; (c) FT of Fig. 2c; and (d) Raman spectrum of naphthalene taken with dispersive system, with the same laser power and integration time as for the MCFT system (135 mW, 5).

tained from 2a by removal of low-frequency components and zero-filling to a total of 2000 points. Figure 3b is the FT of 2b, showing increased data density but no improvement in resolution. Figure 2c shows an interferogram obtained from 2b by the “data reflection algorithm”, which doubles the number of points by reflection about the zero-phase shift point at the centerburst.¹⁹ Its FT (Fig. 3c) shows a full width at half-maximum (FWHM) for the 764-cm⁻¹ band of naphthalene of 27 cm⁻¹. A dispersive Raman spectrum of naphthalene with the same laser power and integration time is shown in Fig. 3d; the FWHM for the same band is 6.4 cm⁻¹.

The MCFT spectra exhibit significantly poorer resolution than the dispersive spectrum, because of the limitations imposed by Eq. 2. $\sigma_{\max}$ for the conditions of Figs. 2 and 3 was 14,500 cm⁻¹, yielding a minimum $\Delta\sigma$ of 28 cm⁻¹ for the 1024-channel detector employed. Increasing N is analogous to increasing the mirror travel in a Michelson interferometer, but N is obviously limited by available CCDs. In addition, mathematical manipulation may yield some improvement in resolution,^{20,21} as well as geometric modifications which exploit the two-dimensional nature of CCDs.^{14,15} However, it is unlikely that MCFT Raman techniques will outperform most dispersive or Michelson systems with respect to resolution.

Nevertheless, the MCFT design improves the trade-off of resolution against spectral coverage or sensitivity inherent in dispersive systems. Resolution improvement with a dispersive/CCD system requires either a narrower slit (and lower throughput) or higher dispersion (and lower spectral coverage). For the MCFT system, sensitivity and throughput are not dependent on resolution, since there is no slit. Like a dispersive system, resolution in MCFT spectroscopy does depend on the number of CCD pixels (Eq. 2), but the entire spectral range is acquired regardless of the number of pixels.

A related advantage is the independence of MCFT response on laser power density. A slit-based instrument can collect only from a region whose image is as wide

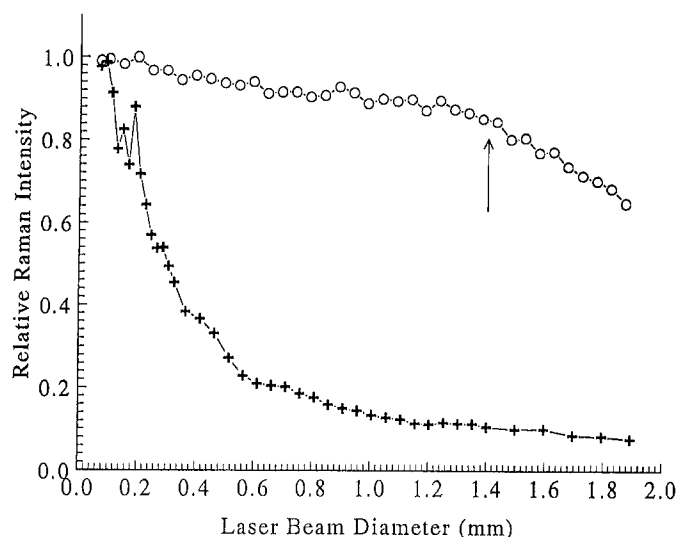


FIG. 4. Laser spot size dependence of the benzene 992-cm⁻¹ band. (○) The MCFT system; (+) the dispersive system with a 50-μm-wide slit. Arrow indicates beam diameter where the MCFT aperture was exceeded.

as the slit, often 25–50 μm for CCD systems. The MCFT has a much larger aperture (>10 mm), which is limited by the size of the beamsplitter and mirror and does not vary with resolution. Figure 4 shows the effect of laser beam focus at the sample for a dispersive system with a 50-μm slit image. In comparison to the signal strength with a tight beam focus (~60 μm), the signal decreases by 90% when the beam diameter is increased to 1.3 mm. For the MCFT spectrometer of Fig. 1, the 11-mm aperture can accept light from a 1.5-mm beam diameter at the sample, because of the collection optics L2 and L3. When the beam diameter is increased from 60 μm to about 1.3 mm, the signal decreases by only about 10%. A 1.3-mm-diameter beam is essentially unfocused and has a power density at the sample only 0.2% as large as the focused, 60-μm beam. The advantage to thermolabile or photochemically unstable materials is obvious, and results from the much larger MCFT aperture (at the sample) of 1.3 mm, compared to 50 μm for a typical slit image.

Since the band positions in the MCFT experiment are determined by rigid optical components and the CCD pixel spacing, frequency precision would be expected to be excellent. Furthermore, the absence of moving parts and the absence of a requirement for precise alignment of laser and slit should yield good intensity precision. Figure 5 is an overlay of 20 MCFT spectra of benzene obtained over an 8-h period. Zero frequency jitter was observed for these spectra, but it should be noted that the resolution of the MCFT system would detect only relatively large frequency shifts of >10 cm⁻¹. Subtraction of spectra obtained 5 h apart yielded no observable residuals (Fig. 5b), indicating the absence of observable frequency shifts. The standard deviation of the 992-cm⁻¹ peak intensity for benzene was 1.4% for the 20 spectra, but most of this deviation resulted from a nitrogen fill after the 15th spectrum. The standard deviation of 992-cm⁻¹ peak intensity for the first 15 spectra (covering 4 h) was 0.7%. A background spectrum obtained under the same conditions, but in the absence of benzene, is shown in Fig. 5c.

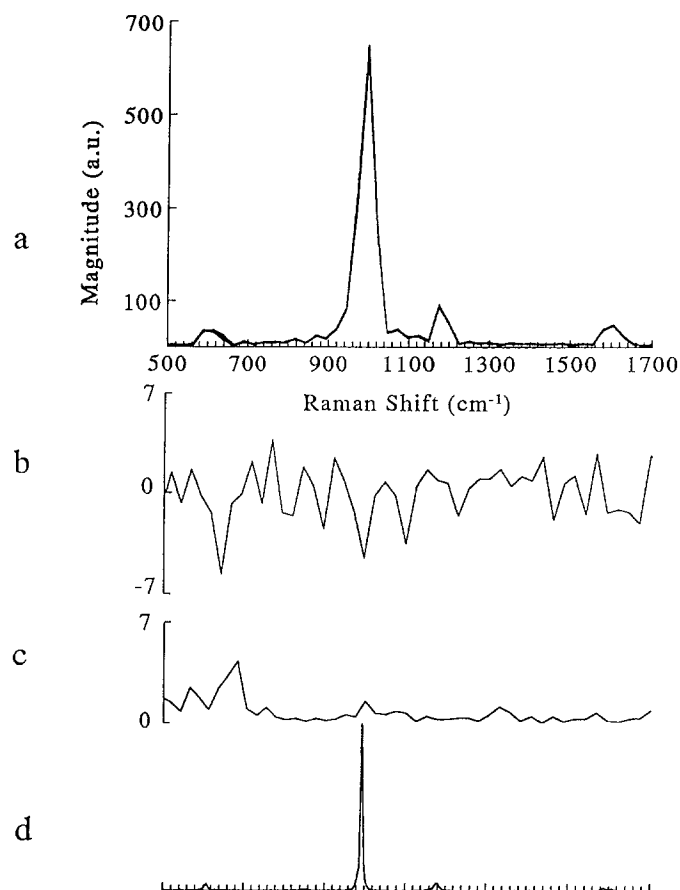


FIG. 5. Stability test of the MCFT system. (a) An overlay of 20 MCFT spectra of benzene obtained over an 8-h period, with 135-mW laser power at the sample and 10-s integration for each spectrum. (b) Subtraction of two benzene spectra obtained 5 h apart. (c) A background spectrum taken from an empty cuvette. (d) A dispersive spectrum with same laser power and integration time.

The small features observed are presumably due to periodic variations in pixel sensitivity or dark signal and to background shot noise. Notice that the baseline in the benzene spectra is very reproducible and definitely non-random. It might be due to the choice of apodization function or to periodic gain variation in the CCD.

The possibility of CCD gain nonuniformity introducing artifacts in the spectrum is a potentially important source of noise or interferences (as pointed out by one of the reviewers). Fixed pattern noise in the CCD, or "cosmic" spikes in the interferogram, will transform to artifactual peaks and baseline noise in the frequency spectrum. The severity of this issue will depend on signal and background conditions and can be reduced by pre-processing of the interferogram to calibrate pixel gain and remove "cosmic" spikes. To provide an initial assessment of the effect of cosemics on MCFT, we artificially added two single pixel spikes to the interferogram of Fig. 7a. This approach caused an increase in the standard deviation of the baseline (in the 1800- to 2000-cm⁻¹ region) of 38% with no change in peak heights. Although this is a noticeable effect which will worsen with a larger number of cosemics, it is not a major problem for weak scattering from glassy carbon and is at least partly correctable. Until the effects of CCD uniformity and cosmic contamination can be more thoroughly assessed, suffice it to

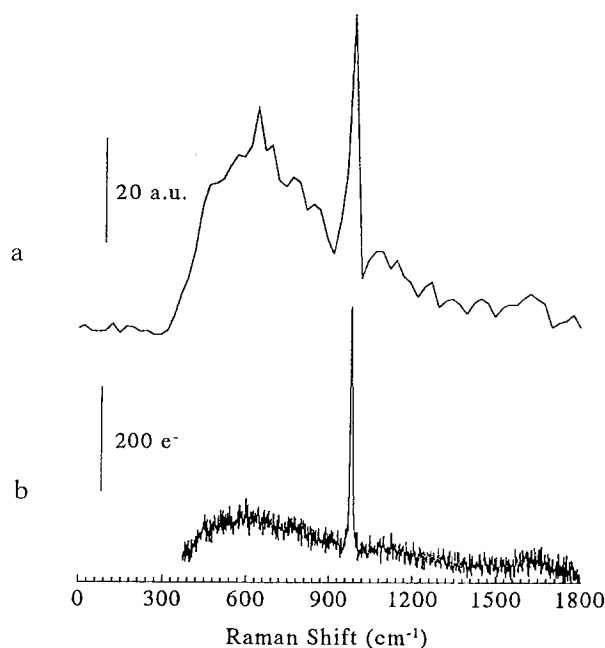


FIG. 6. Raman spectrum of a 0.2 M K_2SO_4 solution taken with the MCFT system (a) and the dispersive system (b). Experimental conditions are the same for both systems: 90° collection geometry, 135-mW laser power at sample, and 60-s integration time.

say that they will affect the noise level of the entire spectrum after Fourier transformation.

Sensitivity comparisons (in terms of $\text{e}^- \text{mW}^{-1} \text{s}^{-1}$) between dispersive and MCFT instruments cannot be made directly, since the MCFT produces a modulated intensity over all the CCD pixels, while a dispersive instrument places all the intensity of a particular band on a few pixels only. It is appropriate, however, to compare the SNR for the two methods for comparable measurement conditions. Figure 6 shows spectra of a weakly scattering solution (0.2 M K_2SO_4 in water) obtained with MCFT and dispersive instruments operating with the same laser power at 832 nm, and the same integration time. This case is an example where the SNR is determined by both analyte and background shot noise. For the dispersive system (Fig. 6b) the SNR determined as the ratio of SO_4^{2-} peak height to the standard deviation of the baseline is 37. The SNR based on the ratio of peak height to the standard deviation of the peak height is 34. For the MCFT system (Fig. 6a), the SNRs determined by the same two relationships are 51 and 39, respectively. Figure 7 shows spectra of glassy carbon²² obtained with dispersive and MCFT instruments. The SNR based on the ratio of the 1315-cm^{-1} peak height to the standard deviation of the baseline is 118 for the dispersive system, and 103 for MCFT. These examples establish that the MCFT technique has comparable SNR for weak scattering from a clear solution and an opaque solid.

DISCUSSION

The MCFT approach to obtaining Raman spectra differs from dispersive Raman and FT-Raman (with a Michelson interferometer) in both fundamental and pragmatic ways. The fundamental benefits of MCFT Raman derive from the combination of a low-noise multichannel

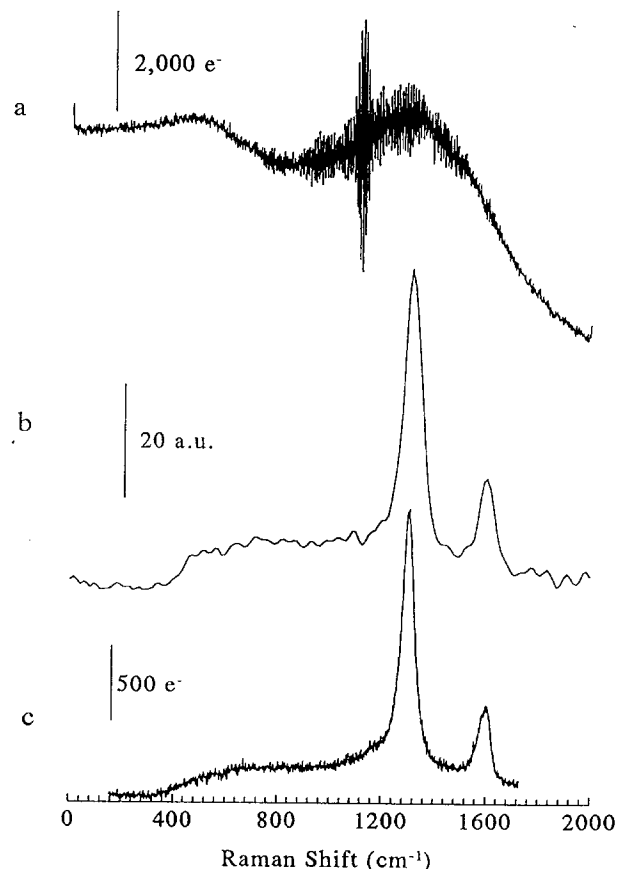


FIG. 7. Raman spectra of glassy carbon. (a) Raw interferogram; (b) FT of the raw interferogram zero-filled to 2000 data points; and (c) a spectrum taken with the dispersive system with back-scattering geometry. Experimental conditions for both systems: 180 mW laser power at sample and 120-s integration time.

detector with a spatial interferometer. The high throughput, wavelength accuracy, and stability of an interferometer are achieved, without sacrificing the low-noise characteristics of modern CCDs. This fundamental difference between MCFT and either dispersive Raman or FT-Raman leads to several useful advantages. First, the entire Stokes Raman shift range is available to the interferometer, with the upper limit in Raman shift being determined by detector sensitivity. Second, the laser line (assuming adequate filtering) may appear in the spectrum, providing a calibration of laser wavelength. Third, spectral coverage is complete (within the limits of detector response), and does not depend on sensitivity or resolution. Fourth, interferometry with no moving parts yields the excellent wavelength precision required for spectral subtraction. Fifth, the large entrance aperture (and corresponding $\Delta\Omega$ product) is usually underfilled, making the intensity much less sensitive to laser focus and position. Sixth, response is weakly dependent on beam focal size and associated power density. Much lower power densities may be employed when sample damage is a concern.

The multichannel advantage of MCFT should not be confused with the multiplex advantage of FT-Raman using a Michelson interferometer and single-channel detector. In the latter technique, all wavelengths of interest are multiplexed onto a single detector, which boosts the signal over the detector noise. In MCFT, however, N (1024

or so) low-noise detectors are monitoring all wavelengths simultaneously. A detailed SNR analysis of MCFT is currently in progress, but we expect the MCFT to have a Fellgett advantage that is similar to that of a Michelson system with a single shot-noise-limited detector. For samples with a few sharp Raman features, the SNR of an MCFT will exceed that of a dispersive system because of a higher *entendue*. For a sample with numerous Raman features or a high baseline, the SNR for an MCFT will decrease.

Accompanying the benefits of MCFT are some drawbacks, some of which are common to multiplex techniques. The Rayleigh line must be adequately filtered to avoid contributing shot noise across the interferogram. The dynamic range will generally be reduced in comparison to that of a dispersive system, possibly leading to difficulty in observing minor components or peaks. There is no spatial filtering provided by an entrance slit, so care must be taken to reduce stray light. As noted earlier, the spectral resolution is limited by the number of CCD channels, N . Although 2000×800 -pixel CCDs are available, increasing N above 2000 in a scientific-grade CCD is costly at present. It appears feasible to reduce $\Delta\sigma$ from 27 cm^{-1} to perhaps $<10 \text{ cm}^{-1}$, but a resolution of a few cm^{-1} is unlikely for the foreseeable future.

Assuming that high resolution is not a requirement, possible applications where MCFT Raman should be useful include those requiring precision and stability and those requiring a low laser power density. The combination of rigid optics without a slit and the inherent precision of interferometric frequency measurement leads to excellent reproducibility of both Raman shift and intensity. An example of an application where high sensitivity and low power density are important is the observation of monolayers on carbon surfaces, where a focused laser beam can easily thermally damage the sample.²³

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation Division of Surface and Analytical Chemistry. The authors thank Robert Messerschmidt for initial discussions on using the common-path interferometer for Raman spectroscopy, and Rio Grande Medical Technology for loan of the interferometer.

1. T. Hirschfeld and D. B. Chase, *Appl. Spectrosc.* **40**, 133 (1986).
2. D. B. Chase, *J. Am. Chem. Soc.* **108**, 7485 (1986).
3. D. B. Chase, *Anal. Chem.* **59**, 881A (1987).
4. N. Lewis, V. F. Kalasinsky, and I. W. Levin, *Anal. Chem.* **60**, 2658 (1988).
5. B. Schrader, A. Hoffman, A. Simon, and J. Sawatzki, *Vibrational Spectrosc.* **1**, 239 (1991).
6. P. Hendra, C. Jones, and G. Warnes, *FT-Raman: Instrumentation and Chemical Application* (Ellis Harwood, New York, 1991).
7. R. L. McCreery, "CCD Array Detectors for Multichannel Raman Spectroscopy", in *Charge Transfer Devices in Spectroscopy*, J. Sweedler, K. Ratzlaff, and M. Denton, Eds. (VCH, New York, 1994), pp. 227–279.
8. A. Campion and S. Perry, *Laser Focus World*, **August**, 113 (1990).
9. C. D. Newman, G. G. Bret, and R. L. McCreery, *Appl. Spectrosc.* **46**, 262 (1992).
10. M. J. Pelletier, *Appl. Spectrosc.* **44**, 1699 (1990).
11. R. L. McCreery, "Instrumentation for Dispersive Raman Spectroscopy", in *Modern Techniques in Raman Spectroscopy*, J. J. Laserna, Ed. (John Wiley and Sons, London, in press).
12. M. Fryling, C. J. Frank, and R. L. McCreery, *Appl. Spectrosc.* **47**, 1965 (1993).
13. J. Sweedler and M. B. Denton, *Appl. Spectrosc.* **43**, 1378 (1989).
14. J. Sweedler, R. Jalkian, G. Sims, and M. B. Denton, *Appl. Spectrosc.* **44**, 14 (1990).
15. S. Takahashi, J. S. Ahn, S. Asaka, and T. Kitagawa, *Appl. Spectrosc.* **47**, 863 (1993).
16. T. Okamoto, S. Kawata, and S. Minami, *Appl. Opt.* **23**, 269 (1984).
17. T. Okamoto, S. Kawata, and S. Minami, *Appl. Opt.* **24**, 4221 (1985).
18. A. Schulte, *Appl. Spectrosc.* **46**, 891 (1992).
19. M. Gorshkov and R. T. Kouves, *Anal. Chem.* **67**, 3412 (1995).
20. S. Kawata, K. Minami, and S. Minami, *Appl. Opt.* **22**, 3593 (1983).
21. K. Minami, S. Kawata, and S. Minami, *Appl. Opt.* **24**, 162 (1985).
22. Y. Wang, D. Alsmeyer, and R. L. McCreery, *Chem. Mater.* **2**, 557 (1990).
23. M. R. Kagan and R. L. McCreery, *Anal. Chem.* **66**, 4159 (1994).