

Raman Spectral Estimation via Fast Orthogonal Search

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A Fourier transform (FT) spectrometer measures the autocorrelation (interferogram) of radiation emitted from a source and estimates the optical power spectral density through application of the discrete Fourier transform (DFT) to the recorded interferogram. Although a widely used method, FT spectrometry suffers because its frequency resolution is limited to the sampling rate divided by the number of time-series data points. A large number of points are therefore required to resolve an optical spectrum properly. In this paper, it is shown that a noise-resistant technique known as fast orthogonal search (FOS) can be used to achieve accurate optical spectrum estimation. Further, it is shown that frequency accuracy comparable to the DFT applied to the full interferogram can be obtained with FOS even if the original interferogram is contaminated with noise and then reduced by a factor of up to 10 by irregularly spaced sampling. The FOS application presented here is for the estimation of Raman spectra from interferograms acquired with an FT Raman spectrometer.

Keywords: Spectrum estimation; Raman spectroscopy; irregular sampling; discrete Fourier transform

Beginning with the early work of Michelson,¹ the Fourier transform (FT) spectrometer has become an increasingly important tool for optical spectral measurement. The FT spectrometer in its most general form is constructed from a two-beam, wavefront- or amplitude-division interferometer. After division of an incident optical field of wavenumber σ_0 ($= 1/\lambda_0$) into two equi-amplitude beams, an optical path length difference, Δs , is imposed on the field of each beam on propagation through the interferometer. Interference of the two fields at the interferometer output generates an irradiance, J , that varies as a function of Δs :

$$J(\Delta s) = B(\sigma_0)\cos(2\pi\sigma_0 \Delta s) \quad (1)$$

where B is the optical power at σ_0 and

$$\Delta s = 2(n_1x_1 - n_2x_2) \quad (2)$$

where, for $i = 1$ or 2 , n_i and x_i are the refractive index and length of the i th interferometer arm, respectively. For a polychromatic field illuminating the interferometer, the interferogram, $J(\Delta s)$, and optical spectrum are a cosine Fourier transform pair:^{2,3}

$$J(\Delta s) = \int_{-\infty}^{+\infty} B(\sigma)\cos(2\pi\sigma\Delta s)d\sigma \quad (3)$$

and the interferogram is formally equivalent to the autocorrelation of the input optical field through the Wiener–Khitnitche theorem.⁴ Hence the essence of FT spectrometry is to measure the optical field autocorrelation with the interferometer and recover the optical power spectrum by application of the discrete Fourier transform (DFT).

DFT-based spectral estimation requires the interferogram to be sampled at equi-spaced intervals and at a rate at least twice

the maximum wavenumber, σ_{\max} , of the optical signal (Nyquist sampling criterion). For an N -point data record sampled at frequency $\sigma_s = 2\sigma_{\max}$, the DFT estimate will have a spectral resolution

$$\Delta\sigma = \frac{2\sigma_{\max}}{N} \quad (4)$$

and a spectral range, $\delta\sigma$, equal to σ_{\max} . The FT spectrometer resolving power R ($= \delta\sigma/\Delta\sigma$) equals $N/2$ or

$$R = \frac{\Delta s_{\max}}{\bar{\lambda}} \quad (5)$$

for a maximum optical path length difference, Δs_{\max} , and light of mean wavelength $\bar{\lambda}$.

The time required to record an N -point interferogram, T , depends on the means by which Δs is systematically varied. Most commonly, one interferometer mirror is moved relative to the other and measurement of J at specified optical path differences yields the interferogram as a time-series signal.^{5–7} If the measurement time per interferogram point equals δt , the total time to measure the interferogram is simply $T = N\delta t$. Assuming that optical shot noise dominates, the FT spectral signal-to-noise ratio (S/N) has been shown to scale as $1/\sqrt{N}$.⁸ Clearly, for an FT spectrometer based on a scanning mirror configuration, operation of the spectrometer at a high resolving power greatly increases the time to acquire an interferogram that yields an acceptable spectral S/N.

Attempts to minimize T can adversely impact on the spectral resolution, spectral range and S/N. These restrictions are alleviated with an FT spectrometer fabricated from a static two-beam interferometer and an array photosensor with N equi-spaced photosensitive elements for recording the interferogram distributed across the detector array.^{9–12} For the same S/N, the acquisition time is decreased by N (known as the multi-channel advantage⁹) compared with a scanning mirror-type FT spectrometer but with a restricted spectral resolution since the number of array photoelements is usually a small fixed number.

Given the above considerations, it would be particularly advantageous in many spectroscopic applications (e.g., imaging or time-resolved measurement) to estimate spectra from a smaller number of sample points, N , in order to minimize total measurement time, T , whilst simultaneously retaining a high spectral S/N and resolving power, R . Alternatively, for the static, two-beam interferometer, minimizing N will result in a smaller instrument or, equivalently, achieve higher resolution of the optical spectrum for a given size of instrument. A number of parametric methods have been proposed, such as the Prony and Pisarenko methods, the maximum entropy method, and various autoregressive moving average-based estimators,¹³ to obtain frequency resolutions comparable to the DFT but with a reduced number of sample points (i.e., smaller N) or, conversely, to obtain finer frequency resolution than is afforded by the DFT for the same N . However, in all of these methods the model order must be selected, and the first two additionally

require solution of a polynomial equation, which may be of high degree.

Accordingly, we demonstrate the application of a recent parametric spectral estimator, fast orthogonal search (FOS),¹⁴ to the estimation of Raman spectra acquired with an FT-Raman spectrometer.⁷ As opposed to the techniques listed above, model order is automatically determined in FOS; moreover, there is no need to solve a polynomial equation. Most important, we will show that reduction in the number of Raman interferogram points by a factor of 10 through irregular sampling and application of FOS to the reduced data set generates a spectral estimate comparable in frequency resolution to a DFT applied to the full interferogram. We also demonstrate that the FOS spectral estimator is relatively insensitive (compared with the DFT estimator) to additive noise over a large range of interferogram S/N. Optical spectrometers utilizing the FOS algorithm and irregularly spaced sampling may have important applications in process control or monitoring.

Method

There is a special benefit provided by FOS which is not readily available with the other spectral methods discussed above, namely the ability to handle conveniently time series which are unequally spaced or missing some data.¹⁴ This capability stems from the implicit orthogonalization procedure that FOS employs, and does not involve interpolation to 'fill in' missing data values, which would introduce error.

The ability of FOS to cope with unequally spaced data permits irregular sampling of the interferogram and, further, the irregular sampling permits accurate resolution of high frequencies in the optical spectrum using fewer interferogram points than required by the DFT and other parametric spectral estimators. This can be understood through consideration of a time series obtained by sampling at the Nyquist frequency. Suppose next that a large number of data points are randomly deleted. Since some points would still remain closely proximate, high-frequency information would not be lost, yet far fewer points would be required for processing the time series to extract its spectral content. As noted, this exploits the capability of FOS to accept unequally spaced data without introducing error, unlike the other above-mentioned spectral methods. Why FOS has this ability is explained next.

Denote the irregularly-spaced data points by $y(n)$, sampled at times $t = t(n)$, $n = 0, \dots, N - 1$. Then FOS enables one to build up a concise sinusoidal series model:

$$y(n) = \sum_{m=0}^M a_m p_m(n) + e(n) \quad (6)$$

where $p_0(n) = 1$, and for $i = 1, 2, \dots$,

$$p_{2i-1}(n) = \cos \omega_i t(n) \quad (7)$$

$$p_{2i}(n) = \sin \omega_i t(n) \quad (8)$$

and $e(n)$ is the equation error.

The frequencies ω_i in eqns. (7) and (8) are found by systematically searching through a candidate set of frequencies $\omega_A, \omega_B, \dots$. These candidate frequencies are not required to be commensurate with, or integral multiples of, the fundamental frequency corresponding to the record length. The candidate frequencies can be selected with *a priori* knowledge of the specific frequencies sought or they could simply be frequencies distributed in frequency bands of interest.

In particular, for $i = 1, 2, \dots$, and $M = 2i$ we set ω_i equal to that candidate frequency resulting in the greatest reduction in mean-square error (MSE) when the term pair

$$T_i(n) = a_{2i-1} p_{2i-1}(n) + a_{2i} p_{2i}(n) \quad (9)$$

is added to the model of eqn. (6). An implicit orthogonalization of the term pairs, achieved *via* a slightly modified Cholesky decomposition, is used to obtain a computationally efficient procedure¹⁴ for building up the sinusoidal series model. Because the $t(n)$ in eqns. (7) and (8) are the actual instants when the samples $y(n)$ were taken, and these instants are used in defining the $T_i(n)$ (which are implicitly orthogonalized), the unequal spacing of the data contributes no error.

Results

A comparative analysis of DFT and FOS spectral estimates is based on a double-sided Raman interferogram for neat methanol measured at equi-spaced scan mirror positions with an FT Raman spectrometer to yield an interferogram containing 6294 data points. The interferogram was zero-padded to 8192 points in order to treat the data set as a time series obtained with a sampling rate of 8192 Hz. After application of the Hamming window, the DFT was applied to obtain the Raman spectrum shown in Fig. 1(a), having a spectral resolution of 26 cm^{-1} (2.6 Hz). As expected, the spectrum derived here compares well with the previously published Raman spectrum of methanol.¹⁵ Application of FOS to the original 6294 point interferogram generates a Raman spectrum similar to that obtained with the 8192 point DFT but with a slightly higher spectral resolution of 20 cm^{-1} (2 Hz) [Fig. 1(b)]. To obtain this Raman spectral estimate, FOS searched through 200 candidate frequencies equi-spaced between 1700 and 2098 Hz (-3480 to 500 cm^{-1}) inclusive and selected the 40 most significant frequencies. The amplitudes of those frequencies are plotted in Fig. 1(b) and the amplitudes of unselected frequencies were set to zero. The small difference in spectral peak positions between the FOS and DFT spectra is attributed to their slightly different spectral resolutions.

We now proceed to demonstrate a major difference between the DFT and FOS spectral estimators by recovering *via* FOS the methanol Raman spectrum with only 10% of the original interferogram data. At the same time, we will illustrate the pronounced capability of FOS to cope with noise contamination

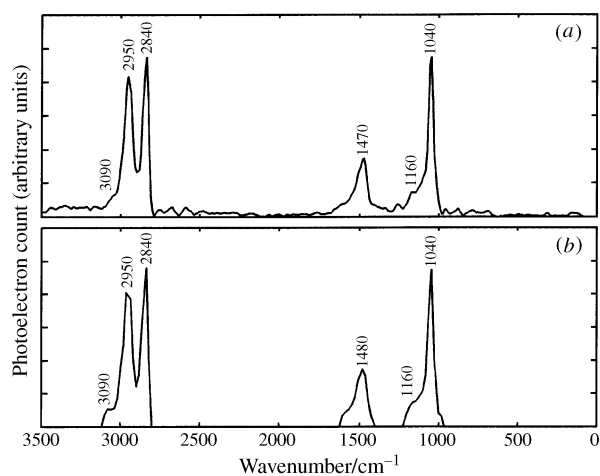


Fig. 1 Comparison of the Raman spectrum of methanol estimated from a 6294 point interferogram with two different algorithms. (a) Raman spectrum resulting from application of the DFT to the 6294 point interferogram, Hamming windowed and zero padded to 8192 points. (b) Raman spectral estimate that results from the direct application of FOS to the 6294 point raw interferogram. Divisions on the vertical axes are proportional to the photoelectron count and the horizontal axes indicate spectral position in wavenumbers.

of the interferogram. We began by adding to the full interferogram zero-mean white Gaussian noise whose variance was 10% of that of the interferogram. Then, 621 points in the noisy interferogram were randomly selected and FOS was directly applied without any additional processing to this reduced data set. Again, FOS searched through 200 candidate frequencies equi-spaced between 1700 and 2098 Hz, and the amplitudes of selected frequencies are shown in Fig. 2(a). The following stopping criterion was used.¹⁶ FOS required, in order to continue, that the greatest reduction achievable by adding a further frequency, divided by the mean square of the current residue, exceed a threshold divided by the number of data points. This criterion (which follows immediately from using a standard correlation test) helps to avoid choosing frequencies which are merely fitting noise. A threshold of 10.9 was used here, roughly corresponding to 99.9% confidence limits. Comparison of Fig. 2(a) with 1(a) shows that the Raman spectrum estimated from 10% of the noisy data using FOS is remarkably similar to the DFT result obtained from the full 6294 point interferogram with no added noise. Fig. 2(b) and (c) show, for 50% and 100% noise contamination, respectively, the FOS estimated Raman spectra using the same 621 point irregular sampling sequence. It is impressive that with only 10% of the original interferogram points and interferogram S/Ns as low as 1 (100% additive noise) that the FOS algorithm recovers the major spectral components of the Raman spectrum.

Note that the irregular spacing of the 621 point reduced data set was crucial to successful recovery of the spectrum. Had, instead, every tenth point been selected from the original data, the sampling rate would have been only about 820 Hz, suitable for recovering frequencies up to about 410 Hz but certainly not those at higher frequencies where most, if not all, of the spectral information in the interferogram is situated. Fig. 3(a) shows the unproductive result of applying the DFT in this situation, where no noise was added to the reduced data set. On the other hand, if the original sampling frequency of 8192 Hz is maintained but

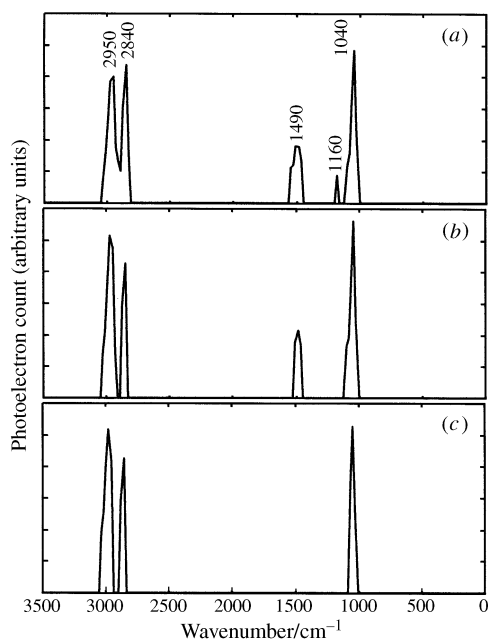


Fig. 2 Raman spectral estimate of methanol by FOS applied to a 621 point reduced interferogram generated by resampling a noisy 6294 point interferogram with a random sampling sequence. In (a), the noise added to the original interferogram had a variance equal to 10% of the variance of the original interferogram. In (b) and (c), the noise variance was 50% and 100%, respectively, and the peaks occurred at the same positions as marked in (a).

621 data points were selected equally spaced to either side of the zero lag position (310 data points to either side) then the resulting DFT spectral estimate will have a resolution limit of 260 cm^{-1} (26 Hz) [Fig. 3(b)], over ten times larger than the resolution observed with FOS applied to a data set with the same number of points. Again, no noise was added to the reduced data set used to obtain the DFT spectral estimate. Thus a FOS spectral analysis of a randomly reduced noisy data set results in a substantially higher spectral resolution than is possible with a DFT spectral estimator applied to a clean interferogram with the same number of points. Comparison of Fig. 3(a) and (b) with Fig. 2(a) is particularly relevant in those situations where the number of sampled interferogram points must be minimized. Similarly accurate FOS Raman spectral estimates from reduced interferograms have also been observed for other condensed phase organic and inorganic samples. Moreover, it has been shown that the recovery of the major spectral components in a Raman spectrum from a randomly reduced interferogram *via* FOS is not critically dependent on the particular random sampling sequence employed.

Conclusions

We have introduced for optical spectrum estimation the use of a recent spectral estimator called fast orthogonal search^{14,16} and compared its performance with the discrete Fourier transform on an interferogram recorded with an FT spectrometer. The specific example given here is the estimation of the Raman spectrum of methanol from its interferogram measured with an FT Raman spectrometer. The FOS algorithm does not impose the same restriction on sampling of the interferogram as the DFT; therefore, FOS requires far fewer interferogram data points than the DFT to obtain a spectral estimate of comparable resolution to a DFT estimate that utilizes the entire interferogram data record. Consequently, the reduced number of interferogram points needed to obtain a given spectral resolu-

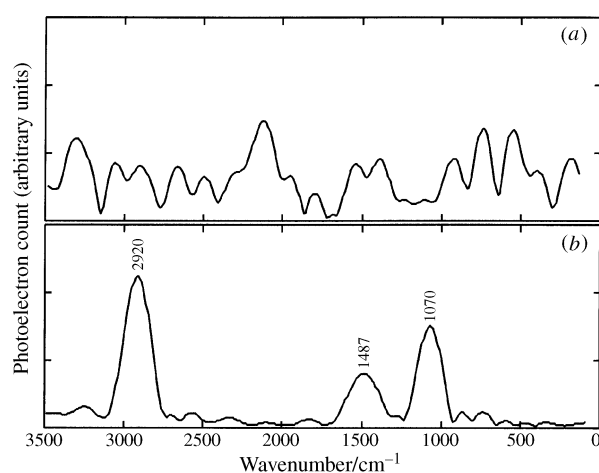


Fig. 3 Comparison of the Raman spectrum of methanol estimated from the DFT applied to (a) a reduced 621 point interferogram produced by resampling the original interferogram at a new sampling rate that is one tenth the original sampling frequency and (b) a reduced 621 point interferogram composed of 310 points equally distributed to either side of the original interferogram zero lag position. The sampling rate of this reduced interferogram is identical with that of the original interferogram. Note that no noise was added to the original interferogram before the reduced interferograms were obtained. In (a) and (b), the reduced interferograms were Hamming windowed and zero padded to 8192 points. These spectra should be compared with that in Fig. 2(a), estimated by FOS from an equal number of interferogram points (which had additionally been corrupted with noise).

tion via FOS implies substantial performance improvements for existing FT spectrometers when measurement time must be minimized and suggests new interferometric spectrometer designs based on the irregular sampling strategy allowed by FOS. This is especially pertinent for a spectrometer having an array photosensor where the number of array photoelements is typically small.

To illustrate the differences between the DFT and FOS spectral estimators, a 6294 point Raman interferogram of neat methanol acquired with an FT Raman spectrometer was analyzed with each algorithm. First, the FOS and DFT Raman spectra computed from the full Raman interferogram were shown to be similar. Next, the interferogram was contaminated with additive Gaussian white noise and then resampled with an irregular (random) sampling sequence to generate a new interferogram having one tenth the points (621 points) of the original data set. Application of FOS to the reduced noisy interferogram generated a Raman spectrum remarkably similar to the DFT spectral estimate using the full clean interferogram data record (6294 points). As expected, application of the DFT to reduced data sets of 621 points failed to generate estimates comparable to the Raman spectrum obtained from the original interferogram even though the reduced sets did not have added noise, unlike those analyzed by FOS.

The FOS method is general and robust and could be an alternative to the DFT in other FT-based spectrochemical analytical techniques. This would include atomic emission, visible or infrared absorption, nuclear magnetic resonance, electron paramagnetic resonance and ion cyclotron spectrometry.

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References

- 1 Michelson, A. A., *Philos. Mag.*, 1891, **5**, 338.
- 2 *Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems*, ed. Ferraro, J. R., and Basile, L. J., Academic Press, New York, 1978.
- 3 Nordstrom, R. J., in *Fourier, Hadamard and Hilbert Transforms in Chemistry*, ed. Marshall, A. G., Plenum Press, New York, 1982, p. 21.
- 4 Saleh, B. E. A., and Teich, M. C., *Fundamental of Photonics.*, Wiley, New York, 1991.
- 5 Hirschfeld, T., and Chase, D. B., *Appl. Spectrosc.*, 1986, **40**, 133.
- 6 Bell, R. J., *Introductory Fourier Transform Spectroscopy*, Academic Press, New York, 1972.
- 7 Brenan, C. J. H., and Hunter, I. W., *Appl. Spectrosc.*, 1995, **49**, 1086.
- 8 Kahn, F. D., *Astrophys. J.*, 1959, **129**, 518.
- 9 Zhao, J., and McCreery, R. L., *Appl. Spectrosc.*, 1996, **50**, 1209.
- 10 Moller, K. D., *Appl. Opt.*, 1995, **34**, 1493.
- 11 Junttila, M.-L., *Appl. Opt.*, 1992, **31**, 4106.
- 12 Okamoto, T., Kawata, S., and Minami, S., *Appl. Opt.*, 1984, **23**, 269.
- 13 Kay, S. M., *Modern Spectral Estimation: Theory and Application*, Prentice-Hall, Englewood Cliffs, NJ, 1988.
- 14 Korenberg, M. J., *Biol. Cybern.*, 1989, **60**, 267.
- 15 *Raman/IR Atlas of Organic Compounds*, ed. Schrader, B., and Meier, W., Verlag Chemie, Weinheim, 1977, p. A3-04.
- 16 Korenberg, M., in *Non-linear Vision: Determination of Neural Receptive Fields, Function, and Networks*, ed. Pinter, R. B., and Nabet, B., CRC Press, Boca Raton, FL, 1992, ch.7.

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