

Fourier-transform infrared derivative spectroscopy with an improved signal-to-noise ratio

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Infrared derivative spectroscopy is a useful technique for finding peaks hidden in broad spectral features. A data acquisition technique is shown that will improve the signal-to-noise ratio (SNR) of Fourier-transform infrared (FTIR) derivative spectroscopy. Typically, in a FTIR measurement one samples each point for the same time interval. The effect of using a graded time interval is studied. The simulations presented show that the SNR of first-derivative FTIR spectroscopy will improve by 15% and that the SNR of second-derivative FTIR will improve by 34%. © 2005 Optical Society of America

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In derivative spectroscopy, instead of analyzing the optical spectrum $J(\nu)$ we study $d^{(m)}J/d\nu^{(m)}$, the m th derivative of the spectrum with respect to ν , where λ is the wavelength, c is the speed of light, and ν is the frequency, $\nu=c/\lambda$. Taking the derivative of the spectrum can give an enhanced spectral signature such that, instead of broad features, the derivative reveals sharp peaks at points of interest. Derivative spectroscopy is used by researchers in many fields, including chemistry and biology.^{1,2} In Refs. 1 and 2, the authors acquired spectra with a Fourier-transform infrared (FTIR) spectrometer and then computed the derivative. In the work of Ref. 3, the researchers modified a monochromator such that the detected signal was a square wave with amplitude that directly corresponds to the derivative of the spectrum.

In this Letter it is shown that, by changing the data acquisition parameters of the FTIR spectrometer, one can improve the signal-to-noise ratio (SNR) of derivative IR spectroscopy. The percentage improvement does not depend on the number of points in the FTIR scan. The cost of improving the derivative IR spectroscopy will be that the SNR of the 0th derivative measurement will decrease. I show that this method can improve the SNR of the 1st derivative by a factor of 15%. For 2nd derivative IR spectroscopy the SNR can be improved by a factor of 34%. As the SNR goes as the square root of the acquisition time, this approach would decrease the measurement time by a factor of 1.8. The technique described here involves changing the times at which the FTIR sample points are taken. No physical modification of the FTIR apparatus is required. Because the FTIR is typically integrated with computer control and analysis, implementation of the technique described here should be straightforward.

We begin with a review of the equations describing FTIR spectroscopy.⁴ The spectrometer design shown in Fig. 1 has two outputs. The path length traversed from beam splitter BS1 to mirror C and then back to

beam splitter BS2 (Fig. 1) is denoted x_C , and the similar path to mirror D from BS1 and then back to BS2 is denoted x_D . Path-length difference x between the two arms is given by $x=x_C-x_D$.

We assume that the detectors in Fig. 1 are photon counters. So, if we make a measurement for a time interval t , output detector signal R will be proportional to the number of photons striking the detector during that time interval. Signal R will be proportional to t , so the term R/t will be independent of t . In this Letter we consider the case when the detector is shot-noise limited. In an optimal measurement, all other noise sources will be reduced to the point where shot noise dominates,⁴ so the shot-noise limit is always of interest. In the shot-noise limit, variance σ^2 associated with detector measurement R will be given by $\sigma^2=R$, where we have dropped proportionality factors such as the detector's responsivity. Because we show the percentage improvement of the SNR by using the modified data acquisition technique described in this Letter, proportionality factors will cancel out when we take the ratio of the SNR from the standard data acquisition to the SNR from the modified data acquisition.

With path-length difference x and measurement time interval t , we denote by $I_A(x,t)$ the signal from detector A and by $I_B(x,t)$ the signal from detector B (refer to Fig. 1). The optical intensity into the spectrometer, integrated for a time interval of 1 s, is denoted I_0 . For a measurement acquisition time t , the output signal from the spectrometer will be given by $(I_0t/1\text{ s})$, where we have omitted the detector responsivity. Initially we assume that the incident light is monochromatic with frequency $\nu=\nu_0$. From Ref. 4,

$$I_A(x,t) = \left(\frac{t}{1\text{ s}} \right) (I_0) \left[\frac{1 + \cos\left(\frac{2\pi x \nu_0}{c} \right)}{2} \right], \quad (1)$$

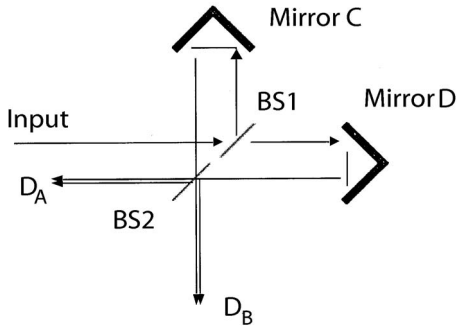


Fig. 1. Optical configuration for the dual-output Michelson interferometer, after Ref. 4. Mirrors C and D are 90°-folding fold mirrors.

$$I_B(x, t) = \left(\frac{t}{1 \text{ s}} \right) (I_0) \left[\frac{1 - \cos\left(\frac{2\pi x \nu_0}{c}\right)}{2} \right], \quad (2)$$

we define $I(x, t)$ by

$$I(x, t) = I_A(x, t) - I_B(x, t) = \left(\frac{t}{1 \text{ s}} \right) I_0 \cos\left(\frac{2\pi \nu_0 x}{c}\right). \quad (3)$$

We define σ_I^2 as the variance associated with $I(x, t)$ and, from Eq. (3), σ_I^2 is the sum of the variances⁵ associated with $I_A(x, t)$ and $I_B(x, t)$, because the shot noise on the two detectors will be uncorrelated. We set incident intensity I_0 to $I_0=1$, as in this Letter we are not studying the SNR as a function of incident intensity, and then from Eqs. (1) and (2) we find that σ_I^2 depends only on measurement time t and not on x :

$$\sigma_I^2 = t/1 \text{ s}. \quad (4)$$

This result for the variance is valid for broadband light, as well.

We now consider the case of broadband light. In a double-sided interferogram measurement,⁴ path-length difference x is centered about $x=0$, and we vary x with a step size of δx , with $2S+1$ equally spaced steps, such that

$$x(q) = q \delta x, \quad (5)$$

where q is an integer ranging from $-S$ to S . We denote the total measurement time τ , and denote by $t(q)$ the time taken to measure the intensity at position $x(q)$, so that

$$\sum_{q=-S}^{q=S} t(q) = \tau. \quad (6)$$

In a typical FTIR measurement we would take equal time intervals at each sample point $x(q)$, such that $t(q) = \tau/(2S+1)$ for all q , but in this Letter we explore the effect of varying time interval $t(q)$ with q . We write the frequency axis $\nu=c/\lambda$ as a set of discrete values:

$$\nu(r) = r \delta \nu, \quad (7)$$

where r is an index ranging from $-S$ to S and $\delta \nu = c/[(2S+1)\delta x]$. The input optical spectrum can be described by $J_A[\nu(r)]$, defined as the optical intensity in the spectral band centered at $\nu(r)$, with width $\delta \nu$, and we take $J_A[\nu(r)]=0$ for $r < 0$. It will simplify our derivation to reflect the spectrum near $\nu=0$, so we define $J[\nu(r)]$ by $J[\nu(r)]=1/2\{J_A[\nu(r)]+J_A[-\nu(r)]\}$. Neglecting proportionality constants yields the generalization of Eq. (3) to broadband light:

$$I[x(q), t(q)] = \left[\frac{t(q)}{1 \text{ s}} \right] \sum_{r=-S}^{r=S} J[\nu(r)] \exp\left[\frac{i2\pi \nu(r)x(q)}{c} \right]. \quad (8)$$

First we multiply both sides of Eq. (8) by $[1 \text{ s}/t(q)]$ and then we take the Fourier transform⁶ to find the desired spectrum $J[\nu(r)]$, ignoring the proportionality constant that is due to the Fourier inversion:

$$J[\nu(r)] = \sum_{q=-S}^{q=S} \left\{ \frac{1 \text{ s}}{t(q)} I[x(q), t(q)] \exp\left[\frac{-i2\pi \nu(r)x(q)}{c} \right] \right\}. \quad (9)$$

As detector signal $I[x(q), t(q)]$ is proportional to t , it follows that the term $I[x(q), t(q)]/t(q)$ does not depend on t . So $J[\nu(r)]$ and also derivatives of $J[\nu(r)]$ with respect to ν do not depend on measurement time intervals $t(q)$.

We denote by $J^{(m)}(\nu)$ the m th derivative of $J(\nu)$ with respect to ν . We take the derivative of both sides of Eq. (9), using the property of the Fourier transform that the derivative in real space is accomplished by a multiplication in Fourier space⁶:

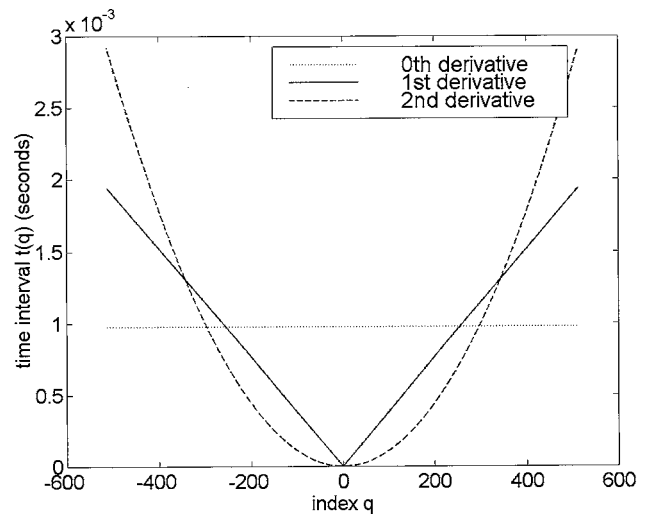


Fig. 2. Numerical analysis of Eq. (13) allowed the optimal time interval $t(q)$ to be found as a function of index q . The total measurement time was $\tau=1 \text{ s}$, and the number of sample points was $2S=1025$. For 0th derivative spectroscopy the ideal time interval is constant for all indices. For 1st derivative spectroscopy the function is linear, and for 2nd derivative spectroscopy the curve is parabolic.

$$J^{(m)}[\nu(r)] = \sum_{q=-S}^{q=S} \left\{ \frac{1 \text{ s}}{t(q)} \left[\frac{2\pi i x(q)}{c} \right]^m I[x(q), t(q)] \right. \\ \left. \times \exp \left[\frac{-i2\pi x(q)\nu(r)}{c} \right] \right\}. \quad (10)$$

Then, the variance associated with $J^{(m)}[\nu(r)]$ from Eq. (10) is⁵

$$\sigma^2 = \sum_{q=-S}^{q=S} \left\{ \left[\frac{1 \text{ s}}{t(q)} \left[\frac{2\pi i x(q)}{c} \right]^m \right. \right. \\ \left. \left. \times \exp \left[\frac{-i2\pi \nu(r)x(q)}{c} \right] \right]^2 \sigma_I^2 \right\}. \quad (11)$$

From Eq. 4, the variance associated with the term $I[x(q), t(q)]$ is given by $\sigma_I^2 = t(q)/1\text{s}$, so that Eq. (11) simplifies to

$$\sigma^2 = \sum_{q=-S}^{q=S} \left\{ \left[\frac{1 \text{ s}}{t(q)} \right]^2 \left[\frac{2\pi x(q)}{c} \right]^{2m} \frac{t(q)}{1 \text{ s}} \right\}. \quad (12)$$

Substituting the expression for $x(q)$ from Eq. (5) into Eq. (11), we find that noise N (we define noise N as equal to standard deviation σ , as in Ref. 4) associated with $J^{(m)}(\nu)$ is given by the following equation when we drop proportionality constants such as 2π , 1 s , and δx :

$$N = \left\{ \sum_{q=-S}^{q=S} \left[\frac{q^{2m}}{t(q)} \right] \right\}^{1/2}. \quad (13)$$

To find the SNR associated with signal $J^{(m)}(\nu)$, as we change time intervals $t(q)$ we need consider only noise N in Eq. (13), because $J^{(m)}(\nu)$ does not change with $t(q)$, as we noted with Eq. (9). We use numerical techniques to find a distribution $t(q)$ that will minimize noise N of Eq. (12), subject to the constraint of Eq. (6). We calculate the SNR improvement by taking the ratio of N when $t(q)$ is constant to N when $t(q)$ varies. The total measurement time τ acts as a scaling factor but does not change the shape of $t(q)$ or the SNR improvement achieved by varying $t(q)$. In my simulations I found that the number of sampling points, $2S + 1$, did not alter the improvement in SNR achieved by varying $t(q)$. So I arbitrarily chose the number of points $2S + 1 = 1025$, and $\tau = 1 \text{ s}$ for our calculation parameters.

In Fig. 2 are shown the results of the numerical analysis plotting the optimized time interval $t(q)$ as a function of index q . For the 0th derivative, taking all points for an equal amount of time was an optimal solution (Fig. 2, dotted line). For 1st derivative spectroscopy, the SNR could be improved by 15% by increasing $t(q)$ linearly with respect to q (Fig. 2, solid curve). For 2nd derivative spectroscopy, the SNR could be improved by 34%, with a quadratic increase in $t(q)$ as a function of q (shown in Fig. 2 by a dashed curve). For all the derivatives, the optimal $t(q)$ satisfies $t(q) = t(-q)$, as expected because the factor q^{2m} in Eq. (13) is the same for positive and negative q .

In this Letter, the specific FTIR architecture in Fig. 1 was chosen, as was taking the double-sided interferogram in Eq. (9). These choices simplify the mathematical development, but further calculation and analysis have shown that the SNR improvement shown here also holds for the single-sided interferogram and for the standard Michelson interferometer.⁴ When the measurement times are graded to provide an increase in the 2nd derivative measurement, the SNR of the 0th derivative measurement will degrade. The calculation given here shows that for the time intervals that provide a 34% increase in the 2nd derivative, the 0th derivative measurement will degrade by a factor of 23.

In conclusion, I have proposed a technique for improving the signal-to-noise ratio in Fourier-transform IR derivative spectroscopy. Instead of measuring each point for the same time interval, I graded the measurement time as a function of path-length difference between the arms of the FTIR interferometer. As the modern FTIR is fully computer controlled, this technique could be implemented through software modifications.

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