Fourier Transform Spectrometry with Fourier Analysis of the Interferogram as Just an Optional Tool

Miguel Lagos,*†‡ Rodrigo Paredes,‡ and César Retamaš§

†Departamento de Tecnologías Industriales, Facultad de Ingeniería, §Departamento de Ciencias de la Computación, Facultad de Ingeniería, and ‡Departamento de Ciencias de la Construcción, Facultad de Ingeniería, Universidad de Talca, Campus Los Niches, Camino a Los Niches km 1, Curicó, Chile

ABSTRACT: Fourier transform spectrometers replace the traditional dispersive frequency analyzer by a Michelson interferometer. The spectrum is the Fourier transform of the interferogram constituting the raw output. The method is a primary tool for chemical analysis because it has decisive advantages over the dispersive one for analyzing infrared electromagnetic radiation (Fourier transform infrared, FTIR). A new procedure for dealing with the raw interferometric output of the instrument, not needing Fourier transformation and having additional advantages, is put forward here. It rests on recent advances in the theory of the interaction of matter with electromagnetic radiation yielding first principles analytic expressions for the Fourier transform of the spectral lineshapes, which can be fitted directly to the experimentally measured interferogram. The relevant physical information, as the integrated intensities of the electronic transitions and their net energy release, not affected by Stokes shifts, is readily obtained in the fitting procedure. Ulterior analysis of the spectra, introducing phenomenological standard interpolation functions to deconvolute and integrate peaks, becomes unnecessary. Both methods, standard FTIR and the one outlined here, demand little computer time and can be used simultaneously with synergistic effects.

1. INTRODUCTION

The scientific basis for an alternate way of processing the raw data constituting the output of Fourier transform spectrometers is expected to improve substantially the precision of both concentration and energy measurements. Good frequency resolution is attained in a standard traditional dispersive spectrometer at the cost of blocking at the slit of the monochromator most of the photons that would otherwise reach the detector. This reduces considerably the signal to noise ratio. A Fourier transform spectrometer replaces the monochromator by a Michelson interferometer, which yields the cosine Fourier transform of the spectrum as the output. The procedure collects information at all frequencies simultaneously, improving dramatically both speed and the signal to noise ratio because the detector captures the full intensity of the light coming from the sample. The output is an interferogram consisting of a graph giving the radiation intensity as a function of the difference in the optical path length of the two arms of the interferometer, which is accurately measured from the interference fringes of a reference laser. This is referred to as raw data and usually exhibits a complex oscillating structure that must be Fourier transformed to bring out the frequency spectrum in a conventional way. The spectrometer then has to be associated with a numerical processor to display the spectrum. Infrared (IR) absorption spectroscopy went through a major advance when Fourier transform spectroscopy came to the fore, and practically no dispersive IR equipment is in the market today. However, the procedure is also practical in optical spectrocopy, nuclear magnetic resonance spectroscopy, and magnetic resonance spectroscopic imaging. The new technique came on the scene associated with the development of the fast Fourier transform (FFT) algorithm, a mathematical method for the fast calculation of Fourier transforms of functions, fast enough to process the highly structured interferograms with acceptable precision. The discovery of the FFT algorithm by Cooley and Tukey initiated a new generation of IR instruments and techniques.

Hence, the mathematical processing of the raw data for displaying them as a standard spectrum in the frequency domain is adequately solved by the FFT algorithm, together with the apodization techniques that control spurious spectral features created by the truncation of the interferogram constituting the raw data. Experimental scans are necessarily finite, and sudden cutoffs at the boundaries have broad unphysical Fourier representations that are discarded by apodization. However, precise quantitative chemical analysis and the accurate determination of the excitation energies of molecular bonds demand additional mathematical processing of the spectra, further to the Fourier transformation of the raw data. The concentration of a chemical species is determined by the area under the peak identifying a characteristic bond of it, whose evaluation demands curve fitting of the data, particularly in the presence of heavy overlapping or structured background.

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Standard Gauss, Lorentz, and Voigt distributions in practice are the analytical expressions used for fitting the shape of the spectral peaks and determining their areas by integration. However, these distributions are merely interpolation functions because, in rigor, they do not follow from solving a real physical model for the processes causing the peak broadenings.6 The symmetry of these model for the lineshape. It has been proven that the assigned peak intensities may show substantial variations with the choice of the lineshape model.6 The symmetry of these standard distributions evidences their limited ability to describe spectral profiles. It has been demonstrated on a general basis that the lineshapes for photon absorption and emission by atomic or molecular species in a condensed environment are always asymmetric with respect to the net energy of the electronic transition.7,8 Hence, a significant source of error is the adoption of a standard distribution not well grounded on the physics of the target to describe the spectral features. The fit of the experimental data by the mathematical curves given by a realistic model for the processes causing the peak broadenings and energy shifts is the photon energy, \( \nu_1 \) is the mean speed of sound of the acoustic modes of vibration of the medium. The adimensional constants \( \alpha \) and \( \beta \), and the adimensional dummy time \( \tau \) are given by

\[
\alpha = \frac{3(\Delta F)^2}{\pi^2 h \nu_1^4} \quad \beta = \frac{h \nu_1}{2ak_B T} \quad \tau = \frac{\nu_1 t}{2a}
\]

where \( \Delta F \) is the bond mean force variation upon excitation, \( \rho \) is the density, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. The auxiliary functions \( f(\tau; T) \) and \( I(\tau) \) are dependent on the symmetry of the surroundings of the orbital undergoing the transition. For the simplest case of octahedral coordination (OC) of the optically active orbital, they read

\[
J(\tau; T) = \int_0^{aq_0} \frac{dx}{x} \left(1 - \frac{\sin x}{x}\right) \coth(\beta x) \sin^2(\tau x) \quad (OC)
\]

\[
I(\tau) = \frac{1}{2} \int_0^{aq_0} \frac{dx}{x} \left(1 - \frac{\sin x}{x}\right) \sin(2\tau x) \quad (OC)
\]

with \( aq_0 \) being the Debye wavevector of the acoustic waves, \( aq_0 = (12\pi^2)^{1/3} \), and

\[
J(\infty; T) = \frac{1}{2} \int_0^{aq_0} \frac{dx}{x} \left(1 - \frac{\sin x}{x}\right) \coth(\beta x) \quad (OC)
\]

The second term on the right-hand side of eq 1 for \( F(h\nu; T) \), containing the delta function, is the zero-phonon line, and the first one is the phonon-broadened distribution. The lineshape function \( F(h\nu; T) \) is normalized as

\[
\int_{-\infty}^{\infty} d(h\nu)F(h\nu; T) = 1
\]

and hence the relative contribution of zero-phonon processes to the total is \( I_{2\Pi} = \exp[-\alpha f(\infty; T)] \).

Other symmetries may give more complicated functional forms for \( f \) and \( I \). For example, for tetrahedral coordination (TC) of the optically active orbitals, one has

\[
J(\tau; T) = \int_0^{aq_0} \frac{dx}{x} \left[ \frac{5}{2} - \frac{3\sin x}{2} - \frac{\sin\left(\frac{1}{2}\sqrt{3}x\right)}{\frac{1}{2}\sqrt{3}x} \right] \coth(\beta x) \sin^2(\tau x) \quad (TC)
\]

\[
I(\tau) = \frac{1}{2} \int_0^{aq_0} \frac{dx}{x} \left[ \frac{5}{2} - \frac{3\sin x}{2} - \frac{\sin\left(\frac{1}{2}\sqrt{3}x\right)}{\frac{1}{2}\sqrt{3}x} \right] \sin(2\tau x) \quad (TC)
\]

The output \( f(x; T) \) of the Michelson interferometer, where \( x \) is the difference in the optical path lengths of the two arms of the interferometer, is the cosine Fourier transform of the spectrum given by the lineshape function \( f \), i.e.

\[
f(x; T) = h\nu \int_{-\infty}^{\infty} d(k) F(h\nu; T)[1 + \cos(2\pi kx)]
\]

where \( k = 1/\lambda \) is the wave number and \( h \) is the Planck constant. Substituting eq 1 and solving the integral, this gives

\[
f(x; T) = 1 + \exp[-\alpha f\left(\frac{x}{c}, T\right)] \cos \left[ \frac{\alpha f\left(\frac{x}{c}, T\right)}{h\nu} + \frac{Ex}{h\nu} \right]
\]
where \( x \), in fact, plays the role of the virtual time \( t = x/c \), conjugated to the angular frequency \( \omega = E/\hbar \). Function \( f(x; T) \) is actually the interferogram, which Fourier transform infrared (FTIR) spectroscopists call the raw data. Therefore, replacing in eq 10, the pairs of auxiliary functions 3 and 4 for octahedral symmetry of the optically active orbitals, or 7 and 8 for tetrahedral coordination of them, one obtains explicit closed-form mathematical expressions for the interferograms. Auxiliary functions for other symmetries can be derived from the general expressions for the electron–phonon coefficients, given in ref 8.

2.2. Proposed Method. As both the experimental technique and the general theory, which is well grounded on the physics of the energy transfers between the radiation field and the charges in a condensed system, arrive both to the interferogram expressed in eq 10, in principle, there is no need to perform any Fourier transform of the data to grasp the physical information from the experimental results. Analytical closed-form expression 10 depends on only a few parameters, \( \alpha, \beta \), and the net transition energy \( E \), per spectral line. Hence, the most practical way to proceed is to find the constants \( \alpha, \beta \), and \( E \) by means of a best-fit analysis of eq 10 to the experimental interferograms. Fourier analysis then becomes just an optional alternative for people who like to identify spectra in the conventional frequency domain.

The method seems to be highly convenient because it retains all the advantages of Fourier spectrometry avoiding the numerical errors associated with the Fourier integration of rapidly oscillating functions. An important example of this is given by the area under the spectral line, which in agreement with eq 9 is given by half the intensity \( I(0, T)/2 \) of the central maximum of the interferogram. This magnitude is unity under the hypothesis of a single emission or absorption center of our theory, but in empirical grounds is proportional to the number of optically active orbitals and gives the concentration of them. However, the implementation of practical procedures for interpreting the measured interferograms directly with eq 10 may not be immediate, particularly when dealing with narrow spectral lines, precisely because their interferograms oscillate strongly with \( x \). In particular, the central maximum may be very narrow and its intensity may be strongly affected by the experimental uncertainty of \( x \).

3. RESULTS AND DISCUSSION

The general procedure can be applied to both wide spectral features, like those displayed by fluorescent compounds, or narrow ones, as the sharp minima observed in the absorption spectra of infrared light passing through many materials. The physical process is essentially the same. Figures 1–3 show the mathematical steps of the calculation of the spectrum of YAG:Ce\(^{3+} \) (yttrium aluminum garnet, \( Y_3Al_5O_{12} \) doped with Ce\(^{3+}\)), a phosphor having many technical applications. This complex unit cell of YAG.13

![Figure 1](image1.png)

**Figure 1.** Auxiliary functions \( J(x/c; T) \) and \( I(x/c) \) defined in eqs 3 and 4 for octahedral symmetry with \( \tau = x/c \).

![Figure 2](image2.png)

**Figure 2.** Filled black circles represent the function \( f(x; T) \), given by eq 11, where \( f_1 \) and \( f_2 \) have the general form 10 with slightly different parameters \( \alpha \) and \( E \). It is expected that \( f(x; T) \) will reproduce the experimentally registered Michelson interferogram of two partially resolved spectral features emitted by centers that have concentrations in the ratio of 2:1. The broken line is only a guide to the eye.

Figure 1 shows the auxiliary functions \( f(x/c; T) \) and \( I(x/c) \) for octahedral symmetry, as given by eqs 3 and 4. Figure 2 represents the theoretically predicted interferogram

\[
f(x; T) = \frac{2}{3} f_1(x; T) + \frac{1}{3} f_2(x; T)
\]  

(11)

t of two competing emissions with weights 2/3 and 1/3. The weighting factors follow from assuming that the quasioctahedral coordinated emission center has degenerated \( x \) and \( y \) lobes and slightly different \( z \) lobes. Both \( f_1 \) and \( f_2 \) have the functional form 10 with constants \( \alpha, \beta, \) and \( E \) chosen to fit the measured spectrum. The transition energies are \( E_x = 2.535 \) eV and \( E_z = 2.343 \) eV (corresponding to the wavenumbers \( k_x = E_x/(\hbar c) = 20 450 \) cm\(^{-1} \) and \( k_z = E_z/(\hbar c) = 18 900 \) cm\(^{-1} \)). The other constants are \( \alpha_1 = 10.00, \alpha_2 = 12.25, \) and \( \beta = \infty \) because \( T \approx 0 \). The value of \( E_x \) is given by the zero-phonon line, and hence is not an adjustable parameter; the other three constants were chosen to fit the experimental data.

Notice in Figure 2 that the number of calculated points in the interval of \( x \), where \( f(x/c; T) \) is appreciable, seems insufficient to represent properly the too-structured function. This is not really a problem to construct the spectrum because the FFT algorithm is an analytical procedure that finds out the function whose Fourier transform (or anti-transform) passes by the given points. The main aspect is the accuracy of these

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points, but care must be taken also to avoid aliasing of the frequency by poor sampling of the data.

Figure 3 shows the cosine Fourier transform of the function 11, calculated by the FFT algorithm included as a standard tool in the Excel spreadsheet. The agreement of the theoretical curve with the experimental spectrum is quite impressive. As the Fourier transform is unique, this indicates that function 11 with the assumed values for the constants should represent with good accuracy the output of the Michelson interferometer. The FFT algorithm was run with 1024 points for $x$, which runs over an interval of optical path differences $0 \leq x \leq 0.02$ mm.

Figure 4 shows a calculated interferogram of the general form

$$f(x; T) = \frac{3}{4} f_1(x; T) + \frac{1}{4} f_2(x; T)$$

(12)

where both $f_1$ and $f_2$ are given by eq 10 with the auxiliary functions 7 and 8 for tetrahedral symmetry. The weighting factors 3/4 and 1/4 assume a single distorted orbital in the subgroup of coordination 4 inserted in the more complex unit cell. The constants $\alpha_1 = 18$ and $\alpha_2 = 22$, and the wavenumbers $\tilde{k}_1 = 20510 \text{ cm}^{-1}$ and $\tilde{k}_2 = 19700 \text{ cm}^{-1}$ ($E_1 = 2.543 \text{ eV}$ and $E_2 = 2.442 \text{ eV}$) are chosen to give the fit of the experimental spectrum of rhodamine 6G shown in Figure 5.

4. CONCLUSIONS

In essence, the method put forward in the previous sections replaces the Fourier analysis of the interferogram ensuing as the output of a Fourier transform spectroscope by best-fit analysis of eq 10 to it. Apodization becomes unnecessary, and all the advantages of traditional Fourier transform spectroscopy, Jacquinot, Fellgett, and Connes, are conserved. However, the main result is the addition of three new advantages:

(i) The procedure gives directly the net energy released or absorbed by the electronic transition, free of Stokes shifts.

(ii) The lineshapes are firmly grounded on the physics of the interaction between the electromagnetic radiation field and the target. Hence, the intensities are obtained with better precision because no standard interpolation functions are necessary to fit the data.

(iii) The theory holds equally well for transitions between vibronic states, in the infrared region, and states of molecular orbitals, associated with the much wider peaks of luminescence spectra.

The situation described above should be quite exact in the presence of a single species. However, in the presence of multiple species, the task should be considerably more computationally intensive and error prone because of the overlap of multiple interferograms. This is not a very important drawback because the difficulty can be solved by combining the two methods. An initial Fourier transform can separate the signal into spectral regions corresponding to the various species present and provide numeric conditions for the subsequent fitting task. The Fourier transform may be useful also to identify the contribution of impurities and noise.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: mlagos@utalca.cl.

ORCID
Miguel Lagos: 0000-0002-6114-0782

Notes
The authors declare no competing financial interest.

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