



# Fourier, Hadamard, and Hilbert Transforms in Chemistry

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# **Fourier, Hadamard, and Hilbert Transforms in Chemistry**

**Dedicated  
to  
the Memory of  
Willis H. Flygare**

## PREFACE

In virtually all types of experiments in which a response is analyzed as a function of frequency (e.g., a spectrum), transform techniques can significantly improve data acquisition and/or data reduction. Research-level nuclear magnetic resonance and infra-red spectra are already obtained almost exclusively by Fourier transform methods, because Fourier transform NMR and IR spectrometers have been commercially available since the late 1960's. Similar transform techniques are equally valuable (but less well-known) for a wide range of other chemical applications for which commercial instruments are only now becoming available: for example, the first commercial Fourier transform mass spectrometer was introduced this year (1981) by Nicolet Instrument Corporation. The purpose of this volume is to acquaint practicing chemists with the basis, advantages, and applications of Fourier, Hadamard, and Hilbert transforms in chemistry. For almost all chapters, the author is the investigator who was the first to apply such methods in that field.

The basis and advantages of transform techniques are described in Chapter 1. Many of these aspects were understood and first applied by infrared astronomers in the 1950's, in order to improve the otherwise unacceptably poor signal-to-noise ratio of their spectra. However, the computations required to reduce the data were painfully slow, and required a large computer. In 1965, Cooley and Tukey published a fast Fourier transform algorithm that reduced the computation time by a factor of  $N/\log(N)$ , making it possible to transform data sets of useful size (say, 8192 points) in an acceptably short time (about 10 sec for 8192 points, compared to about 6 hours with the conventional algorithm). On-line FT computations could thus be done by a minicomputer. Moreover, analog-to-digital converters with suitable speed (50,000 words/sec) and accuracy (12-bit per word) were available, and commercial stand-alone FT-IR and FT-NMR spectrometers were produced within 3 years.

Application of transform methods to other experiments required additional theoretical and/or technical developments, and thus occurred later. For example, FT-rotational spectrometry (first demonstrated in 1974) used the same pulse excitation as FT-NMR, but required a much wider spectral range and thus faster analog-to-digital converters (e.g., 100 MHz at 1 bit per word). Different excitation

waveforms were necessary for FT ion cyclotron resonance mass spectrometry (frequency-sweep, 1973), FT faradaic admittance (pseudo-random noise, 1977), and FT dielectric relaxation (voltage step, 1975). Two-dimensional FT NMR (1975) and the conceptually similar FT ENDOR experiment (1972) required significant theoretical groundwork. FT mu spin resonance analysis (the mu atom is a very light isotope of the hydrogen atom) followed very soon after wide use of the  $\mu$ SR technique itself (ca. 1975). Hadamard transform methods were developed independently (again, first for IR applications) about 1968. Hilbert transform techniques were first applied to spectroscopy (in this case for NMR) in 1978.

Chapter 1 (Marshall) presents a general basis for describing the advantages of Fourier, Hadamard, and Hilbert transform techniques in acquisition of data, enhancement of desired spectral features (e.g., signal-to-noise or resolution), and suppression of instrumental artifacts (deconvolution of imperfect excitation). The next three chapters introduce general aspects of these three transform types. Chapter 2 (Sloane) describes the construction and properties of Hadamard "codes", which are perhaps the conceptually simplest "multiplex" spectrometric method. Chapter 3 (Dumoulin & Levy) contains practical details in applying the fast Fourier transform algorithm to large data sets using a computer with limited memory. Chapter 4 (Marshall) provides the first review of applications for the "DISPA" (dispersion versus absorption) data reduction based on the Hilbert transform, as a means for identifying and distinguishing between spectral line-broadening mechanisms.

The succeeding chapters are loosely organized in order of increasing frequency of the spectrum of interest. Beginning at low frequency (0-2 MHz), Chapter 5 (Comisarow) describes the FT mass spectrometry technique, and gives some very recent applications showing the advantages of the technique for unraveling complex mass spectra at high ionic masses. At somewhat higher radiofrequency, Chapter 6 (Klainer et al.) reviews the state of the art in development and applications of FT nuclear quadrupole resonance spectrometers, and suggests a number of areas for immediate future work. Chapter 7 (Cole & Winsor) gives a history of advances in time-domain reflectometry as a source of dielectric relaxation data, including a review of all detection methods in current use. Chapter 8 (Flygare) is a comprehensive treatment of the theory and experimental complications of FT rotational spectroscopy--this technique appears especially promising for spectra of weakly associated van der Waals molecules.

Chapter 9 (Morris) critically compares the advantages of the principal two-dimensional FT-NMR experiments, and includes a comprehensive literature survey through mid-1980. Chapter 10 (Mims) gives a brief review of the somewhat parallel development of electron spin echo FT spectroscopy. Chapter 11 (Dalal) critically compares the

advantages of the "double-resonance" approach of Chapter 10 and direct FT-NMR for radicals containing quadrupolar nuclei. Chapter 12 introduces FT methods in mu spin resonance spectrometry, an area new to many chemists, but with implications important in the study of isotope effects. Chapter 13 (de Haseth) reviews the continuing development of the FT-IR technique, including the new areas of photo-acoustic spectroscopy, gas- and liquid-chromatography/FT-IR, and silicon impurity determinations. Chapter 14 (Nordstrom) extends interferometric detection to the optical frequency range, with proposed applications in atomic absorption spectroscopy.

The remaining two chapters offer somewhat different approaches. Chapter 15 (Smith) details various possible pseudorandom sequences as spectral sources over the frequency range used for a.c. polarography, and gives several applications of this quite new technique. The final Chapter 16 (McCreery & Rossi) describes a new FT technique which was first published (by those authors) this year (1981), in which Fourier transformation of the pattern of light diffracted near the edge of an electrode is used to discover the concentration profile of electroactive species very near to the electrode.

This volume is a successor to "Transform Techniques in Chemistry", edited by Peter R. Griffiths three years ago (Plenum, 1978). Since virtually all the work described in the present volume has been produced in just those intervening three years, the accelerating increase in use of transform techniques by chemists is obvious. Future directions are expected to include more uses of hard-wired fast Fourier transform processors (a 1024-point FFT can now be performed in about 15 millisec), array processors (especially for two-dimensional Fourier transforms), and use of other excitation waveforms (e.g., pseudo-random excitation in FT mass spectrometry). The market share of FT-spectrometers can be expected to increase in all areas in which commercial FT-instruments are available.

The editor wishes to thank all various contributors for providing authoritative, up-to-date, critical summaries of the state of the art in various transform techniques. The manuscripts were converted to their present form by Alan Marshall and Dixie Fisher. Finally, this volume is dedicated in recognition of the late Professor W. H. Flygare, who contributed his own comprehensive chapter at a time when he was already very ill.



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## ADVANTAGES OF TRANSFORM METHODS IN CHEMISTRY

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### INTRODUCTION

Transform techniques offer three main advantages for chemists. First, transform techniques provide a variety of simple procedures for manipulating digitized data: smoothing or filtering to enhance signal-to-noise ratio; resolution enhancement (via either narrower line width or more points per line width); changing spectral line shapes (as from Lorentzian to Gaussian); generation of a dispersion spectrum from an absorption spectrum; generation of integrals or derivatives; and clipping to reduce data storage requirements. Second, Fourier methods can be used to remove any known irregularities in the excitation waveform, so that the corrected ("deconvoluted") response reflects only the properties of the sample, and not the effect of the measuring instrument. Third, "coded" or "multiplex" detection, followed by Fourier or Hadamard "decoding" can offer a multiplex or Fellgett advantage of up to  $\sqrt{N}$  in signal-to-noise ratio (or  $1/N$  in time) compared to a scanning instrument, where  $N$  is the number of data points in the frequency spectrum.

### Absorption and dispersion spectra: steady-state frequency-response

It is useful to begin by reviewing the origin, form, and detection of absorption and dispersion spectra. All the necessary aspects can be demonstrated from the simple mechanical analog (Figure 1) of a weight of mass  $m$ , suspended from a spring of force constant  $k$ , subject to frictional resistance  $f$ , and driven by an external force  $F$  oscillating at angular frequency  $\omega$ :<sup>1</sup>

$$m \frac{d^2x}{dt^2} = -kx - f \frac{dx}{dt} + F_0 \cos(\omega t) \quad [1]$$

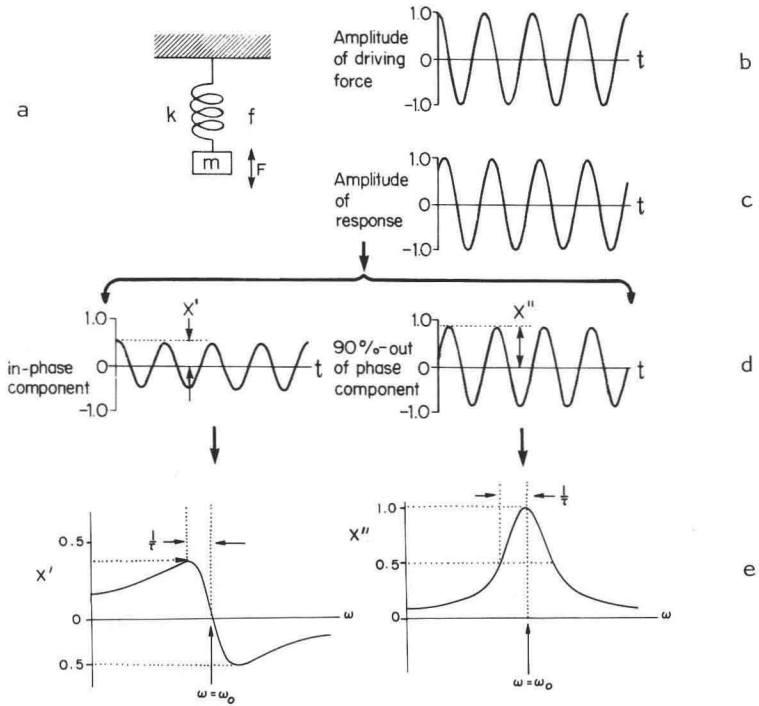


Figure 1. Motion of a driven, damped weight on a spring. (a) Mass  $m$  suspended from spring of force constant  $k$  and frictional coefficient  $f$ , driven by a sinusoidal force  $F_0 \cos(\omega t)$ . (b) Driving force amplitude versus time. (c) Steady-state displacement of driven mass versus time--note that displacement is in general not exactly in step with driver. (d) Displacement analyzed into components that are exactly in-phase or 90°-out-of-phase with driver. (e) Amplitudes (i.e., maximum displacements) of the components in (d), for various choices of driving frequency,  $\omega$ .

The steady-state displacement response (Figure 1c) to a continuous sinusoidally time-varying driver excitation (Figure 1b) always oscillates at the same frequency as the driver, but not usually with the same phase; i.e., the curve in Figure 1c is somewhat displaced in time from that of Figure 1b. The total displacement (Figure 1c) can always be analyzed into components of amplitude  $x'$  and  $x''$  that are exactly in-phase or  $90^\circ$ -out-of-phase with the driver (Figure 1d), in much the same spirit that a vector in a plane is analyzed into its x- and y-components. If the steps shown in Figure 1b-d are repeated for various choices of driving frequency,  $\omega$ , then the component amplitudes  $x'$  and  $x''$  vary with driving frequency as shown in Figure 1e.

The spectroscopic generality of the analysis in Figure 1 is that for relatively small displacement,  $x$ , virtually any driving force,

$$F(x) = a_0 + a_1x + a_2x^2 + \dots \quad [2]$$

can be represented by just the first two terms of Equation 2.  $a_0$  can be eliminated by choosing a suitable reference frame, leaving a force of the form,

$$F(x) = a_1x = -kx \quad [3]$$

which is analogous to the restoring force of a mechanical spring. For example, although an electron may be bound to an atom by a Coulomb attraction, the displacement of the electron by the oscillating electric field of a light wave can be represented by the model of Figure 1, providing that the electron displacement is sufficiently small.

The reason for analyzing the displacement into in-phase and  $90^\circ$ -out-of-phase components is that their amplitude spectra represent the variation of refractive index and power absorption with frequency of the incident radiation. The "dispersion" spectrum is so named because it is the variation of refractive index with frequency that leads to the spreading out ("dispersion") of white light by a prism.

Figure 1e clearly shows that the same information is available from either the dispersion or absorption spectrum. The "natural" or "resonant" frequency

$$\omega_0 = \left(\frac{k}{m}\right)^{1/2} \quad [4]$$

is obtained from the midpoint, and the frictional resistance is resistance is available from the width of either spectrum:

$$\frac{1}{\tau} = \frac{f}{2\pi} \quad [5]$$

The spectral line position thus gives information about the system (i.e., the spring strength and mass), while the line width defines the strength of interaction of the spring with its surroundings (via the frictional coefficient).

It is worth noting that the dispersion-mode frequency spectrum is not simply the derivative,

$$\frac{d A(\omega)}{d \omega} = \text{absorption-mode derivative spectrum.} \quad [6]$$

of the absorption-mode spectrum. Although the dispersion and the absorption-mode derivative spectra have qualitatively similar appearance, their line widths and line shapes are distinctly different. For the Lorentzian line shape of Figure 1e, for example, Figure 2 shows that the peak-to-peak separation for the absorption derivative is smaller than for the dispersion by a factor of  $1/\sqrt{3}$ .<sup>1</sup> Experimentally, the absorption-mode derivative spectrum is the usual display mode in steady-state ESR spectroscopy (see Chapter 4), and is becoming more popular in steady-state optical spectroscopy.<sup>2</sup>

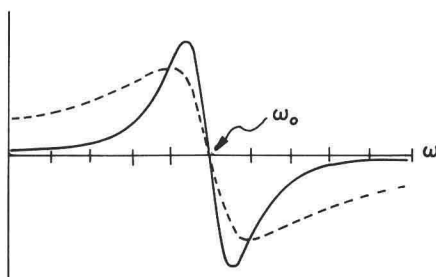


Figure 2. Dispersion (-----) spectrum and corresponding absorption-mode derivative (——) spectrum. Both spectra have been computed from the Lorentzian line shapes of Figure 1e. The line shape differences are clearly evident.

The model based on Equation 1 leads to the fundamental absorption and dispersion line shapes (Figure 1e) of spectroscopy. In addition, various chemically important relaxation phenomena can be modeled by setting  $m = 0$  in Equation 1 (driven, damped, massless weight-on-a-spring):

$$f \frac{dx}{dt} + kx = F_0 \cos(\omega t) \quad [7]$$

The steady-state displacement may again be analyzed into components in-phase and  $90^\circ$ -out-of-phase with the driver as in Figure 1, to give the plots shown in Figure 3. The mathematical line shapes are very similar to those obtained in Figure 1e, except that the curves are now centered at zero frequency, and the width is now given by

$$\frac{1}{\tau} = \frac{f}{k} \quad [8]$$

Experimentally, these line shapes appear in steady-state plots of dielectric or ultrasonic susceptibility versus frequency. The in-phase and  $90^\circ$ -out-of-phase dielectric spectral amplitudes can be combined in a method based on Hilbert transforms (see Chapter 4).

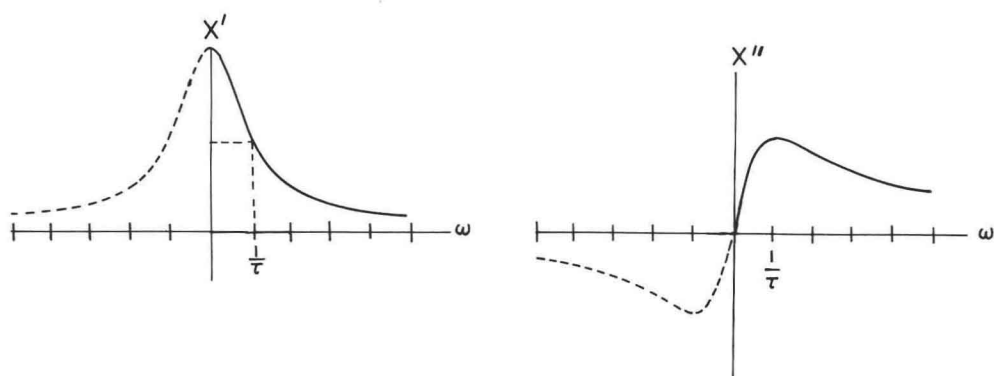


Figure 3. Amplitudes,  $x'$  and  $x''$ , of the in-phase and  $90^\circ$ -out-of-phase components of the steady-state displacement of a frictionally damped, massless spring driven by a sinusoidal force,  $F_0 \cos(\omega t)$ .

### Real and complex notation

Physically,  $x'$  and  $x''$  are properly identified as the in-phase and  $90^\circ$ -out-of-phase steady-state amplitudes defined in Figure 1d. In other words, for a mathematically real driving force,

$$F(t) = F_0 \cos(\omega t), \quad [9]$$

the mathematically real solution to the real Equation [1] or [7] can be expressed,

$$x(t) = x' \cos(\omega t) + x'' \sin(\omega t) \quad [10]$$

However, in solving Equations [1] or [7], it is mathematically convenient to add an imaginary term to the driving force to give

$$\begin{aligned} F(t) &= F_0 \cos(\omega t) + i F_0 \sin(\omega t) \\ &= F_0 \exp[i\omega t] \end{aligned} \quad [11]$$

and then solve the resulting complex Equation [1] or [7] to obtain the complex displacement,

$$X = X \exp[i\omega t] \quad [12]$$

It is then straightforward to show that the complex amplitude can be written

$$X = x' - ix'' \quad [13]$$

The final result of these manipulations is that the real part of (complex)  $X$  is simply

$$\begin{aligned} \text{Re}(X) &= \text{Re}[X \exp[i\omega t]] \\ &= \text{Re}[(x' - ix'')(\cos(\omega t) + i \sin(\omega t))] \\ &= x' \cos(\omega t) + x'' \sin(\omega t) \end{aligned} \quad [14]$$

Therefore, the real part of the complex solution to the complex form of Equation [1] or [7] is the same as the real solution of the real form of Equation [1] or [7]. The two main advantages of complex notation are (a) simpler algebra in solving Equations [1] or [7], and (b) automatic separation of the in-phase and  $90^\circ$ -out-of-phase components (as the real and imaginary parts of a complex amplitude).

It is therefore common to refer to  $x'$  and  $x''$  as the mathematically "real" and "imaginary" parts of a "complex" quantity,  $X$ , even though  $x'$  and  $x''$  clearly represent physically (and mathematically) real in-phase and  $90^\circ$ -out-of-phase amplitudes of a real displacement.



Transient time-domain response to impulse excitation

Historically, most of the spectral responses discussed in the succeeding chapters first came into general use in the form of a steady-state response (usually absorption-mode rather than dispersion-mode) to a "continuous-wave" oscillating driving force. More recently, the same information has come to be extracted from the time-domain response of the same system to a sudden impulse.

Consider the same weight-on-a-spring systems of Equations [1] or [7], but this time in the absence of any driving force:

$$m \frac{d^2x}{dt^2} + f \frac{dx}{dt} + kx = 0 \quad [1a]$$

$$\text{or} \quad f \frac{dx}{dt} + kx = 0 \quad [7a]$$

If the spring is initially at rest (i.e.,  $x = 0$ ), nothing happens. But if the spring is stretched initially to  $x = x_0$  by a sudden pull (impulse excitation), then the spring displacement,  $x$ , will keep changing until friction eventually damps its motion back to zero:

$$x = x_0 \exp[-t/\tau] \cos(\omega_0 t), \quad \frac{1}{\tau} \equiv \frac{f}{2m} \quad [15]$$

$$\text{or} \quad x = x_0 \exp[-t/\tau], \quad \frac{1}{\tau} \equiv \frac{f}{k} \quad [16]$$

as shown in Figure 4.

For the mass-on-a-spring (Figure 4a), we can discover the "natural" spring frequency simply by counting the number of spring oscillations per second. Moreover, we can extract the same damping constant,  $1/\tau$ , from Figure 4a or 4b as from steady-state experiments on the same systems in Figures 1 or 3. In other words, we can discover the natural frequency of a tuning fork, either by humming at it until we find the resonant pitch, or by striking it and listening to its natural oscillation.

Whenever the same parameters are available from two different curves (e.g.,  $\omega_0$  and  $\tau$  from Figure 1 or Figure 4a), there is some mathematical relation between the curves. For the "linear" system we have considered (i.e., displacement is proportional to driving amplitude  $F_0$ ) the time-domain and frequency-domain responses are connected by a Fourier transform. Similarly, absorption and dispersion spectra both yield the same information, and are related by a Hilbert transform (see Chapter 4). In this Chapter, we will next develop some simple Fourier transform properties for continuous curves such as Figures 1-4, and then show the advantages of applying similar relations to discrete data sets consisting of actual physical responses sampled at equally-spaced intervals.