SPECTROMETRIC TECHNIQUES

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Edited by GEORGE A. VANASSE

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Preface

This volume of Spectrometric Techniques contains articles that cover a broader scope than those of Volume I as far as spectral region and techniques are concerned. Specific aspects of the technique of Fourier transform spectroscopy are treated, referring the reader to Volume I for its general description. It was also decided to present the latest work in infrared spectroscopy with tunable lasers. A chapter on vacuum ultraviolet techniques is included to complete the demonstration of the diversity of techniques available to the spectroscopist interested in the ultraviolet visible and infrared spectral regions.

Contents of Volume I

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Chapter **1**

Distortions in Fourier Spectra and Diagnosis

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1.1. Introduction

The main difficulty associated with Fourier spectroscopy has long been the computation of the Fourier transform itself, drastically limited by the limited power of the available computers. The general and tremendous

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progress made in computer technology has overcome this (still recently) impassable barrier and allowed the method of Fourier spectroscopy to blossom. There is currently no serious technical reason preventing the numerical transformation of a great number of points, the computation time being expressed in seconds even for a 10^6 sample transformation (P. Connes, 1971; Delouis, 1971). Indeed, it is considerably more time-consuming to draw the computed spectrum.

Nowadays the main difficulty in performing Fourier spectroscopy rests in the correct realization of the interferogram, the recording of which has strong similarities to the ruling of a grating, which has long been known to be a delicate operation. Also, even if Fourier spectroscopy has exponentially expanded its influence in the past decade, it still remains a new spectroscopic approach. The interpretation of the effects observed in the spectrum due to features occurring in the interferogram often needs unusual mental gymnastics, which are facilitated neither by the general complexity of the recording procedure nor by the time interval (generally considerable) between acquiring the interferogram and obtaining the computed spectrum. This naturally led Fourier people to concentrate their efforts also on the achievement of real-time Fourier computers (Strong and Vanasse, 1958; P. Connes and Michel, 1971), which are now widely used. It is then relatively easy to know in real-time whether the spectrum is good or not. However if it is not, the same unavoidable mental gymnastics must be practiced to detect and correct, in the interferogram or its recording process, the origin of the defects in the spectrum, the correction of which is often not possible. Actually Fourier spectrometry has the specific features that it yields either good results or no results at all. This places even more importance on the examination of all possible kinds of errors affecting the interferogram, how they appear in the spectrum, and how they may be corrected.

The purpose of this chapter is to attempt to review a large number of systematic effects in the recording of an interferogram. The general principles and advantages of Fourier spectroscopy are assumed to be known (see, for instance, J. Connes, 1961; Loewenstein, 1966; Vanasse, 1973; Sakai, 1977). As much as possible, theoretical formulations will only be used if necessary, and replaced by a qualitative approximate representation of the phenomenon. Illustrations of the systematic effects will be given, starting usually from the particular version of interferometers developed by the French group (J. Connes *et al.*, 1970; Guelachvili, 1972). Although this technical choice may seem restrictive, especially concerning the driving mode, no difficulty should be encountered in extending these particular illustrations to the general diagnosis of systematic distortions.

After a brief review of Fourier transform spectrometry, we shall make general remarks on the recording of an interferogram, and give a brief illustration encompassing the particular French choice of approach to Fourier spectroscopy. The systematic errors are then classified in three different specific groups. The review in Section 1.6 of some systematic effects follows a more practical path. We concentrate first on the instrument itself, then on the control of the path difference, and finally on the measurement of the intensity of the interferogram. This section is partly taken from Guelachvili (1973). It is not exhaustive. The contrary would be an impossible task. The old-timers know very well how much the "unexpected" new distortions appearing in a familiar hardware must be expected. Some minor effects have been examined. This is justified by the high accuracy of the results obtained by the Fourier method, together with its extension to other fields (Murphy *et al.*, 1975; Fink and Larson, 1979; Durana and Mantz, 1979).

1.2. Brief Review of Fourier Transform Spectrometry

A. Principle

Suppose a Michelson interferometer is irradiated with a monochromatic source. If the path difference Δ varies linearly with time, the output signal is sinusoidally modulated. The frequency of this signal depends first on the variation of Δ versus time $\Delta(t)$, and second, on the wavenumber σ_0 of the monochromatic analyzed light. If one knows

$$\Delta = vt$$

(v constant), one can easily determine the value of σ_0 from the output signal. This simple way of determining σ_0 remains if, instead of one, the source consists of two monochromatic lines having respectively as wavenumber and intensity σ_1, I_1 and σ_2, I_2. The output signal is then a beat signal due to the combination of two different sinusoidal signals. Given $\Delta(t)$, one obtains without effort σ_1, I_1 and σ_2, I_2. This situation becomes more difficult when the source is complex. Then a complex harmonic analysis of the output signal of the interferometer must be done. The well-known mathematical tool indispensable for the harmonic decomposition of the interferogram is the Fourier transform, which will reconstruct the analyzed spectrum.

The Michelson interferometer is in that case acting as a coding system marking each spectral element (σ_i, I_i) of the optical source by a special and single seal. It works as a frequency divider, transforming each optical frequency σ to a reduced electrical frequency $\sigma \times (v/c)$ (c is the velocity of light) strictly depending on the wavenumber σ. This coding allows obtaining the multiplex advantage. As a matter of fact, each spectral component may be identified even if it has contributed simultaneously with a large number of others to build up the interferogram. No need exists to look at each spectral element without looking at the others which are all detected during all the time of the experiment. Consequently, a gain in the signal-to-noise ratio may be obtained depending on the detector used to record the interferogram.

The fundamental advantage, known as the *étendue* advantage due to the use of an interferometric device, is well known (Fellgett, 1958; Jacquinot, 1958; P. Connes, 1970). Also, the Michelson interferometer is not indispensable either for performing Fourier spectrometry or for getting the multiplex gain (Fellgett, 1967). It plays, however, a particular rôle in the development of this method. It is worth noting that this instrument is now as young as when Michelson conceived it and that it remains curiously the best apparatus for determining the unit of length. All metrological measurements leading to spectacular results have taken advantage of this interferometer. Almost one century after the constancy of the velocity of light was demonstrated by Michelson and Morley, it is needed again in the recent new measurement of c (Evenson and Petersen, 1976), and the instrument built by Michelson himself is still in use at the Bureau International des Poids et Mesures in Paris. This is particularly remarkable at the time when the obsolescence of an apparatus in physics is usually a very rapid phenomenon.

B. Theoretical Apparatus Function

Because it will be useful further in this paper, the formulation of the ideal response of a Fourier interferometer is given here.† It is well known that it is a sinc function due to the limitation of the path difference.

It is supposed that the interferogram starts at the path difference $\Delta_0 \simeq 0$ and stops at the maximum path difference Δ_M. The monochromatic source has a wavenumber σ_0 (wavelength $\lambda_0 = 1/\sigma_0$). The modulated part of the interferogram in this case is given by a sine function

$$I(\Delta) \simeq \sin 2\pi\sigma_0\Delta, \tag{1.1}$$

† No development is done here on the general technique of the Fourier method (sampling theorem, apodization, etc.), which can be found, for example, in J. Connes (1961) and Sakai (1977). Only the formulations necessary for treating the points considered in this paper are retained.

which is then sine transformed from $\Delta = 0$ to $\Delta = \Delta_{max}$ to recover the spectrum. Three cases are considered. First, the interferogram is actually and normally starting from $\Delta = 0$. Second, a slight misadjustment exists, and the interferogram actually starting from $\Delta = \lambda_0/4$ is believed to start from $\Delta = 0$. Third, the interferogram starts from $\Delta = l$, which can take any value.

1. $\Delta_0 = 0$

The spectrum $B(\sigma)$ gives the correct instrumental line shape, which is

$$f(\sigma) = \int_0^{\Delta_M} \sin 2\pi\sigma_0\Delta \sin 2\pi\sigma\Delta \, d\Delta, \tag{1.2}$$

$$= \frac{1}{2}\int_0^{\Delta_M} [\cos 2\pi(\sigma_0 - \sigma)\Delta - \cos 2\pi(\sigma_0 + \sigma)\Delta] \, d\Delta$$

$$= \frac{1}{2}\left[\Delta \frac{\sin 2\pi(\sigma_0 - \sigma)\Delta}{2\pi(\sigma_0 - \sigma)\Delta}\right]_0^{\Delta_M} - \frac{1}{2}\left[\Delta \frac{\sin 2\pi(\sigma_0 + \sigma)\Delta}{2\pi(\sigma_0 + \sigma)\Delta}\right]_0^{\Delta_M}$$

$$= \frac{\Delta_M}{2}\left[\frac{\sin 2\pi(\sigma_0 - \sigma)\Delta_M}{2\pi(\sigma_0 - \sigma)\Delta_M}\right] - \frac{\Delta_M}{2}\left[\frac{\sin 2\pi(\sigma_0 + \sigma)\Delta_M}{2\pi(\sigma_0 + \sigma)\Delta_M}\right]. \tag{1.3}$$

We obtain then two sinc functions of opposite signs centered, respectively, at $+\sigma_0$ and $-\sigma_0$. These are drawn in Fig. 1.1. For the sake of simplicity, only the profile centered at σ_0 will be considered in the rest of this paper.

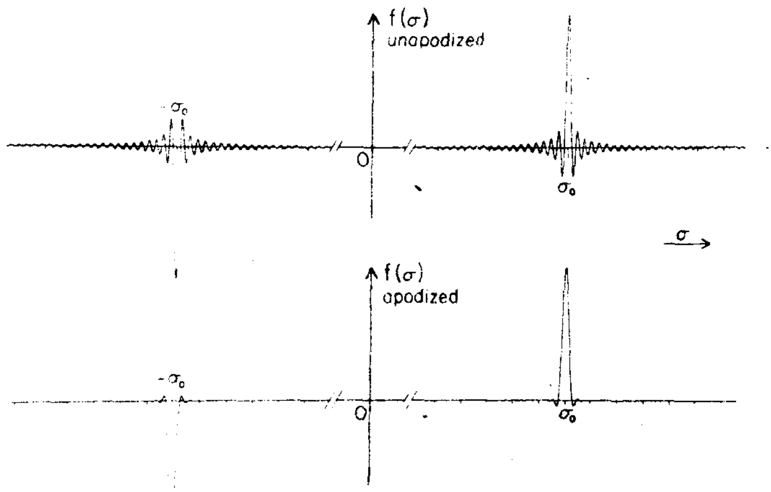

FIG. 1.1. Instrumental line shape $f(\sigma)$, given by the sine transform of the sine interferogram of a monochromatic line at σ_0.

2. $\Delta = \lambda_0/4$

This corresponds to an error in the recording procedure. Then $B(\sigma)$ is

$$\begin{aligned}
h(\sigma) &= \int_0^{\Delta_M} \sin 2\pi\sigma_0\left(\Delta + \frac{\lambda_0}{4}\right) \sin 2\pi\sigma\Delta\, d\Delta \\
&= \int_0^{\Delta_M} \cos 2\pi\sigma_0\Delta \sin 2\pi\sigma\Delta\, d\Delta \\
&= \frac{1}{2}\int_0^{\Delta_M} [\sin 2\pi(\sigma_0 + \sigma)\Delta - \sin 2\pi(\sigma_0 - \sigma)\Delta]\, d\Delta \\
&= \frac{1}{2}\left[-\Delta \frac{\cos 2\pi(\sigma_0 + \sigma)\Delta}{2\pi(\sigma_0 + \sigma)\Delta}\right]^{\Delta_M} - \frac{1}{2}\left[-\Delta \frac{\cos 2\pi(\sigma_0 - \sigma)}{2\pi(\sigma_0 - \sigma)\Delta}\right]_0^{\Delta_M}. \\
&= -\frac{\Delta_M}{2}\left[\frac{\cos 2\pi(\sigma_0 + \sigma)\Delta_M - 1}{2\pi(\sigma_0 + \sigma)\Delta_M}\right] \\
&\quad + \frac{\Delta_M}{2}\left[\frac{\cos 2\pi(\sigma_0 - \sigma)\Delta_M - 1}{2\pi(\sigma_0 - \sigma)\Delta_M}\right], \qquad (1.4)
\end{aligned}$$

which corresponds to two functions of opposite signs, centered respectively at $-\sigma_0$ and σ_0. Figure 1.2 represents $h(\sigma)$ with and without apodization.

3. $\Delta = l$

The resulting incorrect apparatus function is

$$\begin{aligned}
q(\sigma) &= \int_0^{\Delta_M} \sin 2\pi\sigma_0(\Delta + l) \sin 2\pi\sigma\Delta\, d\Delta \\
&= \cos 2\pi\sigma_0 l \int_0^{\Delta_M} \sin 2\pi\sigma_0 \sin 2\pi\sigma\Delta\, d\Delta \\
&\quad + \sin 2\pi\sigma_0 l \int_0^{\Delta_M} \cos 2\pi\sigma_0\Delta \sin 2\pi\sigma\Delta\, d\Delta, \qquad (1.5)
\end{aligned}$$

which is a combination of the shapes $f(\sigma)$ and $h(\sigma)$ weighted by cosine and sine factors depending on $\sigma_0 l$. Figure 1.3 gives an example of such a function with $l = \pi/4$, i.e., an equal contribution of $f(\sigma)$ and $h(\sigma)$ for Eq. (1.5) to give $q(\sigma)$. For example, if

$$l = k\lambda_0,$$

$q(\sigma)$ becomes the correct instrumental line shape $f(\sigma)$ as expected since

$$I(\Delta) = I(\Delta + k\lambda_0) \qquad (k \text{ integer}).$$

As a consequence, any zero of the interferogram of a monochromatic line is suitable for starting the recording, provided one takes care of which side of the sine this zero is located.

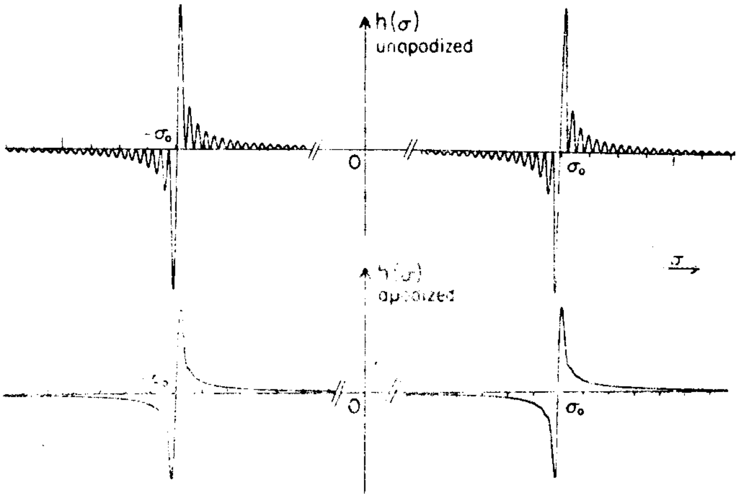

FIG. 1.2. Same as in Fig. 1.1, but a phase error of $\pi/2$ affects the interferogram.

1.3. Recording an Interferogram

A. General Remarks

Essentially two "orthogonal" determinations are necessary for obtaining an interferogram. This is generally expressed by two different simultaneous measurements in the course of an experiment.

As suggested in Section 1.1,A, the first one is connected to the recip-

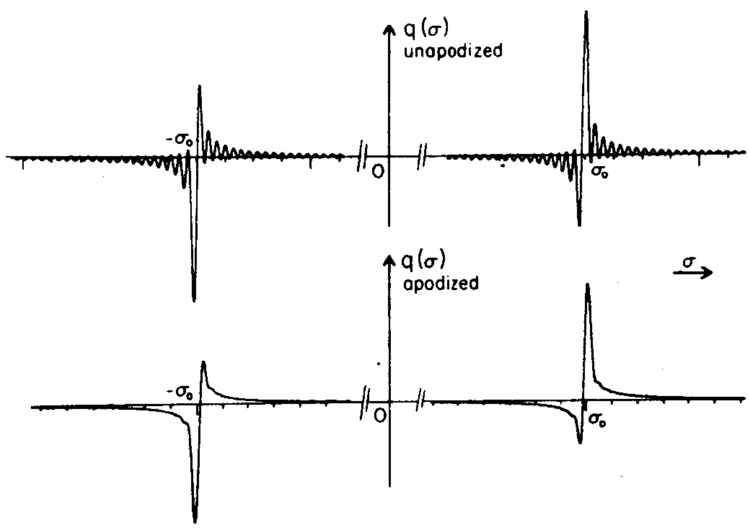

FIG. 1.3. Same as in Figs. 1.1 and 1.2, but the phase error has a value of $\pi/4$.

rocal mathematical relationship existing between Δ and σ in the Fourier transform. Determination of the wavenumber axis in the spectrum depends drastically on the correct measurement of the path difference during the recording of the interferogram. The more accurately Δ is known, the more accurately the spectrum is calibrated. The first care must then be the *rigorous control of* Δ. This is enough to ensure a good wavenumber scale. Generally, the measurement of Δ is obtained using a simultaneously recorded additional interferogram of a monochromatic source whose wavenumber is already well known.

The second determination of importance is that of *the intensity of the interferogram* $I(\Delta)$ as a function of Δ. It is obviously necessary to know Δ very accurately. In particular, its determination using the additional monochromatic interferogram corresponds to slightly different experimental conditions from which the path difference of the recorded interferogram is obtained. The intensity $I(\Delta)$ is also dependent on various parameters starting from the source going to the recorder through the detector, as in any other spectrometric method.

Consequently, at least two types of distortions affecting an interferogram may be defined: the *phase error* and the *intensity error* which, respectively, correspond to distortions on the path difference and on the intensity.

B. CALIBRATION

1. *Wavenumber*

As stated above, only one standard is enough to give a complete calibration of the wavenumber axis. This is at the origin of the consistency of the Fourier results. However, slight misadjustments always exist between the two different paths whereby the monochromatic and the analyzed sources are recorded. When one desires highly accurate results, one must take these into account.

If Δ is the assumed path difference given by the calibration interferogram and if actually the path difference of the recorded interferogram is $(1 + \alpha)\Delta$ (α constant), then an error $d\sigma_0$ exists in the location of the line, normally at σ_0 in the spectrum. Instead of σ_0, one obtains $\sigma_0(1 + \alpha)$. [In Eq. (1.2) replace $\sin 2\pi\sigma_0$ by $\sin 2\pi\sigma_0(1 + \alpha)\Delta$.] Then each wavenumber σ must be corrected by $d\sigma$, with

$$d\sigma/\sigma = \alpha. \tag{1.6}$$

Due to systematic effects, such as the finite angle of the beam, the constant factor α is practically never equal to zero and must be taken into account.

The best way to get a correct estimate of α is to use the *internal standard method* (Guelachvili, 1973). It consists in recording under the same conditions in space and if possible in time the interferograms of the analyzed source and of a complementary standard source, which may not be monochromatic.† In that case the rigorous control of Δ (discussed in Section 1.2,A) by a monochromatic parallel interferogram is no more a measurement of Δ, but only a scaling system which is known to be proportional to Δ. After the computation of the spectrum, the N internal standard lines are measured and their wavenumbers σ_i compared to what they should be, i.e., σ_{0i}. The correct wavenumber scale is then obtained using

$$\alpha = \frac{1}{N} \sum_{i=1}^{N} \frac{\sigma_{0i} - \sigma_i}{\sigma_{0i}}$$

in Eq. (1.6). This calibration method has another important advantage in that it takes into account the slight asymmetries often affecting actual profiles which have, in the whole spectral range, practically the same distorted shape. Since no symmetry exists in these profiles, they should not in principle be exactly measurable. The internal standard method removes this difficulty. Indeed, in that case the standard and the measured lines have the same shape. Provided that they are measured in the same manner, no error remains in the final wavenumber scale that has been determined for the whole spectral range recorded.

2. *Intensity*

The accurate calibration of the intensity axis is strongly dependent on the measurement of the intensity of the interferogram. One finds here all the factors that one has to account for in classical spectrometric methods, the main distortion being nonlinearities. However, here these factors perturb the interferogram and appear Fourier transformed in the spectrum. In Fourier spectrometry their effects are pronounced and specific to the technique (see Section 1.6,C.2b). Distinction must also be made between emission and absorption spectra since the interferograms behave differently, even if the emission spectrum consists of numerous lines spread over a large spectral range.

In emission the modulated part of the interferogram has generally a peak-to-peak amplitude, which slowly varies from $\Delta = 0$ to the maximum path difference. This is not true when a broadband absorption spectrum is looked at. Then the very strong modulation near $\Delta = 0$ rapidly decreases

† For example, in absorption spectra the white-light beam is sent successively through the cell containing the sample of interest and through another additional cell with a standard gas having several well-measured absorption profiles such as the rotational fine structure of a vibrational transition.

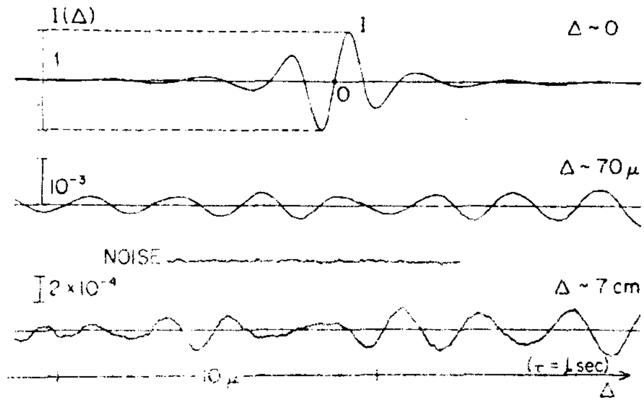

FIG. 1.4. Interferogram of a broadband spectrum (7000 cm^{-1}). With internal modulation the mean level remains zero. Only the small area around $\Delta = 0$ has a high contrast. The sampling interval is too small to be seen on the figure.

for higher values of Δ (see Fig. 1.4). Consequently, detection may easily be linear in emission, whereas in absorption care must be taken because of the great dynamic range of the measurements. A nonlinear detection introduces zero level distortion in the spectrum and harmonic spectral components. The measurement of intensities requires a careful investigation of all the sources of nonlinearities which are, of course, not the only possible sources of error. For example, thermal emission may also introduce parasitic spectral components in the final results.

As in the wavenumber measurement, the *internal standard method* is the best way to get a correct estimate of the intensity. It allows the determination of the transmission of the whole instrument as well as the calibration of the spectral intensities. Also, simple checks in the spectrum may be done to detect the existence of remaining nonlinearities. In case of an emission spectrum, no harmonic lines should appear at two and three times the wavenumber of each line or at their corresponding "images." For absorption spectra, a convenient procedure is to record a slightly larger free spectral range than the one of interest to look at a portion of the spectrum which should be zero; then any displacement of the level in that region indicates remaining nonlinearities.

1.4. One Practical Example of Fourier Transform Spectrometry

The aim of this section is to give an actual illustration of the general previous considerations. It also serves as an introduction to the detailed review, in Section 1.6, of the systematic effects that may disturb a Fourier