Analytical Applications of FT-IR to Molecular and Biological Systems

edited by

JAMES R. DURIG

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PREFACE

In the past few years it has become apparent that Fourier Transform infrared spectroscopy is developing into an excellent technique for solving some of the very difficult problems encountered in analytical chemistry. The applications of FT-IR include the detection and identification of chemical components separated by gas chromatography techniques, determination of low concentration components in a mixture, and problems which have energy limitations such as water samples, opaque samples and biological systems.

The lectures presented in this volume will be utilized at the NATO Advanced Study Institute in Florence, Italy from August 31 to September 12, 1980. These lectures are divided into three main sections: Instrumentation and Theory, Techniques, and Applications. The first section includes a basic introduction to interferometry and the operating parameters. The Techniques section consists of several lectures on accessories used in FT-IR, software and data systems, and special handling techniques. The third section contains an abundance of information on the applications of the FT-IR technique to inorganic and organic molecules, polymers, biological systems, solids and to the determination of molecular structures and conformational analyses. The contents of this volume should provide the reader with the present applications in this field as well as an indication of possible future trends. In general the lectures are of a pedagogical nature and are not to be considered as review articles. These lectures were meant to provide a forum for the exchange of ideas between the student and lecturer and it was hoped that they would engender discussion of topics of current scientific interest in Fourier Transform spectroscopy.

First of all the editor would like to thank Dr. J. F. Sullivan for her administrative assistance and overall supervision of both the Institute and preparation of this book. Also the editor would like to thank the co-directors, Professors W. G. Fateley and A. Müller for their help in various ways with the NATO Advanced Study Institute. Thanks are due to the authors for promptly submitting their manuscripts so that this volume would be available for the students at the Institute. Additionally, the editor would like to thank his wife, Marlene, for copy-editing the manuscripts and for the preparation of the author and subject indexes. Also, thanks

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INSTRUMENTATION AND THEORY

ONE VIEW OF THE ADVANTAGES OF INFRARED INTERFEROMETRY

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1. INTRODUCTION

Since the mid 1950's many papers have appeared emphasizing substantial advantages of interferometry over dispersive spectroscopy. While it is generally recognized that these advantages are qualitatively correct, the magnitudes of these advantages are still subject to debate.

In the beginning it was apparent that with the excitement of this "new" form of spectroscopy, the rational behind many of these arguments was clouded and that the total advantage of interferometry might not be as great as first anticipated. In this chapter we wish to review the advantages and disadvantages of interferometry and attempt to quantify them to the greatest extent possible.

2. DISCUSSION

Let us use a simple optical system for an interferometer (see Fig. 1) with an infrared light source inclined at an angle θ with respect to the optical axis striking a collimator at an angle γ, the differential throughout may be written as:

$$dE = (\cos\theta dA_S)(\cos\gamma dA_C)/r^2 \qquad (1)$$

where:

dA_S = area of the source
dA_C = area of the collimator
r = distance between source and collimator.

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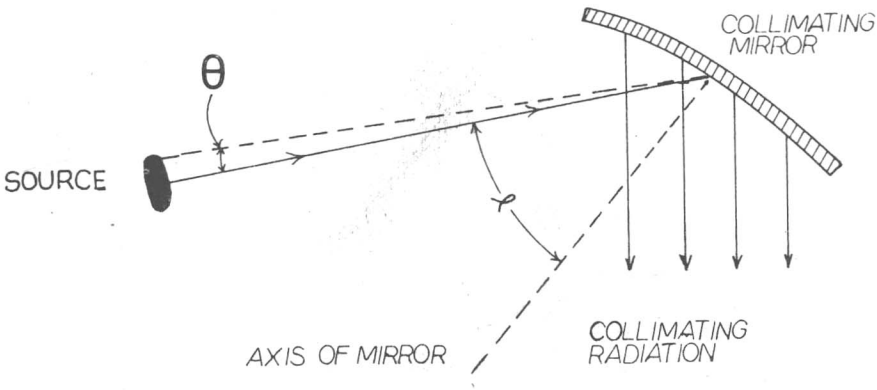

Fig. 1 Simple optical system for an interferometer.

The solid angle subtended by the source can be written as follows:

$$d\Omega = \cos\theta dA_s/r^2 \tag{2}$$

and the projected area can be expressed as:

$$dA = \cos\gamma dA_c . \tag{3}$$

Therefore, Eq. (1) can be rewritten as:

$$dE = d\Omega dA \tag{4a}$$
$$E = \Omega A \tag{4b}$$

Assuming a finite source size, the optical path difference between the two arms of a Michelson interferometer is

$$\Delta = [(\sqrt{3 + \cos^2\theta} - 1)(1 + \cos\theta) - 2]f + (\sec\theta - 1)L + 2d\cos\theta \tag{5}$$

where:

f = focal length of collimating mirror
L = distance from source to fixed mirror
d = distance from fixed to movable mirror (which is equal to the spatial displacement).

The first two terms in Eq. (5) are of different sign and are

very small as compared to the third term. Thus, they tend to cancel in most cases leaving the approximation

$$\Delta \simeq 2d \cos \theta. \tag{6}$$

If the source is considered to be a point, i.e. $\theta = 0$, then Eq. (5) describing the optical path difference between the two arms of an interferometer reduces to

$$\Delta p = 2d. \tag{7}$$

It is this deviation of Δ from Δp which leads to a frequency spread, [1,2] which is

$$\Delta\bar{\nu} = \bar{\nu}_{max}\Omega/2\pi \tag{8}$$

where $\bar{\nu}_{max}$ = the highest wavenumber in the spectrum.

Substituting Eq. (8) into Eq. (4b) we obtain the relation for the throughput of a Michelson Interferometer:

$$E^I = 2\pi A^I \frac{\Delta\bar{\nu}}{\bar{\nu}_{max}} \tag{9}$$

where A^I = area of collimating mirror in the Interferometer. Superscript I will designate interferometry and D will indicate dispersive spectroscopy in our comparison.

For a dispersive spectrometer the solid angle may be written as

$$\Omega^D = \frac{hw}{f^2} \tag{10}$$

where: h = slit height
w = slit width
f = focal length of collimator

since:

$$w = f\frac{(d\theta)}{(d\bar{\nu})}\Delta\bar{\nu} \tag{11}$$

and

$$\bar{\nu} = \frac{m}{d(\sin i + \sin \theta)}. \tag{12}$$

The angular dispersion of the grating becomes

$$\frac{d\theta}{d\bar{\nu}} = \frac{m}{\bar{\nu}^2 \, d \cos \theta} \tag{13}$$

and the solid angle becomes

$$\Omega^D = \frac{hm}{fd \cos \theta} \frac{\Delta\bar{\nu}}{\bar{\nu}^2} \tag{14}$$

where

m = order of the grating
d = the distance between the lines of the grating.

Substituting Eq. (14) and Eq. (3) into Eq. (4b) we obtain for the throughput of a dispersive spectrometer

$$E^D = \frac{hmA^D}{fd} \frac{\Delta\bar{\nu}}{\bar{\nu}^2}. \tag{15}$$

A. Jacquinot Advantage

In 1954 Pierre Jacquinot recognized the throughput advantage of the interferometer over dispersive instruments and the ratio E^I/E^D is now usually termed "Jacquinot's advantage", [3,4].

Using Eq. (9) and Eq. (5) we obtain an equation for Jacquinot's advantage.

$$E^I/E^D = \frac{2\pi fd}{hm} \frac{A^I}{A^G} \frac{\bar{\nu}^2}{\bar{\nu}_{max}} \tag{16}$$

Substituting approximate values for the constants in Eq. (16) one obtains

$$\frac{E^I}{E^D} = \frac{0.075 \, \bar{\nu}^2}{\bar{\nu}_{max}}. \tag{17}$$

It should be noted that gratings are mechanically changed several times during a complete scan of the mid infrared region and therefore d can be a function of the frequencies, as $d = d(\bar{\nu})$. Since the value of d increases stepwise with decreasing frequency the value E^I/E^D may be thought of as being "slightly less than quadratic" in frequency.

It should also be noted that Jacquinot's advantage is a measure of the amount of radiation striking the detector. Thus, this advantage is most important when the amount of radiation is minimal, e.g. such as the measurement of weak emissions, or at high resolution interferometric studies.

B. Fellgett's Advantage

If one measures a spectrum of width $\delta\bar{\nu}$ at a resolution $\Delta\bar{\nu}$ the number of spectral elements is:

$$M = \frac{\delta\bar{\nu}}{\Delta\nu} \tag{18}$$

In a dispersive instrument the time devoted to each spectral element is therefore T/M where T equals the total active time of the scan. The total active time of data acquisition may be considered to be the total time during which the sample was being irradiated.

If the noise is random, the signal-to-noise ratio becomes

$$(S/N)^D \propto \frac{T}{M}. \tag{19}$$

In an interferometer, all frequencies are impinging upon the detector during the entire active time. Therefore, for an interferometer

$$(S/N)_I \propto T, \text{ for } M = 1. \tag{20}$$

Fellgett's advantage [5,6] states that for equal sources, active times, and resolutions, the ratio of signal to noise ratios becomes

$$\frac{(S/N)^I}{(S/N)^D} = M \tag{21}$$

or that for equal signal-to-noise ratios the time required is

$$\frac{T^I}{T^D} = \frac{1}{M}. \tag{22}$$

For a scan of the entire mid infrared region at a resolution of 2 cm^{-1}, the magnitude of Fellgett's advantage may be calculated as:

$$\frac{(S/N)^I}{(S/N)^D} = \frac{(4000 - 400)^{1/2}}{(2)} = 42$$

It should be noted that Fellgett's advantage increases with increasing resolution, and that it becomes very important in high resolution ($\Delta\bar{\nu} < 2\ cm^{-1}$) research.

It must be remembered however, that the active time of Eq. (19) is much less than the total time involved in obtaining a spectrum. In a dispersive instrument where the spectrum is usually plotted as the data are being recorded, the active time is approximately one-fourth to one-half of the total time between the start of the scan and the finished spectrum.

In an interferometer, however, the spectrum cannot be plotted until all of the interferograms have been recorded, averaged, and apodized, then the Fourier transform is performed. If only one interferogram is to be recorded, the inefficiency of the interferometer negates Fellgett's advantage. However, if several interferograms are to be averaged, the Fourier transform of previous interferograms can be averaged while the next interferogram is being collected. This improves the efficiency of the interferometer and brings the actual total time closer to the total active time of Fellgett's advantage. Simply, one can view the Fellgett advantage as one does when he multiplexes the signal.

C. Connes' Advantage

Connes' advantage may be simply stated as the ability of the interferometer to very accurately characterize the frequency. This advantage stems from the accurate measurement of the displacement of the moving mirror, by a He-Ne laser, and allows the subtraction of background spectra.

D. Cooley-Tukey Algorithm

Another way in which the efficiency of the interferometer has been improved lies in the method by which the Fourier transform is calculated. In 1966 Cooley and Tukey described an algorithm by which the total number of operations required to calculate the Fourier transform is greatly reduced, [7]. If sufficient zeros are added such that the total number of data points equals an integral power of two, theory predicts that the time required for the calculation by the "fast method", t_f, should be proportional to $\log_2 N/N$ conventional. In 1966 Forman [8] demonstrated experimentally that the proportionality constant was approximately equal to 1.8.

E. Resolution Advantage

Whereas Connes' advantage deals with the frequency accuracy of spectral data, the resolution advantage deals with the precision or resolution of the band. The resolution of an interfero-

meter may be given as:

$$\Delta\bar{\nu} = \Delta^{-1}. \tag{23}$$

Therefore, for Δ equal to 10 cm, as is common in many commercial interferometers, $\Delta\bar{\nu}$ equals 0.1 cm^{-1}. This high resolution capability has many applications but most obvious is the elucidation of complex rotational structure in gaseous molecules.

F. Detector Performance

One factor which can be a definite disadvantage of the interferometer in our comparison to dispersive spectroscopy is the detector. Unlike a dispersive instrument where all frequencies are modulated, or chopped, at a constant frequency (ca. 10 Hz) the modulation frequency of an interferometer is dependent on the frequency of source radiation. The modulation frequency may be calculated as

$$\nu_{mod} = 2v\bar{\nu} \tag{24}$$

where v = velocity of moving mirror.

Using a typical value of 1.5 mm per sec. for v one finds that modulation frequencies may range from 3 kHz ($\bar{\nu}$ = 10,000 cm^{-1}) to 3 Hz ($\bar{\nu}$ = 10 cm^{-1}). Unfortunately, the thermocouples commonly used in dispersive spectroscopy have response times much greater than 1 ms and therefore cannot detect radiation modulated in excess of 1 kHz. To alleviate this problem most interferometers use triglycine sulfate (TGS) or deuterated triglycine sulfate (DTGS) pyroelectric bolometers. These detectors are capable of detecting radiation modulated in excess of 1 MHz but suffer from a much lower sensitivity (i.e. the D* can be less by an order of magnitude) than thermocouples. This loss of sensitivity can be very serious, reaching more than an order of magnitude difference for high frequency modulation.

If only a small limited portion of the infrared is to be observed, the TGS detector may be replaced with a photoconductive or photovoltaic detector. These detectors are much more sensitive than TGS detectors and are comparable to the thermocouples of dispersive spectroscopy.

3. SUMMARY

With the present state-of-the-art from the above optical considerations, it is evident that the number of advantages clearly favors interferometry over dispersive spectroscopy. However, the magnitude of these advantages is strongly dependent on factors such as required resolution, length of scan, available time, etc.

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