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Fourier Transform Infrared Spectroscopy

The basic principles and current applications of a rapidly expanding technique are reviewed.

J. B. Bates

Fourier transform (FT) spectroscopy has developed during the last 5 years as a very active area of interest among specialists in infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. This interest has been stimulated in part by the efforts of a small but growing industry in the development and manufacture of FT spectrometers. Also, several excellent books (*1*, *2*) and numerous review articles (*3–6*) have been written at all levels of sophistication to describe in detail the principles on which the method is founded and to present examples of current application. For example, Becker and Farrar (*5*) discussed both FT IR and FT NMR spectroscopy, devoting most of their article to the principles and applications of the latter technique. Almost certainly there remains no one among the specialists in IR or NMR spectroscopy or those whose work often depends on these techniques who does not have at least some basic understanding of the important principles and the advantages of FT spectroscopy.

This article is directed primarily to that segment of the scientific community who may not as yet use IR spectroscopy but may find it necessary or desirable to do so in the future. Its purpose is to provide a background in the principles of FT IR spectroscopy and to serve as a guide for possible applications of this technique. A short discussion of Fourier series is presented as an aid to understanding how FT spectroscopy works. Results are stated without proof, and only the most essential concepts are discussed. Some details which are important but are not essential for a basic understanding of FT IR are discussed at the end of the article. A section on applications includes examples from recently published articles which illustrate some of the unique features of FT IR spectroscopy.

Basic Concepts

As the name implies, FT spectroscopy involves a special mathematical treatment of spectral data. It is helpful in understanding how FT spectroscopy works to consider some elementary properties of Fourier series (*7*, *8*). Subject to certain conditions (*7*), a function $f(x)$ can be expressed as a power series expansion of sine and cosine terms

$$f(x) = \frac{A_0}{2} + \sum_{n=1}^{\infty}\left(A_n \cos\frac{n\pi x}{c} + B_n \sin\frac{n\pi x}{c}\right) \qquad (1)$$

where

$$\frac{A_0}{2} = \frac{1}{2c}\int_{-c}^{c} f(x)dx$$

is the mean value of $f(x)$ over the interval $(-c,c)$

$$A_n = \frac{1}{c}\int_{-c}^{c} f(x)\cos\frac{n\pi x}{c}\,dx$$

and

$$B_n = \frac{1}{c}\int_{-c}^{c} f(x)\sin\frac{n\pi x}{c}\,dx$$

The expansion given by Eq. 1 is known as the Fourier series of $f(x)$. In this case, $f(x)$ may be periodic with period $2c$ or, even though it may be defined only on the interval $(-c,c)$, its Fourier series representation will be periodic with period $2c$. Figure 1 shows a familiar textbook example (*8*) of a square-wave function and several partial sums of its Fourier series representation. The point to be illustrated in Fig. 1 is that the function $f(x)$ can be represented as faithfully as desired by including more terms in its Fourier series. In a laboratory application, the question of how many terms to include in order to achieve a desired accuracy is often determined by the storage capacity and perhaps the computation time of a small computer.

The extension of Fourier series representation to include functions that are not periodic or, equivalently, functions that are periodic in the interval $(-\infty, \infty)$ leads to the concept of Fourier integrals. It turns out that certain pairs of functions denoted by $h(\nu)$ and $g(\delta)$ are related as

$$h(\nu) = \int_{-\infty}^{\infty} g(\delta)e^{i2\pi\nu\delta}d\delta \qquad (2a)$$

and

$$g(\delta) = \int_{-\infty}^{\infty} h(\nu)e^{-i2\pi\nu\delta}d\nu \qquad (2b)$$

where $e^{\pm i2\pi\nu\delta} = \cos(2\pi\nu\delta) \pm i\sin(2\pi\nu\delta)$. The use of complex expressions is a convenience in carrying out certain manipulations with Fourier integrals. The transformations given Eqs. 2a and 2b can be expressed in a functional form as

$$h(\nu) = F(\nu,\delta)[g(\delta)] \qquad (3a)$$

and

$$g(\delta) = F^{-1}(\delta,\nu)[h(\nu)] \qquad (3b)$$

where F^{-1} represents the inverse transformation. Note, for example, in Eq. 3a that F transforms a function g which depends on variable δ into another function h which depends on a different variable, ν. This means that if we can perform a measurement to determine $g(\delta)$ for some range of the variable δ, we may be able to recover $h(\nu)$ more rapidly or accurately than we could directly measure it. The functions g and h which are related by the transformations of Eqs. 2 or 3 are known as Fourier pairs. Two sets of Fourier pairs of interest in FT spectroscopy (*9*) are illustrated in Fig. 2. The $h(\nu)$ in Fig. 2A represents a monochromatic signal of frequency ν_0 (cm^{-1}), and its Fourier partner is a cosine wave of wavelength $1/\nu_0$. The $h(\nu)$ in Fig. 2B represents a polychromatic or white source of radiation, and its Fourier partner

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The author is a staff member in the Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

can be viewed as the addition of an infinite number of cosine waves of different amplitudes and wavelengths. The transformation given by Eq. 2a implies that all of the information in $h(\nu)$ can be obtained from a determination of $g(\delta)$. However, the range of values of the variable δ over which $g(\delta)$ can be determined in a measurement will be limited to some interval much smaller than that specified by the transformation—that is, $(-\infty, \infty)$. Thus, experimental limitations result in a truncation of the number of terms included in the integration. This situation is analogous to limiting the number of terms in the Fourier series expansion of a function as given in Eq. 1, and the effect here is to cause a loss of information to be incurred in recovering $h(\nu)$. The fidelity with which $h(\nu)$ can be obtained will then be determined by certain limitations of the apparatus used to measure $g(\delta)$.

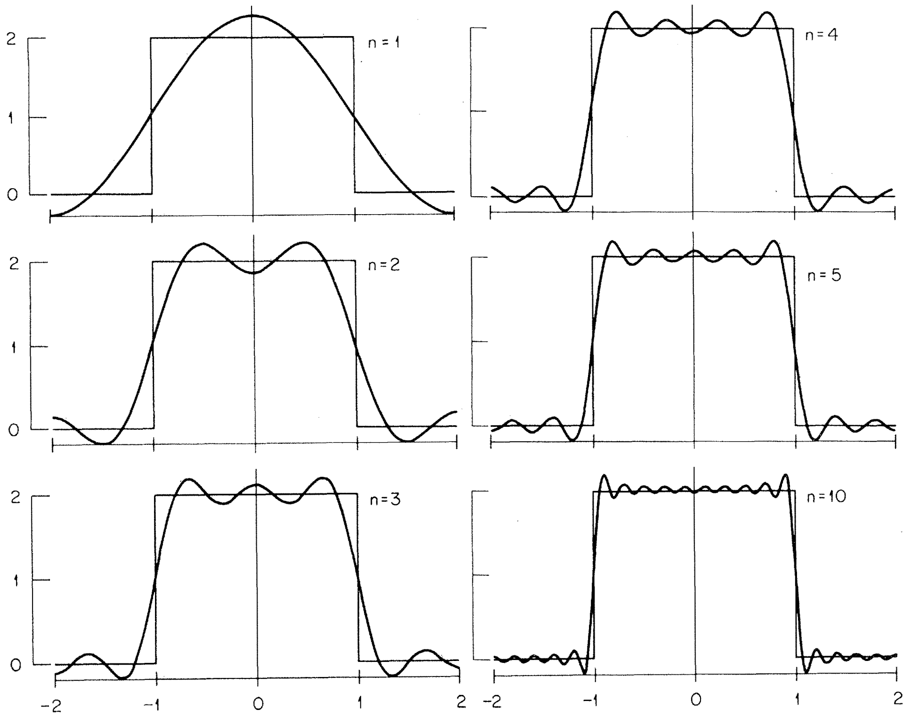


Fig. 1. Partial sums of the Fourier series representation of a square-wave function: $f(x) = 0$, $-2 < x < -1$; $f(x) = 2$, $-1 \leq x \leq 1$; $f(x) = 0$, $1 < x < 2$. The series expansion is $f(x) = 1 + (4/\pi)(\cos \pi x/2 - {}^1\!/_3 \cos 3\pi x/2 + {}^1\!/_5 \cos 5\pi x/2 - \ldots)$.

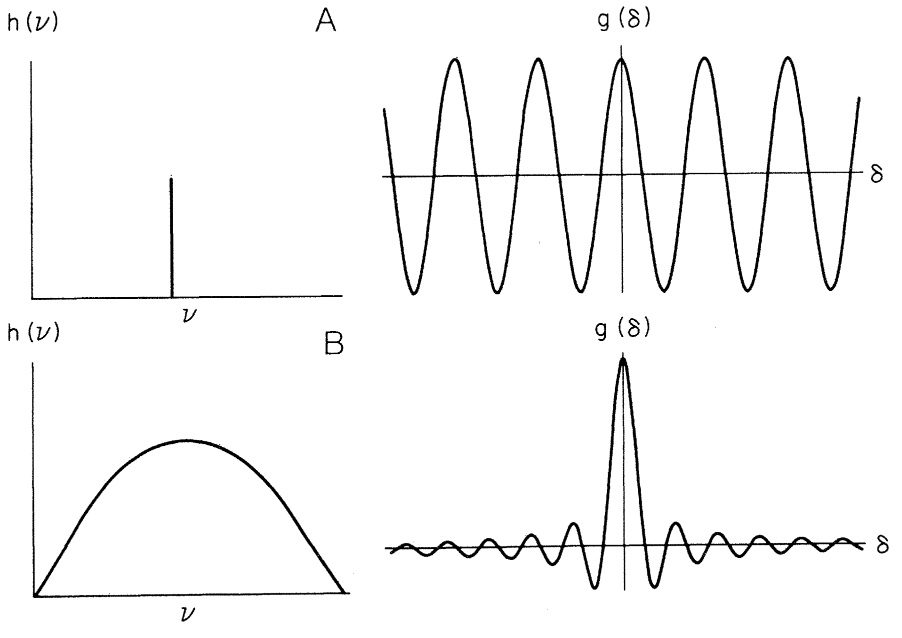


Fig. 2. Pairs of functions related by the Fourier integral transforms in Eq. 2.

Interferometric Spectroscopy

Basically, an FT spectrometer is a device having an optical component which, from an input source, produces $g(\delta)$ over a range of δ values. If immediate results are to be obtained in the form of the transformed spectrum, $h(\nu)$, it will also consist of a small computer system, which is required in carrying out the mathematical operation represented in Eq. 2. The principal optical component of an FT IR spectrometer is a Michelson interferometer, which is illustrated in Fig. 3. Its three basic parts are a fixed mirror (*A*), a moving mirror (*B*), and a beam splitter (*C*). The center of the beam splitter is denoted by *O*. Figure 3 shows the optical path of a parallel light beam through the interferometer. The beam is divided at *O* into two rays. One ray travels to fixed mirror *A* and returns, and the other ray travels to mirror *B* and returns. The two rays are then recombined at the intersection *O*. If initially length (*OB*) = length (*OA*), then the optical path difference, δ, introduced by moving the mirror a distance L is $\delta = 2L$, since the ray travels along the path *OB* twice (out and back) before recombination occurs at *O*. If the interferometer is illuminated with a monochromatic beam of wavelength λ, the output will be a cosine signal, as illustrated in Fig. 2A. When mirror *B* is moved by $L = \lambda/4$, then $\delta = \lambda/2$, and the two beams interfere destructively at *O*—that is, the intensity of the combined beams is zero. When $L = \lambda/2$, $\delta = \lambda$ and the two beams combine constructively at *O* to give the maximum intensity of the incident beam (no losses are assumed). If the interferometer is illuminated with a white or polychromatic source of light, the output is more complicated. Considering this input to consist of (infinitely) many monochromatic sources, then only at $\delta = 0$ will all the input waves add together constructively to produce a maximum signal. The input and output signals for this case are illustrated in Fig. 2B and Fig. 3. The output of the interferometer is measured as a signal intensity, I, as a function of the optical path difference, δ, and is called the interferogram, $I(\delta)$.

The preceding background information provides a simple overview of the function of an FT (that is, interferometric) IR spectrometer. On illumination of the interferometer with a white light source and translation of the moving mirror, an interferogram $I(\delta)$ is produced which is characteristic of the source and the beam splitter. If the output signal is passed through a sample, the sample will absorb certain spectral components from $I(\delta)$, depending on its nature. The signal that emerges from the sample is an interferogram, $\bar{I}(\delta)$, which is characteristic of the sample, the beam splitter, and the source. As discussed in detail in (*1*), the spectrum $S(\nu)$ is related to $I(\delta)$ by means of the Fourier integral

$$S(\nu) = C\int_{-\infty}^{\infty} [\bar{I}(\delta) - {}^{1}\!/_{2}\bar{I}(0)]e^{-i2\pi\nu\delta}d\delta \qquad (4)$$

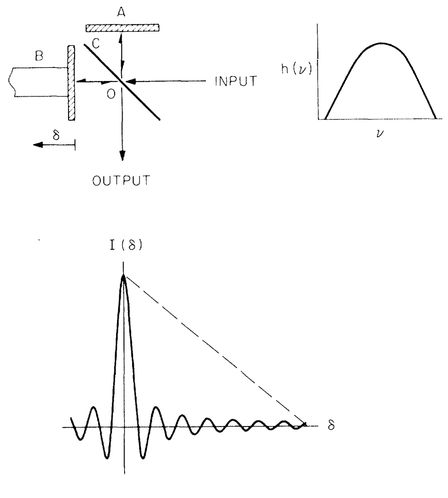
where C is a constant and $\bar{I}(0)$ is the signal intensity at $\delta = 0$. Theoretically, Eq. 4 specifies that the spectrum $S(\nu)$ can be obtained with the highest fidelity since no information has been lost. However, Eq. 4 requires that the optical path difference extend between the limits $(-\infty, \infty)$. This is physically impossible since the mirror scan will be limited to a finite passage $(-L, L)$. The result of limited mirror travel is to cause a loss of information in recovering $S(\nu)$. The Fourier series expansion illustrated in Fig. 1 provides a good analogy to the mirror displacement in an interferometer and the information contained in $S(\nu)$. Increasing the mirror displacement beyond $\delta = 0$ is analogous to including more terms in the series expansion of $f(x)$. The more terms included—that is, the greater the mirror travel—the better the definition or resolution of $S(\nu)$. The relation between resolution, $\Delta\nu$, and mirror displacement, δ, may be derived (*1*, *4*) by considering an interferometer to be illuminated with two monochromatic sources, ν_1 and ν_2, where $\nu_2 - \nu_1 = \Delta\nu(\text{cm}^{-1})$. In order to resolve ν_1 and ν_2, it is necessary to move the mirror far enough so that the two waves come out of phase. How far the mirror must move depends on $\Delta\nu$. The result

$$\Delta\nu = \frac{1}{\delta} = \frac{1}{2L} \qquad (5)$$

is the theoretical resolution of a Michelson interferometer and hence of an FT spectrometer. For example, to achieve a resolution of 1 cm^{-1} the mirror must move by 0.5 cm beyond $\delta = 0$, and for a resolution of 0.1 cm^{-1} it must move 5 cm.

In summary, to measure a spectrum with an FT spectrometer, a Michelson interferometer is illuminated with a white or polychromatic source of radiation and the movable mirror is translated over a distance $(-L, L)$ which depends on the desired resolution. The output signal is passed through a sample (or the sample itself serves as the source), and the resulting interferogram signal is received by an IR detector. The signal produced by the detector is sampled at certain increments of δ, depending on the highest frequency contained in $I(\delta)$. The spectrum $S(\nu)$ is recovered from $I(\delta)$ using the real part of the integral transform (*1*)

$$S(\nu) = C\int^{L} [I(\delta) - {}^{1}\!/_{2}I(0)]\cos(2\pi\nu\delta)d\delta \qquad (6)$$



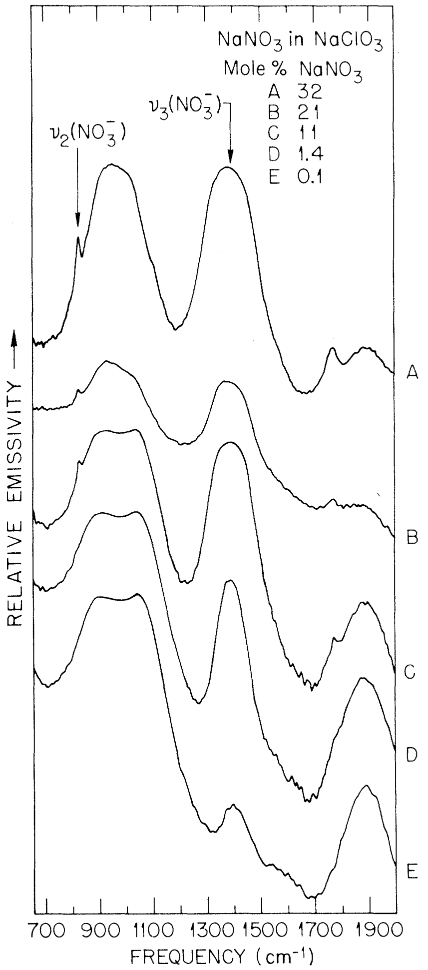
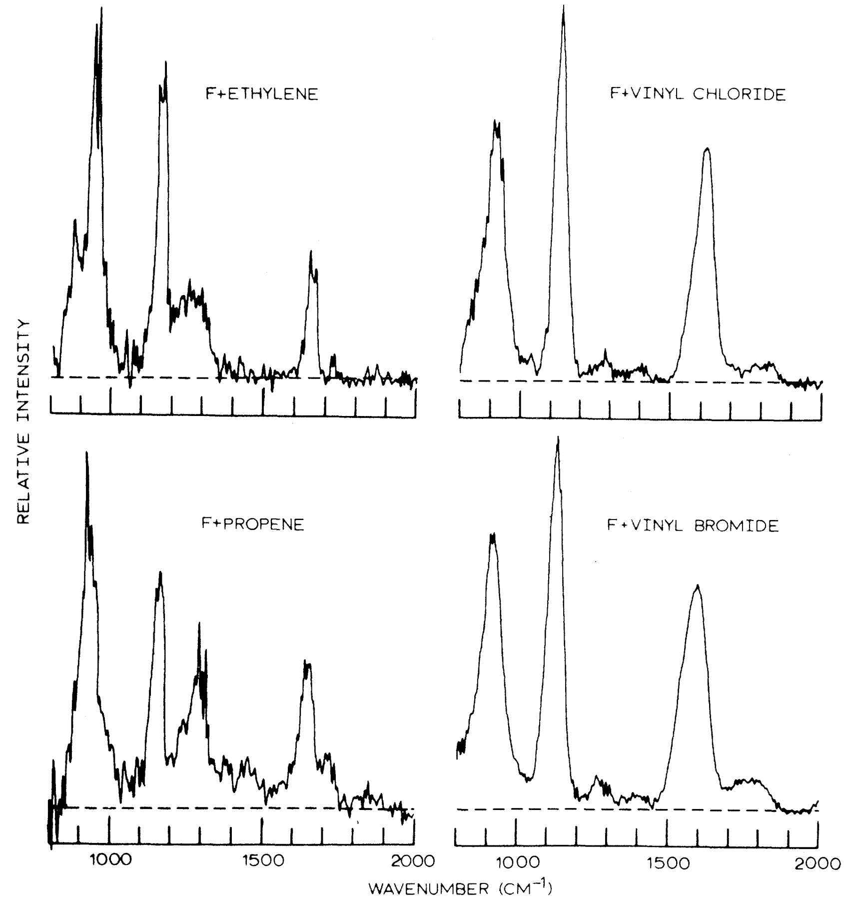


Fig. 3 (top left). Schematic diagram of a Michelson interferometer showing the fixed mirror (*A*), the moving mirror (*B*), and the beam splitter (*C*). The optical path is shown by the arrows. The interferogram output of the broadband input source is shown with a triangular apodization function indicated by the dashed line. Fig. 4 (top right). Infrared emission spectra of $NaNO_3$ dissolved in molten $NaClO_3$ measured at ~ 340°C. [From Bates and Boyd (*13*)] Fig. 5 (bottom). Normalized emission spectra from four reactions of F atoms with C_2H_3X molecules. The zero of intensity for each spectrum is indicated by the dotted line. [From Moehlmann *et al.* (*14*)]



where $L = 2\delta$ is the displacement of the moving mirror. The spectrum characteristic of just the sample can be determined by taking the ratio or difference of two measurements of $S(\nu)$ with and without the sample. A discussion of additional details regarding sampling of the interferogram, beam divergence in an interferometer and resolution, and the effect of truncating the Fourier integral on the spectrum $S(\nu)$ is given in the last section.

The difference in principles of operation between an FT spectrometer and a conventional grating instrument results in two major advantages of FT spectroscopy. These are Fellgett's or the multiplex advantage and Jacquinot's or the throughput advantage. A discussion of these formal advantages is given in the last section. Essentially, these advantages mean that IR spectra can be recorded at a much greater speed or at a greater sensitivity than can be achieved with a dispersive spectrometer. The feasibility of several of the applications described below depends on these advantages. An additional advantage gained with FT IR spectrometers is that the spectrum is measured at a constant resolution over the entire spectral region, as opposed to a grating instrument in which the resolution varies with frequency. This is an important feature in many types of experiments.

There are basically two types of FT spectrometers that are currently in use and are manufactured commercially. These are systems which use slow scanning and rapid scanning Michelson interferometers (*10*). A survey of these interferometric spectrometers from the early instruments to the most recent ones has been given by Griffiths (*3*). The instruments of greatest interest in FT IR, especially among chemical spectroscopists, are the rapid scanning systems. Their advantages have been discussed in some detail previously (*4*). An obvious advantage is the increased speed at which a spectrum can be recorded. Also, in a slow scanning system the input source must be chopped so that the detector receives the full signal from the interferometer only 50 percent of the time. Because a rapid scanning interferometer acts as its own chopper, the detector receives the full signal all of the time, and therefore the instrument is twice as efficient as a slow scanning one. Whereas the early slow scanning instruments were designed for operation in the far infrared region ($\nu < 400$ cm^{-1}) (*11*), a modern rapid scanning instrument is used in this laboratory over the region from ~ 15 to ~ 5000 cm^{-1}. This region is covered in several segments, requiring changes in beam splitter, source, and detector.

Applications of FT IR Spectroscopy

Rapid scanning FT IR instrumentation has made, and is continuing to make, a large impact on IR spectroscopy. The effect is comparable to the renaissance that occurred in Raman spectroscopy with the development of continuous wave gas lasers. The new and interesting experiments that have been conducted with FT IR systems are too numerous to be surveyed completely in an article of this length. A few examples of some recently reported investigations, chosen to illustrate some of the advantages of interferometric techniques in general and rapid scanning FT IR systems in particular, are described in this section.

Emission spectroscopy and IR chemiluminescence. Measurements of the IR emission spectra of materials can be used to study the chemical and physical properties of such systems as molten salts and ceramics at high temperatures. These measurements are most conveniently made by emission techniques in which the sample serves as the source of IR radiation. In the case of molten salts, this avoids the problem of finding an optical material suitable for transmission measurements which can also contain a corrosive liquid at temperatures that are usually above 300°C. While some IR emission measurements have been made with dispersive instruments (*12*), FT IR has been shown to be a superior technique in all instances, and virtually the exclusive method in some, for obtaining emission spectra of heated samples. For example, a study was conducted several years ago in this laboratory to develop techniques for measuring IR emission spectra of molten salts. Spectra of molten nitrates heated in a crude furnace were obtained with a rapid scanning FT IR spectrometer (*13*). An example is shown in Fig. 4 of the emission spectra of sodium nitrate dissolved in molten sodium chlorate. The ν_3 band of NO_3^- at ~ 1400 cm^{-1} was easily observed at concentrations as low as 0.1 mole percent, and should be detectable at NO_3^- concentrations several orders of magnitude smaller by subtracting the $NaClO_3$ solvent spectrum from the $NaClO_3 + NaNO_3$ solution spectrum (see below).

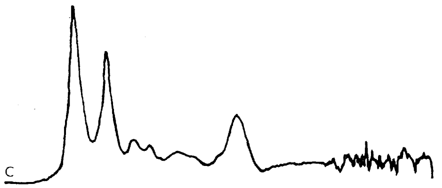


Fig. 6. Infrared spectrum of an aqueous solution of hemoglobin obtained with an FT spectrophotometer. (A) Absorbance spectrum of H_2O, (B) absorbance spectrum of aqueous hemoglobin solution, (C) absorbance spectrum of hemoglobin in aqueous phase (spectrum B minus spectrum A). [From Koenig and Tabb (*16*)]

Measurements of emission spectra from very distant sources at temperatures below 25°C or from a very small number of molecules present experimental problems that are orders of magnitude more difficult to solve than those encountered in measuring emission spectra from heated bulk samples. For all practical purposes, such measurements are accessible only through the use of rapid scanning FT IR instruments. An example of experiments in this category is the IR chemiluminescence measurements of McDonald and co-workers (*14, 15*). These studies were designed to determine how energy released in a chemical reaction is distributed over the vibrational, rotational, and translational degrees of freedom of the product molecules. The effects of collisional deactivation were minimized by carrying out the reactions at very low pressures ($< 10^{-4}$ torr). Under these conditions, the flux of excited molecules observed by the spectrometer was estimated (*14*) to be on the order of $\sim 5 \times 10^{15}$ sec^{-1}. In order to observe the emission from such a small number of molecules, it was necessary to reduce the background radiation by cooling the reaction chamber and the rapid scanning interferometer to ~ 80°K with liquid nitrogen. The mercury-doped germanium detector was held at 5°K by liquid helium. Figure 5 shows the luminescence spectra observed from the reaction of F atoms with C_2H_3X molecules, where X = H, CH_3, Cl, and Br. This reaction proceeds along two pathways to produce either vinyl fluoride or C_2H_2X radicals

$$F + C_2H_3X \begin{cases} \rightarrow C_2H_3F + X \\ \rightarrow C_2H_2X + HF \end{cases}$$

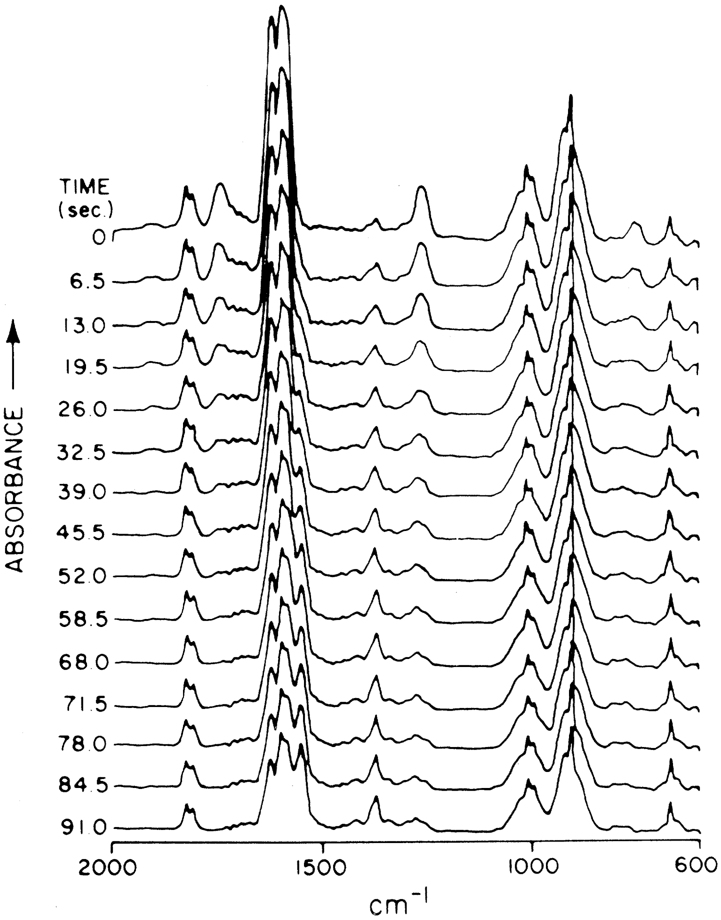
The three emission bands at 1654, 1153, and 929 cm^{-1} were assigned to the ν_1, ν_2, and ν_3 modes, respectively, of C_2H_3F, and the band at ~ 1280 cm^{-1} observed in the ethylene and propene reactions was attributed to CH_3 radicals. From the measured intensity ratios of the bands shown in Fig.

5, the distribution of energy into the ν_1, ν_2, and ν_3 vibrational modes of C_2H_3F for each of the four reactions was determined.

Infrared spectra of aqueous solutions. Measurements of the IR spectra of aqueous solutions are important in many areas of analytical, biological, and physical chemistry. Because water has very strong IR absorption bands, obtaining spectra of dissolved species is often difficult and in many cases is beyond the capabilities of a dispersion instrument, especially for dilute solutions in which the water bands overlap those of the solute. The throughput advantage and the ability to manipulate spectral data make such measurements nearly routine with an FT IR system. Figure 6 shows the IR spectrum of an aqueous solution of hemoglobin reported by Koenig and Tabb (*16*). The hemoglobin spectrum in curve C was obtained by subtracting curve A, the absorption spectrum of water, from curve B, the absorption spectrum of the aqueous hemoglobin solution. Before subtraction, the amide I band at 1657 cm^{-1} is completely obscured by the intense water band in the same region, and the other features in the hemoglobin spectrum are poorly defined. The data processing system of an FT spectrometer allows the operator to scale the spectra, if necessary, before subtraction in order to correct for changes in path length and solvent concentration, for example. As shown in Fig. 6, the correction achieved by subtracting the spectra can be judged by the flat baseline of the difference spectrum in the region of the strong water band near 600 cm^{-1}.

Kinetics of chemical reactions and spectra of transient species. The application of rapid scanning FT IR spectroscopy to kinetic studies was discussed recently by Lephardt and Vilcins (*17*). The ability to rapidly measure and store an IR spectrum makes it possible to study the kinetics of complex reactions with half-lives on the order of seconds. Figure 7 shows the gas phase reaction of butadiene with a mixture of NO_2 and N_2O_4. The spectra recorded at ~ 6.5-second intervals after mixing show the intensity decrease of reactant bands at 1628 cm^{-1} (NO_2), 1260 cm^{-1} (N_2O_4), and 910 cm^{-1} (butadiene) and the increase of the nitro product band at 1550 cm^{-1}. The absorbance profiles of these bands, shown in Fig. 8, provide a quantitative measure of the concentrations of reactants and product as a function of time, from which the kinetics of this reaction can be determined.

The results obtained from the kinetic study demonstrate the general applicability of rapid scanning FT IR instruments in measuring IR spectra of transient species. This feature has been utilized in the development of GC-IR instrumentation, which combines a gas phase chromatograph with a rapid scanning FT spectrometer (*18*). Kizer (*18*) has demonstrated the operation of a commercial GC-IR system by measuring the IR spectra of the constituents of a 1-μl sample of a natural product as each constituent was separated by the gas chromatograph. The chromatogram of this sample is displayed in Fig. 9, and the IR spectrum of the constituent which produces the seventh peak in the chromatogram is shown in Fig. 10. The comparatively high quality of the IR spectrum obtained from the small quantity of the seventh component shows that the detection limit of the GC-IR system extends at least to the microgram range. The extent of this limit has been recently probed by Azarraga (*19*). Figure 11 (*20*) shows the



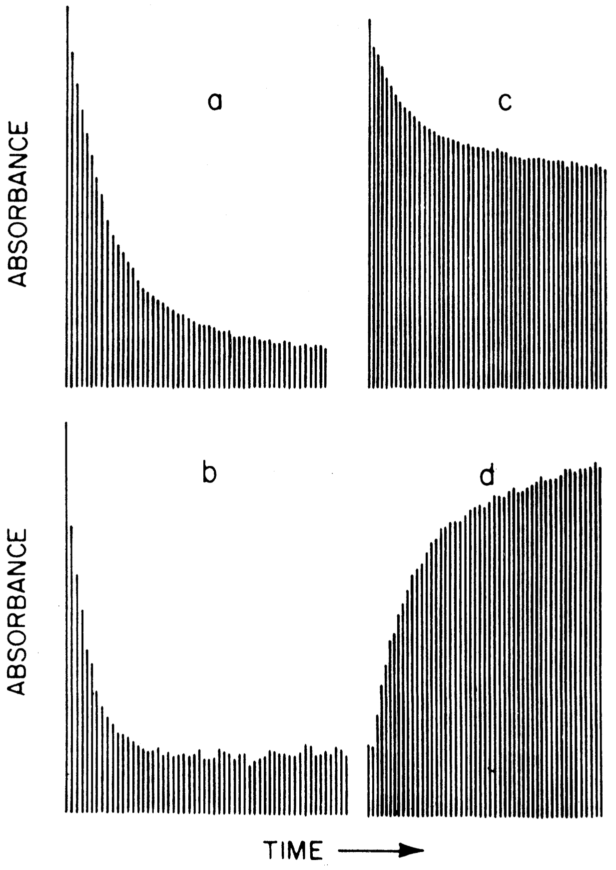


Fig. 7 (left). Infrared spectra of a reaction mixture of butadiene and NO_2-N_2O_4 at 6.5-second intervals after mixing. [From Lephardt and Vilcins (*17*)] Fig. 8 (right). Absorbance profiles of (a) NO_2 (1628 cm^{-1}); (b) N_2O_4 (1260 cm^{-1}); (c) butadiene (910 cm^{-1}); and (d) nitro produce (1550 cm^{-1}) from the reaction of butadiene with an NO_2-N_2O_4 mixture. The time interval between points is 6.5 seconds. [From Lephardt and Vilcins (*17*)] spectra obtained for submicrogram quantities of some organic compounds that were injected into a GC-IR system. These results indicate that IR spectra of a useful quality can be obtained from 5×10^{-7} g quantities of transient species in the gas phase by means of rapid scanning FT spectroscopy.

The examples discussed above are but a few of the many ways in which FT IR spectroscopy has been applied to basic research problems and to the development of new analytical techniques. The list of new applications will continue to grow as more instruments are placed in operation and as technological advances are made to improve the state of the art.

Some Additional Considerations of FT IR Spectroscopy

Effects of beam divergence and finite mirror travel. The resolution of a Michelson interferometer as given in Eq. 5 apparently depends only on the total displacement of the moving mirror past $\delta = 0$. This assumes that the interferometer is illuminated with a perfectly collimated beam of light and that no beam divergence is produced by the mirrors or beam splitter. In practice, however, divergence of the input source does occur, so that rays at the edge of the beam travel along different paths than those near the center of the beam. This means that δ of the extreme rays is different from δ of the axial rays. The result is that for some value of δ, the axial and extreme rays will interfere destructively at all frequencies so that additional mirror displacement produces no further increase in resolution (*4*). The maximum beam divergence that can be tolerated without causing a loss in resolution can be expressed as a maximum half-angle of the beam, $\gamma_{\max} = (\Delta\nu/\nu_{\max})^{1/2}$ radians (*4*). In this expression, $\Delta\nu$ is the resolution and $\nu_{\max}$ is the highest frequency in the spectrum. The reduction in beam divergence as specified by $\nu_{\max}$ is accomplished by inserting an aperture into the output beam from the interferometer. As shown by the expression for $\gamma_{\max}$, the diameter of the aperture must be smaller for higher resolution and as the upper frequency limit of the spectrum increases.

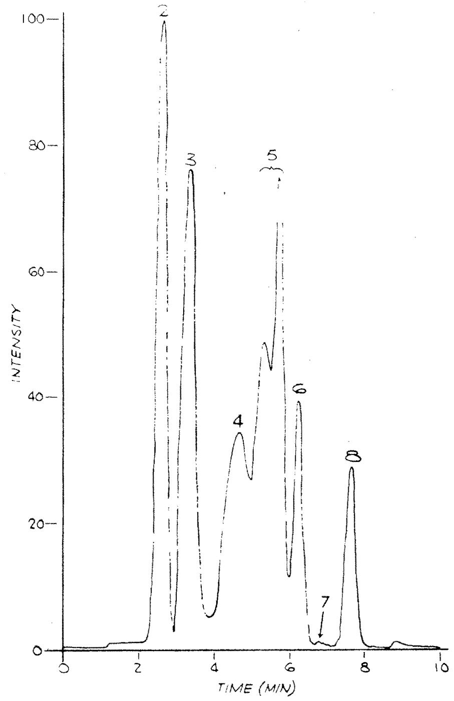


Fig. 9. Chromatogram of a natural product. [From Kizer (*18*)]

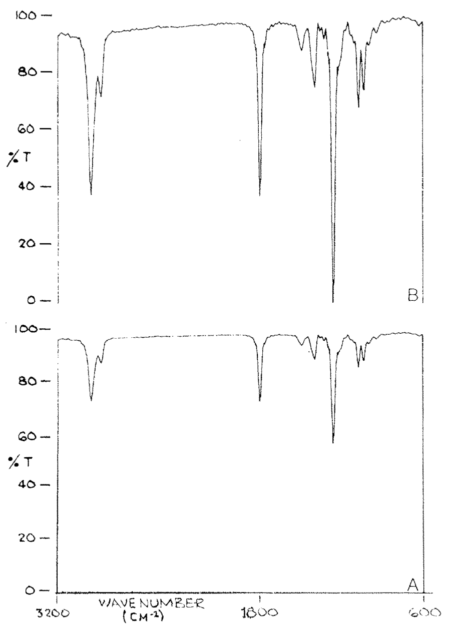


Fig. 10. (A) Infrared spectrum of the seventh peak in the chromatogram shown in Fig. 9 and (B) the same spectrum on an automatically expanded scale. [From Kizer (*18*)]

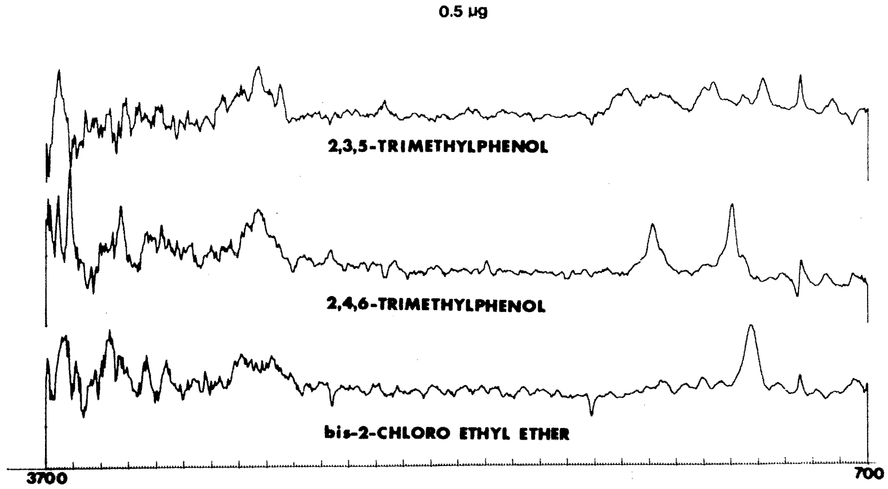


Fig. 11. Infrared spectra of 0.5-μg quantities of some organic compounds measured after injection into a gas chromatograph attached to an FT IR spectrometer. [Courtesy of L. Azarraga]

Aside from the question of beam divergence, we see that the limits of mirror travel $(-L,L)$ in Eq. 4 will determine the resolution achieved in the measurement. Within the limit of this resolution, all of the information contained in the spectrum will be obtained. However, what effect will truncating the integration of Eq. 4 (represented in Eq. 6) have on the appearance of the spectrum? A simple view of the effect is illustrated by the example shown in Fig. 1. Note that for higher values of n, as $f(x)$ is more closely approximated, large oscillations occur near the points of discontinuity (that is, at the corners of the box). This effect is known as the Gibbs phenomenon (*7*), and it is produced by the high-frequency components of the series (terms for large n). In the case of the spectrum, $S(\nu)$, small lobes are produced near the base of absorption bands. These lobes can be viewed as arising from the effect of multiplying the interferogram by a square-wave (or boxcar) function (Fig. 1) before the transformation is carried out. My experience has been that this effect is rarely a problem, but it can be minimized by multiplying $I(\delta)$ with a weighting function before computing the transform. This process is called apodization, and it is part of the computational procedure after the interferogram has been obtained. The most common apodization function is triangular (shown by the dashed line in Fig. 3) such that $I(\delta)$ points at increasing δ values have a decreasing effect on the transformed spectrum. While this process aids in reducing the side lobes at the base of a band, it also results in a loss of resolution (by about a factor of 2 with triangular apodization). The effects of different types of apodization functions on the transformed spectrum have been discussed in detail by Codding and Horlick (*21*).

Sampling the interferogram. A question that arises in computing the Fourier integral to obtain the spectrum is how many data points must be sampled from an interferogram in order to obtain, within the limit of resolution, all of the information contained in $I(\delta)$. This question is very important because certain restrictions will be imposed on the amount of data that can be handled by the computing facilities available. Information theory (*22*) provides the answer that if $\nu_{\max}$ is the highest frequency in a spectrum which extends from $0 \leq \nu \leq \nu_{\max}$, then the interferogram must be sampled each time δ changes by $1/(2\nu_{\max})$. The total number of data points that must be obtained thus depends on $\nu_{\max}$ and on the total change in δ. Using the result from above that $\Delta\nu = 1/\delta$, then the number of data points that must be sampled from the interferogram is given by $2\nu_{\max}/\Delta\nu$. For example, if a spectrum is to be measured at a resolution of 1 cm^{-1}, and if the highest frequency in the spectrum is 4000 cm^{-1}, then 8000 data points must be sampled on each side of the $\delta = 0$ point of the interferogram. If both sides of the interferogram are scanned, then 16,000 data points must be obtained. The amount of data that must be stored and processed thus depends on $\nu_{\max}$ and $\Delta\nu$, and on whether or not points from $I(\delta)$ are sampled on both sides of $\delta = 0$.

Fellgett's and Jacquinot's advantages. The two major formal advantages of FT IR spectroscopy over the conventional dispersive techniques were briefly mentioned above. These advantages are illustrated by assuming that the FT and dispersive instruments have certain common characteristics. In a grating (or prism) spectrometer, a white light source [$h(\nu)$ in Fig. 2B] illuminates a sample (or an emitting sample serves as the source), the resulting radiation is dispersed by a grating (or prism), and small segments of the dispersed light fall on a detector after passing through a slit which is set at some width to produce a resolution of $\Delta\nu$. Suppose that the spectrum of interest lies between ν_2 and ν_1. Then the number of spectral elements, n, is defined by $n = (\nu_2 - \nu_1)/\Delta\nu$. Thus, a spectral element is that part of $S(\nu)$ between ν_2 and ν_1 which is seen by the detector at any given time (*23*). If T_G is the total time required to measure a single spectral element (*24*), then nT_G is the total time required to scan between ν_2 and ν_1. An FT spectrometer contains no dispersing element or slit, and therefore all of the spectral information contained in the interval, $(\nu_2 - \nu_1)$, measured at resolution $\Delta\nu$, is received by the detector in the time, T_{FT}, required to record the interferogram. If it is assumed that the response times of the grating and FT spectrometers are the same, $T_G = T_{FT}$, then the spectrum can be recorded n times faster with the FT spectrometer than with the grating instrument with the same signal-to-noise ratio (S/N). On the other hand, if the same total time, nT_G, is taken by the FT spectrometer to record the spectrum, then the gain in S/N is given by

$$\frac{(S/N)_{FT}}{(S/N)_G} = \left(\frac{nT_G}{T_{FT}}\right)^{1/2} = n^{1/2} \qquad (7)$$

The $n^{1/2}$ gain in S/N is known as Fellgett's advantage or, more descriptively, as the multiplex advantage (*9*). The multiplex advantage is achieved by the way in which an interferometer functions and by the relationship, through the Fourier transform, between the input signal and the output signal. With the assumption $T_G = T_{FT}$, the FT spectrometer examines the entire spectrum in the same period of time that the grating instrument requires to examine a single spectral element. For example, if $\nu_2 - \nu_1 = 4000$ cm^{-1} and $\Delta\nu = \text{cm}^{-1}$, then $n = 4000$. Theoretically, an FT spectrometer can acquire the spectrum from 0 to 4000 cm^{-1} with a resolution of 1 cm^{-1} 4000 times faster than a grating instrument at the same S/N, or, from Eq. 7, a factor of ~ 63 increase in S/N can be gained with the FT spectrometer recording the spectrum in the same amount of time required by the dispersive spectrometer.

Jacquinot's or the throughput advantage results from the loss in energy of the input source in a dispersive instrument because of the presence of a grating and slit between the source and the detector. Such losses do not occur in an FT spectrometer since these components are not required. As discussed by Bell (*1*), the ratio of the throughputs for an FT and a grating instrument is given approximately by $E_{FT}/E_G \cong 2\pi(F/l)$, where F is the focal length of the collimator and l is the slit height. It is assumed that the focal length, the area of the collimator, and the resolving power are the same in both instruments. This expression also assumes that the grating in the dispersive instrument is set at the angle of maximum efficiency. Research quality commercial grating instruments have typical F/l ratios of ~ 22 to ~ 33, so that E_{FT}/E_G ranges between ~ 140 and ~ 200. The high throughput of interferometric spectrometers means that they can be used to great advantage in observing spectra from very weak sources. For this reason, they have been extensively employed in astronomical observations and, more recently, to observe emission spectra from chemical systems at relatively low temperatures.

References and Notes

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