Fourier Transform Infrared Spectrometry

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Summary. The theory and instrumentation for Fourier transform infrared spectrometry are discussed. These instruments measure infrared spectra of the same quality as spectra measured on grating spectrometers in about one thousandth of the time. Their sensitivity advantage for spectra measured in equal times is between a factor of 10 and 100. Commercial spectrometers are now available from nine vendors in North America. Important areas of chemistry include atmospheric monitoring, surface chemistry, and on-line identification of chromatographically separated materials. Many new biochemical and biomedical applications are also becoming apparent, including investigations of phase transitions in lipids and studies of the biocompatibility of implant polymers.

The origin of Fourier transform techniques for the measurement of high-quality infrared spectra can be traced back to the turn of the century, when Michelson first described the interferometer that now bears his name (*1*). In this instrument an input collimated beam of light is divided into two paths by a beamsplitter. The length of one of these paths is constant, while the other may be varied by translating a mirror. The two beams are recombined at the same beamsplitter, so that on the average half the beam returns to the source and the other half passes to a detector, usually after passing through an absorbing sample. The effect of the moving mirror is to introduce a path difference, and hence a phase difference, between the two beams on recombination at the beamsplitter, so that interference between these beams occurs.

For a monochromatic source and a mirror moving at constant velocity, the signal measured at the detector (which is known as the interferogram) is sinusoidal. For a polychromatic source, the interferogram is the resultant of the sinusoidal signals of the individual wavelengths emitted by the source. Only when the fixed and moving mirrors are equidistant are the sinusoidal signals due to each wavelength emitted by the source in phase. At this point the interferogram has a very large amplitude, and this region is often called the "centerburst." In practice, there is usually a very small phase shift between all wavelengths even at the centerburst, so that a typical "real" interferogram in this region is not symmetrical, but usually has the form shown in Fig. 1A.

The interferogram is related to the spectrum through its Fourier transform (FT), and the FT of the interferogram seen in Fig. 1A is shown in Fig. 1B. Transmittance spectra are usually measured by first measuring a single-beam background spectrum such as this; a sample is then placed in the beam and its single-beam spectrum is also measured. The ratio of these two spectra gives the transmittance of the sample, and the negative logarithm of this spectrum is usually computed to yield the absorbance spectrum.

There are several advantages to measuring infrared spectra interferometrically. The first is the multiplex (or Fellgett) advantage, which is derived from the fact that radiation at all wavelengths reaches the detector simultaneously throughout the measurement. All other factors being equal, the Fellgett advantage allows spectra of the same signal-to-noise ratio (SNR) to be measured M times faster on a Fourier spectrometer than on a monochromator, where M is the number of resolution elements in the spectrum. For equal measurement times, the SNR of spectra measured on a Fourier spectrometer is $\sqrt{M}$ times greater. The second advantage is the optical throughput (or Jacquinot) advantage: for spectra measured at the same resolution, the product of the solid angle and the area of the beam at any focus—that is, the throughput, is greater for an interferometer than for a monochromator.

For interferograms to be transformed into spectra, they must be digitized. In essentially all modern Fourier transform infrared (FTIR) spectrometers, this goal is achieved by sampling at equal intervals of optical path difference using the sinusoidal interferogram from a helium-neon laser beam which is passed through a different region of the beamsplitter of the interferometer. The infrared interferogram is generally digitized once per wavelength of the laser interferogram (typically at a zero-crossing). This method of sampling gives rise to the third major advantage of FTIR spectrometry, which is its extremely high wave number precision.

A fourth benefit, which results in part from the good SNR and wave number precision of FTIR spectra, is the ease with which spectra can be manipulated in a computer. Many of the applications of FTIR spectrometry that will be summarized in this article are derived as much from the way in which the data were manipulated as from the high SNR of the spectra themselves.

Commercially Available Instrumentation

Optics. The first two interferometers designed for Fourier transform spectrometry appeared in the marketplace in the mid-1960's. A far-infrared spectrometer was designed and sold by Research and Industrial Instruments Corporation (RIIC) in England. This was a slow-scanning instrument, in which the radiation from a mercury lamp source was chopped, passed through the interferometer and sample, and subsequently focused onto a Golay detector. Interferograms were usually digitized by using a paper-tape punch and transformed at a remote computer. The other Fourier spectrometer, introduced by Block Engineering in Cambridge, Massachusetts, incorporated a small rapid-scanning interferometer. This instrument differed in several important ways from the RIIC spectrometer. First, the modulation frequencies imposed by the interferometer, given by

$$f = 2V\bar{\nu}\ \text{Hz} \tag{1}$$

where V is the velocity of the mirror (cm sec^{-1}) and $\bar{\nu}$ is the wave number (cm^{-1}), were in the audio-frequency region. The signal could therefore easily be detected without the need for a chopper. Mea-

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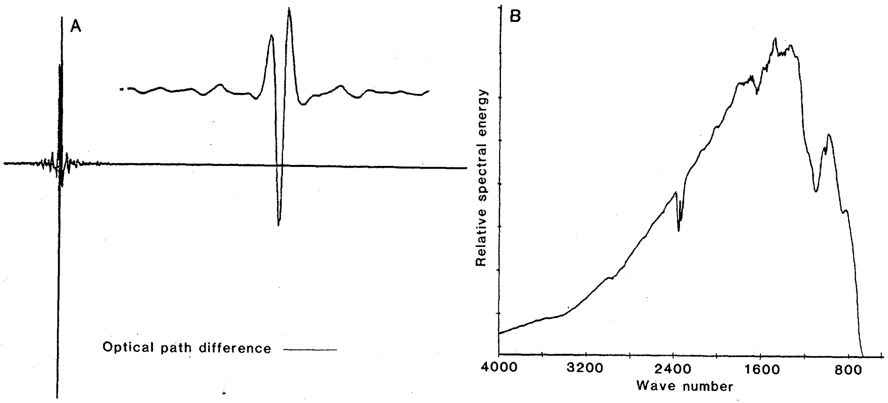

Fig. 1. (A) Typical mid-infrared interferograms measured with an optical path difference of 0.125 cm. An expanded view of the centerburst is also shown. (B) Transform of (A), which is a single-beam spectrum of this interferogram; resolution is 8 cm^{-1}.

surement times were typically less than 1 second per scan, and signal-averaging techniques could be used to increase the SNR. Unlike modern interferometers, the instrument was not laser-referenced, so the mirror could not be translated very far before successive interferograms lost their phase coherence. This meant that the resolution of these instruments was very low, since the nominal spectral resolution of FTIR spectrometers is given by the reciprocal of the maximum path difference between the two beams in the interferometer. Interferograms were co-added by a signal averager and the Fourier transform was performed with an audio-frequency wave analyzer.

By the end of the 1960's, several important developments had been made which paved the way to modern FTIR spectrometry. The so-called fast Fourier transform (FFT) algorithm, reported by Cooley and Tukey (*2*) in 1965, was applied to FTIR spectrometry by Forman (*3*) the following year. This algorithm usually reduces the time required to compute the spectrum by two orders of magnitude (and even more for high-resolution spectrometry). The development of laboratory minicomputers and disks allowed the FFT to be performed rapidly after data acquisition, and permitted spectra to be manipulated interactively. Small reliable He-Ne lasers allowed interferograms to be digitized at precisely equal intervals of path difference, so that the moving mirror could be translated over greater distances, resulting in higher spectral resolution. Finally, use of the triglycine sulfate (TGS) pyroelectric bolometer, which has a better high-frequency response than conventional thermal detectors, permitted the use of faster scan speeds than the original Block Engineering interferometer. This use of fast scan speeds was very important for a rather surprising reason. The SNR of the interferogram could become so high in the region of the centerburst at slow scan speed that it could actually exceed the dynamic range of a 15-bit analog-to-digital converter. With faster scanning, the SNR could be reduced to a level below the dynamic range of the analog-to-digital converter, allowing valid signal averaging to be performed.

The first interferometer to incorporate these innovations was the Digilab FTS-14. This instrument was introduced in late 1969 and Digilab was the dominant vendor of rapid-scanning FTIR spectrometers for several years. During this period, the potential of FTIR spectrometry became clear. However, because of the marginal reliability of early computers, disks, and peripherals, these instruments did not become accepted as rapidly as, say, FTNMR spectrometers did after their introduction. Nevertheless, many of the features that have enabled FTIR spectrometers to become so popular today, such as spectral subtraction and the gas chromatographic interface, were first developed on this instrument.

A few years after the Digilab instruments were introduced, a company called EOCOM developed a competitive interferometer. Although this instrument also did not have immediate appeal to the chemical marketplace, it actually had much to do with the current popularity of FTIR spectrometry, since in 1975 the Nicolet Instrument Corporation took over the infrared product line of EOCOM. They added their own data system to the EOCOM interferometer, to form the Nicolet model 7199 FTIR spectrometer. The healthy competition between Digilab and Nicolet hastened the development of the sensitive, reliable, versatile instruments of the present day.

The Nicolet and Digilab instruments involved similar design concepts. Each used a standard 90° Michelson interferometer, with the moving mirror being driven on an air bearing to ensure that its plane was maintained parallel to better than 1 μm throughout the scan. In both instruments an interferogram of a white visible light source was measured along with the infrared and He-Ne laser interferograms. The centerburst of the white light interferogram acted as a "fiducial mark" to trigger the onset of data acquisition. Both instruments produced excellent spectra and led to a general acceptance of the superiority of FTIR spectometers over grating spectrometers by the end of the decade.

Since the Digilab and Nicolet designs became accepted as standard, many other companies have introduced variations of this basic design. One of the first variations was the Genzel interferometer, which forms the basis of the Bruker IFS 113 and IBM IR/95 spectrometers. In these interferometers, the beamsplitter is located at a focus, after which the reflected and transmitted beams are collimated and passed to the opposite faces of a moving double-sided mirror. This design has one advantage over the standard Michelson interferometer. The small size of the focused beam at the beamsplitter allows several different beamsplitters, each optimized for a certain spectral region, to be mounted on a wheel and brought into the beam on a command from the computer. Thus the instrument can be kept evacuated even when changes between spectral regions are made.

Another trend-setting instrumental design was that of Bomem in Canada. In the Bomem interferometers, the alignment of the moving mirror is monitored by three laser beams throughout the scan, and the plane of the mirror is adjusted continuously to maintain parallelism. In this way Doppler-limited (0.002 cm^{-1}) spectra can be measured without resorting to more complicated optical designs. Recently, Beckman Instruments introduced two relatively inexpensive FTIR spectrometers in which the moving mirror is also dynamically aligned. The Beckman FT-1000 and 2000 series FTIR spectrometers are one example of several inexpensive Fourier spectrometers that are now commercially available. These include the Nicolet 10-DX and 20-DX and the IBM Instruments IR/32, which employ a conventional air-bearing drive 90° Michelson interferometers; the Nicolet 5-MX, which incorporates a "porch-swing" drive; and the Digilab Qualimatic, for which the angle between the fixed and moving mirrors is 60°. A very recent addition to the marketplace was announced by Mattson Instruments; their interferometer has cube-corner mirrors instead of the conventional plane mirrors of the standard Michelson interferometer. This design gives a result similar to the use of dynamic alignment but is less complex electronically.

All the instruments above are variants of the standard Michelson interferometer. There is, however, one design that is radically different. This is the refractively scanned interferometer, which is the basis of the Analect Instruments fX-6200 series and the Perkin-Elmer model 1500. In this design the path difference is generated by scanning a wedge of KBr across another wedge which is coated with germanium, as shown in Fig. 2. The design is claimed to exhibit greater stability to vibrations than a conventional Michelson interferometer (although in a laboratory environment its performance is comparable).

Other than the interferometer itself, several other components affect the performance of FTIR spectrometers, including the source, beamsplitter, and optical throughput. The most important component is the detector, and one detector in particular has revolutionized FTIR spectrometry over the past decade. This is the liquid nitrogen (LN_2) cooled mercury–cadmium telluride (MCT) photoconductive detector. Depending on the highest wave number to which it can respond, this detector may be 4 to 50 times more sensitive than TGS. The very high sensitivity MCT detectors do not respond beyond 750 cm^{-1}, but the lower sensitivity detectors cover most of the useful mid-infrared spectrum. Care must be taken when these detectors are used to monitor large signals, since the SNR close to the centerburst can exceed the dynamic range of the analog-to-digital converter and their response may become nonlinear. Nevertheless, many of the most important applications of FTIR involve use of these detectors. Another LN_2-cooled photodetector that is becoming popular for measurements above 2000 cm^{-1} is indium antimonide, which is about an order of magnitude more sensitive than MCT between 2000 and 4000 cm^{-1}. It is noteworthy that a sandwich detector of InSb over MCT is now available which has greater potential for low-energy measurements. Other detectors that are starting to become popular include the liquid helium (LHe) cooled germanium bolometer for far-infrared measurements and the LHe-cooled copper-doped germanium photodetector for very low energy mid-infrared studies.

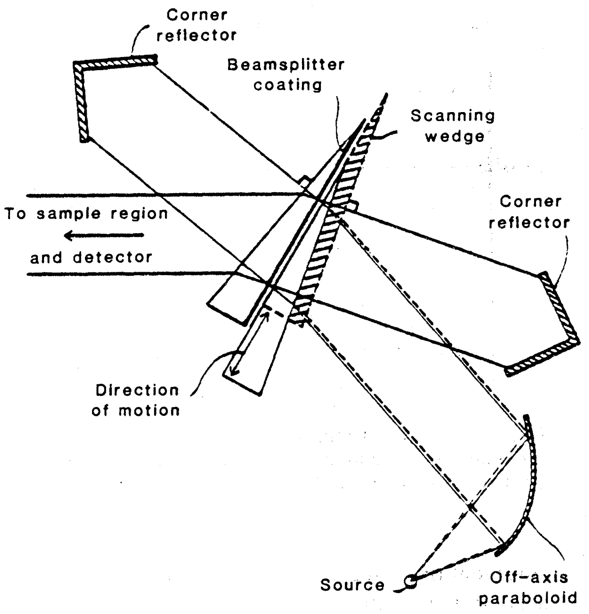

Fig. 2. Refractively scanned interferometer of the type used in Analect and Perkin-Elmer FTIR spectrometers.

In summary, FTIR spectrometers can be used to cover all spectral regions from the ultraviolet to the far-infrared. Their use for electronic spectroscopy has not become widespread because photomultiplier detectors are limited by photon shot noise. Therefore, the Fellgett advantage of FTIR spectrometry is completely offset, and even the Jacquinot advantage is partially lost. Nevertheless, even in this region, some very promising atomic spectra have been measured by Horlick *et al.* (*4*) with an inductively coupled plasma source. In all regions of the infrared spectrum, FTIR spectrometers give superior results to grating monochromators for the vast majority of measurements.

Data systems. FTIR spectrometers consist of two basic components: the optics, which were discussed above, and the data system. Enormous progress has been made over the past decade in the development of both sophisticated, versatile minicomputer-based data systems (of relatively high cost) and, more recently, of cheaper, but still powerful, microcomputer-based data systems. Modern high-performance instruments are typically equipped with minicomputers with at least 64 kilobytes of semiconductor memory and 10 megabytes of disk memory. Peripherals usually include a terminal (often with a color display), printer, and fast digital plotter. Some instruments are equipped with an array processor allowing, among other operations, very rapid FFT's; these are particularly important for processing of data obtained with a gas chromatograph (GC-FTIR).

Only a year ago, most microcomputer-based data systems did not have the power of minicomputer-based systems. This situation is rapidly changing. Microcomputers today are almost as powerful as 3-year-old minicomputers, and they are getting cheaper and more powerful. It is probable that, in only 2 or 3 years, microcomputer data systems will be even more powerful than the best contemporary FTIR data system on any instrument. The data system of the Analect fX-6250 is probably a foretaste of the future. This instrument is equipped with three processors, one for overall control, one for the FFT, and one for display processing. Special-purpose circuit boards are being introduced each month by the electronics industry, and these will undoubtedly also have a tremendous impact on FTIR data processing.

Applications of FTIR Spectrometry

Applications in which FTIR spectrometry has a significant impact can be divided into four areas, which sometimes overlap. These are rapid scanning, high sensitivity, high resolution, and data processing.

Rapid scanning. From the earlier discussion of Fellgett's advantage, it can be seen that measurements which previously took a quarter-hour to make with a scanning monochromator can now be made in a second or less. The fastest instrument sold today permits 25 interferograms yielding spectra of 8 cm^{-1} resolution to be measured and separately stored per second. This performance makes it possible to monitor with some accuracy the concentration of reactants and products in reactions taking place in a time scale of fractions of a second.

The rapid-scanning property of FTIR spectrometers is having its greatest impact in the field of GC-FTIR, which is summarized by Wilkins in this issue. FTIR is now rivaling mass spectrometry (MS) for the identification of unknowns eluting from gas chromotographs, and in one recent study was shown to identify more peaks than MS (*5*). It is clear that GC-FTIR will be of great importance for the analysis of environmental samples. The interface between FTIR and high-performance liquid chromatography (HPLC) is by no means at such an advanced state. Most of the HPLC-FTIR results reported to date have involved the use of size exclusion chromatography with chlorinated solvents (since these have good transmission over much of the infrared). The maximum concentration of most peaks eluting from either normal-phase or reverse-phase HPLC columns rarely exceeds 10 ppm (unless the column has been overloaded), so that on-line detection in a flow cell is very difficult (*6*). For normal- and reverse-phase HPLC, continuous elimination of the solvent is usually required before identifiable infrared spectra can be measured; several prototype systems for this purpose have been described, but none is yet commercially available. For at least one of these systems, a detection limit of 100 ng has been reported for reverse-phase separations with a water-methanol mobile phase (*7*). The next step in this progression will be the interface of an FTIR spectrometer with a supercritical fluid chromatograph, and the first results have already been described (*8*). This work is described in more detail in the article by D. R. Gere on page 253.

Processes occurring in less than the time of a single scan of the moving mirror cannot be monitored with a Fourier spectrometer in its conventional mode. Nevertheless, one technique has been described whereby spectra of processes occurring between 1 msec and 1 μsec can be monitored. In this experiment, which has been called time-resolved or (better) stroboscopic spectroscopy, an event is triggered by a zero-crossing of the He-Ne laser reference interferogram. This might, for example, be a laser pulse to initiate a photochemical reaction. The interferogram is then sampled at various intervals shortly after this event. It is usually not possible to trigger the event for every zero-crossing, but by repeating the experiment many times in a cyclical fashion, each sampling position can be monitored (*9*). The first experimental data of this type were subsequently proved to be incorrect (*10*), with artifacts appearing at many wave numbers. Stroboscopic spectra without these artifacts have recently been measured by two groups, but the measurement times required were quite long—more than 12 hours in one case—so the future popularity of this field is difficult to gauge.

High sensitivity. Many of the more important applications of FTIR spectrometry fall into this category, and only a few selected examples will be discussed. One application close to this author's heart is diffuse reflection spectrometry, in which the spectra of powdered samples can be measured directly (*11*). Many different samples have now been characterized by this technique, including coals, species absorbed on metal oxide and supported metal catalysts, pharmaceuticals, and proteins. In addition, diffuse reflectance spectrometry has formed the basis of two of the solvent elimination HPLC-FTIR interfaces described in the literature. It might be claimed that diffuse reflectance is not really a low-energy technique, since when a Fourier spectrometer is used in conjunction with an MCT detector the signal-to-noise ratio of the measured spectra is very high. Only 20 years ago, however, it was claimed that diffuse reflection techniques would never be easily applicable to mid-infrared spectrometry (*12*).

Another important application where low signals must be measured is photoacoustic (PA) spectrometry. It was seen in Eq. 1 that radiation passing through a Michelson interferometer is modulated at a frequency directly proportional to its wave number. At wavelengths where the sample has some infrared absorption the sample will heat up and cool down at the frequency at which the beam is modulated. If the sample is held in a small enclosed chamber, the gas with which it is in contact will also be heated and cooled at the same frequency. An acoustic signal at this frequency is therefore generated, and this signal can be measured with a small microphone. Since the interferometer modulates all the wavelengths from a continuous infrared source, the signal from the microphone will be an interferogram which, when transformed, will yield the absorption spectrum of the sample directly. Although the signal-to-noise ratio of PA-FTIR spectra is still not as high as, say, transmittance spectra, the technique can be very useful for studying samples that are not amenable to investigation by any other sampling techniques (for instance, polymer chunks). Recent data reported

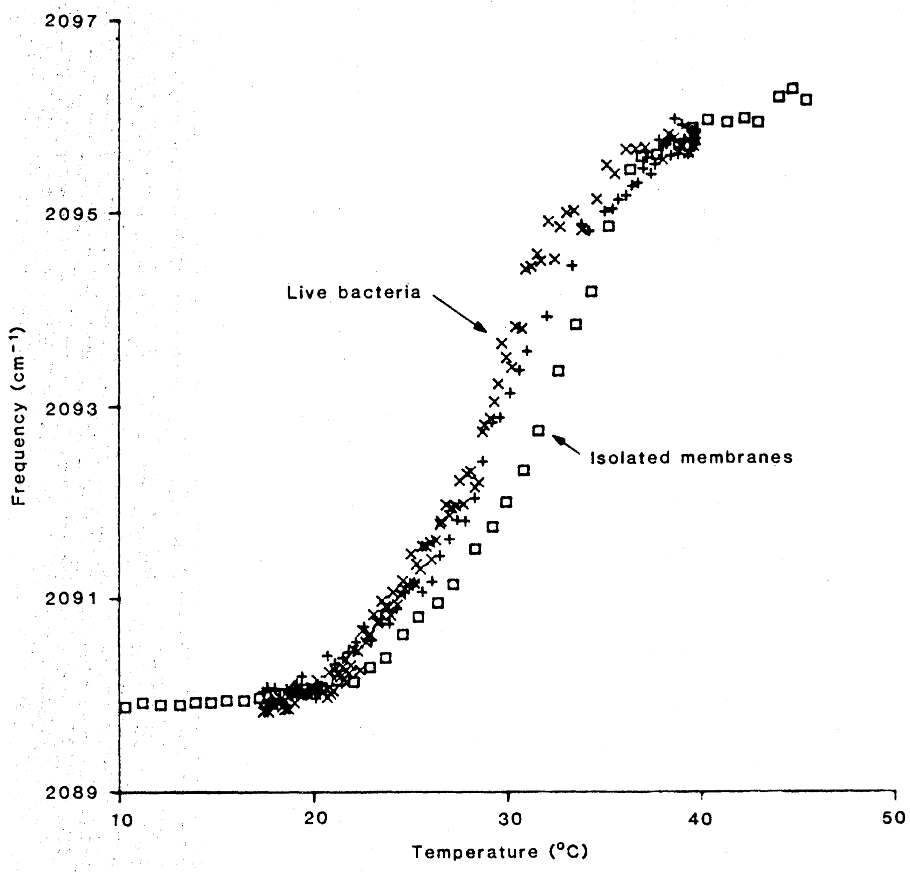

Fig. 3. Variation in the frequency of the C–D stretching bands of live bacteria and the membranes isolated from these bacteria as a function of temperature, showing that the temperature of the gel-to-liquid crystal transition is different [From Cameron *et al.*, (*13*)].

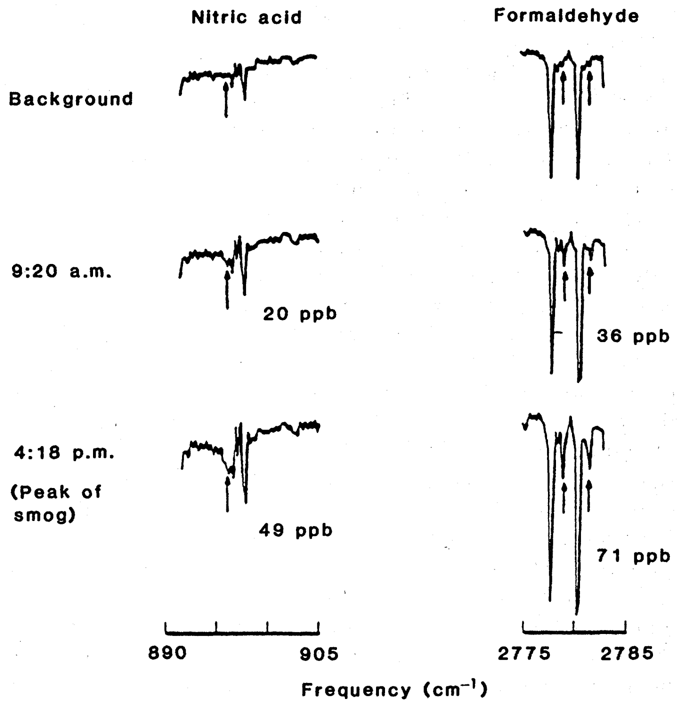

Fig. 4. Spectra used to identify and determine nitric acid and formaldehyde in ambient photochemical smog at a path length of 900 m. [From Tuazon *et al.* (*20*), courtesy of J. N. Pitts, Jr.]

by Digilab suggest that PA-FTIR spectrometry can even be used for quality control of samples of this type.

Certain solvents are often thought to be unsuitable for infrared spectrometry. The most obvious of these is water, but in the past few years several outstanding results have been obtained for species in an aqueous environment. Since water is common to all biochemical and biological systems, it is reasonable to believe that FTIR spectrometry will become increasingly important in these areas. Two examples may suffice to illustrate the importance of measurements of this type performed by FTIR spectrometry.

In the first of these, the thermotropic behavior of lipids was studied by the group led by D. G. Cameron and H. H. Mantsch at the National Research Council of Canada, in Ottawa. Several lipids were selectively deuterated so that their C–H stretching bands were shifted to a region of the spectrum where the absorption of water is relatively weak. The temperature of the cell could be accurately controlled and varied by the computer of the spectrometer. The center of gravity of absorption bands could be calculated to an accuracy of about 0.01 cm^{-1}, so that very small shifts could be measured. The liquid crystal-to-gel phase transition and the pretransition occurring at a slightly lower temperature could be monitored both from changes in band centers and bandwidths. After working with many synthetic lipids, this group grew deuterated samples of *Acholeplasma laidlawii B*, using perdeuteromyristic acid. The cells were harvested, washed, and placed in a 50-μm-thick BaF_2 cell whose temperature was 20°C. The cell temperature was raised to 39°C and then lowered to 16°C in 33 minutes, during which time 200 spectra were collected. After the measurement, the cells were cultured and found to be 98 to 99 percent intact. Subsequently, the plasma membranes were isolated and their spectra were measured in a similar way. The results are summarized in Fig. 3, and it can be seen that the transition from gel to liquid crystal occurs at a lower temperature for the live bacteria (*13*). This result contradicts many assumptions made previously in lipid research and illustrates the potential of FTIR spectrometry for biochemical research.

A series of even more difficult measurements was reported by the group led by R. J. Jakobsen and R. M. Gendreau (*14*) at Battelle's Columbus Laboratories. These experiments were designed to investigate the biocompatibility of various polymers used in artificial implants or organs. A thin layer of the polymer under study is laid on a germanium internal reflection element, and blood is passed from a live animal (dogs and sheep have been used so far) via a shunt over the surface of the internal reflection element and back into the animal. The buildup of proteins from the blood on the polymer film is followed at intervals of 0.8 second or longer by attenuated total reflectance FTIR spectrometry. Differences between the first layer and subsequent layers could be observed after the absorption spectra of the polymer film and the bulk water were subtracted from each spectrum (*10*). This type of experiment not only gives insights into the biocompatibility of polymers, but also illustrates many of the advantages accrued through the use of a Fourier spectrometer—high speed (0.8 second per measurement), high sensitivity (aqueous environment, monolayer detection), and computer manipulation.

Other measurements that require very high sensitivity are those of bands whose peak absorbance is less than 10^{-4} or 10^{-5}. These measurements may be more difficult for a Fourier spectrometer than low-energy measurements because of the limitations of analog-to-digital converters. Several novel approaches have been investigated for the direct measurement of weak absorption bands. One such technique is that of dual-beam FTIR spectrometry, in which both beams emerging from the interferometer are passed onto a single detector (*15*). In this case the interferogram that is measured is the Fourier transform of the absorption spectrum of the sample, and the intense emission spectrum of the source is nulled out. This technique does not yet have wide applicability, but it could well permit detection limits in GS-FTIR to be reduced (*16*).

Another technique can be used if the absorption by the sample of radiation of opposite polarizations is different. Here, a plate of an isotropic crystal such as ZnSe is stressed sinusoidally by using a piezoelectric tranducer. If plane-polarized radiation is passed onto this plate, alternating left and right circularly polarized radiation at the frequency of the modulation, or perpendicular and parallel linear polarized radiation at the second harmonic, is produced with an efficiency that depends on the amplitude of the extension and contraction of the plate. This device, which is known as a photoelastic modulator, has been used for the measurement of vibrational circular dichroism spectra of remarkably high quality by L. A. Nafie's group at Syracuse University (*17*) and for the characterization of species absorbed on flat metal surfaces by C. Marcott at Procter & Gamble (*18*). It is likely that in the future other external high-frequency modulations will be applied to either the infrared beam or the sample in an analogous fashion to polarization modulation. I believe such approaches will become very important in FTIR spectroscopic research in the next decade.

High-resolution measurements. Some of the more impressive early spectra obtained with a Fourier spectrometer were measured in France by the group led by P. Connes. Connes developed an interferometer that incorporated cat's-eye retroreflectors instead of the plane mirrors of a conventional Michelson interferometer. This optical configuration permitted very long optical path differences to be achieved, so that spectra ultimately could be measured at a resolution narrower than the Doppler width of absorption and emission lines (*19*). More recently, the interferometer manufactured by Bomem has made the same type of measurements possible through the use of dynamic alignment of the mirrors at all instants throughout the scan.

High resolution mid- and near-infrared measurements are permitting a more detailed knowledge of molecular vibrations and energetics. From an analytical viewpoint, high-resolution spectra over very long path lengths (1 km or even longer) have allowed components in the atmosphere to be measured at concentrations of a few parts per billion. Spectra of this type measured by J. N. Pitts, Jr., and coworkers at the California Statewide Air Pollution Research Center during a severe smog attack at Claremont, California, in 1978 (*20*) are shown in Fig. 4. Nitric acid and formaldehyde concentrations of ~ 20 and ~ 36 parts per billion, respectively, were detected at midmorning and increased to 49 and 71 ppb in the afternoon, coinciding with the maximum concentrations of ozone. These unequivocal spectroscopic determinations of HNO_3 in polluted air are important in assessing its role in acid deposition and atmospheric chemistry. Formaldehyde is an eye-irritant, suspected animal carcinogen, and initiator of photochemical smog. The use of long-path-length FTIR spectrometry led to the first detailed characterization of the simultaneous concentrations of O_3, HNO_3, peroxyacetyl nitrate, HCO_2H and HCHO in the atmosphere of California's South Coast Basin and is leading to a better understanding of the complex processes involved in the formation of photochemical smog.

Data manipulation. Because these instruments almost invariably incorporate a computer to perform the FFT, and because FTIR spectra are measured with a very high SNR and wave number precision, a great variety of programs has been written to manipulate the spectrum after it has been measured. Several of the experiments described previously have involved this sort of data manipulation. For example, in GC-FTIR and HPLC-FTIR, chromatograms reconstructed from the raw interferometric data may be plotted in real time and very rapid spectral searches performed at the end of the run. Sometimes the speed of these computations is outstanding. With a standard Digilab data system to which their Hi-Comp 32 microprogrammable processor has been added, a spectrum can be compared against 10,000 library reference spectra in 7 seconds. Printing out the results can actually take longer than the search.

Subtraction of the spectrum of a reference material from the spectrum of a mixture is perhaps the most popular operation carried out by users of FTIR spectrometers. In the biocompatibility studies of the Battelle group, not only was subtraction of all the spectra of the polymer and the bulk blood performed, but the spectrum of the first layer of protein deposited was subtracted from that of subsequent layers to amplify the differences in the adsorbed proteins.

Detailed description of the number of programs written for FTIR spectrometers is beyond the scope of this article. The following list represents a few of the more important of these programs. Factor, or principal component, analysis permits the number of components in a mixture to be determined. Curve-fitting routines allow band multiplets to be simulated by the addition of Lorentzian or Lorentzian-Gaussian bands. A particularly important new technique is that of Fourier self-deconvolution (*21*), in which the width of broad bands in a spectrum may be reduced by a factor of up to 3. It is probable that multivariate statistical techniques, which have not yet been fully exploited with these instruments, will also be applied to FTIR spectrometers in the next year or two. In fact, it is probably in the area of computer manipulation of data, rather than instrumental development, that the greatest advances will be observed in the near future.

References and Notes

1. A. A. Michelson, *Philos. Mag.* **31**, 256 (1891); *ibid.* **34**, 28 (1892).
2. J. W. Cooley and J. W. Tukey, *Math. Comput.* **19**, 297 (1965).
3. M. L. Forman, *J. Opt. Soc. Am.* **56**, 978 (1966).
4. G. Horlick, R. H. Hall, W. K. Yuen, in *Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems*, J. R. Ferraro and L. J. Basile, Eds. (Academic Press, New York, 1982), vol. 3, pp. 37–81.
5. K. H. Shafer, T. L. Hayes, J. W. Brasch, R. J. Jakobsen, *Anal. Chem.*, in press.
6. D. Kuehl and P. R. Griffiths, *J. Chromatogr. Sci* **17**, 471 (1979).
7. P. J. Duff, P. R. Griffiths, L. V. Azarraga, in preparation.
8. K. H. Shafer and P. R. Griffiths, *Anal. Chem.*, in press.
9. A. W. Mantz, *Appl. Opt.* **17**, 1347 (1978).
10. A. A. Garrison, R. A. Crocombe, G. Mamantov, J. A. de Haseth, *Appl. Spectrosc.* **34**, 399 (1980).
11. P. R. Griffiths and M. P. Fuller, in *Advances in Infrared and Raman Spectroscopy*, R. E. Hester and R. J. H. Clark, Eds. (Heyden, London, 1981), vol. 9, pp. 63–129.
12. G. Kortüm and H. Delfs, *Spectrochim. Acta* **20**, 405 (1964).
13. D. G. Cameron, A. Martin, H. H. Mantsch, *Science* **219**, 180 (1983).
14. S. Winters, R. M. Gendreau, R. I. Leininger, R. J. Jakobsen, *Appl. Spectrosc.* **36**, 404 (1982).
15. P. R. Griffiths, in *Chemical Fourier Transform Infrared Spectroscopy* (Wiley-Interscience, New York, 1975), chapter 7.
16. D. Kuehl, G. J. Kemeny, P. R. Griffiths, *Appl. Spectrosc.* **34**, 222 (1980).
17. L. A. Nafie and D. W. Vidrine, in *Fourier Transform Infrared Spectroscopy*, J. R. Ferraro and L. J. Basile, Eds. (Academic Press, New York, 1982), vol. 3, pp. 83–123.
18. A. E. Dowrey and C. Marcott, *Appl. Spectrosc.* **36**, 414 (1982).
19. G. Guelachvili and J.-P. Maillard, *in Proceedings of the Aspen International Conference on Fourier Spectroscopy*, G. A. Vanasse, A. T. Stair, D. J. Baker, Eds. (AFCRL-71-0019, Air Force Cambridge Research Laboratories, Cambridge, Mass., 1970), p. 151.
20. E. C. Tuazon, A. M. Winer, R. A. Graham, J. N. Pitts, Jr., *Atmospheric Measurements of Trace Pollutants: Long Path Fourier Transform Infrared Spectroscopy* (Report EPA-600/53-81-026, U.S. Environmental Protection Agency, Washington, D.C., 1981).
21. J. K. Kauppinen, D. J. Moffatt, H. H. Mantsch, D. G. Cameron, *Appl. Spectrosc.* **35**, 271 (1981).