

The Chemical Applications of Advances in Fourier Transform Spectrometry

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1 Introduction

Fourier transform spectrometry (FTS) is now a well-established technique and its use will soon be routine in chemical laboratories needing coverage of the infrared region from 5 cm^{-1} to 1000 cm^{-1} (or more). Recent developments in modulation techniques, in detectors and in computing systems have produced improved signal-to-noise ratios, decreased observation times, and new applications such as time-resolved spectrometry of fast chemical reactions.

The basic advantages of FTS over conventional grating spectrometry are outlined below and the advances are described and illustrated by some examples of chemical interest.

2 Background

After 15 years' development, Fourier transform spectrometry is now widely used, for examination of the infrared spectral region.^{1,2} It owes its present standing to the work of Janine and Pierre Connes, Mertz, Strong, and Gebbie, amongst others. Although Michelson himself was able to draw some conclusions about the structure and widths of spectral lines from visibility curves recorded with his two-beam interferometer, FTS was really born when Fellgett, at the Ohio State Symposium on Molecular Spectroscopy in 1952, pointed out the multiplex advantage to be gained by using a high-speed computer to extract the spectral information from an interferogram trace. Good reviews of the subject have been given by Low³⁻⁵ and Griffiths *et al.*,⁶ who have emphasized the chemical aspects.

A FT spectrometer consists of a source, a two-beam interferometer, a detector, and a computer (Figure 1). The interferometer part of the system is typified by a Michelson interferometer although variants are also used. Since an interferometer

¹ R. J. Bell, 'Introductory Fourier Transform Spectroscopy', Academic Press, New York, 1972; G. W. Chantry, 'Submillimetre Spectroscopy', Academic Press, London, 1971.

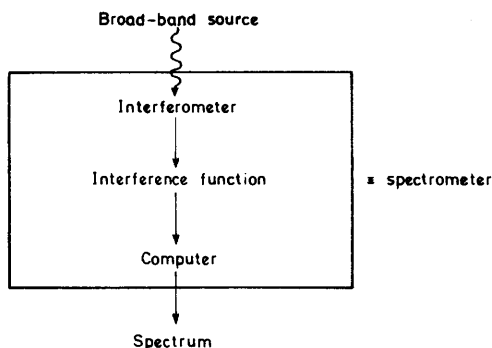
² G. A. Vanasse and H. Sakai, *Progr. Optics*, 1967, **6**, 259.

³ M. J. D. Low, *Analyt. Chem.*, 1969, **41**, 97A.

⁴ M. J. D. Low, *Naturwiss.*, 1970, **75**, 280.

⁵ M. J. D. Low, *Internat. Sci. and Technol.*, February, 1967, p. 52.

⁶ P. R. Griffiths, C. T. Foskett, and R. Curbelo, *Appl. Spectroscopy Rev.*, 1972, **6**, 31.



$$\tilde{F}\{\text{Interference function}\} \rightarrow \text{spectrum}$$

Figure 1 Block diagram showing the essentials of a FT spectrometer

has circular apertures, rather than narrow rectangular slits like a conventional spectrometer it has a greater radiation throughput. This confers an advantage, usually called the Jacquinot⁷ advantage, over the conventional spectrometer.

The basis of FTS is that the frequency distribution of the power incident on the detector (*i.e.* the spectrum) is obtainable by Fourier analysis of the variable part of the interfering power observed by the detector as the path-difference x between the two partial beams of the interferometer is changed. The interfering power [the *interference function* $I(x)$] consists of a constant (x -independent) part I_0 and a variable (x -dependent) part $F(x)$ called the (power) *interferogram*. In the ideal case this is a perfectly symmetrical function. The detected spectral power $B(\tilde{\nu})$ of wavenumber $\tilde{\nu}$ and the interferogram $F(x)$ are a FT pair:

$$F(x) = 2 \int_0^{\infty} B(\tilde{\nu}) \cos 2\pi\tilde{\nu}x \, d\tilde{\nu} = F_{\cos}\{B(\tilde{\nu})\} \quad (1)$$

and

$$B(\tilde{\nu}) = \int_{-\infty}^{\infty} F(x) \cos 2\pi\tilde{\nu}x \, dx = F_{\cos}\{F(x)\} \quad (2)$$

Thus, if $F(x)$ is measured, $B(\tilde{\nu})$, given by (2), is calculable from it. The boxed region of Figure 1 is, therefore, equivalent to a spectrometer. Figure 2 shows the relationship between $I(x)$, $F(x)$, and $B(\tilde{\nu})$,

In practice, (2) can be evaluated only over a finite range of x up to a maximum value D . The effect of this is to introduce finite resolution and spurious structure into the calculated spectrum.* The width and shape of the spectral window can

* Under certain conditions this spurious structure does not appear (see, *e.g.* W. J. Burroughs and J. E. Harries, *Infrared Phys.*, 1971, 11, 99).

⁷ P. Jacquinot, *Reports Progr. Phys.*, 1960, 23, 267.

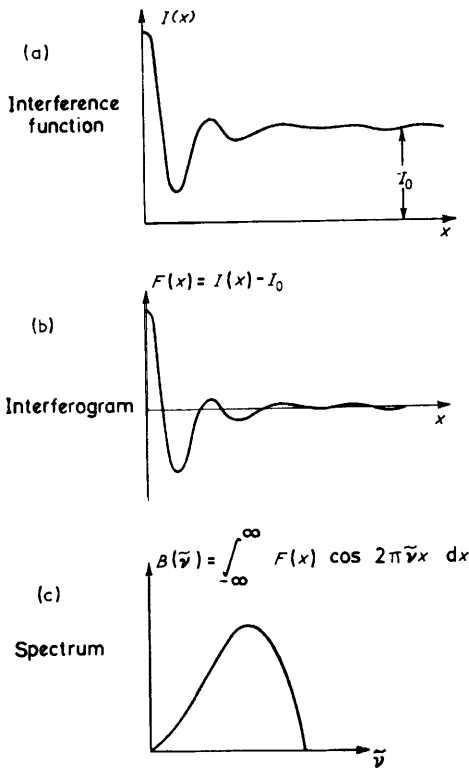


Figure 2 Relationships between (a) the interference function $I(x)$, (b) the interferogram $F(x)$, and (c) the spectrum of the detected radiation $B(\tilde{\nu})$

be adjusted and optimized (apodized) through the introduction into (2) of a weighting function $w(x)$ which tapers $F(x)$ to zero at $x = D$. The resolution R is given by

$$R = 1/wD, \quad (3)$$

where w is a number determined by the weighting function and typically is one. In the absence of weighting, $w = 2$. The resolving power is given by

$$\mathcal{R} = w\tilde{\nu}D \quad (4)$$

though there is a practical limit to the realizable resolving power imposed by the geometrical configuration of the optical system.*

In a practical system it is not the power $I(x)$ incident on the detector that is

* The practical condition to be satisfied is that $D \leq \pi/(\tilde{\nu}\Omega)$, where Ω is the limiting solid angle of the optical system.

recorded but N digitized samples of the voltage $V(x)$ from the detector amplifier.* All detectors produce 'noise', and it is preferable in FTS that the limiting noise should come from the detector. This is because the Fourier spectrometer is a multiplex instrument and all (say M) elements in the observed spectral band are detected for the whole time of observation T (rather as in a spectrograph containing a photographic plate).† As Fellgett⁸ showed, when detector noise is the limiting factor, this gives the multiplex spectrometer a gain in signal-to-noise ratio in the resultant spectrum of $M^{\frac{1}{2}}$ when comparison is made with a scanning spectrometer that also observes the M elements in time T . When the limiting noise is not from the detector, as is frequently the case in the near-i.r., where so-called photon noise can dominate, the multiplex advantage is cancelled (for photon noise) or transformed into a disadvantage (for source or signal noise).

Detector noise increases as the frequency of operation falls, so d.c. detection and amplification are not usually used to record the interference function. Instead, the radiation is modulated and a.c. detection is used. This is a common i.r. practice⁹ and the conventional way to modulate the radiation is by means of a periodic shutter such as a rotating sectored disc (amplitude modulation). The interferogram which results from the x -variation of the rectified output of the amplifier is once again perfectly symmetrical for the ideal case.

Interferometric instruments following these principles have come into widespread use in the infrared, and commercial systems are available for far-i.r. use.¹⁰⁻¹² The operator has in almost all instances used his own computer. FTS has been applied to the measurement of emission, transmission, absorption, and (power) reflection spectra, thereby displacing conventional scanning spectrometers. Chantry¹³ has given a review of applications to inorganic structure chemistry and Chantry and Chamberlain¹⁴ have described applications to the physical chemistry of polymers.

The throughput and multiplex advantages combine to give spectra which have greater radiometric accuracy at a given resolution or higher resolution without loss of signal-to-noise ratio. Alternatively, the observation time is reduced, materials with greater absorption (or weaker reflection) may be studied, or

* $2N$ samples if x is changed from $-D$ through 0 to D , as is often the case if $F(x)$ and $V(x)$ are not symmetrical. However, complete two-sided records are not essential as corrections for asymmetry can be made.

† The number of spectral elements is given by the detected spectral bandwidth divided by the resolution: $(\nu_{\max} - \nu_{\min})/R$.

⁸ P. B. Fellgett, *J. Phys. Radium.*, 1958, 19, 187.

⁹ R. A. Smith, F. E. Jones, and R. P. Chasmar, 'The Detection and Measurement of Infrared Radiation,' Oxford University Press, Oxford, 1968.

¹⁰ J. N. A. Ridyard, *J. Phys. Radium.*, 1967, 28, C-2, 62.

¹¹ G. W. Chantry, H. M. Evans, J. Chamberlain, and H. A. Gebbie, *Infrared Phys.*, 1969, 9, 85.

¹² R. C. Milward, *Infrared Phys.*, 1969, 9, 59.

¹³ G. W. Chantry, in 'Essays in Structural Chemistry', ed. A. J. Downs, D. A. Long, and L. A. K. Staveley, MacMillan, London, 1971, p. 91.

¹⁴ G. W. Chantry and J. Chamberlain, in 'Polymer Science', ed A. D. Jenkins, North-Holland, Amsterdam, 1972, p. 1330.

weaker sources may be examined. Which of these improvements applies depends on the experimental conditions. Three further advantages are the virtually complete absence of stray radiation, the ability to place the specimen just in front of the detector rather than near the source, where it may deteriorate, and the ability to place a good-quality specimen in one arm of the interferometer and obtain a refractive index spectrum¹⁵⁻¹⁷ from the resultant shift and distortion of the interferogram (dispersive¹⁷ or asymmetric^{15,16} FTS). This is valuable throughout the infrared generally for the evaluation of integrated absorption strengths^{18,19} without recourse to intensity measurements, and in the far-i.r. in particular where the complex permittivity can be evaluated, thereby giving continuity with microwave data.^{14,20} In certain specialized applications, however, Fourier spectrometers are not easily used, *e.g.* in the measurement of the spatial variation of the spectrum of a source such as a flame. Some (chemists particularly) have considered a particular drawback to be the generation by the instrument of a record which requires transformation in a computer before the desired spectrum is available. Where interferometric technique is the only way to obtain a spectrum, this drawback is only of academic interest but where there are competing conventional methods it does represent a real psychological factor affecting the choice of spectrometer. However, recently there have been advances in modulation techniques, in detectors, and in computers and computing generally, all of which have enhanced the advantages just listed and have improved the quality and extended the scope of spectra obtained by FTS. Some of these developments are now becoming commercially available. With these advances, a spectrum is available from the interferometer-computer combinations in much shorter time than any conventional system could achieve, for the same spectral quality, and this particular objection should rapidly become a thing of the past.

3 Recent Improvements

A. Modulation.—In the majority of interferometers, the path-difference is changed slowly and monotonically from 0 to D (or $-D$ to D). The interference record is then said to be generated aperiodically, and superimposed modulation of the radiation is required for a.c. detection. In amplitude modulation (AM) the entire magnitude of the detected signal is chopped periodically at a frequency f_0 (Figure 3a). The tuned (synchronous) amplifier delivers to the analogue-to-digital converter a rectified voltage whose magnitude is directly proportional to the power in the interference function.²¹ This includes the steady x -independent

¹⁵ E. E. Bell, *Infrared Phys.*, 1966, 6, 57.

¹⁶ E. E. Bell, 'Proceedings of the International Conference on Fourier Spectroscopy, Aspen, 1970', Air Force Cambridge Special Report, No. 114, 1971, p. 71.

¹⁷ J. Chamberlain, J. E. Gibbs, and H. A. Gebbie, *Infrared Phys.*, 1969, 9, 185.

¹⁸ J. Chamberlain, *J. Quant. Spectroscopy Radiative Transfer*, 1967, 7, 151.

¹⁹ J. G. Chambers, A. J. Barnes, and W. J. Orville-Thomas, *Chem. Physics.*, in press; J. G. Chambers, M. J. Phillips, A. J. Barnes, and W. J. Orville-Thomas, *Adv. Mol. Relaxation Processes*, in press.

²⁰ J. Goulon, J.-L. Rivail, J. W. Fleming, J. Chamberlain, and G. W. Chantry, *Chem. Phys. Letters*, 1973, 18, 211.

²¹ J. Chamberlain, *Infrared Phys.*, 1971, 11, 25.

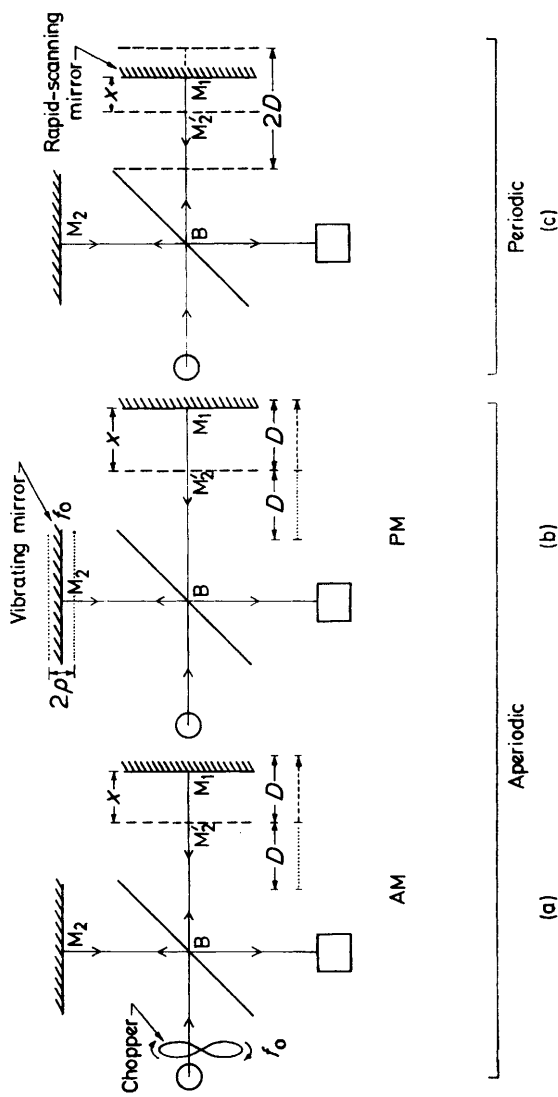


Figure 3 Modulation in two-beam interferometers: (a) aperiodic generation with amplitude modulation, (b) aperiodic generation with phase modulation, (c) periodic generation-rapid scanning. M₁ = 'movable' mirror, M₂ = 'fixed' mirror, M₂' = image of M₂ in arm 1 of interferometer, B = beam divider

contribution and superimposed signal-carried noise, both of which are unwanted for the Fourier transformation. Moreover, on average, the chopper halves the power available for detection. Until this year, all commercial aperiodic interferometers had this type of modulation.

A recent advance has been to use modulation based on interference, which gives strong discrimination in favour of the x -dependent part of the interference function. This improvement was first suggested by Mertz²² in 1958 but was not successfully applied until the period 1965–70 in the near- and mid-i.r. (by J. Connes *et al.*²³ in France) and in the far-i.r. (by Chamberlain, Gebbie, and their colleagues^{24,25} in the U.K.). This has been variously called internal modulation,²³ path-difference modulation (PDM), or phase modulation²¹ (PM). No chopper is used and modulation of the radiation is achieved by vibrating one of the interferometer mirrors (Figure 3b). The form of modulation is selective over a broad spectral band, and so the amplitude of the vibration is usually chosen to be half a wavelength for radiation near the centre of the spectral band of interest.

The result of the vibrating mirror motion is to produce a phase-modulated interference record which resembles the first derivative of the AM interference record and which is ideally antisymmetrical (Figure 4). The background contribution I_0 is not detected. Zero path-difference, manifested by the grand maximum in AM, is given by a negative-going zero-crossing which occurs where the voltage variation is virtually linear with path difference.

Phase modulation is most effective in improving signal-to-noise ratio where

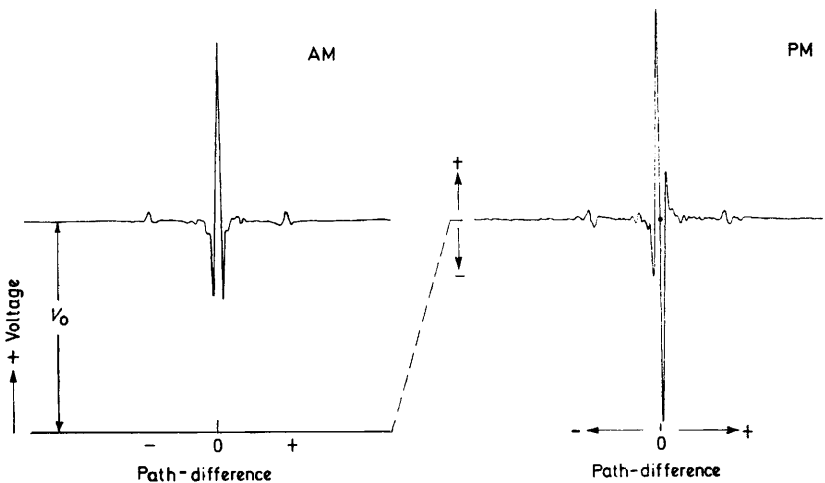


Figure 4 Aperiodic interference records: AM and PM

²² L. Mertz, *J. Phys. Radium*, 1958, **19**, 233.

²³ J. Connes, P. Connes, and J. P. Maillard, *J. Phys. Radium*, 1967, **28**, C-2, 120.

²⁴ J. Chamberlain and H. A. Gebbie, *Infrared Phys.*, 1971, **11**, 56.

²⁵ J. Chamberlain, W. J. Burroughs, and J. E. Harries, in 'Mesospheric Models and Related Experiments', ed. G. Fiocco, Reidel, Dordrecht, Holland, 1971.

signal-carried noise dominates. A significant part of this noise is carried by the background component I_0 and it is reduced, if not eliminated, with the suppression of I_0 . Thus, PM has been used with enormous success in atmospheric and astrophysical spectrometry by P. Connes²⁶ and Harries and Burroughs.²⁷ Even in the laboratory, however, it offers advantages;^{24,28,29} the elimination of the chopper effectively doubles the detected power; the effects of source drift and fluctuation are reduced; and since the voltage interference record has a stable zero background, the digital scale may be filled with the variations of the interference signals simply by changing the amplifier gain, and no offset is required (as in AM). This latter aspect is particularly valuable in dispersive FTS, where I_0 may be an appreciable fraction of the maximum interfering power¹⁷ and overload due to it can occur long before the interferogram fills the digital scale. The linearity of the PM record near the principle zero-crossing enables interpolation, for the evaluation of fringe shifts, to be more accurately performed than when AM records are used and non-linear interpolation is required.²⁴

PM is now commercially available with the Grubb-Parsons far-i.r. cube interferometer,¹¹ and Figure 5 shows an example of a spectrum from 10 to 40 cm^{-1} obtained with such an interferometer fitted with a Rollin indium antimonide

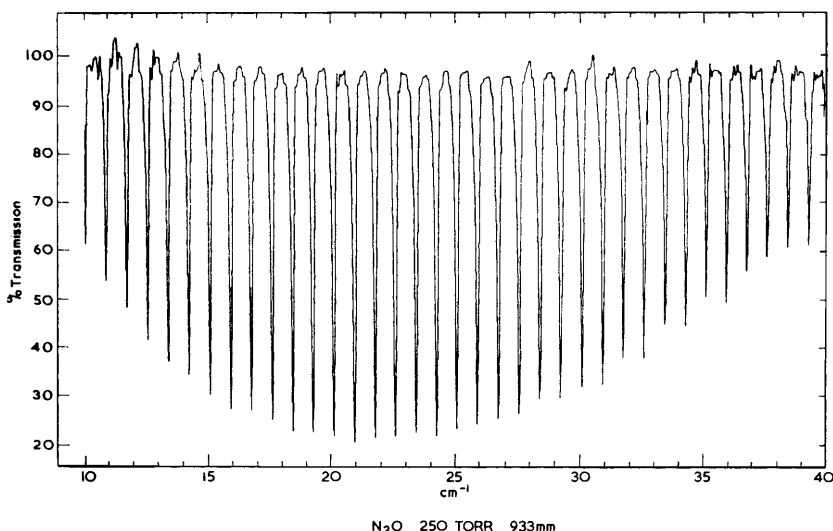


Figure 5 Transmission spectrum of N_2O . The resolution (unapodized) is 0.05 cm^{-1} . The gas cell was 933 mm in length and the gas was at pressure 250 Torr and temperature 23.5°C . The interferometer had PM and a liquid-helium-cooled Rollin detector. The observation time was 50 min

²⁶ P. Connes, *Ann. Rev. Astronomy*, 1970, **8**, 209.

²⁷ J. E. Harries and W. J. Burroughs, *Quart. J. Roy. Meteorological Soc.*, 1971, **97**, 519.

²⁸ P. Connes, in ref. 16, p. 121.

²⁹ G. J. Davies and J. Chamberlain, *J. Phys. (A)*, 1972, **5**, 767.

detector. The spectrum,^{30,31} which is unapodized and has a resolution 0.05 cm^{-1} , represents the transmission of N_2O obtained from the ratio of a specimen spectrum to a background spectrum, each obtained by Fourier transformation of a single interferogram. It is possible to achieve higher resolution than this in the far-i.r. but it is not common because the weakness of available sources sets a practical limit. The ultimate resolution in a spectrum, both emission and absorption, is set by the available integration time and by the relative magnitudes of the power in the resolution bandwidth compared to the overall noise level. FTS techniques permit a much higher resolution to be achieved before practical limitations set in, because of the more efficient use of the energy of the source, but it does not seem likely that resolution better than 0.01 cm^{-1} will be attainable in practice.

For very many of the observations which the chemist would want to make, high resolution is unnecessary, and then the advantages of PM FTS can be turned to providing much better radiometric precision than can be obtained with dispersive instruments. This is most desirable in many connections but one

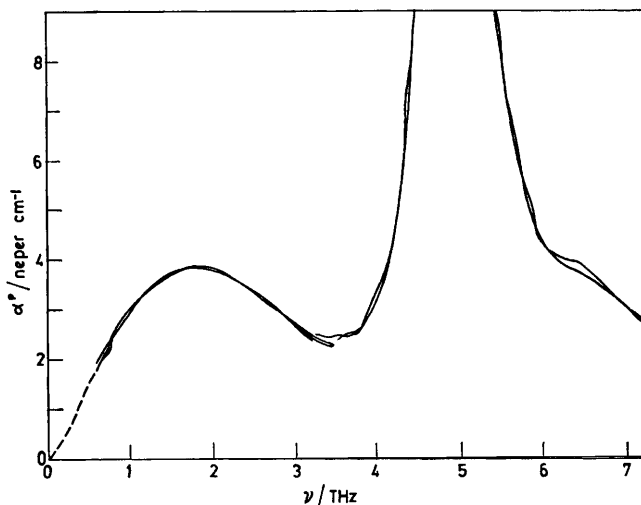


Figure 6 Power absorption coefficient of a solution of *p*-difluorobenzene (6.16 mol l^{-1} in carbon tetrachloride). Three independent spectra are superimposed to demonstrate the reproducibility. The resolution is 4 cm^{-1} and the temperature of the solution was $20 \pm 2^\circ\text{C}$. The effects of reflection losses at the boundary between the liquid layer and the cell windows have been eliminated. The spectrum clearly shows the broad absorption centred on 60 cm^{-1} that is characteristic of the liquid state. The interferometer had PM and a Golay-cell detector

[Adapted from *J. Phys. (A)*, 1972, 5, 767]

³⁰ J. W. Fleming, private communication.

³¹ J. W. Fleming and J. Chamberlain, *Infrared Phys.*, 1974, 14, 277; J. W. Fleming, 'I.E.E.E. Transactions on Microwave Theory and Techniques, 1974,' MTT-22, p. 1023.

important case is the dielectric spectroscopy of liquids at submillimetric wavenumbers. Figure 6 gives an indication of the reproducibility obtainable with PM even when a Golay-cell detector is used.²⁹

Perhaps the most striking results to be obtained by FTS have been recorded in the near- and mid-i.r. by J. and P. Connes and their colleagues, using interferometers equipped with PM and other refinements. Figures 7 and 8 show examples of the spectra that have been obtained,³² these being of holmium in emission and of N₂O at low pressure in absorption, respectively. The combined advantages of modern FT spectrometers have enabled J. Connes *et al.*³³ to record i.r. spectra with the highest resolving power yet achieved ($\mathcal{R} \approx 10^6$). This is clearly of importance to those interested in the detailed quantum properties of molecules.

Apart from the aperiodic type of interferometer described above, a second type, the rapid-scan interferometer, has been developed in recent years. The movable mirror is translated rapidly, but at constant speed, repetitively from $-D$ to $+D$, scanning the whole interference function with each sweep.^{6,34,35} A common mode for the drive is the sawtooth of Figure 9, which gives a periodic interference record as shown. The frequency structure of the voltage leaving the

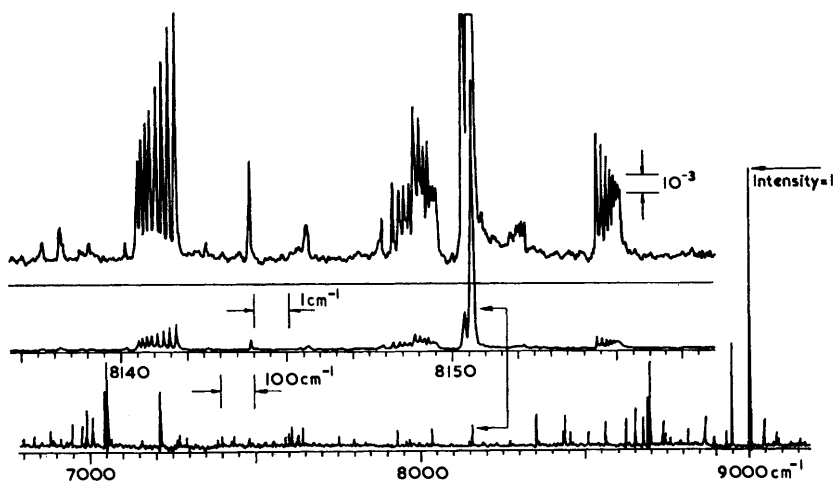


Figure 7 Holmium emission spectrum. The resolution in the upper two traces is 0.02 cm^{-1} , in the lower trace it is 2 cm^{-1} . The intensity scale in the upper trace is ten times that in the middle trace. For the maximum resolution 10^6 interferogram samples were required and the observation time was 10 h. The interferometer has PM and a PbS detector. The lines show the hyperfine structure in the holmium spectrum (Adapted from *Nouv. Rev. d'Optique Appl.*, 1970, 1, 3)

²⁹ G. Guelachvili and J. P. Maillard, in ref. 16, p. 151.

³² J. Connes, H. Delouis, P. Connes, G. Guelachvili, J. P. Maillard, and G. Michel, *Nouv. Rev. d'Optique Appl.*, 1970, 1, 3.

³⁴ L. Mertz, *J. Phys. Radium*, 1967, 28, C-2, 87.

³⁵ E. V. Loewenstein, in 'Far Infrared Spectroscopy', ed. K. D. Möller and W. G. Rothschild, Wiley, New York, 1971, p. 672.

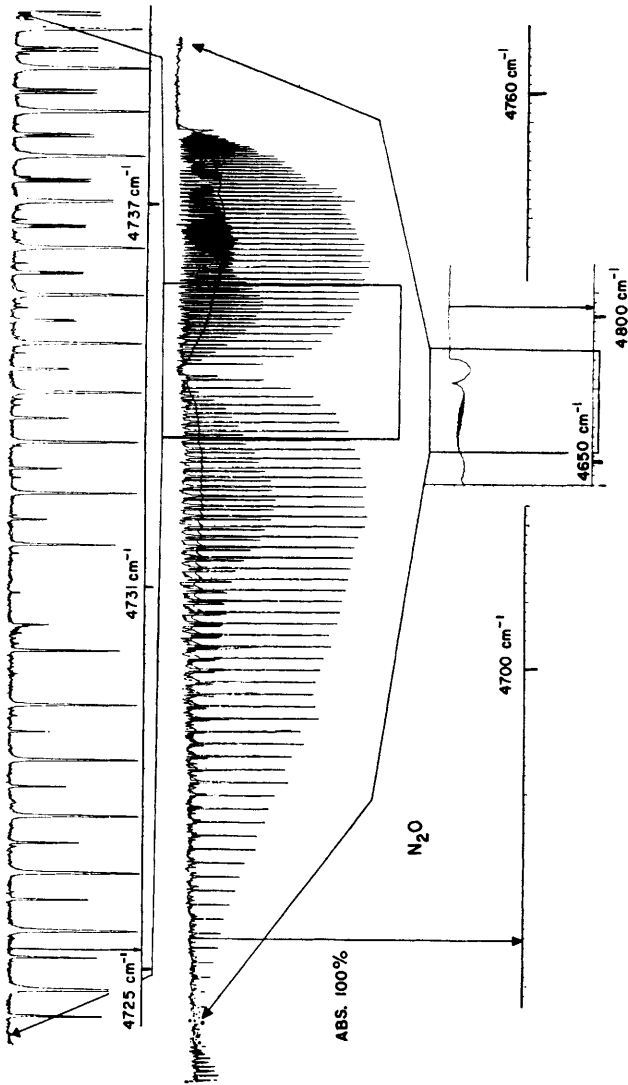


Figure 8 N₂O transmission spectrum in the region of the ($2\nu_1 + \nu_2$) band at 4730 cm⁻¹. The resolution in the lower trace is 0.8 cm⁻¹ ($N = 4500$, $T = 4$ min); in the middle trace $R = 0.08$ cm⁻¹ ($N = 45\ 000$, $T = 45$ min); and in the upper trace, showing a 10 cm⁻¹ slice near the band centre, $R = 0.008$ cm⁻¹ ($N = 450\ 000$, $T = 5\frac{1}{2}$ h). Two spectra are superimposed in the upper trace. The path in the gas was 10 m and the gas pressure was 2 Torr. The interferometer had PM and a PbS detector (Adapted from *Nouv. Rev. d'Optique Appl.*, 1970, 1, 3)

detector depends on the scan speed and the spectrum being observed, and usually lies in the audio-frequency range. Wavenumber $\bar{\nu}$ is converted into frequency according to $f = v\bar{\nu}$, where v is the speed of the moving mirror. The detector and amplifier must have a sufficiently wide and flat response to accommodate this range or else there will be some loss of the multiplex advantage. Samples of the periodic interference record are taken at each of the required values of x , put into store, and corresponding samples of successive scans are co-added for as long as necessary (usually until the signal-to-noise ratio is adequate). Rapid scanning (like PM) was first suggested by Mertz,³⁴ who applied it to astrophysical and astronomical problems where the scan rate can be made fast enough to 'beat' scintillation noise superimposed on the incident radiation. The work of Mertz led to the construction by Block Engineering of the near-i.r. rapid-scanning cube interferometer.

In the laboratory, rapid scanning enables single interferograms to be recorded very quickly⁶ (in a few seconds or less, depending on resolution) and co-added as necessary; as there is no chopper, all the power leaving the source is detected. However, the method becomes increasingly hard to use if D and/or N become very large, or if the rate of data acquisition becomes very high. Subject to these restrictions, the technique works very well, as Griffiths *et al.*⁶ have shown using the commercial Digilab instrument designed for the near- and far-i.r. Rapid scanning has also been particularly rewarding in atmospheric and astrophysical spectrometry, as Hanel *et al.*³⁶ have demonstrated.

In addition to the usual types of spectrometry, rapid-scanning is particularly suitable for studying time-varying processes for which the variation is similar to or slower than the period of scan T_0 .^{3,37} An important example for chemists is gas chromatography monitored by its i.r. spectrum: Figure 10 illustrates a g.c.

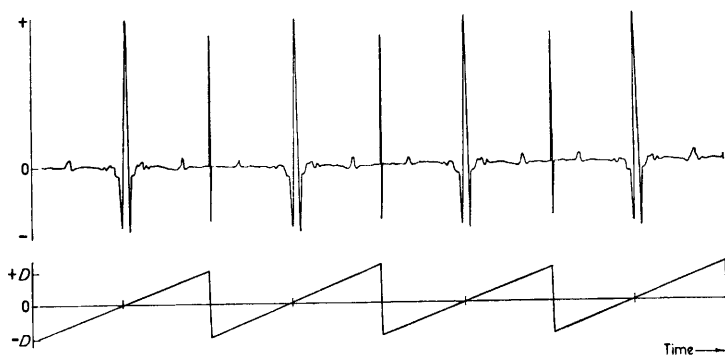


Figure 9 Periodic interference record (upper trace) produced by periodic saw-tooth change of path-difference (lower trace).

³⁶ R. Hanel, B. J. Conrath, W. A. Hovis, V. G. Kunde, P. D. Lowman, J. C. Pearl, C. Prabhakara, B. Schlachman, and G. V. Levin, *Science*, 1972, **175**, 305.

³⁷ J. O. Lephardt and P. R. Griffiths, private communication.

result of Lephardt and Griffiths³⁷ in which three distinct spectra separated by seven seconds overall are shown. The spectra were recorded 'on the fly'. A measurement such as this would be impossible without trapping if a grating spectrometer or aperiodic interferometer were used.

B. Detectors.—The second significant advance has been in detector design and construction.^{38,39} This has led to detectors with higher sensitivity, lower noise, and greater speed than hitherto. In addition to improving signal-to-noise ratios it is possible to use high frequencies for the modulation of the radiation, and it has proved feasible to use FTS to obtain time-resolved spectra with microsecond resolution. Cooling by liquid nitrogen (as in PbS for the near-i.r.—see Figure 8) or by liquid helium (as in InSb for the far-i.r.—see Figure 5) is common but not universal. The use of liquid refrigerants presents few problems, for modern cryostats are easily filled and have long holding times. Even the ambient-temperature Golay cell can give good quality spectra well into the far-i.r. if used with PM (see Figure 6). However, the Golay cell has a slow response, and a particu-

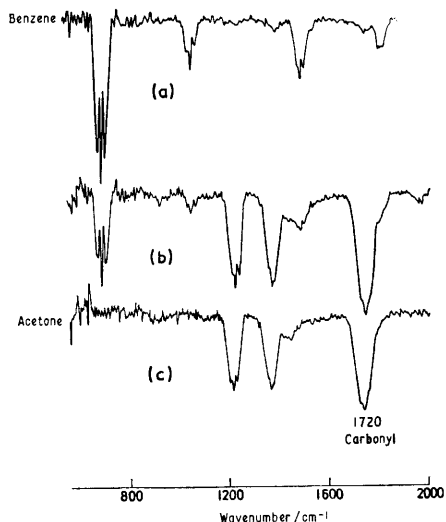


Figure 10 Transmission spectra obtained for one microlitre of 50:50 mixture of acetone and benzene injected into gas chromatograph so that separation of acetone and benzene peaks was 7 s. The spectra were recorded as follows: (a) between leading and trailing edges of acetone; (b) between trailing edge of acetone and leading edge of benzene; (c) between leading and trailing edges of benzene. The interferometer had rapid scanning and a TGS detector

³⁸ K. D. Moller and W. G. Rothschild, 'Far Infrared Spectroscopy', Wiley, New York, 1971, p. 57.

³⁹ 'Infrared Detection Techniques for Space Research', ed. V. Munro and J. Ring, Reidel, Dordrecht, Holland, 1972.

larly important ambient-temperature detector is the pyroelectric device based on triglycine sulphate. Its performance is comparable to that of the much-used Golay cell in nearly all respects except response time, which is much faster. It can, therefore, be used in rapid-scan interferometers⁶ (see Figure 10).

C. Computing.—The third major development has been in computing,⁴⁰ where hardware and software with greater speed and capacity have become available. The total time T_{tot} taken to obtain a spectrum is the sum

$$T_{\text{tot}} = T + T_{\text{trans}} + T_{\text{comp}} \quad (5)$$

of the time T taken to observe the interference record, the time T_{trans} taken to transfer the data to and from the computer, and the time T_{comp} taken to compute the spectrum. The value of T can range from a few seconds to a few hours depending on the spectrum under observation. It is less than the time that would be required for a comparable measurement using a grating spectrometer. The value of T_{comp} depends on the size and type of computer as well as the nature of the program used with it and the quantity of data to be computed; it is rare nowadays for T_{comp} to be inconveniently large. If the interferometer is operated separately from the computer (off-line) T_{trans} may represent the major contribution to T_{tot} (e.g., $T_{\text{trans}} \approx 24$ h for a central batch-process general-purpose computer). If there is a remote-access data-link or if the computer is local and used by the spectroscopist himself, T_{trans} may be markedly reduced (although T_{comp} may increase slightly owing to the need to use a smaller computer). If the interferometer is operated on-line to the computer, T_{trans} can be ignored. For most general-purpose on-line computers, computation immediately follows observation (this is 'false' real-time computation) while for some modern special-purpose hard-wired computers, computation accompanies observation (real-time computation) and $T_{\text{tot}} \rightarrow T$. The advantages of on-line operation are firstly that the interferogram need never be seen by the operator, who may regard the whole assembly of interferometer – detector – amplifier – A/D converter – computer simply as a spectrometer (Figure 1) and use it as such; secondly, the computer may also be used to control the interferometer. The Digilab Fourier spectrometers⁶ are of this type.

4 Time-resolved Fourier Spectrometry

The advent of very fast detectors (response times less than $0.1 \mu\text{s}$) has made it possible to extend FTS to the measurement of time-resolved spectra such as are emitted during reactions between transient species⁴¹ or by pulsed plasmas.^{42,43} All parts of the interferometer are fixed, with the movable mirror set to give a path-difference x_1 ; the pulse of radiation is emitted and the corresponding detector signal $V(x_1; t)$ is sampled at a series of preselected times and stored (Figure

⁴⁰ J. Connes, in ref. 16, p. 83.

⁴¹ R. E. Murphy and H. Sakai, in ref. 16, p. 301.

⁴² J. Chamberlain, A. E. Costley, and D. D. Burgess, 'Proceedings of the Symposium on Submillimetre Waves, 1970', Polytechnic, New York, 1971, p. 573.

⁴³ A. E. Costley, J. Chamberlain, and D. D. Burgess, I.E.R.E. Conference Proceedings No. 22: Infrared Techniques, 1971, p. 191.

11). This process is repeated for each value of x_i . A sequence of data is then assembled for all x for each time t_j of interest. These sequences constitute the interference records that would have been obtained if observations could have been over all x at each time t_j . Fourier transformation follows as usual. It is assumed that the pulsed source is reproducible: if it is not, some form of monitoring and compensation is necessary.

The technique has been applied in the millisecond domain by Murphy and Sakai⁴¹ (in the U.S.A.) to chemical reactions (Figure 12) and in the microsecond domain by Costley *et al.*^{43,44} (in the U.K.) to pulsed plasmas. As an example, the time development of the spectrum emitted by a discharge in active nitrogen is shown in Figure 12. Nitrogen is excited to high vibrational levels by a microwave discharge and de-excited by a resonant transfer during collisions with CO_2 molecules. The CO_2 molecules then decay, emitting radiation in the vibrational hot bands. The spectrum is dominated by the decay over 100 ms of the CO_2 band at 2340 cm^{-1} . There is also evidence for emission from N_2O near 2223 cm^{-1} .

5 Summary

From what has gone before, it will be realized that FTS instruments are now superior to dispersive instruments throughout the entire i.r. region. In the far-i.r., where the cost of an interferometer plus mini-computer is less than that of a grating spectrometer, the superiority is absolute, but in the middle-i.r., where the

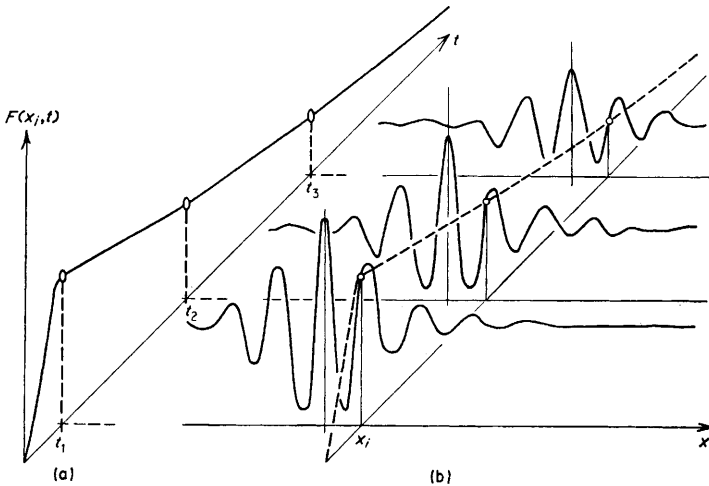


Figure 11 Construction of time-dependent interferograms with a two-beam interferometer. (a) Pulse $V(x_i, t)$ detected at a particular setting x_i and sampled at a series of times t_j ($j = 1, 2, 3, \dots$). (b) The interferograms that can be constructed by repeating the procedure in (a) at a series of values of x_i

⁴⁴ A. E. Costley, R. J. Hastie, J. W. M. Paul, and J. Chamberlain, *Phys. Rev. Letters*, 1974, 33, 758.

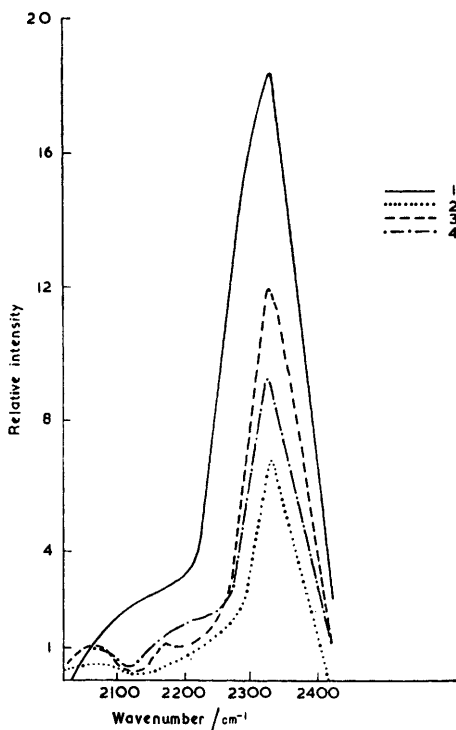


Figure 12 Time-dependence of spectrum emitted during reaction between active nitrogen and CO_2 . The resolution is 40 cm^{-1} . The times (referred to peak emission as origin) are (1) 0, (2) 35, (3) 55, and (4) 75 ms. The detector was InSb (Adapted from Proceedings of the International Conference on Fourier Spectroscopy, Aspen, 1970, Air Force Cambridge Special Report, No. 114, 1971, p. 301)

cost of an FTS system is still greater than that of a grating instrument of comparable quality, the superiority is qualified. One must ask therefore what a chemist wants from an i.r. spectrometer and then see how the two systems perform in providing what is required before one can come to form conclusions about their relative standing. It is also important to consider other instrumental approaches to the same problem: thus laser Raman spectroscopy covers the same frequency range as does i.r. spectroscopy, and there are now available tunable lasers which can provide high-resolution non-dispersive spectroscopy throughout much of the infrared.

The purposes to which a chemist puts a spectroscopic instrument are multifarious,⁴⁵ but some of the principal ones are:

I Static systems:

- (i) structural diagnosis of organic molecules,

⁴⁵ See e.g. I. R. Beattie, *Chem. Soc. Rev.*, 1975, 4, 107.

- (ii) determination of the symmetry and detailed structure of small molecules, particularly inorganic molecules,
- (iii) determination of equilibrium data,
- (iv) determination of the microstructure of complex solids, particularly polymers,
- (v) study of intermolecular interactions in high-pressure gases and condensed phases,
- (vi) detection of constituents in a mixture, especially those present at low concentrations,
- (vii) the study of adsorbed layers and of chemical-physical effects at interfaces,

II Dynamic systems:

- (i) detection of transients and short-lived intermediates,
- (ii) detection of unstable complexes,
- (iii) determination of rate constants,
- (iv) elucidation of reaction mechanisms.

For I(i) the extension of spectral range down into the far-i.r., which FTS techniques have made practicable, is of little consequence, for most characteristic features lie above 200 cm^{-1} . However, the much higher signal-to-noise ratio which is available in the 'fingerprint' region with FTS does permit the extension of micro-sampling techniques and does permit organic substances to be studied in normally prohibitive milieu, aqueous solution for example. In the case of I(ii), the far-i.r. capability is essential since all the vibrational fundamentals that can be observed (*i.e.* are not forbidden) need to be observed before an unambiguous assignment can be arrived at. Modern laser-Raman spectroscopy has made, of course, an enormous contribution in this field, but it cannot replace i.r. observations entirely. Even for non-centrosymmetric molecules, it is commonly found that both the Raman and the i.r. spectrum are necessary before a confident assignment can be attempted. A good example of this can be found in the recent determination at the National Physical Laboratory (N.P.L.) of the structure of phenyl isocyanate in the liquid phase.⁴⁶ Vibration-rotation spectroscopy of molecules in the vapour phase can give considerable information about the shapes of the absorbing molecules, and here the high resolution capability of modern FTS instruments is very relevant. Even if individual lines cannot be resolved, the form of the band envelope can often be interpreted unambiguously, but again it is preferable to work at the highest resolution that can be achieved. FTS systems are commercially available that can do 0.1 cm^{-1} in the mid-i.r., and there is talk of a commercial instrument that could achieve 0.01 cm^{-1} . There does not seem any insuperable difficulty which would prevent the 'home constructor' making an instrument that could do 0.03 cm^{-1} . However, these high-resolution instruments are, or would be, very expensive, and this factor has to be

⁴⁶ G. W. Chantry, E. A. Nicol, D. J. Harrison, A. Bouchy, and G. Roussy, *Spectrochim. Acta*, 1974, 30A, 1717.

considered in arriving at a balance. Also, the competition from tunable lasers has to be borne in mind, for the spin-flip laser is capable of 0.01 cm^{-1} in two bands centred at 5 and $10\ \mu\text{m}$,⁴⁷ and diode lasers capable of 0.001 cm^{-1} are available over much of the important mid-i.r. region.⁴⁸ These are not cheap, but for meaningful research in the field of structural physical chemistry there does not seem to be any choice but expensive instrumentation. It is difficult at this stage to see how the market for, and use of, very-high-resolution i.r. spectrometers will develop in the future, but it is possible that resolution up to 0.03 cm^{-1} in the laboratory will be the province of FTS instruments, that resolution beyond this will be the realm of the tunable diode laser, and that the spin-flip laser will be used in applications where monochromatic power is desirable, in field work and in double-resonance experiments for example.

The determination of equilibrium data means in essence the determination of concentrations to high precision, and that implies the use of an instrument which gives good radiometric precision. FTS instruments are far superior to dispersive instruments in this respect, and the competition from Raman instruments is only minor, because of the narrow concentration range over which Raman instruments can be used. There is no simple equivalent in Raman spectroscopy to the variable path-length cell in i.r. spectroscopy and, of course, in the study of equilibrium systems one is not usually at liberty to change the concentration.

The determination of the microstructure of solids is usually done by means of X-rays or neutron diffraction but there are some systems where these techniques give ambiguous results. This usually occurs where one is prevented from growing a suitably large single crystal, and prime examples are found in the area of macromolecular studies. Crystalline polymers generally consist of spherulites connected by amorphous regions, and X-ray studies are therefore usually made on drawn fibres, so that there will be some degree of orientation. The interpretation of these fibre results is often not easy, and there always remains the doubt that possible changes of morphology might occur in going from the bulk material to the fibre. Also, X-ray observations at low temperature are notoriously difficult. Reservations must therefore be entertained about low-temperature crystal structures of polymers derived by X-ray methods. Far-i.r. studies can be of enormous value here⁴⁹ since the number of segments per unit cell and the symmetry of the unit cell can often be deduced from observations of the lattice spectrum in the wavenumber region $10\text{--}120\text{ cm}^{-1}$. Raman and neutron-diffraction observations have tended to be complementary rather than competitive, leaving FTS methods of unchallenged value. At higher wavenumbers, related effects are noticed (*e.g.* crystal-field splitting) but these are usually well within the compass of a good dispersive

⁴⁷ C. K. N. Patel, *Phys. Rev. Letters*, 1972, **28**, 649, R. A. Wood, R. B. Dennis, and J. W. Smith, *Optics Comm.*, 1972, **4**, 383; R. L. Allwood, R. B. Dennis, W. J. Forth, S. D. Smith, B. S. Wherrett, and R. A. Wood, in ref. 43, p. 107, *Radio and Electronic Engineer*, 1972, **42**, 243.

⁴⁸ See *e.g.* K. W. Nill, F. A. Blum, A. R. Calawa, and T. C. Harman, *Appl. Phys. Letters*, 1972, **21**, 132, and W. H. Weber, P. D. Maker, K. F. Yeung, and C. W. Peters, *Appl. Optics*, 1974, **13**, 1431.

⁴⁹ G. W. Chantry, J. W. Fleming, E. A. Nicol, H. A. Willis, M. E. A. Cudby, and F. J. Boerio, *Polymer*, 1974, **15**, 69.

instrument, and FTS techniques, though desirable, are not essential.

The topic of intermolecular interactions, and particularly those in liquids, has become a major research field of far-i.r. spectroscopy in recent years.⁵⁰ This work had its origin in the confirmation at N.P.L. of the existence of the characteristic liquid-phase absorption bands which had been predicted by Poley. Unlike all the topics so far discussed, effective investigation of liquid-phase interactions requires the experimental observation of both parts of the complex refractive index—*i.e.* both the absorption coefficient and the refractive index. The development of asymmetric dispersive FT techniques has permitted the direct observation of both components and has therefore led to the extension of dielectric spectroscopy into the tens of gigahertz region. Much valuable chemical information is flowing from this experimental advance—one example being the elucidation of 'chemical-relaxation processes' by the group at Nancy.⁵¹

The detection and determination of constituents present at low concentration have always been important jobs for the i.r. spectroscopist but in recent years, with the growth of concern about the pollution of the environment, this field has become very important indeed. The successful achievement of the objectives involves a sampling problem, *i.e.* either a method for concentrating the trace constituents or else ensuring a sufficiently long path length, a sensitivity problem, and a radiometric accuracy problem. FTS methods solve the latter problems very well indeed, though for specific problems, *i.e.* monitoring a single pollutant, the superior resolving power of injection lasers can give them the edge. Nevertheless, for general surveys or for monitoring several gases, FTS methods reign supreme. At far-i.r. frequencies, FTS instruments have been used to monitor the ozone layer in the stratosphere⁵² and to detect the presence of the nitrogen oxides which it is thought might affect it deleteriously.⁵³ In the mid-i.r., FTS instruments have been used extensively to monitor atmospheric pollution, especially that due to the exhaust gases of motor cars.

The study of adsorbed layers and the chemical effects at interfaces gains in motivation from the practical importance of heterogeneous catalysis. The layers involved may be only a few tens of nanometres thick and there are severe problems in getting sufficient absorption for a reasonable quality spectrum. ATR techniques can magnify the absorption, but even so the multiple-reflection forms of ATR are essential, and these require a quasi-parallel beam, with the consequent severe loss of energy throughput. The loss in energy throughput can be compensated for by going over to FTS techniques, and this is almost universal practice in modern research. A variant on absorption spectroscopy, namely emission spectroscopy, is also possible with FTS instruments used to study chemisorption.

When one considers the study of dynamic systems it might be thought that

⁵⁰ G. W. Chantry, 'Submillimetre Spectroscopy', Academic Press, London, 1971, pp. 157—162 and pp. 177—187.

⁵¹ J. Goulon, J. L. Rivail, J. Chamberlain, and G. W. Chantry, in 'Molecular Motions in Liquids', ed. J. Lascombe, Reidel, Dordrecht, Holland, 1974, p. 163.

⁵² J. E. Harries, N. R. W. Swann, J. E. Beckman, and P. A. R. Ade, *Nature*, 1972, 236, 159.

⁵³ J. E. Harries, *Nature*, 1973, 241, 515.

FTS operates under a severe handicap in that it produces a spectrum which is the time average of the physical (and in general time-varying) spectrum. Thus whereas with grating instruments one can set the instrument to observe only a very narrow band of wavelengths, this is possible only in exceptional cases with FTS instruments. FTS techniques are of value as mentioned earlier if the variation of spectrum occurs in a time longer than the rapid-scan time, if the phenomena can be reproducibly repeated many times, or if there is a way of 'freezing-in' the transient phenomena so that static methods may be used to study them. Standard 'rapid-scan' instruments can cover a length of interferogram equivalent to a resolution of 4 cm^{-1} in under a second, and special modifications are available that permit this time to be reduced to 1/80th of a second for an equivalent resolution of 16 cm^{-1} . These times are sufficiently short for most gas-phase chromatography to be monitored by FTS 'on-the-fly'; that is, in real time and without recourse to trapping. The extra dimension given to gas chromatography by the addition of an i.r. spectrometer is opening up new possibilities in diagnostic chromatography. The study of fast chemical reactions by time-resolved FTS, on the other hand, has not so far made very much progress beyond the early work of Murphy and Sakai,⁴¹ unlike the equivalent situation in physics, where the study of rapidly evolving pulsed plasmas is progressing at a rapid rate. The difference undoubtedly arises from the more severe problems which chemists experience in getting their reactants into the flash zone and the products out of it, but in the future this may well be a significant growth area in experimental kinetics. The 'freezing-in' technique most commonly used is matrix isolation, in which free radicals or other transients formed at a high temperature are quickly trapped in a solid argon matrix at cryogenic temperature. The spectroscopic problems arise because (i) the radicals have to be at low concentration to prevent recombination and (ii) scattering of radiation by the matrix leads to heavy energy loss. Once again, the energy-throughput advantage of FTS comes to the aid of the spectroscopist and permits the observation of good-quality vibrational spectra of transients.

In summary, therefore, the availability of FTS systems for the entire i.r. region has given chemists powerful new ways of investigating chemical systems, and the keen rivalry between FTS and other instrumental techniques will ensure that the chemist is well served with an ever-increasing range of instruments to bring to bear on his problems.