

Fourier transformed

R. P. Wayne

Reprinted From *May*
Chemistry in Britain
Vol. 23 No. 5 1987

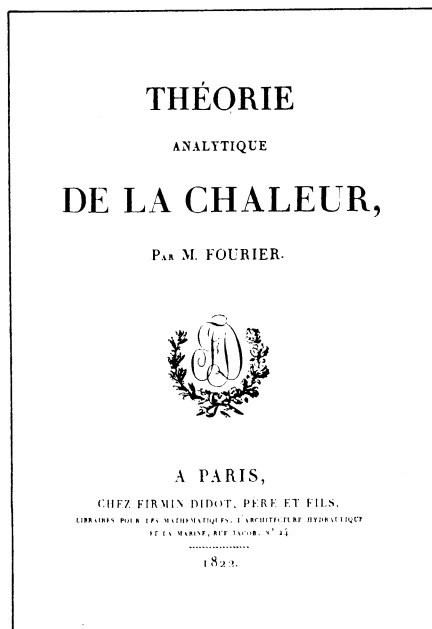
Fourier transformed

R. P. Wayne

Robespierre fell from power on 27 July 1794, and Jean Baptiste Joseph Fourier, a diplomat and scientist who was to be executed the next day because of his involvement with revolutionary affairs, was spared. In 1807, Fourier was attempting to solve mathematically a problem concerning the conduction of heat by using a series expansion of sine and cosine terms that became the familiar Fourier series.¹ The principles that Fourier established laid the foundation for mathematical methods of extraordinary power and flexibility that have not only stimulated continuing original contributions to pure mathematics, but have found a variety of applications in applied mathematics and science. Fourier transform infrared and NMR spectroscopy are now fully fledged analytical techniques used in chemical laboratories throughout the world. This article describes why Fourier methods are enabling chemists to foster, and sometimes revolutionise, their endeavours.

The basic idea of the Fourier series is that 'any' periodic function can be expressed as a sum of a trigonometric series of sines and cosines of the same period. The trigonometric functions are easy to deal with in a way that the more complex functions are not. Concepts touching on Fourier's had been around for some time. The Babylonians seem to have used a primitive 'Fourier series' to predict celestial events.² By the mid-18th century, d'Alembert, Euler, D. Bernouilli and Lagrange were studying the motions of vibrating strings, and by 1777 Euler had the recipe for computing the coefficients

Fourier's publication (1822) of his analysis of heat conduction, which was the foundation of the Fourier series.



of the series that Fourier had yet to formulate!

Physically, the Fourier series represent functions that are periodic and defined in a fixed finite interval as a superposition of sinusoidal functions. For functions defined over an infinite interval, and with no periodicity, the summation of the harmonic series must be replaced by an integration of a continuum of trigonometric functions. This Fourier integral is the Fourier transform (FT) of the function represented by the original sinusoidal components (see box).

One of the most remarkable mathematical properties of the FT is that a second transform can generate the original function from which the first transform was obtained. That is, if $F(t)$ is the transform of $f(\nu)$, then $f(\nu)$ is the transform of $F(t)$ (see box). This result suggests that the superposition of sinusoidal waveforms in physical processes *eg* from vibrating strings, radiation scattered by a diffraction grating or crystal *etc* could be unravelled by mathematical transformation of the complex sound pattern, diffraction pattern, interferogram *etc*. For example, we might be able to recover the individual frequencies and their amplitudes from a fortissimo orchestral chord. The process is that of spectral analysis. The human ear is quite good at separating the component frequencies of sound, but the eye is incapable of resolving mixed colours, even though colour itself can carry important information. A spectroscope or a spectrum analyser allows us to see optical or electrical spectra of waveforms just as the ear hears spectra. Waveforms and spectra are the FTs of each other. Spectral analysis into frequency com-

ponents is often valuable, because the responses of many systems, such as electrical circuits, or, indeed, atoms and molecules depend on the frequency content of the input stimulus.

FTs are not concerned only with time-dependent waveforms and frequency-dependent spectra. If $F(t)$ is the FT of $f(\nu)$, as used in our mathematical example, then t and ν are said to be the two 'domains' of the transform. The variables t and ν could be time and frequency; but equally well could be length and wave-number. These pairs have reciprocal dimensions (*eg* s and s⁻¹, or m and m⁻¹). The two domains occupied by the functions and their FTs are sometimes referred to as upper and lower, implying a function and a counterpart connected uniquely with it through the FT, and changing as the function changes. The FT is therefore a mathematical recipe for moving from one domain to the other.

Advantages

For about the first 150 years of their existence, the practical application of Fourier methods was restricted mainly to problems in mathematical physics and engineering that could be expressed in an analytical algebraic form. The approach was to express all the functions in a problem as sinusoidal components by using the FT, carry through the difficult procedures on the simple trigonometric functions, and then reconstitute the output functions by a second transformation. It is true that towards the end of this first period, X-ray crystallographers had used Fourier concepts, although the procedures often involved a synthesis of the diffraction pattern expected from a hypothetical structure, rather than the analysis of the structure from the pattern. The advent of fast digital computers has changed the way in which Fourier methods can be applied. The continuing increase in speed and memory of computers, and the development of array processors and even single chip FT devices, has meant that the FT operation is now no more of an obstacle than addition or multiplication were in the past.

FT techniques permit efficient and precise data manipulation. Traditional methods for removing 'noise'—those signals of higher or lower frequency than that of the signal of interest—have

ranged from the incorporation of electrical or electronic 'filters' to hand smoothing of a rough recorder trace or scattered graph. Now, by using an FT, the data can be transformed to the other Fourier domain, manipulated mathematically, and transformed back to the first domain to provide the filtered output. For example, the record of a noisy chart trace is a waveform in the time domain; transformation yields the frequency spectrum of the data whose frequency range can be modified by truncation; reverse transformation to the time domain gives back the waveform with the unwanted frequency elements eliminated. The ad-

vantage of this technique is the precision with which the modifications can be specified, because they are achieved by mathematical functions rather than electronic components. Single chip integrated circuits (ICs) are now available that perform the two FTs in 'real time'. Related FT methods are available to enhance or recover resolution and contrast in a variety of image processing applications, including spectroscopy. With physical techniques, such as FT-IR or FT-NMR, in which one transformation is an obligatory element, the modifications are applied directly to the primary data set recorded.

Use of FTs

The use of FTs in spectroscopy can be considered by looking at the spectral analysis of radio signals. We might want to measure the frequencies at which radio stations were transmitting in a particular broadcast band, and how strong was the reception of each. That is, we want to obtain the spectrum. We could attach a radio set to an antenna, scan through the band and log the frequencies and amplitudes of all the stations that can be heard. In practice, the particular frequency range would be divided into a chosen number, *n*, of discrete intervals, and the measurements

The basic principles of Fourier mathematics

The proposition is that if *F(t)* is any periodic function, with a repetition frequency ν , then it is possible to represent the function as the sum of a series:

$$F(t) = 2 \sum_{n=1}^{\infty} [f'(n) \cos 2\pi n \nu t + f''(n) \sin 2\pi n \nu t] \quad (i)$$

where *f'(n)* and *f''(n)* terms are the amplitudes of cosine and sine components of frequency $n\nu$. (A constant term representing a non-varying offset is omitted here for simplicity). It is convenient to write the trigonometric functions in the exponential notation:

$$F(t) = \sum_{n=-\infty}^{\infty} f(n) e^{2\pi i n \nu t} \quad (ii)$$

where *f(n)* is a complex coefficient.

The transforms

For functions with no periodicity, the summations are replaced by integrations, the size of the frequency step ν tending to zero. Thus equation (ii) becomes:

$$F(t) = \int_{-\infty}^{\infty} f(\nu) e^{2\pi i \nu t} d\nu \quad (iii)$$

or, expanding the exponential:

$$F(t) = \int_{-\infty}^{\infty} f(\nu) \cos 2\pi \nu t d\nu + i \int_{-\infty}^{\infty} f(\nu) \sin 2\pi \nu t d\nu \quad (iv)$$

The function *F(t)* is said to be the *Fourier transform* of *f(ν)*. An important property of Fourier transforms is that *f(ν)* is related to *F(t)* by an inverse transform:

$$f(\nu) = \int_{-\infty}^{\infty} F(t) e^{-2\pi i \nu t} dt \quad (v)$$

The Fourier transform and its inverse are not quite symmetrical because of the negative sign in the exponent of the inverse transform. Commonly, however, *F(t)* may be an *even* function of *t*: that is *F(t)=F(-t)*. Because $\sin(-\theta) = -\sin(\theta)$, the trigonometric inverse transform becomes:

$$f(\nu) = \int_{-\infty}^{\infty} F(t) \cos 2\pi \nu t dt \quad (vi)$$

which is symmetrically equivalent to the cosine part of the forward transform.

f'(ν) and f''(ν)

The quantities *f'* and *f''* were introduced as real coefficients in the Fourier series. The real part of equation (iv) could have been obtained by expressing equation (i) in continuous form

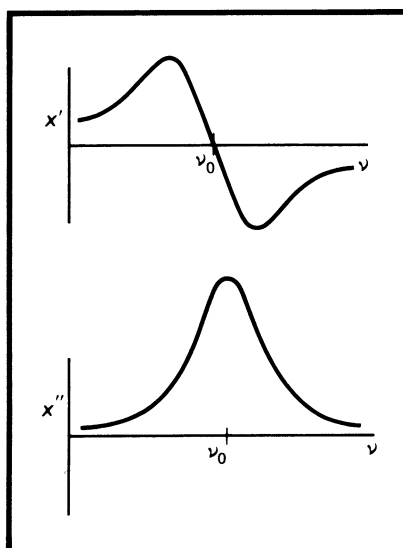
$$F_{\text{real}}(t) = \int_{-\infty}^{\infty} f'(\nu) \cos 2\pi \nu t d\nu + \int_{-\infty}^{\infty} f''(\nu) \sin 2\pi \nu t d\nu \quad (vii)$$

Comparison of equations (iv) and (vii) then gives

$$f(\nu) = f'(\nu) - i f''(\nu) \quad (viii)$$

f' and *f''* thus represent the magnitude of the real and imaginary components of the complex amplitude *f*; they are commonly referred to as 'real' and 'imaginary'. But the use of *f'* and *f''* in equation (i), and equation (vii), shows that they are also the real in phase and 90° out of phase amplitudes that make up the complex waveform. This conclusion is important in spectro-

The frequency dependence of the spring motions.



scopy, because two modes of representing spectra are sometimes distinguished—dispersion and absorption—corresponding to the *f'(ν)* and *f''(ν)* components of the complex spectrum *f(ν)*.

We can explain the origin of the two modes by using a mechanical analogy—the damped oscillations of a mass on a spring, driven by a variable frequency external source—to represent situations such as displacement of electrons bound to a nucleus by Coulombic attraction. In general, the displacement is not exactly in phase with the driver, even though its frequency is the same. For driver frequencies much smaller or larger than the resonant frequency, ν_0 , of the mass-spring system, the displacements are nearly in phase, but they are of low amplitude. At resonance, the amplitude is much greater, but the spring oscillations lag behind the driving oscillations by 90°. Analysis of the spring motions, *x*, into in phase, *x'*, and 90° phase, *x''*, components gives rise to the frequency dependence shown in the *Figure*. The negative sign of *x'* for $\nu > \nu_0$ shows that there is a phase reversal on passing through ν_0 . The behaviour of *x'* results from changes in wave propagation velocity with frequency. In the optical analogue, these velocities are reflected in the refractive index, and the changes are associated with the term 'dispersion'. The behaviour of the *x''* motions corresponds to the coupling of energy from the driver into the oscillations, and thus to 'absorption'. The relationship of the in phase and 90° out of phase motions *x'*, *x''* with the components *f'* and *f''* of the complex spectrum is evident.

Dispersion or absorption spectra, *f'(ν)* or *f''(ν)*, can be obtained from *F(t)* by performing cosine or sine transforms on *F(t)*. The mathematical link between *f'(ν)* and *f''(ν)* is sometimes called the *Kramers-Kronig relation* by spectroscopists (and the *Bode relation* by engineers); it is really a facet of another transform, that of *Hilbert*.

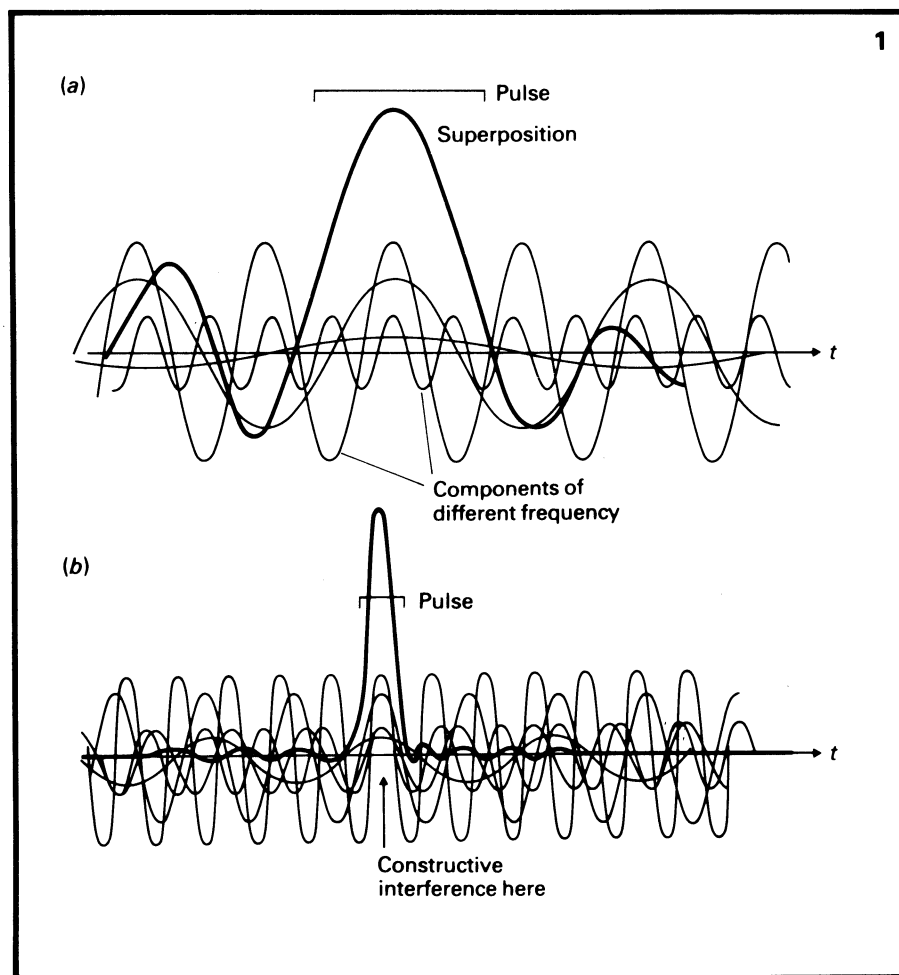


Fig. 1. A pulse has Fourier components of many frequencies needed for destructive interference at all times before and after the pulse. A narrower pulse (b) demands a wider range of frequencies than the wider 'pulse' shown in (a).

made at each point in turn: the intervals thus correspond to spectral elements. The process will take a finite time, even if the scanning and logging operations could be automated.

Moreover, noise is always present because the electronic devices are operating above absolute zero temperature. Thermal agitation, corresponding to Brownian motion, produces what is called Johnson noise; and the antenna collects thermal radiation from the surroundings that are also above absolute zero. Therefore, sufficient time must be taken to scan our radio spectrum to determine if there is a signal at every point; the weaker the signal, the longer it will take to decide whether there is a signal present. As a result, the output of the radio receiver must be integrated for long enough for the signal to noise ratio (S:N) to be satisfactory. A similar problem is encountered in conventional optical spectroscopy, where long 'time constants' or integration times must be used to record weak spectra.

The scanning method is not a very efficient way of obtaining a spectrum—it might take a long time if the signals are weak, or a misleading result might be obtained if some stations started or stopped broadcasting during the course of the scan. Although energy from all the stations is reaching the antenna and the input to the radio set, most of this energy

is being rejected by the radio receiver because it is tuned to a specific small frequency band. Only when the receiver is on resonance with a station is that station's energy accepted.

When a lack of energy is slowing the scanning procedure, it would be advantageous to use several radio receivers simultaneously, up to the limit of having one receiver for each of the n channels or spectral elements. The signals are independent of each other, so that the total signal recorded is increased by a factor of n . But the noise is random and increases only by a factor of \sqrt{n} . If the noise is independent of the signal, the S:N of the determinations should improve by a factor of \sqrt{n} for any fixed measurement. This improvement is the 'multiplex advantage' of a multichannel technique; in spectroscopy it is often called the Fellgett advantage. The drawback is the number of radio receivers required to operate the multichannel measurement. Some waveform analysers do depend on the use of many independently tuned circuits, but the multiplex advantage is most evident in the most difficult case, *ie* where n is large.

Fourier methods offer a completely different solution to the multichannel problem. Instead of using tuned circuits to extract the various sinusoidal components from the antenna signal, mathematics is put to work. Because the

alternating voltages derived from the antenna result from the superposition of all the received transmissions, they make up a Fourier sum or integral. The reciprocal nature of FTs allows the recovery of the frequency spectrum by applying the FT operation mathematically to a (digitised) waveform that is obtained from the transmitted electromagnetic waves. Although there may be practical difficulties in recording the time-domain waveform at radio frequencies, in principle the FT method permits the spacing of the spectral elements to be as close as is wanted. The ultimate frequency resolution of the measurements is determined by the time for which the waveform is recorded. Simultaneous multi-channel recording of many spectral elements is also of immense value in the spectroscopies used by chemists, and the FT route to achieving the multiplex advantage is more likely to bring success than the application of banks of IR, NMR or MS instruments, one for each channel.

One further point can be illustrated by use of radio transmission. An additional contribution to radio noise is caused by lightning discharges. The noise spreads throughout the radio frequency spectrum, and is caused by the short pulsed nature of the discharge phenomena—a large current flows for a short time. Electromagnetic waves are radiated over a wide frequency range. If the short burst of energy can be represented by the superposition of continuous sinusoidal signals, as Fourier theory leads us to believe, then those waves must destructively interfere both before the beginning of the pulse and after it ends. Constructive interference occurs only while the pulse exists. A range of frequencies is needed, shown in *Fig. 1*. The narrower the pulse, the greater the spread of frequencies needed. In the limit, a spike of energy corresponds to 'white' radiation: that is, all frequencies are present at equal amplitudes. These ideas can be expressed quantitatively by the use of the FT which enables us to move to the frequency domain from the time domain. We can exemplify this result by considering the distribution of frequencies, or the spectrum, that constitutes a Gaussian ('normal distribution') shaped pulse of radiation. The example is chosen for its simplicity, because the FT of a Gaussian is itself a Gaussian. If the width (RMS deviation) of the Gaussian in the time domain is Δt , then the width of the Gaussian in the frequency domain, $\Delta \nu$, is equal to $(2\pi\Delta t)^{-1}$. That is,

$$\Delta \nu \Delta t = \frac{1}{2\pi} \quad (a)$$

showing that the deviations or spreads in ν and t are inversely related. Similar relations connect other Fourier pairs such as wavenumber, $k(=1/\lambda)$, and spatial position, x

$$\Delta k \Delta x = 1 \quad (b)$$

These relationships are forms of the uncertainty principle, independent of quantum mechanics. Because we are

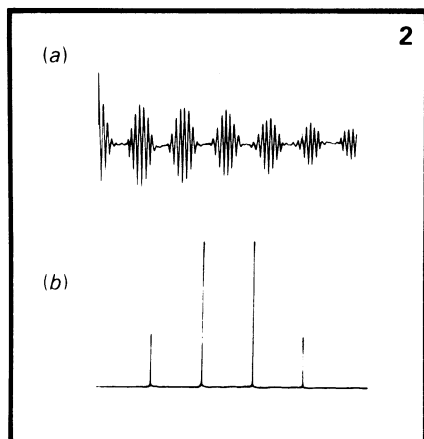


Fig. 2. FT-NMR spectrometry of $^{13}\text{CH}_3\text{I}$. (a) Free induction signal after applying a 90° pulse. (b) The ^{13}C spectrum.⁶

describing how FTs are used in chemistry, we should make the connection with the quantum mechanical form. Particles behave as waves, the square of the wavefunction representing the probability distribution. If the squares of the Gaussian pulses are taken, the two uncertainty relations become half the products— $1/2\pi$ and 1 —of equations (a) and (b). Combining the Planck–Einstein relation ($E=h\nu$) with equation (a) gives $\Delta E\Delta t=h/4\pi$, the formula for lifetime broadening of a spectral energy level; and combining the de Broglie expression for momentum ($p=h/2\pi\lambda=hk/2\pi$) with equation (b) gives the usual form of the Heisenberg uncertainty principle, $\Delta p\Delta x=h/4\pi$.

It is now relatively straightforward to describe the various applications of FT spectroscopy.^{3,4}

FT-NMR spectroscopy

In conventional swept field NMR the signals are rather weak and the data acquisition rate is further impeded by the need for the sweep to be slow on the nuclear spin timescale, because the spin system must be at equilibrium at all times. Spin–lattice relaxation times can be of the order of seconds in high resolution NMR, so that sweep rates may be confined to a few tenths of a hertz. If a wide frequency range needs to be explored, the experiment will take an intolerable time. This is exactly the situation where the multiplex advantage of FT spectroscopy can help. A rough estimate of the sensitivity improvement achieved by FT-NMR might be 10–50 for ^1H and 40–100 for ^{13}C , but such figures conceal an even greater advantage, because the S:N increases as the square of the time taken to integrate noisy signals—so that a ^{13}C spectrum can be obtained more than 5000 times faster by FT-NMR than in a swept field experiment.

In the FT-NMR experiment the sample of nuclei held in a magnetic field is irradiated by a pulse (or pulse sequence) of radiofrequency (RF) energy.⁵ Because the short burst of RF contains components spanning a wide frequency range, all the magnetic nuclei of interest can interact with the RF field. Those

nuclei then induce, in receiver coils, currents that are characteristic of their precession frequencies in the applied magnetic field. Signals from all nuclei are superimposed in the electrical response; they decay with time because of the various relaxation phenomena. This decaying complex oscillation in the time domain is called the free induction decay (FID). The FID is amplified, digitised and stored in a memory. The FT operation then gives the spectrum in the frequency domain. *Figure 2* shows an example of an FID, together with the spectrum, obtained as the ^{13}C response from $^{13}\text{CH}_3\text{I}$. Because the simple spectrum consists of equally spaced lines, the FID displays a beat frequency equivalent to the ^{13}C –H coupling constant. Even here, however, it would not be possible to predict the

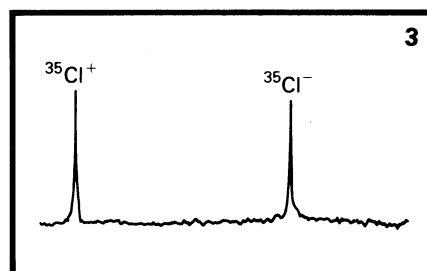


Fig. 3. FT mass spectra of $^{35}\text{Cl}^+$ and $^{35}\text{Cl}^-$ at a mass resolution of ca 1 500 000. The Cl^+ and Cl^- ion signals were alternately acquired, stored and transferred. The FT mass spectrometer cannot simultaneously store positive and negative ions.⁹

number of lines or their relative intensities from the time domain FID. Various 'massaging' procedures can be imposed on the FID before transformation to adjust, for example, resolution, generally at the expense of the S:N ratio. Improvements in the S:N ratio can be achieved by coherent addition, or by 'time averaging', of the FID signals. It is the speed with which individual FIDs can be obtained that makes this averaging technique so useful.

Although the short pulses used to excite the nuclei are not perfect 'impulses', they do provide a more or less uniform power spectrum over the defined frequency range. Uniform power may not always be desirable, and so 'tailored' excitation may be used. For example, a notch or a spike in the excitation signal may be required to remove strong solvent lines or to study double resonance. Tailoring the pulses is yet another use of Fourier methods. After the power spectrum has been defined, it is subjected to a mathematical Fourier transformation to derive the waveform necessary to give that spectrum, and the RF pulse train may be modulated accordingly.

The increase in sensitivity afforded by FT-NMR has opened up many new possibilities. Proton, ^1H , resonance spectroscopy can be performed on more dilute materials than was previously possible. In the ^{13}C example, 1000 scans at 1 s each would take under 20 min, while the swept experiment would take

5000 times longer, or nearly 60 days, and would never be undertaken at all.⁶ The possibility of ^{13}C and ^{15}N nuclear spectroscopy is a direct consequence of the advent of the FT technique. New experiments have become possible because high resolution spectra can be obtained on the timescale of nuclear relaxation. Relaxation times can be measured, thus providing scope for the study of molecular motions, and fast reactions can now be studied by NMR.

FT-mass spectroscopy

The first FT mass spectrometer was described in 1974.⁷ Instruments built to date are based on ion cyclotron resonance (ICR) spectrometers.⁸ (An ion moving in a magnetic field is constrained to a circular path at right angles to the magnetic field. It orbits at a fixed cyclotron frequency proportional to the charge and magnetic field strength, but inversely proportional to its mass.) Cyclotron frequencies for typical fields (1 T) and masses (15–1500 amu: 1 amu = 1.67×10^{-27} kg) lie in the range 10^4 – 10^6 Hz. If two plates define the sample volume, and an RF field of the correct frequency is applied, then energy will be absorbed from the field by the ions as their cyclotron resonance is excited. The resonance may be detected either by the absorption of power from the exciting field or by the induction of charge on separate detector plates. The spectrometer is maintained at high vacuum, and an ion source must be provided. In the conventional ICR-MS, the resonances are recorded at fixed RF frequency as the magnetic field is swept.

By using the FT technique, the cyclotron motion of ions of different masses is excited essentially simultaneously, and the presence of cyclotron motion detected by the AC voltages induced after the exciting field has been turned off. The gains in data acquisition time resulting from multichannel operation are as dramatic as with FT-NMR. To sweep the mass range 15–200 amu would typically take 30 min using a conventional ICR spectrometer. With the FT instrument, the same S:N ratio can be achieved in 1.6 s, and the mass range is extended to 1200 amu, a value that cannot be reached with the scanning spectrometer.⁸

There are two differences between FT-NMR and FT-ICR worth noting. First, ICR involves the interaction of alternating electric fields with electrically charged ions, whereas NMR involves alternating magnetic fields and magnetic dipoles. Secondly, relaxation times in the FT-NMR signal are controlled partly by intramolecular couplings outside the control of the experimenter, while the ion trapping lifetimes in ICR depend on intermolecular collisions whose rate can be minimised by use of low pressures. Because the spectral line width is determined by the relaxation time of the excited signal, ICR can give extremely narrow linewidths, corresponding to very high mass spectral resolution. A resolution of 10^8 has been demonstrated for

an FT-ICR machine—the best commercially available magnetic sector mass spectrometer has a resolution of 150000. *Figure 3* shows the FT-mass spectra of $^{35}\text{Cl}^+$ and $^{37}\text{Cl}^+$: the separation between the peaks is just two electron masses!⁹ High mass ions can also be studied by using the FT-MS technique. Although an ion trap has a maximum mass of ion that it can maintain in a stable cyclotron orbit, it seems that masses as high as 100000 amu could be studied.

IR, visible and UV spectroscopy

The FT techniques described so far have had in common the digital recording of a complex waveform in the time domain and the use of the FT operation to obtain the frequency domain spectrum. Fourier variants of IR, visible and UV spectroscopy employ a rather different approach. Direct sampling and digitising in the time domain are currently impossible at the frequencies of interest. The problem is that the rate of sampling of the waveform must be twice the highest spectral frequency present. Frequencies involved in the 'optical' spectroscopies range from about 10^{11} Hz to nearly 10^{16} Hz, while 'fast' electronic devices are already in difficulty by 10^9 Hz.

Instead of direct sampling, therefore, a trick is adopted to overcome the sampling difficulties. Two beams of radiation are split off from the same source, one is delayed with respect to the other, and they are then recombined, producing interference. The delay is introduced to the second beam by making it travel on a longer path before being overlaid with the first, and the intensity after interference is then recorded as a function of optical path difference. The spectrum produced by the constructive and destructive interference of light from a conventional diffraction grating is formed by this mechanism, but with many beams of radiation rather than two.

The instrument used in FT spectroscopy to split the beams and incorporate the delay into one is an interferometer, usually a Michelson. A semireflecting mirror divides the incident beam into two. One of the beams passes to a fixed mirror, and returns (through the splitter) to reach the detector, while the other beam is directed to a movable mirror, from which reflected radiation is also directed (by reflection from the splitter) to the detector. By altering the position of the movable mirror the optical path travelled by the second beam is changed and so are the phase relations between the waves of the two beams. Constructive and destructive interference occurs between the waves in the two beams as a result of the phase differences. The intensity at the detector is measured as the optical path difference is varied, the record constituting an interferogram.

We may consider two simple cases to illustrate the nature of the interferograms. For monochromatic radiation, full constructive interference occurs when there is no optical path difference between the two beams, and whenever

the path differences are a multiple of the wavelength. Total destructive interference arises for path differences that are multiples of $\lambda/2$. The interferogram is thus a continuing series of bright and dark fringes—the intensity-pathlength relation is shown in *Fig. 4a*. Conversely, for polychromatic radiation constructive interference can occur only with zero optical path difference, some cancellation of waves of different wavelengths always occurring when there is a phase delay. The intensity thus drops off rapidly on either side of the 'central maximum'.

Figure 4b shows the spectrum and resulting interferogram from wide band radiation. In cases lying between the two extremes, the spectral characteristics of the incoming radiation will determine a unique interferogram. An interferogram obtained by mixing one waveform with the same waveform delayed by progressively greater times is mathematically the autocorrelation function of the waveform. This function corresponds to the Fourier integral of the individual components of the waves in space. The FT of the interferogram recorded in the distance domain thus recovers the spectral distribution in the reciprocal distance (wavenumber) domain that produced it. The appearance of the spectra and their resultant interferograms in *Fig. 4* illustrates the Fourier relation between them. It embodies again the uncertainty principle.

FT interferometric spectroscopy brings with it Fellgett's multiplex advantage described for FT-NMR and FT-MS. All spectral elements are examined simultaneously, with the resulting improvement of the S:N ratio or decreased recording time. A further gain in S:N results from the cylindrical optical geometry of the interferometer compared with the slit-governed geometry of a conventional spectrometer. The resulting improvement in throughput or *étendue* is

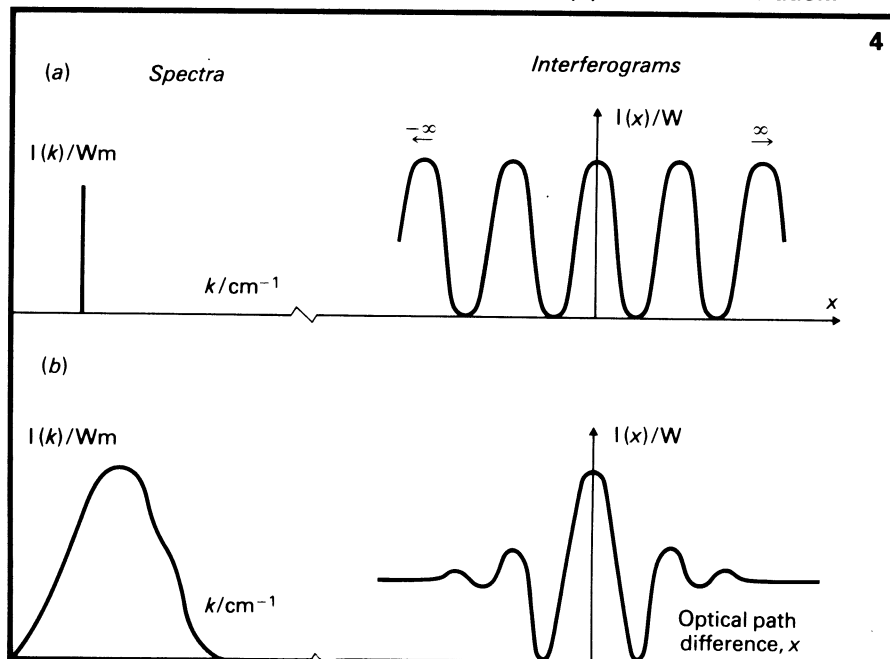
referred to as the Jacquinot advantage. The Fellgett advantage in FT spectroscopy corresponds to opening the exit slit of a spectrometer, and thus to using all the radiation that passes through the instrument; the Jacquinot advantage corresponds to opening the entrance slit as well, and allowing all the radiation to enter the spectrometer!¹⁰ The improved sensitivity means that experiments can be done more rapidly on more dilute samples, with weaker sources, or at higher resolution than can be done with conventional spectroscopy.

The far infrared (in the region $10\text{--}200\text{cm}^{-1}$) offers experimental difficulties because light sources are inefficient and detectors poor. This region, where many pure rotational transitions lie, has been opened up by FT spectroscopy. In the conventional infrared region, the increased sensitivity is being exploited, for example, in the study of trace gases in the atmosphere.¹¹ The potential for rapid scanning has made possible experiments in reaction kinetics, and the analysis of effluents from gas chromatographs to obtain the IR spectra of the separate fractions as they appear in the gas stream.¹²

Other important applications of FT-IR spectroscopy include diffuse reflectance spectrometry on powdered samples, and photoacoustic IR spectrometry.¹² One recent application of both high resolution and sensitivity has been in the ATMOS (atmospheric trace molecule spectroscopy) experiment on Spacelab 3. The spectra obtained by a Michelson FT spectrometer orbiting the Earth are compared with high resolution (down to 0.002cm^{-1}) laboratory spectra to determine global altitude profiles for molecules, including radicals, important in the Earth's atmospheric chemistry. *Figure 5* shows the quality of the data that are obtained.¹³

Of course, FT spectroscopy has its

Fig. 4. Spectra and their resulting interferograms, showing the intensity-pathlength relations. (a) Monochromatic radiation. (b) Broad band radiation.



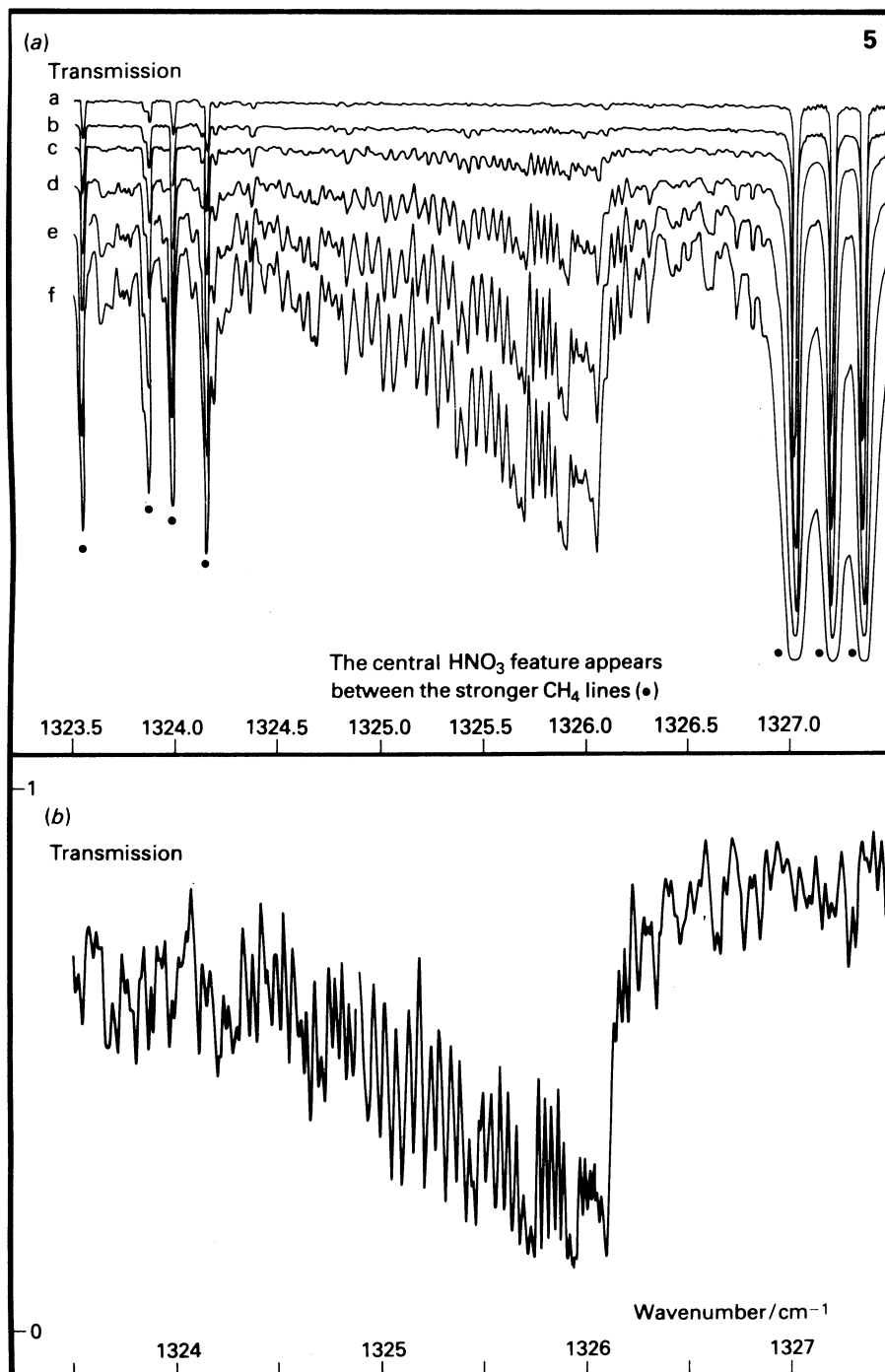


Fig. 5. (a) A small portion of a series of ATMOS spectra taken at sunset over latitude 30°N . The instrument records the spectra once every 2 s over the mid-infrared range $600\text{--}4300\text{ cm}^{-1}$ and at a resolution of better than 0.015 cm^{-1} . The tangent heights, or the closest approach to the Earth of the ray path from the Sun to the instrument decreases from (a) 42 km to (b) 38 km to (c) 34 km, to (d) 30 km, to (e) 26 km, to (f) 23 km. (Reproduced by permission of C. B. Farmer, Jet Propulsion Laboratory, California Institute of Technology.) (b) A laboratory spectrum of the same HNO_3 Q-branch at 1326 cm^{-1} , recorded at a resolution of 0.005 cm^{-1} using a BOMEM interferometer. (The resolution has been degraded to match the Spacelab spectra.) Reproduced by permission of P. J. Wassell and recorded at the Rutherford Appleton Laboratory.

drawbacks. Mertz, a pioneer in FT spectroscopy, once remarked¹⁴ that the technique is 'a disagreeable indirect method to record a spectrum'. It may be that you want to observe an absorption or emission in a single narrow band of the electromagnetic spectrum, without scanning. In that case the multiplex capabilities of the FT method offer no advantage. If noise is carried on the signal, rather than independently of it, then the multiplex characteristic can confer a disadvan-

tage, with a reduced S:N ratio that cannot be improved by time averaging. In any spectroscopic experiment, the product of S:N and spectral resolution is a constant for a particular time over which an observation is made, the maximum value of the product being dictated by the classical uncertainty principle. Fourier spectroscopy can help to approach the ideal, but cannot overcome the fundamental limitation. It does provide the convenience that S:N and resolution can

be varied at will (and at each other's expense) without any physical alteration to the spectrometer.

Information theory

The application of the uncertainty principle in the form of a product between S:N and resolution is an aspect of a more general central proposition of information theory. That is, that the rate at which information can be conveyed by a signal has an upper limit determined by the product of the signal bandwidth and a function of the S:N ratio. The ideal transfer rate may not be reached. For example, it is estimated¹⁵ that speaking on the telephone conveys information about 1000 times less efficiently than the ideal rate; sending data as binary pulses, on the other hand, can reach nearly 10 per cent of the ideal. These differences are just the sort that distinguish conventional from FT spectroscopy: efficient use of the available communication channel. The mathematical formulation of information theory, begun by Shannon and coworkers,¹⁶ itself uses Fourier methods extensively.^{15,17} One frequently encounters ideas familiar in one branch of study appearing slightly altered in another, and this observation seems particularly pertinent in the case of Fourier theory. Many different physical and mathematical shapes are adopted by the one underlying theorem, making the tool with which Fourier provided us one of the most pervasive and versatile in all science.

Dr Richard P. Wayne is Dr Lee's Reader in chemistry, Christ Church College, Oxford, and lecturer in the Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ.

References

1. J. B. J. Fourier, *Théorie analytique de la chaleur*. Paris: Firmin Didot, 1822.
2. O. E. Neugebahr, *The exact sciences in antiquity*. Princeton, NJ: Princeton University Press, 1952.
3. P. R. Griffiths (ed), *Transform techniques in chemistry*. New York: Plenum, 1978.
4. A. G. Marshall (ed), *Fourier, Hadamard, and Hilbert transforms in chemistry*. New York: Plenum, 1982.
5. R. R. Ernst and W. A. Anderson, *Rev. Sci. Inst.*, 1966, **37**, 93.
6. E. D. Becker and T. C. Farrar, *Science*, 1972, **178**, 361.
7. M. B. Comisarow and A. G. Marshall, *Chem. Phys. Letts.*, 1974, **25**, 282.
8. M. B. Comisarow, *Fourier transform ion cyclotron resonance spectroscopy*, in reference 4.
9. D. L. Rempel, *Science*, 1984, **226**, 261.
10. A. G. Marshall, *Advantages of transform methods in chemistry*, in reference 4.
11. R. P. Wayne, *Chemistry of atmospheres*. Oxford: OUP, 1985.
12. P. R. Griffiths, *Science*, 1983, **222**, 297.
13. C. B. Farmer, 1987, private communication.
14. L. Mertz, *Transformations in optics*. New York: Wiley, 1975.
15. M. J. Usher, *Information theory for information technologists*. London: Macmillan, 1984.
16. C. E. Shannon and W. Weaver, *A mathematical theory of communication*. Illinois: Illinois University Press, 1949.
17. J. R. Pierce, *Signals: the telephone and beyond*. San Francisco: W. H. Freeman, 1981.