Vibrational, Rotational and Raman Spectroscopy, Historical Perspective

AS Gilbert, Beckenham, Kent, UK

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After a slow start in the nineteenth century, infrared (IR) spectroscopy saw a rapid increase in use and for a while, from 1945 onwards, was the most widespread method for determining the chemical structures of molecules. In the 1960s it became increasingly supplemented and overshadowed by other techniques, but developments in instrumentation have vastly improved its sensitivity and speed and enabled it to be applied to previously intractable problems. While research applications are many, there is overwhelming analytical and industrial usage.

The development of Raman spectroscopy has generally lagged behind that of IR owing to greater technical difficulties. The advent of the laser was the most important event in its history and has enabled many special and esoteric Raman experiments to be conceived. It is no longer confined mainly to the laboratory and is now used extensively in industry.

Beginnings: IR and Raman Spectroscopy before the Second World War

The astronomer William Herschel, better known as the discoverer of the planet Uranus, first detected IR radiation in 1800. Using a glass prism to refract the rays of the sun, he observed a rise in temperature in a thermometer positioned beyond the red limit of the visible spectrum (Figure 1).

Over the next hundred years the essential nature of IR radiation was slowly established, electrical methods of measurement were developed and a number of materials such as rock salt were found to be largely transparent to it and thus useful as refracting elements. Interest was mainly directed to the physics of the subject, with little attention given to any possibilities for application to chemistry.

Near the end of the nineteenth century, however, a number of workers observed that many specific classes of organic compounds absorbed in characteristic regions of the IR spectrum. A monumental compilation of such bands, mostly from his own measurements, was published by W.W. Coblentz in 1905. One of his spectra is shown in Figure 2 (plotted in terms of % transmittance) and can be compared with a modern-day version of the same compound in Figure 3 (plotted in terms of absorbance). At the time, the precise mechanism for absorption was unclear, but it was soon realized that it was derived from what could be considered to be intramolecular vibrations. By the 1930s, a fairly complete theory encompassing the relation of dipole moment change to band intensity, selection rules, molecular symmetry and anharmonicity was available for both vibrational and rotational motions.

In 1928, C.V. Raman announced the discovery of the effect that now bears his name. In fact he had already observed it a few years before as a weak ‘residual fluorescence’ from highly purified organic liquids. It is generally considered, however, that the effect had been predicted by A. Smekal. Raman was awarded the Nobel Prize, the second Indian to be so honoured. Although the Raman effect was found to be very weak, the relation of selection rules to symmetry differed, so that results could complement those from IR absorbance.

Instrumentation

Detection of IR radiation could be done by using bolometers or thermocouples, but point-by-point plotting of galvanometer readings made measurement of spectra somewhat tedious. IR-sensitive photographic film was available later and was occasionally used. Technical obstacles were many, however; for example, the DC output from detectors could not be amplified and most galvanometers had long response times. Material for dispersion of IR radiation was scarce, rock salt of the quality and size suitable for prisms being difficult to obtain. Machines for single-beam and baselines were a major problem owing to the normal variations in laboratory heat background. Most instruments were built in-house, though commercial models were available, the first being introduced by Adam Hilger Ltd of the UK in 1913. It is illustrated in Figure 4.

The KBr disk method was not to be invented until 1952, so solids were usually sampled by mulling or reflection from whole crystals. The majority of samples studied were either liquids or gases.

By contrast, Raman spectra were usually easier to acquire so long as the sample was not coloured or turbid. Working in the visible region allowed simple spectographs with silica/glass optics to be used and suitable photographic films were readily available, though long exposures were generally required. Discharge lamps, usually mercury vapour, provided a rather weak source of excitation radiation with a broad, diffuse background.

Studies between the Wars

The benefits of theory soon allowed vibrational spectroscopy to move away from simple characterization to deductions about the shape and symmetry of simple molecules. The observation that gaseous CO₂ yielded three fundamental modes of vibration, of which two were seen in the IR only and the other in the Raman only, immediately determined that it must be linear and symmetric. The tetrahedral structure of methane was confirmed by the lack of any observable pure rotational Raman spectrum. Such results gave valuable support to the developing theories of chemical bonding.

Knowledge of the actual frequency values enabled the calculation of the vibrational partition functions. Thermodynamic
Figure 1  Picture of William Herschel’s experimental setup. Using blackened-bulb mercury thermometers, he observed a difference in temperature between one positioned at the red end of the visible and one positioned beyond. Originally from *Philosophical Transactions*, Pt II 80: 289 (1800). Photograph courtesy of Professor N. Sheppard, FRS.

Figure 2  Point-by-point IR spectrum of ethyl cyanide, plotted as % transmittance. From Coblentz WW (1905) *Investigations of Infrared Spectra*. Washington, DC: Carnegie Institution of Washington. Photograph courtesy of Professor N. Sheppard, FRS.
quantities of interest such as the heat capacity in the gas phase at different temperatures could then be estimated with great precision. In addition, the force constants of very simple molecules could be determined.

IR spectroscopy gave a dramatic illustration of the existence of hydrogen bonding, a suspected new type of molecular attraction. For instance, at high temperatures in the gas phase, formic acid yielded the expected single fundamental from O–H stretching at about 3570 cm\(^{-1}\). But at lower temperatures and in the liquid, this band disappeared to be replaced by a new one at near 3080 cm\(^{-1}\).

While most attention was naturally given to the IR region below 4000 cm\(^{-1}\), some measurements were made in the near IR (NIR), i.e. above 4000 cm\(^{-1}\), often for no other reason than ease of experimentation. Overtones and combination bands were of course of interest in their own right but could also sometimes be used to make deductions about lower-frequency fundamental modes.
First Flowering: IR Spectroscopy to the 1970s

Developments in electronics during the 1930s made measurements of IR spectra somewhat easier. Successful application to a number of tasks connected with the Second World War, such as monitoring the composition of Axis petroleum samples to determine origin, led to a considerable expansion in activities. Considerable effort was put into organic group frequency correlations, and compilations soon became available for general use. These were utilized extensively for detailed structural characterization of organic compounds. The boon to organic chemists can be appreciated by considering the methods that had been available to them before. Elemental analysis could only give overall composition and ultraviolet–visible (UV-visible) spectroscopy little more than some idea of the degree or type of unsaturation. A limited number of chemical group types were detectable by chemical spot tests.

Moreover, IR spectroscopy was also applied to other work such as quantitative analysis and the study of physical interactions between molecules. The general rise of scientific activities in both universities and industry naturally led to a rise in demand for IR facilities and the 1940s saw the first commercial automatically recording spectrometers. Spectra were now produced routinely as continuous plots. Single-beam instruments were rapidly superseded by double-beam ones and gratings came into general use.

Dispersive Double-Beam Spectrometers

In double-beam instruments compensation was, with one or two exceptions, by the optical null method whereby a servomotor drove a comb into the reference beam to minimize the signal difference between it and the sample beam as it was attenuated to varying degrees by absorbance. Movement of the comb was mechanically geared to a pen, which thus recorded the spectrum as a trace on a moving chart.

Sample and reference beams were alternately presented to the detector by means of mirrors and a chopper rotating at a frequency of several hertz, thus allowing selective amplification of the signal difference, which was fed to the servomotor. Thermal detectors continued to be used for many years but with developments, such as the pneumatic Golay cell, for greater sensitivity.

Good-quality large alkali halide crystals could now be grown on an industrial scale, so that fabrication of prisms and other optical components did not present any difficulties. In particular, use of synthetic KBr allowed spectra to be measured down to 400 cm$^{-1}$; pre-war natural NaCl (rock salt) prism spectrometers had a lower limit of about 650 cm$^{-1}$ owing to the higher frequency absorption edge of the salt.

Rotation of the prism or grating was controlled by a cam to allow the spectral trace to be recorded in either constant wavelength or wavenumber. This cam was coupled to the slits to vary their width in order to keep the radiation reaching the detector roughly constant. Resolution therefore varied over the spectrum. Positional accuracy and repeatability were poor owing to backlash and wear in the mechanical linkages; most specifications quoted values around ±0.5 cm$^{-1}$.

The inherent disadvantage of the optical null mechanism was the attenuation of the reference beam, so that accuracy and response time became worse as sample transmittance (%T) decreased. Linearity of response depended on how well the comb had been machined. Theoretically it was impossible for the equipment to measure 0%T. Scanning had to be slow to avoid excessive pen lag. Reliable quantitative analysis was difficult though possible.

The amounts of sample required for good spectra of a solid was generally of the order of a milligram. By utilizing beam condensers and the best instruments, adequate spectra could be obtained from small samples of the order of a hundred nanograms.

Commercial Instruments

Several companies built spectrometers; based in the USA were Perkin-Elmer, Beckman, Baird and Cary; in the UK, Grubb-Parsons, Hilger (Figure 5) and Unicam (later Pye-Unicam).

Figure 5  An early automatically recording IR spectrometer, the Hilger model D209 introduced in 1940. The spot from a mirror galvanometer was focused onto photographic film fixed to a rotating drum. Later during the Second World War, this machine was developed into the first commercial double-beam (ratio recording) IR spectrometer. Photograph courtesy of Professor N. Sheppard, FRS, and reproduced by permission of Hilger Analytical.
Instruments were also built in France, Germany (both West and East), Japan and the USSR. The commonest optical layout used was the Littrow arrangement which had the virtue of compactness. Low-cost instruments were introduced in the 1950s, some only with prisms though all were soon sold with gratings instead. Their relative cheapness and ease of use were major factors in the rapid expansion in the practice of IR spectroscopy. Research-grade models usually had a grating monochromator with a fore-prism. Two or more gratings with auto changeover were required to cover the whole range.

During the latter part of the period, prisms disappeared and more advanced features were built into dispersive spectrometers such as computer interfaces, principally for data acquisition only. Ratio recording became standard in place of the optical null. However, the Perkin-Elmer model 983, introduced in 1982, demonstrated the benefits that computerization could bring to instrument control. Grating rotation was carried out directly by a stepper motor under the command of a microprocessor. With no mechanical cam, position repeatability (±0.005 cm⁻¹) was, in consequence, almost as good as that of FT-IR instruments.

Applications
A pre-eminent use already described was structure determination of organic compounds. The KBr disk technique allowed complete and unmarred spectra of solids to 400 cm⁻¹. Extensive collections of spectra (both literature and commercial) of organics, inorganics, pharmaceuticals and industrial chemicals now appeared.

A result of great topical interest in the late 1940s was the recognition that penicillin contained a fused four-membered lactam ring on the basis of several bands, including one at an unusually high value, near 1780 cm⁻¹, from the amadic carbonyl stretching mode.

Because of the distinctive fingerprint nature of the spectra of individual substances, a very common application was, and continues to be, compound verification in forensic identification and quality assurance to meet pharmacopoeial and other standards set by regulatory authorities.

The sensitivity of IR bands to changes in physical state led to numerous studies concerned with the thermodynamics of hydrogen bonding in solvents and the influence of solvent effects (donor/acceptor capacities). Phase transitions (polymorphism) in solids could easily be detected by changes in band intensity and position.

Inorganic and metal–organic compounds also received attention in structural studies. For instance, IR spectroscopy of metal carbonyl complexes could easily distinguish between terminal and bridging ligands.

Access to computing (mainframe) facilities from the 1950s onwards provided the means to analyse the fundamental mode frequencies of a polyatomic molecular structure on the basis of harmonic oscillation and obtain force constants. These could be transferred to other structures and the procedure reversed so as to estimate frequencies for cases where a spectrum was difficult to interpret. While fraught with difficulties, mainly because there were usually many more force constants to estimate than frequencies, such work did at least highlight the fact that many vibrational modes are strongly coupled to each other and that few bands can normally be assigned to specific bond motions.

Data handling was never more than very primitive. Although the largest commercial collections of spectra offered searching facilities, for example by matching of most prominent bands, these were not very successful in practice even for pure compounds.

The rapid spread of mass spectrometry (MS) and nuclear magnetic resonance (NMR) spectroscopy from the 1960s caused IR spectroscopy to be sidelined in many areas of analysis. NMR was much better at elucidating many fine details of molecular structure, while detection limits were lower using MS.

Renaissance: The (Fourier) Transformation of IR Spectroscopy
IR interferometers seem first to have been tried out for examining the very low signal levels of IR emission from astronomical sources. They were shortly also employed for far-IR spectroscopy where low source output made measurement extremely difficult using conventional spectrometers below 200 cm⁻¹.

There was sufficient interest for several far-IR instruments to be made available commercially from the late 1950s, but one drawback was the difficulty of numerically converting the interferograms to recognizable spectra. With only mainframe computers available, instrument-based digital computing was not feasible. RII/C/Beckman marketed a machine that stored data, after analogue-to-digital conversion, on magnetic core memory. The data were then reconverted back to analogue to be fed into an electronic wave analyser to generate the spectrum.

Ironically, these interferometers could not be used to advantage in the mid-IR region (4000–400 cm⁻¹) in most circumstances. This was because, with scan speeds in minutes, signal levels were so large that the noise was well below the threshold of even the smallest bit of the best (16-bit) ADCs obtainable. However, by the early 1960s, Block Engineering of the USA had developed a fast scanning interferometer. Provisionally, lasers (for accurate path difference referencing), minicomputers and the Cooley–Tukey fast Fourier transform (FFT) algorithm soon all appeared. A Block subsidiary, Digi- lab, exploited these devices to produce the first commercial mid-IR Fourier transform (FT-IR) spectrometer, the model FTIR-14, in 1969.

They were followed during the 1970s by other companies, most of whom had had no previous experience in the IR field but made computers and data loggers, such as Nicolet and Bruker. The machines offered were principally research grade, though Digilab made an early and substantial entry into the specialist market for quality control of semiconductors.

Most manufacturers of dispersive instruments opted not to enter the new arena, presumably because of the costs involved in investment in the new technology, and in consequence left the business altogether as demand for dispersive instruments dried up. A major exception was Perkin-Elmer who, although starting late, had the resources to participate in a big way. Although offering research-grade instruments as well, they
particularly targeted the analytical market, in which they were soon to be a major supplier.

At least twenty manufacturers worldwide have offered FT-IR spectrometers in recent years, several of them for niche markets such as dedicated gas analysis and space science.

**Advantages of Interferometry in the Mid IR**

Two factors were judged to be of major importance: the Fellgett (multiplex) and Jacquinot (throughput) advantages. The Jacquinot advantage, though large, and foremost at higher wave-numbers, was found, however, to be largely cancelled out by the much decreased performance (at the high modulation frequencies imposed by fast scanning interferometers) of the early pyroelectric detectors used, both factors having a roughly similar wavenumber dependency. Traditional thermal effect detectors such as thermocouples were far too slow.

As other factors (e.g. beam splitter versus grating efficiency) were of lesser importance, this meant that overall advantage in signal to noise (S/N) ratio of mid-IR FT instruments over dispersives was basically determined by multiplexing only. Strict comparisons were not possible, though, because FT instruments ran at constant resolution unlike dispersives where resolution varied somewhat across the spectrum.

Thus for spectra run at moderate resolution and over limited spectral range, FT machines with pyroelectric detectors were not strikingly better than dispersives. This was because the multiplex advantage (for FTIR) is no better than $1/2M$, where $M$ is the number of resolution elements.

However, for low signal levels a quantum detection, MCT (mercury cadmium telluride) was soon developed that had much greater sensitivity at high modulation rates and thus did not trade off the Jacquinot advantage. This allowed FT spectrometers to tackle situations that dispersives could not even attempt and to go some way in competing with and complementing MS in trace analysis. Various advances in component design (e.g. sources) saw a considerable improvement in general performance during the 1970s.

The Connes advantage claimed for interferometers was that laser referencing would yield much greater wavelength accuracy and reproducibility. The latter was crucial for both signal averaging and spectral subtraction but, as the Perkin-Elmer company had shown, this could almost be matched by dispersives.

Photometric accuracy and reproducibility were actually worse than with the best ratio-recording grating instruments, owing mainly to sample reflection and emission back into the interferometer.

Fashion probably played a significant role in the cessation of dispersive spectrometer manufacture as the high S/N provided by FT machines was not required when sample was abundant and sample preparation took much longer than measurement.

**Applications**

Interferometers made far-IR spectroscopy possible, and enabled observation of lattice vibrations of crystals, low-frequency skeletal motions of organics and the stretching modes of heavy atoms. In the mid-IR region interest was not so much in new vibrations as in old ones in new and difficult situations, now accessible because of the high S/N available. Multitudes of hitherto indifferent samples suffering from low transmission were now directly amenable without resort to complex pre-preparation. Because data were obtained and stored in digital form, spectra could readily be manipulated and spectral subtraction to remove solvent bands from solution spectra, assess purity and reveal impurities became a popular activity.

High S/N, and in addition fast scanning, enabled events as rapid as fractions of seconds to be monitored. Thus FT-IR spectroscopy was applied with considerable success as a detection method for gas chromatography (GC) and manufacturers were obliged to offer suitable devices. However, optimizing the interface took a surprisingly long time; waiting on GC column technology was partly to blame. Some 20 years elapsed from the early 1970s before minimum identifiable limits, starting in micrograms, reached the mid-picogram level with the advent of cryogenic trapping methodology.

While many biological/biochemical samples had been studied by dispersive instruments, the difficulties of dealing with aqueous solutions was a severe limitation. Now, however, this general field became a major area of research attention for application of FT-IR in the 1980s. Of interest was the sensitivity of vibrational modes to subtle changes in molecular environment of the type crucial to biological mechanism and structure studies. Particular topics were how cell membrane conformations were affected by interactions with other chemicals or general physicochemical effects, and analyses of protein secondary structure.

**Instrumentation**

The GC–IR interface was the first of many specialized accessories that began to appear in increasing numbers during the 1980s. They included interfaces to various forms of chromatography (the combination being known as a hyphenated method), photoacoustic and diffuse reflectance cells and microscopes. Spectrometer design was influenced so as to avoid the inconvenience of changeover. Interferometers were therefore built with multiple beam ports to allow two or more accessories to be permanently connected. With such developments and the continuing miniaturization of computing hardware, the large floor-standing FT spectrometers of the 1970s were superseded by the modular benchtop machines of the 1980s.

One of the more recent significant developments of the interferometer has been the step scanning modification. This has allowed, among other things, the monitoring of fast processes on the timescale of single data point acquisition so that, for example, vibrational spectra of some excited states can be obtained.

Finally, the interferometer was not to be all-conquering, however, as simple filter spectrometers were found to be useful for many dedicated monitoring purposes. Tuneable IR lasers have also been applied to gas monitoring, but their general usefulness has been limited by the range of wavelengths that can be output.
The Coming of the Black Box

The necessary provision of computers in FT-IR soon led to much more than simple data manipulation. After much unfulfilled promise and wasted effort, data transfer systems became fairly standardized and reliable by the late 1980s. With the universal adoption of the JCAMP format, spectra in digital form became truly portable and could become part of the business of laboratory information management systems (LIMS). More interestingly, they could be directly matched into large digital spectral databases for automatic identification or structural analysis by expert systems.

In parallel, the 1980s also saw considerable development in the application of software for data analysis and instrument control. By this time, software was accounting for more than half the development cost of an FT-IR system.

Acronyms Galore: The Impact of the Laser on Raman Spectroscopy

Unlike the case for IR spectroscopy, there was little development in the immediate post-war years, so that for a long time practice was mainly confined to a few academic institutions.

An improved source, the mercury arc, a helical discharge lamp surrounding a cylindrical sample tube, yielded much-increased light energy, though probably equal in importance was the advent of photoelectric recording. The latter facility enabled the production of scanning instruments. Two companies, Cary and Hilger & Watts, offered models, the former fielding an image slicing device that attempted to overcome the optical incompatibility of the extended area of the mercury arc source and the narrow spectrometer slits.

Apart from the weakness of the spectra, the range of materials that could be examined was restricted by problems thrown up by the sample itself. Coloured samples absorbed source and scattered signal and possessed the propensity to fluoresce, which could easily drown out the Raman signal.

The advantages offered by the laser to Raman spectroscopy were recognized almost as soon as it had been demonstrated in 1960. It was to revolutionize the technique by providing dramatic increases in sensitivity (Figure 6) and the opportunity for unusual experiments by virtue of nonlinear effects that it could induce in many materials.

The continuous gas lasers were found to be most useful. The principal advantage of the laser in general over the mercury arc lay in the small point-source area that allowed larger flux throughput for a given spectrometer etendue.

Where formerly grams of material were needed, now milligram quantities, as solid powders, liquid or solutions in capillary tubes, were routinely amenable to examination.

![Figure 6](https://example.com/figure6.png)  
*Figure 6* Comparison of the Raman spectra of isotactic polypropylene. (a) Mercury arc, 435.8 nm; densitometer trace of a photographic negative. (b) Laser, 632.8 nm; photoelectric recording. Reproduced by permission from Tobin MC (1971) *Laser Raman Spectroscopy*. New York: Wiley.
The beckoning opportunities soon led several manufacturers (e.g. Spex, Jarrel-Ash, Coderg and Perkin-Elmer) to bring out new equipment, while older designs (Cary) were modified to accommodate the new type of source. Instruments were of course expensive compared to dispersive IR spectrometers as the optical requirements were far more stringent. Two coupled monochromators were necessary to cut down stray light from the exciting line. The Czerny-Turner layout was most common, the monochromators usually, but not always, being arranged for additive dispersion. Figure 7 shows a very early photographic/mercury arc Raman spectrum of CCl₄ for comparison with what could be achieved with an automatically recording spectrometer of the late 1960s (Figure 8).

Photoelectric detection for Raman spectroscopy initially suffered from poor sensitivity in the red, but this was rectified during the 1980s when many cheap photomultiplier tubes became available. Rather more expensive were multichannel detectors, originally used for fast time-resolved experiments in the 1970s. Their take-up was slow but by the late 1980s very sensitive charge-coupled devices (CCDs) developed for astronomy were being incorporated in spectrographs for relatively mundane analytical work.

**Complementing Infrared**

Compared to IR spectroscopy, the Raman technique was found to possess some advantages, one particular being the comparative ease in dealing with aqueous solutions. In the biochemical sphere this meant, for example, that ionization behaviour and pH change could be studied; even before the arrival of the laser, amino acids had been demonstrated to exist as zwitterions.

For a long time a major disadvantage was the common occurrence of interference from fluorescence, especially often encountered in biological material. A redeeming feature of Raman spectroscopy, however, was the many special experiments that could be performed.

**Nonlinear Effects and Other Esoterica**

The high power densities available from lasers were found to be capable of inducing a number of strange (nonlinear) Raman effects, though many were of limited applicability to problems in chemistry. Typical examples included SIRS (stimulated inverse Raman scattering), RIKES (Raman-induced Kerr effect spectroscopy) and the hyper Raman effect.

Probably the most useful was found to be CARS (coherent anti-Stokes Raman scattering), in which the signal could be detected largely free of background such as fluorescence. It was particularly beneficial in examining combustion processes in flames. Hopes that it might provide the complete answer to the fluorescence problem were to be largely unfulfilled owing mainly to its technical complexity.

Other interesting and useful discoveries did not require high-power excitation. Resonance Raman scattering (RRS) arises in certain samples when the laser excitation wavelength falls within an electronic absorbance band. RRS bands can be several orders of magnitude stronger than normal. One application was to employ small-molecule ligands exhibiting RRS as probes in the active sites of enzymes, thus avoiding major interference from the complex spectrum of the protein.

In 1974 news came that the Raman spectrum of pyridine was considerably enhanced when absorbed on a roughened silver substrate. This effect was named SERS (surface-enhanced Raman scattering) and has since been observed from many other compounds and other metals. Electrochemistry was an early application. Inevitably, experimenters were to combine the effect with RRS to create SERRS, which in some circumstances can equal fluorescence for sensitivity of detection.
**Instrumental Developments**

FT-Raman spectroscopy was introduced in 1986 and it is now available as a bolt-on to many FT-IR machines. Interestingly, interferometers might have been used earlier for Raman spectroscopy if the laser had not been invented, as their large circular aperture could have coped advantageously with the extended source area of the mercury arc. As it was, the multiplexing capability was needed to boost sensitivity so as to satisfactorily observe the weak spectra produced by a near-IR laser. The rationale was that fluorescence was largely eliminated. Thus, high-quality spectra of dyes, for instance, could be obtained that had formerly been impossible. Unfortunately, as overtones and combinations of H₂O vibrations possess significant absorbance in the near IR, spectra from aqueous solutions were affected.

An earlier development was the reintroduction of the spectrograph made possible by the availability of multichannel detectors. CCDs, with sensitivity equal to the traditional photomultiplier and up to 1024 channels, thus provided a considerable multiplexing advantage. They allowed the construction of small, rugged instruments able to acquire good-quality spectra very rapidly. Coupled to fibreoptic sampling devices, such spectrographs have recently found considerable use for process monitoring in industry.

A very useful accessory has been the microscope. Here there is a significant advantage over IR spectroscopy as spatial resolution is higher owing to the shorter wavelength of the source radiation.

**Out of the Orphanage: The Rise of Near-IR Spectroscopy**

The NIR region was for long neglected, a curiosity for users of many research-grade UV-visible and mid-IR spectrometers that had been provided with extended range capabilities. This was not unexpected, as absorption bands in the region originate from either uncommon electronic transitions in inorganic compounds or broad and heavily overlapped overtones and combinations of vibrational fundamentals. The latter are mostly derived from X–H stretching modes in organic compounds. In consequence, spectra, particularly of mixtures, are not easy to interpret.

Experimentally, however, the spectra are easy to observe, thick samples being tractable in either transmission or reflection without preparation. As the spectra seldom possess many narrow features that could be unduly affected by instrumental or other factors, robust methods for quantitation were possible. With the arrival of cheap instrumental computing from the 1980s onwards and the development of multivariate analysis methodology, NIR spectroscopy has undergone considerable expansion in use. It is now widely applied to automated, rapid and precise quantitative analyses in agriculture, industrial process control and noninvasive medical examinations. A typical and early example was determination of the protein content of grain and flour.

Most work is now done with dispersive and simple filter analysers. Though S/N is not usually a problem, FT-NIR and filter/CCD machines are more popular.

**Full Circle: IR and Raman Spectroscopy into the New Millennium**

Originally IR spectra were measured point by point; they then became continuous and now are again digital in nature. Spectrometers were single-beam, then double-beam, and now are almost all single-beam once more. With the introduction of spectrographs coupled to multichannel detectors, Raman spectroscopy is also in a sense back where it used to be, when photographic film effectively provided a multiplicity of channels. NIR CCDs are presently available that cover some of the range and the future possibilities of usable array detection right down into the mid IR could eventually spell a general return to dispersive techniques. Further into the future, fully tuneable IR lasers would remove even the need for a dispersing element for IR spectroscopy. If the rationale for interferometers, hitherto their advantage in throughput, is lost, then their disadvantages such as poor photometric accuracy and mechanical complexity could mean retention only in special circumstances.

Hand in hand with increasing sophistication of spectrometers and software, much of which runs transparently to the user, has gone an overall de-skillling of operatives. This is inevitable (and usually desirable) given the workload and demands on modern analytical laboratories and industrial processes. There are obvious dangers, however, as the theory behind the methodology is beyond many scientific workers, as are the ramifications of many spectrometer function operations on the input data. The days are long gone when spectroscopists built their own machines, synthesized the chemicals they studied and contributed to advance of theory.
Spectroscopy, Surface Studies; IR Spectroscopy, Theory; Near-Infrared Spectra, Interpretation; Near-Infrared Spectroscopy; Near-IR Spectrometers; NIR FT-Raman; Nonlinear Raman Spectroscopy, Applications; Nonlinear Raman Spectroscopy, Instruments; Nonlinear Raman Spectroscopy, Theory; Protein Structure Analysis by CD, FTIR, and Raman Spectroscopies; Raman and Infrared Microspectroscopy; Raman Optical Activity, Applications; Raman Optical Activity, Macromolecule and Biological Molecule Applications; Raman Optical Activity, Small Molecule Applications; Raman Optical Activity, Spectrometers; Raman Optical Activity, Theory; Raman Spectrometers; Raman Spectroscopy, Biochemical Applications; Raman Spectroscopy, Medical Applications: A New Look Inside Human Body With Raman Imaging; Raman Spectroscopy, Soil Analysis Applications; Rayleigh Scattering and Raman Effect, Theory; Resonance Raman Applications; Spatially Offset Raman Spectroscopy; Spatially Resolved IR; Surface-Enhanced Raman Optical Activity (SEROA); Surface-Enhanced Raman Scattering (SERS), Applications; Surface-Enhanced Raman Scattering (SERS) Biochemical Applications; Time-Resolved Raman Spectroscopy; Transmission Raman: Methods and Applications; Vibrational CD, Applications; Vibrational CD Spectrometers; Vibrational CD, Theory and Application to Determination of Absolute Configuration; Vibrational CD, Theory; Vibrational Spectroscopy in Drugs Analysis; Vibrational Spectroscopy, Flame and Temperature Measurement; Vibrational Spectroscopy in Food Processing.

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