1

A brief history of spectroscopy

The earliest reference to optical spectroscopy that we have in modern times appears to be the *phenomenon of colours* in Isaac Newton's *Opticks*, in which he describes his famous experiments with prisms and the shaft of sunlight coming through the hole in his window shutter. There was much philosophical conjecture at the time but scientific silence from then on until William Hyde Wollaston (1766–1828) in 1802, also in Cambridge, used a lens to focus images of a narrow, sunlight-illuminated slit through a prism on to a screen. Wollaston appears to have observed the dark lines across the spectrum transverse to the dispersion direction but ascribed them to the divisions between the colours. He may be forgiven for this, because with a single lens the spectral resolution would have been derisory. At about the same time William Herschel (1738–1822) discovered the infra-red radiation by the rise in temperature of the bulb of a thermometer when he held it beyond the red part of the spectrum in his spectroscope. Joseph von Fraunhofer (1787–1826) saw more dark lines but did not guess or deduce their origin. The currently accepted explanation – the absorption of continuous white light by vapours in the atmosphere of the Sun – was given by Gustav Kirchhoff and Robert Bunsen in the University of Heidelberg who, we may be reasonably certain, passed a collimated beam through their prism before focusing it, and thereby secured a reasonable resolution. It is probably to these two but perhaps to Fraunhofer as well that we owe the classical form of the optical spectroscope: the sequence of collimator, prism and telescope. Little has changed fundamentally since then.

Developments in geometrical optics kept pace with developments in photography. From Lord Rayleigh we have the complete theory of the prism spectroscope and of the diffraction grating. Comparatively crude but useful diffraction gratings could be ruled on the bed of any screw-cutting lathe and many individual workers made gratings for their own use, but without passing on the art. Practical details of grating construction were given by R. W. Wood of Johns Hopkins University. At this stage though, they were little more than scientific curiosities emphasising the

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wave nature of light. This was at a time when the corpuscular theory was by no means dead.

However, diffraction gratings were first realised at a serious and practical level by H. A. Rowland, also of Johns Hopkins University, who first devised ruling engines capable of the necessary precision.

The prism spectroscope continued in its role as the chief instrument of astronomical botany – the taxonomy or classification of stars, that is – but the resolution available then was insufficient to do more than measure wavelengths, identify and discover elements and to allow wise comments on the mysterious ‘fluted’ spectra sometimes found in flames as well as in cool stars, so described by their resemblance, at low dispersion, to the flutings on the columns of classical temples. It was a major achievement for a spectroscope to be able to resolve the six angstroms separating the ‘D’ lines of sodium, and Rayleigh computed that a prism base length of ‘at least 1 centimetre’ would be needed for this, that is to say a resolving power of $\sim$1000.

Sir Arthur Schuster achieved a resolving power of more than 10 000 at Manchester University with a twelve-prism[1] spectroscope made for him by Cooke of York, with 30 glass–air interfaces (excessive even in a modern coated zoom lens!) and prism bases of 25.4 mm. With incidences near the Brewster angle there should have been near perfect transmission for one state of polarisation, but in practice a transmission coefficient of about 0.05 made it virtually useless except as a sort of tour de force of the spectroscope-maker’s art. The way forward in those days was the manufacture of ever-larger prisms from ever-denser glasses.

The finely ruled diffraction grating by contrast improved the spectral resolution immeasurably and led to the evolution of the spectrograph at the hands of H. Ebert, who in 1889 removed chromatic aberration and a great deal more besides by replacing the lenses of the collimator and the camera with a single concave mirror. The symmetry was intended to eliminate coma as well as chromatic aberration but the apparent symmetry is removed by the tilt of the grating and, although reduced, the coma is still there.

Ebert’s invention was inexplicably lost until rediscovered by W. G. Fastie 50 years later, by which time the single mirror had been replaced by two separate mirrors in the now standard Čzerny–Turner configuration.

It was the invention of efficient vacuum pumps which led to the investigation of gas-discharge phenomena by Crookes and others and the consequent exploration of gaseous emission line spectra. This led in turn to the empirical discoveries by Balmer, Paschen and Rydberg which gave rise to the need for an explanation and the consequent invention of the Bohr model of the atom and the subsequent evolution of quantum mechanics.

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[1] In practice six prisms each passed twice.

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In the twentieth century the spectroscope developed in accordance with the best detector technology available at the time. Little happened before 1950 in the optical part of the spectrum although infra-red detectors made considerable progress, and at wavelengths below 0.8 μm the photographic emulsion was the universal detector, the spectroscopic art advancing along with improvements in its sensitivity and panchromaticity. By *c*. 1950 the whole electromagnetic spectrum from soft X-rays to about 1.2 μm was available to silver halide emulsions and the short-wave limit to practical spectrography was set by the reflection coefficients of the optical components, which were – and are – dismal below about 1200 Å. This limitation was offset by the gradual development of improved sources of XUV light such as the synchrotron for absorption spectrography and later spectrometry.

Semiconductor detectors improved the accessibility of the infra-red, and the photomultiplier, which became generally available *c.* 1950, revolutionised optical spectroscopy. This device yielded a detective quantum efficiency (DQE) in the region of 0.2–0.35 as opposed to the DQE of a silver halide crystal of about 0.0005 and, just as importantly, gave a linear response.[2] One of the bugbears of the silver halide emulsion, especially at the low surface brightness of many astronomical sources, was *reciprocity failure*, the inability to respond adequately to long exposures at a low light level. Consequently a monochromator with a photomultiplier detector, free from the constraints of low focal ratio, could easily out-perform a spectrograph and moreover could be made to concentrate its efforts on the parts of the spectrum important to the investigation being made.

Geometrical optical design was then brought to bear, resulting not only in high efficiency but in much greater resolving power, sometimes reaching 80–85% of the theoretical level imposed by the constraints of physical optics.

In parallel with the development of the grating spectrograph, interference spectrometry extended the high-resolution end of the art. Rayleigh again observed that the signal from a Michelson interferometer was the Fourier transform of the spectrum of the incoming light but little note was taken of it at the time except as a scientific curiosity, and it was Charles Fabry and Alfred Pérot in the University of Marseille who in 1899 devised the interferometer which revealed fine and hyperfine structure in spectral lines. Other simultaneous devices, such as the echelon grating,[3] the Lummer plate[4] and the echelle[5] gave equally high resolution but were far less convenient to use and were not widely copied. In the visible and UV region it is the

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[2] Based upon the experimental finding that ∼1000 photoelectrons must be liberated within a microcrystal of silver bromide, irrespective of its size, to make it developable.

[3] A. A. Michelson, *Astrophys. J.*, **8** (1898), 37.

[4] O. Lummer, *Verh. Deutsch. Phys. Ges.*, **3** (1901), 85.

[5] G. R. Harrison, *J. Opt. Soc. Amer.*, **39** (1949), 522.

Fabry–Perot interferometer in its various guises which still rules the high-efficiency end of the spectrographic art.

Meanwhile high resolution was being achieved by more-or-less heroic means, with plane-grating instruments of two or three metres focal length and focal ratios of F/20 or F/30. This ensured at least that the optical resolution would be diffraction limited and that photographic exposures would take an inordinately long time. Academic research was simultaneously being carried out using concave gratings of up to ten metres radius, in spectrographs which filled a whole room in a laboratory or the whole of the Coudé focus room of a large astronomical telescope. There appears to have been some confusion at the time between *dispersion* and resolution, as though one depended on the other, and dispersion itself was taken as a measure of quality or performance. With the passage of time has come improved knowledge and a spectrograph much bigger than one metre or perhaps two in focal length is now a rarity. Provided that an adequate design is chosen, all the information that can be extracted from a spectrograph can be revealed with a 1.5-metre instrument.

The period between 1950 and 1970 saw a great surge in activity in the art of optical spectroscopy. This followed Jacquinot's revelation that 'L-R product' or 'efficiency' in a spectrometer, defined as the product of 'throughput' or 'light-grasp'[6] and resolving power, was a constant and that one quality could be traded for the other. There was consequently a huge blossoming of ingenious, weird and wonderful inventions, including the mock-interferometer,[7] the Sisam,[8] the Girard grille,[9] the Möbius-band interferometer,[10] the tilting Michelson interferometer,[11] the lamellar grating interferometer[12] and various 'chirped' and field-compensated Michelson Fourier spectrometers.[13] Much time and effort were expended to bring these ideas to practical use and the two famous 'Bellevue' conferences of 1957 and 1967 brought all these people together for an exchange of ideas.

However, this insubstantial pageant has faded and very few of the devices described there have survived the test of time–convenience–cost-benefit analysis.

The concept of L-R product is important, indeed fundamental. The idea of resolving power, defined as $R = \lambda/\delta\lambda$ where λ is the wavelength being observed and $\delta\lambda$ the smallest wavelength separation that can be distinguished as two separate

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[6] A felicitous phrase from H. A. Gebbie.

[7] L. Mertz, N. O. Young & J. Armitage, *Optical Instruments and Techniques*, K. J. Habell, Ed. (London: Chapman & Hall, 1962).

[8] **S**pectromètre **I**nterférentiel à **S**élection par l'**A**mplitude de **M**odulation. P. Connes, *J. Phys. Rad.*, **19** (1958), 197.

[9] A. Girard, *Opt. Acta*, **7** (1960), 81.

[10] W. H. Steel, *Opt. Acta*, **11** (1964), 211.

[11] R. S. Sternberg & J. F. James, *J. Sci. Instrum.*, **41** (1964), 225.

[12] J. D. Strong & G. A. Vanasse, *J. Phys. Rad.*, **19** (1958), 192.

[13] L. Mertz, *J. Opt. Soc. Am.*, **49** (1959), iv; P. Bouchareine & P. Connes, *J. Phys.*, **24** (1963), 134; Y. P. Elsworth, J. F. James & R. S. Sternberg, *J. Phys. E*, **7** (1974), 813.

spectrum lines, is an old, dimensionless quantity and a useful parameter of quality in a spectroscope. ‘Light grasp’ on the other hand, also known as ‘luminosité’ or ‘étendue’ and generally denoted by the letter L, is less familiar and is a measure of the rate at which an optical instrument can process the power it receives from the incident electromagnetic field. It can be defined as the product of detector sensitive area and the solid angle subtended by the detector at the exit pupil of the system[14] or alternatively as the product of the area of the exit pupil and the solid angle subtended by the detector sensitive area. Both of these definitions are derived from the *Helmholtz–Lagrange* invariants of the system. The constancy of the product can be envisaged easily by referring to a simple prism spectroscope. If the entry-slit width is doubled, twice as much light passes through but the resolution is halved.

The concept is much more universal than this and it became apparent that high-resolution devices such as the Fabry–Perot interferometer, possessing a much higher L-R product than a grating spectrometer, could be used at moderate resolution to examine low-luminosity sources. Soon afterwards the ‘multiplex’ or Fellgett[15] (so named after its discoverer) advantage made Fourier-transform spectroscopy with a Michelson interferometer a highly desirable goal despite its formidable technological problems – now happily solved.

For more than 30 years the monochromator in one form or another ruled supreme until it was rudely overthrown by the arrival of the charge-coupled device, the ‘CCD’. When cooled to the temperature of liquid nitrogen the CCD has a detective quantum efficiency of $\sim$0.5 or more and it is, in effect, a photographic plate with an ISO rating in the region of 3 000 000 and a resolution of anything up to 100 line-pairs/mm.[16] The other improvements which it brought are legion: the lack of reciprocity failure, the enormous dynamic range in the region of 50 000,[17] the virtually instant read-out on to a computer screen, and so on. To develop its full potential in spectrography it has been necessary to return to geometric optics in spectrograph design, as there is a strict requirement for a flat field, and a distinct advantage in a low focal ratio; and there are modern advances which would have benefited the Victorian spectrograph had the problem been tackled at the time.

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[14] Which for F-numbers ≥ 1.5 is related to the focal ratio F by $\Omega = \pi/4F^2$.

[15] P. Fellgett, *J. de Phys.*, **19** (1958), 187, 237.

[16] As compared with the fastest and consequently coarsest silver halide emulsions with ISO ratings in the region of 2000 and $\sim$50 line-pairs/mm.

[17] Silver halide has a dynamic range of about 100: it saturates at $\sim$100 times the minimum exposure needed to produce blackening.

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The relevant regions of the electromagnetic spectrum

The extent of the electromagnetic spectrum is too well known to require description here. We shall be chiefly concerned with the so-called ‘optical’ region, of which the boundaries are determined partly by the methods of detection and partly by the methods of dispersing and analysing the radiation. What is common to all parts of the region is the type of optical element and materials of construction of spectroscopic instruments. Beyond the region on the long-wave side, coherent detectors, paraboloidal aerials, waveguides and dipole arrays are used, and on the short-wave (X-ray) side, optical elements other than diffracting crystals and grazing incidence reflectors are generally unknown. Radiation of 100 Å wavelength liberates photoelectrons with more than 100 eV of energy and the appropriate detection methods are those of radiography and nuclear physics.

Broadly we can identify six wavelength divisions appropriate to optical design techniques:

- 50–15 μm. The far infra-red (FIR), where bolometric, superconductor and semiconductor detectors are the chief methods of detection and measurement, and only specialised materials such as selenium, thallium bromide and various polymer resins such as sulphones have the necessary transparency to make useful refracting components. Optical elements may well be polymer plastics of high dielectric constant. Reflecting elements are coated with gold. New FIR-transparent materials with desirable optical properties are appearing all the time. Nevertheless, the principles of design which make use of them are unchanging and it is important to pay attention to their refractive index and partial dispersion or v-value when deciding whether to use them.
- 15–1.2 μm, 0.1–1 eV. The near infra-red, where there are many suitable refracting materials, and where semiconductor, superconductor and bolometric detectors prevail. This region includes the two ‘windows’, the 2–4 μm band and the 8–13 μm band where the atmosphere is transparent. The opacity does not much concern laboratory work, but is important if aeronomy, telecommunications or astronomical research is in view. The edges

of the regions, where absorption is slight but noticeable, are particularly difficult regions to work in.

- 1.2–0.35 μm, 12 000–3500 Å, 1–3.5 eV. The near infra-red, visible and near ultra-violet (UVOIR)[1] region where both semiconductors, photoconductors, photochemical reactions and photoemitters can be used, the latter directly as so-called 'photon-counters' (in reality photoelectron counters). This, not unnaturally, is the best understood region of the spectrum and where the greatest variety of refracting materials are known. It is also the region between 1 eV and 3 eV of energy, where interesting things happen in chemistry and physics, where atoms and molecules display their properties, where chemical reactions take place. At wavelengths above 8000 Å atmospheric transmission is patchy with extensive regions of opacity caused by water-vapour and oxygen molecules. Laboratory work is unaffected but aeronomers, astronomers and surveyors may have problems when they need long path lengths through the atmosphere.
- 0.35–0.20 μm, 3500–2000 Å, 3.5–6 eV. The far ultra-violet, where optical components must be selected carefully for adequate transmission[2] and phosphors are required to convert the radiation into longer wavelengths for registration by optical detectors. Again laboratory work is unaffected but the ozone layer of the atmosphere at 45 km effectively absorbs all extra-terrestrial UV radiation below 2900 Å. Laboratory sources emitting these wavelengths (a quartz-envelope mercury vapour lamp for example, which emits the 2537 Å Hg $^1S_0$–$^3P_1$ resonance line) are harmful and must be shielded, together with any surfaces which may reflect that radiation into the surrounding laboratory. Such sources may also stimulate the production of ozone (O_3) which has a characteristic 'electric' smell and has well-known corrosive properties on some materials such as rubber.
- 0.2–0.12 μm, 2000–1200 Å, 6–10 eV. The vacuum ultra-violet, where atmospheric gases absorb the radiation (O_2 below 2424 Å and N_2 below 1270 Å), where most materials have lost their transparency and where the reflecting powers of metals are beginning to decline. Optical instruments for this region must be in a vacuum chamber or in a non-absorbing atmosphere such as helium, which is transparent down to 911 Å, and other rare gases similarly down to their respective ionisation potentials. It is an interesting and not yet thoroughly explored region where autoionisation series spectra can be detected with their concomitant 'superallowed' transitions and broad line absorption spectra. Filling the spectrograph with helium does not ease the vacuum problem so far as leak prevention is concerned but it may ease the stress on thin-film windows.
- 0.12–0.01 μm, 1200–100 Å, 10–100 eV. The far- or extreme-vacuum ultra-violet, sometimes called the XUV, where radiation is ionising, where there are no transparent materials except in the form of thin (∼1–2 μm) films, where reflection coefficients are down to ∼0.1–0.2 and apart from synchrotron radiation there are no reliable, steady sources of radiation for absorption spectroscopy.

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[1] **U**ltra-**V**iolet-**O**ptical-**I**nfra-**R**ed.

[2] Most optical glasses are opaque below 3500 Å.

Gas molecules have absorption cross-sections measured in megabarns (1 Mb $= 10^{-18}$ cm^2) and this, in an optical path of $\sim$1 m, implies a need for a vacuum better than 10^{-4} mm Hg, which in turn requires a diffusion pump or, if especially pure samples are to be examined, a turbo-molecular pump. This is probably the most difficult region of the spectrum for which to design spectrographs and in which to do research. The vacuum requirements are demanding and not to be undertaken lightly.

At wavelengths below $\sim$100 Å materials start to become transparent again[3] and this is the beginning of the soft X-ray region where different techniques supervene.

In each of these regions of the spectrum the optical design requirements have much in common. There are exceptions.

- In the infra-red, alternative techniques such as Fourier-transform spectroscopy, usually with a Michelson interferometer,[4] are possible, are advantageous and are capable of enormous resolving power. A warning, however: the method lacks spectrometric simultaneity. A flickering source can have catastrophic effects on the spectrum unless rapid sawtooth scanning is used at a frequency well above the highest flicker frequency or below the lowest. In commercially available Fourier spectrometers this rapid scanning is unusual. Fourier spectroscopy has no advantage elsewhere than in the infra-red.
- In the UVOIR region the plane diffraction grating is the radiation analyser of choice although there are circumstances where a prism has advantages. The Fabry–Perot interference spectrograph, too, has its place where high resolution is needed or where very low light levels are encountered.
- In the vacuum ultra-violet between $\sim$2000 Å and 1200 Å prism and lens materials such as calcite and lithium fluoride are available with the required transmission but generally the concave grating possesses advantages which increase rapidly as the wavelength of interest decreases. At wavelengths below 2000 Å the concave grating is the analyser of choice. Below 1200 Å there is no realistic alternative.

So far as refracting materials are concerned for these various regions, technology is advancing all the time, especially in the infra-red and the Internet should be consulted for details of their transmitting and refracting properties and for the names of their manufacturers.

2.1 The limits of optical spectrography

An optical spectrograph or spectrometer of one sort or another can be made to give a resolution up to $R \sim 10^7$ without a struggle. It is difficult to imagine a practical application for a conventional spectrograph with a greater resolving power than

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[3] Or the radiation more penetrating!

[4] But see Section 7.6.

this.[5] A Fabry–Perot étalon with a 3-metre spacer and a finesse of 50 will give $\sim 4.10^8$ at optical wavelengths, enough to reveal the natural widths of allowed atomic transitions, provided of course that you can first eliminate all the temperature effects. Extraordinary precautions are needed to ensure stability (in the source as well as the instrument) since the étendue is tiny and the exposure time long. It has the merit of being absolute, since the various quantities involved are directly measurable with a metre-stick. But at this sort of resolving power, more sophisticated spectroscopic techniques are available and preferable.

[5] The measurement of small Doppler shifts, for example, does not require high resolving power, only high spatial resolution at the focal plane. A wavelength shift of a small fraction of a resolved element is measurable.

3

Geometrical optics

This is the branch of optics which deals with image-forming instruments, including of course spectrographs and interferometers. Such instruments employ lenses, mirrors and prisms and it is the art of combining these elements to make useful devices which is the subject of the next two chapters.

3.1 Rays and wavefronts

Image-forming instruments are intended to project *images* of real objects on a *screen* or *focal surface* – usually though not always plane, and instrumental optics is the study of ways of doing this.

The subject comprises two chief parts: *instrument design* and *lens design*.

The former is the design of instruments so that light is conveyed through their optical components from one to another to arrive eventually at the focal surface. The technique is essentially a graphical one, using a drawing board or a computer drafting program to lay out the components at their proper places.

The latter involves the accurate tracing of rays through various optical surfaces of different types of glass, and reflections from mirrors of various shapes to achieve a correction of the optical aberrations and to ensure that light of all wavelengths from a point on an object is focused to a corresponding point on its image.

Traditionally this was done by *ray tracing*, the accurate computation of ray paths using seven-figure logarithms and trigonometrical tables, but now is done chiefly by iterative ray tracing in a small computer, using a program specifically designed for that purpose.

A word of warning: an optical system such as a spectrograph cannot be designed on a ray-tracing program. The proper positions for the various elements must be found by means of the drawing board or the CAD program. An iterative ray-tracing program can then be used to optimise the performance of the instrument by altering