Spectrophysics

ANNE P. THORNE

SECOND EDITION

Spectrophysics

ANNE P. THORNE

Senior Lecturer in Physics,
Imperial College,
University of London

SECOND EDITION

Preface to the first edition

This book describes the methods of experimental spectroscopy and their use in the study of physical phenomena. The applications of optical spectroscopy may be grouped under three broad headings: chemical analysis, elucidation of atomic and molecular structure, and investigations of the interactions of radiating atoms and molecules with their environment. I have used the word 'Spectrophysics' for the third of these by analogy with spectrochemistry for the first and in preference to 'quantitative spectroscopy'.

A number of textbooks treat atomic and molecular structure at varying levels of profundity, but elementary spectrophysics is not, so far as I am aware, covered in any one existing book. There is moreover a lack of up-to-date books on experimental techniques that treat in a fairly elementary fashion interferometric, Fourier transform and radiofrequency methods as well as prism and grating spectroscopy. In view of the importance of spectrophysics in astrophysics and plasma physics as well as in atomic and molecular spectroscopy there seemed a place for a book describing both the experimental methods and their spectrophysical applications.

This book is directed at students on a first degree course in physics and at postgraduates beginning research in the fields of experimental atomic or molecular spectroscopy, plasma physics or astrophysics. It is hoped this book will enable such students to set their own particular research problems in the context of similar problems and to compare the various methods of tackling them. The book is not, however, intended as a research manual, for it does not contain sufficient experimental detail for this purpose. In particular, Chapter 7 on microwave and radiofrequency spectroscopy describes only the principles of the various methods and the types of problem to which they can be applied.

The rather long chapter on atomic and molecular structure, Chapter 2, has been included to explain the concepts and terminology used in the later chapters for the benefit of any student who is not familiar with the subject. It is in no sense intended as a potted course on atomic structure. Some acquaintance with elementary wave mechanics is assumed in both this and later chapters.

A few remarks on the contents of Chapters 8 to 11 should help to indicate the scope of this book. Pressure broadening of spectral lines is discussed more fully

than is usual in elementary textbooks, but from a physical rather than a mathematical point of view. Transition probabilities, line and oscillator strengths, absorption coefficients, and the relations between these quantities are treated at some length because they seem to engender considerable confusion among students. Moreover, topics such as optical depth, equivalent width, curves of growth and radiative transfer are often totally unfamiliar to students because they are usually to be found only in textbooks on astrophysics. The last chapter introduces some basic ideas of plasma physics, discusses ionization, continuous radiation and thermodynamic equilibrium, and shows how spectroscopy may be applied to problems in both laboratory and astrophysical plasmas.

This book has been completed at a time when the rapid development of tunable dye lasers is opening up new possibilities in all branches of spectroscopy. I have remarked on some of the new techniques at appropriate places in the text, but undoubtedly many more will pass into common usage in the next few years.

I owe my sincere thanks to a number of friends and colleagues who have helped me in writing this book. In particular, Dr H. G. Kuhn, FRS, of Oxford University most kindly read the whole manuscript and made numerous suggestions for its improvement. Dr R. C. M. Learner of Imperial College has provided a wealth of constructive criticism of most of the book, and Dr D. D. Burgess, also of this college, has done likewise for the remainder. Finally, I must thank my husband and children for putting up, on the whole patiently, with a constantly pre-occupied wife and mother.

Preface to the second edition

Spectrophysics has been out of print for some years, and a number of colleagues who have found it useful in their teaching and as a quick reference for some of their research have persuaded me to resurrect it. The minimal changes and additions I at first envisaged have actually turned into a substantial rewriting of the book, although it still covers the same field at the same general level.

As to the changes, one's colleagues are much better at making suggestions for what should be added than for what should be removed. The principal addition is a chapter on laser spectroscopy. I remarked in the Preface to the first edition on the possibilities then opening up with the development of tunable dye lasers, and it is unthinkable now not to include laser spectroscopy with the other experimental techniques. The difficulties have been to avoid turning the chapter into a book, and to restrict it to techniques and applications that will not be out of date almost before the book is published.

The other main structural change is the splitting of the summary of atomic and molecular structure into two chapters. The molecular chapter now contains a little more discussion of interatomic potentials as background for the subsequent treatment of pressure broadening.

Much more spectroscopy is still done by 'conventional' methods than with lasers. I have updated the material on sources and detectors, particularly the latter, and paid more attention to signal-to-noise limitations. In the three chapters on prisms, gratings and interferometers I have improved (I hope) the presentation of resolving power and throughput and have rewritten and added somewhat to the section on Fourier transform spectroscopy (largely as a result of personal experience of this technique in the last few years). Raman spectroscopy and coherent anti-Stokes Raman spectroscopy (CARS) now put in a brief appearance at the end of the chapter on the 'other techniques'; they are not entirely logical companions to radiofrequency and magnetic resonance spectroscopy, but because of their increased importance it seemed right to include some mention of them. The remaining chapters have been updated and partly rewritten, but the content has not been greatly changed.

It proved impossible, without cutting out a whole chapter, to omit as much material as I have put in, but I have eliminated parts that seemed redundant or

out of date, and the book is not very much longer than it was. I hope it will continue to serve as a readable undergraduate text and as a handy background survey in research.

I should like to thank the many colleagues who have helped me, wittingly or unwittingly, in correcting errors and bringing the book up to date – in particular, Drs K. Burnett, P. L. Knight and R. C. M. Learner of this college, Dr J. W. Brault of the National Solar Observatory, Dr P. L. Smith of Harvard College Observatory and Dr M. C. E. Huber of ETH–Zürich. Finally, thank you to my husband for putting up with it all over again.

Contents

ONE

Introduction

1.1 The uses of spectroscopy

Spectroscopy can be used to determine the identity, the structure and the environment of atoms and molecules by analysis of the radiation emitted or absorbed by them. The light from a gaseous discharge, when analysed by wavelength to form a spectrum, is found to consist of discrete lines and bands, perhaps overlying a continuum. Each line or band is characteristic of a particular atom or molecule, and once the characteristic line pattern of an atom is known its appearance in the spectrum establishes the presence of the atom in the source. This aspect of spectroscopy is known as spectrochemical analysis, and it may be made quantitative by measuring relative intensities as well as wavelengths. Secondly, one may deduce from the line or band pattern the characteristic energy levels, or stationary states, of the atom or molecule. This provides the experimental basis from which the theories of atomic and molecular structure have been developed and are still developing. Finally, the physical properties (temperature, pressure, etc.) of the gas or plasma containing the emitting or absorbing particles affect the intensity and wavelength distribution of the radiation in various ways. The study of these effects, with a view to establishing the physical parameters of the source, may be called, by analogy to spectrochemistry, spectrophysics.

For the first couple of centuries after Newton first observed a spectrum, spectroscopy was put to none of these uses. Although the wavelengths of many spectral lines were measured during the first half of the nineteenth century – including the absorption lines in the Sun's spectrum discovered by Fraunhofer and emission lines in the spectra of flames – it was not until about 1860 that Kirchhoff and Bunsen confirmed the link between particular wavelengths and particular atoms and so inaugurated spectrochemistry. In the following few years several elements were first discovered spectroscopically (rubidium, cesium, thallium and indium, for example). In addition to its laboratory applications, the new technique was immediately directed to the identification of the Fraunhofer lines in the Sun's spectrum. Helium was 'discovered' in the Sun by Lockyer in 1868, many years before it was isolated in the laboratory.

The identification of atoms and molecules in other stars, in nebulae and in interstellar space, together with estimates of their relative abundances, has continued to the present and is of the utmost importance to astrophysics and cosmology.

The spectroscopic foundations of atomic structure were laid from 1885 onwards with the attempts by Balmer, Rydberg and others to group the observed spectral lines of a given atom in some meaningful fashion. The splitting of spectral lines in a magnetic field, discovered by Zeeman in 1896, was interpreted by Lorentz in terms of an oscillating charged particle whose charge/mass ratio identified it with the electron discovered at about the same time by Thompson. However, it was not until 1913 that Bohr, using the atomic model recently proposed by Rutherford, produced the theory of the hydrogen atom that really established the link between spectra and structure. The part played by spectroscopy in atomic physics grew rapidly in scope in the 1920s and 1930s with the introduction of quantum mechanics and the discovery of electron spin and nuclear spin, and it is far from being played out now. The unravelling of the spectra of complex atoms (such as the rare earths) and of highly ionized species, the determination of transition probabilities, and the study of hyperfine structure and isotope shifts are examples of the continuing role of 'conventional' spectroscopy. Even simple atoms give rise to complex spectra when electrons are excited from inner valence shells, and their study has helped in the development of many-body theories as well as in the understanding of recombination and scattering processes. The development of microwave and radiofrequency spectroscopy has allowed small energy differences such as those arising from hyperfine structure and quantum electrodynamical effects to be measured far more accurately than is possible by optical spectroscopy. The advent of tunable lasers has opened up a multitude of new techniques and, indeed, new fields of research concerned with the interactions of atoms with very high electromagnetic fields and non-linear optics. On the theoretical side the availability of powerful computers has enabled far more sophisticated calculations to be made. A high degree of co-operation between theory and experiment is vital in the interpretation of all these current fields of research.

The third application of spectroscopy, here designated spectrophysics, is concerned with interactions between atoms, molecules, electrons and photons insofar as these determine the intensities, widths and shifts of spectral lines and the intensity and spectral distribution of continuous radiation. There are two aspects to investigating these interactions: to interpret and understand what is happening, and to use this understanding to determine abundances, temperatures, pressures, velocities, electron densities and radiative transfer and dynamic rate processes in the emitting or absorbing gas. Spectrophysics has been an important branch of astrophysics ever since the identification of the Fraunhofer lines with applications both to true astrophysics and to what is sometimes called laboratory astrophysics. The importance of quantitative spectroscopy in both of these fields has increased rapidly in recent years for two main reasons. Until

1930 astrophysicists were limited in the range of wavelengths they could study by the 'optical window' in the Earth's atmosphere: 300 nm to 2 μm, in round figures. The opening of the 'radio window' (roughly 1 cm to 10 m range) set off the rapidly growing and immensely important science of radio astronomy. Of more direct relevance to the subject of this book, the development of rocket and satellite spectroscopy from 1945 onwards enabled 'optical' spectroscopists to see beyond the edges of their window to the infra-red and the highly important ultra-violet region below 300 nm. The second main reason for spectrophysical advance has been the development of high-temperature plasmas, initially for fusion work. The need for spectroscopic investigation of these plasmas stimulated lines of research that were immediately applicable to the study of astrophysical plasmas as well as to basic collisional and radiative procesess in atomic physics.

1.2   Scope of this book

This book is mainly concerned with those aspects of experimental spectroscopy that have definite physical applications – the third of the three uses described in the previous section. Chapters 2 and 3 survey atomic and molecular structure in order to give the necessary background for the rest of the book and to introduce the quantum numbers and the terminology. Chapters 4–7 describe the experimental techniques of optical spectroscopy, by which is meant spectroscopy from the soft X-ray region to the sub-millimetre region – the wavelength range from 1 nm to 100 μm (in round numbers). The emphasis in these chapters is on high resolution and intensity measurements, because these are necessary for the determinations of line shapes, transition probabilities and number densities. Absolute wavelength measurements and line identifications are of much greater importance in spectrochemistry and atomic structure than in spectrophysics. Chapter 8 surveys the current state of the continuously developing field of laser spectroscopy. Concluding the experimental techniques, Chapter 9 gives an overview of microwave, radiofrequency, level-crossing and Raman spectroscopy, with the object of pointing out alternative ways of measuring some of the quantities discussed in optical spectroscopy.

Chapter 10 discusses the broadening of spectral lines by radiation damping, Doppler effect and interactions with other particles. Chapter 11 defines and relates transition probabilities, absorption coefficients, oscillator strengths and connected quantities, and discusses such astrophysically important concepts as optical depth and curves of growth. Chapter 12 describes the various methods of measuring transition probabilities, partly because of their intrinsic importance in spectrophysics and partly because many such methods may equally well be used on lines of known transition probability to determine abundances and temperatures. Chapter 13 deals with energy distributions and equilibrium conditions and describes specifically some of the more important applications of spectroscopy to laboratory and astrophysical plasmas.

The book makes no attempt to cover a number of forms of spectroscopy – notably radio-astronomy, photoelectron, X-ray and Mössbauer spectroscopy – on the grounds either that they use very different experimental techniques or that they are not very relevant to spectrophysics.

1.3   The electromagnetic spectrum

The electromagnetic spectrum extends from the longest radio waves, whose wavelengths are measured in kilometres, through the medium and short radio waves to the microwave, infra-red and visible regions. Beyond the visible, the ultra-violet merges into the X-ray region, and at shorter wavelengths still come γ-rays and cosmic rays.

Figure 1.1 is a diagram of the spectrum on which are marked the conventional spectral regions. The divisions are necessarily rather arbitrary, except for the closely defined visible region. The wavelength λ is marked in metres and subunits: micrometres, μm (or microns) and nanometres, nm. Ångström units, Å, and X-units, XU, are also shown since they are still recognized units and are frequently found in the literature. Since $1\,\text{Å} = 10^{-10}$ m, the nanometre and the ångström are related by $1\,\text{nm} = 10\,\text{Å}$. The XU was originally defined independently in such a way that its relation to the ångström unit was $1002.06\,\text{XU} = 1\,\text{Å}$. It is now defined as exactly $10^{-3}\,\text{Å}$, or 10^{-13} m.

Despite the common classification by wavelength, the important quantity from the point of view of atomic and molecular structure is the frequency ν, which is related directly to the energy difference between two stationary states of the system by $\Delta E = h\nu$, where h is Planck's constant. Frequency is measured in Hz (s^{-1}) and multiples thereof (kHz, MHz, GHz, . . .) and is related to the wavelength measured in vacuum by

$$\nu = c/\lambda_{\text{vac}} \tag{1.1}$$

where c is the velocity of light in vacuum. In optical spectroscopy ν is usually replaced by a unit proportional to it, the wavenumber σ defined by

$$\sigma = \nu/c = 1/\lambda_{\text{vac}} \tag{1.2}$$

Different authors use different symbols for wavenumber: ν', $\tilde{\nu}$, k and σ will all be found in the literature, but we shall use σ in this book. The unit of wavenumber in the SI system should logically be the m^{-1}, but the unit cm^{-1} is firmly entrenched in actual usage. Attempts to designate it by the name Kayser (K) have not met with general acceptance, although the sub-unit millikayser (mK) is sometimes used in hyperfine structure and linewidth work. A convenient relation to remember is $1\,\text{mK} = 30\,\text{MHz}$. Finally, very high photon energies, corresponding to very short wavelengths, are often expressed in electron volts (eV): 1 eV is equal to 1.6×10^{-19} J and corresponds to $8066\,\text{cm}^{-1}$. These three 'energy units' are marked below the wavelength scale in Fig. 1.1, and the numerical relations are collected in the Appendix.

log λ (m)	+3	0	−3	−6	−9	−12

λ: 1 km   1 m   1 mm   1 μm   1 nm   1 Å   1 XU

ν: 33 MHz   33 GHz   33 THz

σ: 1 cm^{-1} 100 cm^{-1} $10\,000 \text{ cm}^{-1}$

ΔE: 1.2 eV   1.2 keV   1.2 MeV

γ-ray →

Name

Radio wave — Medium | Short — Microwave — Infra-red — Far IR | Near IR — Visible — Ultra-violet — Vacuum UV — X-ray

Physical phenomena

Free electrons

Atomic and molecular hfs molecular rotation

Atomic and molecular outer electron transitions

Inner electron transitions

Ionic transitions

Molecular vibration-rotation

Nuclear effects

Experimental notes

Tunable sources and detectors

Quartz transmission

Crystal transmissions

Ruled diffraction gratings

Crystal gratings

Fourier-transform spectroscopy

Dye lasers

Tunable lasers

Photo-ionization detectors

Photomultipliers and photographic plates

Photoconductive detectors

Photodiodes

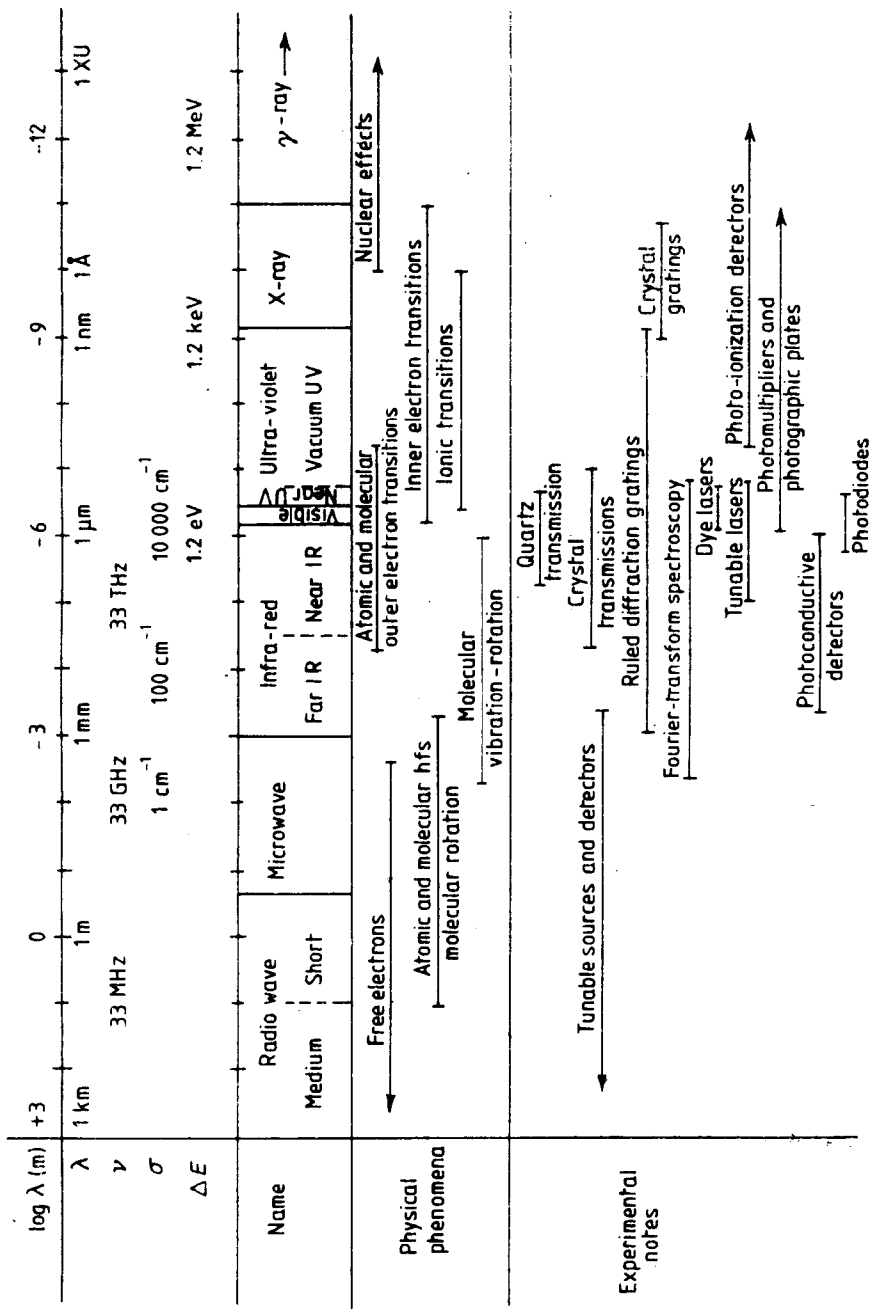**Figure 1.1** The electromagnetic spectrum.

The atomic and molecular energy levels themselves are also often expressed in wavenumbers, cm^{-1}. Conversion from absolute energy units, joules, requires in addition to the factor hc a further factor of 100 to change m^{-1} to cm^{-1}:

$$\Delta E \text{(joules)} = h\nu = hc/\lambda_{vac} \text{(m)} = 100\, hc\, \sigma(cm^{-1}) \tag{1.3}$$

The use of λ_{vac} should be stressed. If the wavelength is measured in air, it must be multiplied by n, the refractive index of air, before conversion to frequency or wavenumber units:

$$\nu = c/n\lambda_{air}, \qquad \sigma = 1/n\lambda_{air} \tag{1.4}$$

The correction is about 3 parts in 10^4, and is itself slightly wavelength-dependent. The tables for conversion of air wavelengths compiled by the National Bureau of Standards [21] include the refractive index correction in taking the reciprocal.

Returning to Fig. 1.1, it is seen that the visible region (750–400 nm) is bounded by the infra-red to longer wavelengths and the ultra-violet to shorter wavelengths. It is convenient to subdivide these regions into near and far infra-red at about 40 μm, and near and far ultra-violet at about 200 nm, these being roughly the practical limits of transparency of optical materials suitable for prisms and lenses. Until the middle of this century there were wavelength gaps, both between the far infra-red and radio and between the far ultra-violet and X-ray regions, in which it had not been found possible to excite and detect radiation. The invention of radar in the Second World War opened the door to the very short radio wave, or microwave, techniques, while at the same time infra-red spectroscopists were pushing up to longer wavelengths. The two now overlap in the sub-millimetre region. The short-wavelength gap has meanwhile been well filled, partly because of its interest to plasma- and astrophysicists. Optical spectroscopy now reaches wavelengths below 0.2 nm, while soft X-rays extend to 5 nm. The distinction between 'optical' and 'X-ray' in the overlap region is in the origin of the spectra. Optical spectroscopy is concerned with transitions of the outer or valence electrons, and X-ray spectroscopy with transitions of the innermost electrons. However, the distinction is somewhat blurred by 'inner shell' spectroscopy, dealing with excitation of electrons more tightly bound than the valence electrons. Very short wavelength 'optical' spectra may come either from these 'inner shell' electrons or from the outer electrons of very highly ionized species.

A book on optical spectroscopy may therefore take as a logical lower limit a wavelength just below 1 nm (a few ångströms). The upper limit is conventionally set in the far infra-red. However, the very smallest energy level splittings of interest are of order 0.01 cm^{-1}, corresponding to a wavelength of 1 m or so; this is the justification for including a chapter on microwave and radiofrequency spectroscopy. Apart from this one chapter, we shall be concerned with the conventional 'optical' region below 100 μm, with the emphasis on the three decades from 10 μm to 10 nm.