

# **Spectroscopy**

**edited by  
B.P. Straughan  
and S. Walker**

**Atomic, n.m.r., n.q.r., e.s.r., and  
Mössbauer Spectroscopy**



# Spectroscopy

## VOLUME ONE

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# Preface

It is fifteen years since Walker and Straw wrote the first edition of 'Spectroscopy' and considerable developments have taken place during that time in all fields of this expanding subject. In atomic spectroscopy, for example, where the principles required in a student text have been laid down for many years, there have been advances in optical pumping and double resonance which cannot be neglected at undergraduate level. In addition, nuclear quadrupole resonance (n.q.r.) and far infrared spectroscopy now merit separate chapters while additional chapters dealing with Mössbauer spectroscopy, photoelectron spectroscopy and group theory are an essential requisite for any modern spectroscopy textbook.

When the idea for a new edition of Spectroscopy was first discussed it quickly became clear that the task of revision would be an impossible one for two authors working alone. Consequently it was decided that the new edition be planned and co-ordinated by two editors who were to invite specialists, each of whom had experience of presenting their subject at an undergraduate level, to contribute a new chapter or to revise extensively an existing chapter. In this manner a proper perspective of each topic has been provided without any sacrifice of the essential character and unity of the first edition.

The expansion of subject matter has necessitated the division of the complete work into three self contained volumes.

Volume 1 includes atomic, n.m.r., n.q.r., e.s.r. and Mössbauer spectroscopy.

Volume 2 contains chapters on molecular symmetry and group theory, microwave, infrared and Raman, far-infrared spectroscopy, force constants, evaluation of thermodynamic functions.

Volume 3 centres on the information which results when a valence electron(s) is excited or removed from the parent molecule. It includes electronic spectroscopy, quantum numbers, dissociation energies, fluorescence and phosphorescence spectroscopy, astrochemistry, photoelectron spectroscopy.

The complete work now provides a single source of reference for all the spectroscopy that a student of chemistry will normally encounter as an undergraduate. Furthermore, the depth of coverage should ensure the books' use on graduate courses and for those starting research work in one of the main branches of spectroscopy.

A continued source of confusion in the spectroscopic literature is the duplication of symbols and the use of the same symbol by different authors to represent different factors. The literature use of both SI and non SI units further complicates the picture. In this book we have tried to use SI units throughout or units such as the electron volt which are recognised for continued use in conjunction with SI units. The symbols and recognised values of physical constants are those published by the Symbols Committee of the Royal Society 1975.

B.P. Straughan  
S. Walker

October, 1975

## Acknowledgements

Although not involved in the production of this second edition, we would like to express our sincere thanks to Mr. H. Straw whose vital contribution to the first edition of Spectroscopy helped to ensure its widespread success and hence the demand for a new edition. One of us (S.W.) wishes to thank his wife, Kathleen, without whose help at many stages part of this work could not have gone forward.

## Terms and symbols describing magnetic phenomena

When discussing magnetic phenomena, the chemist has been accustomed to write  $H$  instead of  $B$  when  $H$  is the *magnetic field strength* and  $B$  is the *magnetic flux density* (or *magnetic induction field*). When using electromagnetic units (e.m.u.)  $H$  and  $B$  have the same magnitude but in SI units they differ by  $4\pi \times 10^{-7}$ . Consequently,  $B$  has been used throughout this book and in imprecise contexts it has been referred to as the *magnetic field*.

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# 1 Atomic spectroscopy

## 1.1 INTRODUCTION TO ATOMIC SPECTROSCOPY

Atomic spectra are principally concerned with the interchange of energy between the atom and electromagnetic radiation where the exchange in energy may be associated on the simplest pictorial model with a valence electron changing its orbit. Energy may be absorbed from the radiation field (absorption spectra) or may be added to it (emission spectra). The actual change in energy ( $\Delta E$ ) between two energy levels in an atom is related to the frequency of the radiation absorbed or emitted by the equation:

$$E' - E'' = \Delta E = h\nu \quad (1.1)$$

where  $h$  is Planck's constant and  $\nu$  is the frequency in hertz (previously 'cycles per second' was employed).  $E'$  is the total energy of the atom in its higher energy state, and  $E''$  is the value for the lower state. The quantity  $h\nu$  is really the photon of energy, either absorbed or emitted.

Even for the hydrogen atom there are many possible energy levels. On the basis of the simple circular orbit model a few of the various orbits in which the electron may exist are represented as in Fig. 1.1, the proton being at the centre of the innermost orbit. The values of energy levels corresponding to the principal quantum numbers ( $n$ ) (see later) 1, 2, 3, 4, 5, are  $E_1, E_2, E_3, E_4$ , and  $E_5$ , respectively. If hydrogen is present in an electric discharge, some of the molecules split up into atoms, and some of these hydrogen atoms may reach an excited electronic state, that is have  $n$  values greater than 1. Some of the excited atoms lose the whole of their excess energy, returning to the lowest level (that is,  $n = 1$ , the ground state) and emit radiation with frequencies  $\nu_1, \nu_2, \nu_3, \nu_4 \dots$ , for example:

$$E_2 - E_1 = h\nu_1 \quad (1.2)$$

$$E_3 - E_1 = h\nu_2 \quad (1.3)$$

$$E_4 - E_1 = h\nu_3 \quad \text{and so on} \quad (1.4)$$

Some electrons return to the  $n = 2^\dagger$  state, and these produce another set of frequencies  $\nu'_1, \nu'_2, \nu'_3$  given by:

$$E_3 - E_2 = h\nu'_1 \quad (1.5)$$

$$E_4 - E_2 = h\nu'_2 \quad (1.6)$$

$$E_5 - E_2 = h\nu'_3 \quad \text{and so on} \quad (1.7)$$

These different frequencies are sorted out either by passage through a prism or by means of a diffraction grating; the separation of the radiation into its component frequencies gives *spectrum of the element*. If, however, it is impossible to separate the frequencies—and this applies over a fairly wide frequency region—the spectrum is said to be continuous; an example of a continuous spectrum is exhibited by filament lamps.

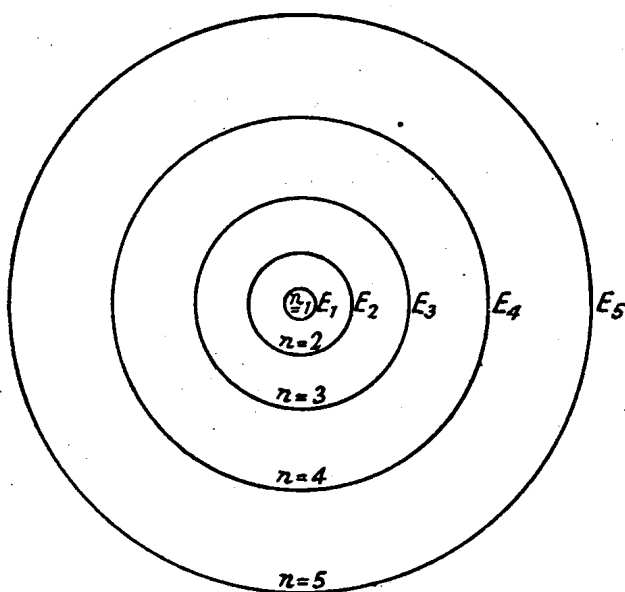


Fig. 1.1 Circular orbit model for the hydrogen atom

An apparatus for producing the hydrogen atom emission frequencies is shown in Fig. 1.2. To the end of a quartz tube an optical quartz window is attached, and two metal electrodes are sealed through the quartz in the side arms A and B. The gas to be examined (in this case hydrogen) is introduced into the tube, and a discharge is produced by applying a voltage of  $\sim 3000$  V across the electrodes from a transformer. The swiftly moving electrons in the discharge

<sup>†</sup> This is, of course, only an intermediate stop because they must finally return to the lowest energy state ( $n = 1$ ).



bombard the hydrogen molecules; this bombardment results in the formation of some excited hydrogen atoms which are capable of emitting light. Light from this source is lined up with a *spectroscope* (i.e. an instrument which splits the light up into a spectrum). This in principle consists of a slit, a collimating lens producing a parallel beam of light which is then passed through the prism, and a telescope lens. The latter brings the frequencies, separated by the prism, to a focus. For example, if the frequencies  $\nu_1, \nu_2, \nu_3 \dots$  are directed on to the slit, as in Fig. 1.3, a narrow beam of light is allowed to enter; the lens B collimates the light on to the prism which disperses the light into its respective frequencies. The lens C then focuses these separated frequencies (which are monochromatic images of the slit) on to a photographic plate. When the plate is developed, sharp black lines are observed corresponding to each of the emitted frequencies  $\nu_1, \nu_2, \nu_3 \dots$ , and this photographic record of the spectrum is termed a *spectrogram*. When the instrument gives a photographic record it is called a *spectrograph*; the term *spectroscope* is usually reserved for instruments where the spectrum is viewed by the eye.

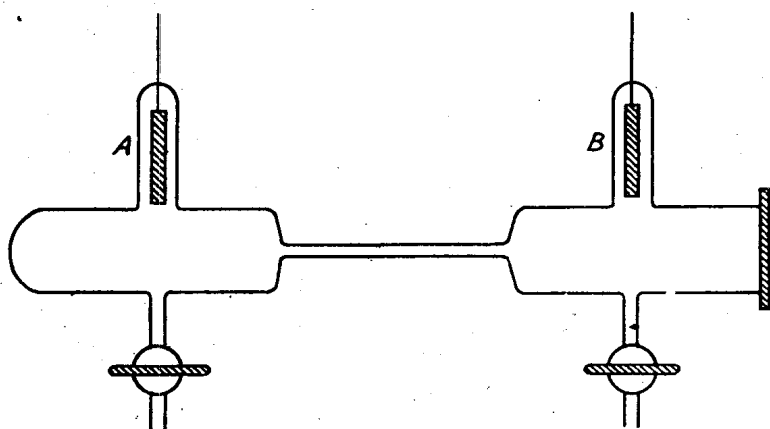


Fig. 1.2 One type of discharge tube

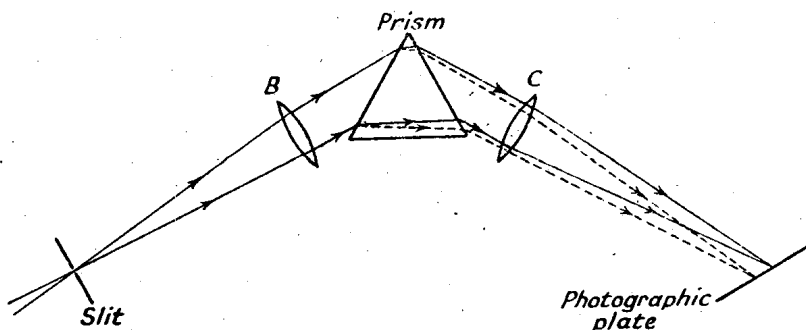


Fig. 1.3 Optical arrangement of a medium quartz type of spectrograph

In Fig. 1.4 the frequencies resulting from transitions from the  $n > 2$  levels to the  $n = 2$  level are given for the hydrogen atom. This gives a series of lines known as the *Balmer series*. For transitions to the  $n = 1$  level another series (*Lyman*) is obtained.

In Fig. 1.3 the simplest kind of spectrograph has been shown, and this type would not be able to distinguish between two lines only a fraction of an Ångström unit apart in the visible region of the spectrum ( $1 \text{ Å} = 10^{-10} \text{ m}$ ). A most important function of a spectrograph is to separate wavelengths of approximately the same value. This ability is measured by the *resolving power*, which is defined as  $\lambda/d\lambda$ , where  $d\lambda = \lambda_1 - \lambda_2$ . This is the wavelength separation between the two closest lines  $\lambda_1$  and  $\lambda_2$  of similar intensity which can just be separated (resolved) by the spectrograph at the average wavelength,  $\lambda$ , where  $\lambda = (\lambda_1 + \lambda_2)/2$ . The resolving power may vary considerably, depending on the type of spectrograph used. Much fundamental information is derived from a study of spectral 'lines' with a spectrograph which has a high resolving power.

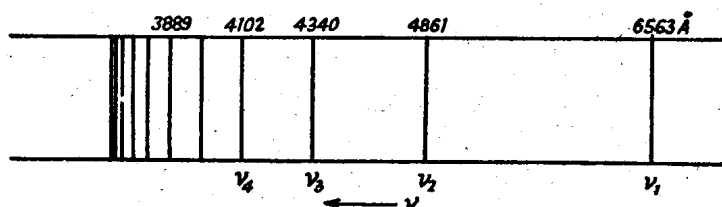


Fig. 1.4 Hydrogen atom emission spectrum (Balmer series)

The absorption of energy may be studied by directing energy from a filament lamp (e.g. a tungsten filament lamp which provides a continuous range of wavelengths from about 3000 Å to 10 000 Å) through a cell containing the atoms† whose absorption spectrum is required. The frequencies which are required to accomplish the permitted energy transitions are selected by the atoms from the continuous source of radiation, and when the photographic plate is developed these appear as light lines on a dark background. When a transition between  $E'$  and  $E''$  levels occurs in both emission and absorption for separate experiments on a particular atom, the corresponding frequencies are in agreement within the limits of experimental error.

The complexity of the spectrum varies quite considerably with the atom concerned. The emission spectrum for mercury is given in Fig. 1.5 for the 2400 to 6000 Å region and does not appear overwhelmingly complex. The spectrum for iron, however, consists of an extremely large number of lines which are distributed right across the ultraviolet and visible regions, and, in fact,

† The atoms could be produced, for example, by the dissociation of a compound, if a high-temperature furnace were employed as the absorption cell.

these lines are often used for interpolating the value of the wavelengths for the lines of other elements. In Fig. 1.6 the 2400 to 6000 Å region of the iron emission spectrum may be observed, while in Fig. 1.7 part of the absorption spectrum for the principal series of sodium is given (see later).

The primary standard of wavelength which is now employed is the orange emission line of krypton ( $\text{Kr}_{36}^{86}$ ) resulting from a cathode discharge tube situated in a cryostat at the triple point of nitrogen (63 K), a standard which is claimed to be reproducible to 1 part in  $10^8$ . This line is employed to define the basic SI unit (see later) the metre of which is 1 650 763.73 vacuum wavelengths of this radiation. Many other lines have been measured relative to this and defined as secondary standards, although to be classed as such the measured wavelengths from several laboratories have to be in agreement.

It will be observed from Figs. 1.5–1.7 that the intensity of the different lines within a spectrum varies considerably, and in addition to determining the frequencies accurately, quantitative studies can be made of the intensities of these lines, where the intensity of the lines is dependent on the concentration of the element producing it. The study of both frequency and intensity is known as *spectrophotometry*.

### 1.1.1. Units and fundamental constants

In recent years there has been a trend to adopt a more logical system of units termed the *Système International d'Unités* (SI units) which was the ultimate outcome of a resolution of the 9th General Conference of Weights and Measures in 1948. It was adopted in 1960 and was based on the seven units listed in (A) below.

SI units may be divided into the following three categories:

(A) *Base units*. These are the standards of:

- (a) length, the metre (m);
- (b) time, the second (s);
- (c) mass, the kilogram (kg);
- (d) electric current, the ampere (A);
- (e) temperature, the kelvin (K);
- (f) amount of substance, the mole (mol), where the mole is the amount of substance which contains the same number of molecules (atoms) as there are atoms of carbon in 0.012 kg of carbon-12;
- (g) luminosity intensity, the candela (cd).

The initial practice in electrical and magnetic quantities was to define them in terms of the centimetre, gramme, and second which were then the units employed in mechanics. Later it became apparent that if the metre, kilogramme, and second were made the fundamental units, a consistent system of electrical and magnetic units could be built up. Known as the mks system, this with the ampere as the electrical base unit has been adopted for SI units.

(B) *Derived units*. These result from combining the above base units as is



Fig. 1.5 Emission spectrum of the mercury atom between 2400 and 6000 Å (The marked scale is in Angstrom units). (After Pearse and Gaydon [1.1]).



Fig. 1.6 Iron arc spectrum between 2400 and 6000 Å (The marked scale is in Angstrom units). After Pearse and Gaydon [1.1]).

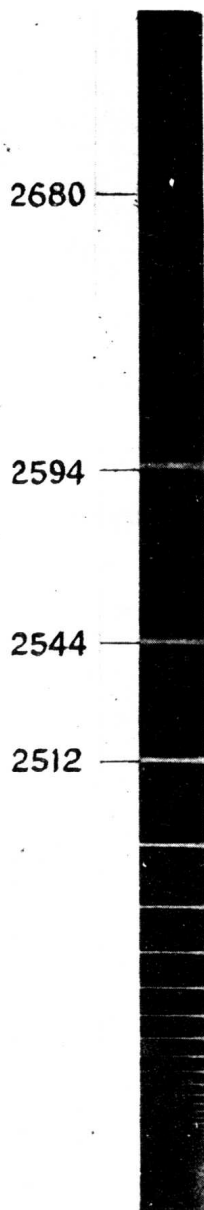


Fig. 1.7 Part of the absorption spectrum of the principal series of sodium. (After Kuhn [1.2]. Courtesy of Springer Verlag, Heidelberg).

indicated in the two examples below.

For energy ( $E$ ) the derived unit is the joule, and thus it is the practice now to consider energy changes in joules whereas it was previously considered in terms of ergs or calories. The joule may be defined by inserting the SI units in the Einstein equation  $E = mc^2 = \text{kg m}^2 \text{s}^{-2}$ .

The derived unit of force is the newton (N), and since energy = force  $\times$  distance, the newton may be defined as follows:

$$\text{force} = \text{J m}^{-1} = \text{kg m s}^{-2}$$

The derived unit for pressure is the pascal (Pa) and may be defined as newton per square metre, that is from the formula force/unit area.

Some derived units without special names are those for:

- (i) volume, which has the unit of cubic metre ( $\text{m}^3$ );
- (ii) density, which has the unit of kilogramme per cubic metre ( $\text{kg m}^{-3}$ );
- (iii) molar mass, which has the unit of kilogramme per mole ( $\text{kg mol}^{-1}$ ).

The derived units in electric and magnetic systems of spectroscopic application are:

- (a) the charge ( $Q$ ), where the quantity of unit charge is the coulomb (C) and may be defined as the quantity of electricity carried per second by a current of one ampere, i.e.,  $C = A \text{ s}$ ;
- (b) the capacitance ( $C$ ) the unit of which is the farad (F) which may be defined as the capacitance of a capacitor of which there is a difference of one volt potential between the plates when they hold one coulomb of charge;
- (c) the unit of magnetic flux which is the weber (Wb). This may be defined as the amount of flux which produces an electromotive force of one volt in a one-turn conductor as it reduces uniformly to zero in one second ( $1 \text{ Wb} = 1 \text{ kg m}^2 \text{s}^{-2} \text{ A}^{-1} = 1 \text{ V s} = 10^8$  lines of flux);
- (d) the magnetic flux density or induction ( $B$ ) may be defined by means of the equation for the force on a current element placed in a magnetic field  $B$ , is measured in tesla units where a tesla unit can be identified with  $\text{kg s}^{-2} \text{ A}^{-1}$  ( $= \text{V s m}^{-2} = \text{Wb m}^{-2}$ ).
- (e) the magnetic moment ( $\mu$ ) is the couple experienced by a magnet placed at right angles to a uniform field with unit flux density and is measured in ampere metre<sup>2</sup>;
- (f) the electrical intensity ( $E$ ) at a point in an electric field is the force experienced by a unit charge of one coulomb situated at that point and is measured in volt metre<sup>-1</sup> ( $= \text{newton coulomb}^{-1}$ );
- (g) the electric potential difference is the volt (V) and may be defined as  $\text{J A}^{-1} \text{ s}^{-1}$ .

As a result of common usage certain multiples and sub-multiples of length are treated as derived units although none is recognized as being strictly an SI unit, e.g. micron ( $\mu$ ) =  $10^{-6}$  m, ångström (Å) =  $10^{-10}$  m, and fermi (fm) =

$10^{-15}$  m. The ångström unit is particularly useful since internuclear distances are of that order, and the literature of physical chemistry abounds with its use. Consequently, it will be retained here. The conversion to metres is a straightforward one since 1 Å is now precisely  $10^{-10}$  m based on the  $\text{Kr}_{86}$  standard line (see Section 1.1); this was not the case before 1960 when the previous standard of wavelength was the red line of cadmium which made  $1 \text{ Å} = 1.0000002 \times 10^{-10}$  m.

(C) *Supplementary units.* At present these are the radian (rad) which is the unit for a plane angle while the term steradian (sr) is employed for solid angles.

*Multiples and submultiples of a particular unit.* These are obtained by employing such prefixes as those listed in Table 1.1 and have been agreed upon internationally for use with SI units.

Table 1.1 Multiplication factors used in conjunction with SI units

| <i>Prefix</i> | <i>Multiplication factor</i> | <i>Symbol</i> |
|---------------|------------------------------|---------------|
| giga          | $10^9$                       | G             |
| mega          | $10^6$                       | M             |
| kilo          | $10^3$                       | k             |
| centi         | $10^{-2}$                    | c             |
| milli         | $10^{-3}$                    | m             |
| micro         | $10^{-6}$                    | $\mu$         |
| nano          | $10^{-9}$                    | n             |
| pico          | $10^{-12}$                   | p             |

The application of such prefixes may be seen as follows. It is common practice in spectroscopy to write a wavelength of  $10 \times 10^{-8}$  cm as 10 Å. However, in SI units this would be  $10^{-9}$  m, and in terms of the appropriate prefix this would be written as 1 nm. In SI units the first line of the Balmer series would be 656.28 nm whereas it has normally been quoted as 6562.8 Å. In spectroscopic studies of dissociation energies and barriers to internal rotation the energies are best expressed in terms of kJ (i.e. units of  $1000 \times$  the basic unit). The use of prefixes allows some flexibility in the expression of results. For example, the van der Waals radius of the chlorine atom is  $1.80 \times 10^{-8}$  cm, and this in SI units could be written as  $1.80 \times 10^{-10}$  m or as 180 pm; the former procedure would be preferable for use in calculations whereas the latter would seem more appropriate when results were being tabulated.

To summarize, the main changes which have been brought about by the adoption of SI units are:

- (a) to replace the centimetre and gram by the metre and kilogram respectively, although the first pair are still retained as sub-multiples;

- (b) to make the newton ( $\text{kg m s}^{-2}$ ) the unit of force and the joule ( $\text{kg m}^2 \text{s}^{-2}$ ) the unit of energy;
- (c) to replace the electrostatic and electromagnetic units by SI electrical units.

A comparison of some SI and previously employed units is made in Table 1.2 for some quantities of spectroscopic interest, and includes some of the derived units.

**Table 1.2** Comparison for some quantities of spectroscopic interest of SI and the previously employed units

| Quantity                    | Symbol | SI unit                  | Previously employed units |
|-----------------------------|--------|--------------------------|---------------------------|
| Dissociation energy         | $D$    | joule $\text{mol}^{-1}$  | cal $\text{mole}^{-1}$    |
| Energy                      | $E$    | joule (J)                | erg                       |
| Frequency                   | $\nu$  | hertz (Hz)               | $\text{s}^{-1}$           |
| Moment of inertia           | $I$    | $\text{kg m}^2$          | $\text{g cm}^2$           |
| Force constant (stretching) | $f$    | $\text{N m}^{-1}$        | dyne $\text{cm}^{-1}$     |
| Force constant (bending)    | $f$    | joules $\text{rad}^{-1}$ | ergs $\text{rad}^{-1}$    |

A number of physical constants are of frequent use in spectroscopic work, and it is useful to have the values of these quantities in cgs and SI units. Some such data are listed in Table 1.3

Most textbooks on spectroscopy have not yet adopted SI units, and, in addition, the bulk of previous literature has not employed these units. It often becomes necessary to make use of conversion factors from data such as:

$$1 \text{ e.v./molecule} = 8065.7 \text{ cm}^{-1} = 23.061 \text{ kcal mol}^{-1} = 1.6021 \times 10^{-12} \text{ ergs/molecule}$$

$$= 1.6021 \times 10^{-19} \text{ joules/molecule}$$

### 1.1.2 Frequency, wavenumber, and wavelength

In spectroscopic studies which take place in the absence of an applied electric or magnetic field the absorption or emission of radiation is recorded at particular frequencies ( $\nu$ ), wavelengths ( $\lambda$ ), or wavenumbers ( $\sigma$ ), where:

$$\nu \times \lambda = \text{velocity of light} = c \quad (1.8)$$

where the values of  $\lambda$  and  $c$  depend slightly on whether the measurements are made in vacuum or in air; the frequency, however, in each case, is given by:

$$\nu = \frac{c_{\text{air}}}{\lambda_{\text{air}}} = \frac{c_{\text{vac}}}{\lambda_{\text{vac}}} \quad (1.9)$$



Table 1.3 The values of some physical constants expressed in SI and cgs units

| Quantity                                 | Symbol     | SI Units                                    | cgs Units   |
|--|------------|---|---|
| Speed of light in vacuo                  | $c$        | $2.997924580 \times 10^8 \text{ ms}^{-1}$   | $2.997924580 \times 10^{10} \text{ cm s}^{-1}$            |
| Electric charge of a proton              | $e$        | $1.6021892 \times 10^{-19} \text{ C}$       | $1.6021892 \times 10^{-20} \text{ e.m.u.}$                |
| Planck's constant                        | $h$        | $6.626176 \times 10^{-34} \text{ J s}$      | $6.626176 \times 10^{-27} \text{ erg s}$                  |
| Mass of electron at rest                 | $m_e$      | $9.109534 \times 10^{-31} \text{ kg}$       | $9.109534 \times 10^{-28} \text{ g}$                      |
| Mass of proton at rest                   | $m_p$      | $1.6726485 \times 10^{-27} \text{ kg}$      | $1.6726485 \times 10^{-24} \text{ g}$                     |
| Avogadro constant                        | $N_A$      | $6.022045 \times 10^{23} \text{ mol}^{-1}$  | $6.022045 \times 10^{23} \text{ mol}^{-1}$                |
| Faraday constant                         | $F$        | $9.648456 \times 10^4 \text{ C mol}^{-1}$   | $9.648456 \times 10^3 \text{ e.m.u. mol}^{-1}$            |
| Gas constant ( $=N_A k$ )                | $R$        | $8.31441 \text{ JK}^{-1} \text{ mol}^{-1}$  | $8.31441 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$ |
| Boltzmann constant                       | $k$        | $1.380662 \times 10^{-23} \text{ K J}^{-1}$ | $1.380662 \times 10^{-16} \text{ erg K}^{-1}$             |
| Rydberg constant (nucleus infinite mass) | $R_\infty$ | $1.097373177 \times 10^7 \text{ m}^{-1}$    | $1.0973731 \times 10^5 \text{ cm}^{-1}$                   |
| Bohr magneton ( $=eh/2m_e$ )             | $\mu_B$    | $9.274078 \times 10^{-24} \text{ J T}^{-1}$ | $9.050824 \times 10^{-24} \text{ e.m.u.}$                 |
| Nuclear magneton ( $=eh/2m_p$ )          | $\mu_N$    | $5.050824 \times 10^{-27} \text{ J T}^{-1}$ | $5.050824 \times 10^{-24} \text{ e.m.u.}$                 |

The spectroscopist measures the wavelength in air, and this may be corrected to  $\lambda_{\text{vac}}$  by  $\lambda_{\text{vac}} = n\lambda_{\text{air}}$ , where  $n$  is the refractive index of air at that particular wavelength. With a view to the subsequent analysis of the spectral lines it is often more satisfactory to employ frequency than wavelength. In addition, frequency is more fundamental than the wavelength, since the frequency of monochromatic light does not alter in different media. The wavelength, however, does alter as is obvious from Equation (1.9). A value proportional to frequency may be chosen ( $1/\lambda_{\text{vac}}$ ); this is known as the *wavenumber* ( $\sigma$ ). It has been the practice to use different units in different spectral regions. For example, Ångström units (Å) are normally used for atomic spectra, where:

$$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 10 \text{ nm}$$

Other procedures employed for recording wavelength in other regions are the micron ( $\mu\text{m}$ ), and the nanometre (nm). Hence:

$$1 \mu\text{m} = 10^{-4} \text{ cm} = 10^{-6} \text{ m}$$

$$1 \text{ nm} = 10^{-7} \text{ cm} = 10^{-9} \text{ m} = 1 \text{ nm}$$

$$1 \mu\text{m} = 10000 \text{ Å} = 1000 \text{ nm} = 10^{-6} \text{ m} = 1 \mu\text{m}$$

Here the  $\mu$  employed as a prefix has the value of  $10^{-6}$  and the symbol  $n$  has the value of  $10^{-9}$ .

In the infrared region wavelengths are recorded in microns so that the results

may be expressed in terms of simple numbers between  $\sim 1$  to  $1000\mu\text{m}$ .

No one spectrometer can separate all the radiation ranging in wavelength from  $\sim 10\text{\AA}$  to  $\sim 10^4\text{ cm}$  into a spectrum; instead, several different types of instruments have to be used. The type of spectral technique employed sometimes lends its name to a certain region of electromagnetic radiation; for example, the region between  $\sim 10\text{\AA}$  and  $2000\text{\AA}$  is known as the *vacuum ultraviolet*. Since the oxygen in the air and many other gases absorb in this region and would interfere with the spectrum, a vacuum spectrograph is used; that is why this region is called the vacuum ultraviolet.

The various spectral regions are listed in Fig. 1.8. By different types of spectrographs it is possible to study the entire region from long wavelength X-radiation to radio wavelengths, although in the case of atomic spectra we shall

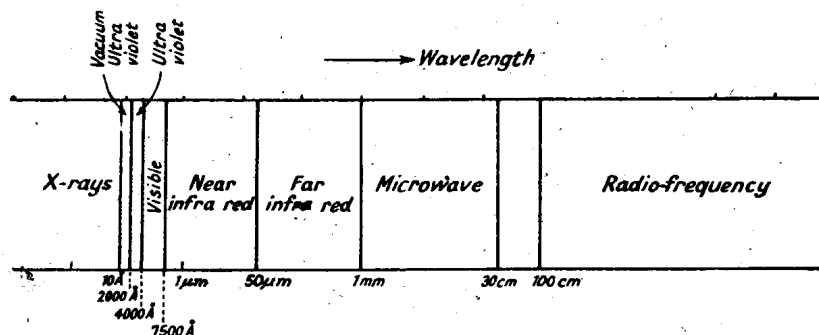


Fig. 1.8 Spectroscopic regions of the electromagnetic spectrum

be mainly concerned with the ultraviolet and visible, and occasionally the vacuum ultraviolet and the infrared regions. However, this division into regions in terms of a particular type of energy change in the atoms or molecules is to some extent arbitrary.

## 1.2 THE HYDROGEN ATOM AND THE THREE QUANTUM NUMBERS ( $n$ , $l$ and $m_l$ )

### 1.2.1 Introduction

As might be expected, the hydrogen atom yields the simplest analysable spectrum. It consists of five series of lines which can be represented by the equation:

$$\sigma = R_H (1/n_2^2 - 1/n_1^2) \quad (1.10)$$

where  $R_H$  is its Rydberg constant. When  $n_2 = 1$ , then  $n_1 = 2, 3, 4, \dots$ , and each of the lines calculated from Equation (1.10) corresponds to the wavenumber in the Lyman series. For the case where  $n_2 = 2$ , lines in the Balmer series are obtained corresponding to  $n$  values of  $3, 4, 5, \dots$ . In general, for these five series, if the appropriate values of  $n_1$  and  $n_2$  are inserted in Equation (1.10),