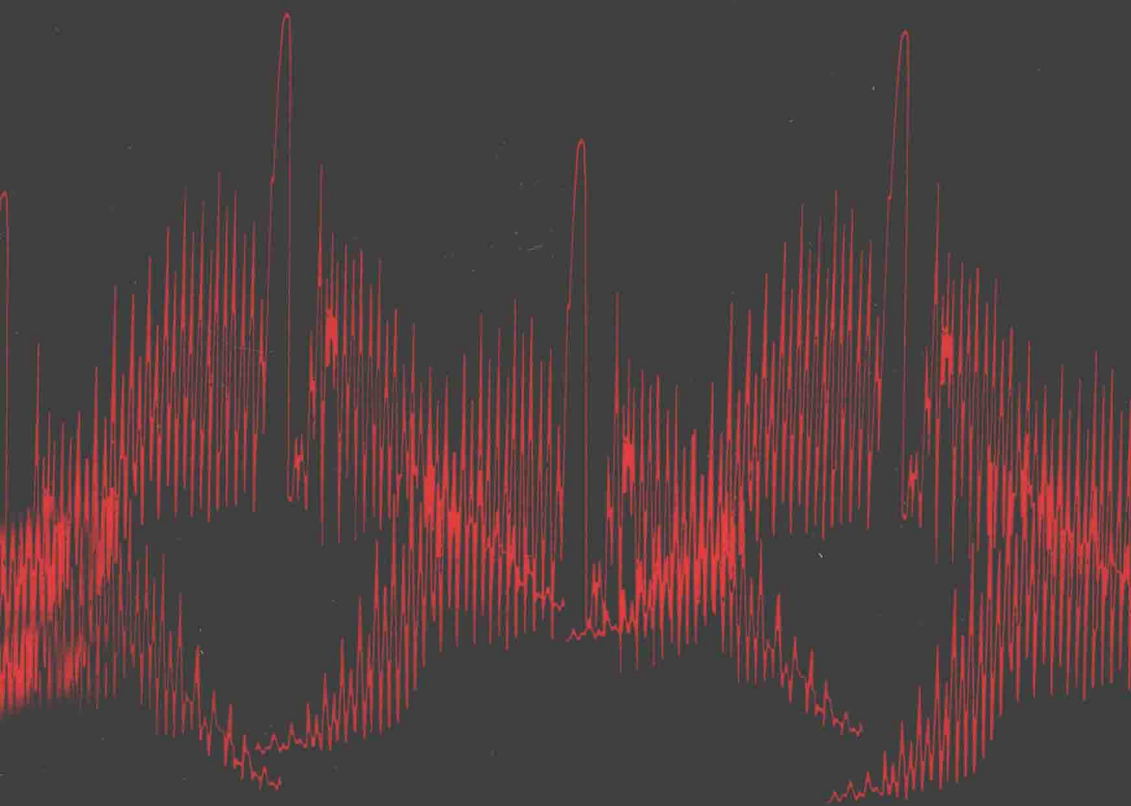


Fundamentals of Molecular Spectroscopy

THIRD EDITION



C.N. Banwell

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PREFACE

During the writing of this, the third edition of *Fundamentals of Molecular Spectroscopy*, I have borne very firmly in mind the aims of the original book—to emphasize the overall unity of the subject, and to offer a pictorial rather than a mathematical description of the principles of spectroscopy. The latter aim has received some criticism (although, it must be said, from teachers of the subject rather than from those trying to learn it); but, while it is true that universities and polytechnics now offer excellent courses in subjects such as quantum mechanics, a grasp of which can illuminate many areas of spectroscopy, experience shows that most students approaching spectroscopy for the first time prefer the simpler treatment offered here.

The general organization of the book remains unchanged, each chapter after the first presenting the fundamentals of a particular spectroscopic technique. Although each chapter is thus essentially self-contained, the intention is that the book shall be read as a whole, since concepts introduced in early chapters are often used later without further discussion.

In fact, although it is an almost unbelievable ten years since the second edition was published, there has been relatively little change in the basic ideas of spectroscopy, and much of the book is essentially unaltered. What changes have occurred have been mainly in the extension of existing techniques, and their increasing availability due to improvements in instrumentation. In this respect the two main areas of interest are the use of lasers as radiation sources, and the very rapid expansion in the use of Fourier transform techniques. Accordingly I have added a section on lasers to Chapter 1

and expanded the references to them in later chapters, particularly in Chapter 3. Equally, a general description of the Fourier transform method has been included in Chapter 1, and Chapter 7 has been extensively rewritten to take account of the wealth of additional information accessible from the application of this technique to nuclear magnetic resonance spectroscopy.

When a book has been in use for 15 years it becomes impossible to acknowledge the help received from the very many people, students and teachers, who have commented on it. My greatest debt is, of course, to Professor Sheppard of the University of East Anglia, who first introduced me to the beauty and fascination of spectroscopy, but I hope that all those who see their comments and suggestions incorporated into this edition will accept this general acknowledgement of my indebtedness, and will not think me churlish for leaving them unnamed.

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INTRODUCTION

1.1 CHARACTERIZATION OF ELECTROMAGNETIC RADIATION

Molecular spectroscopy may be defined as the study of the interaction of electromagnetic waves and matter. Throughout this book we shall be concerned with what spectroscopy can tell us of the structure of matter, so it is essential in this first chapter to discuss briefly the nature of electromagnetic radiation and the sort of interactions which may occur; we shall also consider, in outline, the experimental methods of spectroscopy.

Electromagnetic radiation, of which visible light forms an obvious but very small part, may be considered as a simple harmonic wave propagated from a source and travelling in straight lines except when refracted or reflected. The properties which undulate—corresponding to the physical displacement of a stretched string vibrating, or the alternate compressions and rarefactions of the atmosphere during the passage of a sound wave—are interconnected electric and magnetic fields. We shall see later that it is these undulatory fields which interact with matter giving rise to a spectrum.

It is trivial to show that any simple harmonic wave has properties of the sine wave, defined by $y = A \sin \theta$, which is plotted in Fig. 1.1. Here y is the displacement with a maximum value A , and θ is an angle varying between 0 and 360° (or 0 and 2π radians). The relevance of this representation to a travelling wave is best seen by considering the left-hand side of

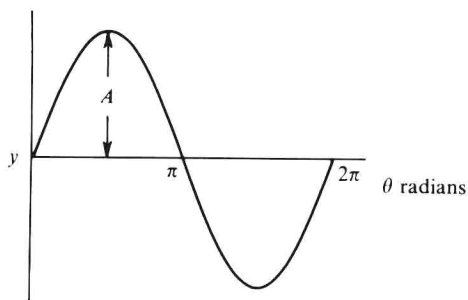


Figure 1.1 The curve of $y = A \sin \theta$.

Fig. 1.2. A point P travels with uniform angular velocity $\omega \text{ rad s}^{-1}$ in a circular path of radius A ; we measure the time from the instant when P passes O' and then, after a time t seconds, we imagine P to have described an angle $\theta = \omega t$ radians. Its vertical displacement is then $y = A \sin \theta = A \sin \omega t$, and we can plot this displacement against time as on the right-hand side of Fig. 1.2. After a time of $2\pi/\omega$ seconds, P will return to O' , completing a 'cycle'. Further cycles of P will repeat the pattern and we can describe the displacement as a continuous function of time by the graph of Fig. 1.2.

In one second the pattern will repeat itself $\omega/2\pi$ times, and this is referred to as the *frequency* (ν) of the wave. The SI unit of frequency is called the hertz (abbreviated to Hz) and has the dimensions of reciprocal seconds (abbreviated s^{-1}). We may then write:

$$y = A \sin \omega t = A \sin 2\pi \nu t \quad (1.1)$$

as a basic equation of wave motion.

So far we have discussed the variation of displacement with time, but in order to consider the nature of a *travelling* wave, we are more interested in

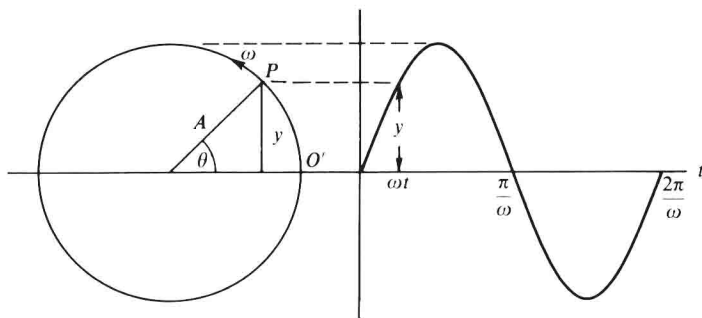


Figure 1.2 The description of a sine curve in terms of the circular motion of a point P at a uniform angular velocity of $\omega \text{ rad s}^{-1}$.

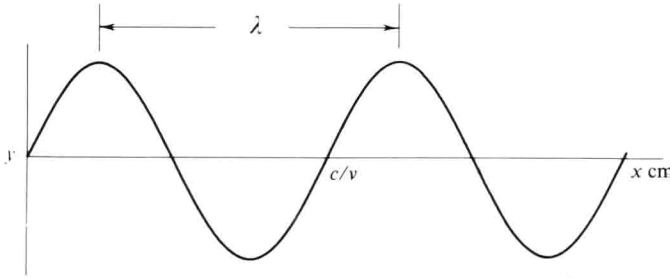


Figure 1.3 The concept of a travelling wave with a wavelength λ .

the distance variation of the displacement. For this we need the fundamental distance–time relationship:

$$x = ct \quad (1.2)$$

where x is the distance covered in time t at a speed c . Combining (1.1) and (1.2) we have:

$$y = A \sin 2\pi vt = A \sin \frac{2\pi vx}{c}$$

and the wave is shown in Fig. 1.3. Besides the frequency v , we now have another property by which we can characterize the wave—its *wavelength* λ , which is the distance travelled during a complete cycle. When the velocity is c metres per second and there are v cycles per second, there are evidently v waves in c metres, or

$$v\lambda = c \quad \lambda = c/v \text{ metres} \quad (1.3)$$

so we have:

$$y = A \sin \frac{2\pi x}{\lambda} \quad (1.4)$$

In spectroscopy wavelengths are expressed in a variety of units, chosen so that in any particular range (see Fig. 1.4) the wavelength does not involve large powers of ten. Thus, in the microwave region, λ is measured in centimetres or millimetres, while in the infra-red it is usually given in micrometres (μm)—formerly called the *micron*—where

$$1 \mu\text{m} = 10^{-6} \text{ m} \quad (1.5)$$

In the visible and ultra-violet region, λ is still often expressed in Ångstrom units (\AA) where $1 \text{\AA} = 10^{-10} \text{ m}$, although the proper SI unit for this region is the nanometre:

$$1 \text{ nm} = 10^{-9} \text{ m} = 10 \text{\AA} \quad (1.6)$$

There is yet a third way in which electromagnetic radiation can be usefully characterized, and this is in terms of the *wavenumber* $\bar{\nu}$. Formally this is defined as the reciprocal of the wavelength expressed in *centimetres*:

$$\bar{\nu} = 1/\lambda \quad \text{cm}^{-1} \quad (1.7)$$

and hence

$$y = A \sin 2\pi\bar{\nu}x \quad (1.8)$$

It is more useful to think of the wavenumber, however, as the number of complete waves or cycles contained in each centimetre length of radiation. Since the formal definition is based on the centimetre rather than the metre, the wavenumber is, of course, a non-SI unit; it is, however, so convenient a unit for the discussion of infra-red spectra that—like the Ångström—it will be many years before it falls into disuse.

It is unfortunate that the conventional symbols of wavenumber ($\bar{\nu}$) and frequency (ν) are similar; confusion should not arise, however, if the units of any expression are kept in mind, since wavenumber is invariably expressed in reciprocal centimetres (cm^{-1}) and frequency in cycles per second (s^{-1} or Hz). The two are, in fact, proportional: $\nu = c\bar{\nu}$, where the proportionality constant is the velocity of radiation expressed in *centimetres* per second (that is, $3 \times 10^{10} \text{ cm s}^{-1}$); the velocity in SI units is, of course, $3 \times 10^8 \text{ m s}^{-1}$.

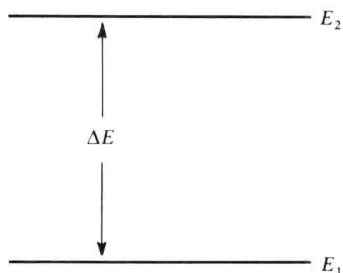
1.2 THE QUANTIZATION OF ENERGY

Towards the end of the last century experimental data were observed which were quite incompatible with the previously accepted view that matter could take up energy continuously. In 1900 Max Planck published the revolutionary idea that the energy of an oscillator is discontinuous and that any change in its energy content can occur only by means of a jump between two distinct energy states. The idea was later extended to cover many other forms of the energy of matter.

A molecule in space can have many sorts of energy; e.g., it may possess rotational energy by virtue of bodily rotation about its centre of gravity; it will have vibrational energy due to the periodic displacement of its atoms from their equilibrium positions; it will have electronic energy since the electrons associated with each atom or bond are in unceasing motion, etc. The chemist or physicist is early familiar with the electronic energy states of an atom or molecule and accepts the idea that an electron can exist in one of several discrete energy levels: he learns to speak of the energy as being *quantized*. In much the same way the rotational, vibrational, and other energies of a molecule are also quantized—a particular molecule can exist in a variety of rotational, vibrational, etc., energy levels and can move from

one level to another only by a sudden jump involving a finite amount of energy.

Consider two possible energy states of a system—two rotational energy levels of a molecule, for example—labelled E_1 and E_2 in the following diagram. The suffixes 1 and 2 used to distinguish these levels are, in fact,



quantum numbers. The actual significance of quantum numbers goes far deeper than their use as a convenient label—in particular, we shall later see that analytical expressions for energy levels usually involve an algebraic function of one or more quantum numbers. Transitions can take place between the levels E_1 and E_2 provided the appropriate amount of energy, $\Delta E = E_2 - E_1$, can be either absorbed or emitted by the system. Planck suggested that such absorbed or emitted energy can take the form of electromagnetic radiation and that the frequency of the radiation has the simple form:

$$\nu = \Delta E/h \quad \text{Hz}$$

i.e.,

$$\Delta E = h\nu \quad \text{joules} \quad (1.9)$$

where we express our energies E in terms of the joule, and h is a universal constant—Planck's constant. This suggestion has been more than amply confirmed by experiment.

The significance of this is that if we take a molecule in state 1 and direct on to it a beam of radiation of a single frequency ν (monochromatic radiation), where $\nu = \Delta E/h$, energy will be absorbed from the beam and the molecule will jump to state 2. A detector placed to collect the radiation after its interaction with the molecule will show that its intensity has decreased. Also if we use a beam containing a wide range of frequencies ('white' radiation), the detector will show that energy has been absorbed *only* from that frequency $\nu = \Delta E/h$, all other frequencies being undiminished in intensity. In this way we have produced a spectrum—an *absorption* spectrum.

Alternatively the molecule may already be in state 2 and may revert to state 1 with the consequent emission of radiation. A detector would show

this radiation to have frequency $\nu = \Delta E/h$ only, and the *emission* spectrum so found is plainly complementary to the absorption spectrum of the previous paragraph.

The actual energy differences between the rotational, vibrational, and electronic energy levels are very small and may be measured in joules per molecule (or atom). In these units Planck's constant has the value:

$$h = 6.63 \times 10^{-34} \text{ joules s molecule}^{-1}$$

Often we are interested in the total energy involved when a gram-molecule of a substance changes its energy state: for this we multiply by the Avogadro number $N = 6.02 \times 10^{23}$.

However, the spectroscopist measures the various characteristics of the absorbed or emitted radiation during transitions between energy states and he often, rather loosely, uses frequency, wavelength, and wavenumber as if they were energy units. Thus in referring to 'an energy of 10 cm^{-1} ', he means 'a separation between two energy states such that the associated radiation has a wavenumber value of 10 cm^{-1} '. The first expression is so simple and convenient that it is essential to become familiar with wavenumber and frequency energy units if one is to understand the spectroscopist's language. Throughout this book we shall use the symbol ϵ to represent energy in cm^{-1} .

It cannot be too firmly stressed at this point that the frequency of radiation associated with an energy change does *not* imply that the transition between energy levels occurs a certain number of times each second. Thus an electronic transition in an atom or molecule may absorb or emit radiation of frequency some 10^{15} Hz , but the electronic transition does not itself *occur* 10^{15} times per second. It may occur once or many times and on each occurrence it will absorb or emit an energy quantum of the appropriate frequency.

1.3 REGIONS OF THE SPECTRUM

Figure 1.4 illustrates in pictorial fashion the various, rather arbitrary, regions into which electromagnetic radiation has been divided. The boundaries between the regions are by no means precise, although the molecular processes associated with each region are quite different. Each succeeding chapter in this book deals essentially with one of these processes.

In increasing frequency the regions are:

1. Radiofrequency region: 3×10^6 – $3 \times 10^{10} \text{ Hz}$; 10 m – 1 cm wavelength. Nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) spectroscopy. The energy change involved is that arising from the reversal of spin of a nucleus or electron, and is of the order 0.001 – 10 joules/mole (Chapter 7).

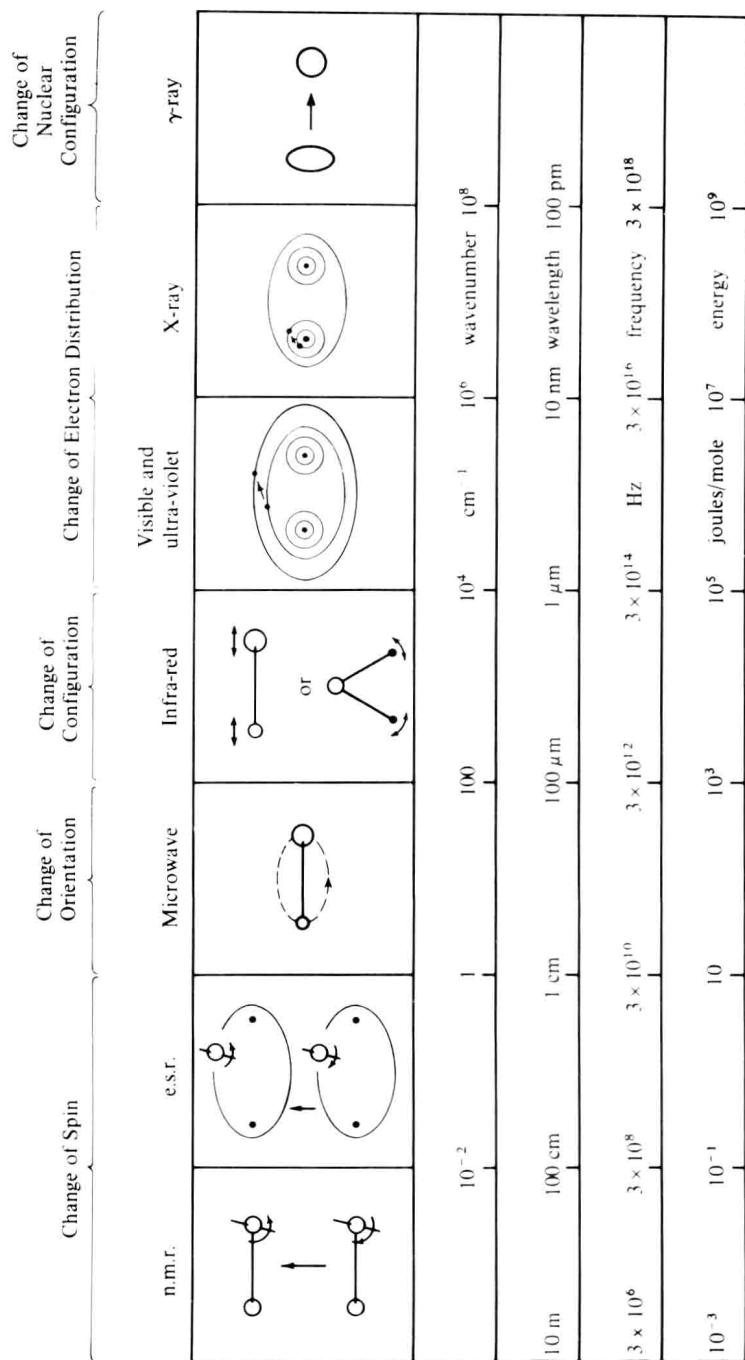


Figure 1.4 The regions of the electromagnetic spectrum.

2. Microwave region: 3×10^{10} – 3×10^{12} Hz; 1 cm–100 μm wavelength. Rotational spectroscopy. Separations between the rotational levels of molecules are of the order of hundreds of joules per mole (Chapter 2).
3. Infra-red region: 3×10^{12} – 3×10^{14} Hz; 100 μm –1 μm wavelength. Vibrational spectroscopy. One of the most valuable spectroscopic regions for the chemist. Separations between levels are some 10^4 joules/mole (Chapter 3).
4. Visible and ultra-violet regions: 3×10^{14} – 3×10^{16} Hz; 1 μm –10 nm wavelength. Electronic spectroscopy. The separations between the energies of valence electrons are some hundreds of kilojoules per mole (Chapters 5 and 6).
5. X-ray region: 3×10^{16} – 3×10^{18} Hz; 10 nm–100 pm wavelength. Energy changes involving the inner electrons of an atom or a molecule, which may be of order ten thousand kilojoules (Chapter 5).
6. γ -ray region: 3×10^{18} – 3×10^{20} Hz; 100 pm–1 pm wavelength. Energy changes involve the rearrangement of nuclear particles, having energies of 10^9 – 10^{11} joules per gram atom (Chapter 8).

One other type of spectroscopy, that discovered by Raman and bearing his name, is discussed in Chapter 4. This, it will be seen, yields information similar to that obtained in the microwave and infra-red regions, although the experimental method is such that observations are made in the visible region.

In order that there shall be some mechanism for interaction between the incident radiation and the nuclear, molecular, or electronic changes depicted in Fig. 1.4, there must be some electric or magnetic effect produced by the change which can be influenced by the electric or magnetic fields associated with the radiation. There are several possibilities:

1. The radiofrequency region. We may consider the nucleus and electron to be tiny charged particles, and it follows that their spin is associated with a tiny magnetic dipole. The reversal of this dipole consequent upon the spin reversal can interact with the magnetic field of electromagnetic radiation at the appropriate frequency. Consequently all such spin reversals produce an absorption or emission spectrum.
2. The visible and ultra-violet region. The excitation of a valence electron involves the moving of electronic charges in the molecule. The consequent change in the electric dipole gives rise to a spectrum by its interaction with the undulatory electric field of radiation.
3. The microwave region. A molecule such as hydrogen chloride, HCl, in which one atom (the hydrogen) carries a permanent net positive charge and the other a net negative charge, is said to have a permanent electric dipole moment. H_2 or Cl_2 , on the other hand, in which there is no such charge separation, have a zero dipole. If we consider the rotation of HCl