

Spectroscopy

CHAPTER ONE

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

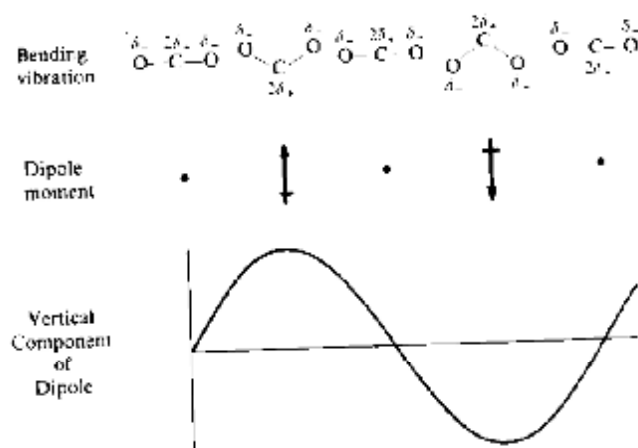


Figure 1.8 The bending motion of the carbon dioxide molecule and its associated dipole fluctuation.

5. There is a rather special requirement for a molecular motion to be 'Raman active'; this is that the electrical *polarizability* of the molecule must change during the motion. This will be discussed fully in Chapter 4.

1.4 REPRESENTATION OF SPECTRA

We show in Fig. 1.9 a highly schematic diagram of a spectrometer suitable for use in the visible and ultra-violet regions of the spectrum. A 'white' source is focused by lens 1 on to a narrow slit (arranged perpendicularly to the plane of the paper) and is then made into a parallel beam by lens 2. After passing through the sample it is separated into its constituent frequencies by a prism and is then focused on to a photographic plate by lens 3; the vertical image of the slit will thus appear on the plate. Rays have been drawn to show the points at which two frequencies, ν_1 and ν_2 , are focused.

If the sample container is empty, the photographic plate, after development, should ideally show an even blackening over the whole range of frequencies covered (i.e., from A to B). The ideal situation is seldom realized, if only because the source does not usually radiate all frequencies with the same intensity, but in any case the blackening of the plate serves to indicate the relative intensities of the frequencies emitted by the source.

If we now imagine the sample space to be filled with a substance having only two possible energy levels, E_1 and E_2 , the photographic plate, after development, will show a blackening at all points except at the frequency $\nu = (E_2 - E_1)/h$, since energy at this frequency will have been absorbed by

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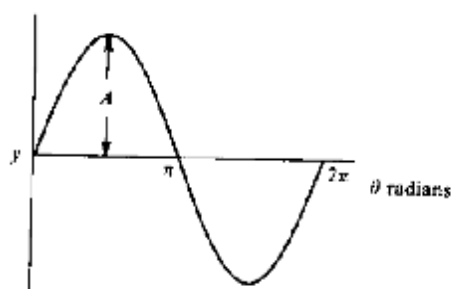


Figure 1.1 The curve of $y = A \sin \theta$.

Fig. 1.2. A point P travels with uniform angular velocity ω 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

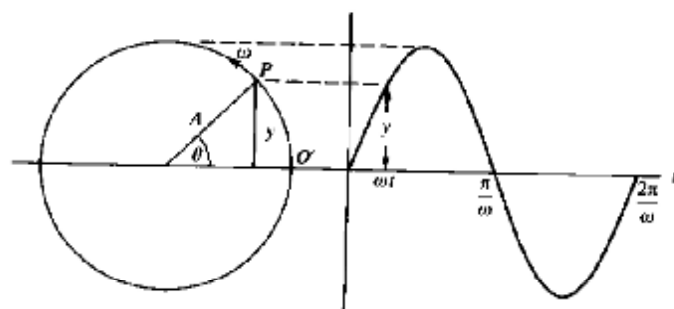


Figure 1.2 The description of a sine curve in terms of the circular motion of a point P at a uniform angular velocity of ω rad s^{-1} .

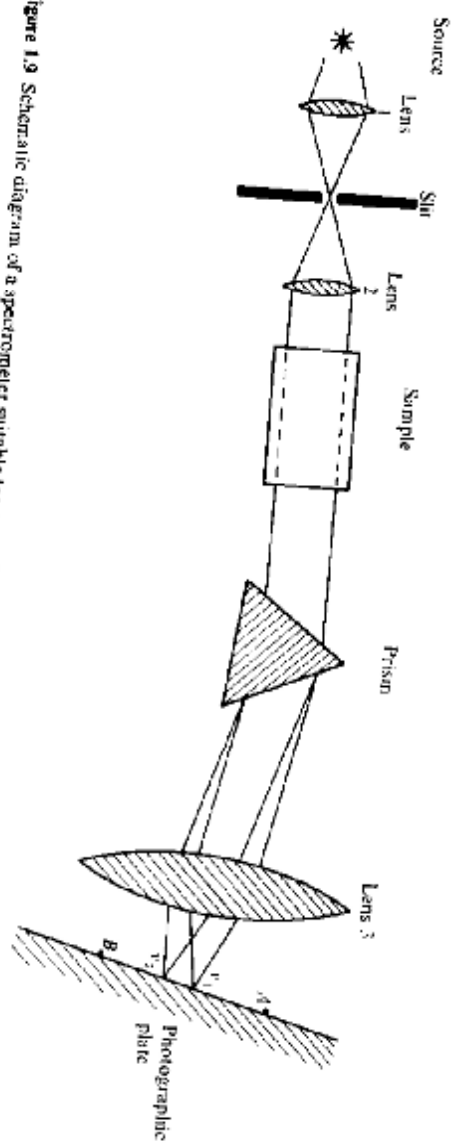


Figure 1.9 Schematic diagram of a spectrometer suitable for operation in the visible region.

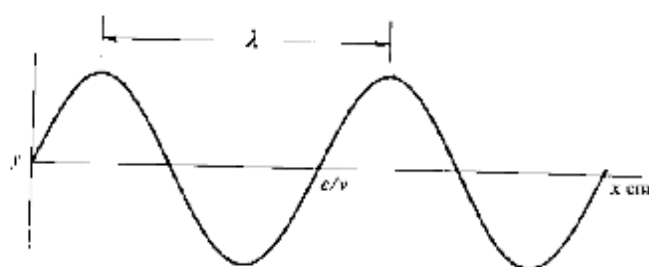


Figure 1.3 The concept of a travelling wave with a wavelength λ .

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 ν , 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 ν cycles per second, there are evidently ν waves in c metres, or

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

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 Ångström units (\AA) where $1 \text{\AA} = 10^{-10} \text{ m}$, although the proper SI unit for this region is the nanometre:

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

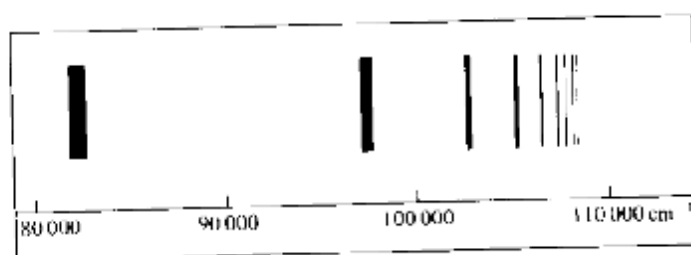


Figure 1.10 Schematic diagram of the absorption spectrum of atomic hydrogen recorded on a photographic plate.

the sample in raising each molecule from state 1 to state 2. Further if, as is almost always the case, there are many possible energy levels, $E_1, E_2, \dots, E_j, E_k, \dots$ available to the sample, a series of absorption lines will appear on the photographic plate at frequencies given by $\nu = (E_j - E_k)/h$. A typical spectrum may then appear as in Fig. 1.10.

At this point it may be helpful to consider what happens to the energy absorbed in the sort of process described above. In the ultra-violet, visible, and infra-red regions it is an experimental fact that a given sample continues to show an absorption spectrum for as long as we care to irradiate it—in other words, a finite number of sample molecules appear to be capable of absorbing an infinite amount of energy. Plainly the molecules must be able to rid themselves of the absorbed energy.

A possible mechanism for this is by thermal collisions. An energized molecule collides with its neighbours and gradually loses its excess energy to them as kinetic energy—the sample as a whole becomes warm.

Another mechanism is that energy gained from radiation is lost as radiation once more. A molecule in the ground state absorbs energy at frequency ν and its energy is raised an amount $\Delta E = h\nu$ above the ground state. It is thus in an excited, unstable condition, but by emitting radiation of frequency ν again, it can revert to the ground state and is able to reabsorb from the radiation beam once more. In this case, it is often asked how an absorption spectrum can arise at all, since the absorbed energy is re-emitted by the sample. The answer is simply that the radiation is re-emitted in a random direction and the proportion of such radiation reaching the detector is minute—in fact re-emitted radiation has as much chance of reaching the source as the detector. The net effect, then, is an absorption from the directed beam and, when re-emission occurs, a scattering into the surroundings. The scattered radiation can, of course, be collected and observed as an emission spectrum which will be—with important reservations to be discussed in Chapter 4—the complement of the absorption spectrum. Under the right conditions much of the radiation emitted from a sample can be in a very coherent beam—so-called laser radiation. We discuss this in Sec. 1.10.

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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

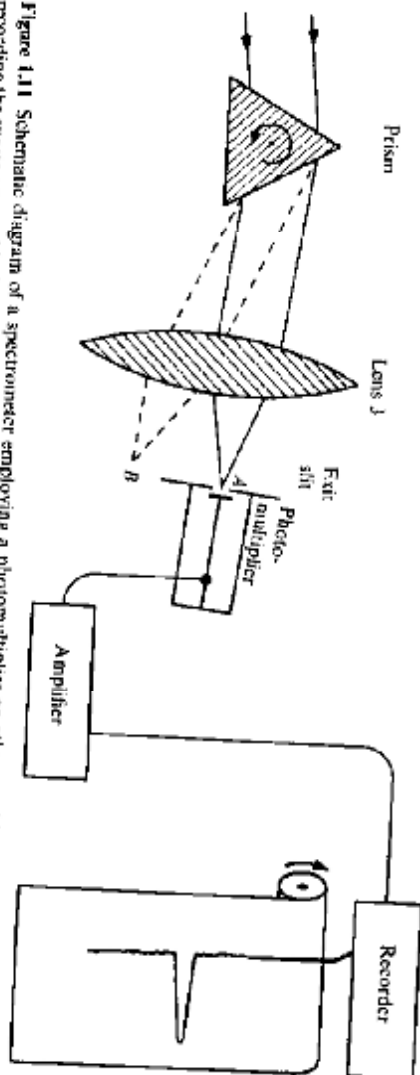


Figure 1.11 Schematic diagram of a spectrometer employing a photomultiplier or other sensitive element as detector and recording the spectrum graphically on chart paper.

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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).

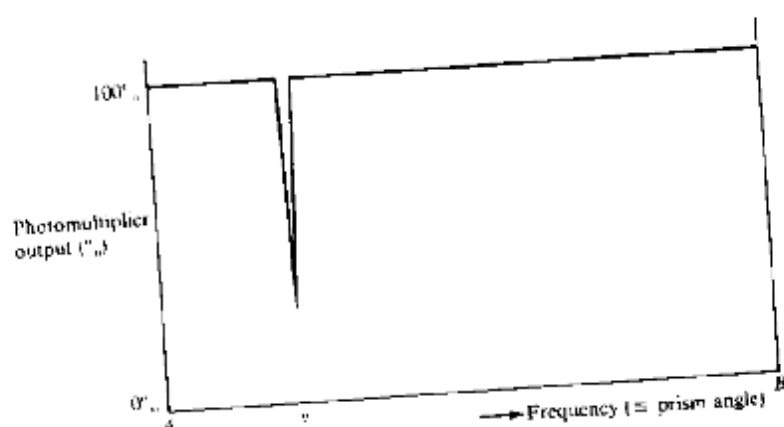


Figure 1.12 The idealized spectrum of a molecule undergoing a single transition.

In modern spectrometers the detector is rarely the simple photographic plate of Fig. 1.9. One of the most sensitive and useful devices in the visible and ultra-violet region is the photomultiplier tube, consisting of a light-sensitive surface which emits electrons when light falls upon it. The tiny electron current may be amplified and applied to an ammeter or pen recorder. The spectrometer would then appear somewhat as in Fig. 1.11, where the sensitive element of the photomultiplier is situated at the point *A* of Fig. 1.9. The physical width of the beam falling on the detector can be limited by the provision of an 'exit slit' just in front of the detector entrance.

The frequency of the light falling on the photomultiplier may be altered either by physically moving the latter from *A* to *B* or, more usually, by steady rotation of the prism. If, as before, we imagine the sample to contain a substance having just two energy levels, the photomultiplier output will, ideally, vary with the prism orientation as in Fig. 1.12. We say that the spectrum has been *scanned* between the frequencies represented by *A* and *B*, and such a picture is referred to, rather grandly, as a spectrum in the 'frequency domain', to indicate that it records the detector output against frequency. In Sec. 1.8 we shall discuss 'time domain' spectroscopy, where the detector output is recorded as a function of time.

Again, the ideal situation of Fig. 1.12 is seldom attained. Not only does the source emissivity vary with frequency, but often the sensitivity of the photomultiplier is also frequency-dependent. Thus the baseline—the 'sample-empty' condition—is never horizontal, although matters can usually be arranged so that it is approximately linear. Further, since it is impossible to make either of the slits infinitely narrow, a *range* of frequencies, rather than just a single frequency, falls on the photomultiplier at any given setting of the prism. This results in a broadening of the absorbance peak, and the final spectrum may appear rather as in Fig. 1.13. In this

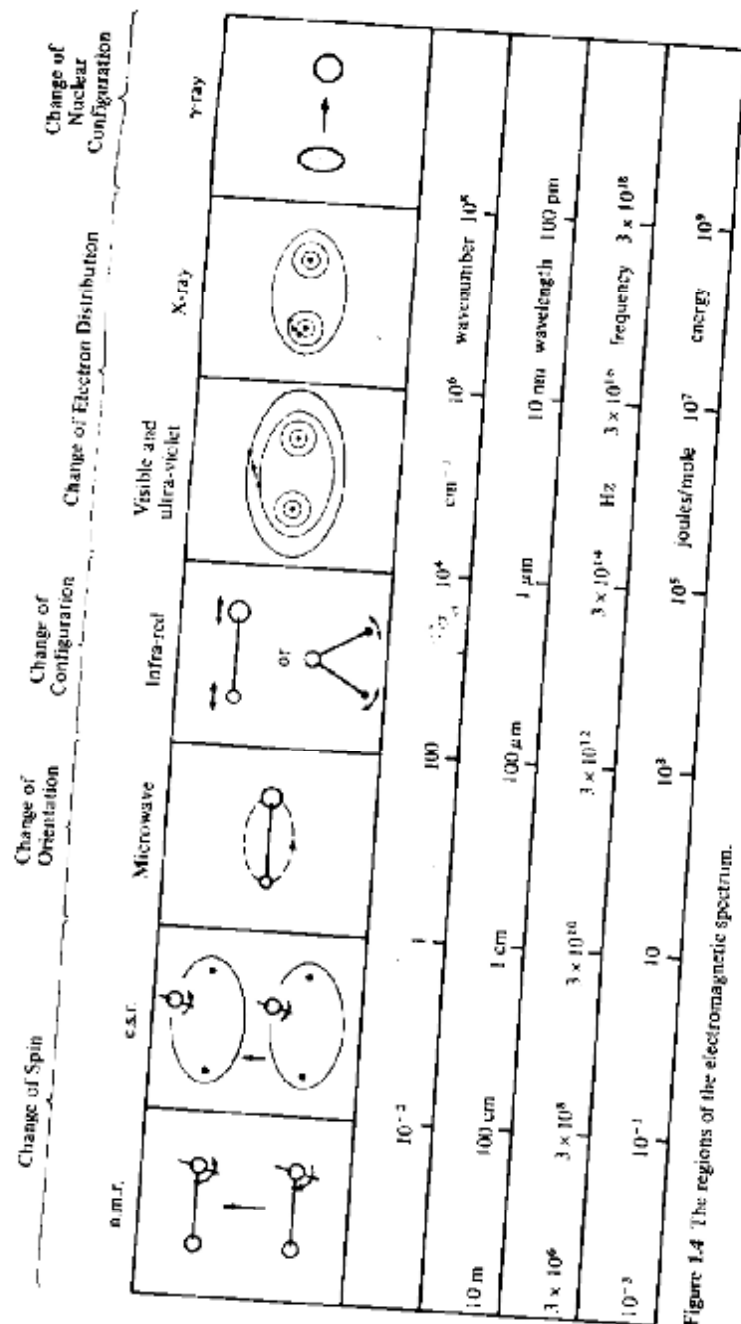


Figure 1.4 The regions of the electromagnetic spectrum.



instrumental reasons, it is often better to measure the relative intensities of absorbance peaks from the derivative curve than from the direct trace.

1.5 BASIC ELEMENTS OF PRACTICAL SPECTROSCOPY

Spectrometers used in various regions of the spectrum naturally differ widely from each other in construction. These differences will be discussed in more detail in the following chapters, but here it will probably be helpful to indicate the basic features which are common to all types of spectrometer. We may, for this purpose, consider absorption and emission spectrometers separately.

1. *Absorption instruments.* Figure 1.15(a) shows, in block diagram form, the components of an absorption spectrometer which might be used in the infra-red, visible, and ultra-violet regions. The radiation from a white source is directed by some guiding device (e.g., the lens of Fig. 1.9, or mirrors) on to the sample, from which it passes through an analyser (e.g., the prism of Fig. 1.9), which selects the frequency reaching the detector at any given time. The signal from the latter passes to a recorder which is synchronized with the analyser so as to produce a trace of the absorbance as the frequency varies.

Placed, often, between the sample and the analyser is a *modulator*; this mechanical or electronic device interrupts the radiation beam a certain number of times per second, usually fixed somewhere between 10 and 1000 times, and its effect is to cause the detector to send an alternating current signal to the recorder, with a fixed frequency of 10-1000 Hz, rather than the direct current signal which would result from a steady, uninterrupted beam. This has two main advantages: (a) the amplifier in the recorder can be of a.c. type which is, in general, simpler to construct and more reliable in operation than a d.c. amplifier, and (b) the amplifier can be tuned to select only that frequency which the modulator imposes on the signal, thus ignoring all other signals. In this way stray radiation and other extraneous signals are removed from the spectral trace and a better, cleaner spectrum results.

In the microwave and radiofrequency regions it is possible to construct monochromatic sources whose emission frequency can be varied over a range. In this case, as Fig. 1.15(b) shows, no analyser is necessary, the source being, in a sense, its own analyser. Now it is necessary for the recorder to be synchronized with the source-scanning device in order that a spectral trace be obtained.

2. *Emission instruments.* The layout now differs in that the sample, after excitation, is its own source, and it is necessary only to collect the emitted radiation, analyse, and record it in the usual way. Figure 1.16

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2. Microwave region: 3×10^{10} – 3×10^{12} Hz; 1 cm–100 μ m 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 μ m–1 μ m 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 μ m–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 10^5 – 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

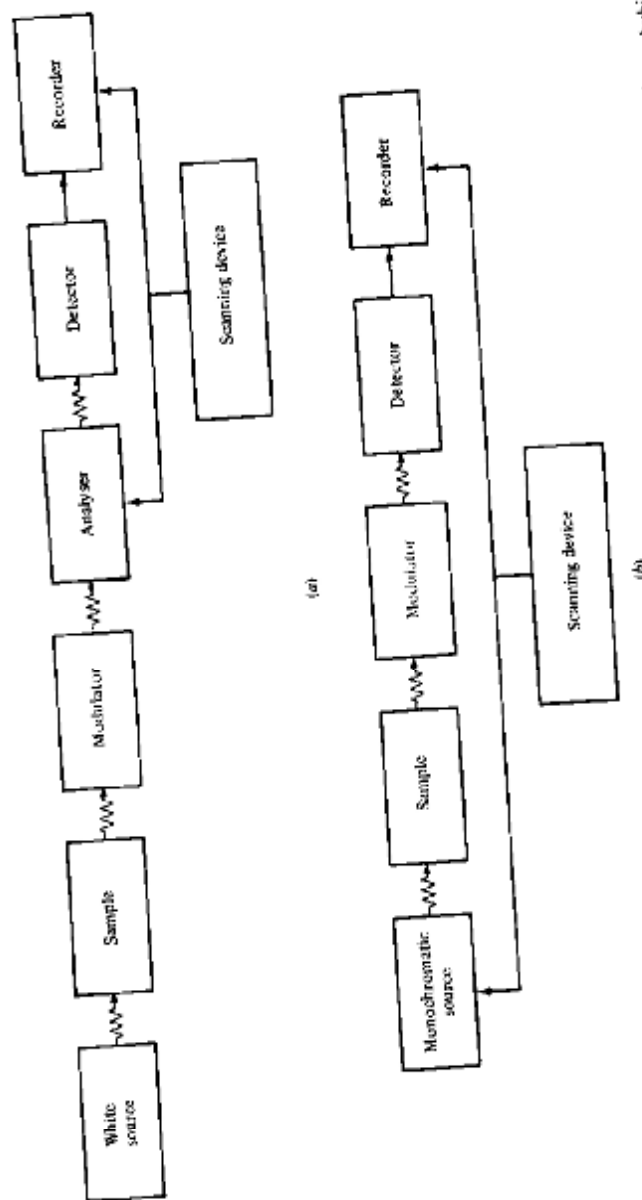


Figure 1.15 Block diagram of a typical absorption spectrometer for use in (a) the infra-red, visible, and ultra-violet regions where a 'white' source is available, and (b) the microwave and radiofrequency regions where the source can be tuned over a considerable range of frequencies.

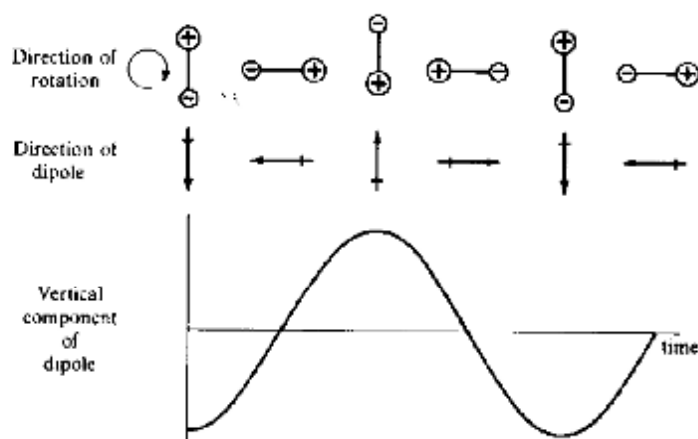
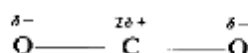


Figure 1.5 The rotation of a diatomic molecule, HCl, showing the fluctuation in the dipole moment measured in a particular direction.

(Fig. 1.5, where we notice that if only a pure rotation takes place, the centre of gravity of the molecule must not move), we see that the plus and minus charges change places periodically, and the component dipole moment in a given direction (say upwards in the plane of the paper) fluctuates regularly. This fluctuation is plotted in the lower half of Fig. 1.5, and it is seen to be exactly similar in form to the fluctuating electric field of radiation (cf. Fig. 1.2). Thus interaction can occur, energy can be absorbed or emitted, and the rotation gives rise to a spectrum. All molecules having a permanent moment are said to be 'microwave active'. If there is no dipole, as in H_2 or Cl_2 , no interaction can take place and the molecule is 'microwave inactive'. This imposes a limitation on the applicability of microwave spectroscopy.

4. The infra-red region. Here it is a vibration, rather than a rotation, which must give rise to a dipole change. Consider the carbon dioxide molecule as an example, in which the three atoms are arranged linearly with a small net positive charge on the carbon and small negative charges on the oxygens:



During the mode of vibration known as the 'symmetric stretch', the molecule is alternately stretched and compressed, both C—O bonds changing simultaneously, as in Fig. 1.6. Plainly the dipole moment remains zero throughout the whole of this motion, and this particular vibration is thus 'infra-red inactive'.

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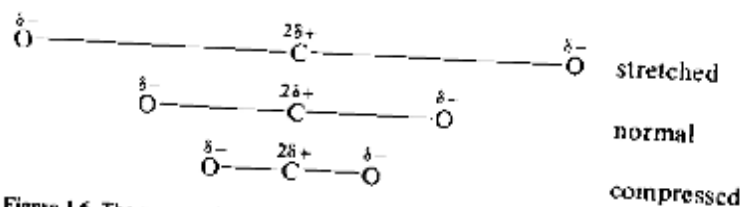


Figure 1.6 The symmetric stretching vibration of the carbon dioxide molecule

However, there is another stretching vibration called the anti-symmetrical stretch, depicted in Fig. 1.7. Here one bond stretches while the other is compressed, and vice versa. As the figure shows, there is a periodic alteration in the dipole moment, and the vibration is thus 'infra-red active'. One further vibration is allowed to this molecule (see Chapter 3 for a more detailed discussion), known as the bending mode. This, as shown in Fig. 1.8, is also infra-red active. In both these motions the centre of gravity does not move.

Although dipole change requirements do impose some limitation on the application of infra-red spectroscopy, the appearance or non-appearance of certain vibration frequencies can give valuable information about the structure of a particular molecule (see Chapter 3).

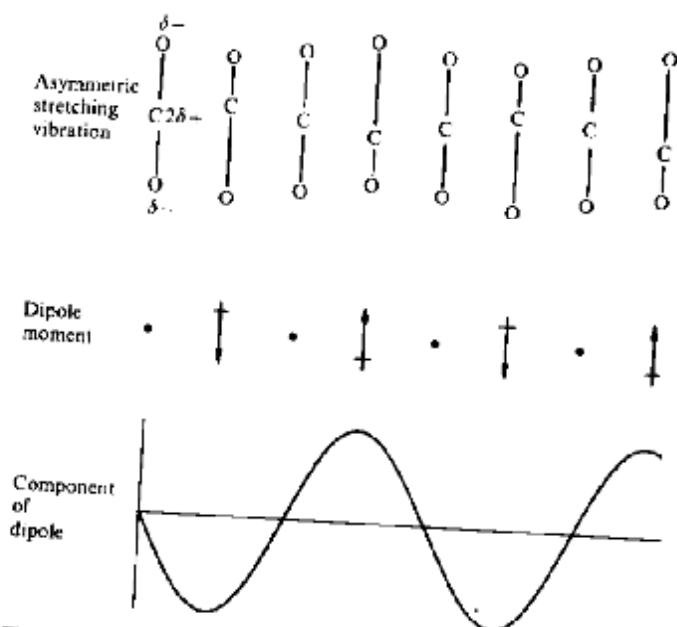


Figure 1.7 The asymmetric stretching vibration of the carbon dioxide molecule showing the fluctuation in the dipole moment.