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

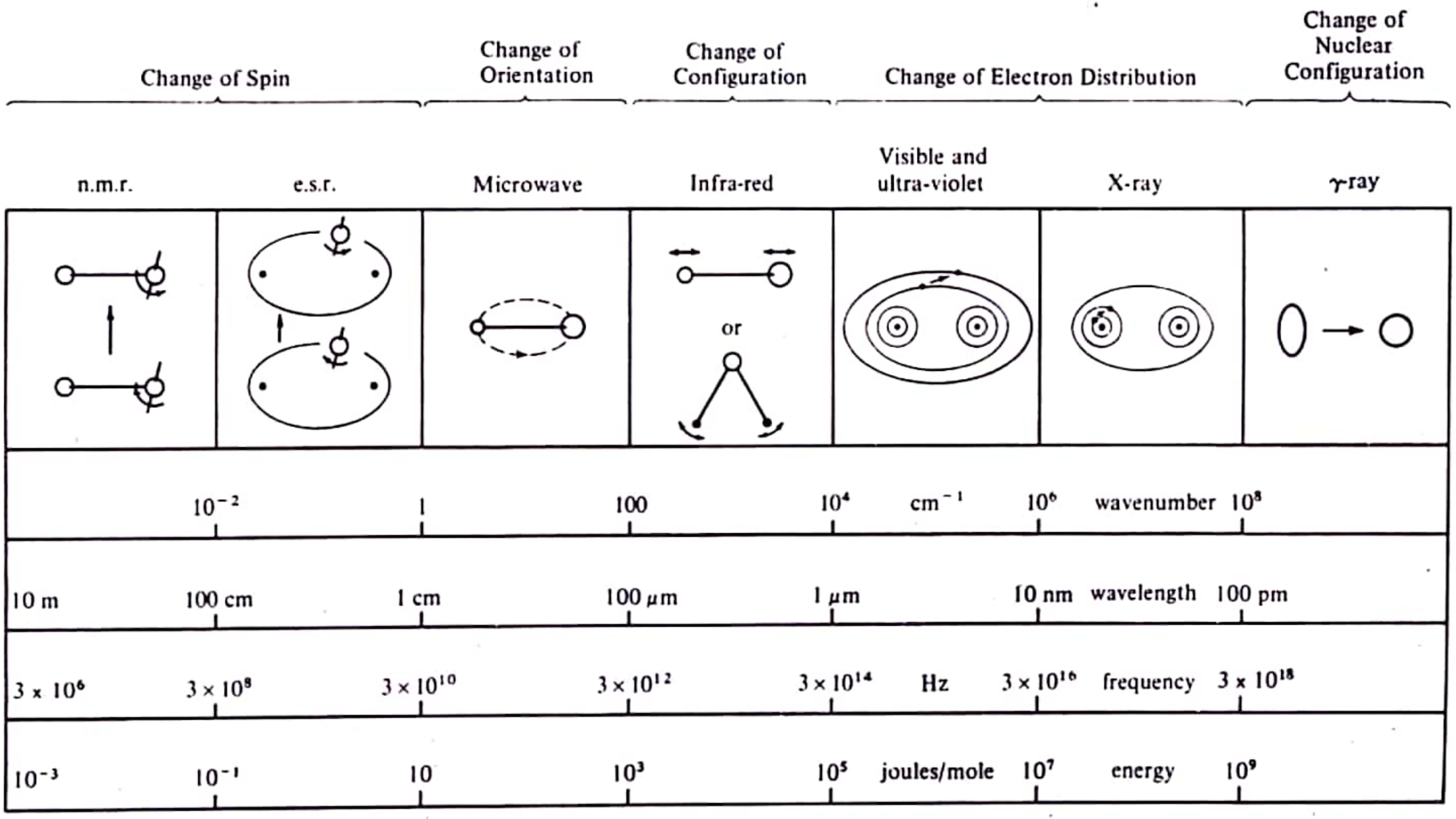

Figure 1.4 The regions of the electromagnetic spectrum.

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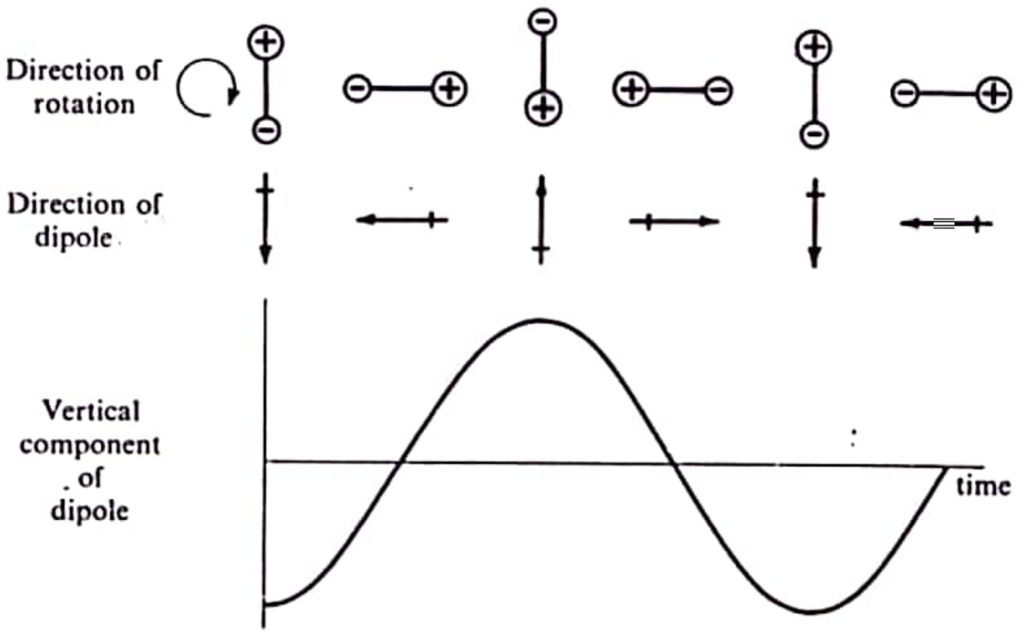
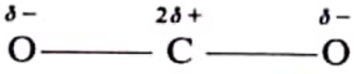


Figure 1.5 The rotation of a diatomic molecule, HCl, showing the fluctuation in the dipole moment measured in a particular direction.

(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:



$$\overset{\delta -}{O} — \overset{2\delta +}{C} — \overset{\delta -}{O}$$

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'.

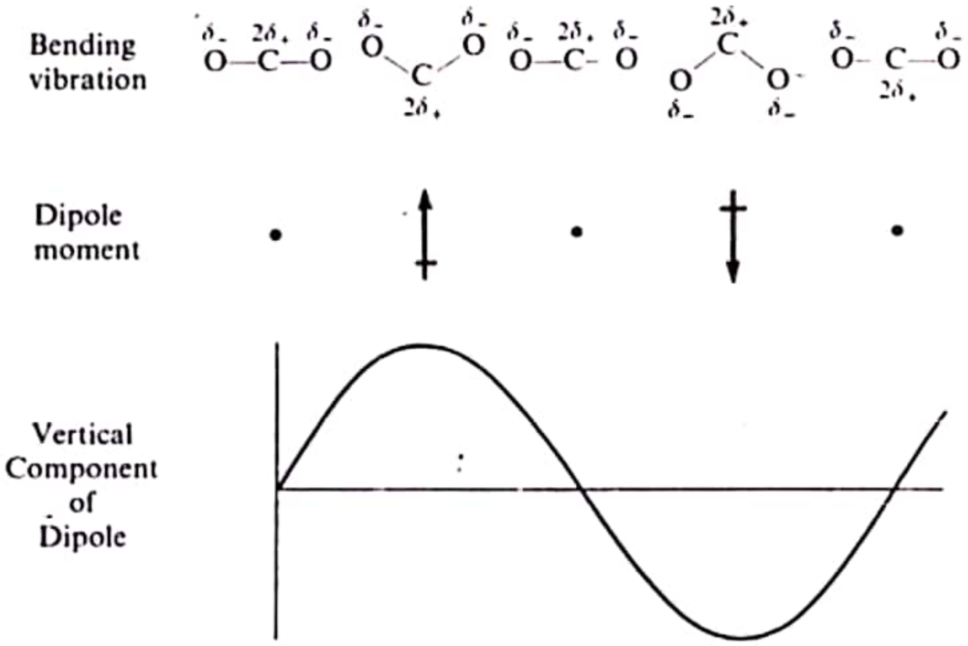


Figure 1.8 The bending motion of the carbon dioxide molecule and its associated dipole fluctuation.

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

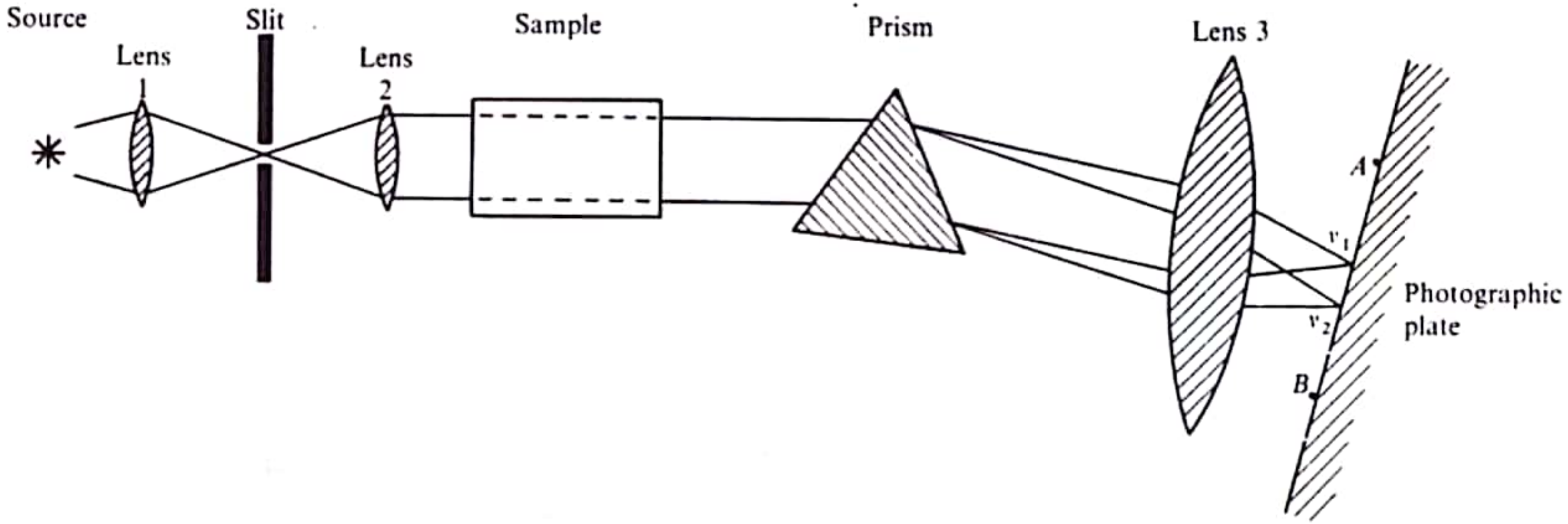


Figure 1.9 Schematic diagram of a spectrometer suitable for operation in the visible region.

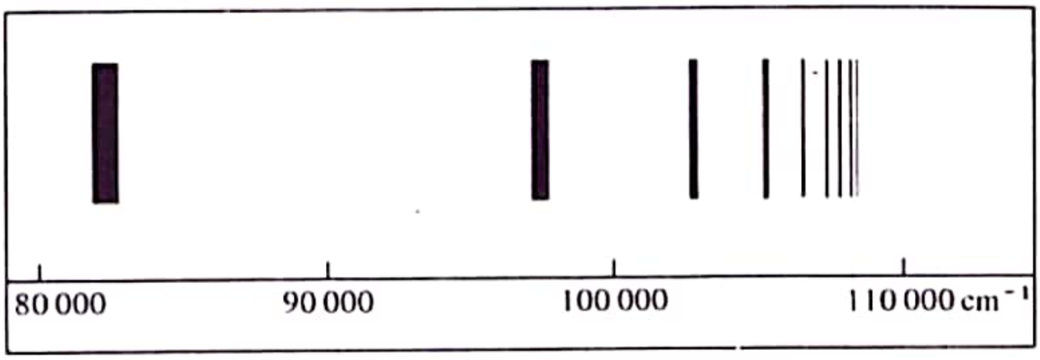


Figure 1.10 Schematic diagram of the absorption spectrum of atomic hydrogen recorded on a photographic plate.

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, ..., E_j, E_k, ... 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.

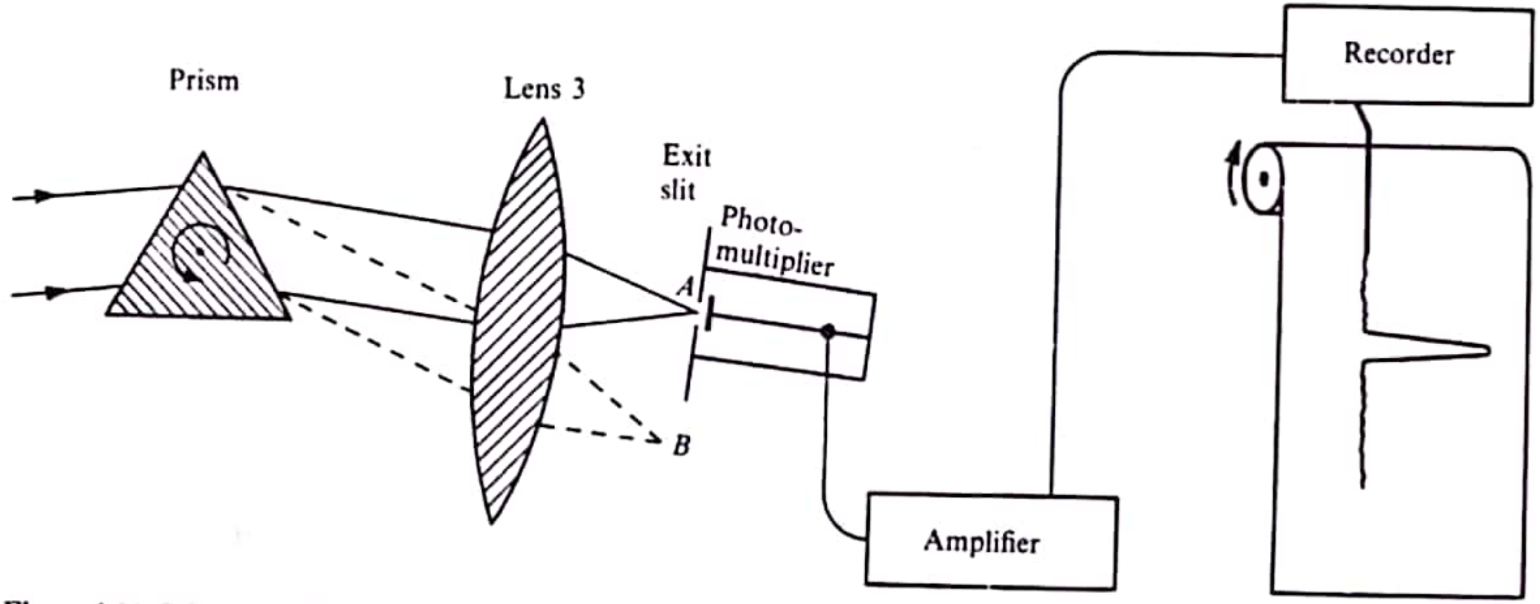


Figure 1.11 Schematic diagram of a spectrometer employing a photomultiplier or other sensitive element as detector and recording the spectrum graphically on chart paper.

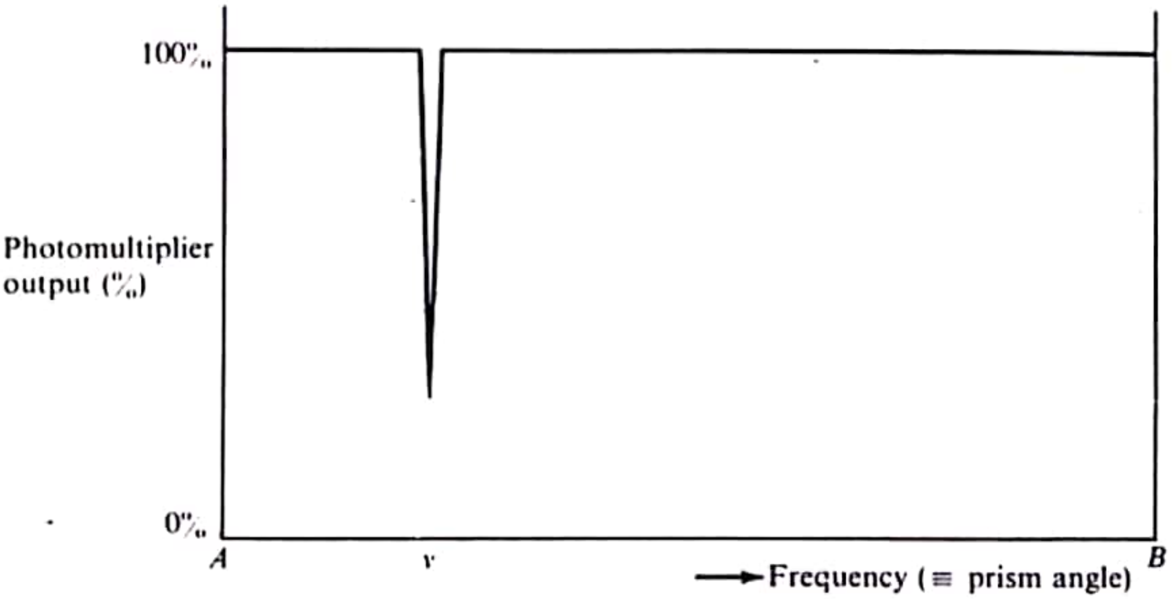


Figure 1.12 The idealized spectrum of a molecule undergoing a single transition.

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

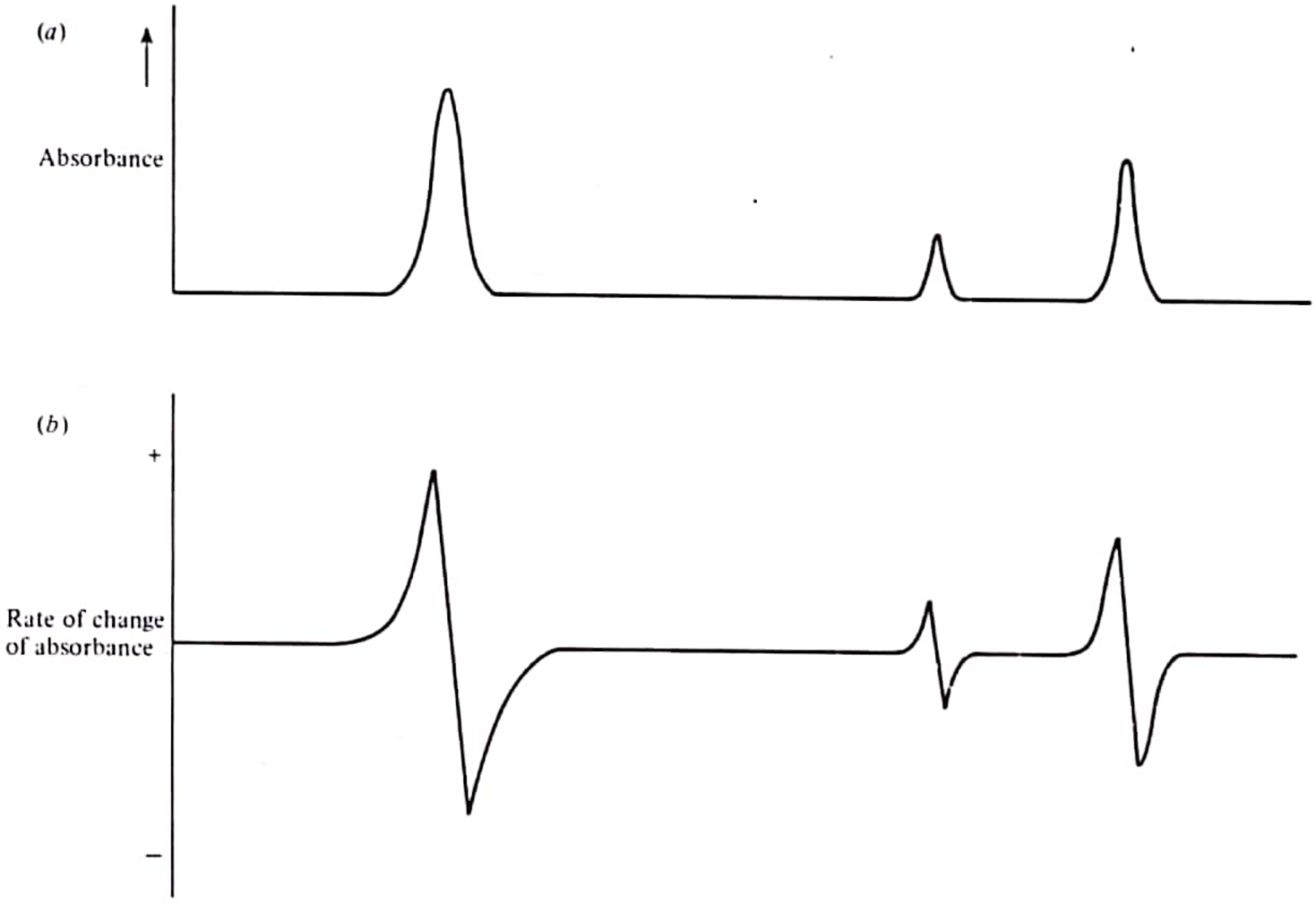


Figure 1.14 To illustrate the relation between absorption and derivative spectra: in (*a*) the absorption nuclear magnetic resonance spectrum of benzyl alcohol, $C_6H_5CH_2OH$, is shown, and in (*b*) the derivative (or dispersion) spectrum of the same molecule.

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

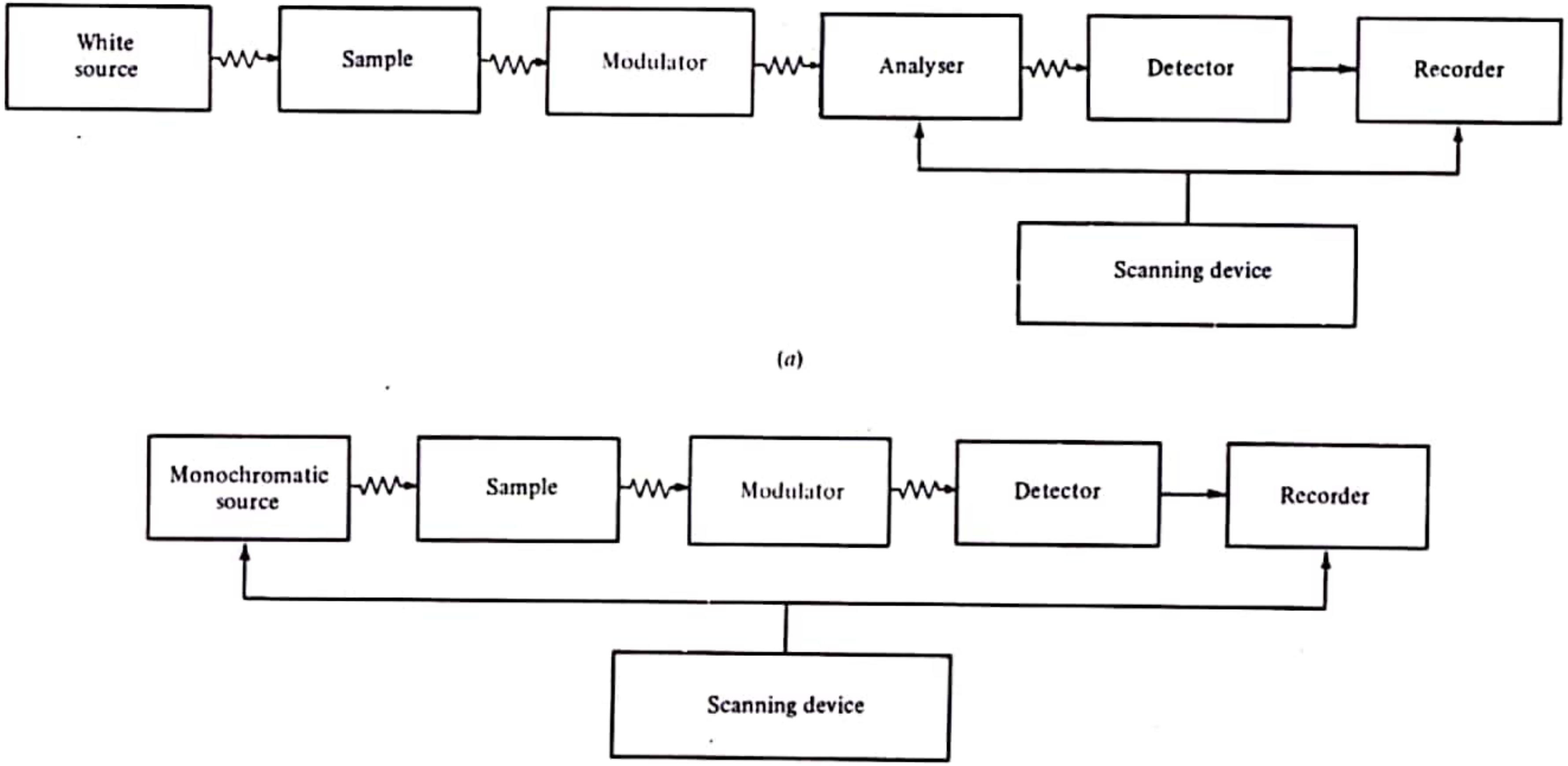
1.5 BASIC ELEMENTS OF PRACTICAL SPECTROSCOPY

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



(a)

(b)

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.

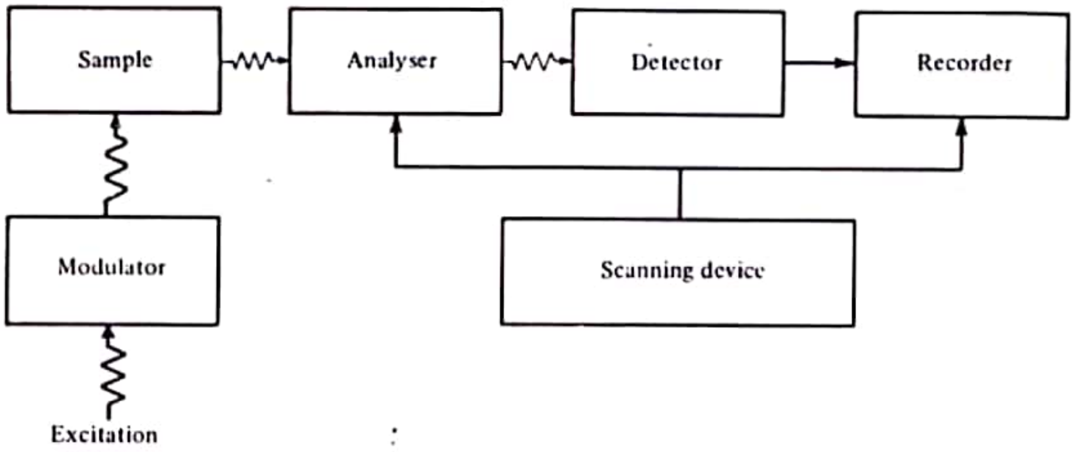


Figure 1.16 Block diagram of a typical emission spectrometer.

shows, schematically, a typical spectrometer. The excitation can be thermal or electrical, but often takes the form of electromagnetic radiation. In the latter case it is essential that the detector does not collect radiation directly from the exciting beam, and the two are placed at right angles as shown. A modulator placed between the source of excitation and the sample, together with a tuned detector-amplifier, ensures that the only emission recorded from the sample arises directly from excitation; any other spontaneous emission is ignored.

1.6 SIGNAL-TO-NOISE: RESOLVING POWER

Two other spectroscopic terms may be conveniently discussed at this point since they will recur in succeeding chapters.

Signal-to-Noise Ratio

Since almost all modern spectrometers use some form of electronic amplification to magnify the signal produced by the detector, every recorded spectrum has a background of random fluctuations caused by spurious electronic signals produced by the detector, or generated in the amplifying equipment. These fluctuations are usually referred to as 'noise'. In order that a real spectral peak should show itself as such and be sufficiently distinguished from the noise, it must have an intensity some three or four times that of the noise fluctuations (a signal-to-noise ratio of three or four). This requirement places a lower limit on the intensity of observable signals. In Sec. 1.9 we refer briefly to a computer-averaging technique by which it is possible to improve the effective signal-to-noise ratio.

Resolving Power

This is a somewhat imprecise concept which can, however, be defined rather arbitrarily and is often used as a measure of the performance of a spectrometer. We shall here consider it in general terms only.

No molecular absorption takes place at a single frequency only, but always over a spread of frequencies, usually very narrow but sometimes quite large (see Sec. 1.7); it is for this reason that we have up to now drawn spectra with broadened line shapes (cf. Fig. 1.14(*a*)).

Let us consider two such lines close together, as on the right of Fig. 1.17(*a*): the dotted curve represents the absorption due to each line separately, the full line their combined absorption. We shall first take the exit slit width to be larger than the separation between the lines. Scanning the

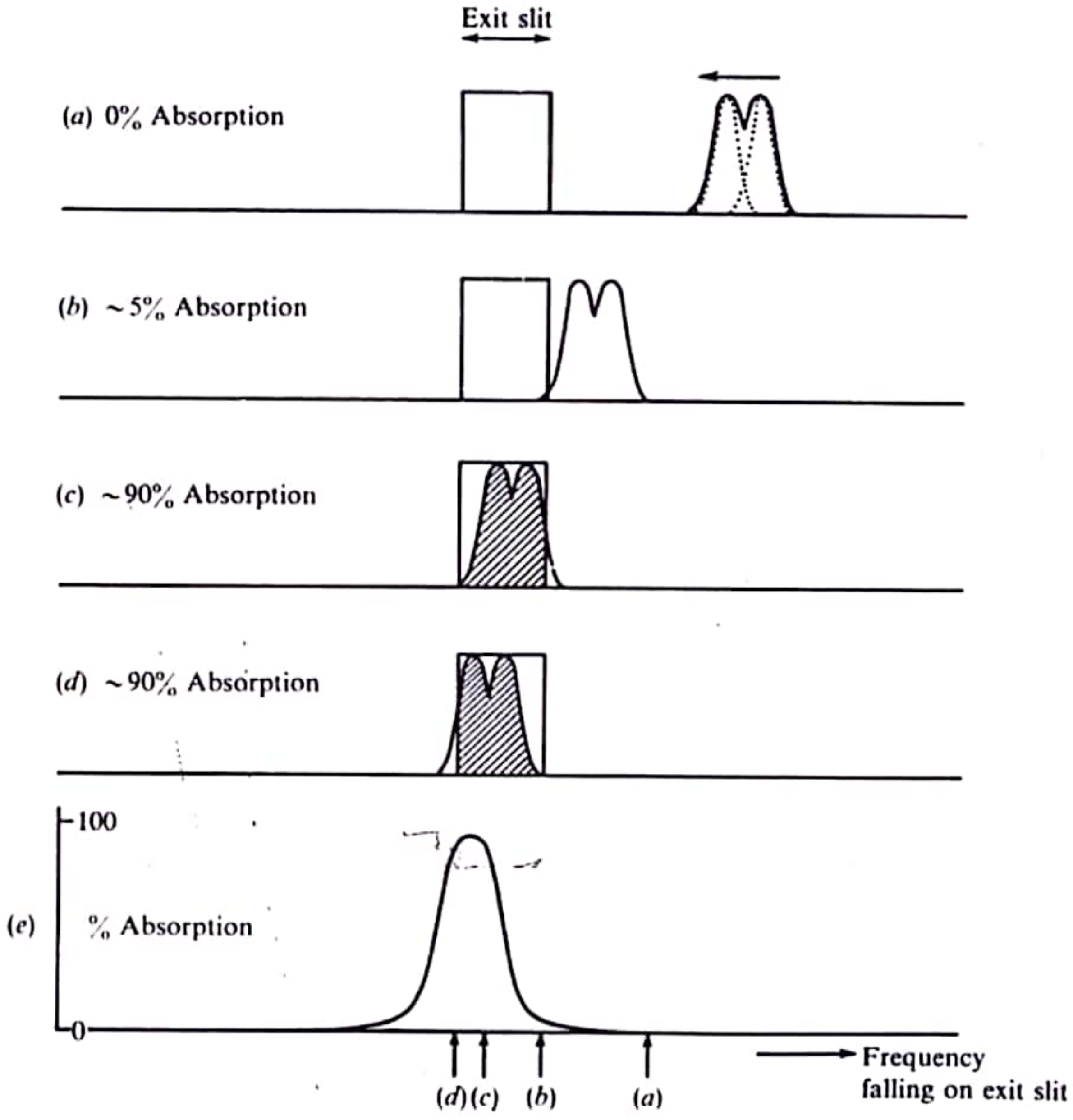


Figure 1.17 Illustrating the relation between slit width and resolving power: see text for discussion.

spectrum plainly involves moving the twin absorbance peaks steadily to the left so that they pass across the exit slit and into the detector; the situation at successive stages is shown in (*b*), (*c*), and (*d*) of Fig. 1.17, the shaded area showing the amount of absorbance which the detector would register. At (*e*) of this figure, the absorbance is plotted against frequency, together with the approximate positions of stages (*a*), (*b*), (*c*), and (*d*).

It is quite evident that the separation between the lines has disappeared under these conditions—the lines are not *resolved*. It is equally evident that the use of a much narrower slit would result in their resolution—the *resolving power* would be increased. In fact, provided the slit width is less than the separation between the lines, the detector output will show a minimum between them.

However, it must be remembered that a narrower slit allows less total energy from the beam to reach the detector and consequently the intrinsic signal strength will be less. There comes a point when decreasing the slit width results in such weak signals that they become indistinguishable from the background noise mentioned in the previous paragraph. Thus spectroscopy is a continual battle to find the minimum slit width consistent with acceptable signal-to-noise values. Improvements in resolving power may arise not only as a result of obtaining better dispersion of the radiation by the analyser (e.g., by the use of a diffraction grating rather than a prism for the ultra-violet and infra-red regions) but also by using a more sensitive detector.

1.7 THE WIDTH AND INTENSITY OF SPECTRAL TRANSITIONS

In the preceding sections we have seen that a spectral transition has the important property of *position*, measured in terms of its frequency, wavelength, or wavenumber; there are two other important properties, its *width* and its *intensity*, and we shall consider these briefly here.

1.7.1 The Width of Spectral Lines

Throughout this chapter we have drawn spectral absorptions and emissions not as infinitely sharp lines but as more or less broad peaks; we have seen that one reason for this is that the mechanical slits in spectrometers are not infinitely narrow and thus allow a *range* of frequencies, rather than a single frequency, to fall on the detector, hence blurring the pattern. While improvements in spectrometer design can improve the resolving power of an instrument, however, there is nonetheless a minimum width inherent in any atomic or molecular transition—the *natural line width*—beyond which no instrument, however superior, will show a sharpening. This width arises essentially because the energy levels of atomic and molecular systems are not precisely determined, but have a certain fuzziness or imprecision. Several factors contribute to this.

1. *Collision broadening.* Atoms or molecules in liquid and gaseous phases are in continual motion and collide frequently with each other. These collisions inevitably cause some deformation of the particles and hence perturb, to some extent, the energies of at least the outer electrons in each. This immediately gives a possible explanation for the width of visible and ultra-violet spectral lines, since these deal largely with transitions between outer electronic shells. Equally vibrational and rotational spectra are broadened since collisions interfere with these motions too. In general, molecular interactions are more severe in liquids than in gases, and gas-phase spectra usually exhibit sharper lines than those of the corresponding liquid.

   In the case of solids, the motions of the particles are more limited in extent and less random in direction, so that solid-phase spectra are often sharp but show evidence of interactions by the splitting of lines into two or more components.
2. *Doppler broadening.* Again in liquids and gases the motion of the particles causes their absorption and emission frequencies to show a Doppler shift; since the motion is random in a given sample, shifts to both high and low frequencies occur and hence the spectral line is broadened. In general, for liquids collision broadening is the most important factor, whereas for gases, where collision broadening is less pronounced, the Doppler effect often determines the natural line width.
3. *Heisenberg uncertainty principle.* Even in an isolated, stationary molecule or atom the energy levels are not infinitely sharp, due to the operation of a fundamental and very important principle, the Uncertainty Principle of Heisenberg. In effect this says that, if a system exists in an energy state for a limited time δt seconds, then the energy of that state will be uncertain (fuzzy) to an extent δE where

   $$\delta E \times \delta t \approx h/2\pi \approx 10^{-34} \text{ J s} \tag{1.10}$$

   where h is again Planck's constant. Thus we see that the lowest energy state of a system *is* sharply defined since, left to itself, the system will remain in that state for an infinite time; thus $\delta t = \infty$, and $\delta E = 0$. But, for example, the lifetime of an excited electronic state is usually only about 10^{-8} s, which gives a value for δE of about $10^{-34}/10^{-8} = 10^{-26}$ J. A transition between this state and the ground state will thus have an energy uncertainty of δE, and a corresponding uncertainty in the associated radiation frequency of $\delta E/h$, which we can write as:

   $$\delta \nu = \frac{\delta E}{h} \approx \frac{h}{2\pi h \delta t} \approx \frac{1}{2\pi \delta t} \tag{1.11}$$

Thus for our example of an excited electronic state lifetime of 10^{-8} s, $\delta\nu \approx 10^8$ Hz. This apparently large uncertainty is, in fact, small compared with the usual radiation frequency of such transitions, 10^{14}–10^{16} Hz, and so the natural line width is said to be small; in fact, the apparent widths of electronic transitions are far more dependent on collision and Doppler broadening than on energy uncertainties.

On the other hand an excited electron *spin* state may exist for some 10^{-7} s which, from Eq. (1.11), leads to a frequency uncertainty of some 10^7 Hz for a transition. This, compared with the usual frequency of such transitions, 10^8–10^9 Hz, represents a very broad transition indeed, and here the Heisenberg uncertainty relation is by far the most important effect.

Further examples of the application of Heisenberg's principle will be given in later chapters.

1.7.2 The Intensity of Spectral Lines

When discussing spectral intensities there are three main factors to be considered: the likelihood of a system in one state changing to another state—the *transition probability*; the number of atoms or molecules initially in the state from which the transition occurs—the *population*; and the amount of material present giving rise to the spectrum—the *concentration* or *path length* of the sample.

1. *Transition probability.* The detailed calculation of absolute transition probabilities is basically a straightforward matter, but as it involves a knowledge of the precise quantum mechanical wave functions of the two states between which the transition occurs, it can seldom be done with accuracy and is, in any case, beyond the scope of this book. We shall generally content ourselves with qualitative statements about relative transition probabilities without attempting any detailed calculations.

   At a much lower level of sophistication, however, it is often possible to decide whether a particular transition is forbidden or allowed (i.e., whether the transition probability is zero or non-zero). This process is essentially the deduction of *selection rules*, which allow us to decide between which levels transitions will give rise to spectral lines, and it can often be carried out through pictorial arguments very like those we have already used in discussing the activity or otherwise of processes in Sec. 1.3.
2. *Population of states.* If we have two levels from which transitions to a third are equally probable, then obviously the most intense spectral line will arise from the level which initially has the greater population. There

is a simple statistical rule governing the population of a set of energy levels.

For example, if we have a total of N molecules distributed between two different energy states, a lower and an upper with energies E_{lower} and E_{upper}, respectively, we would intuitively expect most of the molecules to occupy the lower state. Proper statistical analysis bears this out and shows that, *at equilibrium*

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp(-\Delta E/kT) \tag{1.12}$$

where $\Delta E = E_{\text{upper}} - E_{\text{lower}}$, T is the temperature in K, and k is a universal constant. The expression is known as the Boltzmann distribution, after its originator, and k, which has a value of $1{\cdot}38 \times 10^{-23}$ J K^{-1}, as Boltzmann's constant. Examples showing the use of this very important expression will recur throughout the remaining chapters.

3. *Path length of sample.* Clearly if a sample is absorbing energy from a beam of radiation, the more sample the beam traverses the more energy will be absorbed from it. We might expect that twice as much sample would give twice the absorption, but a very simple argument shows that this is not so. Consider two identical samples of the same material, S_1 and S_2, and assume that S_1 or S_2 alone absorb 50 per cent of the energy falling on them, allowing the remaining 50 per cent to pass through. If we pass a beam of initial intensity I_0 through S_1, 50 per cent of I_0 will be absorbed and the intensity of the beam leaving S_1 will be $\frac{1}{2}I_0$; if we then pass this beam through S_2 a further 50 per cent will be absorbed, and $\frac{1}{2} \times \frac{1}{2}I_0 = \frac{1}{4}I_0$ will leave S_2. Thus two 50 per cent absorptions in succession do not add up to 100 per cent but only to 75 per cent absorption. An exactly similar relationship exists between the *concentration* of a sample and the amount of energy absorption—a doubling of the concentration produces something less than a doubling of the absorption.

These relationships are best expressed in terms of the Beer–Lambert law, which is:

$$\frac{I}{I_0} = \exp(-\varepsilon cl) \tag{1.13}$$

where I_0 is the intensity of radiation falling on the sample, and I that part transmitted, c and l are the sample concentration and length, and ε is the extinction coefficient or absorption coefficient, which is a constant for a given type of transition (e.g., electronic, vibrational, etc.) occurring within a particular sample. Clearly ε is closely connected with the transition probability discussed above, a large probability being associated with a large ε, and vice versa.

1.8 FOURIER TRANSFORM SPECTROSCOPY

One of the major disadvantages of the conventional method of producing a spectrum, such as that of Fig. 1.13, is its inherent slowness. Essentially each point of the spectrum has to be recorded separately—the spectrometer is set to start reading at one end, the frequency is swept smoothly across the whole span of the spectrum, and the detector signal is monitored and recorded. The inefficiency of such a method is clear when one considers taking a spectrum with only one or two 'lines' in it—we have to sweep from one end to the other in order to find the lines, but most of the time is spent recording nothing but background noise. Until recently it was only in the visible and ultra-violet regions that the whole of a spectrum could be recorded simultaneously—on a photographic plate—but a new development, Fourier transform spectroscopy, is providing simultaneous and almost instantaneous recording of the whole spectrum in the magnetic resonance, microwave, and infra-red regions. In this section we shall briefly discuss the basic ideas of the technique, leaving to later chapters more detailed consideration of its methods and applications.

Although equally applicable to both emission and absorption spectroscopy, it is probably easier to visualize Fourier transform (FT) spectroscopy in terms of emission, so let us take the spectrum of Fig. 1.13 to represent the emission of radiation by a sample. Further we shall, for the moment, ignore the line-broadening discussed in the previous section, and think of this radiation as a pure sine wave at some quite precise frequency, ν. If a detector capable of responding sufficiently rapidly receives this emitted radiation, its output will be an oscillating signal, again of frequency ν. Note that we here consider the detector output as a function of *time* ('time domain' spectroscopy) rather than as the function of frequency ('frequency domain') plotted in Fig. 1.13.

Now consider a sample-emitting radiation at two different frequencies; a detector receiving the total radiation will 'see' the *sum* of the two sine waves. We illustrate, diagrammatically, the two separate but superimposed waves in Fig. 1.18(*a*), and their sum in (*b*), and we note that the detector output shows an oscillation due to the frequency of the two waves, but also a slow increase and decrease in overall amplitude. This latter is often called the 'beat' frequency, by analogy with a similar phenomenon for musical tones, and it arises because the two component waves are sometimes 'in step' (as at points *A* and *B* in Fig. 1.18 where their amplitudes reinforce each other), and sometimes out of step (as at *C* where they cancel). In fact the beat frequency is always equal to the *difference* in frequency of the component waves—if they differ in frequency by 10 cycles per second (Hz) then the beat oscillation is also at 10 Hz. This is illustrated by Fig. 1.18(*c*) and (*d*) where we show sine waves with half the frequency separation of those in Fig. 1.18(*a*) and (*b*), and we see that the beat frequency has also halved.

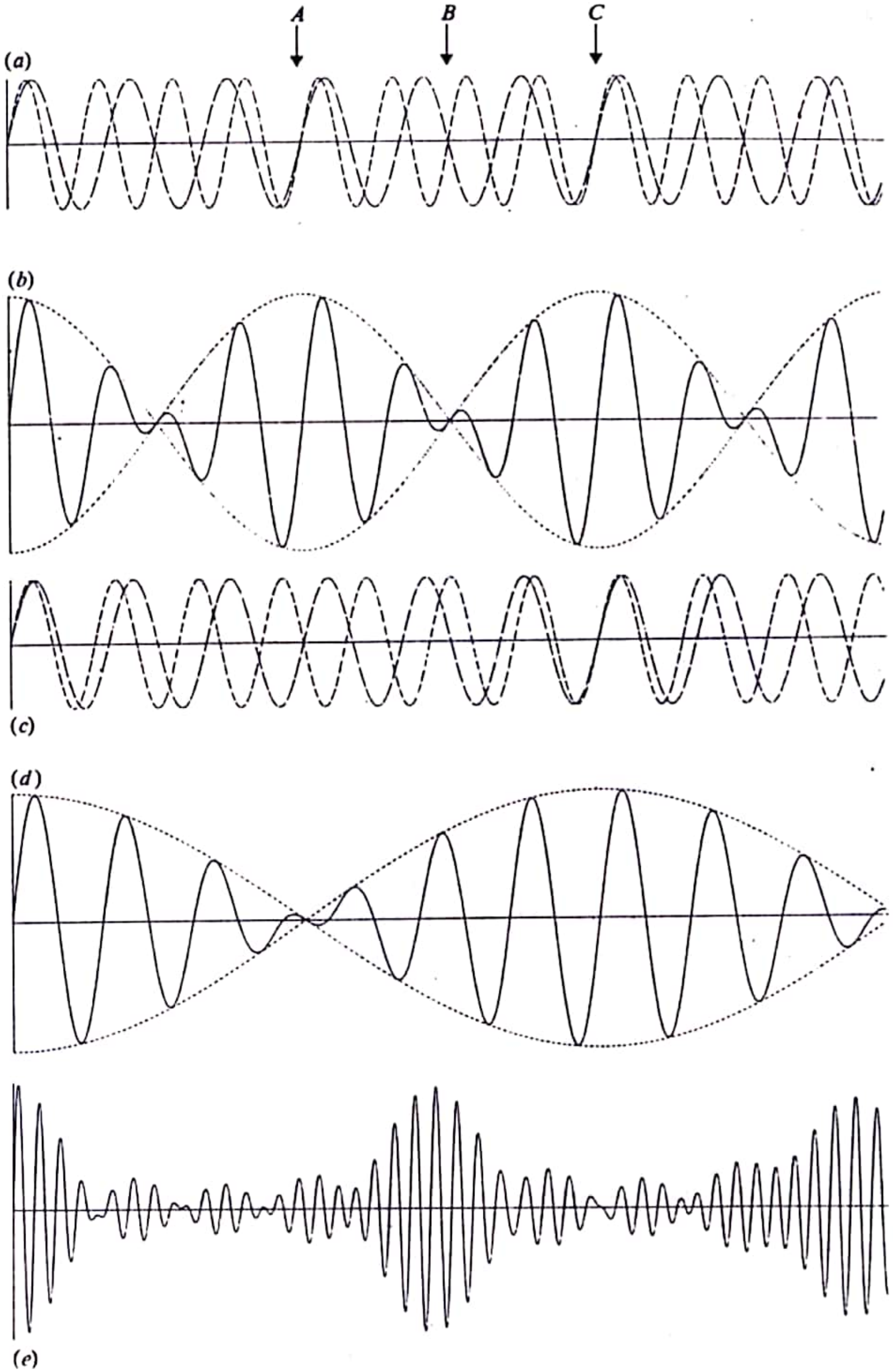


Figure 1.18 Adding of sine waves. (*a*) and (*c*) show the superposition of two sine waves with slightly different frequency, with (*b*) and (*d*) their sums; (*e*) shows the summation of five sine waves with different frequencies.

Mathematically it is simple, but tedious, to resolve a combined wave such as Fig. 1.18(*b*) into its components. Essentially each component wave has its own frequency and maximum amplitude, so two components require us to evaluate four unknowns from the composite curve. In principle, observation of the time domain signal at four points and solution of four simultaneous equations will yield the information we seek.

Adding more than two sine waves complicates the resultant combined wave and makes the resolution into components even more tedious, but does not change the principle. Figure 1.18(*e*) shows the result of superimposing five sine waves each of slightly different frequency. It would need 10 measured points and the solution of 10 simultaneous equations to determine the frequency and relative amplitude of each component. Fortunately there is a simple and quite general way to resolve a complex wave into its frequency components; this is the mathematical process known as the Fourier transform, named after the French mathematician Jean Baptiste Fourier who developed the method in the early 1800s. Even more fortunately we do not need to know how the process works: it suffices to say that it is essentially a matter of integration of the complex waveform, and that it may be carried out very conveniently nowadays by computer.

As an example of its operation let us consider the complex waveform of Fig. 1.18(*b*) and imagine that a suitable detector is responding to this waveform. A computer receiving the detector output might typically be set to sample it once every millisecond and to store, say, 2000 samplings in separate memory locations: it would thus need to collect the signal for just two seconds. The computer would then apply the Fourier transform process to the stored data, taking a further second or so, and the component sine wave frequencies and intensities would be displayed. Conventionally the display would not take the form of Fig. 1.18(*a*), where the actual periodic variation of the waves is shown, but would simply be the *spectrum* of the waves, i.e., two very sharp peaks of equal height plotted on a suitable frequency scale to show where the two frequencies occur. This is shown in Fig. 1.19, where the complex wave in Fig. 1.19(*a*) (taken from Fig. 1.18(*b*)) is seen to give rise to the spectrum of Fig. 1.19(*b*). Essentially the Fourier transform has converted the *time* domain plot of Fig. 1.19(*a*) into the *frequency* domain spectrum of Fig. 1.19(*b*). The process described above would have taken, perhaps, four or five seconds only. Essentially the detector collects *all* the spectral information simultaneously, and the computer 'decodes' that information into the conventional spectrum. It is in this way that the FT method speeds the collection of spectral data, typically, by factors of 10 to 1000.

There are one or two further points to consider before we leave this basic discussion of FT spectroscopy. Firstly we must recall that real samples do not emit radiation at precise frequencies; as we saw in the previous section, each emission is more or less broadened by various processes, and

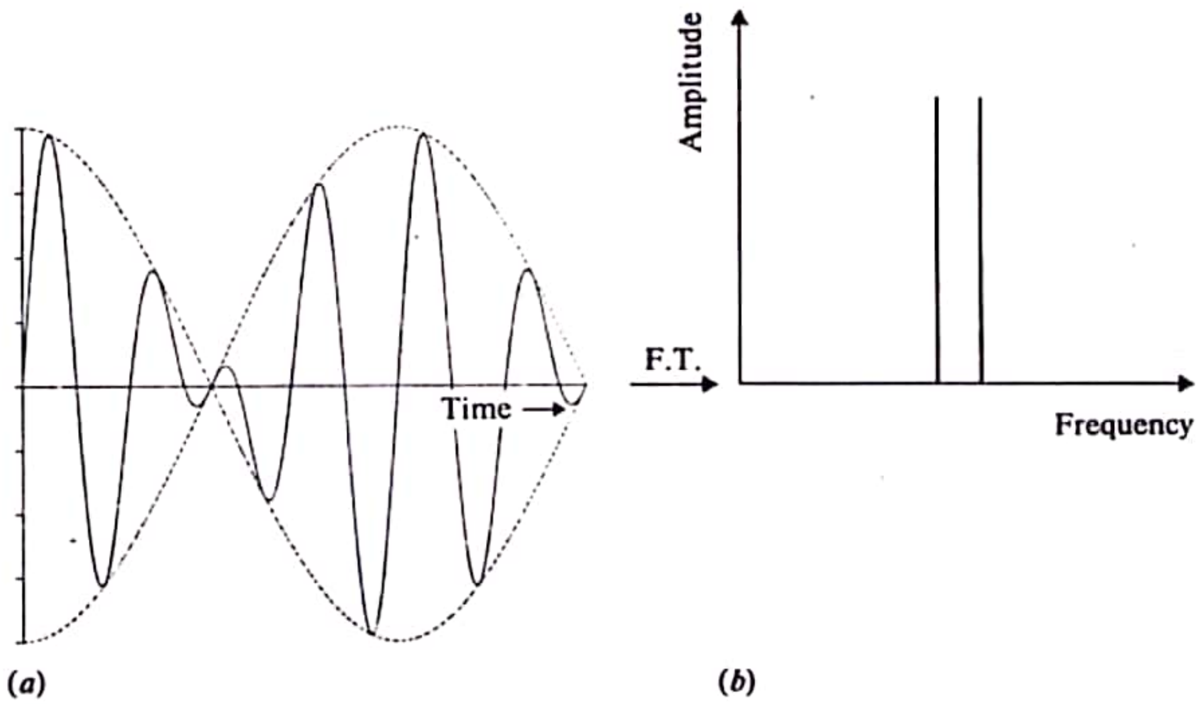


Figure 1.19 The use of the Fourier transform to convert the summed sine waves of (*a*) into their frequency spectrum, (*b*).

so each 'line' is really a small package of slightly different frequencies. We show a typical package in Fig. 1.20(*a*). In Fig. 1.20(*b*) we see that the package can be considered as arising from a large number of sample molecules radiating at exactly ν_{max}, the frequency maximum of the package, with a smaller number of molecules radiating at frequencies away from that maximum, the number decreasing as the separation increases. Now, if we want to discover the total signal emitted by such a package we could, if we had the time, plot out a sine wave for each frequency using an intensity proportional to the number of molecules radiating at that frequency, and then add all the sine waves together. We are fortunately spared this task because it turns out that the Fourier transform is a reciprocal process; just as FT converts a time domain signal to a frequency domain spectrum, so it will carry out the reverse conversion. Thus if we supply the frequency curve of Fig. 1.20(*a*) to a computer and carry out the FT, the resultant display will be exactly the same as adding the component sine waves. The result is shown in Fig. 1.20(*c*).

We see that a detector receiving the total radiation from a single broad-line emission will show an oscillating signal whose overall amplitude decays smoothly to zero. The oscillation is the beat pattern set up by all the superimposed, but slightly different, sine waves emitted by the samples; and the signal decays because, if we imagine all the waves in the package to be 'in step' initially, after some time has elapsed the many different frequencies concerned will be very much out of step, and on average half will have their amplitudes in the positive sense and half in the negative, thus giving a

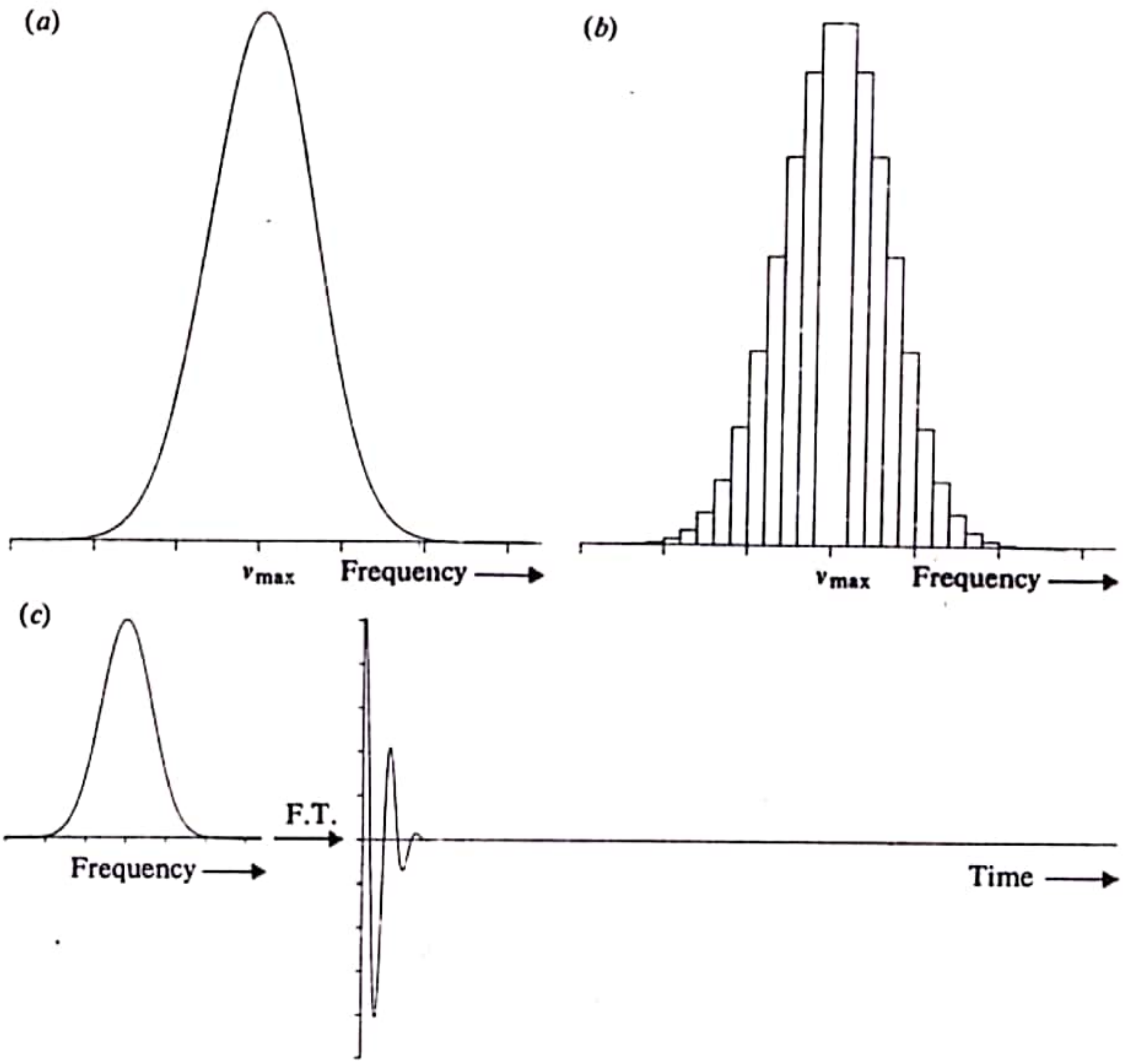


Figure 1.20 (*a*) shows the frequency distribution of a broad spectral line and (*b*) an approximate histogram of the frequencies; (*c*) is the Fourier transform of (*a*).

resultant sum of zero. Another way to think of this is to remember that two waves setting out in step with an infinitesimally small difference in frequency will take an infinite time to get back in step again, i.e., they will never do so. The distribution of Fig. 1.20(*a*) has many infinitely close frequencies within it and so, after a few cycles, none of the individual waves ever get back into step again. If the band had been *infinitely* broad, i.e., containing an infinite number of infinitesimally close neighbours, none would have ever been in step after the first instant, and the FT of such a 'white' source is a single decaying signal with no beats. We shall return to this in a moment.

The corollary of these arguments is that the *rate of decay* of the overall signal is dependent on the *width* of the original spectral peak. This is illustrated in Figs. 1.21(*a*) and (*b*) where (*a*) shows the FT of a relatively narrow signal and (*b*) that of a broader signal at the same central frequency.

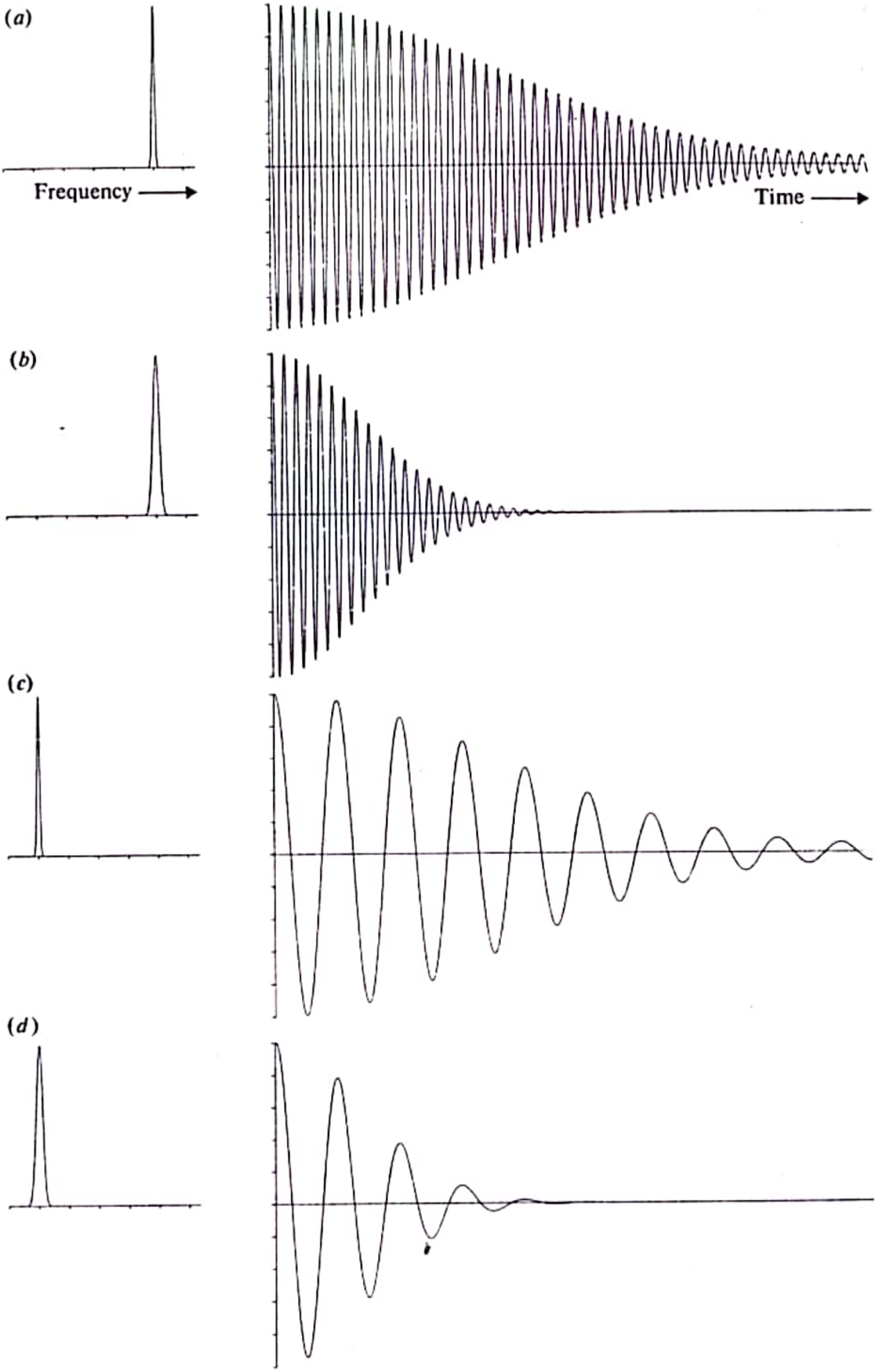


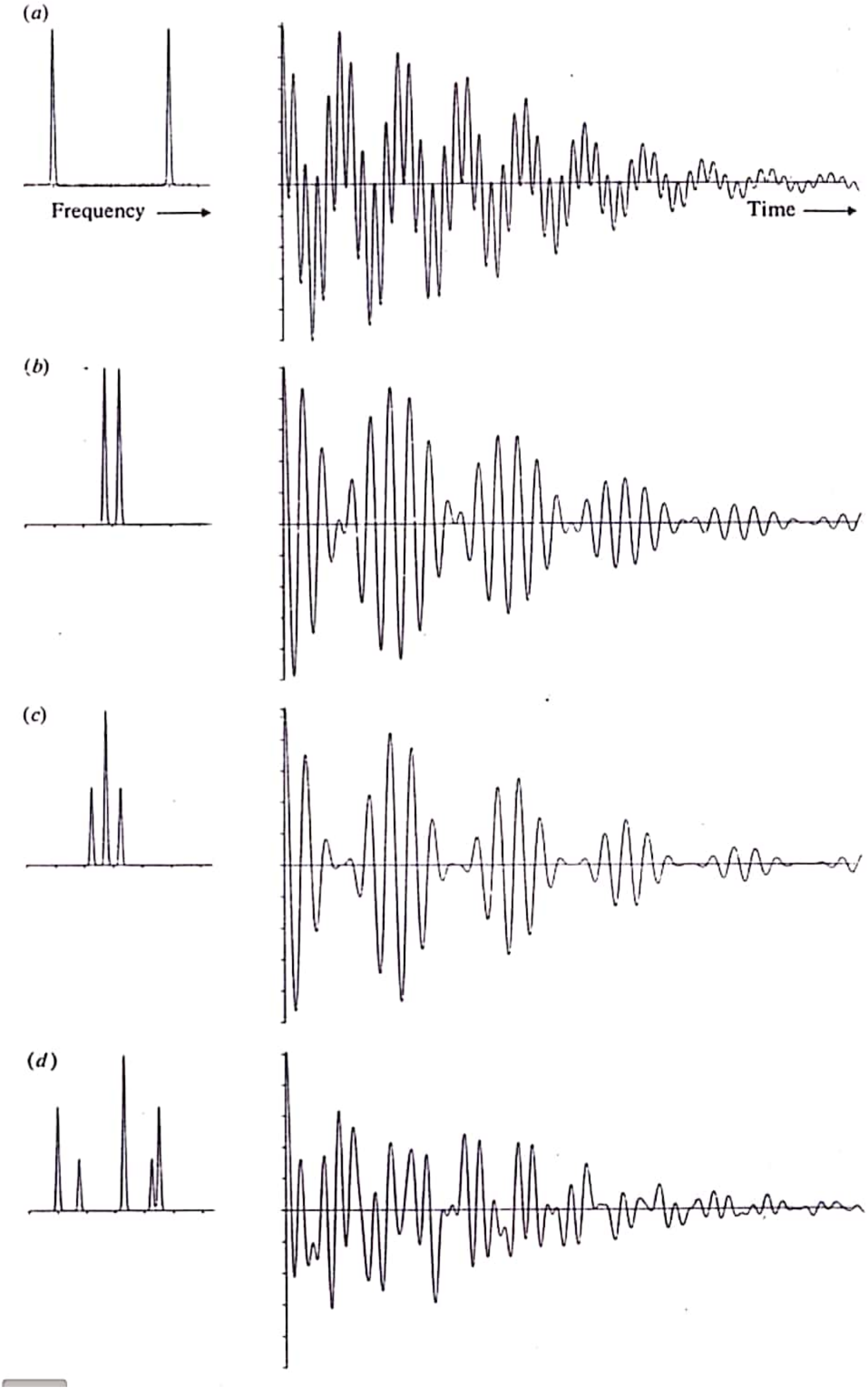
Figure 1.21 Showing the variation in the time domain signal from a spectral line as its position and breadth vary.

The beat frequency is identical, but the decay is more rapid in the latter. On the other hand, Figs. 1.21(*c*) and (*d*) show the FT of two more lines with peaks the same *width* as in Fig. 1.21(*a*) and (*b*) respectively, but at a different central *frequency*. We see that increasing the frequency of the line gives rise to an increased beat frequency. In general it is clear that the position and width of a frequency package can be recovered from the time domain signal by FT.

Next we must consider the situation when a sample emits radiation at more than one frequency, i.e., has more than one spectral peak. Not surprisingly the overall result is again the summation of the individual peaks, and beat patterns of varying complexity are built up. Thus Fig. 1.22(*a*) shows the time domain signal detected from two separate spectral peaks, choosing the frequencies used in Fig. 1.21(*a*) and (*c*). Figure 1.22(*b*) shows the effect of moving the two peaks close together. The beat pattern becomes more pronounced if three spectral lines are involved (Fig. 1.22(*c*)), and rather complex when several randomly spaced lines of different intensities are emitted, as in Fig. 1.22(*d*). As before, however, we should remember that brief observation of the signals whose patterns are shown on the right of Fig. 1.22 can be rapidly Fourier-transformed into their resultant spectra shown on the left.

Finally, although we stated initially that the FT process is most easily visualized in terms of emission of radiation, the technique is just as readily applied to absorption. We have already seen that a 'white' source would show a single decay signal with no beats; an approximation to this is given in Fig. 1.23(*a*), where a very broad emission line (which can be considered as a white source covering a limited region of the spectrum) and its Fourier transform are shown. We can now imagine an absorbing sample making a 'hole' in this radiation, as approximated by the left-hand side of Fig. 1.23(*b*), with its resulting FT shown on the right. Although we may find it difficult to imagine Fourier-transforming (or even just adding up) the *absence* of radiation at a particular frequency, in practice a detector will collect a perfectly sensible signal which can be stored by a computer, transformed, and displayed as the normal adsorption spectrum. The experimental technique for absorption FT spectroscopy in the infra-red region is described briefly in Sec. 3.8.

We see, then, that the FT method allows us to record spectra much more rapidly than the conventional sweep technique. This in itself is valuable; spectrometers are costly instruments, and the more work we can get from them in a given time, the more justified is the initial investment. But rapid data collection brings other benefits, for example, in being able to record the spectra of transient species such as unstable molecules or intermediates in a chemical reaction. Since the technique essentially reduces the


(a)
Frequency
Time
(b)
(c)
(d)

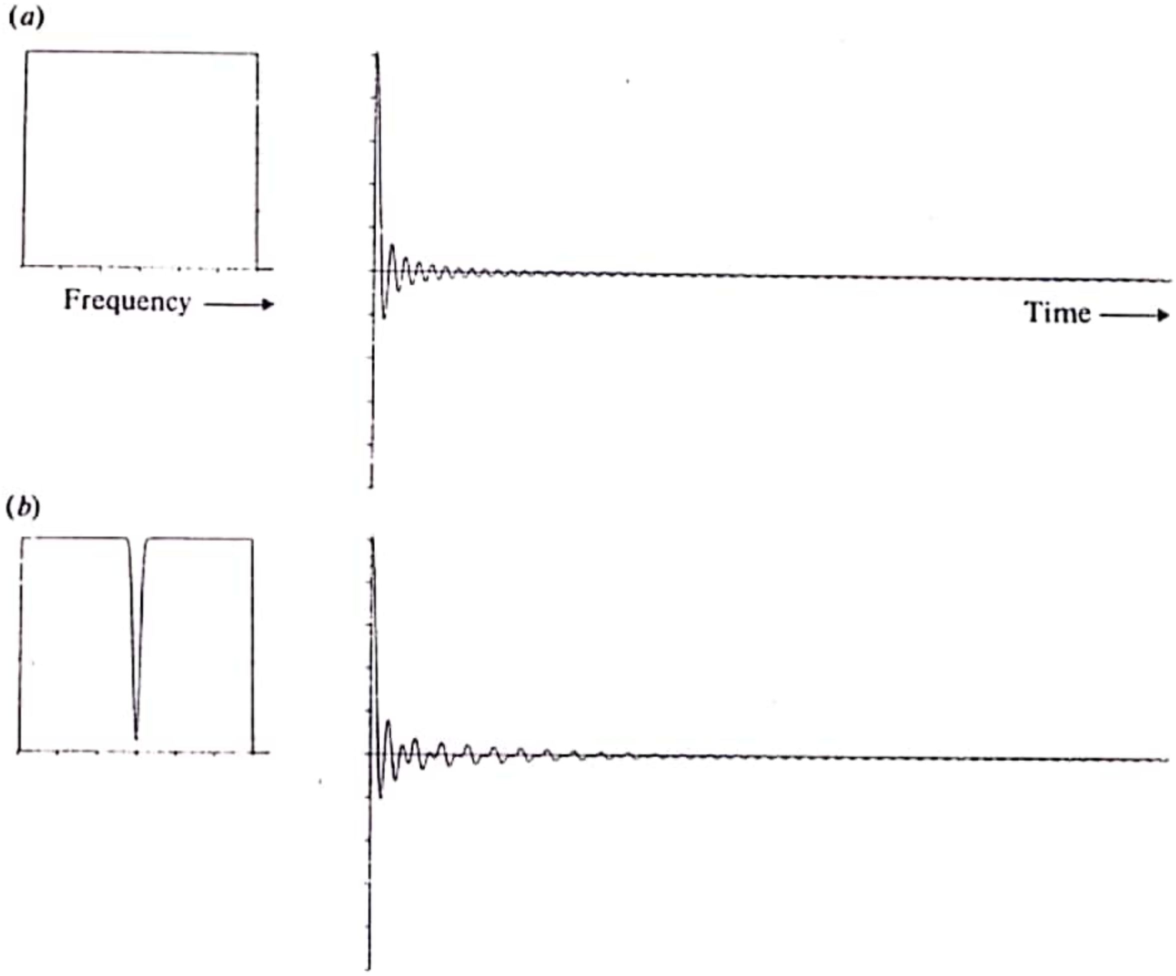


Figure 1.23 (*a*) An approximation to a 'white' source and its Fourier transform. (*b*) The effect on the Fourier transform of an absorption from the 'white' source.

time spent obtaining a spectrum from minutes to seconds or even fractions of a second, it vastly increases the range of materials which can be studied. There are other advantages in using FT instruments, but we shall leave discussion of them until the relevant chapters on magnetic resonance and infra-red spectroscopy.

1.9 ENHANCEMENT OF SPECTRA: COMPUTER AVERAGING

We have already mentioned, in Sec. 1.6, that the problem of background noise imposes a limitation on the sensitivity of any spectroscopic technique—unless a real signal peak stands out clearly from noise fluctuations it is impossible to be sure that it *is* a signal. A signal-to-noise (S/N) ratio of 3 or 4 is usually reckoned necessary for unambiguous recognition of a signal. There are several ways in which S/N can be improved for a given sample, but all require the expenditure of time. Thus it is possible electronically to damp out oscillations of the recorder pen so that it is less susceptible to high-frequency noise. The baseline of the spectrum will then be smoother, but, because the pen responds more slowly to any change (including changes in signal), one must sweep more slowly across the spectrum. Nor is FT spectroscopy immune from noise—detector and amplifier noises occur during the collection of data, and are transformed into spurious frequencies in the spectrum.

The advent of cheaper and more powerful computers offers another method of signal enhancement, known as 'computer averaging of transients' or the CAT technique, which involves recording the spectrum stepwise into a computer. Of course, this is already done if FT is intended, but it is just as easy to sample a frequency domain spectrum at, say, 2000 closely spaced points, and to store the intensity at each point in 2000 separate computer memory locations. This process may then be repeated as many times as we wish, but each time *adding* the new data into that already existing. Although in any one scan a weak signal may not be visible above the noise level, after n summed scans the signal will be n times larger in the store, whereas the noise, being random, will sometimes contribute to the store in a positive sense and sometimes negatively, so it will accumulate less rapidly. In fact it may be shown that n scans increase the noise level in the store by $n^{1/2}$, so the net gain in S/N is $n/n^{1/2} = n^{1/2}$.

If a single scan takes several minutes, as is usually the case in conventional frequency-sweep spectroscopy, the necessity to store 100 scans in order to give an improvement in S/N by a factor of 10 is rather costly in instrument time, so CAT techniques are not often applied to such measurements. However, the combination of CAT with FT is very powerful indeed. Here one time-domain scan can be completed in a second or two, and 100 scans will only occupy a couple of minutes; thus a tenfold gain in S/N can be achieved in a total time often less than that required for a non-enhanced spectrum by ordinary sweep methods. So useful is the combination of CAT with FT that virtually all FT spectrometers are routinely equipped with CAT facilities.

Other benefits follow from the addition of a computer to a spectrometer. The spectrum of a solvent or other background can be stored in the computer and subtracted from the observed spectrum in order to isolate the spectrum of the substance, or peak intensities can be automatically measured and converted to sample concentrations. Even the operation of the spectrometer itself can usefully be entrusted to the computer—samples can be changed automatically, and the optimum operating conditions can be determined and set for each new sample.

1.10 STIMULATED EMISSION: LASERS

We have already mentioned that, once radiation has been absorbed by a sample, the sample can lose its excess energy either by thermal collisions or by re-emission of radiation. In this section we shall consider the latter process in more detail, because it leads to the very important topic of laser radiation.

Radiation may be emitted by an excited molecule or atom either *spontaneously* or as the result of some stimulus acting on the molecule, called *stimulated emission*. Which of these two processes is most likely to occur in any given case depends on the energy jump involved, i.e., on the frequency of the radiation being emitted. For high-frequency transitions (infra-red, visible, and ultra-violet upwards) spontaneous emission is by far the most likely; conversely, for low-frequency changes (microwave and magnetic resonance) spontaneous emission is unlikely and, if the right conditions obtain, stimulated emission will occur.

Stimulated emission is a resonance phenomenon—an excited state drops to the ground state (emitting radiation of frequency $\nu = \Delta E/h$, where ΔE is the energy gap), only when a photon (i.e., radiation) of the same frequency ν interacts with the system. We illustrate the situation in Fig. 1.24. On the left, in both (*a*) and (*b*), we show the excitation of a molecule by absorption of radiation of frequency $\nu_{\text{ex.}}$. At the right in (*a*) we show spon-

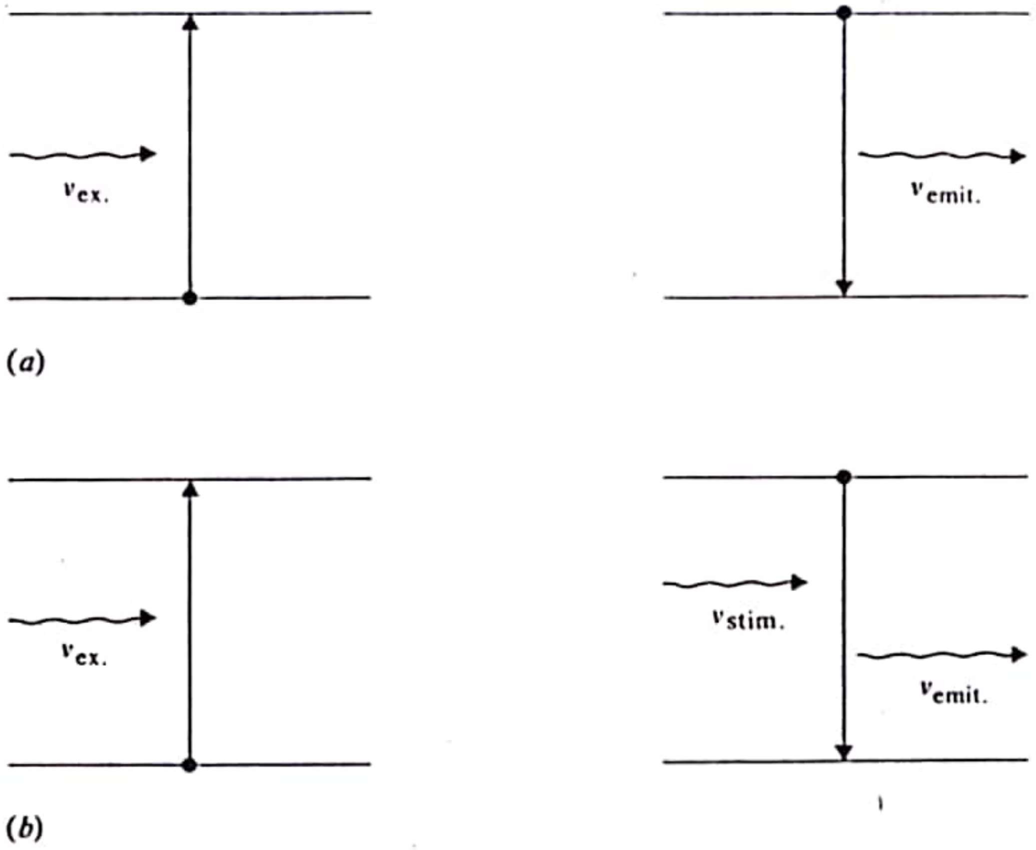


Figure 1.24 Showing (*a*) spontaneous and (*b*) stimulated emission from an excited energy state.

taneous emission, when radiation $\nu_{\text{emit.}}$ is spontaneously given out, and, in (*b*) stimulated emission where a photon of frequency $\nu_{\text{stim.}}$ interacts with the excited state and causes radiation of frequency $\nu_{\text{emit.}}$ to be released. Note particularly that, although we have given different subscripts to $\nu_{\text{ex.}}$, $\nu_{\text{emit.}}$, and $\nu_{\text{stim.}}$ in order to indicate their origins, they all represent *exactly the same frequency*, the frequency $\Delta E/h$.

Radiation emitted under stimulation of this sort has three very important qualities. Firstly it is of a very *precisely defined* frequency: the excited state does not spontaneously decay, so it is inherently long-lived, which implies (see the discussion of Heisenberg uncertainty in Sec. 1.7.1) a narrow energy level. Secondly the emitted radiation is *in phase* with the stimulating radiation: the excited state is stimulated to emit by interaction with the oscillating electromagnetic field of $\nu_{\text{stim.}}$, so it is not surprising that the maximum amplitude of the emitted wave coincides with that of $\nu_{\text{stim.}}$. And, since the waves are exactly the same frequency, they remain in phase as they leave the sample. Finally, the stimulating and emitted radiation are *coherent*, which means that they travel in precisely the same direction. In contrast *spontaneous* emission can occur at any time (so each emitted photon is not necessarily in phase with any other), in any direction, and within a more or less broad range of frequencies.

Of course the stimulating radiation of Fig. 1.24 is still present in the system after emission has occurred—it is in no way absorbed—so it can go on to interact with another excited molecule to induce more emission. Equally the emitted radiation has the right frequency to stimulate emission from yet another excited molecule. Clearly, all the time a supply of excited molecules exists, this process is likely to cascade and a great deal of radiation may be emitted coherently. This *amplification* of the original stimulating photon is reflected in the name of the process—*l*ight *a*mplification by *s*timulated *e*mission of *r*adiation, or *laser*.

In fact, as we have said, light (or, more properly, visible radiation) is far more likely to be emitted *spontaneously*, and so not to have the coherent properties of laser radiation. It was in the microwave region that the first successful amplification by stimulated emission was performed (and the process was therefore christened *maser*, standing for *m*icrowave *a*mplification by *s*timulated *e*mission of *r*adiation). For the process to be possible in higher-frequency regions it is necessary to find systems with long-lived excited states so that stimulated, rather than spontaneous, emission may predominate, and this may only be achieved if more than two energy levels are involved.

Consider the three energy levels of Fig. 1.25(*a*). Excitation from the ground state, level 1, to the normal excited state, level 2, can occur by absorption of radiation, as usual. Provided that, as well as emitting spontaneously, level 2 can transfer some molecules into a metastable state (level 3) which cannot easily revert spontaneously to the ground state, then the

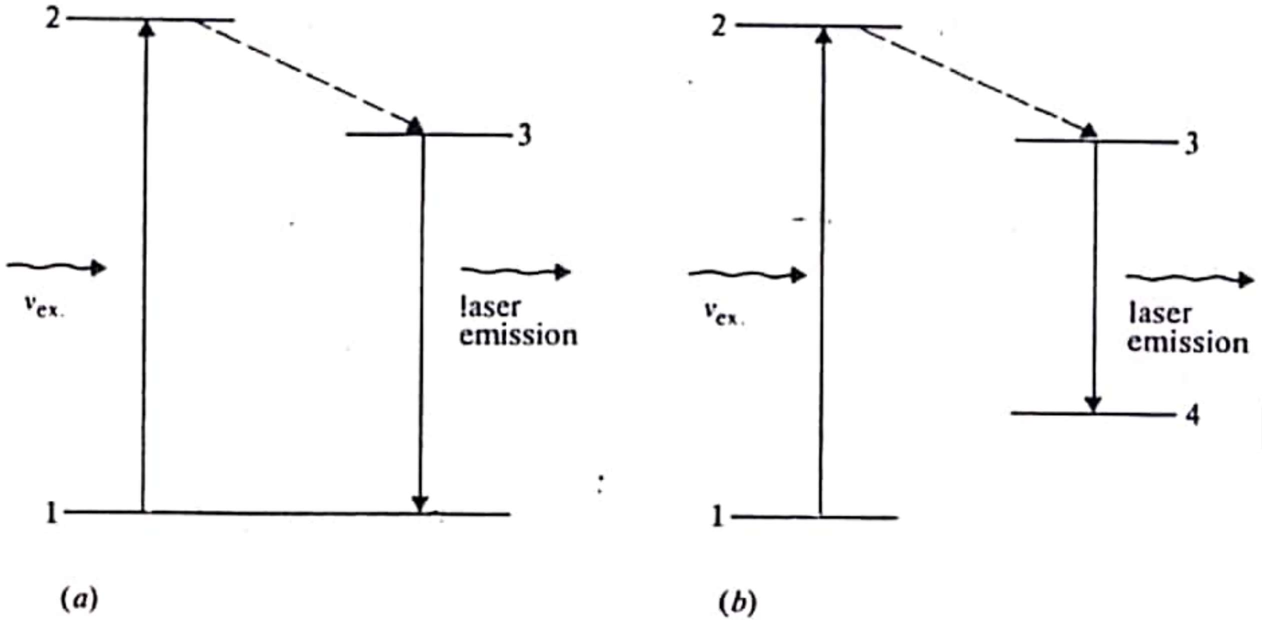


Figure 1.25 Showing the energy levels of (*a*) a three-level and (*b*) a four-level system operating as a laser.

population of level 3 builds up, and laser action becomes feasible. The ruby laser is an example of this type of three-level system. Ruby is basically aluminium oxide containing a trace (about 0·05 per cent) of chromium ions, which gives it its characteristic colour. A discharge tube wound round a rod of ruby is flashed very briefly to raise the chromium ions into an excited electronic state; they drop rapidly by thermal, non-radiative processes, into a metastable state some 14 000 cm^{-1} above the ground state, and they then revert to the ground state, by laser action, emitting radiation at about 690 nm wavelength. The decay from excited to metastable state releases quite large amounts of heat, so the ruby must be allowed to cool before another excitation cycle is commenced; it is thus operated as a pulsed laser.

In some cases the laser emission arises by reversion of level 3 to a lower state other than the original level 1, as shown in the four-level system of Fig. 1.25(*b*). This situation occurs particularly when, as is quite possible, levels 3 and 4 belong to an entirely *different* molecular species from levels 1 and 2. For example in the helium–neon laser it is the helium atoms which are initially excited (level 1 to 2), and which then transfer their excitation energy to neon atoms by collisions; this can happen only because neon has an excited state with almost exactly the same energy as the excited state of helium, so a resonance transfer of energy is possible. It also happens that the excited state of neon does not readily undergo an ordinary spectroscopic transition back to its ground state, so the conditions are ideal for laser action. Provided the exciting radiation for helium is maintained, so replenishing the population of excited helium atoms, this type of laser can operate continuously. We shall discuss the precise electronic energy levels involved in more detail in Chapter 5.

The extreme coherence of laser radiation makes it ideal in applications like communications, distance measurement, etc., but from the spectroscopic point of view its very narrow frequency spread makes it directly useful in only one area. This is Raman spectroscopy where, as we shall see in Chapter 4, the requirement is for an intense monochromatic source. For this the laser—almost *any* laser—is ideal.

For virtually all other spectroscopic measurements, however, either a wide-band or a tunable source is desirable. Lasers cannot be wide-band (although the CO_2 laser, to be described in Sec. 3.8.4, comes close to this), but recent developments have led to their becoming tunable. In order to change the emission frequency of a laser system it is necessary to be able to modify the energy levels between which transitions take place. Solids emitting laser radiation can be subjected to varying temperatures or pressures in order smoothly to change the relevant energies, but the extent of such changes is relatively small. More usefully, lasers made from coloured organic substances in solution—the so-called dye lasers—are widely tunable. In these the active material is usually a rare-earth ion held in the centre of an organic 'ligand' which complexes firmly to the ion. The tuning is brought about by changes in temperature, solvent, or concentration, and it is now possible to produce laser emission anywhere from the near infra-red to the ultra-violet. The possibilities for using such intense, sharply defined but variable-frequency sources routinely in spectroscopy are tremendous, and this technique will certainly become increasingly important in the near future.

PROBLEMS

(Useful constants: $N = 6{\cdot}023 \times 10^{23}$ mol^{-1}; $k = 1{\cdot}381 \times 10^{-23}$ J K^{-1}; $h = 6{\cdot}626 \times 10^{-34}$ J s; $c = 2{\cdot}998 \times 10^{8}$ m s^{-1}.)

1.1 The wavelength of the radiation absorbed during a particular spectroscopic transition is observed to be 10 μm. Express this in frequency (Hz) and in wavenumber (cm^{-1}), and calculate the energy change during the transition in both joules per molecule and joules per mole. If the energy change were twice as large, what would be the wavelength of the corresponding radiation?

1.2 Which of the following molecules would show (*a*) a microwave (rotational) spectrum, (*b*) an infra-red (vibrational) spectrum: Br_2, HBr, CS_2?

1.3 A particular molecule is known to undergo spectroscopic transitions between the ground state and two excited states, (*a*) and (*b*), its lifetime in (*a*) being about 10 s, and in (*b*) about 0·1 s. Calculate the approximate uncertainty in the excited state energy levels and the widths of the associated spectral 'lines' in hertz.

1.4 A certain transition involves an energy change of $4{\cdot}005 \times 10^{-22}$ J molecule^{-1}. If there are 1000 molecules in the ground state, what is the approximate equilibrium population of the excited state at temperatures of (*a*) 29 K, (*b*) 145 K, (*c*) 290 K and (*d*) 2900 K? What would your answer have been if the energy change were 10 times greater?