Semester VI
Paper M 601 Spectroscopy

Unit 6.1 Introduction to Spectroscopy (Marks 10)

The nature of electromagnetic radiation. The regions of spectrum. Mechanism of interaction of electromagnetic radiation with matter. Absorption and emission spectroscopy. Basic elements of practical spectroscopy. Representation of spectrum – the width of spectral line. Intensity of spectral lines. Selection rules for various transitions. The Beer-Lambert law, molar absorption coefficient and absorbance. Molecular motion and energy – degree of freedom. Moment of inertia.

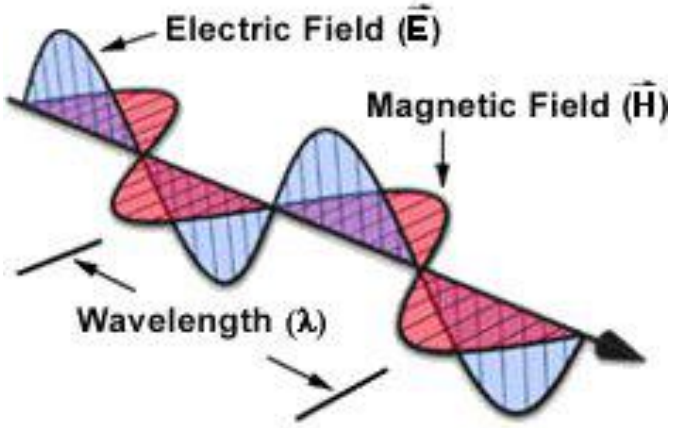
Nature of Electromagnetic Radiation – *Wave Nature*

❖Electromagnetic (EM) radiation is a form of energy propagated through free space or through a material medium in the form of electromagnetic waves.

❖EM radiation is so-named because it has electric and magnetic fields that simultaneously oscillate in planes mutually perpendicular to each other and to the direction of propagation through space.

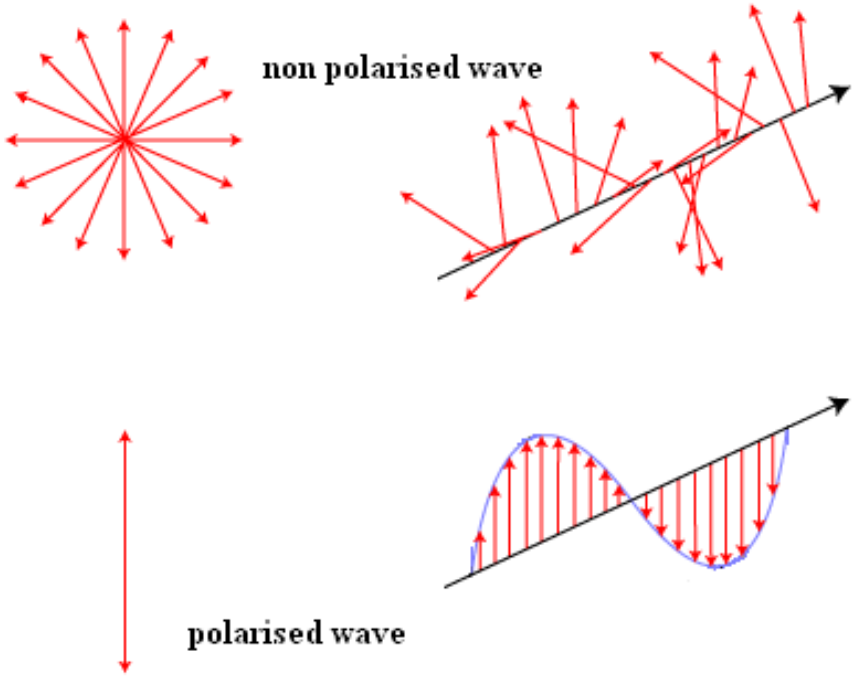
❖Electromagnetic radiation has the dual nature: its exhibits wave properties and particulate (photon) properties.

❖Wave nature of radiation: Radiation can be thought of as a traveling transverse wave.



Nature of Electromagnetic Radiation

❖As a transverse wave, EM radiation can be polarized. **Polarization is the** distribution of the electric field in the plane normal to propagation direction.

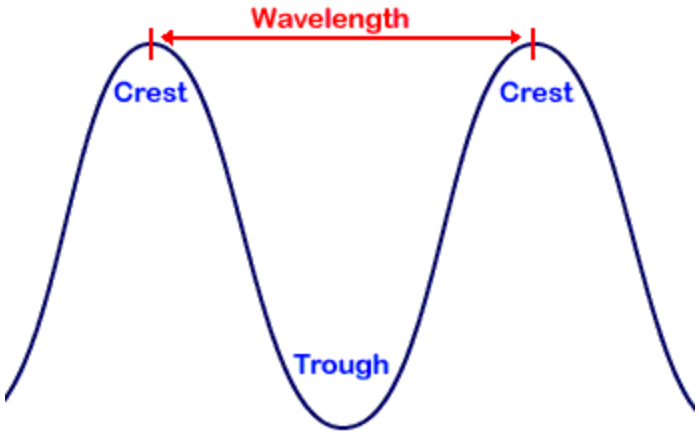


❖Waves are characterized by frequency, wavelength, speed and phase.

❖Frequency is defined as the number of waves (*cycles) per second that pass a given point* in space (symbolized by ν).

❖**Wavelength is the distance between two consecutive peaks or troughs in a wave** (symbolized by the λ).

Nature of Electromagnetic Radiation



❖Relation between λ and ν : $\lambda \times \nu = c$

❖Since all types of electromagnetic radiation travel at the speed of light, short wavelength radiation must have a high frequency.

❖Unlike speed of light and wavelength, which change as electromagnetic energy is propagated through media of different densities, frequency remains constant and is therefore a more fundamental property.

❖Wavenumber is defined as a count of the number of wave crests (or troughs) in a given unit of length (symbolized by $\tilde{\nu}$):

$$\tilde{\nu} = \nu / c = 1/\lambda$$

Nature of Electromagnetic Radiation

❖***UNITS:***

Wavelength units: length

Angstrom (A) : 1 A = $1x10^{-10}$ m;
Nanometer (nm): 1 nm=$1x10^{-9}$ m;
Micrometer (μm): 1 μm = $1x10^{-6}$ m;

Wavenumber units: inverse of length (often in cm^{-1})

❖**Frequency units: unit cycles per second 1/s (or s^{-1}) is called hertz (abbreviated Hz)**

Properties of Electromagnetic Radiation

1. The oscillating charged particles produce oscillating electric and magnetic fields which are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.

2. Electromagnetic waves do not require a medium i.e., they can travel in a vacuum too.

3. There are many kinds of electromagnetic radiation, differing from one another in terms of wavelength or frequency. This electromagnetic radiation as a whole constitutes the electromagnetic spectrum. For example radio frequency region, microwave region, infrared region, ultraviolet region, visible region etc.

4. The electromagnetic radiation is characterized based on various properties like frequency, wavelength, time period etc.

Nature of Electromagnetic Radiation – *Particle Nature*

❖Radiation can be also described in terms of particles of energy, called photons

❖The energy of a **photon is given as**

$$\varepsilon_{photon} = h\nu = hc/\lambda = hc\tilde{\nu}$$

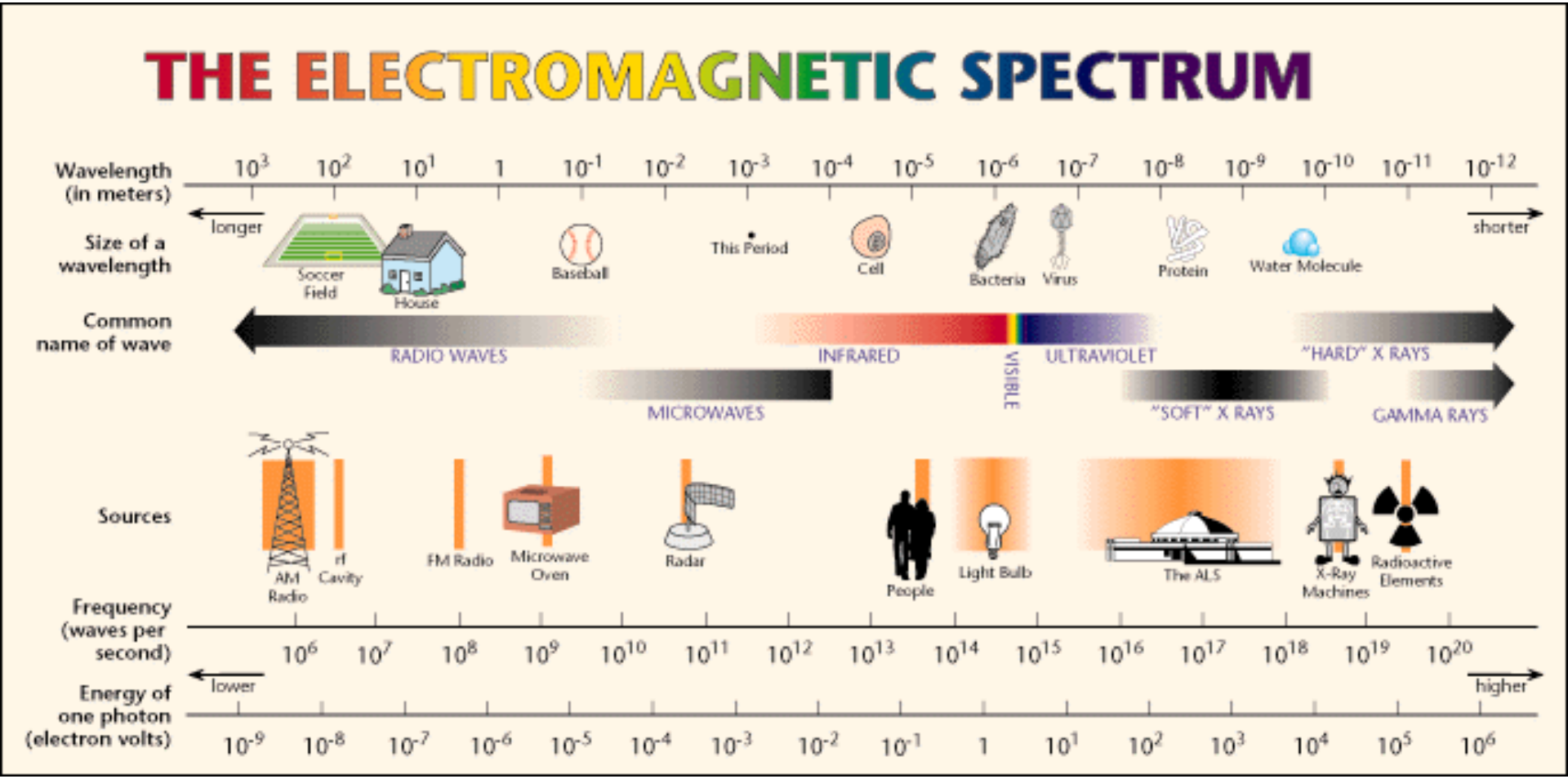
✓where ***h is Plank's constant (h = 6.6256x10^{-34} J s)***

✓Photon has energy but it has no mass and no charge.

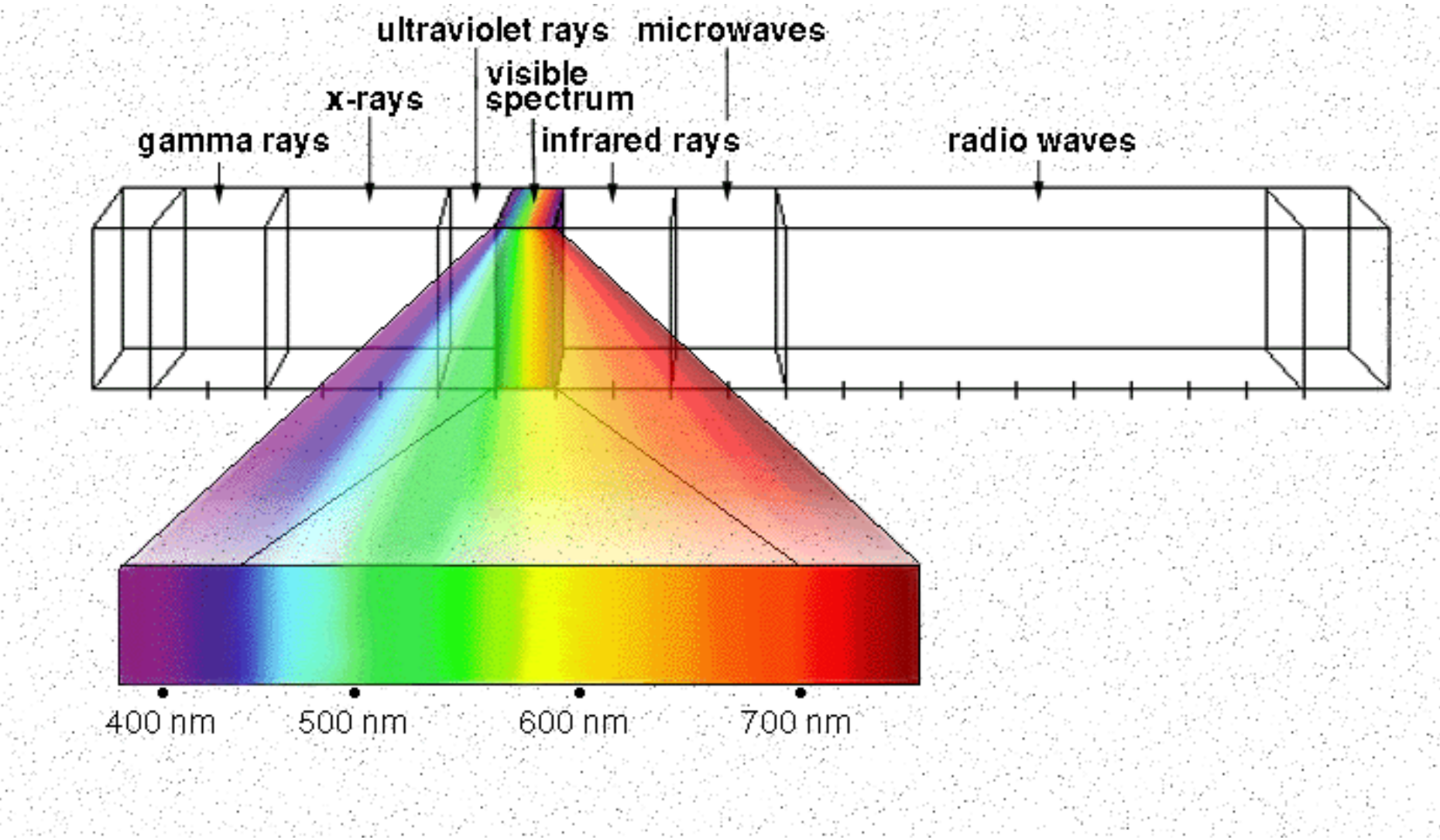
✓Relates energy of each photon of the radiation to the electromagnetic wave characteristics.

Spectrum of Electromagnetic Radiation

❖The electromagnetic **spectrum is the distribution of electromagnetic radiation according** to energy or, equivalently, according to the wavelength or frequency.



Spectrum of Electromagnetic Radiation



Spectrum of Electromagnetic Radiation

Electromagnetic Spectrum

Type of Radiation	Frequency Range (Hz)	Wavelength Range	Type of Transition
gamma-rays	10^{20}-10^{24}	<1 pm	nuclear
X-rays	10^{17}-10^{20}	1 nm-1 pm	inner electron
ultraviolet	10^{15}-10^{17}	400 nm-1 nm	outer electron
visible	4-7.5x10^{14}	750 nm-400 nm	outer electron
near-infrared	1x10^{14}-4x10^{14}	2.5 μm-750 nm	outer electron molecular vibrations
infrared	10^{13}-10^{14}	25 μm-2.5 μm	molecular vibrations
microwaves	3x10^{11}-10^{13}	1 mm-25 μm	molecular rotations, electron spin flips*
radio waves	<3x10^{11}	>1 mm	nuclear spin flips*

Absorption Spectroscopy

❖**Absorption spectroscopy** refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e., photons, from the radiating field. The intensity of the absorption varies as a function of frequency, and this variation is the absorption spectrum. Absorption spectroscopy is performed across the electromagnetic spectrum.

❖The most common arrangement is to direct a generated beam of radiation at a sample and detect the intensity of the radiation that passes through it. The transmitted energy can be used to calculate the absorption. The source, sample arrangement and detection technique vary significantly depending on the frequency range and the purpose of the experiment.

Absorption Spectroscopy

❖**Applications: Absorption spectroscopy** is employed as an analytical chemistry tool to determine the presence of a particular substance in a sample and, in many cases, to quantify the amount of the substance present. Infrared and ultraviolet–visible spectroscopy are particularly common in analytical applications. Absorption spectroscopy is also employed in studies of molecular and atomic physics, astronomical spectroscopy and remote sensing.

❖**Types of Absorption Spectroscopy:**

Sr. No	Electromagnetic Radiation	Spectroscopic type
1	X-ray	X-ray absorption spectroscopy
2	Ultraviolet–visible	UV–vis absorption spectroscopy
3	Infrared	IR absorption spectroscopy
4	Microwave	Microwave absorption spectroscopy
5	Radio wave	Electron spin resonance spectroscopy Nuclear magnetic resonance spectroscopy

Absorption Spectroscopy

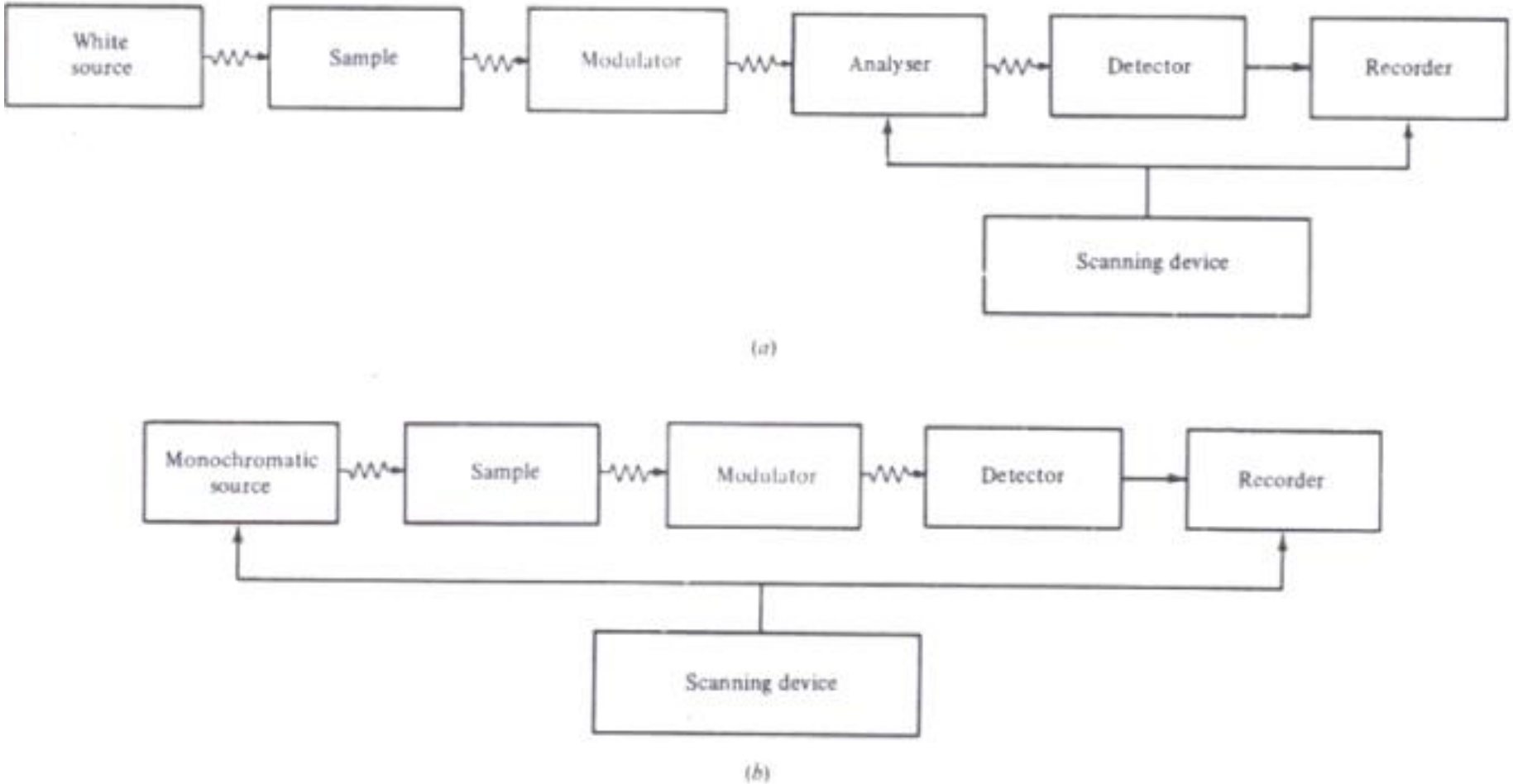
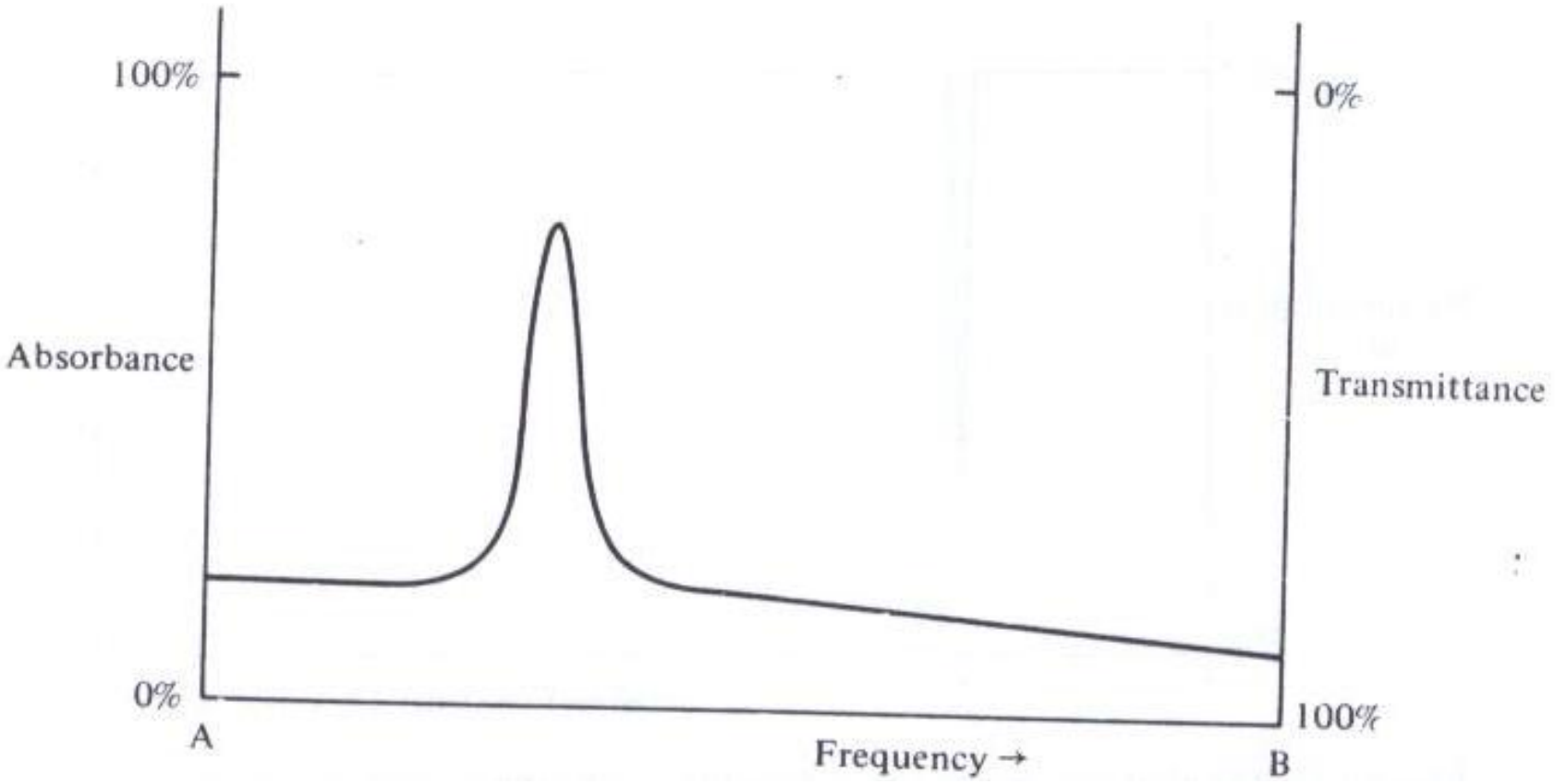


Figure 1.15 Block diagram of a typical absorption spectrometer for use in (*a*) the infra-red, visible, and ultra-violet regions where a 'white' source is available, and (*b*) the microwave and radiofrequency regions where the source can be tuned over a considerable range of frequencies.

Absorption Spectroscopy



Absorption Spectroscopy

❖**Mechanism:** A material's absorption spectrum is the fraction of incident radiation absorbed by the material over a range of frequencies. The absorption spectrum is primarily determined by the atomic and molecular composition of the material. Radiation is more likely to be absorbed at frequencies that match the energy difference between two quantum mechanical states of the molecules. The absorption that occurs due to a transition between two states is referred to as an absorption line and a spectrum is typically composed of many lines.

❖The frequencies where absorption lines occur, as well as their relative intensities, primarily depend on the electronic and molecular structure of the sample. The frequencies will also depend on the interactions between molecules in the sample, the crystal structure in solids, and on several environmental factors (e.g., temperature, pressure, electromagnetic field). The lines will also have a width and shape that are primarily determined by the spectral density or the density of states of the system.

Absorption Spectroscopy - Home Assignments

1. We have an absorption line at 642 nm. Calculate the energy of the absorbed photons.

2. Calculate the energy difference between two absorption lines occurring at 642 nm and 720 nm.

3. Calculate the frequency of following absorption lines and indicated the region of the electromagnetic spectrum.

(i) 640 nm (ii) 411 nm (iii) 180 nm (iv) 900 nm (v) 1100 nm

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Emission Spectroscopy

The **emission spectrum** of a chemical element or chemical compound is the spectrum of frequencies of electromagnetic radiation emitted due to an atom or molecule making a transition from a high energy state to a lower energy state. The photon energy of the emitted photon is equal to the energy difference between the two states. There are many possible electron transitions for each atom, and each transition has a specific energy difference. This collection of different transitions, leading to different radiated wavelengths, make up an emission spectrum. Each element's emission spectrum is unique. Therefore, spectroscopy can be used to identify elements in matter of unknown composition. Similarly, the emission spectra of molecules can be used in chemical analysis of substances. emission is the process by which a higher energy quantum mechanical state of a particle becomes converted to a lower one through the emission of a photon, resulting in the production of light. The frequency of light emitted is a function of the energy of the transition.

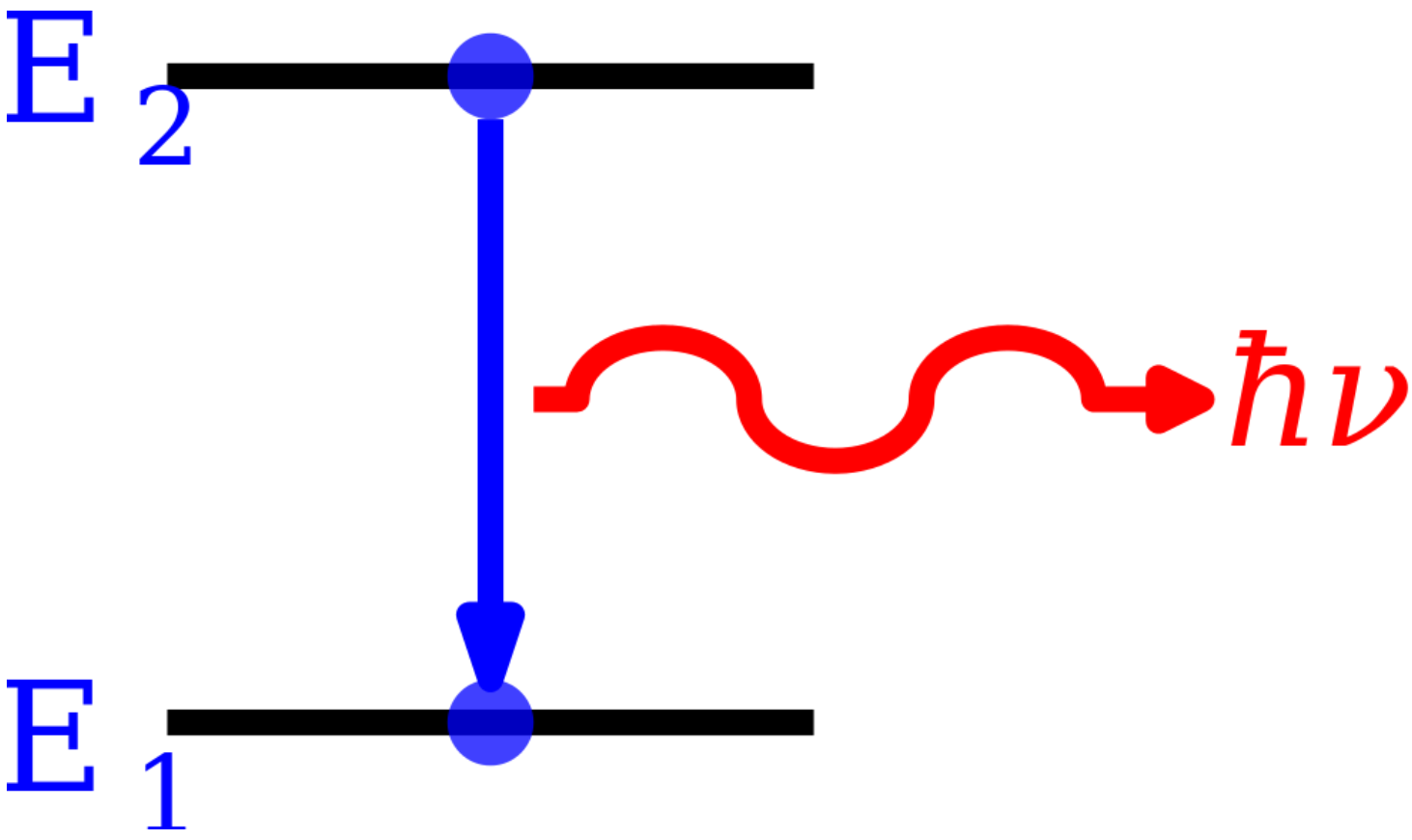
Emission Spectroscopy

When the electrons in the atom are excited, for example by being heated, the additional energy pushes the electrons to higher energy orbitals. When the electrons fall back down and leave the excited state, energy is re-emitted in the form of a photon. The wavelength (or equivalently, frequency) of the photon is determined by the difference in energy between the two states. These emitted photons form the element's spectrum. The fact that only certain colors appear in an element's atomic emission spectrum means that only certain frequencies of light are emitted. Each of these frequencies are related to energy by the formula:

$$E_{photon} = h\nu$$

Ephoton is the energy of the photon, *v* is its frequency, and h is Planck's constant. This oncludes that only photons with specific energies are emitted by the atom. The principle of the atomic emission spectrum explains the varied colors in neon signs, as well as chemical flame test results

Emission Spectroscopy



Emission Spectroscopy

❖**Mechansim:** Light consists of electromagnetic radiation of different wavelengths. Therefore, when the elements or their compounds are heated either on a flame or by an electric arc they emit energy in the form of light. Analysis of this light, with the help of a spectroscope gives us a discontinuous spectrum. A spectroscope or a spectrometer is an instrument which is used for separating the components of light, which have different wavelengths. The spectrum appears in a series of lines called the line spectrum. This line spectrum is called an atomic spectrum when it originates from an atom in elemental form. Each element has a different atomic spectrum. The production of line spectra by the atoms of an element indicate that an atom can radiate only a certain amount of energy. This leads to the conclusion that bound electrons cannot have just any amount of energy but only a certain amount of energy.

Emission Spectroscopy

❖**Applications:** The emission spectrum can be used to determine the composition of a material, since it is different for each element of the periodic table. One example is astronomical spectroscopy: identifying the composition of stars by analysing the received light. The emission spectrum characteristics of some elements are plainly visible to the naked eye when these elements are heated. For example, when platinum wire is dipped into a sodium nitrate solution and then inserted into a flame, the sodium atoms emit an amber yellow color. Similarly, when indium is inserted into a flame, the flame becomes blue. These definite characteristics allow elements to be identified by their atomic emission spectrum. Not all emitted lights are perceptible to the naked eye, as the spectrum also includes ultraviolet rays and infrared radiation. An emission spectrum is formed when an excited gas is viewed directly through a spectroscope.

Emission Spectroscopy

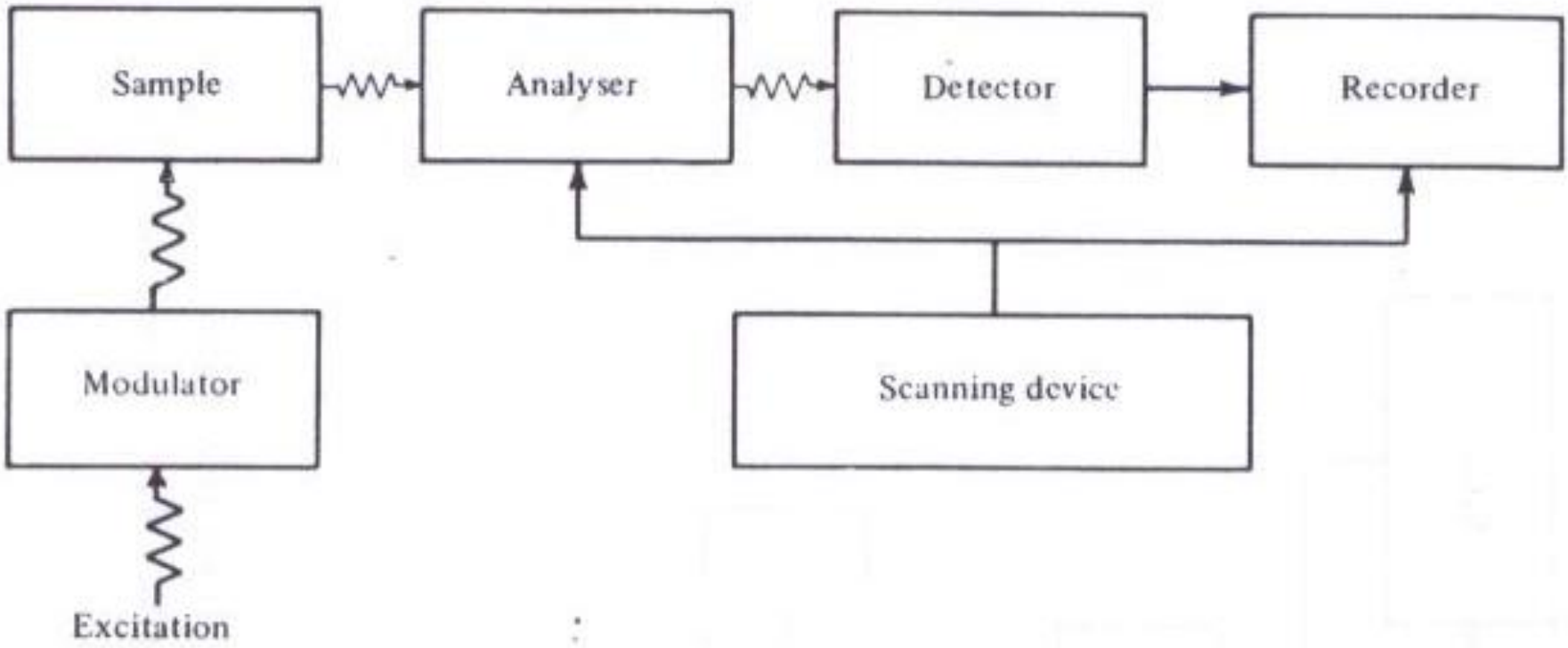


Figure 1.16 Block diagram of a typical emission spectrometer.

Representation of spectrum

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

Representation of spectrum

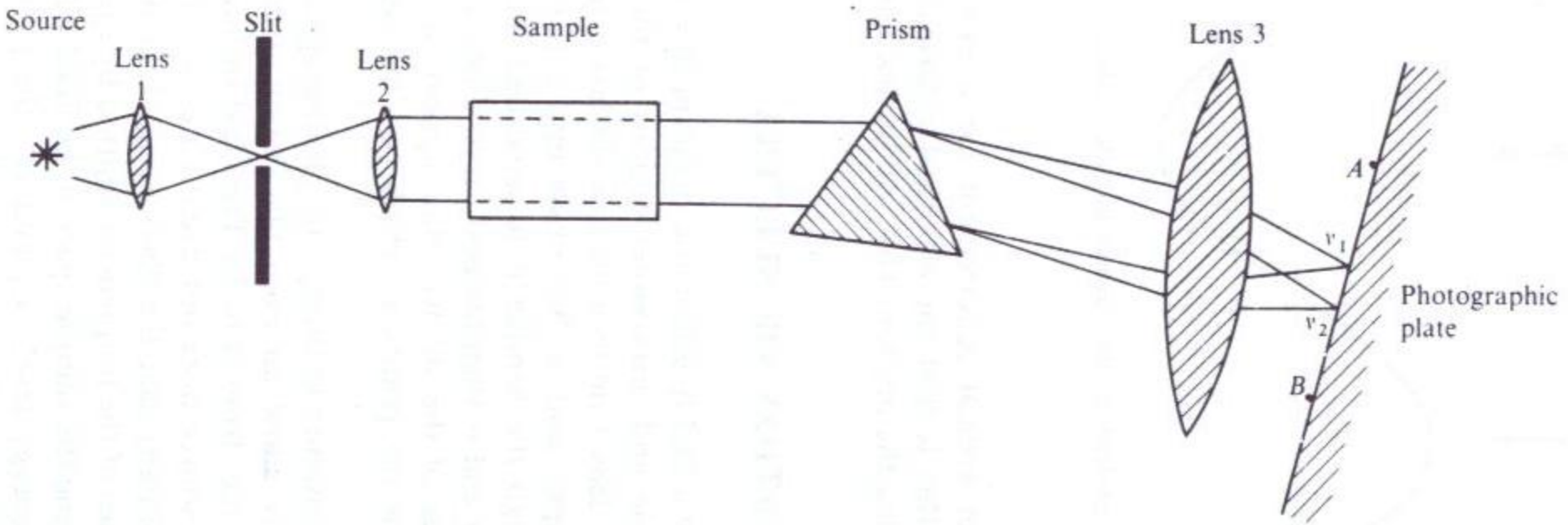


Figure 1.9 Schematic diagram of a spectrometer suitable for operation in the visible region.

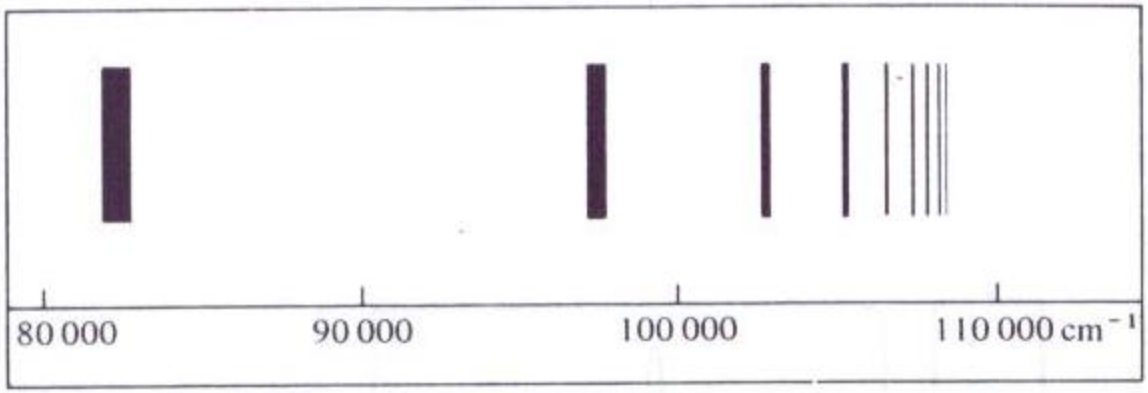


Figure 1.10 Schematic diagram of the absorption spectrum of atomic hydrogen recorded on a photographic plate.

Representation of spectrum

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.

Representation of spectrum

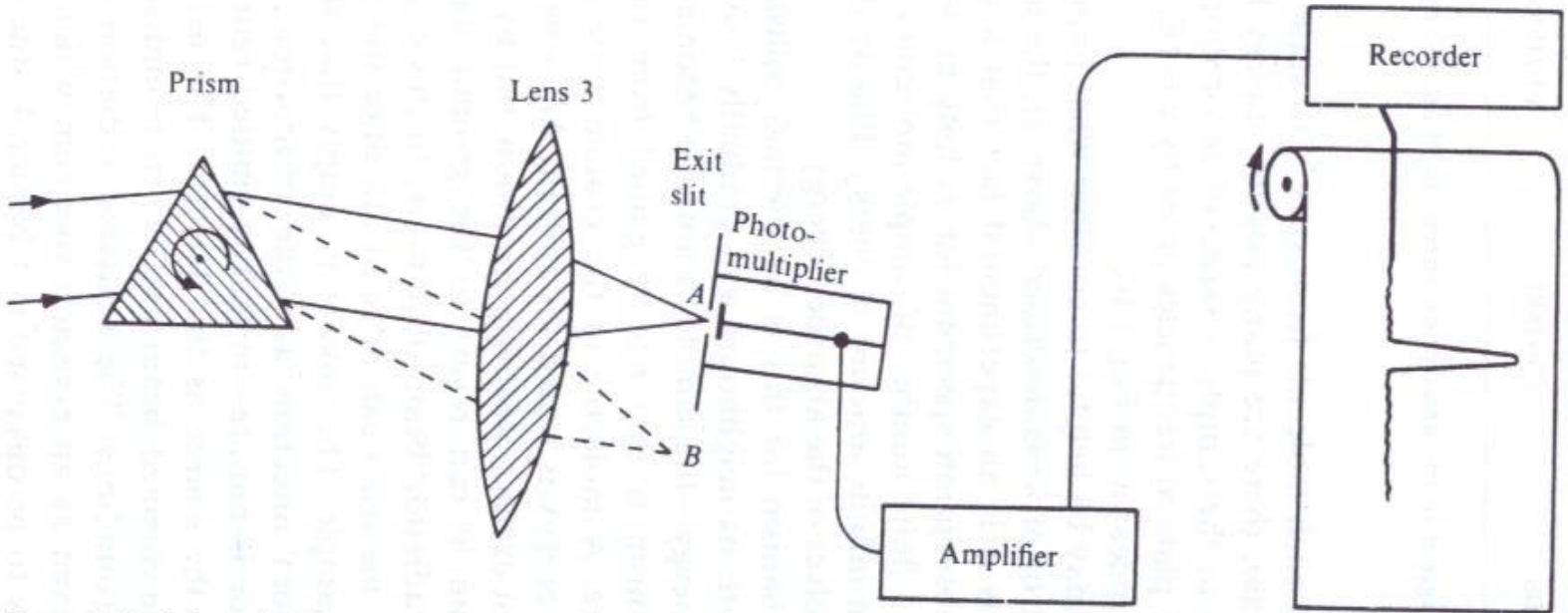


Figure 1.11 Schematic diagram of a spectrometer employing a photomultiplier or other sensitive element as detector and recording the spectr

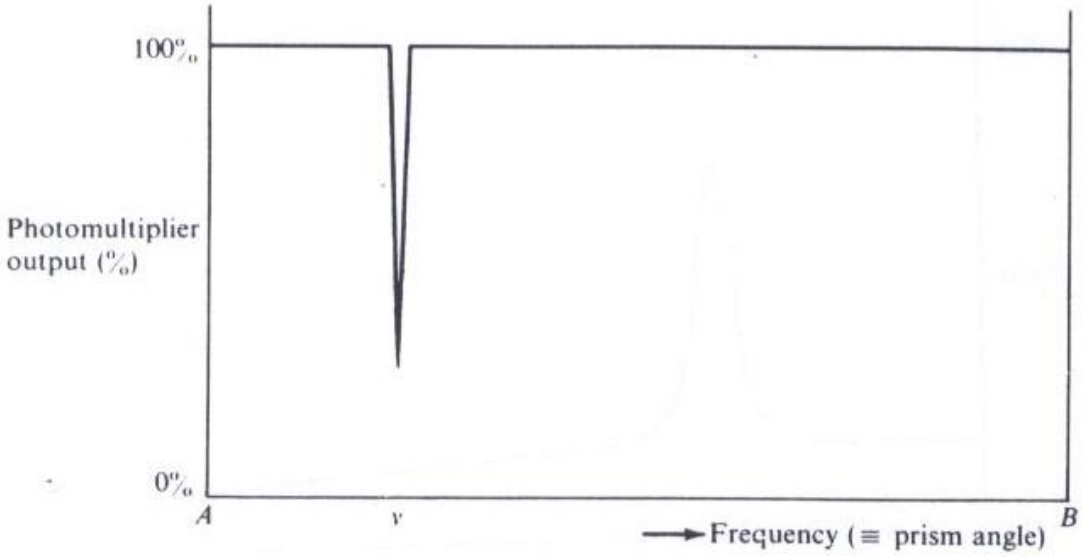


Figure 1.12 The idealized spectrum of a molecule undergoing a single transition.

Representation of spectrum

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

Representation of spectrum

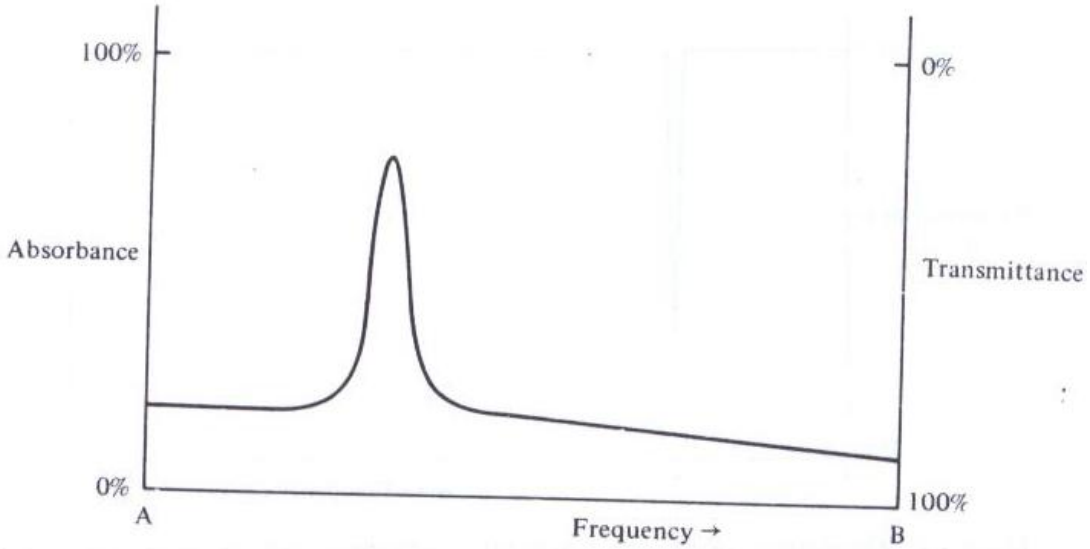


Figure 1.13 The usual appearance of the spectrum of a molecule undergoing a single transition (cf. Fig. 1.12); here the background is no longer constant and the absorption region is of finite width.

figure, too, we have plotted absorbance upwards from 0 to 100% and transmittance—its complement—downwards. This is the usual way in which such spectra are represented.

If there are again several energy levels available to the sample, it is very unlikely that there is the same probability of transition between the various levels. The question of transition probability will be discussed more fully in Sec. 1.7 but here we may note that differences in transition probability will mean that the absorbance (or transmittance) at each absorbing frequency will differ. This is shown by the varying intensities of the lines on the photographic plate of Fig. 1.10 and, more precisely, by the recorder trace of Fig. 1.14(*a*).

Representation of spectrum

Figure 1.14(*a*) shows the sort of record which is produced by most modern spectrometers, whatever the region in which they operate. One other form of presentation is often adopted, however, particularly in the microwave and radiofrequency regions, and this is to record the *derivative* of the spectral trace instead of the trace itself. The derivative of a curve is simply its slope at a given point. In calculus notation, the derivative of the spectral trace is $dA/d\nu$, where A is the absorbance. The derivative record is thus a plot of the slope $dA/d\nu$ against ν; this is shown in Fig. 1.14(*b*) corresponding to the plot of Fig. 1.14(*a*).

Although at first sight more complex, the derivative trace has advantages over the direct record in some circumstances. Firstly, it indicates rather more precisely the centre of each absorbance peak: at the centre of a peak, the A curve is horizontal, hence $dA/d\nu$ is zero, and the centres are marked by the intersection of the derivative curve with the axis. Further, for instrumental reasons, it is often better to measure the relative intensities of absorbance peaks from the derivative curve than from the direct trace.

Representation of spectrum

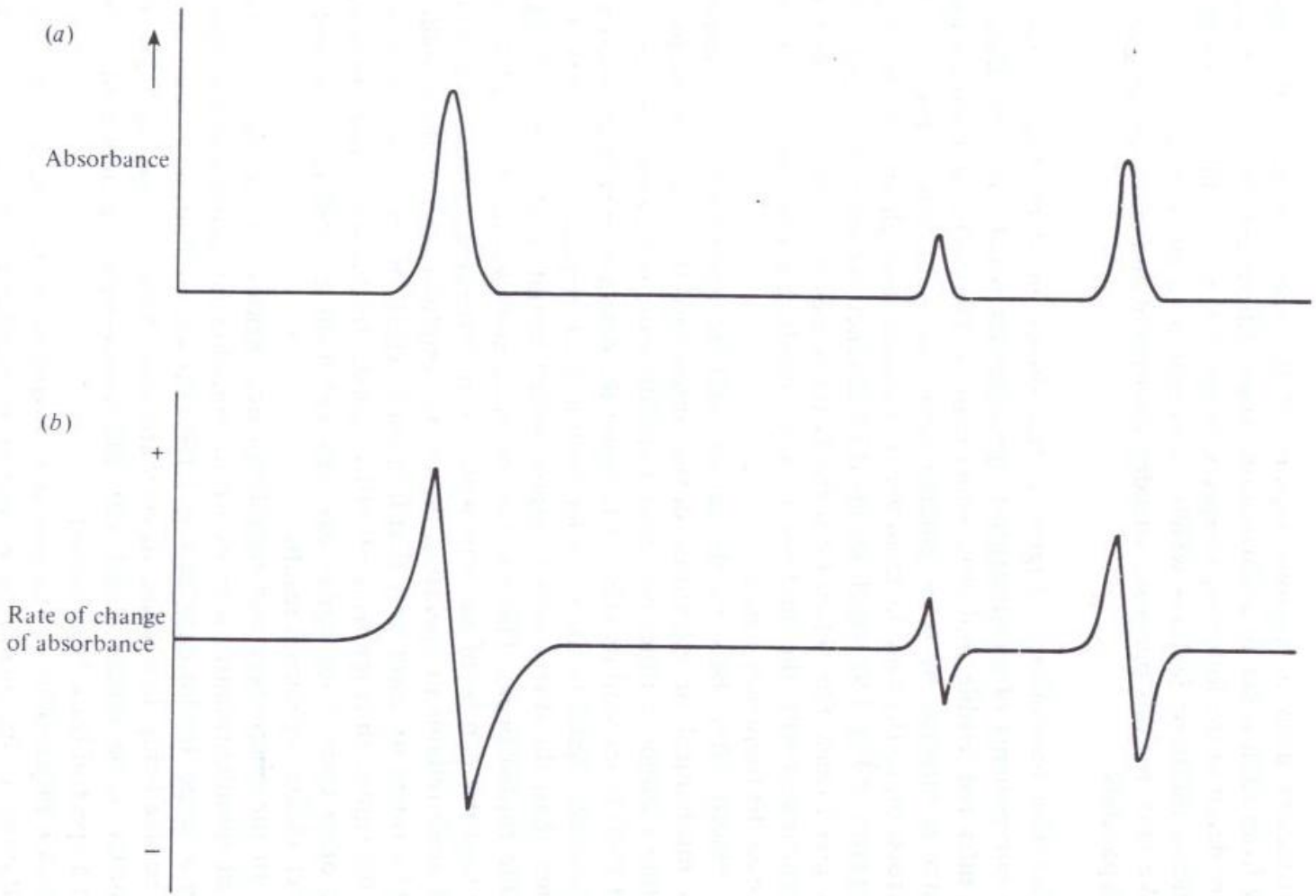


Figure 1.14 To illustrate the relation between absorption and derivative spectra: in (*a*) the absorption nuclear magnetic resonance spectrum of benzyl alcohol, $C_6H_5CH_2OH$, is shown, and in (*b*) the derivative (or dispersion) spectrum of the same molecule.

Basic elements of practical spectroscopy.

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.

Basic elements of practical spectroscopy.

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 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.

Basic elements of practical spectroscopy.

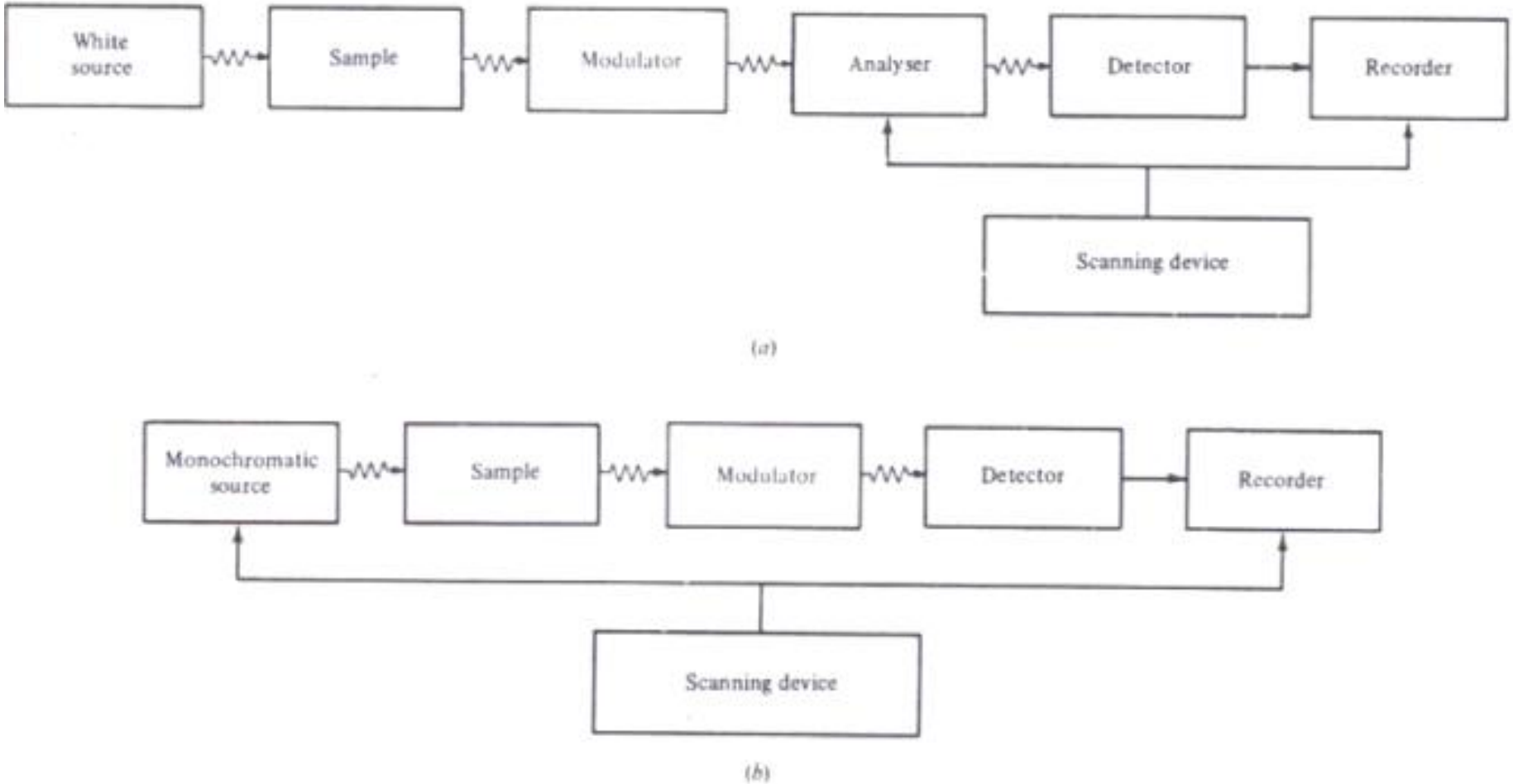


Figure 1.15 Block diagram of a typical absorption spectrometer for use in (*a*) the infra-red, visible, and ultra-violet regions where a 'white' source is available, and (*b*) the microwave and radiofrequency regions where the source can be tuned over a considerable range of frequencies.

Basic elements of practical spectroscopy.

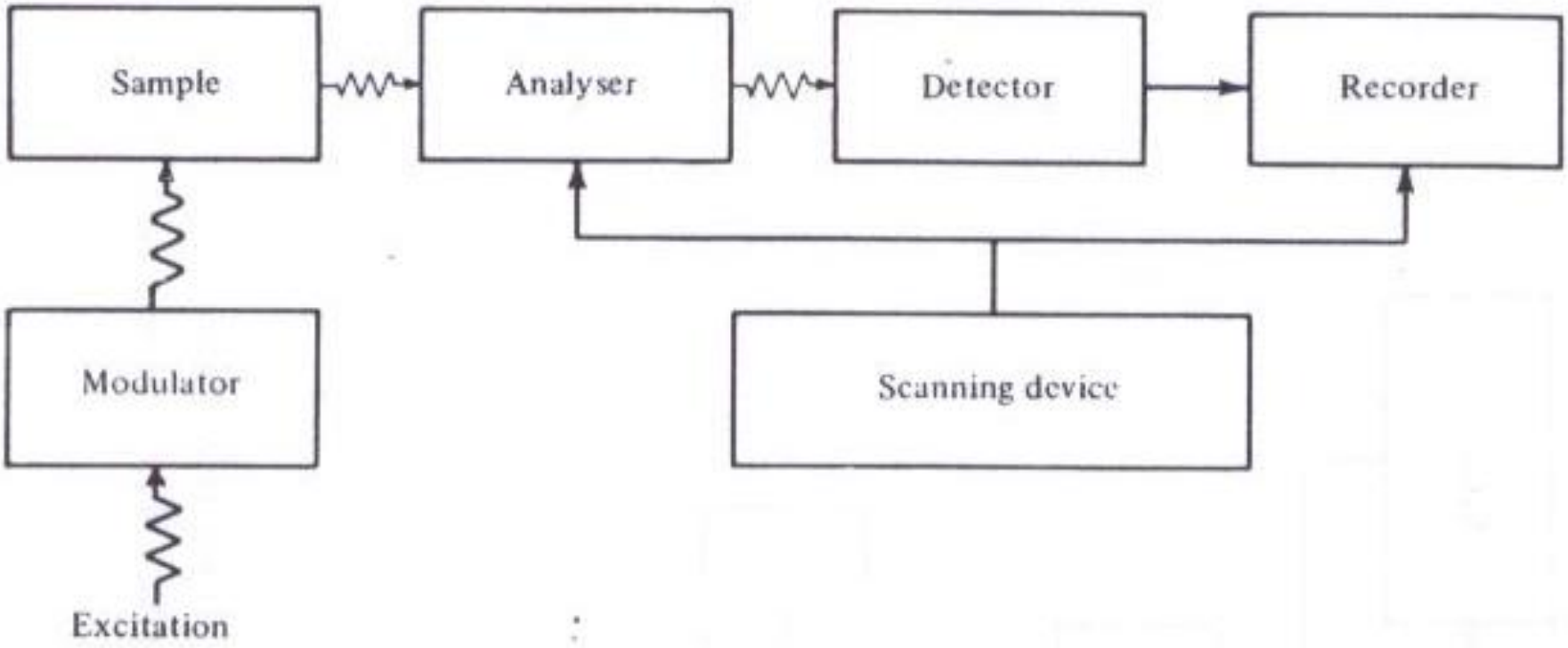


Figure 1.16 Block diagram of a typical emission spectrometer.

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

Signal-to-noise ratio

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.

Signal-to-noise ratio

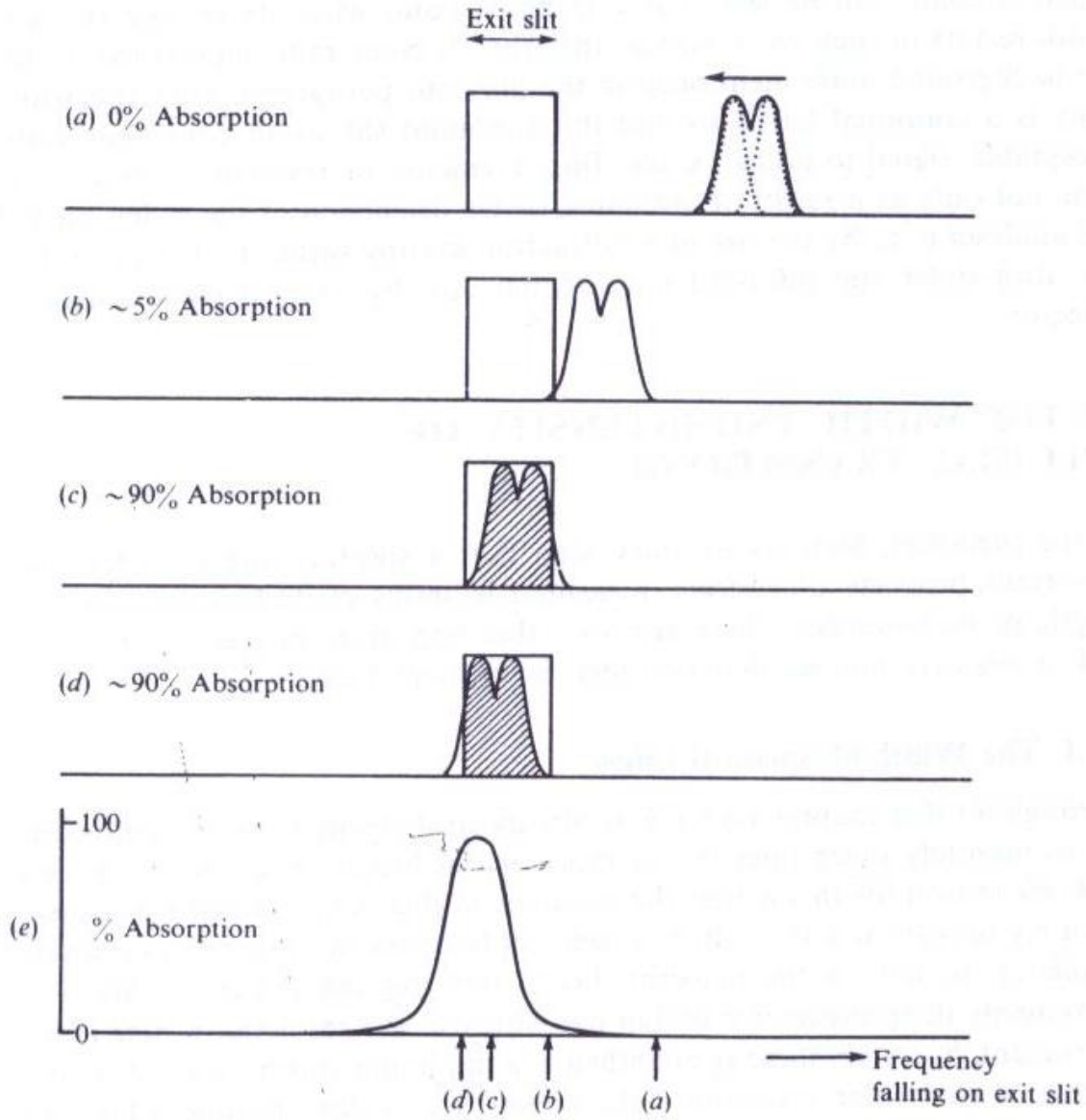


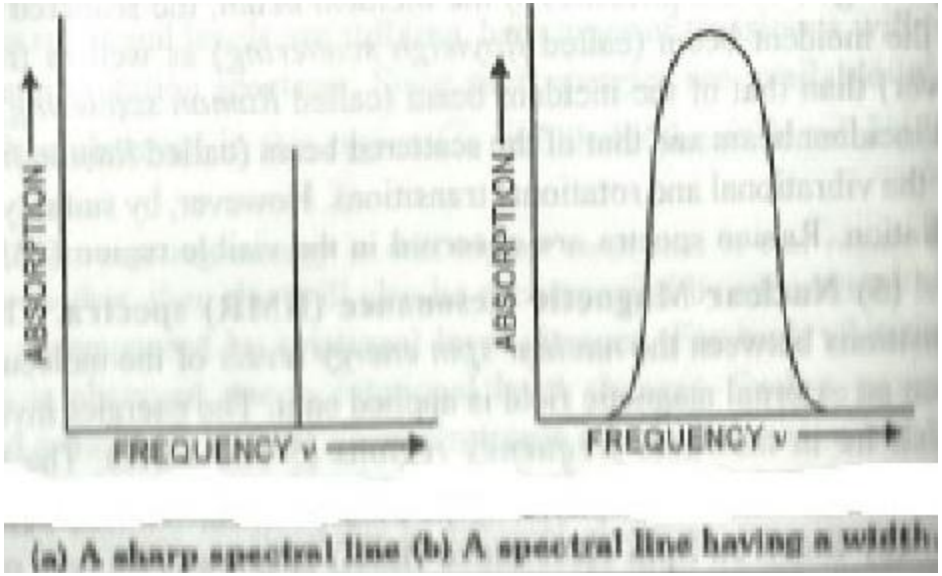
Figure 1.17 Illustrating the relation between slit width and resolving power

Representation of spectrum – the width and intensity of spectral lines

❖**In molecular spectroscopy, the spectral lines depend on two factors :**

(i) Width of the spectral lines decides the sharpness or broadness of the line

ii) Intensity of the spectral lines decides the strength of the signal



(a) A sharp spectral line (b) A spectral line having a width

Factors affecting the width of spectral lines

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.

Factors affecting the width of spectral lines

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.

Factors affecting the width of spectral lines

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:

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

Factors affecting the intensity of spectral lines

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.

Factors affecting the intensity of spectral lines

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*

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

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.

Factors affecting the intensity of spectral lines

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:

$$\frac{I}{I_0} = \exp(-\varepsilon c l) \qquad (1.13)$$

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.

Selection rules for various spectroscopic transitions

❖In chemistry and physics, selection rules define the transition probability from one energy state to another energy state.

❖In this topic, we are going to discuss the transition moment, which is the key to understanding the intrinsic transition probabilities.

❖

❖Selection rules have been divided into the electronic selection rules, vibrational selection rules (including Franck-Condon principle and vibronic coupling), and rotational selection rules.

Selection rules for various spectroscopic transitions

The transition probability is defined as the probability of particular spectroscopic transition to take place. When an atom or molecule absorbs a photon, the probability of an atom or molecule to transit from one energy level to another depends on two things: the nature of initial and final state wavefunctions and how strongly photons interact with an eigenstate. Transition strengths are used to describe transition probability. Selection rules are utilized to determine whether a transition is allowed or not.

Transition Moment

In an atom or molecule, an electromagnetic wave (for example, visible light) can induce an oscillating electric or magnetic moment. If the frequency of the induced electric or magnetic moment is the same as the energy difference between one eigenstate Ψ1 and another eigenstate Ψ2 , the interaction between an atom or molecule and the electromagnetic field is resonant (which means these two have the same frequency). Typically, the amplitude of this (electric or magnetic) moment is called the transition moment. In quantum mechanics, the transition probability of one molecule from one eigenstate Ψ1 to another eigenstate Ψ2 is given by $|M21|^2$, and $M21$ is called the transition dipole moment, or transition moment, from Ψ1 to Ψ2. In mathematical form it can be written as

$$\vec{M}_{21} = \int \Psi_2 \vec{\mu} \Psi_1 d\tau$$

Selection rules for various spectroscopic transitions

The Ψ1 and Ψ2 are two different eigenstates in one molecule, *M21* is the electric dipole moment operator. If we have a system with n molecules and each has charge Qn, and the dipole moment operator is can be written as

$$\vec{\mu} = \sum_n Q_n \vec{x}_n$$

Electronic Selection rules

Atoms:

Atoms are described by the primary quantum number n, angular momentum quantum number L, spin quantum number S, and total angular momentum quantum number J. Based on Russell-Saunders approximation of electron coupling, the atomic term symbol can be represented as $^{(2S+1)}L_J$.

1. The total spin cannot change, ΔS=0;
2. The change in total orbital angular momentum can be ΔL=0, ±1, but L=0↔L=0 transition is not allowed;
3. The change in the total angular momentum can be ΔJ=0, ± 1, but J=0↔J=0 transition is not allowed;
4. The initial and final wavefunctions must change in parity. Parity is related to the orbital angular momentum summation over all elections Σli , which can be even or odd; only even ↔ odd transitions are allowed.

Selection rules for various spectroscopic transitions

Vibrational Selection rules

1. Transitions with Δv= ±1, ± 2, ... are all allowed for anharmonic potential, but the intensity of the peaks become weaker as Δv increases.
2. v=0 to v=1 transition is normally called the fundamental vibration, while those with larger Δv are called overtones.
3. Δv=0 transition is allowed between the lower and upper electronic states with energy E1 and E2 are involved, i.e. (E1 , v''=n) →(E , v'=n), where the double prime and prime indicate the lower and upper quantum state.

The geometry of vibrational wavefunctions plays an important role in vibrational selection rules. For diatomic molecules, the vibrational wavefunction is symmetric with respect to all the electronic states. Therefore, the Franck-Condon integral is always totally symmetric for diatomic molecules. The vibrational selection rule does not exist for diatomic molecules.

For polyatomic molecules, the nonlinear molecules possess 3N-6 normal vibrational modes, while linear molecules possess 3N-5 vibrational modes. Based on the harmonic oscillator model, the product of 3N-6 normal mode wavefunctions contribute to the total vibrational wavefunction, i.e.

$$\psi_{vib} = \prod_{3N-6} \psi_1 \psi_2 \psi_3 \cdots \psi_{3N-6}$$

Selection rules for various spectroscopic transitions

Rotational Selection rules

1. Transitions with $\Delta J = \pm 1$ are allowed;

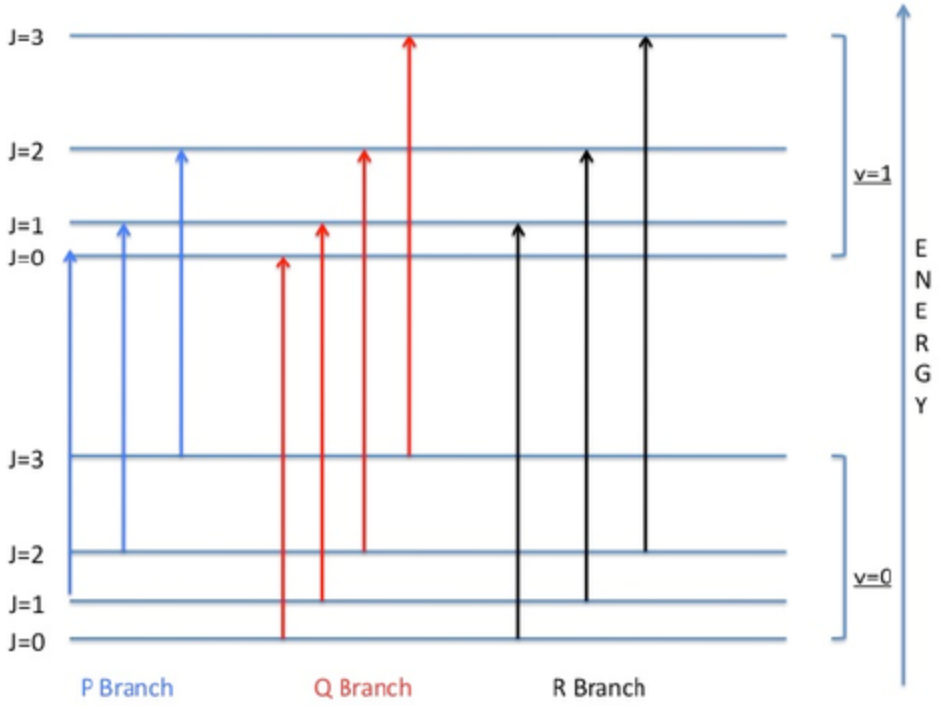
Photons do not have any mass, but they have angular momentum. The conservation of angular momentum is the fundamental criteria for spectroscopic transitions. As a result, the total angular momentum has to be conserved after a molecule absorbs or emits a photon. The rotational selection rule relies on the fact that photon has one unit of quantized angular momentum. During the photon emission and absorption process, the angular moment J cannot change by more than one unit.

Let's consider a single photon transition process for a diatomic molecule. The rotational selection rule requires that transitions with $\Delta J = \pm 1$ are allowed. Transitions with $\Delta J = 1$ are defined as R branch transitions, while those with $\Delta J = -1$ are defined as P branch transitions. Rotational transitions are conventional labeled as P or R with the rotational quantum number J of the lower electronic state in the parentheses. For example, R(2) specifies the rotational transition from J=2 in the lower electronic state to J=3 in the upper electronic state.

Selection rules for various spectroscopic transitions

Rotational Selection rules

2. $\Delta J=0$ transitions are allowed when two different electronic or vibrational states are involved: (X'', J''=m) → (X', J'=m). The Q branch transitions will only take place when there is a net orbital angular momentum in one of the electronic states. Therefore, Q branch does not exist for $^1\sum \leftrightarrow ^1\sum$ electronic transitions because $\sum$ electronic state does not possess any net orbital angular momentum. On the other hand, the Q branch will exist if one of the electronic states has angular momentum. In this situation, the angular momentum of the photon will cancel out with the angular momentum of the electronic state, so the transition will take place without any change in the rotational state. The schematic of P, Q, and R branch transitions are shown below:



Beer Lambert Law

The Beer-Lambert law relates the attenuation of light to the properties of the material through which the light is traveling.

The Absorbance of a Solution

For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as - *Io* that's for Intensity.

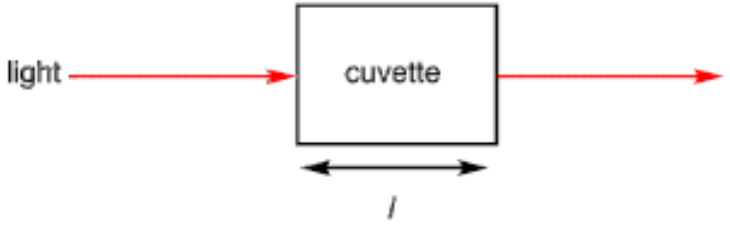


Figure 1: Light absorbed by sample in a cuvette

The intensity of the light passing through the sample cell is also measured for that wavelength – given the symbol, *I* . If is less than , then the sample has absorbed some of the light (neglecting reflection of light off the cuvette surface).

Beer Lambert Law

The absorbance of a transition depends on two external assumptions.

1. The absorbance is directly proportional to the concentration (c) of the solution of the sample used in the experiment.
2. The absorbance (A) is directly proportional to the length of the light path (l), which is equal to the width of the cuvette.

Assumption one relates the absorbance to concentration and can be expressed as

$$A \propto c$$

The absorbance (*A*) is defined via the incident intensity *Io* and transmitted intensity *I* by

$$A = \log_{10}\left(\frac{I_o}{I}\right)$$

Assumption two can be expressed as

$$A \propto l$$

Beer Lambert Law

Combining both the equations, we have

$$A \propto cl$$

This proportionality can be converted into an equality by including a proportionality constant (ε).

$$A = \epsilon cl$$

This formula is the common form of the *Beer-Lambert Law, although it can be also written in terms of intensities as*

$$A = \log_{10}\left(\frac{I_o}{I}\right) = \epsilon lc$$

Beer Lambert Law

The constant ε is called **molar absorptivity or molar extinction coefficient and is a measure of the probability of the** electronic transition. On most of the diagrams you will come across, the absorbance ranges from 0 to 1, but it can go higher than that. An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed. The intensities of the sample and reference beam are both the same, so the ratio *Io/I* is 1 and the $\log_{10}$ of 1 is zero.

The Greek letter epsilon in these equations is called the **molar absorptivity - or sometimes the molar absorption coefficient.** The larger the molar absorptivity, the more probable the electronic transition. In uv spectroscopy, the concentration of the sample solution is measured in mol/L and the length of the light path in cm. Thus, given that absorbance is unitless, the units of molar absorptivity are L/mol.cm . However, since the units of molar absorptivity is always the above, it is customarily reported without units.

Beer Lambert Law

The Importance of Concentration

The proportion of the light absorbed will depend on how many molecules it interacts with. Suppose you have got a strongly colored organic dye. If it is in a reasonably concentrated solution, it will have a very high absorbance because there are lots of molecules to interact with the light. However, in an incredibly dilute solution, it may be very difficult to see that it is colored at all. The absorbance is going to be very low. Suppose then that you wanted to compare this dye with a different compound. Unless you took care to make allowance for the concentration, you couldn't make any sensible comparisons about which one absorbed the most light.

The importance of the container shape

Suppose this time that you had a very dilute solution of the dye in a cube-shaped container so that the light traveled 1 cm through it. The absorbance is not likely to be very high. On the other hand, suppose you passed the light through a tube 100 cm long containing the same solution. More light would be absorbed because it interacts with more molecules. Again, if you want to draw sensible comparisons between solutions, you have to allow for the length of the solution the light is passing through. Both concentration and solution length are allowed for in the Beer-Lambert Law.

Beer Lambert Law

Molar Absorptivity

The Beer-Lambert law can be rearranged to obtain an expression for (the molar absorptivity):

$$\epsilon = \frac{A}{lc}$$

Remember that the absorbance of a solution will vary as the concentration or the size of the container varies. Molar absorptivity compensates for this by dividing by both the concentration and the length of the solution that the light passes through. Essentially, it works out a value for what the absorbance would be under a standard set of conditions - the light traveling 1 cm through a solution of 1 mol dm^{-3}. That means that you can then make comparisons between one compound and another without having to worry about the concentration or solution length.

Values for molar absorptivity can vary hugely. For example, ethanal has two absorption peaks in its UV-visible spectrum – both in the ultra-violet. One of these corresponds to an electron being promoted from a lone pair on the oxygen into a pi antibonding orbital; the other from a π - bonding orbital into a π anti-bonding orbital. Table 1 gives values for the molar absorptivity of a solution of ethanal in hexane. Notice that there are no units given for absorptivity. That's quite common since it assumes the length is in cm and the concentration is $moldm^{-3}$, the units are $mol^{-1}dm^3cm^{-1}$.

Table1

electron jump	wavelength of maximum absorption (nm)	molar absorptivity
lone pair to π anti-bonding orbital	290	15
π bonding to π anti-bonding orbital	180	10,000