

### 1.3 REGIONS OF THE SPECTRUM

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

In increasing frequency the regions are:

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

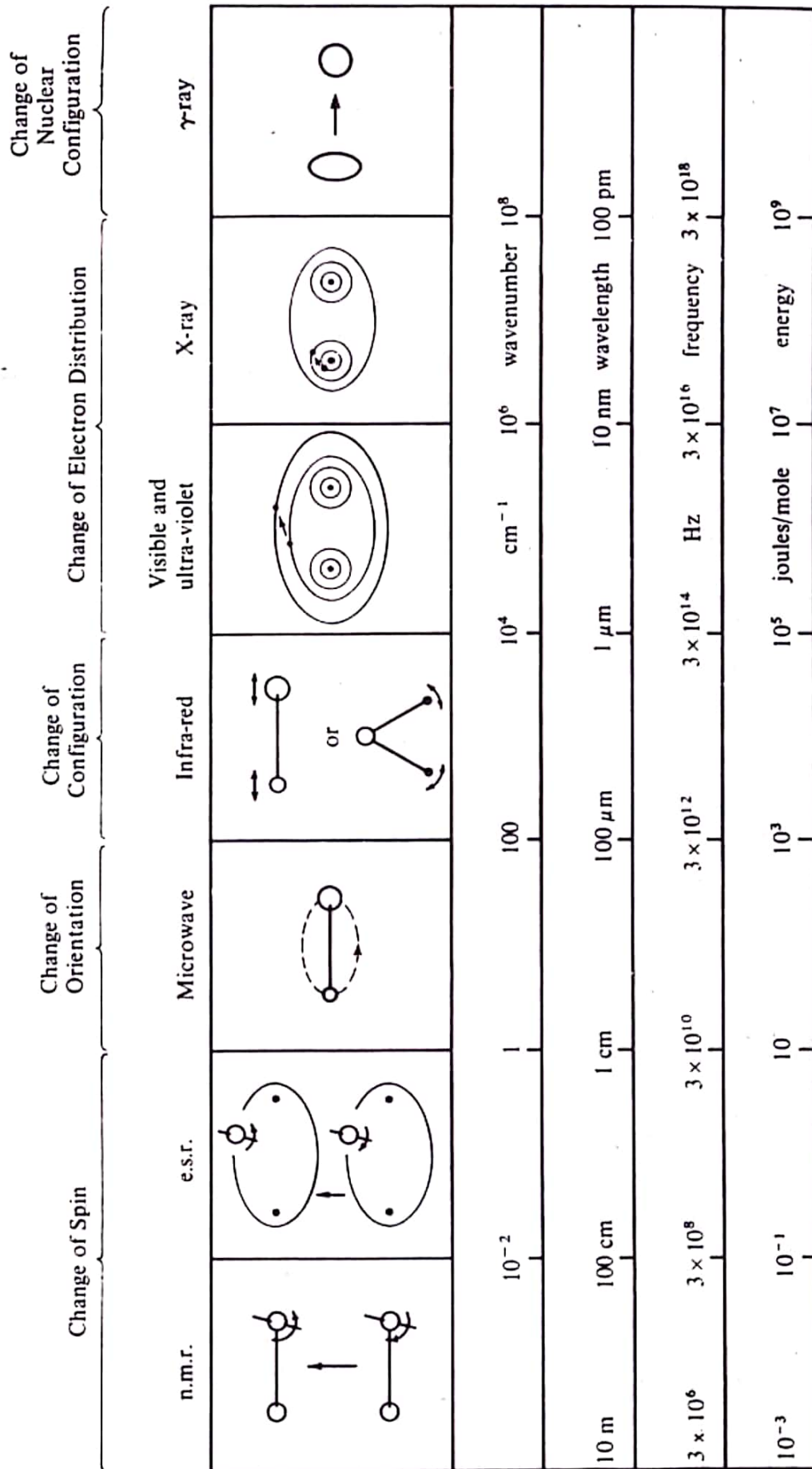


Figure 1.4 The regions of the electromagnetic spectrum.

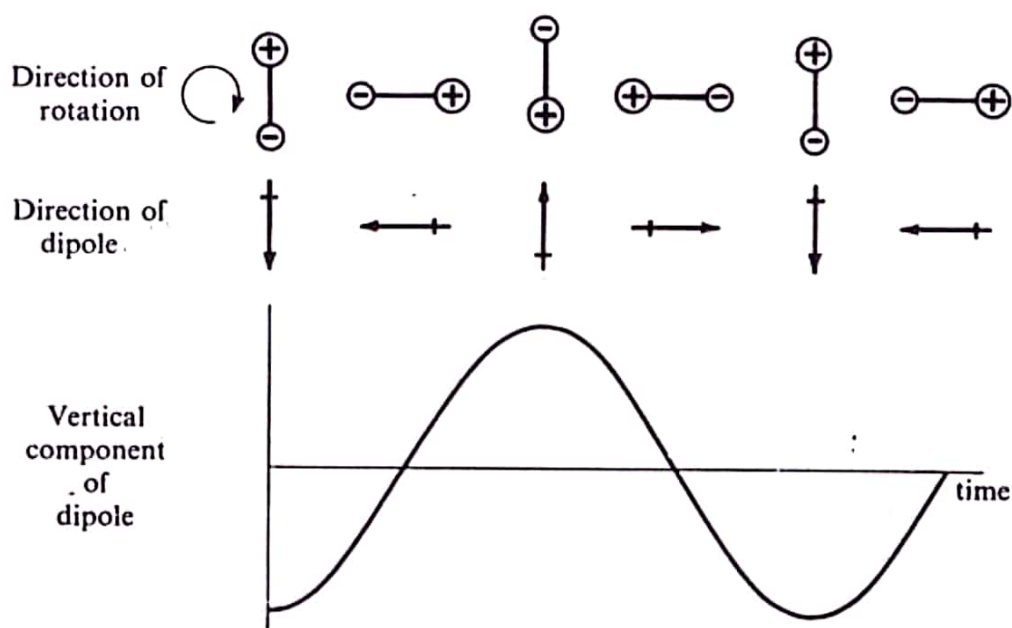
2. Microwave region:  $3 \times 10^{10}$ – $3 \times 10^{12}$  Hz; 1 cm–100  $\mu\text{m}$  wavelength. Rotational spectroscopy. Separations between the rotational levels of molecules are of the order of hundreds of joules per mole (Chapter 2).
3. Infra-red region:  $3 \times 10^{12}$ – $3 \times 10^{14}$  Hz; 100  $\mu\text{m}$ –1  $\mu\text{m}$  wavelength. Vibrational spectroscopy. One of the most valuable spectroscopic regions for the chemist. Separations between levels are some  $10^4$  joules/mole (Chapter 3).
4. Visible and ultra-violet regions:  $3 \times 10^{14}$ – $3 \times 10^{16}$  Hz; 1  $\mu\text{m}$ –10 nm wavelength. Electronic spectroscopy. The separations between the energies of valence electrons are some hundreds of kilojoules per mole (Chapters 5 and 6).
5. X-ray region:  $3 \times 10^{16}$ – $3 \times 10^{18}$  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.  $\gamma$ -ray region:  $3 \times 10^{18}$ – $3 \times 10^{20}$  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.  $\text{H}_2$  or  $\text{Cl}_2$ , on the other hand, in which there is no such charge separation, have a zero dipole. If we consider the rotation of HCl

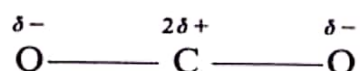




**Figure 1.5** The rotation of a diatomic molecule, HCl, showing the fluctuation in the dipole moment measured in a particular direction.

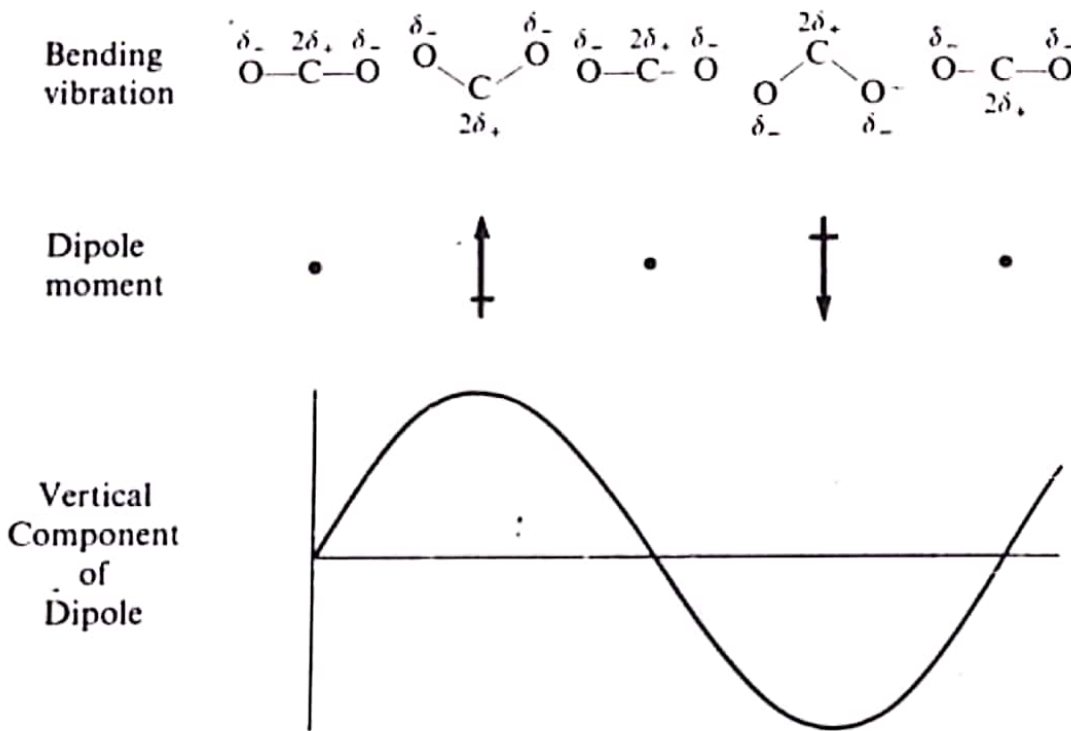
(Fig. 1.5, where we notice that if only a pure rotation takes place, the centre of gravity of the molecule must not move), we see that the plus and minus charges change places periodically, and the component dipole moment in a given direction (say upwards in the plane of the paper) fluctuates regularly. 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  $\text{H}_2$  or  $\text{Cl}_2$ , no interaction can take place and the molecule is 'microwave inactive'. This imposes a limitation on the applicability of microwave spectroscopy.

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



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





**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.