Unit 6.2 Rotational, Vibrational and Raman Spectroscopy (Marks 20)

Rotational spectra of diatomic molecules – rigid rotator concept – determination of bond length – effect of isotopic substitution – spectra of non-rigid rotator. Vibrational spectra of diatomic molecules – harmonic and anharmonic oscillator model – Morse potential - calculation of force constants – effect of isotope - vibrations of polyatomic molecules, overtone and combination bands (H_2O, CO_2). Diatomic vibrating rotor – vibration rotation spectrum of CO. Principle of Raman spectroscopy – rotational and vibrational Raman spectra of linear molecules – rule of mutual exclusion.

Structure elucidation by IR spectroscopy – finger print region and group frequencies – effect of hydrogen bonding (alcohol, keto-enol) and coordination to metal.

Microwave Region

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
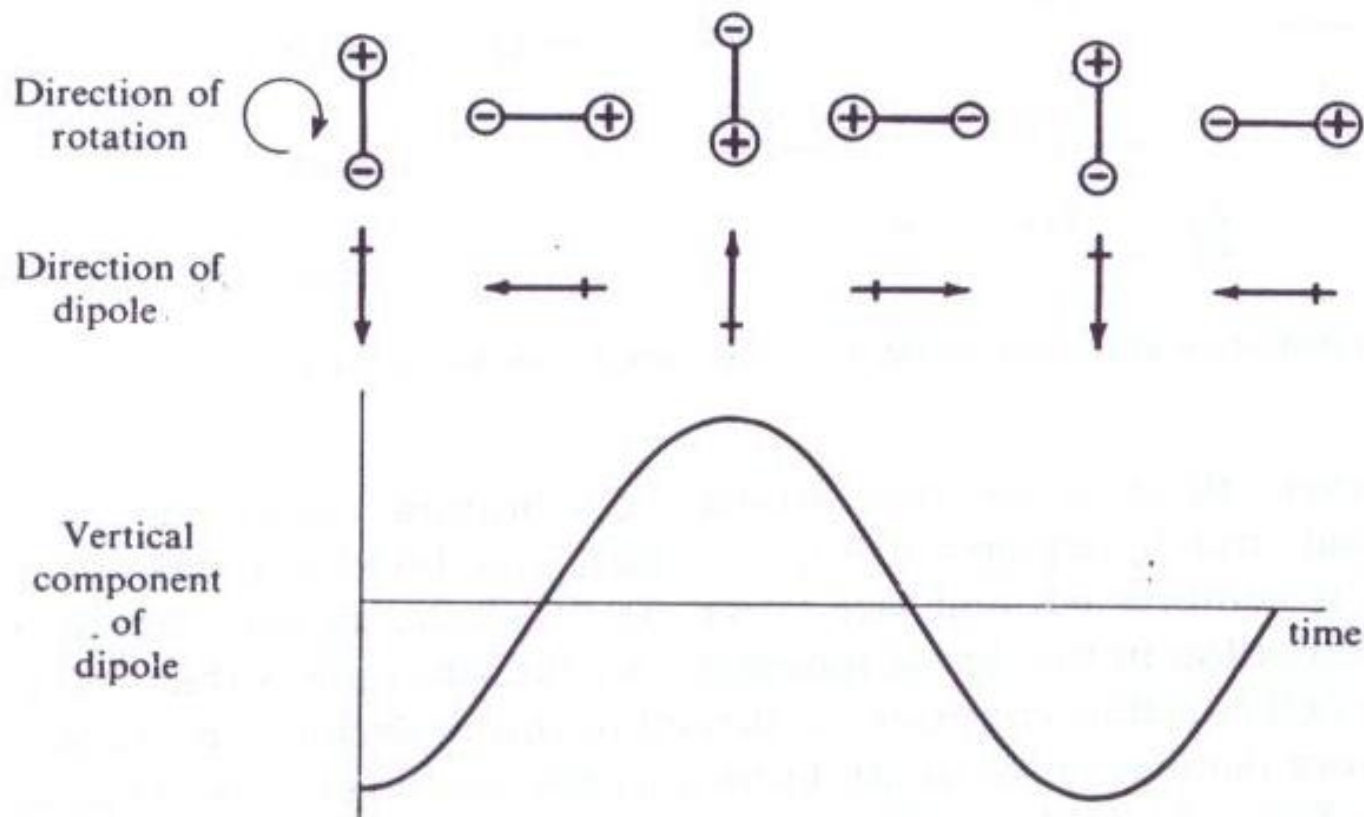

Figure 1.5 The rotation of a diatomic molecule, HCl, showing the fluctuation in the dipole moment measured in a particular direction.

(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.

Infra-red Region

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:

$$\overset{\delta-}{O} \text{———} \overset{2\delta+}{C} \text{———} \overset{\delta-}{O}$$
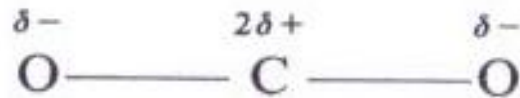
During the mode of vibration known as the 'symmetric stretch', the molecule is alternately stretched and compressed, both C—O bonds changing simultaneously, as in Fig. 1.6. Plainly the dipole moment remains zero throughout the whole of this motion, and this particular vibration is thus 'infra-red inactive'.
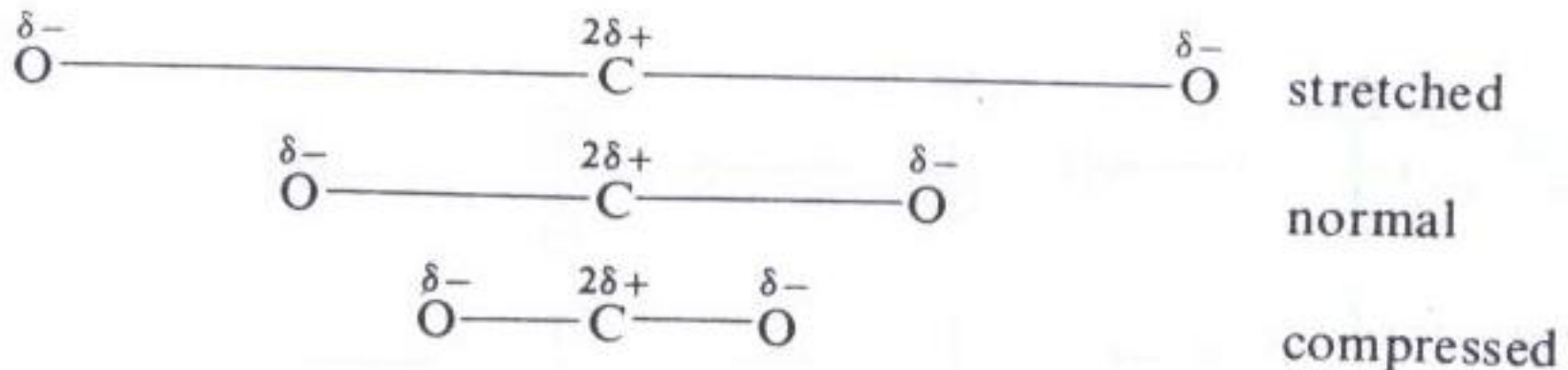

Figure 1.6 The symmetric stretching vibration of the carbon dioxide molecule.

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

Although dipole change requirements do impose some limitation on the application of infra-red spectroscopy, the appearance or non-appearance of certain vibration frequencies can give valuable information about the structure of a particular molecule (see Chapter 3).
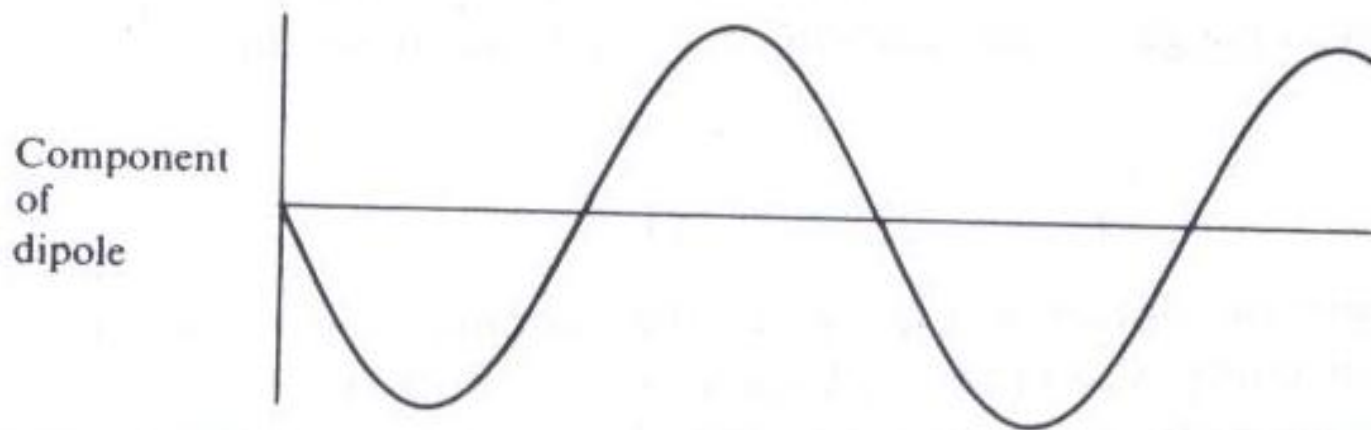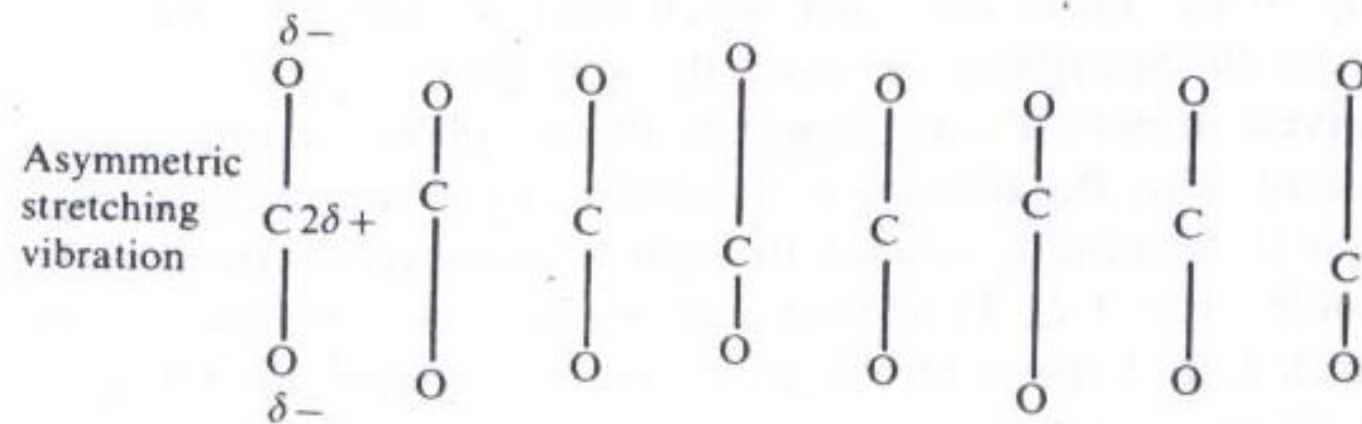
Figure 1.7 The asymmetric stretching vibration of the carbon dioxide molecule showing the fluctuation in the dipole moment.
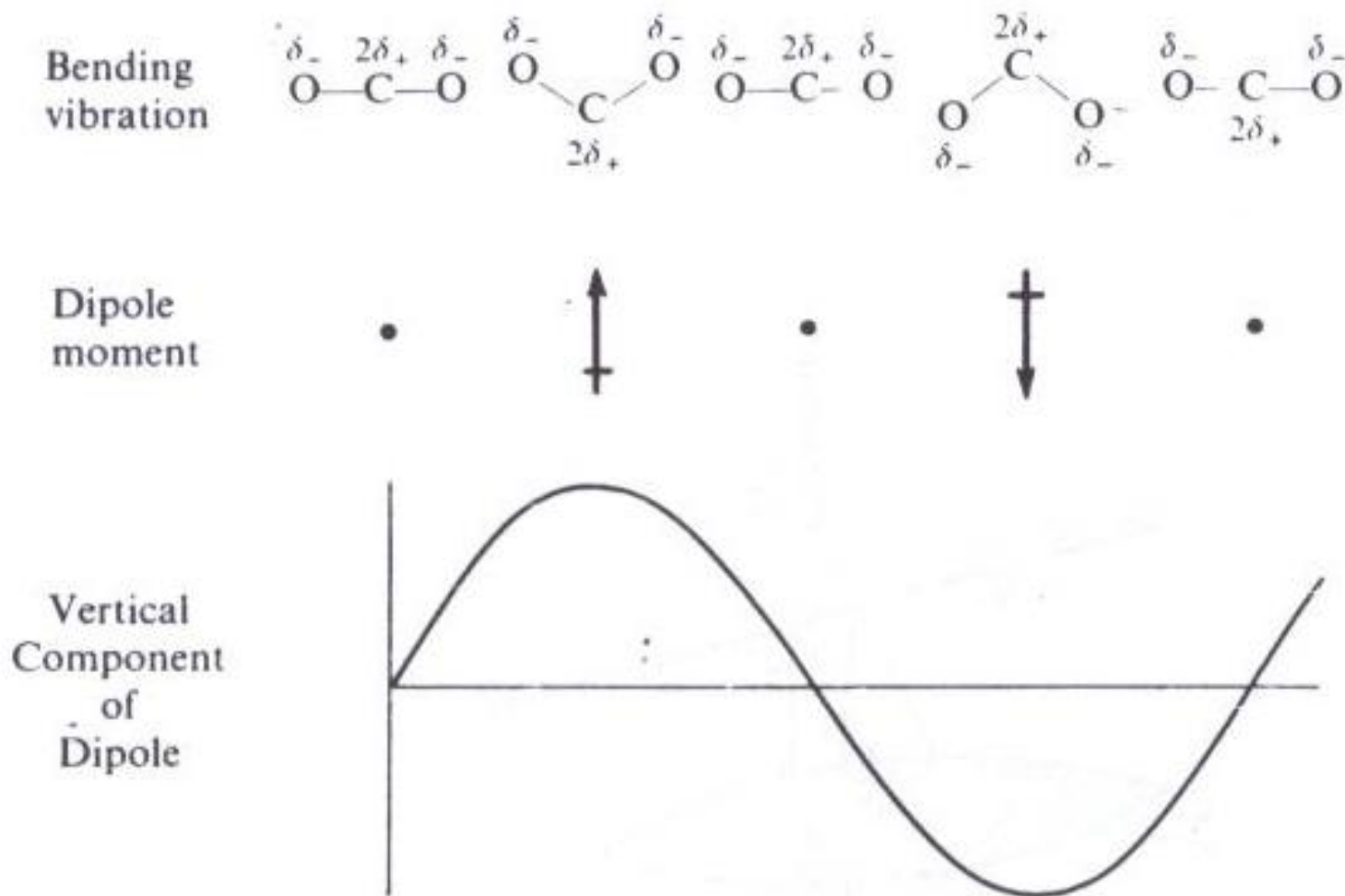
Figure 1.8 The bending motion of the carbon dioxide molecule and its associated dipole fluctuation.