

CHAPTER FOUR

Molecular Spectroscopy

4.1 Introduction

The subject of molecular spectroscopy deals with the interaction of electromagnetic radiations with the matter. The absorption (or emission) of electromagnetic radiations by a molecule is highly selective and follows the relation

$$\Delta E = h\nu = E_2 - E_1 \quad (4.1.1)$$

where ν is the frequency of absorption, and E_1 and E_2 are the energies of lower and higher molecular levels, respectively. Thus, the molecule is excited from a lower molecular energy level to the higher one when it absorbs radiation. In emission of radiation, the reverse of the above is observed.

It is possible to correlate the experimentally observed data on absorption or emission with the nature of molecular changes which are responsible for the absorption or emission. With the help of these correlations, much useful information regarding the size, shape, flexibility of the bond and electronic arrangements of a molecule can be deduced. Before considering such correlations, a brief discussion on different types of molecular energies is in order.

DIFFERENT TYPES OF MOLECULAR ENERGIES

A molecule possesses many forms of energies. These are:

- (1) Translational energy : by virtue of its translatory motion.
- (2) Rotational energy : by virtue of bodily rotation of the molecule about its centre of gravity.
- (3) Vibrational energy : by virtue of the periodic displacement of its atoms from their equilibrium positions.
- (4) Electronic energy : by virtue of different electronic arrangements in the molecule.

It was seen in Chapters 1 and 2 that the energies listed above are all quantised, i.e., a molecule cannot have any arbitrary energies of rotation, vibrational or electronic, but can exist only in the allowed energy levels. According to the Born-Oppenheimer approximation, the energies listed above can be treated separately and we can write the total energy of the molecule as

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}$$

where E_{trans} , E_{rot} , E_{vib} and E_{el} represent translational, rotational, vibrational and electronic energies, respectively. In general

$$E_{\text{el}} \gg E_{\text{vib}} \gg E_{\text{rot}} \gg E_{\text{trans}}$$

The approximate difference between the two levels of any one of the energies listed above may be worked out from the following expressions.

$$(1) \quad E_{trans} = \frac{h^2}{8mL^2} \quad \text{Joule}$$

where n is the translational quantum number and has integral values 1, 2, 3, 4, ...

$$(2) \quad E_{rot} = J(J+1) \frac{h^2}{8\pi^2 I} \quad \text{Joule}$$

where J is the rotational quantum number. The permitted values of J are 0, 1, 2, 3, ...

$$(3) \quad E_{vib} = \left(v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{Joule}$$

where v is the vibrational quantum number and possesses values of 0, 1, 2, 3, ...

$$(4) \quad E_{el} = - \frac{2\pi^2 e^4 m_e Z^2}{h^2 n^2}$$

where n is the electronic quantum number and has values 1, 2, 3, 4, ...

At the very outset, an important conclusion regarding the energy difference between the two translational levels may be stated. The energy difference between the two successive translational levels is of the order of $10^{-20} \text{ J mol}^{-1}$ for a normal molecule moving in a container of ordinary size. This separation is too small to be determined experimentally. It is for this reason that the translational energy is considered to be continuous and thus the corresponding translational spectroscopy to be observed is completely excluded.

The order of energy difference between the two successive energy levels for other motions alongwith the approximate wavelengths of radiation to be employed for the required transitions are shown in Table 4.1.1.

Table 4.1.1 Energy Differences between the Two Successive Energy Levels

Motion	$\approx \Delta E / \text{molecule}^{-1}$	$\approx \lambda / \text{m}$
Rotation	10^{-20}	10^{-4}
Vibration	10^{-18}	10^{-4}
Electronic	10^{-17}	10^{-7}

From Table 4.1.1, it follows that the separation between the two electronic energy levels are larger than those between the two vibrational energy levels, which in turn are larger than those between the two rotational levels.

In Fig. 4.1.1 only a few energy levels have been shown. In fact, a very large number of vibrational levels going up to the dissociation limit exist for each electronic level. Similarly, a series of rotational levels exist with each of the vibrational level.

DIFFERENT TYPES OF SPECTROSCOPY

Transitions between rotational levels belonging to a particular vibration level are observed in the microwave region of the electromagnetic spectrum ($\lambda \approx 10^{-2}$ to 10^{-4} m); these are called *pure rotational spectra*. Transitions between vibrational levels within the same electronic state lie in the infrared region ($\lambda \approx 10^{-6}$ to 10^{-4} m) and are responsible to exhibit *pure vibrational* and *vibrational-rotational spectra*. Finally, transitions between electronic levels give rise to the spectra in the visible or ultraviolet region ($\lambda \approx 10^{-8}$ to 10^{-7} m) and are called *electronic spectra*.

In addition to the various spectra listed above, there exist two other important spectra which lie in the radiofrequency region of the spectrum (10 m to 1 cm wavelength). These are connected with the reversal of spin of a nucleus and an electron, and are known as *nuclear magnetic resonance spectrum* and *electron-spin resonance spectrum*, respectively.

Lastly, we may mention another type of spectroscopy which is known as *Raman spectroscopy*. This yields information similar to that obtained in microwave and infrared regions. The incident light used in this spectroscopy lies in the visible region. Figure 4.1.2 depicts a schematic diagram of the various electromagnetic spectra listed above.

In the following sections, we describe the different types of spectroscopy in the increasing magnitude of energy of absorbed or emitted electromagnetic radiations.

THE ABSORPTION OF RADIATION

The absorption of microwave, infra-red, visible, and ultra-violet radiations by a gaseous or liquid sample is often expressed by the Beer-Lambert law¹:

$$\log \frac{I}{I_0} = -\epsilon cl \quad (4.1.2)$$

where c and l are the concentration and path length of the sample, I_0 and I are the intensities of incident and transmitted light and ϵ is the molar absorption coefficient which has a characteristic value for a particular absorption of a molecule.

THE PROBABILITY OF TRANSITION

The absorption of a photon of frequency ν by a molecule causes a transition from the lower energy state m to the higher energy state n provided the following expression is satisfied:

$$E_n - E_m = h\nu$$

¹See Equations 7.1 and 7.2 for the derivation.

It is customary to show the different energy separations in a diatomic molecule by a diagram shown in Fig. 4.1.1. Each stable electronic level exhibits a minimum in the potential energy diagram. The upper level relative to the ground level has a smaller depth which lies at a larger internuclear distance. In the minimum valley, the different vibrational and rotational levels are shown by straight lines. The vibrational energy levels are almost equidistant (strictly true only for a harmonic vibration) and the energy separation between the two successive rotational levels increases in a definite manner (strictly true only for a rigid rotator).

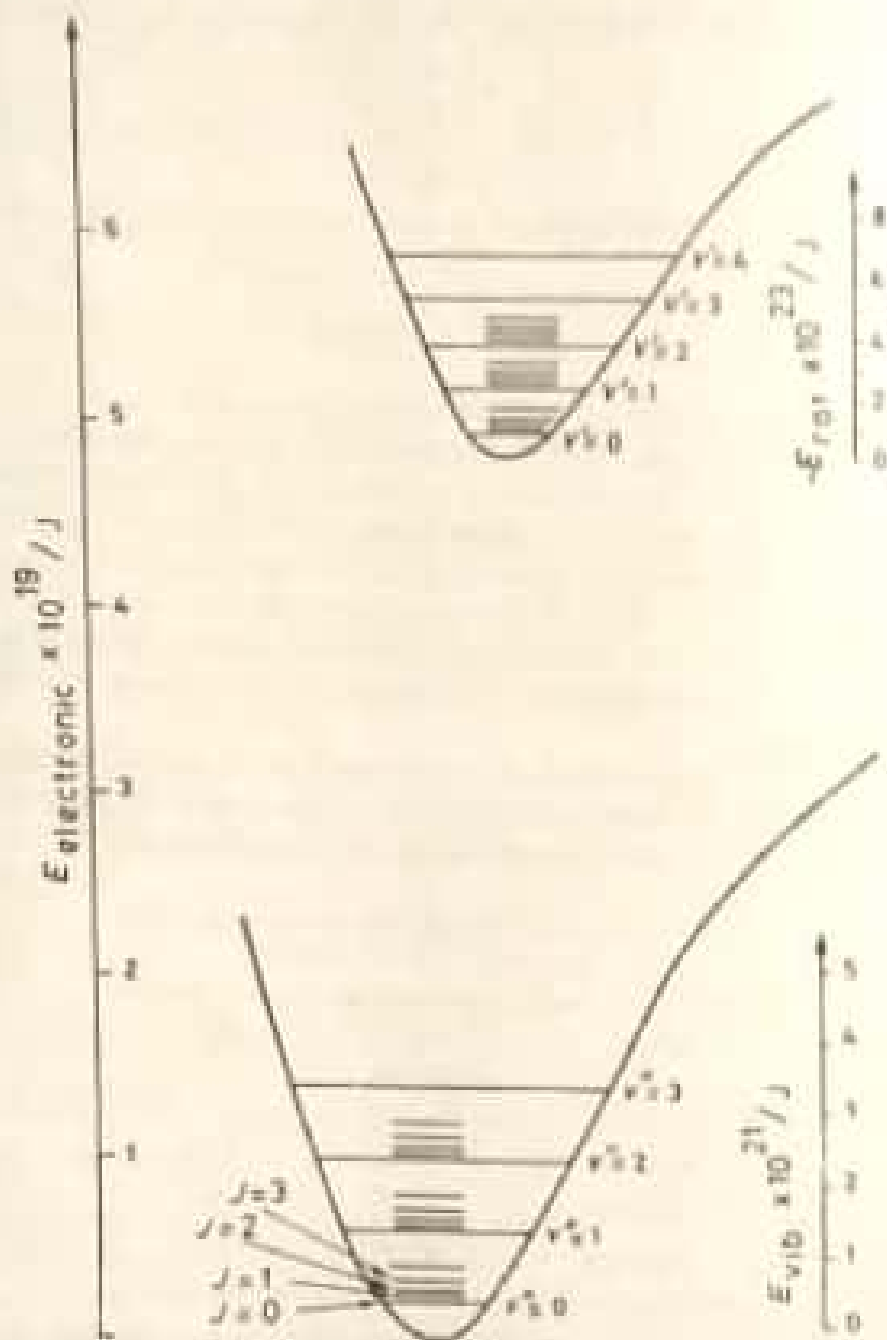


Fig. 4.1.1 A schematic representation of various energy levels