2

Theory of the Atom and Origin of Spectra

2.1 HYDROGEN SPECTRUM

A characteristic feature of line spectra is that the spectral lines could be grouped in one or more series in which the separation and intensity of lines decrease gradually towards shorter wavelength side. For example, in hydrogen, the line spectrum revealed a series of lines with separation and intensity decreasing regularly towards the shorter wavelengths and the series converges to a limit at about 3646 Å. The line with the longest wavelength (6563 Å) is designated H_α, the next (λ = 4861 Å) is designated H_β and so on (see Fig. 2.1).

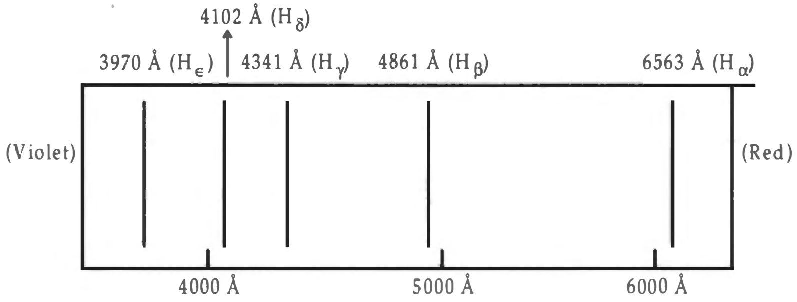

Fig. 2.1: The hydrogen spectrum (Balmer lines)

Attempts were made to explain such line spectra in analogy of overtones in acoustics to find harmonic relations in lines found in the spectrum of a given element. In this regard, though, initially, attempts were in vain, however, in 1880, Liveing and Dewar emphasized that there existed a certain sort of series relation (*iv*) **Asymmetric Top Molecules:** In these molecules, $I_a \neq I_b \neq I_c$. A few examples are H_2O, CH_3OH. The majority of the molecules belong to this category.

9.6 THE DIATOMIC MOLECULE AS A SYMMETRIC TOP

A diatomic molecule is considered equivalent to a simple rigid rotator with the tacit assumption that the moment of inertia about the line joining the nuclei is zero. Actually, due to a number of electrons revolving about the two nuclei, the moment of inertia about the line joining the nuclei is not exactly zero, rather it has a small magnitude characterised by an angular momentum ***K***.

and $$|\boldsymbol{K}| = K \cdot \frac{h}{2\pi}$$

where *K* is the quantum number of the angular momentum of the electrons about the internuclear axis. (The system is like a dumbbell carrying a flywheel on its axis—a more general case of a symmetric top). The total angular momentum designated by ***J*** can take only the values

$$|\boldsymbol{J}| = \sqrt{J(J+1)} \cdot \frac{h}{2\pi}$$

Figure 9.6 gives a diagram of the angular momentum vectors. The component of the total angular momentum at right angles to the internuclear axis is designated ***N*** (it represents essentially the rotation of the nuclei alone). The magnitude $|\boldsymbol{N}|$ is completely determined by ***K*** and ***J*** and ***N*** cannot have integral values, so there is no quantum number associated with ***N***. The total angular momentum ***J*** is perpendicular to the axis only when $K = 0$ (in that case $\boldsymbol{N} \equiv \boldsymbol{J}$). For $K \neq 0$, the total angular momentum ***J*** subtends an angle smaller than 90° with the internuclear axis. It is clear from Fig. 9.6 that $|\boldsymbol{J}| \geq |\boldsymbol{K}|$. Therefore for a given *K*, the possible values of *J* are

$$J = K,\ K + 1,\ K + 2,\ \ldots \qquad ..(55)$$

This means that the rotational levels corresponding to $J < K$ are missing and this provides a means of identifying symmetric-top molecules.

From Fig. 9.6 (*b*), it is clear that for a given value of $|\boldsymbol{J}|$, there are two modes of motion of the system, corresponding to two directions ***K*** and –***K***.

Reduced mass $$\mu = \frac{M_H M_{Cl}}{M_H + M_{Cl}} = \frac{1 \times 35}{1+35} M_H$$

$$= \frac{35}{36} \times 1.68 \times 10^{-24} \text{ gm} = 1.63 \times 10^{-24} \text{ gm}$$

$$\therefore \quad k = 4 \times (3.14)^2 \times (1.63 \times 10^{-24} \text{ gm}) \times (2886 \text{ cm}^{-1})^2 \times (3 \times 10^{10} \text{ cm s}^{-1})^2$$

$$= 4.8 \times 10^5 \text{ dynes/cm.}$$

10.2 VIBRATIONS OF POLYATOMIC MOLECULES

The study of vibrations of polyatomic molecules provides a background for an understanding of the absorption spectrum in the infrared region.

Number of Independent Vibrations: Imagine that a molecule contains N atoms which are held together by extremely weak bonds, the collective motion being described in terms of nearly independent motions of the constituent N atoms. If x_i, y_i, z_i are the coordinates of ith atom, there will be a total of $3N$ such coordinates, either of these will represent a degree of freedom, so that there will be $3N$ degrees of freedom.

For actual molecules, however, the $3N$ coordinates are not in fact convenient. It is convenient to describe their motions in terms of the motion of their centre of mass. The centre of mass will have 3 coordinates needed to describe the rotation of the molecule about the centre of mass. If one imagines a gradual strengthening of the bonds between the atoms as one goes from a set of independent to the rather firmly held (compact) set that constitutes the molecule, one will find that none of the $3N$ degrees of freedom will be destroyed. Then if 3 translational and 3 rotational degrees of freedom are recognised there will be remaining $3N - 6$ degrees of freedom which must be accounted for by the internal coordinates of the molecular system. Then displacements and velocities in accordance with these $(3N - 6)$ coordinates constitute vibrations of the molecule.

If the molecule is linear, molecular rotations can occur only about the two axes that can be drawn perpendicular to the molecular axis. For such molecules, three overall translations and

$$N_v = \frac{N}{Q_v} e^{-\varepsilon_0(v)hc/kT}$$

For all practical purposes, we can consider $Q_v = 1$ as the second and the other higher terms in expression for Q_v are small compared to the first term 1. Hence

$$N_v = Ne^{-\varepsilon_0(v)hc/kT}$$

10.9 INTERPRETATION OF VIBRATIONAL SPECTRA

The vibrational spectrum of a molecule consists of two major regions-the group frequency region and finger-print region. Group frequencies are vibrations that are associated with certain structural units such as $—CH_3$, —NH, $—C \equiv N$ etc. and appear in fairly constant regions in the spectrum. The approximate constancy of the position of group frequencies form the basis for the structural analysis of the compounds. The region 900–1460 cm^{-1} is very rich in absorption bands and contains mainly bending and certain stretching vibrations. A molecular or structural moiety may often be identified by the assignments of the bands in this region. Though molecules having similar groups show very similar spectra outside this region, they show bands typical of the molecule in this region (hence the name *fingerprint region*). Some of the important group frequencies are listed in Table 10.1. More extensive data are available in the literature. It is to be noted here that confirmation of the findings based on the above concept is needed for the complete identification of compounds. Only practice can give the necessary intuition for making correct assignment of group frequencies.

10.10 APPLICATIONS OF INFRA RED SPECTROSCOPY

Infra Red Spectroscopy, and in particular, Fourier transform Infra-red spectroscopy, is one of the most widely used analytical tools available today. It has a rapidly increasing demand for a routine analysis of a wide range of compounds and the present data handling capabilities have generated this interest. Applications of infrared spectroscopy are of varied types. Some major applications are as follows.