2.3.5 The Spectrum of a Non-Rigid Rotator

The Schrödinger wave equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \text{ J}$$

or

$$\varepsilon_J = E_J/hc = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \tag{2.24}$$

where the rotational constant, B, is as defined previously, and the *centrifugal distortion constant* D, is given by:

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1} \tag{2.25}$$

which is a positive quantity. Equation (2.24) applies for a simple harmonic force field only; if the force field is anharmonic, the expression becomes:

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \cdots \text{ cm}^{-1} \tag{2.26}$$

where H, K, etc., are small constants dependent upon the geometry of the molecule. They are, however, negligible compared with D and most modern spectroscopic data are adequately fitted by Eq. (2.24).

From the defining equations of B and D it may be shown directly that

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\bar{\omega}^2} \tag{2.27}$$

where $\bar{\omega}$ is the vibrational frequency of the bond, and k has been expressed according to Eq. (2.22). We shall see in Chapter 3 that vibrational frequencies are usually of the order of 10^3 cm^{-1}, while B we have found to be of the order of 10 cm^{-1}. Thus we see that D, being of the order 10^{-3} cm^{-1}, is very small compared with B. For small J, therefore, the correction term $DJ^2(J+1)^2$ is almost negligible, while for J values of 10 or more it may become appreciable.

Figure 2.9 shows, much exaggerated, the lowering of rotational levels when passing from the rigid to the non-rigid diatomic molecule. The spectra are also compared, the dashed lines connecting corresponding energy levels and transitions of the rigid and the non-rigid molecules. It should be noted that the selection rule for the latter is still $\Delta J = \pm 1$.

We may easily write an analytical expression for the transitions:

$$\begin{aligned}\varepsilon_{J+1} - \varepsilon_J = \bar{\nu}_J &= B[(J+1)(J+2) - J(J+1)] \\ &\quad - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1}\end{aligned} \tag{2.28}$$

where $\bar{\nu}_J$ represents equally the upward transition from J to $J+1$, or the downward from $J+1$ to J. Thus we see analytically, and from Fig. 2.9, that the spectrum of the elastic rotor is similar to that of the rigid molecule except that each line is displaced slightly to low frequency, the displacement increasing with $(J+1)^3$.

A knowledge of D gives rise to two useful items of information. Firstly, it allows us to determine the J value of lines in an observed spectrum. If we have measured a few isolated transitions it is not always easy to determine from which J value they arise; however, fitting Eq. (2.28) to them—provided three consecutive lines have been measured—gives unique values for B, D, and J. The precision of such fitting is shown by Table 2.1 where the wavenumbers are calculated from the equation:

$$\bar{\nu}_J = 41{\cdot}122(J+1) - 8{\cdot}52 \times 10^{-3}(J+1)^3 \text{ cm}^{-1} \tag{2.29}$$

Secondly, a knowledge of D enables us to determine—although rather inaccurately—the vibrational frequency of a diatomic molecule. From the above data for hydrogen fluoride and Eq. (2.27) we have:

$$\bar{\omega}^2 = \frac{4B^3}{D} = 16{\cdot}33 \times 10^6 \text{ (cm}^{-1})^2$$

i.e.,

$$\bar{\omega} \approx 4050 \text{ cm}^{-1}$$

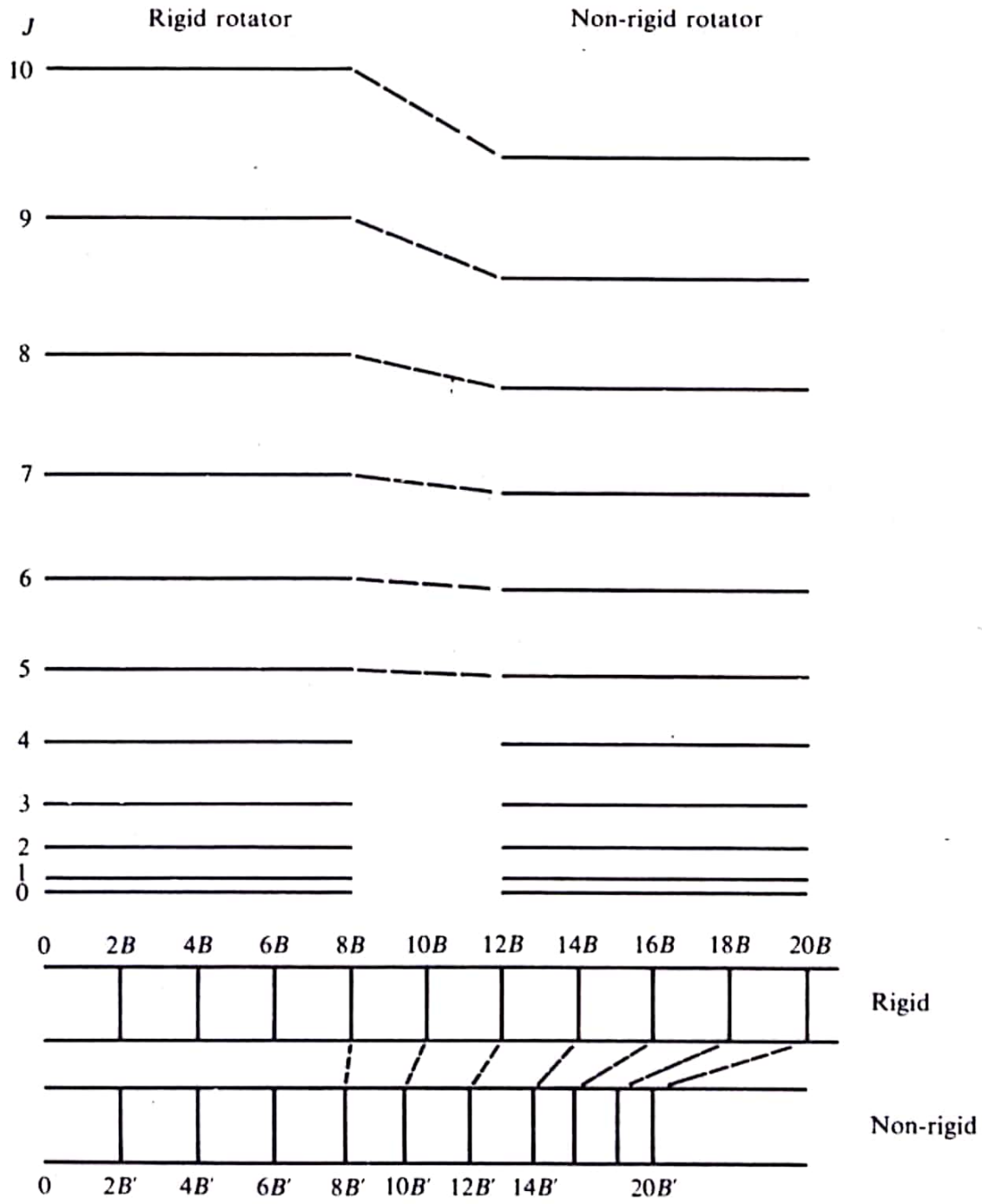

Figure 2.9 The change in rotational energy levels and rotational spectrum when passing from a rigid to a non-rigid diatomic molecule. Levels on the right calculated using $D = 10^{-3}B$.

In the next chapter we shall see that a more precise determination leads to the value 4138·3 cm^{-1}; the two per cent inaccuracy in the present calculation is due partly to the assumption of simple harmonic motion, and partly to the very small, and hence relatively inaccurate, value of D.

The force constant follows directly:

$$k = 4\pi^2 c^2 \bar{\omega}^2 \mu = 960 \text{ N m}^{-1}$$

which indicates, as expected, that H—F is a relatively strong bond.