

Figure 2.8 The effect of isotopic substitution on the energy levels and hence rotational spectrum of a diatomic molecule such as carbon monoxide.

from which m' , the atomic weight of carbon-13, is found to be 13.0007. This is within 0.02 per cent of the best value obtained in other ways.

It is noteworthy that the data quoted above were obtained by Gilliam et al. from $^{13}\text{C}^{16}\text{O}$ molecules in natural abundance (i.e., about 1 per cent of ordinary carbon monoxide). Thus, besides allowing an extremely precise determination of atomic weights, microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorption intensities.

2.3.4 The Non-Rigid Rotator

At the end of Sec. 2.3.1 we indicated how internuclear distances could be calculated from microwave spectra. It must be admitted that we selected our data carefully at this point—spectral lines for carbon monoxide, other than the first, would not have shown the constant $2B$ separation predicted

Table 2.1 Rotation spectrum of hydrogen fluoride

J	$\bar{\nu}_{\text{obs.}}^\dagger$ (cm^{-1})	$\bar{\nu}_{\text{calc.}}^\ddagger$ (cm^{-1})	$\Delta\bar{\nu}_{\text{obs.}}$ (cm^{-1})	B ($= \frac{1}{2}\Delta\bar{\nu}$)	r (nm)
0	41.08	41.11			
			41.11	20.56	0.0929
1	82.19	82.18			
			40.96	20.48	0.0931
2	123.15	123.14			
			40.85	20.43	0.0932
3	164.00	163.94			
			40.62	20.31	0.0935
4	204.62	204.55			
			40.31	20.16	0.0938
5	244.93	244.89			
			40.08	20.04	0.0941
6	285.01	284.93			
			39.64	19.82	0.0946
7	324.65	324.61			
			39.28	19.64	0.0951
8	363.93	363.89			
			38.89	19.45	0.0955
9	402.82	402.70			
			38.31	19.16	0.0963
10	441.13	441.00			
			37.81	18.91	0.0969
11	478.94	478.74			

\dagger Lines numbered according to $\bar{\nu}_J = 2B(J+1) \text{ cm}^{-1}$. Observed data from 'An Examination of the Far Infra-red Spectrum of Hydrogen Fluoride' by A. A. Mason and A. H. Nielsen, published as Scientific Report No. 5, August 1963, Contract No. AF 19(604)-7981, by kind permission of the authors.

\ddagger See Sec. 2.3.5 for details of the calculation.

by Eq. (2.16). This is shown by the spectrum of hydrogen fluoride given in Table 2.1; it is evident that the separation between successive lines (and hence the apparent B value) decreases steadily with increasing J .

The reason for this decrease may be seen if we calculate internuclear distances from the B values. The calculations are exactly similar to those of Sec. 2.3.1 and the results are shown in column 6 of Table 2.1. Plainly the bond length increases with J and we can see that our assumption of a rigid bond is only an approximation; in fact, of course, all bonds are elastic to some extent, and the increase in length with J merely reflects the fact that the more quickly a diatomic molecule rotates the greater is the centrifugal force tending to move the atoms apart.

Before showing how this elasticity may be quantitatively allowed for in rotational spectra, we shall consider briefly two of its consequences. First,

when the bond is elastic, a molecule may have vibrational energy—i.e., the bond will stretch and compress periodically with a certain fundamental frequency dependent upon the masses of the atoms and the elasticity (or force constant) of the bond. If the motion is simple harmonic (which, we shall see in Chapter 3, is usually a very good approximation to the truth) the force constant is given by:

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu \quad (2.22)$$

where $\bar{\omega}$ is the vibration frequency (expressed in cm^{-1}), and c and μ have their previous definitions. Plainly the variation of B with J is determined by the force constant—the weaker the bond, the more readily will it distort under centrifugal forces.

The second consequence of elasticity is that the quantities r and B vary during a vibration. When these quantities are measured by microwave techniques many hundreds of vibrations occur during a rotation, and hence the measured value is an average. However, from the defining equation of B we have:

$$B = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 c \mu r^2}$$

or

$$B \propto 1/r^2 \quad (2.23)$$

since all other quantities are independent of vibration. Now, although in simple harmonic motion a molecular bond is compressed and extended an equal amount on each side of the equilibrium distance and the average value of the distance is therefore unchanged, the average value of $1/r^2$ is not equal to $1/r_e^2$, where r_e is the equilibrium distance. We can see this most easily by an example. Consider a bond of equilibrium length 0.1 nm vibrating between the limits 0.09 and 0.11 nm. We have:

$$\langle r \rangle_{\text{av.}} = \frac{0.09 + 0.11}{2} = 0.1 = r_e$$

but

$$\left\langle \frac{1}{r^2} \right\rangle_{\text{av.}} = \frac{(1/0.09)^2 + (1/0.11)^2}{2} = 103.05 \text{ nm}^2$$

and therefore $\langle r \rangle_{\text{av.}} = \sqrt{1/103.5} = 0.0985 \text{ nm}$. The difference, though small, is not negligible compared with the precision with which B can be measured spectroscopically. And in fact the real situation is rather worse. We shall see in Chapter 3 that real vibrations are not simple harmonic, since a real bond may be stretched more easily than it may be compressed, and this usually results in $r_{\text{av.}}$ being greater than $r_{\text{eq.}}$

It is usual, then, to define three different sets of values for B and r . At the equilibrium separation, r_e , between the nuclei, the rotational constant is B_e ; in the vibrational ground state the average internuclear separation is r_0 associated with a rotational constant B_0 ; while if the molecule has excess vibrational energy the quantities are r_v and B_v , where v is the vibrational quantum number.

During the remainder of this chapter we shall ignore the small differences between B_0 , B_e , and B_v —the discrepancy is most important in the consideration of vibrational spectra in Chapter 3.

We should note, in passing that the rotational spectrum of hydrogen fluoride given in Table 2.1 extends from the microwave well into the infra-red region (cf. Fig. 1.4). This underlines the comment made in Chapter 1 that there is no fundamental distinction between spectral regions, only differences in technique. Since hydrogen fluoride, together with other diatomic hydrides, has a small moment of inertia and hence a large B value, the spacings between rotational energy levels become large and fall into the infra-red region after only a few transitions. Historically, indeed, the moments of inertia and bond lengths of these molecules were first determined from spectral studies using infra-red techniques.

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:

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

or

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

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

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

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:

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

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

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

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:

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

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:

$$\bar{\nu}_J = 41.122(J+1) - 8.52 \times 10^{-3}(J+1)^3 \text{ cm}^{-1} \quad (2.29)$$

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:

$$\bar{\omega}^2 = \frac{4B^3}{D} = 16.33 \times 10^6 \text{ (cm}^{-1}\text{)}^2$$

i.e.,

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

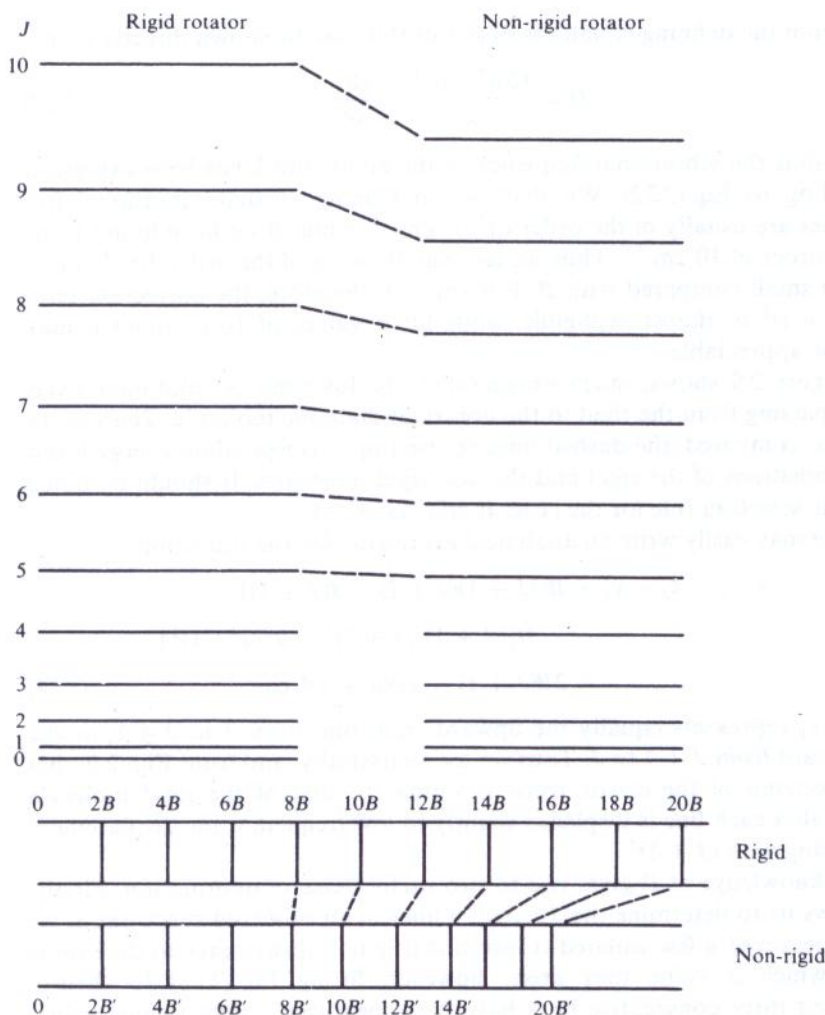


Figure 2.9 The change in rotational energy levels and rotational spectrum when passing from a rigid to a non-rigid diatomic molecule. Levels on the right calculated using $D = 10^{-3}B$.

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.