

### 2.3.3 The Effect of Isotopic Substitution

When a particular atom in a molecule is replaced by its isotope—an element identical in every way except for its atomic mass—the resulting substance is identical chemically with the original. In particular there is no appreciable change in internuclear distance on isotopic substitution. There is, however, a change in total mass and hence in the moment of inertia and  $B$  value for the molecule.

Considering carbon monoxide as an example, we see that on going from  $^{12}\text{C}^{16}\text{O}$  to  $^{13}\text{C}^{16}\text{O}$  there is a mass increase and hence a decrease in the  $B$  value. If we designate the  $^{13}\text{C}$  molecule with a prime we have  $B > B'$ . This change will be reflected in the rotational energy levels of the molecule and Fig. 2.8 shows, much exaggerated, the relative lowering of the  $^{13}\text{C}$  levels with respect to those of  $^{12}\text{C}$ . Plainly, as shown by the diagram at the foot of Fig. 2.8, the spectrum of the heavier species will show a smaller separation between the lines ( $2B'$ ) than that of the lighter one ( $2B$ ). Again the effect has been much exaggerated for clarity, and the transitions due to the heavier molecule are shown dashed.

Observation of this decreased separation has led to the evaluation of precise atomic weights. Gilliam et al., as already stated, found the first rotational absorption of  $^{12}\text{C}^{16}\text{O}$  to be at  $3.84235\text{ cm}^{-1}$ , while that of  $^{13}\text{C}^{16}\text{O}$  was at  $3.67337\text{ cm}^{-1}$ . The values of  $B$  determined from these figures are:

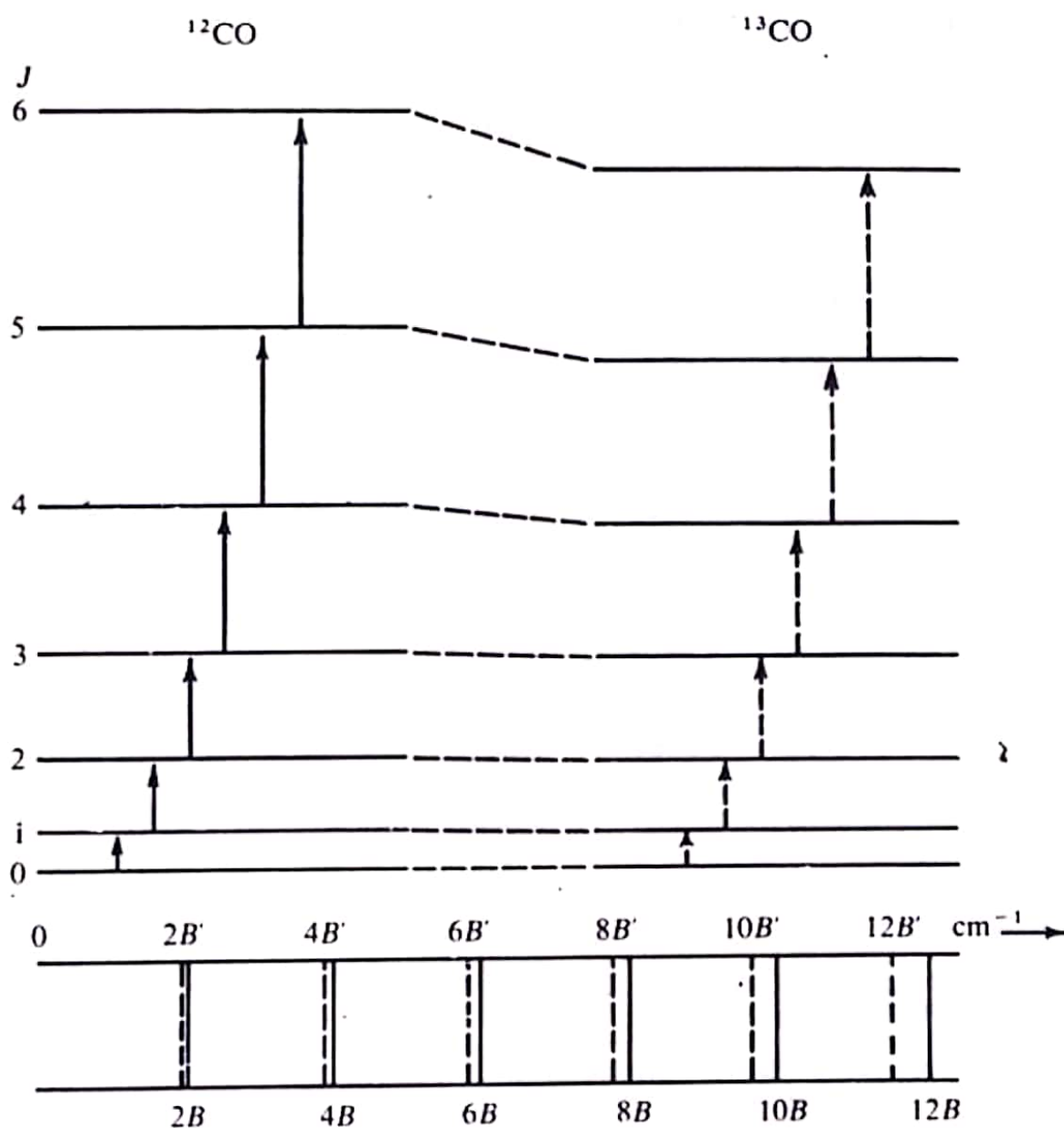
$$B = 1.92118\text{ cm}^{-1} \quad \text{and} \quad B' = 1.83669\text{ cm}^{-1}$$

where the prime refers to the heavier molecule. We have immediately:

$$\frac{B}{B'} = \frac{h}{8\pi^2 I c} \cdot \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where  $\mu$  is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12.00, we have:

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.9994m'}{15.9994 + m'} \times \frac{12 + 15.9994}{12 \times 15.9994}$$



**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.