

# Rotational Spectroscopy

## 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, it can be seen 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 Figure 10 Shows, much exaggerated, the relative lowering of  $^{13}\text{C}$  levels with respect to those of  $^{12}\text{C}$ . Plainly, as shown by the diagram at the foot of Figure 10, 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 transition due to the heavier molecule are shown dashed.

Observation of this decreased separation has led to the evaluation of precise atomic weights. As per spectroscopic data, it is found that the first rotational absorption of  $^{12}\text{C}^{16}\text{O}$  is at  $3.84235 \text{ cm}^{-1}$ , while that of  $^{13}\text{C}^{16}\text{O}$  is at  $3.67337 \text{ cm}^{-1}$ . The values of B determined from these figure are:

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

Where the prime refers to the heavier molecule. It can be seen that :

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

# Rotational Spectroscopy

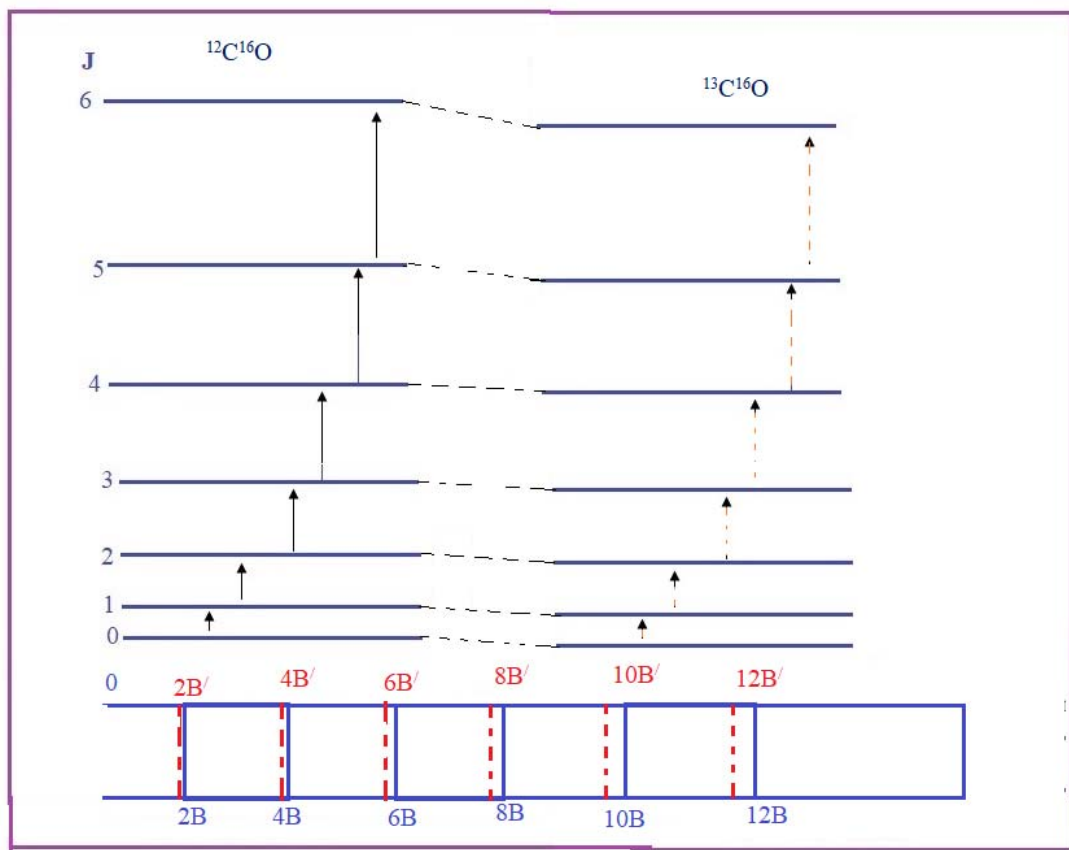


Figure 10: The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as carbon monoxide

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

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

from which  $m'$ , the atomic weight of carbon -13, is found to be 13,0007. This is within 0.02 percent of the best value obtained in other ways.

So this can be conclude that this process allow an extremely precise determination of atomic weights.



# Rotational Spectroscopy

**Non –Rigid Rotator:** 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 distance from the B values. 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 atom apart.

Before showing how this elasticity may be quantitatively allowed for in rotational spectra, we shall consider briefly two of its consequences. Firstly, 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 the force constant is given by :

$$k=4\pi^2\tilde{\omega}^2c^2\mu \dots\dots\dots(17)$$

where  $\tilde{\omega}$  is the vibrational frequency ( expressed in  $\text{cm}^{-1}$ ), and , c and  $\mu$  have their previous definition. 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 **secondly** 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:

$$B=h/8\pi^2Ic=h/8\pi^2c\mu r^2$$

or  $B\propto 1/r^2 \dots\dots\dots(18)$

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.

Due to this second cause the concept of non –rigid rotator is introduced.

# Rotational Spectroscopy

## The Spectrum of a Non-rigid Rotator

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

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

or  $\epsilon_J = \frac{E_J}{hc} = BJ(J+1) - DJ^2(J+1)^2 \quad \text{cm}^{-1}$  .....(19)

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

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k} \quad \text{cm}^{-1}$$
 .....(20)

which is a positive quantity. Equation (19) applies for a simple harmonic force field only; if the force field is anharmonic, the expression becomes:

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \dots \text{cm}^{-1}$$
 .....(21)

where H, K, etc., are small constants dependent upon the geometry of the molecule. They are however, negligibly small compared with D and most modern spectroscopic data are adequately fitted by Eq.(19).

### Selection rule : ΔJ=±1

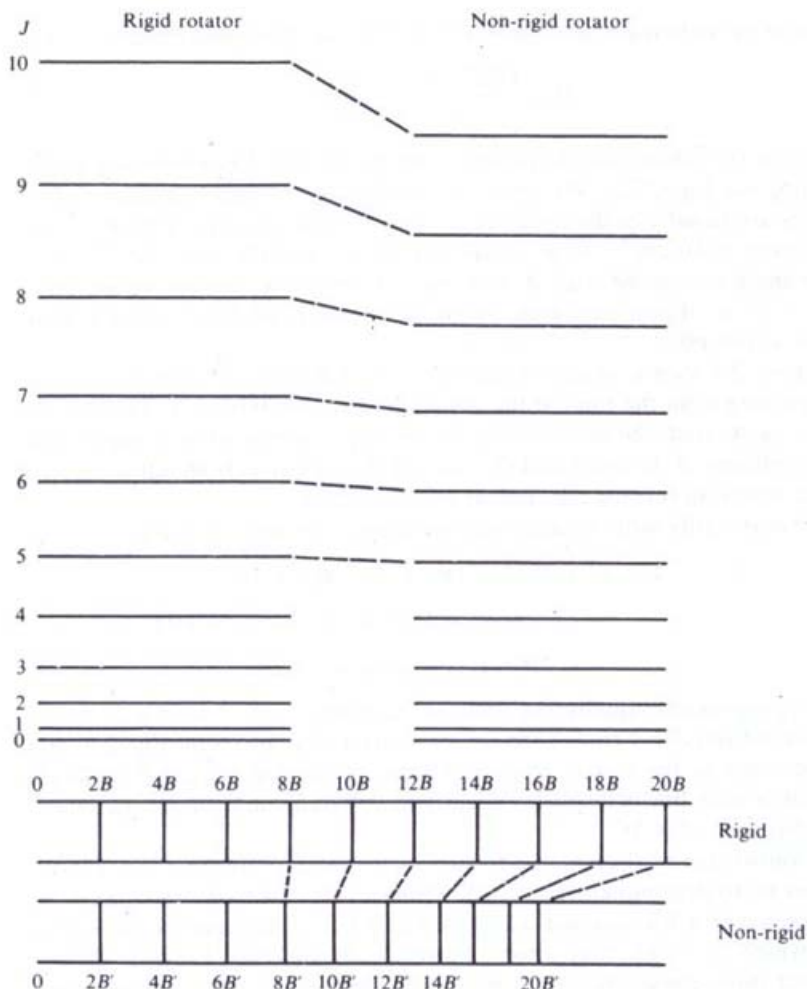
Analytical expression for the transition :

$$\epsilon_{J+1} - \epsilon_J = \bar{\nu}_J = B[(J+1)(J+2) - J(J+1)] - D[(J+1)^2(J+2)^2 - J^2(J+1)^2]$$

$$= 2B(J+1) - 4D(J+1)^3 \quad \text{cm}^{-1}$$
 .....(22)

where  $\bar{\nu}_J$  represents equally the upward transition from J to J+1, or the downward from J+1 to J.

# Rotational Spectroscopy



**Figure11: The change in rotational energy levels and spectrum when passing from a rigid to non rigid diatomic molecule. Energy levels on the right are calculated using  $D=10^{-3}B$**

## Linear Tri-atomic Molecule

We consider first molecule such as carbon oxysulphide OCS or chloroacetylene  $HC\equiv CCl$ , where all the atoms lie on a straight line, since this type gives rise to particularly simple spectra in the microwave region. Since  $I_B=I_C; I_A=0$ , as for diatomic molecules the energy levels are given by a formula identical with Equation 21 :

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 + \dots \text{ cm}^{-1} \dots \dots \dots (23)$$

and the spectrum will show the same  $2B$  separation modified by the distortion constant. In fact, the whole of the discussion on diatomic molecules applies equally to all linear molecules; three points, however, should be underlined:



# Rotational Spectroscopy

1. Since the moment of inertia for the end-over-end rotation of a polyatomic linear molecule is considerably greater than that of a diatomic molecule, the B value will be much smaller and the spectral lines more closely spaced. Thus B values for diatomic molecules are about  $10\text{cm}^{-1}$ , while for triatomic molecules they can be  $1\text{cm}^{-1}$  or less, and for larger molecules smaller still.

2. The molecule must, as usual, possess a dipole moment if it is to exhibit a rotational spectrum. Thus OCS will be microwave active, while  $\text{OCS}$  (more usually written  $\text{CO}_2$ ) will not. In particular, it should be noted that isotopic substitution does not lead to a dipole moment since the bond lengths and atomic charges are unaltered. Thus  $^{16}\text{O}^{18}\text{O}$  is microwave inactive.

3. A non-cyclic polyatomic molecule containing N atoms has altogether N-1 individual bond lengths to be determined. Thus in the triatomic molecule OCS there is the CO distance,  $r_{\text{CO}}$ , and the CS distance,  $r_{\text{CS}}$ . On the other hand, there is only one moment of inertia for the end-over-end rotation of OCS, and only this one value can be determined from the spectrum.

From the microwave spectra data of OCS, taking the value of B as  $0.2027\text{cm}^{-1}$ , we can calculate :

$$I_B = h/8\pi^2 Bc = 137.95 \times 10^{-47} \text{kg m}^2$$

From this one observation it is plainly impossible to deduce the two unknowns,  $r_{\text{CO}}$  and  $r_{\text{CS}}$ . The difficulty can be overcome, however, if we study a molecule with different atomic masses but the same bond length—i.e. an isotopically substituted molecule—since this will have a different moment of inertia.