# Microwave Spectroscopy Note 2

**Effect of Isotopic substitution**

When a particular atom in a molecule is replaced by its isotope, the resulting substance is chemically identical with the original. There is no appreciable changes in the internuclear distances on isotopic substitution, but mass, moment of inertia and hence the value of B changes.

With increase in isotope mass ($^{12}C^{16}O$ to $^{13}C^{16}O$), the B decreases. If the substituent molecule is designated with B' then B>B'. This change is reflected in the rotational energy level of the molecule. The spectrum of the heavier species will so a smaller separation between the lines (2B') then the lighter one (B).

Observation of this decrease separation has led to the evaluation of precise atomic weight.

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

where μ and μ' are the reduced mass of the lighter and a heavier species. Knowing the value of B, B' and μ, the value of μ' hence the mass of the isotope can be determined.

Non rigid router or elastic rotor

All bonds are elastic and the increase in bond length with the increasing J reflects the fact that the more quickly a diatomic molecule rotate, the greater is the centrifugal force tending to move the atoms apart. When the bonds are elastic, a molecule may have vibrational energy with a certain fundamental frequency depending on the mass of atom and the elasticity of the bond.

A second consequence of the elasticity is that the quantity I and B vary during a vibration.

On solving the Schrodinger equation for a non-rigid molecule, the rotational energy level is found to be

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

Where rotational quantum number J = 0, 1, 2, 3, 4…

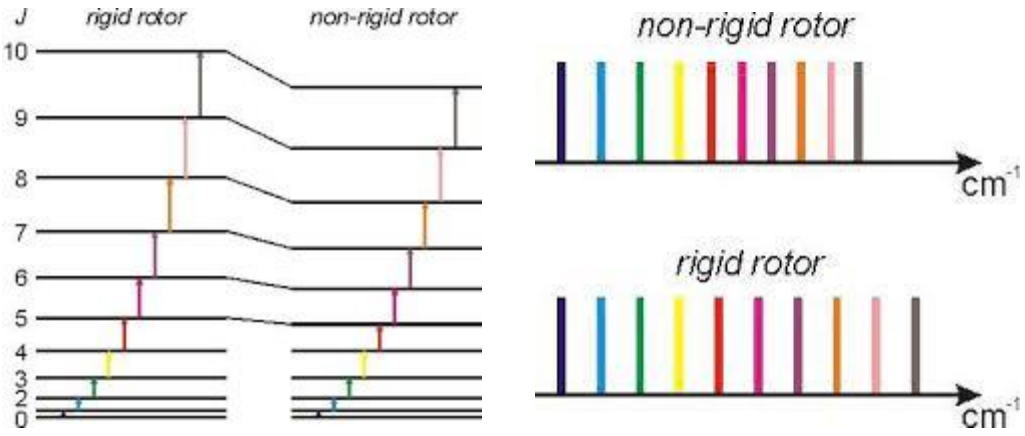
In spectroscopic unit

$$E_J = \frac{h}{8\pi^2 Ic} J(J+1) - \frac{h^3}{32\pi^4 I^2 r^2 kc} J^2(J+1)^2 \text{ cm}^{-1}$$

Or

$$E_J = BJ(J+1) - DJ^2(J+1)^2$$

Where B is rotational constant and D is centrifugal Distortion constant.




The figure shows the lowering of rotational level on passing from the rigid to the nonrigid diatomic molecule. The selection rule for non-rigid rotor is ΔJ = +/-1.

Determination of bond length for a rigid diatomic rotor the wave number of the radiation absorb to raise it from J to j + 1 state

$\bar{\nu} = 2B(J+1)\ cm^{-1}$

Where rotational quantum number J = 1, 2, …. etc and rotational constant $B=h/8\pi^2Ic\ cm^{-1}$. Hence knowing the $\bar{\nu}$ for a transition and reduce mass of the molecule the bond length may be determined.