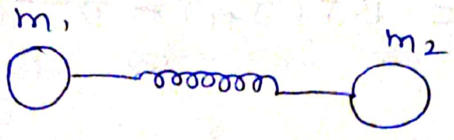
# Non rigid rotator



① In non rigid rotator the bond is ~~Not~~ elastic. ~~but rigid~~

② When the bond is elastic a molecule, may have vibrational energy hence the bond stretches and compress periodically with a certain fundamental frequency depending uppon the mass and elasticity of the atoms. The vibrational motion simple harmonic and the force constant is given by $k = 4\pi^2 \bar{\nu}^2 c^2 \mu$ where $\bar{\nu}$ is the vibrational frequency in $cm^{-1}$

~~The Schrodinger equation is $H\psi = E\psi$ In this case we consider the additional vibrational energy in addition to the rotational energy.~~

We know the Schrodinger equation is $H\psi = E\psi$

In this case we have to consider the Hamiltonian for a non rigid rotator

On scholving the Schrodinger equation the energy eigen value is

$E_J =$ -

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

$$J = 0, 1, 2 \quad \text{———} \quad ①$$

where 'D' is the centrifugal distortion constant

$$D = \frac{4B^3}{\bar{\nu}^2} \text{ cm}^{-1} \quad \text{———} \quad ②$$

$\bar{\nu}$ — fundamental vibration frequency

$B$ — rotational constant

The fundamental frequency of vibration is

$$\bar{\nu} = \frac{\nu}{c}$$

$$\nu = \frac{1}{2\pi}\sqrt{k/\mu}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{k/\mu} \quad \text{———} \quad ③$$

$k$ — force constant

$\mu$ — reduced mass of the molecule

Substituting the value of $\bar{\nu}$ and $B$ in eqn ②

$$D = 4\left(\frac{h}{8\pi^2 I c}\right)^3 \left(\frac{4\pi^2 c^2 \mu}{k}\right)$$

$$= \frac{h^3 \mu}{32\pi^4 I^3 c k} \quad \text{———} \quad ④$$

$$I = \mu r^2$$

$$= \frac{h^3 \mu}{32\pi^4 \mu^3 r^6 c k}$$

$$D = \frac{h^3}{32\pi^4 \mu^2 r^6 c k}$$

From the above equation it is clear that the centrifugal distortion effects are greater for a molecule with small moments of inertia and small force constant (refer eqn 4)

As the distortion increases the rotational energy decreases. As the value of J ~~[illegible]~~ increases i.e for higher rotational levels D also correspondingly increases and energy ~~value~~ decreas

Applying the selection rule $\Delta J = \pm 1$ the frequency of the transition is

$$\bar{\nu}_j = \varepsilon_{j+1} - \varepsilon_j$$

$$= B\cancel{[(J+1)(J+2) - J(J+1)]}$$

$$- \cancel{D[(J+1)^2(J+2)^2 - J^2(J+1)^2]}$$

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

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

$$= B(J+1)[J+2-J] - D(J+1)^2[(J+2)^2 - J^2]$$

$$= 2B(J+1) - D(J+1)^2[\cancel{J^2} + 4J + 4 - \cancel{J^2}]$$

$$= 2B(J+1) - 4D(J+1)^2(J+1)$$

$$= 2B(J+1) - 4D(J+1)^3 \qquad J = 0, 1, 2 \ldots$$

The first term is the same as the one due to a rigid molecule

The additional term gives the shift of the lines from that of the rigid molecule ~~That shift~~. The spectrum of the rigid rotator and non rigid rotator is given in figure for comparison of the non rigid rotator with that of the rigid rotator. ~~If the J value of the transitions are fixes~~

If the J value of transitions are fixed, from the frequencies of the two lines one can determine the constants B and D from which an estimate of the fundamental vibrationa frequency of the diatomic molecule may be rotated.

Rotational spectra

## Microwave spectroscopy

### Linear polyatomic molecules

Linear polyatomic molecules can also be treated similar to the diatomics. Since $I_a = 0$, $I_b = I_c$ as for diatomics the energy levels $E_J$ are given by a formula identical to that of diatomics.

The selection rule is $\Delta J = \pm 1$ and the frequency of the $J \rightarrow J+1$ transition is

$$\bar{\nu}_J = 2B(J+1) - 4D(J+1)^3 \ \text{cm}^{-1} \quad J = 0, 1, 2, \ldots$$

The spectrum will show the same 2B separation modified by the distortion constant.

(The moment of inertia for the end-to-end rotation of the linear polyatomic molecule is considerably greater)

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

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 $cm^{-1}$, while for triatomic molecules they can be 1 $cm^{-1}$ or less, and larger molecules still smaller.

2. The molecule must possess a dipole moment in order to exhibit a rotational spectrum. Thus OCS will be microwave active OCO will be microwave in active.

3. A linear molecule containing n atoms altogether has (n-1) individual bond lengths to be determined. Thus in a triatomic molecule OCS there is the CO distance $r_{CO}$ and the CS distance $r_{CS}$. But experiment we ~~of~~ from the spectrum ~~we can find out the~~ there is only one moment of inertia for the end-over-end rotation of OCS.

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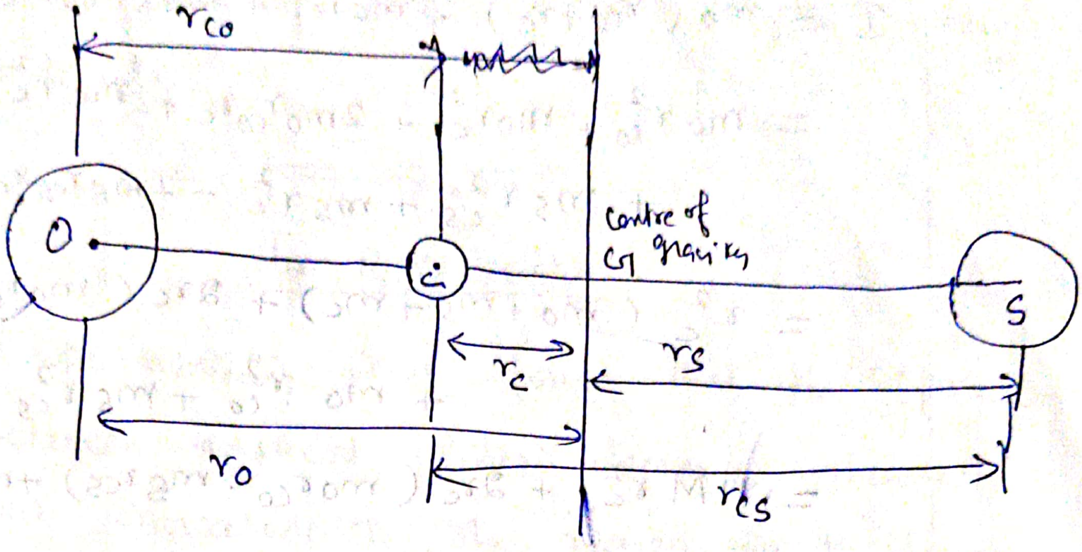
However if we study a isotopically substituted molecule we will have a different moment of inertia with the same bond lengths. Hence for the determination of $r_e$ (inter nuclear distance) $r_{CO}$ and $r_{CS}$ parameters we requires a study of isotopically substituted molecule.

Let us consider the rotation of OCS in detail



$r_o$, $r_c$ and $r_s$ represent the distances of the atoms from the centre of gravity.

Consideration of moments of OCS molecule

$$m_o r_o + m_c r_c = m_s r_s \quad \text{———} \quad ①$$

The moment of inertia is

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \quad \text{———} \quad ②$$

$$\left.\begin{aligned} r_o &= r_{co} + r_c \\ r_s &= r_{cs} - r_c \end{aligned}\right\} \quad \text{———} \quad ③$$

Substituting ⑤ in ①

$$m_o(r_{co} + r_c) + m_c r_c = m_s(r_{cs} - r_c)$$

$$m_o r_{co} + m_o r_c + m_c r_c = m_s r_{cs} - m_s r_c$$

$$m_o r_{co} - m_s r_{cs} = -r_c(m_s + m_c + m_o)$$

$$M r_c = m_s r_{cs} - m_o r_{co} \quad \text{———} \quad ④$$

M total mass of the molecule

Substituting ③ in ②

$$I = m_O(r_{CO}+r_C)^2 + m_C r_C^2 + m_S(r_{CS}-r_C)^2$$

$$= m_O r_{CO}^2 + m_O r_C^2 + 2m_O r_{CO} r_C + m_C r_C^2$$
$$+ m_S r_{CS}^2 + m_S r_C^2 - 2m_S r_{CS} r_C$$

$$= r_C^2(m_O + m_S + m_C) + 2r_C(m_O r_{CO} - m_S r_{CS})$$
$$+ m_O r_{CO}^2 + m_S r_{CS}^2$$

$$= M r_C^2 + 2r_C(m_O r_{CO} - m_S r_{CS}) + m_O r_{CO}^2 + m_S r_{CS}^2$$

Substituting the value of $r_C$ from eqn ④ and simplifying we get

$$I = m_O r_{CO}^2 + m_S r_{SS}^2 - \frac{(m_O r_{CO} - m_S r_{CS})^2}{M} \quad ⑤$$

This is the eqn for $^{16}O\,^{12}C\,^{32}S$

Considering now the isotopic molecule

$^{18}O\,^{12}C\,^{34}S$

$\underline{I'} =$ ~~[illegible]~~

$$I' = m_O' r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_O' r_{CO} - m_S r_{CS})^2}{M'} \quad ⑥$$

We can solve eqn ⑤ and ⑥ and find out the value of $r_{CO}$ and $r_{CS}$ provided if we know the value of $I'$ from the microwave spectrum of isotopic molecule

The extension of the above discussion with more than three atoms is straight forward; it suffices to say here that microwave studies have led to very precise determination of many bond lengths in such molecules.

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This D being r
correction term $DJ^2(J+1)^2$

fundamental vibration frequency of the diatomic molecule may be estimated.

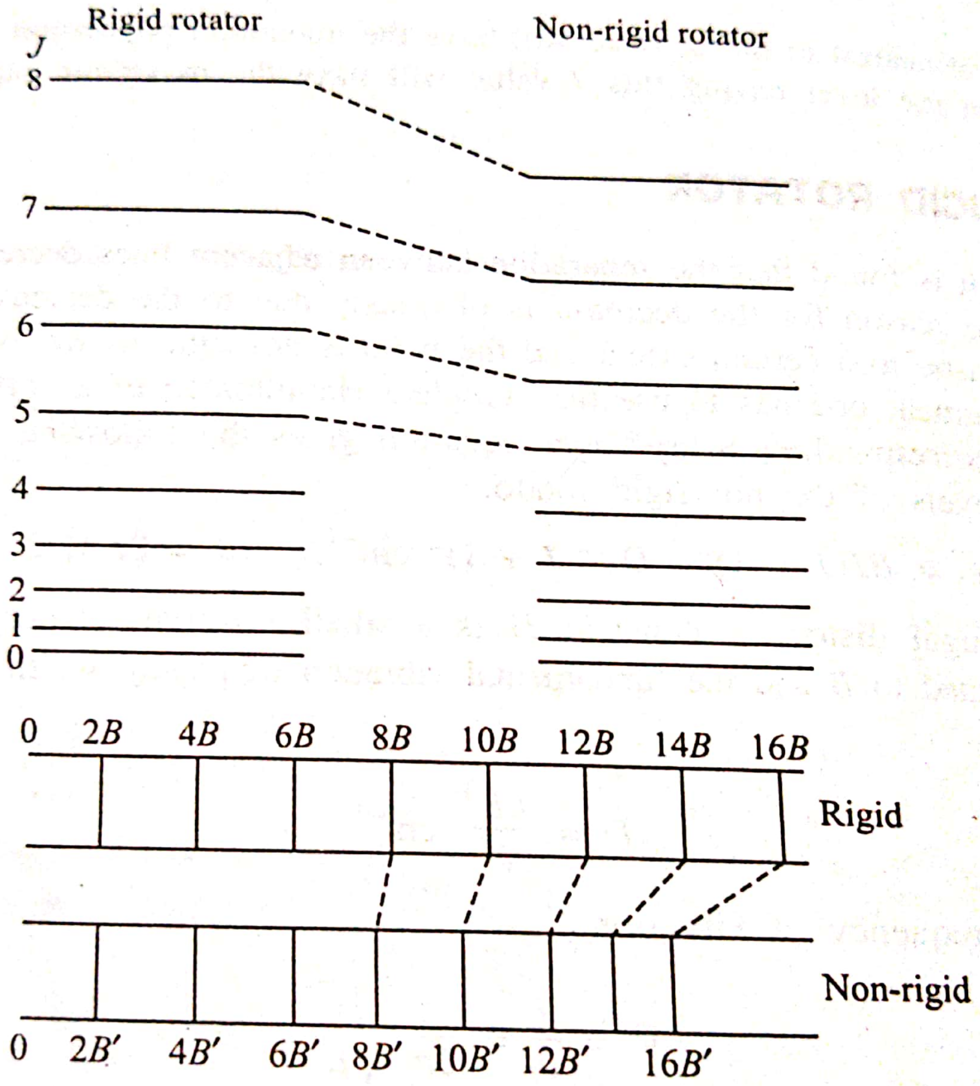

**Figure 6.5** Schematic representation of the energy levels and spectrum of rigid and rigid rotors.