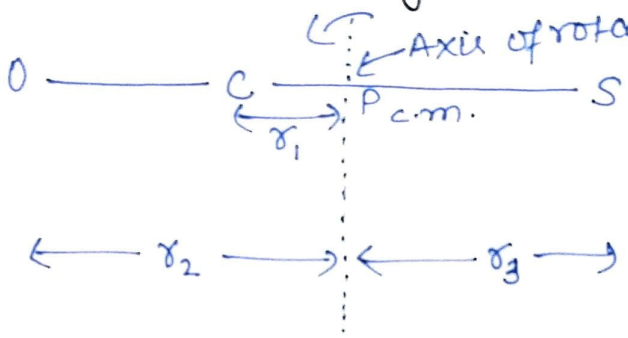
Application of Microwave spectroscopy for the determination of Bond distances in polyatomic molecules:-



consider the gaseous molecule O=C=S (linear triatomic molecule) for determination of two bond distances O-C and C-S. This can be done by <u>isotopic substitution method</u>.

(1) For $^{16}O = {}^{12}C = {}^{32}S$

The centre of mass is given as P where

$$m_c r_1 + m_o r_2 = m_s r_3 \quad \text{—— (1)}$$

The moment of inertia is given by

$$I = m_c r_1^2 + m_o r_2^2 + m_s r_3^2 \quad \text{—— (2)}$$

Also

$$r_2 = r_{co} + r_1 \;, \text{ And } r_3 = r_{cs} - r_1 \quad \text{—— (3)}$$

where r_{co} and r_{cs} are interatomic distances

$$m_c r_1 + m_o (r_{co} + r_1) = m_s (r_{cs} - r_1) \quad \text{— (4)}$$

{ substituting eq. (3) to eqn (1) }

or $$(m_c + m_o + m_s) r_1 = m_s r_{cs} - m_o r_{co} \quad \text{— (5)}$$

$$r_1 = (m_s r_{cs} - m_o r_{co}) M \quad \text{— (6)}$$

where $M = m_c + m_o + m_s$

$$I = m_c r_1^2 + m_o (r_{co} + r_1)^2 + m_s \quad \text{— (7)}$$

or $$I = (m_s r_{cs}^2 - m_o r_{co}^2 + 2 m_o m_s r_{co} r_{cs} - m_s r_{cs}^2) / M$$

— (8)

r_{co} and r_{cs} are unknown factors in this equation.

→ Assuming that isotopic substitution does not alter the interatomic distances.

Applying assumption to $^{16}O = ^{12}C = ^{34}S$, the inertia for the molecule:-

$$I' = (m_s' r_{cs}^2 - m_o r_{co}^2 + 2 m_o m_s' r_{co} r_{cs} - m_s' r_{cs}^2)/M \quad \text{—⑨}$$

I and I' can be obtained from microwave spectra of $^{16}O = ^{12}C = ^{32}S$ and $^{16}O = ^{12}C = ^{34}S$ molecules and from these moment of inertia the unknown r_{co} and r_{cs} can be determined.

→ The small difference in bond length caused by the changing isotopes. This is due to zero-point vibrations whose amplitudes depends upon the masses of the atom. Measured bond lengths change upon isotopic substitution.

* Microwave Oven:- What's wrong with them?

The mode of microwave operation depends upon the absorption by the food of the microwave radiation in which it is placed. The biological molecules is are too big and thus are unable to rotate but the water molecules being small excited easily and rotate easily. The heating being internal rather than external as in conventional, stays excited and kept on re-emitting.

Rotational Spectra of polyatomic molecules

The rotational spectra of polyatomic molecules shows feature is not found in the spectra of diatomic molecules. While the diatomics have single bond distance to deal with polyatomics may have more moments of inertias.

According to cartesian system (x, y, z) there are nine components of moment of inertia.

In principal axis system (A, B, C) these components reduce to three moment of inertia I_A, I_B and I_C where I_A, I_B and I_C are principal moment of inertia about axis A, B and C respectively.

Polyatomic molecules are classified into various types of rotators:-

① Linear rotors:-

In such rotors

$$I_A = I_B \text{ and } I_C = 0$$

They simply follow the eq.

$$F(J) = BJ(J+1)$$ for calculation of energy.

Here, isotopic substitution method used to determine the bond distances.

Some of the examples are HX, O=C=S, H-C≡N.

(2) Spherical top molecules:-

Since a spherical top molecule such as CH_4 or SF_6 does not possess a permanent dipole moment, it may not be ~~dipole~~ microwave active.

In such molecules

$$I_A = I_B = I_C$$

And molecules such as CH_4, SF_6, UF_6 come under this category.

(3) Symmetric Top molecules:-

For solution of Schrodinger wave equation for a symmetric top molecule gives the following expression for the energy levels of the rotors:-

$$E_{J,K} = BJ(J+1) + (A-B)K^2 \quad \text{——} (1)$$

where K is the component of J about the unique axis and rotational constants A and B (in cm^{-1}) are defined as

$$A = \frac{h}{8\pi^2 I_A C} \quad \text{and} \quad B = \frac{h}{8\pi^2 I_B C}$$

Also in such molecules

$I_A > I_B = I_C$ (for prolate symmetry) → ~~such~~ and $I_A < I_B = I_C$ (for oblate symmetry)

$2J+1$ given by K, $K = 0, \pm 1, \pm 2 \cdots \pm J$

and selection rule being $\Delta J = 0, \pm 1$ and $\Delta K = 0$.

(4) Asymmetric Top molecule:-

$$I_A \neq I_B \neq I_C$$

and includes H_2O like molecules.