Microwave (Rotational) Spectroscopy

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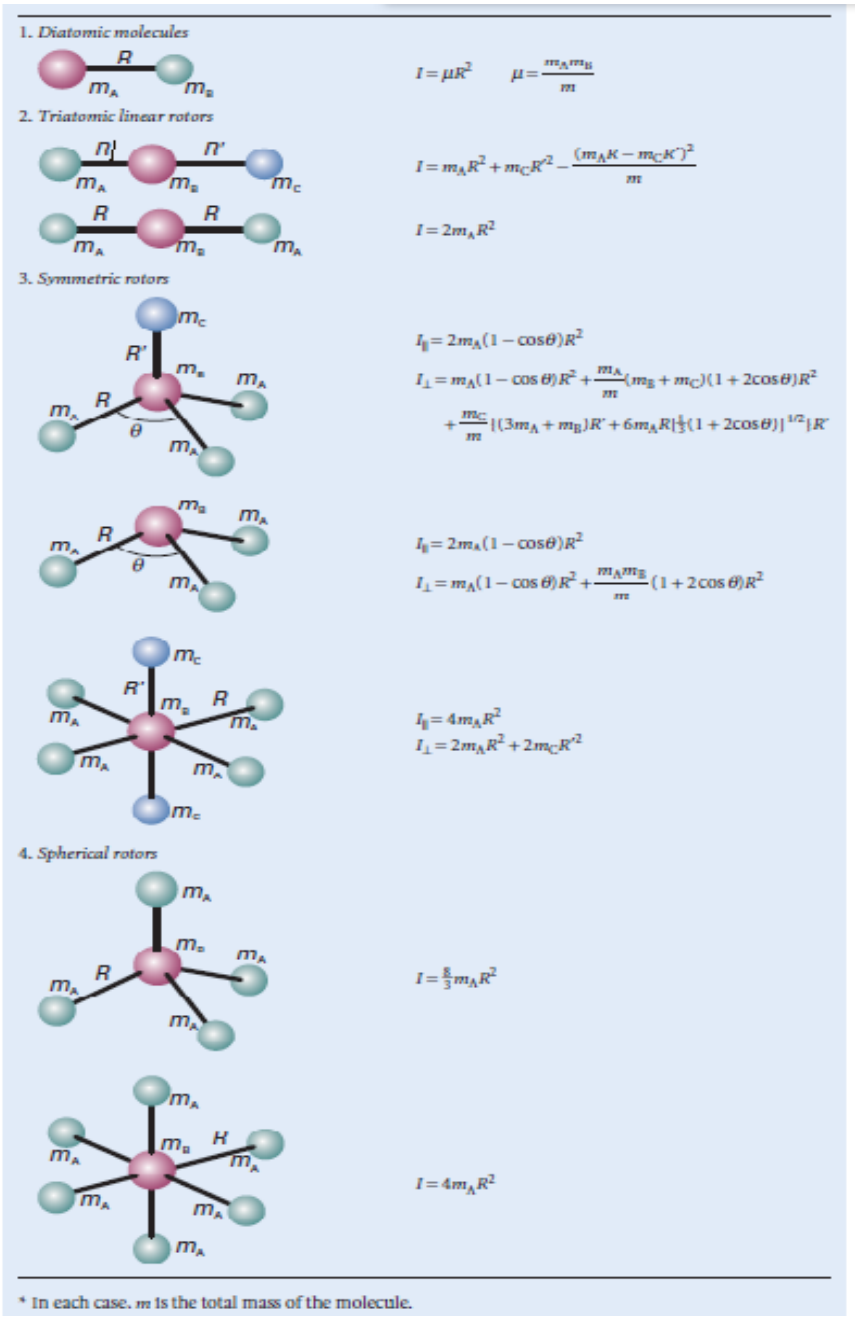
1.1 Classification of Molecules

The moment of inertia of a molecule is defined as the mass of each atom multiplied by the square of its distance from the rotational axis through the centre of mass of the molecule. It opposes any change in its state of rest or uniform rotation.

$$I = \Sigma m_i r_i^2$$



For asymmetric tops like H_2O,

Ia = $2m_H R^2(\sin 52.3)^2$, where mH = mass of hydrogen and R is bond length.

The molecules are usually classified into four groups based on the relative values of principal moments of Inertia I_a, I_b and I_c, where *a,b,c* are axes and are selected in such a way that $I_a > I_b > I_c$

(i) Linear Molecules:

In this type, all the atoms of the molecules are arranged in a straight line. For example, HCl, CO_2, OCS, HCN, C_2H_2 etc are some of the molecules of this category. The three mutually perpendicular principal axes *a,b,c* of rotation may be taken as:

$a \rightarrow$ the molecular axis

$b \rightarrow$ the direction in the plane of the paper passing through the centre of gravity of the molecule and perpendicular to it a – axis.

$c \rightarrow$ the axis perpendicular to both a and b axes, and passing through the centre of gravity of the molecule.

For a linear molecule, the principal moments of Inertia are $I_a = 0$ and $I_b = I_c$. The moments of Inertia I_b and I_c correspond to the end over end rotation of the molecule and therefore they are equal, and $I_a = 0$. Since the nuclei of the atoms which give the main contribution of mass are situated in the axis *a*.

ii) Symmetric Tops: -

In a symmetric top, two of the principal moments of inertia are equal and all the three are non-zero.

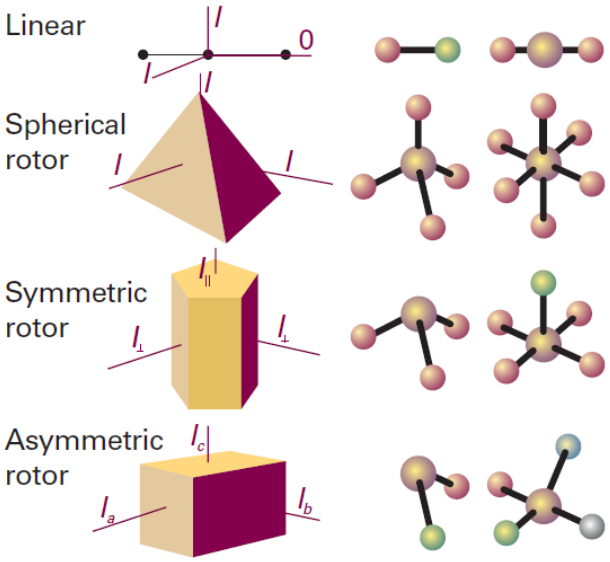
The molecule in this class is further subdivided into the groups prolate symmetric top and oblate symmetric top. In probate, $I_a < I_b = I_c$ (Ex. CH_3Cl, CH_3F, CH_3CN, NH_3, etc.,) and in oblate, $I_a > I_b = I_c$ (Ex. BH_3, BCl_3, etc.,).

iii) Spherical Tops:

When all the three principal moments of inertia of a molecule are equal, it is called a spherical top. (Ex. CH_4, OsO_4, SF_6, CCl_4, etc.,)

iv. Asymmetric Tops :-

In an asymmetric top molecule, all the three moments of Inertia are distinct $I_a \neq I_b \neq I_c$. Some of the examples are H_2O, CH_3OH CH_3CH_2Cl etc., The majority of the molecules belong to this group.



1.2 Rotational Spectra of Rigid diatomic molecules

The rotational energy of a linear molecule consisting atoms with mass m1 and m2 and bond length r is

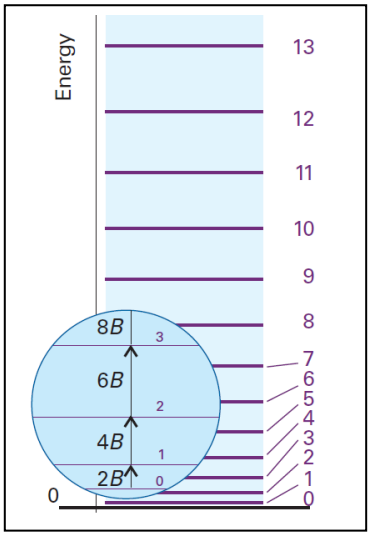
$$E_j = \frac{\hbar}{2I}J(J+1), \text{ where } J = 0, 1, 2, \ldots..$$

Here, J is rotational quantum number.

$$\frac{\hbar^2}{2I} = B = \frac{h^2}{2I \times 4\pi^2} = \text{Rotational constant for particular molecule (in Joule)}$$

$$B = \frac{h}{8Ic\pi^2} \text{ cm}^{-1}$$

E0 = B×0×(0+1) = 0
E1 = B×1×(1+1) = 2B
E2 = B×2×(2+1) = 6B
E3 = B×3×(3+1) = 12B
E4 = B×4×(4+1) = 20B



For J' to J transition
$\Delta E = EJ - EJ'$
$\Delta E = BJ(J+1) - BJ'(J'+1)$
$\Delta E = B\{(J^2+J) - (J'^2+J')\}$

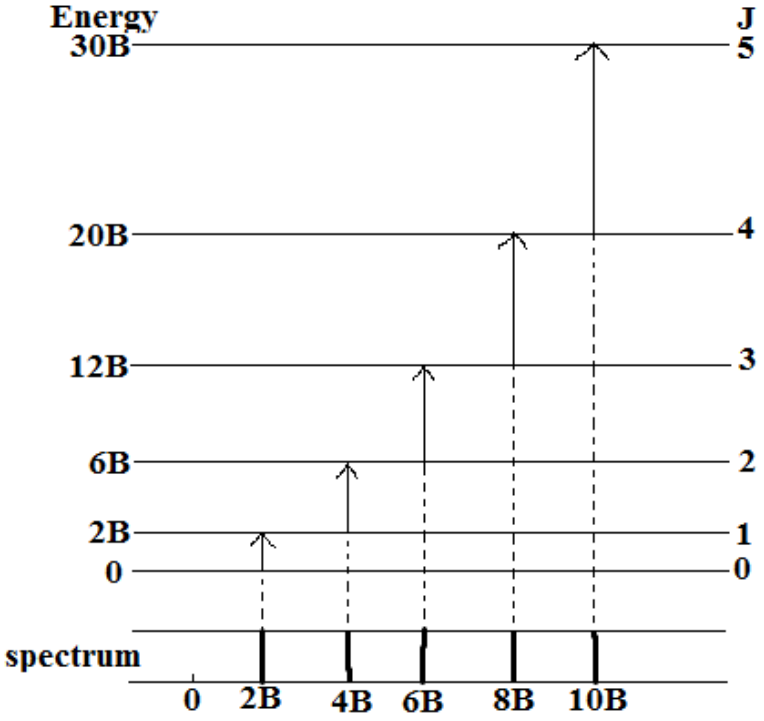
For 0⟶1 transition,
$\Delta E = B\{(1^2+1) - (0^2+0)\}$
$\Delta E = 2B$

For 3⟶4 transition,
$\Delta E = B\{(4^2+4) - (3^2+3)\}$
$\Delta E = B\{(16+4) - (9+3)\}$
$\Delta E = B\{20 - 12\}$
$\Delta E = 8B$

1.3 Selection rule of rotational spectrum:-

For the molecule to be able to interact with the electromagnetic field and absorb or create a photon of frequency ν, it must possess, at least transiently, a dipole oscillating at that frequency. We saw in Section 9.10 that this transient dipole is expressed quantum mechanically in terms of the transition dipole moment, μ fi, between states ψ
i and ψ

1. The molecule must have a permanent dipole moment.
2. Transitions are allowed only between adjacent rotational levels, ie., $\Delta J = \pm 1$ (plus sign for absorption and minus sign for emission).



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