

Pure Rotational Spectra:-

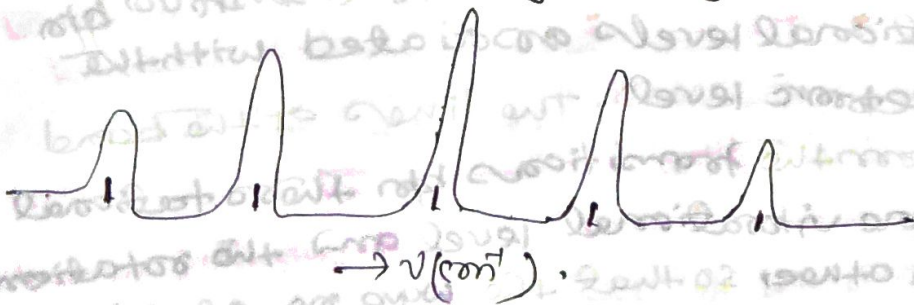
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Salient Features of Rotational Spectra

Pure rotational molecular spectra arise from transitions b/w rotational energy states and are observed in the far infrared ($\approx 10^2 \mu - 10^3 \mu$) or microwave ($\approx 10^3 \mu - 10^4 \mu$) region of the electromagnetic spectrum. Only molecules that have permanent electric dipole moments can absorb or emit electromagnetic radiation in such transition. This means that homonuclear diatomic molecules such as H_2, O_2, N_2 symmetrical linear molecules such as CO_2 ($O=C=O$) and spherical-top polyatomic molecules such as CH_4 do not exhibit rotational spectra.

In rotational spectra are observed in absorption. For heteronuclear diatomic molecules such as HF, HCl, HBr, CO , etc. the rotational spectra consist of a simple series of absorption maxima which are very nearly equidistant on a wave no. scale.

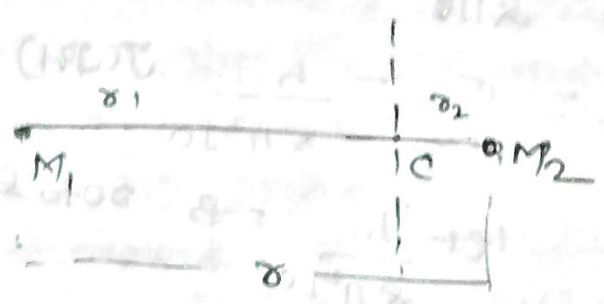


A measurement of frequencies of these maxima leads to a determination of the M.O.I and the internuclear distance of the molecule. For homonuclear molecules, which do not give rotational spectra, the moment of inertia and the internuclear distance can be found from the rotational fine structure of electronic bands and from rotational Raman spectra.

Molecular Requirement for Rotational Spectroscopy

The Molecule as a rigid Rotator :-
Examination of Rotational Spectra

The simplest model of a rotating diatomic molecule is that of a Rigid rotator, i.e. the internuclear separation is assumed to be fixed at the equilibrium value.



M.O.I. of I is centre of mass $I = M_1 r_1^2 + M_2 r_2^2$

By simple, lever rule, $M_1 r_1 = M_2 r_2$

$$\Rightarrow r_1 = \frac{M_2}{M_1} r_2 = \frac{M_2}{M_1} (r - r_1)$$

$$\text{or } r_1 + r_2 = r$$

$$\Rightarrow r_1 = \frac{M_2}{M_1 + M_2} r$$

Similarly, $r_2 = \frac{M_1}{M_1 + M_2} r$

The eqn for I therefore, becomes

$$I = M_1 \left(\frac{M_2}{M_1 + M_2} r \right)^2 + M_2 \left(\frac{M_1}{M_1 + M_2} r \right)^2$$

$$= \frac{M_1 M_2}{M_1 + M_2} r^2$$

But $\frac{M_1 M_2}{M_1 + M_2}$ is called reduced mass μ of the molecule

$$I = \mu r^2$$

Thus the diatomic molecule is equivalent to a single point mass μ at a fixed distance r from the axis of rotation. Such a system is called a simple rigid rotator.

$$L^2 \psi = J(J+1) \frac{h^2}{4\pi^2} \psi$$

$$L^2 \psi = \frac{Mh}{2\pi} \psi$$

$$E = \frac{h^2}{8\pi^2 I} J(J+1) \quad \left\{ \begin{array}{l} J = 0, 1, 2, 3, \dots \\ \text{which can take the integral} \end{array} \right.$$

$$L = \sqrt{2EI} \\ = \frac{h}{2\pi} \sqrt{J(J+1)}$$

$$F(J) = \frac{E}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1}$$

let $\frac{h}{8\pi^2 I c} = B$ rotational constant

$$F(J) = BJ(J+1) \text{ cm}^{-1} \quad J = 0, 1, 2, \dots$$

$$F(J) = 0, 2B, 6B, 12B, 20B, 30B, \dots$$

When a transition takes place between an upper level J' and a lower level J'' the wave no. of the emitted or absorbed radiation would be

$$\begin{aligned} \nu &= F(J') - F(J'') \\ &= BJ'(J'+1) - BJ''(J''+1) \end{aligned}$$

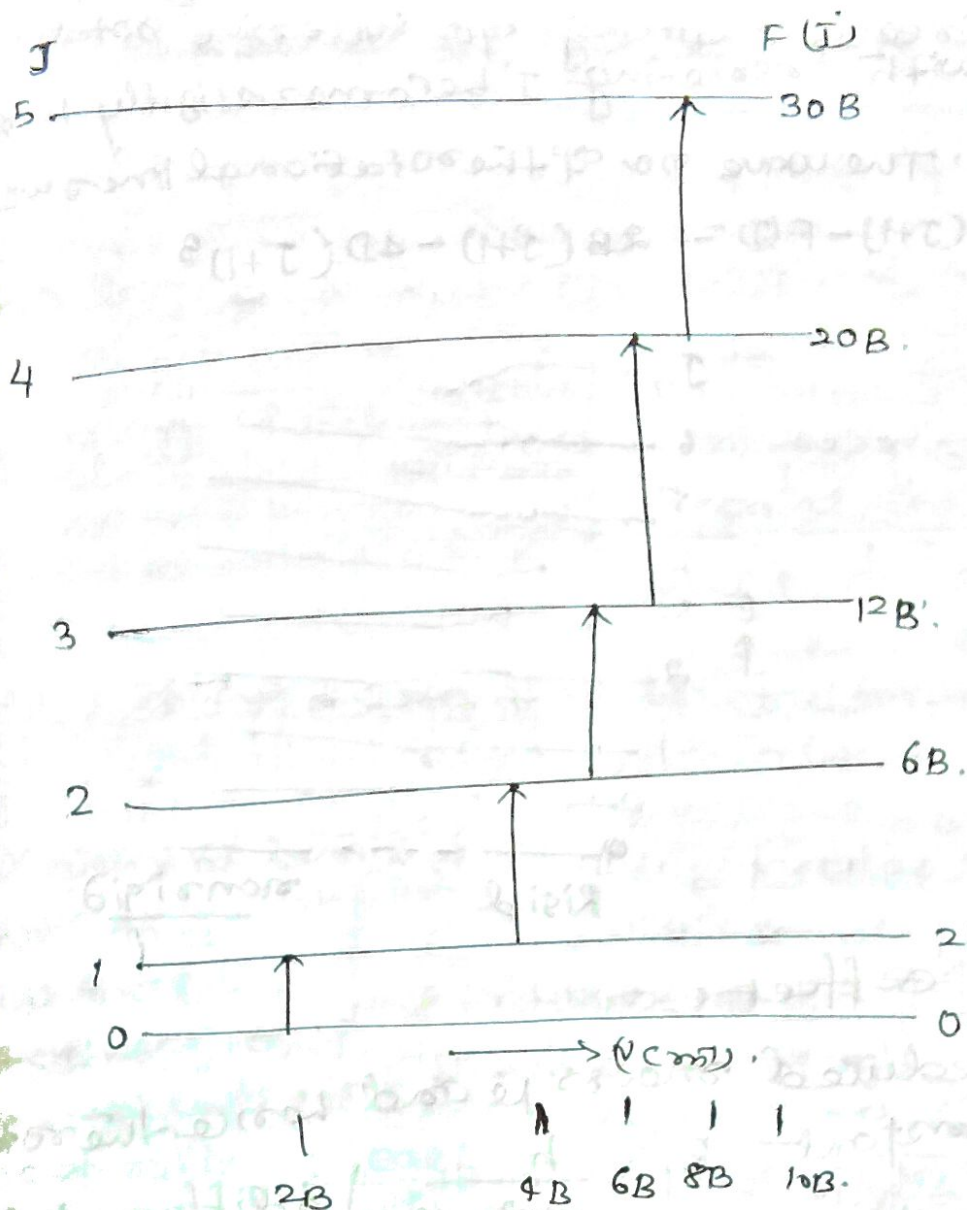
Selection rule is

$$\Delta J = \pm 1$$

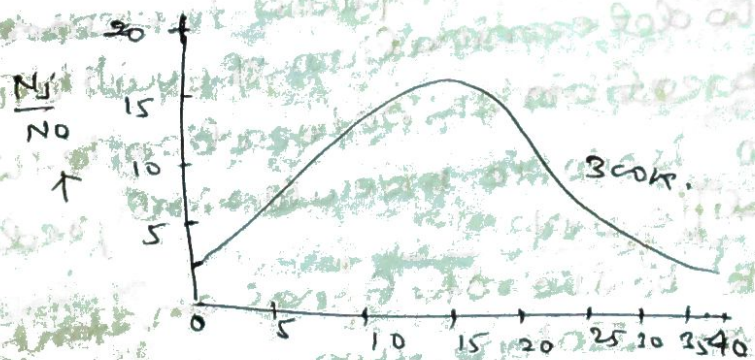
$$J' > J''$$

$$J' = J'' + 1$$

$$\begin{aligned} \text{Thus, } \nu &= B(J''+1)(J''+2) - BJ''(J''+1) \\ &= 2B(J''+1) \end{aligned}$$



$$J = 2B(J+1)$$



⑤ Thermal-rigid rotator -

The rotational lines are not exactly equidistant
 the separation decreases slightly with increasing J

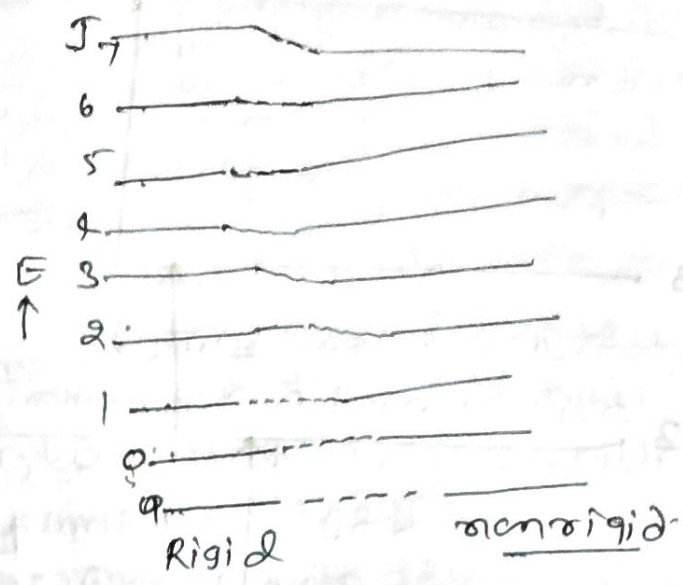
$$F(J) = B(J+1) - DJ^2(J+1)^2$$

and much smaller than B.

where D is centrifugal distortion constant.

The increase in spacing b/w successive rotational levels with increasing J becomes slightly less rapid. The wave no. of the rotational lines are

$$v = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3$$



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Isotope effect:-

The reduced mass μ and hence the rotational constant $B (= \frac{h}{8\pi^2 \mu r^2})$ is different for different isotopic molecules. Since mass effects are negligible compared to electronic effects w.r.t to determination of equilibrium inter nuclear separation this separation is the same in two isotopic molecules, only reduced masses are different.

If B' be the rotational constant for the heavier isotope, then

$$B' < B$$

$$F'(J) < F(J)$$

Thus the separation of levels for the heavier isotope will be smaller than those of the corresponding levels of the lighter isotope. Hence spectral lines will also be closer.