

We thus need two quantum numbers to describe <sup>(19)</sup> the degree of rotation, one for  $I_A$  and one for  $I_B$  or  $I_C$ . It is convenient to have a quantum number to represent the total angular momentum of the molecule, which is the sum of the separate angular momenta about the two different axes.

$J \rightarrow$  usually chosen.

For linear molecule  $J \rightarrow$  end-over-end rotation of molecule, the only sort of rotation allowed, so it is quite consistent to use  $J$ , in general, to represent the total angular momentum.

$k \rightarrow$  represent the angular momentum about the top axis - i.e. about the C-F bond in this case.

Values allowed to  $k$  and  $J \rightarrow$  both must, by the conditions of Q.M., be integral or zero.

$J \rightarrow$  can be as large as we like, i.e.

$J$  can be  $0, 1, 2, \dots \rightarrow \infty$ . ~~One~~ we have

chosen  $J$ ,  $k$  is rather more limited.

For a total angular momentum,  $J$ , we see that  $k$  can take values:

$$k = J, J-1, J-2, \dots, 0, \dots, -(J-1), -J \quad (20)$$

which is a total  $(2J+1)$  values (1) altogether.

for a rigid symmetric top - i.e., one in which the bonds are supposed not to stretch under centrifugal forces - the Schrödinger eq<sup>n</sup> may be solved to give the allowed energy levels for rotation as;

$$\begin{aligned} E_{J,k} &= E_{J,k}/hc \\ &= B J(J+1) + (A-B) k^2 \quad \text{cm}^{-1} \end{aligned} \quad (2)$$

where

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

Energy depends on  $k^2$ , so that it is immaterial whether the top spins clockwise or anticlockwise.  $\rightarrow$  the energy is the same for a given angular momentum. For all  $k > 0$ , therefore the rotational energy levels are doubly degenerate.

The selection rules for this molecule may be shown to be

$$\Delta J = \pm 1 \quad (\text{as before}) \quad \text{and} \quad \Delta k = 0$$

— (3)

and when applied to eq<sup>n</sup> (2), the spectrum is given by

(21)

$$\begin{aligned} \Sigma_{J+1, k} - \Sigma_{J, k} &= \bar{\nu}_{J, k} \\ &= B (J+1) (J+2) + (A-B) k^2 \\ &\quad - [B J (J+1) + (A-B) k^2] \\ &= 2 B (J+1) \text{ cm}^{-1} \quad \text{--- (4)} \end{aligned}$$

Thus, the spectrum is independent of  $k \rightarrow$  rotational changes about the symmetry axis do not give rise to a rotational spectrum.

Reason  $\rightarrow$  rotation about the symmetry axis does not change the dipole moment perpendicular to the axis (which always remains zero), and hence the rotation can not interact with radiation.

Eq<sup>n</sup> (4)  $\rightarrow$  The spectrum is just the same as for a linear molecule  $\rightarrow$  only one moment of inertia  $\rightarrow$  that for end-over-end rotation can be measured.

Eq<sup>n</sup> (2) and (4) are for a rigid molecule. When centrifugal stretching is taken into account, the energy levels become:

$$\begin{aligned} \Sigma_{J, k} &= B J (J+1) + (A-B) k^2 - D_J J^2 (J+1)^2 \\ &\quad - D_{JK} J (J+1) k^2 - D_K k^4 \text{ cm}^{-1} \quad \text{--- (5)} \end{aligned}$$

$D_J$ ,  $D_{JK}$  and  $D_K \rightarrow$  small correction terms for non-rigidity

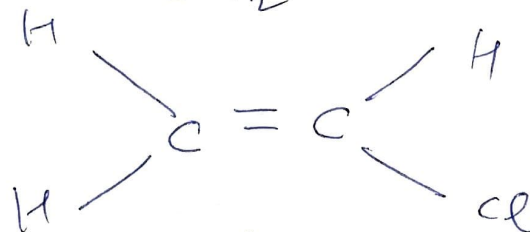
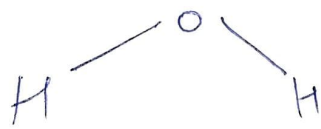
The selection rules are unchanged,  
 so the spectrum is

$$\begin{aligned} \bar{\nu}_{J,k} &= \Sigma_{J+1,k} - \Sigma_{J,k} \\ &= 2B(J+1) - 4D_J(J+1)^2 - 2D_{JK}(J+1)k^2 \end{aligned} \quad \text{cm}^{-1} \quad (6)$$

Basically as for a linear molecule (including centrifugal stretching) with an additional term depending on  $k^2$ .

Asymmetric Top Molecules: All three moments of inertia different  $I_A \neq I_B \neq I_C$  --- (7)

Example  $H_2O$  and Vinyl chloride  $CH_2=CHCl$



Rotational energy levels and spectra are very complex - impossible to give one simple expression for all energy levels.

Each molecule and spectrum must, therefore, be treated as a separate case, much tedious computation is necessary. Best method

→ To consider the asymmetric top as falling somewhere between the oblate and prolate symmetric top

Problem The  $J = 1 \leftarrow 0$  transition in HCl occurs at  $10.68 \text{ cm}^{-1}$ . Regarding the molecule to be rigid rotator, Calculate the wavelength of the transition  $J = 15 \leftarrow 14$

Sol<sup>n</sup> 
$$\nu_r = B J' (J' + 1) - B J'' (J'' + 1)$$

Here  $J' = 1, J'' = 0$

So  $10.68 = 2B$

$$\Rightarrow \nu_r' = B [15(15+1) - 14(14+1)]$$

$$= 2B \times 15$$

$$= 10.68 \times 15$$

$$\lambda' = \frac{1}{10.68 \times 15 \text{ cm}^{-1}} = 64 \mu$$

Problem The moment of inertia of the CO molecule is  $1.46 \times 10^{-46} \text{ kg.m}^2$ . Calculate the energy in eV, and the angular velocity in the lowest rotational energy level of the CO molecule.

Sol<sup>n</sup> 
$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \text{ or classically } E_J = \frac{h^2}{8\pi^2 I} J^2$$

For the lowest energy level,  $J=1$  so that

$$E_r = \frac{h^2}{8\pi^2 I}$$

$$E_r = \frac{(6.62 \times 10^{-34})^2}{8 \times (3.14)^2 \times (1.46 \times 10^{-46})} \text{ Joule}$$

$$= 2.37 \times 10^{-4} \text{ eV}$$

angular velocity

$$E_r = \frac{1}{2} I \omega^2$$

$$\omega = \sqrt{\frac{2E_r}{I}} = 7.21 \times 10^{11} \text{ rad/sec}$$