

## Centrifugal Distortion

We showed that the selection rule for rotational transition is  $\Delta J = \pm 1$  and:

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

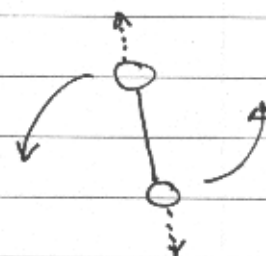
where  $F(J)$  is the energy value for the level  $J$ .

Then:  $\nu_{J+1 \leftarrow J} = F(J+1) - F(J)$   
or simply

$$\begin{aligned} \nu_{J'' \leftarrow J'} &= F(J') - F(J'') \\ &= B(J+1)(J+2) - B J(J+1) \\ &= 2B(J+1) = F(J \leftarrow J'') \end{aligned}$$

A diatomic molecule is not strictly a rigid rotor.

Fast rotation causes the bonds to stretch



The rotational energy can be expressed more accurately as:

$$\begin{aligned} F(J) &= B J(J+1) - D [J(J+1)]^2 \\ &= B J(J+1) - D J^2 (J+1)^2 \end{aligned}$$

$D$ : the centrifugal distortion constant

Higher  $J$  means faster rotation and more distortion.

$$D = \frac{4B^3}{\nu_{\text{vib}}^2} \quad ; \quad \nu_{\text{vib}} \text{ is the vibrational frequency.}$$

$B$ ,  $D$  and  $\nu_{\text{vib}}$  must all have the same unit.

For more accurate data, additional terms are needed and the rotational energy level can be expanded as:

$$F(J) = B J(J+1) - D J^2(J+1)^2 + H J^3(J+1)^3 + \dots$$

The transition wave number ( $\bar{\nu}$ ) in frequency ( $\nu$ ) is:

$$\bar{\nu}(J+1) - F(J) - 5B(J+1) - 4D(J+1)^2$$

## Splitting Due to Stark Effect

The effect of the splitting of rotational levels in the presence of an electric field ( $E$ ) is called the Stark effect.

In the presence of an electric field  $E_r$  (The rotational energy) is modified to  $E_r + E_E$  where  $E_E$  is the energy due to the electric field.

$$E_E = \frac{\mu^2 E^2 [J(J+1) - 3M_J^2]}{2hB J(J+1)(2J-1)(2J+3)}$$

$E$  is the electric field voltage.

$\mu$  is the permanent dipole moment.

Its unit is debye (D); where  $1D = 3.34 \times 10^{-30} \text{ C.m}$

$M_J$  is the angular momentum quantum number

$$M_J = J, J-1, \dots, 0, -1, -2, \dots, -J$$

Because  $E_E$  contains only an  $M_J^2$  term (and not  $M_J$ ) it depends on the magnitude but not the sign of  $M_J$ . That is why each  $J$  level is split into only  $J+1$  components with:

$$|M_J| = 0, 1, \dots, J$$

## Selection Rule:

Transitions between the Stark components are governed by the below selection rule:

$$\Delta M_J = 0$$

$$\Delta J = \pm 1$$

In most spectrometers,  $E$  polarized is parallel to the Stark field. Thus, only  $\Delta M_J = 0$  transitions are observed.

Stark effect helps in determining the  $J$  values.

It is also considered one of the most accurate method with which the permanent dipole moments for molecules can be measured.

## Nuclear Hyperfine Splitting

The angular momentum due to nuclear spin is given by:

$$P_I = \sqrt{I(I+1)} \hbar$$

$I$ : The nuclear spin quantum number

It could be zero, integer or half-integer.

The value of  $I$  is dependent on the protons and neutrons contained in a nucleus.

General rules to determine  $I$ :

①  $I$  is half-integer for nuclei with an odd mass number, e.g.  $^{13}\text{C}$  has  $I = \frac{1}{2}$  ( $P_I \neq 0$ )

②  $I$  is an integer number for nuclei with an even mass number but an odd charge number, e.g.  $^{14}\text{N}$ , for which  $Z=7$ , has  $I=1$  ( $P_I \neq 0$ )

③  $I$  is zero for nuclei with an even mass number and an even charge number, e.g.  $^{12}\text{C}$ , for which  $Z=6$ , has  $I=0$ . ( $P_I=0$ )

For a nucleus, the total angular momentum <sup>( $P_F$ )</sup> is the addition of the spin angular momentum ( $P_I$ ) and the rotational angular momentum ( $P_J$ )

$$P_J = \sqrt{J(J+1)} \hbar$$

$$P_F = P_I + P_J = \sqrt{F(F+1)} \hbar$$

where  $F = J+I, J+I-1, J+I-2, \dots, |J-I|$

This is called Clebsch-Gordan series.

$F$  values must not be negative.

An important condition is that:

if  $J > I$  then the lowest values of  $F$  is:  $J-I$

if  $J < I$  " " " " " "  $F$  is:  $I-J$

Example: Take  $J=1$  coupled with  $I = \frac{3}{2}$

$J < I$  and the lowest value for  $F$   
is  $I-J = 1 - \frac{3}{2} = \frac{1}{2}$

$$J+I = 1 + \frac{3}{2} = \frac{5}{2}$$

$$J+I-1 = \frac{5}{2} - 1 = \frac{3}{2}$$

$$|J-I| = \left| 1 - \frac{3}{2} \right| = \frac{1}{2}$$

### Selections Rule

Transitions between nuclear-spin-rotational-level split are governed by:

$$\Delta F = 0, \pm 1$$

## Pure Rotational Spectra of Symmetric Molecules

Classically, the rotational energy ( $E_r$ ) of a rotor with one degree of freedom is:

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

where  $\omega = v/r$  (angular velocity)

$$\text{Notice that: } E_r = \frac{L^2}{2I} = \frac{m^2 v^2 r^2}{2mr^2} = \frac{1}{2} mv^2$$

In Three dimension:  $L^2 = L_x^2 + L_y^2 + L_z^2$

More conveniently we use  $P$  symbol for overall angular momentum. Thus,

$$P^2 = P_a^2 + P_b^2 + P_c^2$$

$$E_r = \frac{P_a^2}{2I_A} + \frac{P_b^2}{2I_B} + \frac{P_c^2}{2I_C}$$

For prolate symmetric top molecules;  $I_c = I_b > I_a$

$$\therefore E_r = \frac{P_a^2}{2I_A} + \frac{(P_b^2 + P_c^2)}{2I_B}$$

For oblate symmetric top molecules,  $I_c > I_b = I_a$

$$\therefore E_r = \frac{(P_a^2 + P_b^2)}{2I_B} + \frac{P_c^2}{2I_C}$$

For example, for a prolate symmetric top molecule:

$$P_a^2 + P_b^2 + P_c^2 = P^2$$

$$P - P_a^2 = P_b^2 + P_c^2$$

which gives:

$$\bar{E}_r = \frac{P_a^2}{2I_A} + \frac{P - P_a^2}{2I_B}$$

$$= \frac{P_a^2}{2I_A} + \frac{P}{2I_B} - \frac{P_a^2}{2I_B}$$

$$= \frac{P^2}{2I_B} + \left( \frac{1}{2I_A} - \frac{1}{2I_B} \right) P_a^2$$

In order to work out the Q.M. solution for a prolate symmetric top molecule, the Hamiltonian operator applied is:

$$\hat{H} = \frac{1}{2I_B} \hat{P}^2 + \left( \frac{1}{2I_A} - \frac{1}{2I_B} \right) \hat{P}_a^2$$

Quantum mechanical solutions can be derived and are expressed for symmetric top system.

"Prolate"  
top  $E_{JK_a}$  [or  $F(J, K)$ ] =  $B J(J+1) + (A-B) K_a^2$

"Oblate"  
top  $E_{JK_c}$  [or  $F(J, K)$ ] =  $B J(J+1) + (C-B) K_c^2$

The rotational constants (in joules) are:

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

"  $A \geq B \geq C$  as  $I_C \geq I_B \geq I_A$  "



It should be noticed that:

$P^2$  is quantized by  $P^2 = J(J+1)\hbar^2$ , and

$P_a^2$  is quantized by  $P_a^2 = \pm K^2\hbar^2$  (prolate top)

$J$  and  $K$  are Q.N. for symmetric top molecules

$$J = 0, 1, 2, \dots, J$$

$K = 0, \pm 1, \pm 2, \dots, \pm J$  (degeneracy of rotational levels for symmetric top systems)

and that:

$$K \leq J$$

Degeneracy

for symmetric top molecules

The rotational levels with  $K > 0$  are <sup>nearly</sup> degenerate.  
 Rotational levels with  $J > 0$  at given <sup>non-zero</sup> value of  $K$  (such as  $J=1, K=1$ ) are doubly degenerate.

Also notice that:

(a) For a given  $J$  value, the levels as going from  $K=0$  to higher  $K$  values;

① The energy increases for a prolate top system.

② The energy decreases for an oblate top system.

(b) For a given  $J'' - J'$  energy spacing, the spacing is found to be wider as you go for higher values of  $K$  in the prolate top than in the case of oblate top.

Notes (a) and (b) are explained based on the energy expressions for the prolate and oblate top symmetries.

(a) and (b) are true since:

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

$$F(J, K) = BJ(J+1) + (C-B)K^2 \quad \text{"oblate"}$$

where  $A > B = C$  for prolate top ; compared to:  
 $A = B > C$  for oblate top.

Selection Rule:

$$\Delta J = \pm 1 ; \Delta K = 0$$

Thus transition frequencies is

$$F(J+1, K) - F(J, K) = 2B(J+1)$$

which is similar to that for linear systems.