Selection Rules — for molecules, depends on the type of transition

For a molecule to absorb or emit – it must possess – transiently — a dipole oscillating at that frequency

Transient dipole is expressed in terms of the transition dipole moment

Transition between states ψ_i & ψ_f must have an instantaneous dipole moment

$$\mu_{fi} = -e\int \psi_f^* \, r \, \psi_i \, d\tau$$

$$I \propto |\mu_{fi}|^2$$

$\therefore$ need to find when $|\mu_{fi}|^2 \neq 0$

General Beginning Rules

- A polar molecule appears to possess a fluctuating dipole when rotating

  For Rotational Transitions, must have a permanent electric moment

- Vibrations – electric dipole moment of the molecule must change during vibration (does not need to have a permanent dipole)

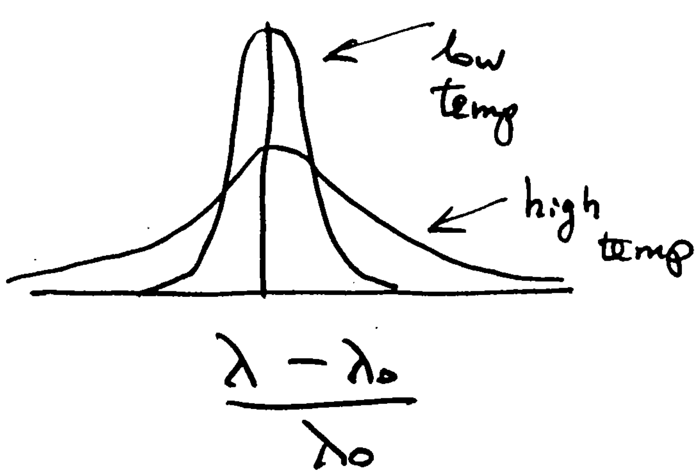
- Other Selection Considerations

  Conservation of angular momentum

Linewidths / Doppler Shift

$$\lambda_{detected} = \left(1 + \frac{v}{c}\right)\lambda$$

$$\lambda_d = \left(1 - \frac{v}{c}\right)\lambda$$



due to movement of molecules in a stagnant gas

Gaussian Curve e^{-x^2}

Consider a system Changing in Time

Photon emitted or absorbed
get Life time Broadening
(Collisions can deactivate & hence influence time)

No excited state has an
infinite Lifetime

The shorter the lifetime, the
broader the spectral lines

Uncertainty broadening:

$$\Delta E \, \Delta t \approx \hbar$$

Spontaneous emission has a "natural"
lifetime $= \tau_{natural}$ and hence a
natural Linewidth

$$\delta E = hc(\delta \tilde{\nu})$$

$$\delta \tilde{\nu} = \left[\frac{5.31}{\tau/ps} \right] \ cm^{-1}$$

increase as ν^3

Pure Rotational Spectra

Energy of a rotating body

$$E = \frac{1}{2} I_{xx} u_x^2 + \frac{1}{2} I_{yy} u_y^2 + \frac{1}{2} I_{zz} u_z^2$$

$u_i \equiv$ angular velocity in radians/sec

(Recall classical angular momentum $= J_i = I_{ii} u$

$$E_c = J_x^2 / 2 I_{xx} + J_y^2 / 2 I_{yy} + J_3^2 / 2 I_{33}$$

(discussed for a rigid body)

moment of inertia – $I_{xx} = \sum_i m_i X_i^2$

Usually label moments of inertia : I_A, I_B, I_C

Consider Spherical Rotors

CH_4
SF_6

see pg 475

$$I_{xx} = I_{yy} = I_{zz} = I$$

$$E_J = J(J+1)\hbar^2/2I$$

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

$$\hbar^2/2I = hcB$$

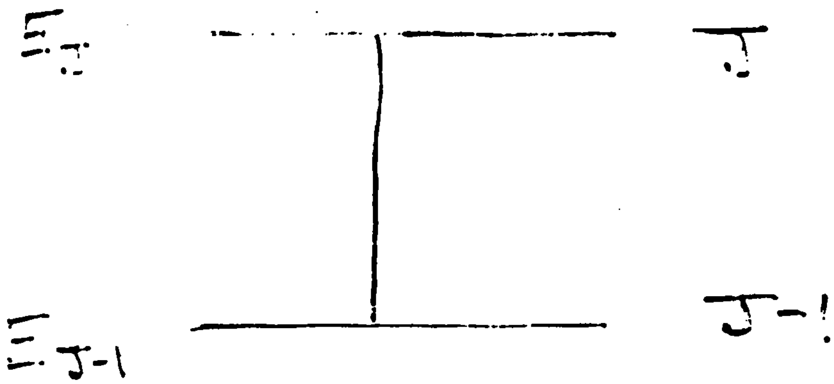
↑ rotational constant

$$E_J = hcB\,J(J+1)$$

Where:

$$B = \hbar/4\pi cI$$

Consider the Energy Difference Between Two Levels



Two Rotational Levels

$$E_J - E_{J-1} = hcB\left[J(J+1) - (J-1)J\right]$$

$$= hcB\left[J^2 + J - J^2 + J\right]$$

$$= 2hcBJ$$

$$\frac{1}{\lambda_J} - \frac{1}{\lambda_{J-1}} = 2BJ$$

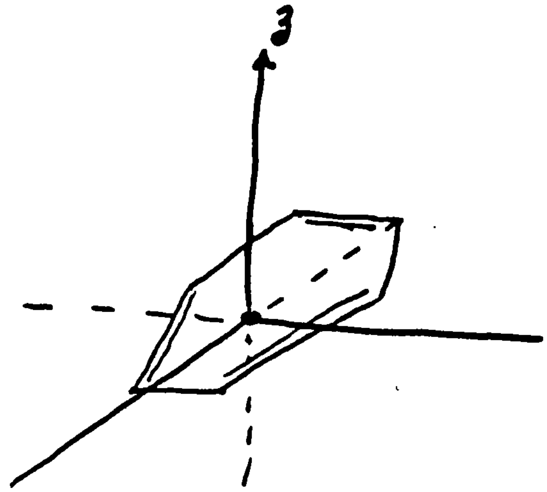
$$\tilde{\nu}_J - \tilde{\nu}_{J-1} = 2BJ$$

Separation decreases as I increases $\left(B = \hbar / 4\pi c I\right)$

$\therefore$ heavy molecules have closely spaced levels

Symmetric Rotors CH_3Cl, NH_3, C_6H_6

$$I_{xx} = I_{yy} \neq I_{zz}$$



$I_{zz} = I_{\parallel}$ – parallel to distinct axis
= figure axis

$$I_{xx} = I_{yy} = I_{\perp}$$

Oblate (pancake, flying saucer) – C_6H_6

$$I_{\parallel} > I_{\perp}$$

Prolate (cigar) – PCl_5

$$I_{\parallel} < I_{\perp}$$

Symmetric Rotors (cont.)

Consider Classical Approach

$$E = \frac{1}{2I_\perp}\left(J_x^2 + J_y^2\right) + \frac{1}{2I_\parallel} J_z^2$$

add and subtract

$J_z^2 / 2I_\perp$

$$E = \frac{1}{2I_\perp}\left(J_x^2 + J_y^2 + J_z^2\right) + \frac{1}{2I_\parallel} J_z^2 - \frac{1}{2I_\perp} J_z^2$$

$$E = \frac{1}{2I_\perp} J^2 + \left\{\frac{1}{2I_\parallel} - \frac{1}{2I_\perp}\right\} J_z^2$$

Quantum approach – replace J^2 with $J(J+1)$

$J_z \equiv$ Component about the figure axis $\equiv$ called K

Symmetric Rotors (cont.)

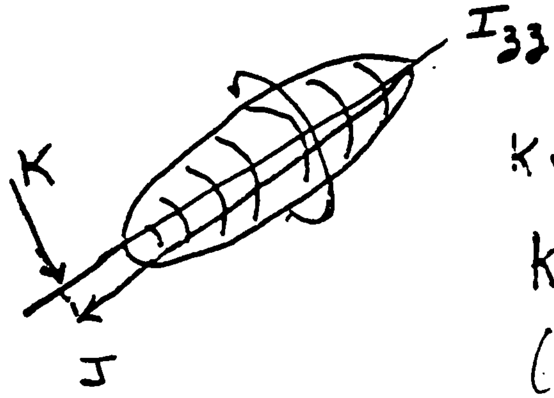
$$E_{JK}/hc = B\,J(J+1) + (A-B)\,K^2$$

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

$$K = 0, \pm 1, \ldots \pm J$$

$$A = \frac{\hbar}{4\pi c I_{\parallel}} \qquad B = \frac{\hbar}{4\pi c I_{\perp}}$$

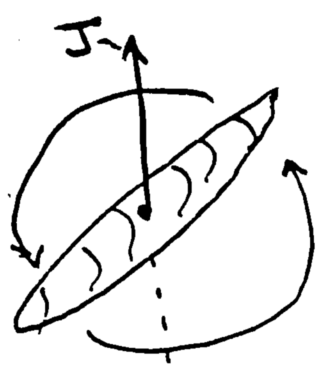
Consider Prolate Example



K nearly equal to J

K is large; most of the motion (rotation) is about the (figure) symmetry axis

depends mainly on $I_{\parallel}$



$K=0$

end-over-end rotation; depends mainly on $I_{\perp}$

Linear Rotors – like diatomics

(CO_2, HCl, C_2H_2)

Rotation only about axis $\perp$ to the line of atoms

$\therefore$ no angular momentum around this line

$\therefore K = 0$

$$E_J / hc = B J(J+1)$$

$$J = 0, 1, 2, ---$$