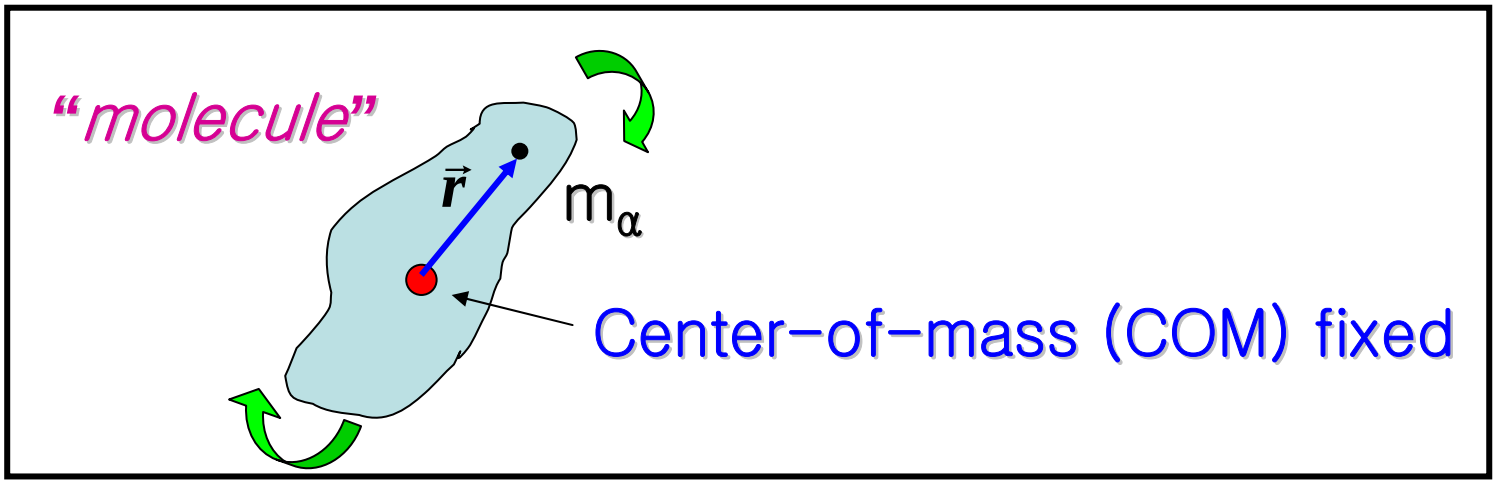
Basics-4

Rotational Spectroscopy

Classical Mechanics of Rotations



$$\vec{L} = \sum_\alpha \vec{r}_\alpha \times \vec{p}_\alpha = \sum_\alpha \vec{r}_\alpha \times m_\alpha \vec{v}_\alpha = \sum_\alpha m_\alpha \vec{r}_\alpha \times (\vec{\omega}_\alpha \times \vec{r}_\alpha)$$

$$\vec{r}_\alpha = x_\alpha \hat{i} + y_\alpha \hat{j} + z_\alpha \hat{k},\ \vec{\omega}_\alpha = \omega_{\alpha x} \hat{i} + \omega_{\alpha y} \hat{j} + \omega_{\alpha z} \hat{k}$$

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} \sum m_\alpha (y_\alpha^2 + z_\alpha^2) & -\sum m_\alpha x_\alpha y_\alpha & -\sum m_\alpha x_\alpha z_\alpha \\ -\sum m_\alpha x_\alpha y_\alpha & \sum m_\alpha (x_\alpha^2 + z_\alpha^2) & -\sum m_\alpha z_\alpha y_\alpha \\ -\sum m_\alpha x_\alpha z_\alpha & -\sum m_\alpha z_\alpha y_\alpha & \sum m_\alpha (y_\alpha^2 + x_\alpha^2) \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

$$\therefore \vec{L} = \vec{\vec{I}} \bullet \vec{\omega}$$

Principal rotational moment of inertia:

Diagonalization: $\vec{\vec{I}}' = \vec{\vec{X}}^{-1} \bullet \vec{\vec{I}} \bullet \vec{\vec{X}} = \begin{pmatrix} I_A & 0 & 0 \\ 0 & I_B & 0 \\ 0 & 0 & I_C \end{pmatrix}$ $\quad I_A \le I_B \le I_C$

Principal rotational axes : $\vec{r}' = \vec{\vec{X}}^{-1} \bullet \vec{r}$

* Principal rotational constants:

$$A = \frac{\hbar^2}{2I_A},\ B = \frac{\hbar^2}{2I_B},\ C = \frac{\hbar^2}{2I_C};\ A \geq B \geq C$$

* Rotational energy:

$$E_{rot} = \frac{1}{2}\vec{\omega}^t \cdot \vec{\vec{I}} \cdot \vec{\omega} = \frac{1}{2}I_A\omega_A^2 + \frac{1}{2}I_B\omega_B^2 + \frac{1}{2}I_C\omega_C^2 = \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C}$$

* Rotational tops:

Linear tops: $I_A = 0,\ I_B = I_C \rightarrow B = C$

Spherical tops: $I_A = I_B = I_C \rightarrow A = B = C$

Symmetric tops – prolate: $I_A < I_B = I_C \rightarrow A > B = C$

oblate: $I_A = I_B < I_C \rightarrow A = B > C$

Asymmetric tops: $I_A < I_B < I_C \rightarrow A > B > C$

near-prolate: $A > B \approx C$

near-oblate: $A \approx B > C$

Diatomic and Linear Molecules

* Energies and eigenfunctions

$$\hat{H}_{rot} = \frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} = \frac{\hat{J}^2}{2I} \leftarrow I = I_x = I_y,\ \hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2$$

$$\hat{H}_{rot}\psi = \frac{\hat{J}^2}{2I}\psi = E\psi$$

$$\rightarrow \psi = Y_{J M_J}(\theta,\phi);\ \textit{spherical harmonics}$$

$$E_J = \frac{J(J+1)\hbar^2}{2I} = BJ(J+1),\quad J = 0,1,2,\ldots$$

$$* \ B = \frac{\hbar^2}{2I}(joule) = \frac{h}{8\pi^2 I}(Hz) = \frac{h}{8\pi^2 Ic}(cm^{-1})$$

$$= \frac{16.8576314}{I(amu\cdot \text{Å}^2)}(cm^{-1})$$

* Selection rules

Transition dipole moment $M = < J' M_J' | \hat{\mu} | J M_J >$

$$| J M_J >= Y_{J M_J}(\theta,\phi) = \Theta_{J M_J}(\theta) \frac{1}{\sqrt{2}} e^{iM_J\phi}$$

$$\mu = \mu_0 (\sin\theta\cos\phi\,\hat{x} + \sin\theta\sin\phi\,\hat{y} + \cos\theta\,\hat{z})$$

$$\therefore M = \frac{\mu_0}{\sqrt{2\pi}} \left(\hat{x} \iint \Theta_{J'M'} e^{-iM'\phi} \sin\theta\cos\phi \;\; \Theta_{J M} e^{-iM\phi} \sin\theta\cos\phi\, d\theta d\phi + \hat{y}... + \hat{z}... \right)$$

$M \neq 0 \rightarrow$

$\hat{z}-component: \Delta J = \pm 1,\ \Delta M_J = 0$

$\hat{y}-component: \Delta J = \pm 1,\ \Delta M_J = \pm 1$

$\hat{x}-component: \Delta J = \pm 1,\ \Delta M_J = \pm 1$

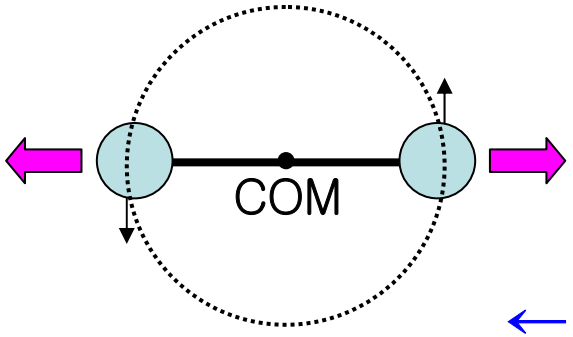
$and\ \mu_0 \neq 0$

} $\Delta J = \pm 1,\ \Delta M_J = 0,\ \pm 1$

* Degeneracy: (2J+1)
* Population of rotational states: determine relative intensities

$$P_J = \frac{(2J+1)e^{-E_J/kT}}{\sum_J (2J+1)e^{-E_J/kT}}, \quad J_{\max} = \left(\frac{kT}{2hB}\right)^{1/2} - \frac{1}{2} \leftarrow \frac{dP_J}{dJ} = 0$$

* Centrifugal distortion: due to non-rigidity of molecules



Centrifugal force

$$F_c = \mu \frac{v^2}{r} = \frac{J^2}{\mu r^3}$$

← *balanced by restoring force* $F_r = k(r_e - r_c)$

After some mathematics,

$$E_J = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 + \ldots$$

D, H: centrifugal distortion constant

D= $4B_e^2/\omega_e^2$ (Kratzer relationship)

$$E_J \approx [B - DJ(J+1)]J(J+1)] = B_{eff}J(J+1)$$

Vibrational and electronic state dependence of B, D:

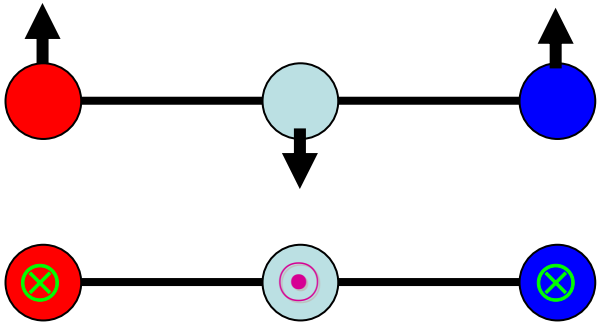
$$B_v = B_e - \alpha_e(v+1/2) + \gamma_e(v+1/2)^2 + \ldots$$

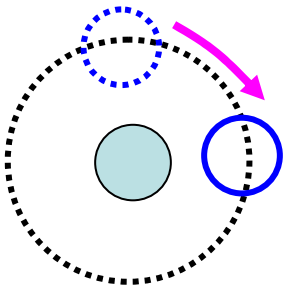
$$D_v = D_e + \beta_e(v+1/2) + \ldots$$

$$\textit{Overall, } (E_J)_v = B_v J(J+1) - D_v[J(J+1)]^2 + \ldots$$

* Vibrational angular momentum

"occur when two degenerate bending modes are excited"





side view

In polar coordinate (ρ, ϕ)

$$\psi_{vl}(\rho,\phi) = R_{vl}(\rho)e^{il\phi}$$

← l : *vibrational AM quantum number*

$l = \pm v, \pm(v\text{-}2), \ldots 0 \text{ or } \pm 1$

Energy levels split according to $|l| = 0(\Sigma), 1(\Pi), 2(\Delta), \ldots$

Total angular momentum: $J = R(rot) + l(vib)$

Quantum number: $l = 1 \rightarrow J = 1,2;\ l = 2 \rightarrow J = 2,3\ldots$

Symmetric Top Molecules

* Hamiltonian of 3-D rotations:

$$E_{rot} = \frac{J_a^2}{2I_A} + \frac{J_b^2}{2I_B} + \frac{J_c^2}{2I_C}, \quad J^2 = J_a^2 + J_b^2 + J_c^2$$

$$(prolate) = \frac{J_a^2}{2I_A} + \frac{1}{2I_B}(J_b^2 + J_c^2) = \frac{J^2}{2I_B} + (\frac{1}{2I_A} - \frac{1}{2I_B})J_a^2$$

$$(oblate) = \frac{1}{2I_B}(J_a^2 + J_b^2) + \frac{J_c^2}{2I_C} = \frac{J^2}{2I_B} + (\frac{1}{2I_C} - \frac{1}{2I_B})J_c^2$$

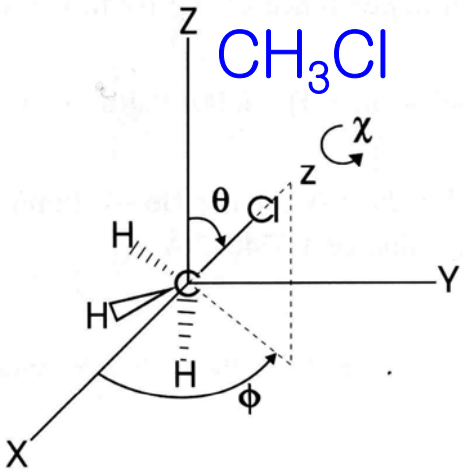
$$\therefore \hat{H}_{prolate} = \frac{\hat{J}^2}{2I_B} + (\frac{1}{2I_A} - \frac{1}{2I_B})\hat{J}_a^2$$

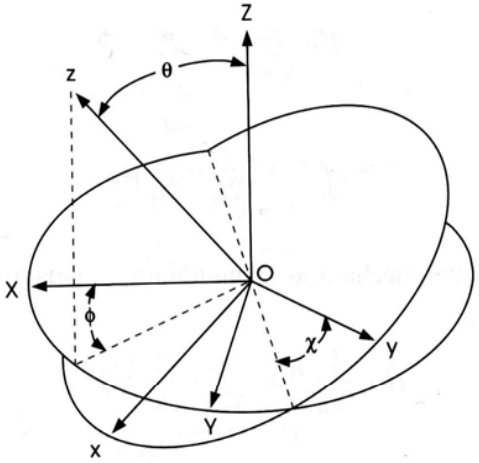
$$\hat{H}_{oblate} = \frac{\hat{J}^2}{2I_B} + (\frac{1}{2I_C} - \frac{1}{2I_B})\hat{J}_c^2$$

* Molecule-fixed coordinate versus space-fixed coordinate:

$$MFC(x,y,z;J_x,J_y,J_z) \Leftrightarrow SFC(X,Y,Z;J_X,J_Y,J_Z)$$

by Euler angles (θ, ϕ, κ), direction cosines (α_i, β_i, γ_i)





"(θ, ϕ) angles define the orientation of molecular z-axis (B, C) and κ angle define the internal orientation of x-y axes (A)"

Commutation relationship:

$$[\hat{J}_x,\hat{J}_y]=-i\hbar\hat{J}_z,\ [\hat{J}_y,\hat{J}_z]=-i\hbar\hat{J}_x,\ [\hat{J}_z,\hat{J}_x]=-i\hbar\hat{J}_y$$

$$[\hat{J}_X,\hat{J}_Y]=i\hbar\hat{J}_Z,\ [\hat{J}_Y,\hat{J}_Z]=i\hbar\hat{J}_X,\ [\hat{J}_Z,\hat{J}_X]=i\hbar\hat{J}_Y$$

* Eigenfunctions and AM operators:

$\hat{H}$ *commute with* $\hat{J}^2, \hat{J}_z, \hat{J}_Z$

$\rightarrow$ *Quantum numbers* J, K, M

Hypergeometric function

$$\rightarrow \textit{Eigenfunction } |JKM> = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} d^J_{MK}(\theta)\, e^{iM\phi}\, e^{iK\chi}$$

but not necessary to list exact forms!

$$\hat{H}\,|JKM> = E\,|JKM>, \quad \hat{J}^2\,|JKM> = J(J+1)\hbar^2\,|JKM>$$

$$\hat{J}_Z\,|JKM> = M\hbar\,|JKM>, \quad \hat{J}_z\,|JKM> = K\hbar\,|JKM>$$

$$\hat{J}^+ = \hat{J}_x + i\hat{J}_y; \ \textit{(lowering op. in MFC)},$$

$$\hat{J}^- = \hat{J}_x - i\hat{J}_y; \ \textit{(raising op. in MFC)}$$

$$\hat{J}^+\,|JKM> = [J(J+1) - K(K-1)]^{1/2}\,|JK-1M>$$

$$\hat{J}^-\,|JKM> = [J(J+1) - K(K+1)]^{1/2}\,|JK+1M>$$

* Energies and transitions:

For prolate tops

$$\hat{H}\psi = \left[\frac{\hat{J}^2}{2I_B} + \left(\frac{1}{2I_A} - \frac{1}{2I_B}\right)\hat{J}_z^2\right] | JKM >$$

$$\therefore\ E_{JK} = BJ(J+1) + (A-B)K^2$$

For oblate tops

$$\hat{H}\psi = \left[\frac{\hat{J}^2}{2I_B} + \left(\frac{1}{2I_C} - \frac{1}{2I_B}\right)\hat{J}_z^2\right] | JKM >$$

$$\therefore\ E_{JK} = BJ(J+1) + (C-B)K^2$$

Degeneracy: $2(2J+1) \leftarrow K = -J, -(J-1), \ldots 0 \ldots (J-1), J$

Selection rules: $\Delta J = \pm 1,\ \Delta M = 0, \pm 1,\ \Delta K = 0$

$$\therefore \Delta E_{J+1, K \leftarrow J, K} = 2BJ(J+1)$$

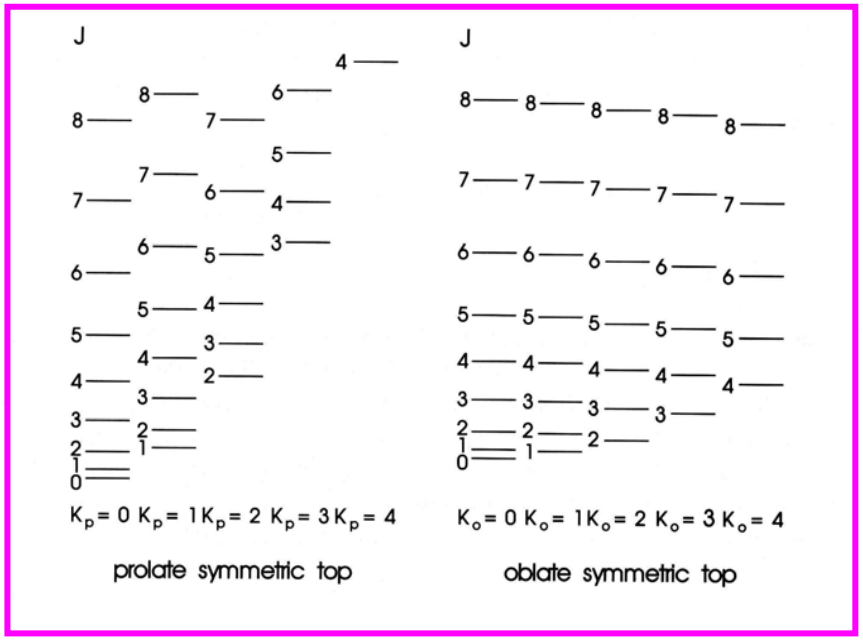
Centrifugal distortions (D_J, D_K, D_{JK}):

$$E_{JK} = BJ(J+1) - D_J[J(J+1)]^2 + (A-B)K^2 - D_K K^2 - D_{JK} J(J+1)K^2$$

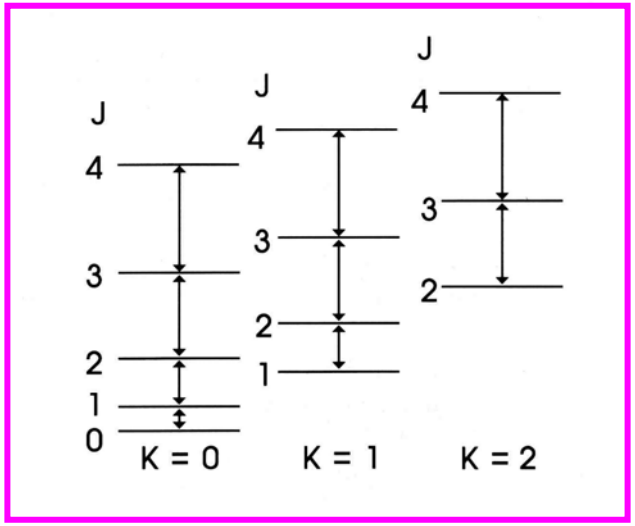
$$\therefore \Delta E_{J+1, K \leftarrow J, K} = 2BJ(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2$$

$$"K-dependent"$$

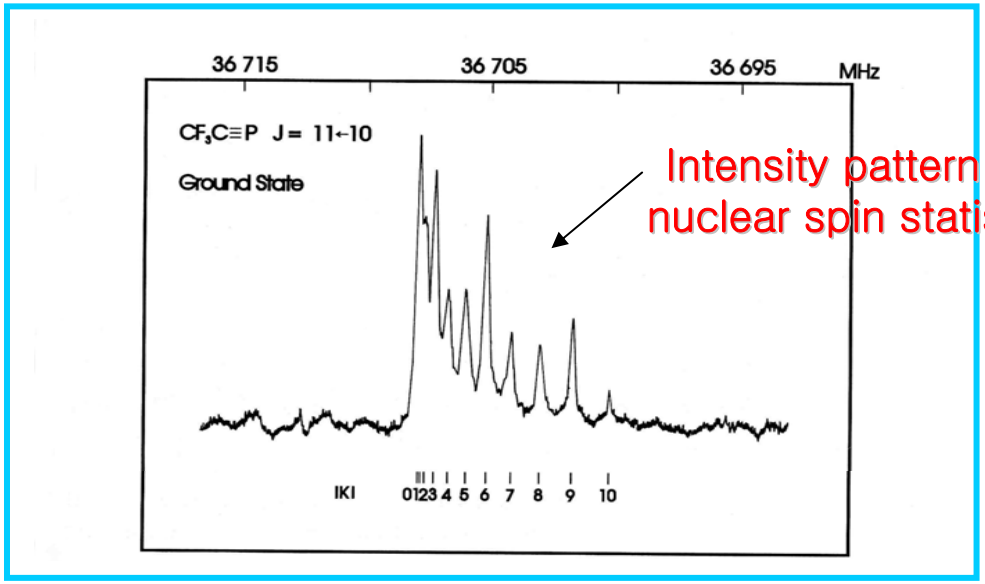
Energy levels



Allowed transitions



Example: CF_3CP spectrum



Asymmetric Top Molecules

* Hamiltonian operator

$$\hat{H}_{rot} = \frac{\hat{J}_a^2}{2I_A} + \frac{\hat{J}_b^2}{2I_B} + \frac{\hat{J}_c^2}{2I_C}, \quad \hat{J}^2 = \hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2$$

$$\hbar^2 \hat{H}_{rot} = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2$$

$$= \left(\frac{A+B}{2}\right)\hat{J}^2 + \left(C - \frac{A+B}{2}\right)\hat{J}_z^2 + \left(\frac{A-B}{4}\right)\left((\hat{J}^+)^2 + (\hat{J}^-)^2\right)$$

(oblate limit)

$$= \left(\frac{B+C}{2}\right)\hat{J}^2 + \left(A - \frac{B+C}{2}\right)\hat{J}_z^2 + \left(\frac{B-C}{4}\right)\left((\hat{J}^+)^2 + (\hat{J}^-)^2\right)$$

(prolate limit)

"Due to $(J^+)^2$, $(J^-)^2$ in H_{rot}, K is not good quantum number. But we use symmetric top basis set ($|JKM\rangle$) to describe asymmetric top problem. Also, we use prolate and oblate limiting cases to label asymmetric top states"

* Matrix methods: Energies

$$\langle JKM|\hat{J}^2|JKM\rangle = J(J+1)\hbar^2,\ \langle JKM|\hat{J}_z^{\,2}|JKM\rangle = K^2\hbar^2$$

$$\langle JK+2M|(\hat{J}^-)^2|JKM\rangle = \sqrt{J(J+1)-K(K+1)}\,\sqrt{J(J+1)-(K+1)(K+2)}\,\hbar^2$$

$$\langle JK-2M|(\hat{J}^-)^2|JKM\rangle = \sqrt{J(J+1)-K(K-1)}\,\sqrt{J(J+1)-(K-1)(K-2)}\,\hbar^2$$

.... others all zero → real symmetric matrix

"Diagonalization gives eigenvalues" → "Solve secular equation"

e.g. J=1

$$\begin{array}{c} \\ \langle 1,1| \\ \langle 1,0| \\ \langle 1,-1| \end{array}\begin{array}{c} \begin{array}{ccc} |1,1\rangle & |1,0\rangle & |1,-1\rangle \end{array} \\ \begin{pmatrix} C+\frac{A+B}{2} & 0 & \frac{A-B}{2} \\ 0 & A+B & 0 \\ \frac{A-B}{2} & 0 & C+\frac{A+B}{2} \end{pmatrix} \end{array} \rightarrow \begin{array}{c} \\ \langle 1,1| \\ \langle 1,-1| \\ \langle 1,0| \end{array}\begin{array}{c} \begin{array}{ccc} |1,1\rangle & |1,-1\rangle & |1,0\rangle \end{array} \\ \begin{pmatrix} C+\frac{A+B}{2} & \frac{A-B}{2} & 0 \\ \frac{A-B}{2} & C+\frac{A+B}{2} & 0 \\ 0 & 0 & A+B \end{pmatrix} \end{array}$$

secular equation:

$$\begin{vmatrix} C+\frac{A+B}{2}-\lambda & \frac{A-B}{2} \\ \frac{A-B}{2} & C+\frac{A+B}{2}-\lambda \end{vmatrix} = 0 \quad \therefore\ \lambda = C+A,\ C+B$$

$$\lambda = A+B$$

* Labeling of energy levels

$$" J_{K_{prolate}\ K_{oblate}} " \rightarrow 0_{00}, 1_{01}, 1_{11}, 1_{01}, 2_{0,2}, \ldots$$

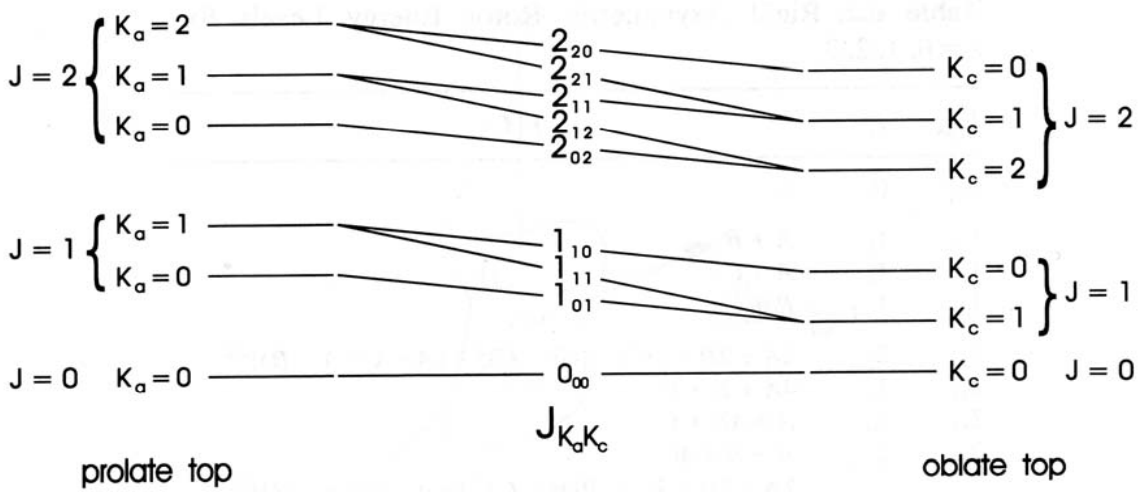
$$cf. \ " J_{\tau} " \leftarrow \tau = K_{prolate} - K_{oblate} = -J, \ldots + J$$

"... each J state has (2J+1) nondegenerate K states..."

Degeneracy: (2J+1) for each |JK>

Asymmetry parameter: $\kappa = \dfrac{2B - A - C}{A - C} \rightarrow \kappa = -1\,(prolate), +1(oblate)$

Correlation diagram:

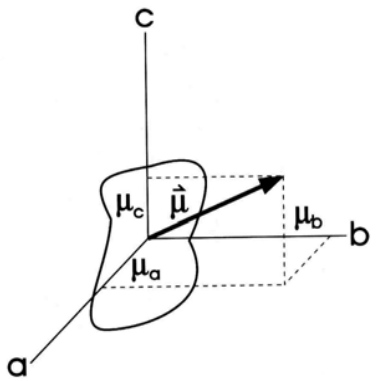


Energy levels and labels of asymmetric top

$J_{K_aK_c}$	J_τ	$F(J_\tau)$
0_{00}	0_0	0
1_{10}	1_1	$A + B$
1_{11}	1_0	$A + C$
1_{01}	1_{-1}	$B + C$
2_{20}	2_2	$2A + 2B + 2C + 2[(B - C)^2 + (A - C)(A - B)]^{1/2}$
2_{21}	2_1	$4A + B + C$
2_{11}	2_0	$A + 4B + C$
2_{12}	2_{-1}	$A + B + 4C$
2_{02}	2_{-2}	$2A + 2B + 2C - 2[(B - C)^2 + (A - C)(A - B)]^{1/2}$
3_{30}	3_3	$5A + 5B + 2C + 2[4(A - B)^2 + (A - C)(B - C)]^{1/2}$
3_{31}	3_2	$5A + 2B + 5C + 2[4(A - C)^2 - (A - B)(B - C)]^{1/2}$
3_{21}	3_1	$2A + 5B + 5C + 2[4(B - C)^2 + (A - B)(A - C)]^{1/2}$
3_{22}	3_0	$4A + 4B + 4C$
3_{12}	3_{-1}	$5A + 5B + 2C - 2[4(A - B)^2 + (A - C)(B - C)]^{1/2}$
3_{13}	3_{-2}	$5A + 2B + 5C - 2[4(A - C)^2 - (A - B)(B - C)]^{1/2}$
3_{03}	3_{-3}	$2A + 5B + 5C - 2[4(B - C)^2 + (A - B)(A - C)]^{1/2}$

* Selection rules:

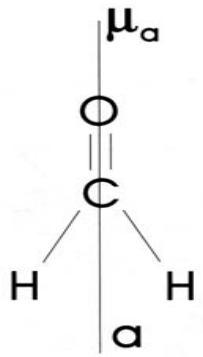
$$\Delta J = 0, \pm 1, \ \Delta M = 0, \pm 1, \ \Delta K = ?$$



(i) a–type transitions ($\mu_a \neq 0$, $\mu_b = \mu_c = 0$):

$$\Delta K_{prolate} = 0, (\pm 2, \pm 4, ...)$$

$$\Delta K_{oblate} = \pm 1, (\pm 3, \pm 5 ...)$$



(ii) b–type transitions ($\mu_b \neq 0$, $\mu_a = \mu_c = 0$):

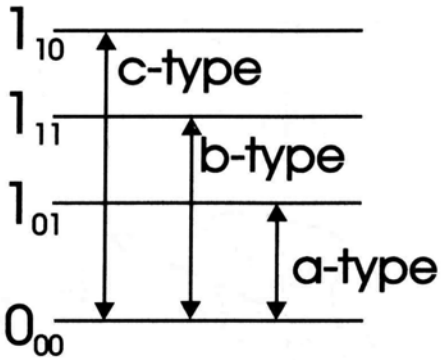
$$\Delta K_{prolate} = \pm 1, (\pm 3, ...)$$

$$\Delta K_{oblate} = \pm 1, (\pm 3, ...)$$

(iii) c–type transitions ($\mu_c \neq 0$, $\mu_a = \mu_b = 0$):

$$\Delta K_{prolate} = \pm 1, (\pm 3, ...)$$

$$\Delta K_{oblate} = 0, (\pm 2, ...)$$



* Structure determination

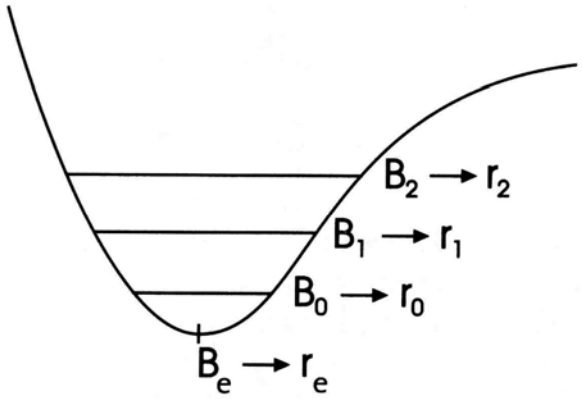
Diatomic molecules:

$$B_v = B_e - \alpha_e(v+\frac{1}{2}) + \gamma_e(v+\frac{1}{2})^2 + \ldots$$

$$\therefore B_0 = B_e - \frac{1}{2}\alpha_e + \frac{1}{4}\gamma_e + \ldots$$

$$B_1 = B_e - \frac{3}{2}\alpha_e + \frac{9}{4}\gamma_e + \ldots$$

$$\Rightarrow B_0, B_1 \rightarrow B_e \rightarrow r_e$$



(more accurate than crystallography!!!)

Polyatomic molecules:

$$A_v = A_e - \sum_{i=1}^{3N-6} \alpha_i^A (v_i + \frac{1}{2})$$

$$B_v = B_e - \sum_{i=1}^{3N-6} \alpha_i^B (v_i + \frac{1}{2})$$

$$C_v = C_e - \sum_{i=1}^{3N-6} \alpha_i^C (v_i + \frac{1}{2})$$

"So many α_i's to be determined"
→ Isotope exchange is needed