5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #23: Asymmetric Top

$\mathbf{R} = \mathbf{I}\boldsymbol{\omega}$

$\mathbf{H}^{ROT} = \frac{1}{2}\mathbf{T}^{\dagger}\mathbf{I}^{-1}\mathbf{T}$

inverse inertia matrix

$J = R + L + S + \ell$

$\mathbf{H}^{ROT} = \frac{1}{2}(J - L - S - \ell)^{\dagger}\mathbf{I}^{-1}(J - L - S - \ell)$

see Watson, *Mol. Phys.* **15**, 479 (1968)

forget about L, S, ℓ for now

$\mathbf{H}^{ROT} = AJ_a^2 + BJ_b^2 + CJ_c^2$

a-axis is "light" c-axis is "heavy"

$A \geq B \geq C$

$A / cm^{-1} = \frac{h}{c}\frac{1}{8\pi^2 I_a}$ $\qquad I_a = \sum_i m_i (b^2 + c^2)$

etc. B, C b,c are perpendicular distances from named axis

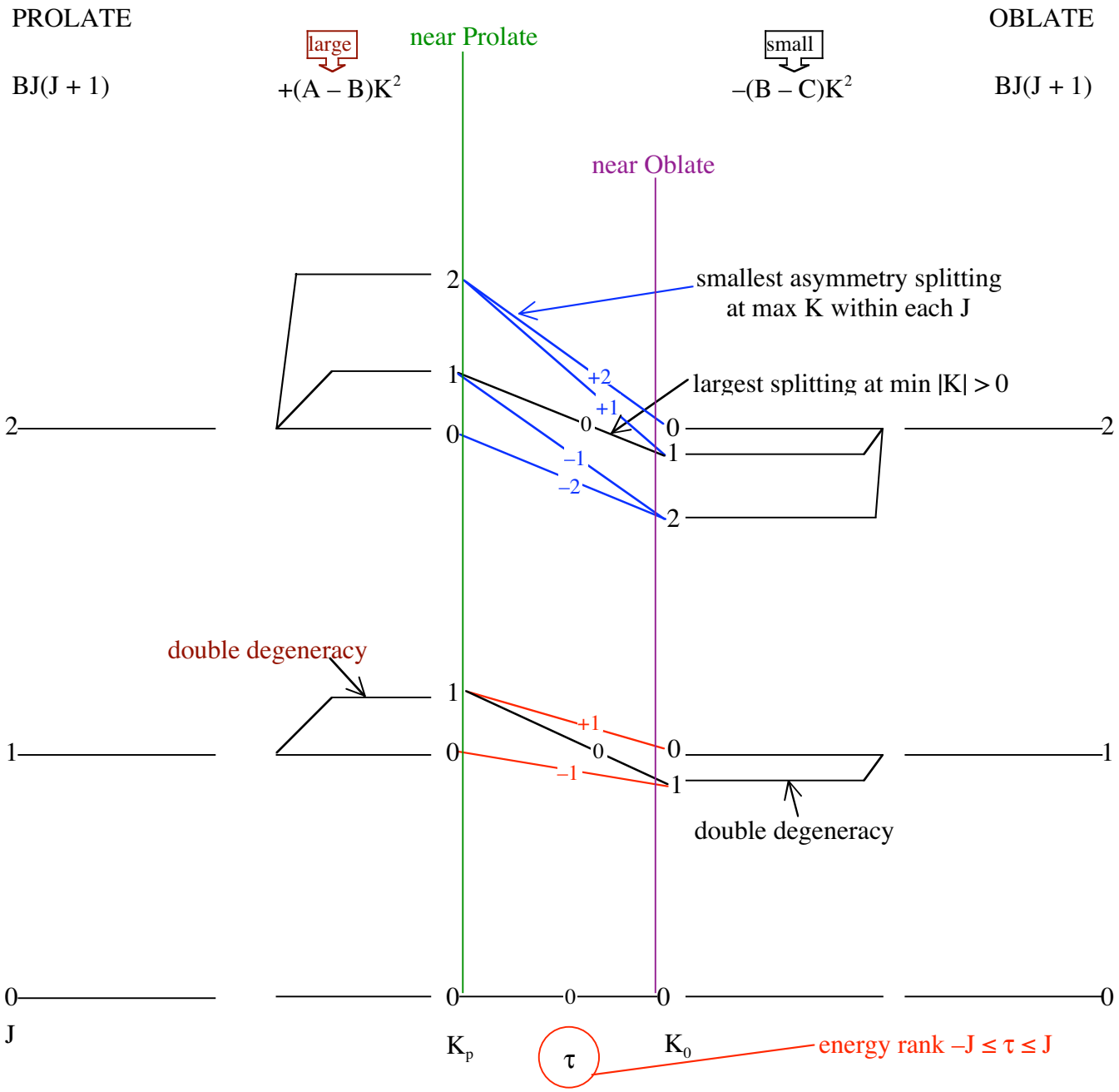
prolate top $I_b = I_c$ $\qquad E_p^{ROT}(J,K) = BJ(J+1) + \underbrace{(A-B)}_{>0}K^2$

oblate top $I_a = I_b$ $\qquad E_o^{ROT}(J,K) = BJ(J+1) + \underbrace{(C-B)}_{<0}K^2$

TODAY: Asymmetric Top

1. Correlation Diagram { qualitative pattern for Energy levels; notation $J_{K_aK_c}$ and J_τ
2. $\mathbf{H}^{ROT}$ in $|JKM\rangle$ basis set
   $\Delta K = 0$ and $\Delta K = \pm 2$ matrix elements
3. perturbation theory and $\kappa \equiv \frac{2B - A - C}{A - C}$ asymmetry parameter
4. Wang factorization: 4 symmetry species
5. Townes and Schawlow Tables for Asymmetric Top Levels

What do we expect energy levels for an asymmetric top to look like? Intermediate between prolate and oblate limits. Correlation diagram is based on non-crossing rule. Imagine a continuous transformation of a molecule from prolate to oblate limit. Levels belonging to different values of a rigorously good quantum number can cross, all others cannot. J is good, K is not good.



Levels within a J can't cross. K > 0 are doubly degenerate and the degeneracy is lifted as soon as top becomes asymmetric. Near the corresponding limit, high K has small "asymmetry splitting" and low K has large splitting.

Vertical lines give a good sense of the level-pattern at any point between prolate and oblate limits.

Two notation schemes:

$J_{K_p K_o}$ (projection on a-axis, projection on c-axis) or $J_{K_a K_c}$

note that $K_p + K_o = J$ or $J + 1$ (asymmetry doublet)

J_τ (eigenvalue rank) $-J \le \tau \le +J$

Near the prolate limit $K_p + K_o = J$ is the higher energy member of the doublet, near the oblate limit $K_p + K_o = J$ is the lower member.

OK. Now we know what to expect qualitatively, and how to label the levels, but how do we compute accurate energy levels and wavefunctions?

Set up $\mathbf{H}^{ROT}$ in symmetric top basis set $|JKM\rangle$. Initially, we do not even have to worry about whether to select a, b, or c axis as the quantization axis.

$$\hat{\mathbf{H}}^{ROT} = \frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} + \frac{\hat{J}_z^2}{2I_z}$$

$$\hat{J}_z^2 |JKM\rangle = \hbar^2 K^2 |JKM\rangle$$

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

$$J_\pm = J_x \pm iJ_y$$

$$\hat{J}_\pm |JKM\rangle = \hbar\left[J(J+1) - K(K\mp 1)\right]^{1/2} |JK\mp 1M\rangle \qquad (\hat{J}_+ \text{ is lowering operator})$$

$$J_x = \frac{1}{2}(J_+ + J_-) \quad J_x^2 = \frac{1}{4}\left[J_+^2 + J_-^2 + \underbrace{J_+J_- + J_-J_+}_{2\left(J_x^2 + J_y^2\right) = 2\left(J^2 - J_z^2\right)}\right]$$

$$J_y = -\frac{i}{2}(J_+ - J_-)$$

So

$$\hat{J}_x^2 = \underbrace{\frac{J_+^2}{4} + \frac{J_-^2}{4}}_{\Delta K = \pm 2} + \underbrace{\frac{J^2 - J_z^2}{2}}_{\Delta K = 0}$$

$$\hat{J}_y^2 = \underbrace{-\frac{J_+^2}{4} - \frac{J_-^2}{4}}_{\Delta K = \pm 2} + \underbrace{\frac{J^2 - J_z^2}{2}}_{\Delta K = 0}$$

be careful of commutation rules!

both $\hat{J}_x^2$ and $\hat{J}_y^2$ have same diagonal part

both have same off-diagonal magnitude but opposite sign

$$\mathbf{H}^{ROT} = \underbrace{\left\{\frac{\hat{J}^2 - \hat{J}_z^2}{2}\left[\frac{1}{2I_x} + \frac{1}{2I_y}\right] + \frac{\hat{J}_z^2}{2I_z}\right\}}_{\Delta K = 0} + \underbrace{\left\{\left[\frac{J_+^2}{4} + \frac{J_-^2}{4}\right]\left(\frac{1}{2I_x} - \frac{1}{2I_y}\right)\right\}}_{\Delta K = \pm 2}$$

Diagonal part of $\mathbf{H}^{ROT}$

$$\left\langle JK\left|\hat{\mathbf{H}}^{ROT}\right|JK\right\rangle = \frac{\hbar^2}{2}\left[\frac{1}{2I_x} + \frac{1}{2I_y}\right]J(J+1) + \frac{\hbar^2}{2}\left[\frac{1}{2I_z} - \frac{1}{2I_x} - \frac{1}{2I_y}\right]K^2$$

(z = a)	near prolate	$\frac{B+C}{2} \equiv \bar{B}$	$A - \bar{B}$	> 0
(z = c)	near oblate	$\frac{B+C}{2} \equiv \bar{B}$	$C - \bar{B}$	< 0
(z = b)	midway (basis for perturbation theory treatment of either limit)	$\frac{A+C}{2}$	$B - \frac{A+C}{2}$	?

Off-Diagonal part of $\mathbf{H}^{ROT}$

$$\left\langle JK \pm 2 \left| \widehat{\mathbf{H}}^{ROT} \right| JK \right\rangle = \frac{\hbar^2}{2}\left[\frac{1}{2I_x} - \frac{1}{2I_y}\right]\left[J(J+1) - K(K\pm 1)\right]^{1/2}\left[J(J+1) - (K\pm 1)(K\pm 2)\right]^{1/2}$$

(Remember the K's in $[\ ]^{1/2}$ are product of initial and final K values.)
Coefficient for $\Delta K = \pm 2$ matrix elements

(z = a)	near prolate	$\frac{B-C}{4}$
(z = c)	near oblate	$\frac{A-B}{4}$
(z = b)	midway (basis for perturbation theory treatment of either limit)	$\frac{A-C}{4}$

$\Delta K = \pm 2$ matrix elements would be = 0 if B = C or A = B (i.e. symmetric top limit)

Since the only off-diagonal matrix elements are $\Delta J = 0$, $\Delta K = \pm 2$, $\mathbf{H}^{ROT}$ factors into even-K and odd-K sub-blocks.

Use perturbation theory to get an idea about $\frac{\mathbf{H}'}{\Delta E^{\circ}}$. Use b-axis as quantization axis, because this is midway between prolate and oblate limits.

$$\frac{\mathbf{H}'_{ij}}{\Delta E^{o}_{ij}} = \frac{\mathbf{H}^{ROT}_{K,K\pm 2}}{E^{o}_{JK} - E^{o}_{JK\pm 2}} = \mp\frac{1}{8}\left[\frac{J^2(J+1)^2}{(K\pm 1)^2} + K(K\pm 2) - 2J(J+1)\right]^{1/2}\frac{A-C}{2B-A-C}$$

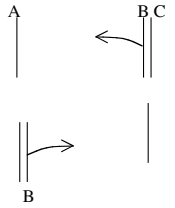
(result of some algebra)

$\kappa \equiv \frac{2B - A - C}{A - C}$ is called "asymmetry parameter".

prolate	B = C	$\kappa = -1$
oblate	A = B	$\kappa = +1$

$\kappa = 0$ is most asymmetric (also spherical top) possible. $B = \frac{A+C}{2}$

Rule out A = B = C (spherical top).



Use κ^{-1} as order-sorting parameter for perturbation theory.

Perturbation Theory (using b-axis for quantization) will give bad approximation when $\left|\frac{\mathbf{H}'}{\Delta E^{o}}\right| \gtrsim 1$.

This occurs when:

1. $\kappa \to 0$

2. $K \ll J$, $J \gg 0$ because then $[\ ]^{1/2}$ gets large. We already saw with correlation diagram that asymmetry splittings are largest for $K \ll J$.

The only time perturbation theory can work (with b-axis quantization) is if J ≈ K and J small. Otherwise we must diagonalize a matrix.

Factor $\mathbf{H}^{ROT}$.

1. No $\Delta J \neq 0$ matrix elements. Each J-block has 2J + 1 eigenvalues.

2. Within each J-block, only $\Delta K = \pm 2, 0$ matrix elements.
   So factor into even-K (J or J + 1 eigenvalues)
   and odd-K (J + 1 or J eigenvalues).

3. Within each odd or even subset, we can form $2^{-1/2}[|JK\rangle \pm |J - K\rangle]$ linear combinations.

This corresponds to constructing eigenfunctions of σ_v (zx or zy) as for a diatomic molecule.

2 senses of rotation about z axis must have same energy

$[\mathbf{H}^{ROT}, \sigma_v] = 0$

$\sigma_v(xz)|JKM\rangle = (-1)^{J-K}|J-KM\rangle$

assertion! need to see form of $|JKM\rangle$ wavefunction to be sure.

not a geometric symmetry element for the rigid molecule itself, but the symmetric top basis functions must always have symmetry properties with respect to σ_v

sense of rotation reversed by σ(xz) or σ(yz)

Wang Symmetrizing Transformation constructs:

$$\left\{\begin{array}{l} |J0M\rangle \\ 2^{-1/2}\left[|J\,|\,K\,|\,M\rangle \pm |J-|\,K\,|\,M\rangle\right] \end{array}\right\} \text{basis functions}$$

works because

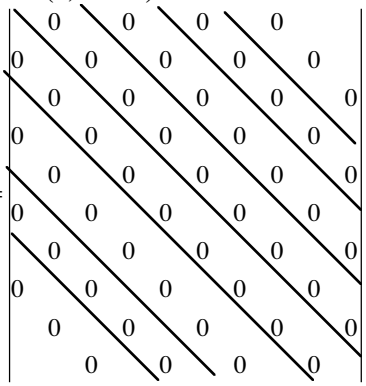
Wang Transformation

$$\mathbf{X}^{-1} = \mathbf{X} = 2^{-1/2} \begin{vmatrix} -1 & & & & & & 1 \\ & \ddots & & & & \iddots & \\ & & -1 & & 1 & & \\ & & & 2^{1/2} & & & \\ & & 1 & & 1 & & \\ & \iddots & & & & \ddots & \\ 1 & & & & & & 1 \end{vmatrix}$$

$$K = \quad J \quad J-1 \quad \cdots \quad 0 \quad \cdots \quad -J$$

$\mathbf{X}^{-1}\,\mathbf{H}^{ROT}(J, \text{all K})\mathbf{X}$

$\mathbf{H}(J) =$



Get 4 types of sub-blocks after rearrangement of $\mathbf{X}^{-1}\mathbf{H}\mathbf{X}$

(K_p, K_o)	e,e	These are 4 distinct symmetry species (Group Theory later)
(K_a, K_c)	e,o	
	o,o	
	o,e	

exact Asymmetric Top Energy Levels

J = 0	is	1×1					
1	is	3	1×1				exactly soluble algebraically
2	is	3	1×1	and	1	2×2	
3	is	1	1×1	and	3	2×2	
4	is	3	2×2	and	1	3×3	must diagonalize numerically
5	is	1	2×2	and	3	3×3	
6							
7							

# of each symmetry

J even $\quad \frac{J}{2}, \frac{J}{2}, \frac{J}{2}, \frac{J}{2}+1$

J odd $\quad \frac{J-1}{2}, \frac{J+1}{2}, \frac{J+1}{2}, \frac{J+1}{2}$

Trivial to set up and diagonalize $\mathbf{H}^{ROT}$.

Guide to tables from T & S (not needed with computers, except for checking programs).

1. pages 522-526 Asymmetric top energies for near-symmetric tops given as power series in

$$b_p = \frac{C - B}{2A - B - C} \text{ near prolate}$$

or

$$b_o = \frac{A - B}{2C - B - A} \text{ near oblate}$$

$$E = \bar{B}J(J+1) + \begin{bmatrix} (A - \bar{B}) \\ \text{or} \\ (C - \bar{B}) \end{bmatrix} w$$

$$w \equiv K^2 + C_1 b + C_2 b^2 + \ldots C_n b^n$$

2. pages 527-555 explicit eigenvalues for $\mathbf{H}^{ROT}$ for J = 0 – 12 and $|\kappa| = 0 \rightarrow 1$ in steps of 0.01.

Listed as $E = \frac{1}{2}(A + C)J(J + 1) + \frac{1}{2}(A - C)E_\tau$ where E_τ is tabulated.

Levels labeled by $J_{K_p K_o}$ and $J_\tau \begin{bmatrix} \tau = -J & E_{min} \\ \tau = +J & E_{max} \end{bmatrix}$.

Next time, intensities and selection rules for pure rotation transitions of symmetric and asymmetric tops.