5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #24: Pure Rotation Spectra of Polyatomic Molecules

Last time: Asymmetric tops

$$\mathbf{H}^{\mathrm{ROT}} = \left[\bar{B}J(J+1) + \begin{pmatrix} A-\bar{B} \\ C-\bar{B} \end{pmatrix} K^2 \right] |JK\rangle\langle JK|$$

$$+ \begin{pmatrix} B-C \\ A-B \end{pmatrix} \frac{1}{4} [(J \mp K)(J \mp K - 1)(J \pm K + 2)(J \pm K + 1)]^{1/2} |JK\rangle\langle JK \pm 2|$$

asymmetry parameter $\kappa \equiv \dfrac{2B - A - C}{A - C}$

prolate	$B = C$	$\kappa = -1$
oblate	$A = B$	$\kappa = +1$
most asymmetric	$B = \dfrac{A+C}{2}$	$\kappa = 0$

Perturbation Theory: $\dfrac{H'_{JK,JK\pm 2}}{\Delta E^\circ} = \dfrac{1}{\kappa} f(J,K)$

Factor $\mathbf{H}^{\mathrm{ROT}}$ into four blocks — can label these blocks according to whether K_p and K_o (or K_a and K_c) are even or odd

e,e e,o o,e o,o — correspond to rotational symmetry species — good quantum numbers [not related to geometric symmetry operations applied to rigid molecule].

TODAY

pure rotation spectra

SYMMETRIC TOP → $M_x = M_y = 0$, $\Delta K = 0$ like diatomic. Only get information about B from pure rotation spectrum.

ASYMMETRIC TOP → $\vec{M}$ can have 1, 2, or 3 non-zero components

Transition	$\mathbf{\Delta K_p}$	$\mathbf{\Delta K_o}$
a-type	even	odd
b-type	odd	odd
c-type	odd	even

NOTATION/ASSIGNMENT

$$P_{if} \propto \left| \sum_{S,b} \varepsilon_S \left\langle v_i \left| \underset{\substack{\text{pure rotation} \\ \big\downarrow \\ M_b(Q_e)}}{M_{b,if}(\mathbf{Q})} \right| v_f \right\rangle \left\langle \Omega_i J_i M_i \left| \underset{\substack{\big\downarrow\ \text{Hougen, p. 31} \\ f(J_i,J_f)\underset{\text{body polarization}}{g(J_i\Omega_i;J_f\Omega_f)}\underset{\text{lab polarization}}{h(J_iM_i;J_fM_f}}}{\alpha_{Sb}} \right| \Omega_f J_f M_f \right\rangle \right|^2$$

BODY COMPONENT b → (a, b, or c) $K \leftrightarrow \Omega$

Symmetric Tops - can't have nonzero dipole ⊥ to unique axis: z

z → a prolate

z → c oblate

"parallel" type transitions only

$\Delta K = 0, \Delta J = \pm 1$ ($\Delta J = 0$ weak, except for J = K)

if there were a ⊥ μ component, it would have to point in same direction after a $C_n(z)$ or $S_n(z)$ operation. $\mu_\perp = 0$ for $n \geq 2$.

$$E_{ROT} = BJ(J+1) + \begin{pmatrix} A-B \\ C-B \end{pmatrix} K^2$$

identical BJ(J + 1) stacks shifted by $\begin{pmatrix} A-B \\ C-B \end{pmatrix} K^2$

no inter-stack transitions

no information about other rotational constants

$$\Delta E_{JK \leftrightarrow J-1K} = 2BJ$$

(small splittings due to centrifugal distortion

$$E_{JK} = E^{o}_{JK} - D_J J^2 (J+1)^2 - \underbrace{D_{JK} J(J+1) K^2} - D_K K^4\ )$$

but these give no information about A or C!

Get information about $\left\{ \begin{array}{l} \text{other rotational constants} \\ \text{equilibrium structure} \end{array} \right. \left\{ \begin{array}{l} \text{from IR and UV spectra} \\ \text{or from isotopomers} \end{array} \right.$

$^{14}NH_3$ $^{15}NH_3$ $^{14}ND_3$ etc. and from non-symmetric species (non-symmetric tops!)

Asymmetric Tops - more than 1 component of $\vec{M}$ can be nonzero.

K ≠ 0 levels split by asymmetry splitting.

Same $^{\Delta K}\Delta J$ type transitions from different K's not superimposed.

No resemblance to diatomic molecule spectrum!

symmetry label - C_2 about specified axis

$$J_{K_p,K_o} \qquad \begin{pmatrix} \text{prolate axis} & & \text{oblate axis} \\ \text{e or o} & , & \text{e or o} \\ K_p & & K_o \end{pmatrix}$$

M_a	(e, o)
M_b	(o, o)
M_c	(o, e)

$$\left\langle J'_{K'_pK'_o}\right| M_{\substack{a\\b\\c}} \left| J''_{K''_pK''_o}\right\rangle \rightarrow \begin{array}{c} \begin{array}{cc} K'_p & K'_o \end{array} \\ \begin{pmatrix} e & e \\ o & o \end{pmatrix} \end{array} \begin{pmatrix} \begin{array}{ccc} M & \Delta K_p & \Delta K_o \\ a & e & o \\ b & o & o \\ c & o & e \end{array} \end{pmatrix} \begin{array}{c} \begin{array}{cc} K''_p & K''_o \end{array} \\ \begin{pmatrix} e & e \\ o & o \end{pmatrix} \end{array}$$

e × e × e = e   o × o × e = e   etc.

This is not matrix multiplication. It is just a summary of possibilities.

integrand must be (e, e) with respect to both K_p and K_o for integral to be $\neq 0$

a-type selection rule	ΔK_a = even	ΔK_c = odd
b-type selection rule	ΔK_a = odd	ΔK_c = odd
c-type selection rule	ΔK_a = odd	ΔK_c = even

Want ΔK to be as small as possible. 0 or ±1 for near symmetry axis, ±2 or ±3 possible for other axes.

K_p and K_o are (related to) symmetry labels. Only one of these two quantum numbers is an almost good projection quantum number.

$\Delta J = 0$ strong or weak depending on whether $\Delta K_{\text{near sym}} = \underline{\pm 1}$ or 0.

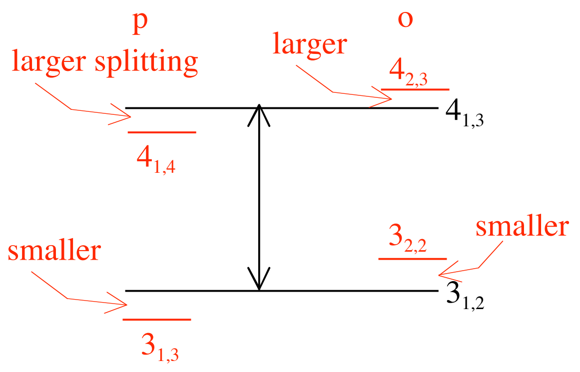
		near prolate		near oblate
a	‖	$\Delta J = 0$ weak $\Delta K_a = 0$	⊥	$\Delta J = 0$ strong $\Delta K_c = \pm 1$
b	⊥	$\Delta J = 0$ strong $\Delta K_a = \pm 1$	⊥	$\Delta J = 0$ strong $\Delta K_c = \pm 1$
c	⊥	$\Delta J = 0$ strong $\Delta K_a = \pm 1$	‖	$\Delta J = 0$ weak $\Delta K_c = \pm 0$

NOTATION examples

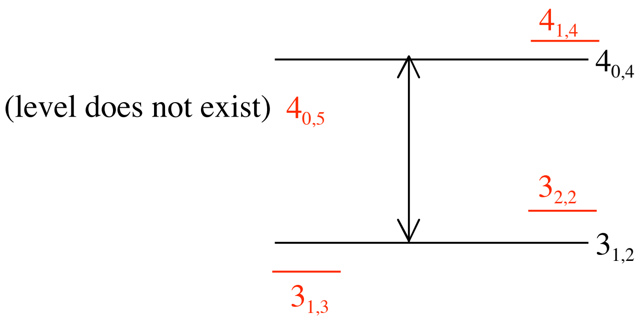
⇓ expressed as …nopqrst…

$${}^{\Delta K_{p\text{ or }o}}\Delta J_{a\text{ or }b\text{ or }c}\left(J_{K_p,K_o}\right)$$

(other asymmetry component in respective limit)



near prolate	near oblate
${}^{q}R_a(3_{1,2})$	${}^{r}R_a(3_{1,2})$



${}^{p}R_c(3_{1,2})$

${}^{s}R_c(3_{1,2})$
weak $\Delta K_o = 2$

Can decide whether the other asymmetry doublet transition is at higher or lower frequency. Asymmetry splitting is largest for largest J–K: $\nu\left({}^{q}R_a\left(3_{1,2}\right)\right) > \nu\left({}^{q}R_a\left(3_{1,3}\right)\right)$.
I am not sure that qualitative predictions can be made when $\Delta K = \Delta J$.

A lot of information about expected patterns can be deduced from qualitative prolate↔oblate correlation diagram and simple transition intensity ideas.

NON-LECTURE

Table of transition intensities in Townes and Schawlow, pages 557-612 (similar to diatomic M-averaged rotational linestrength factors).

$$
{}^{x}S_{J_{k\ell}J'_{mn}}\underset{\boxed{\begin{matrix}\text{listed for}\\ \kappa = \pm 1, \pm 0.5, 0\end{matrix}}}{\underset{\Uparrow}{(\kappa)}} \equiv 10^4(2J+1)\left|\left\langle J_{k\ell}\middle|M_x\overset{\text{M averaged}}{\alpha_{x\bar{S}}}\middle|J'_{mn}\right\rangle\right|^2
$$

x = a, b, c
K_p: k, m
K_o: ℓ,n

Transitions are listed by sub-branch and labeled by lower state quantum numbers. Notation for rotational level and rotational transition.

$$
J_{\underset{K_{-1}}{\underset{\uparrow}{K_p}}\underset{K_{+1}}{\underset{\uparrow}{K_o}}} \qquad {}^{x}R_{\Delta K_p\,\Delta K_o}\left(J_{K_p,K_o}\right)
$$

2 left columns in T and S table are for upper sign of κ
2 right columns in T and S table are for lower sign of κ

But we are modern and have computers. How to do it?

* specify A, B, C

* diagonalize $\mathbf{H}^{\mathrm{ROT}}\begin{cases} \mathrm{E}\left(\mathrm{J}_{\mathrm{K_pK_o}}\right) \\ \psi_{\mathrm{J}_{\mathrm{K_pK_o}}} \end{cases}$

* evaluate $M_b\alpha_{bS}$ matrix elements following Hougen, pp. 32-41 (especially 37-41)

* sum over M_J components

What does actual microwave spectrum look like?

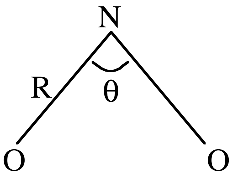
Complicated $J \rightarrow 2J + 1$ sublevels for each J
Many rotational branches
No obvious pattern for Q branches

Do H_2CO instead of NO_2.
Which is a, b, c
oblate or prolate? (possibility of switch to oblate?)
where is μ? what is type? selection rules?

Example: NO_2

$$\boxed{\kappa \equiv \frac{2B - A - C}{A - C}}$$

$A_0 = 8.0012\ \mathrm{cm}^{-1}$
$B_0 = 0.43364$
$C_0 = 0.41040$
$\kappa = -0.8857$ (near prolate)
μ is in-plane ⊥ to O—O direction



$R_0 = 1.1934\text{Å}$
$\theta_0 = 134.1°$

light axis: a, ∥ to O—O direction (through center of mass)
heavy axis: c, ⊥ to plane
$\therefore\ \mu$ is ∥ b axis

Special relationship for planar molecules

$$\frac{1}{A} + \frac{1}{B} = \frac{1}{C}$$

inertial defect: $-\left(\frac{1}{A_e} + \frac{1}{B_e} - \frac{1}{C_e}\right) = +5.6 \times 10^{-3}$
(not quite 0 because v = 0 not $_e$ constants used

<u>b-type transitions</u>: ΔK_p = odd, ΔK_o = odd, $\Delta J = 0$ strong, $\Delta J = \pm 1$

types of branches	$^{p}\mathbf{P}$	$^{p}\mathbf{Q}$	$^{p}\mathbf{R}$	$^{r}\mathbf{P}$	$^{r}\mathbf{Q}$	$^{r}\mathbf{R}$
	downward	downward	downward at low J	upward at low J	upward	upward

~3 upward transitions for each $J_{K_aK_c}$
~3(2J + 1) upward transitions for each J

How to assign?

* Look for patterns

series of lines spaced by ~$2\bar{B}$ (R-branches)
also repeated K-stack spacings
pairs of lines corresponding to asymmetry doublets (R-branches)
    size of asymmetry splitting - large for large J–K
    absence of asymmetry splitting : $K = 0 \leftrightarrow 0, 1 \leftrightarrow 0, 0 \leftrightarrow 1$

* T-dependence

high $\mathbf{E}^{\mathrm{ROT}}$ lines increase in intensity rapidly as T↑
low $\mathbf{E}^{\mathrm{ROT}}$ lines decrease in intensity slightly as T↑

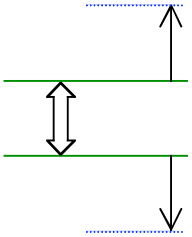
* guess structure and compute spectrum — frequencies and relative intensities

* tricks: Stark (ε-field) modulation

picks out low-J lines where asymmetry splitting is small J ≈ K

Double Resonance — bootstrap — transfer one assignment to neighboring linked transitions

saturate modulate label



Recall, for planar molecule there are only 2 independent bits of information. 2 correct assignments lead to accurate prediction of entire spectrum.

* isotope shifts. Change mass of atom that lies on one a, b, or c axis - corresponding rotational constant unchanged, others affected!