5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #11: Pictures of Spectra and Notation

Last Time Selection, propensity and intensity rules

$\vec{M}(R)_{if}$ $\alpha_{Sb}(\theta,\phi)$

absolute rotational linestrengths $\underbrace{S^{\Omega_i\Omega_f}_{J_iJ_f}}$

rotation	permanent dipole	$P \propto \mu^2 g_i$ or S
vibration	$\frac{dM}{dQ}$	$P \propto \left(\frac{dM}{dQ}\right)^2 v g_i$
electronic	$M_{if}\langle v_i \mid v_f\rangle$	$P \propto M^2 q_{v_i v_f} g_i$

Sum rule

typical form for
universal angular
factor → must
sum to 1 or to
total degeneracy

TODAY:

Patterns in spectra
Typical constants
How to assign spectra - problems and tricks
Notation

PURE ROTATION

μ-wave sources limit range of J sampled (more difficult to assign than expected)
superposition of lines from vastly different energy regions, isotopomers
population effects.
How to tell up from down. ← Think about this!

VIBRATION-ROTATION
J range limited by T, not by radiation source. P and R branch structure - open, no heads, zero gap (easy to assign)
PQR notation
hot bands and isotopomers

ELECTRONIC
Band heads due to large $|\Delta B|$

blue vs. red degraded → sign of ΔB (hard to assign because of overlapping lines)
J_{Head}

vibrational Sequences vs. Progressions
Qualitative Franck-Condon Principle

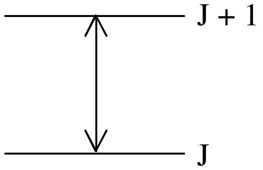
Universal notation for *all* molecular spectroscopy.

Upper level denoted by ′ always stated first
Lower level denoted by ″ always stated second

$\Delta Z \equiv Z' - Z''$ (for any quantity, Z)

	$\Delta J = J' - J''$
O	-2
P	-1
Q	0
R	1
S	2

i.e. R(J) means



Denote whether transition is absorption or emission by direction of arrow. Always state upper level first.

PURE ROTATION SPECTRA – μ-wave (e.g. heteronuclear diatomic)

requires permanent dipole moment

ν 10-300 GHz [$\bar{\nu} = \nu/c$ $c = 3 \times 10^{10}$ cm/s]

λ 3cm – 1mm "cm-wave" and "mm-wave" regions

for $^1\Sigma^+$ $\Delta J = \pm 1$ only because $\Omega = 0$. recall $S^{\Omega\Omega}_{J_iJ_f}$

$$F_v(J) = B_v J(J+1) - \overset{\boxed{\text{centrifugal distortion}}}{D_v} J^2(J+1)^2 \qquad D \approx \frac{4B^3}{\omega^2} \sim 10^{-6}B$$

$$J \leftarrow J-1 \qquad F_v(J) - F_v(J-1) = 2\overset{\boxed{\text{J of higher level}}}{J}B_v - 4J^3D_v$$

Typical B-value $\approx 1\ \text{cm}^{-1} = 30$ GHz

B: Cs_2 $0.01\ \text{cm}^{-1}$ I_2 $0.04\ \text{cm}^{-1}$ H_2 $61\ \text{cm}^{-1}$

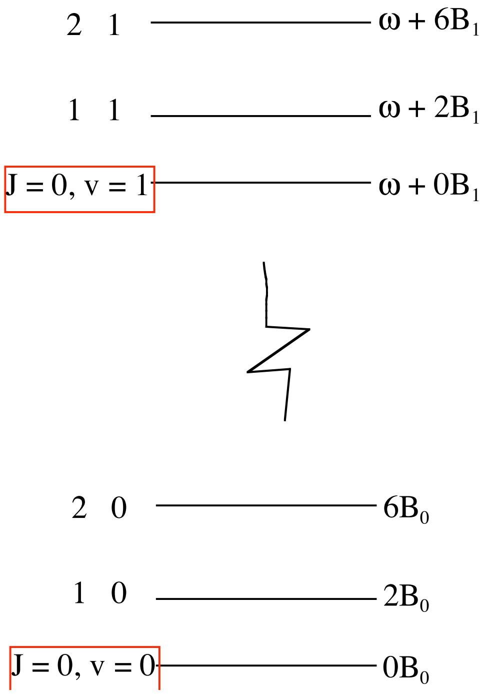
$$B(\text{cm}^{-1}) = \frac{1}{R^2(\text{cm})}\,\frac{1}{\underset{\boxed{^{12}C = 12.000\ldots}}{\mu(\text{amu})}}\,1.685763 \times 10^{-15} \qquad \mu = \frac{m_1m_2}{m_1+m_2}$$

Microwave Spectrum: "Klystron", "Backward Wave Oscillator" (BWO)

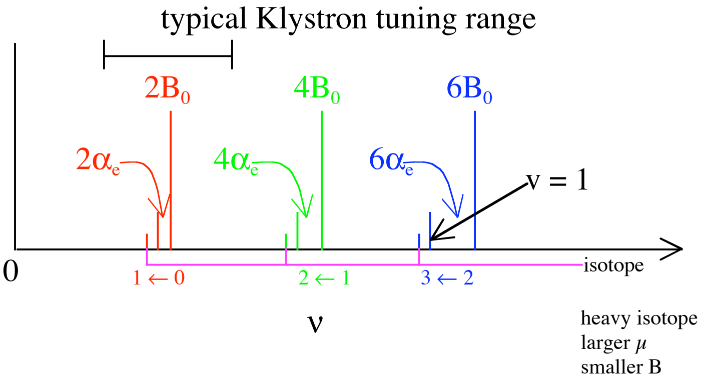
typical tuning range < 1/2 octave ± ~25% 8-12 GHz
12-18
18-24
24-40

not DC to 100 GHz. See only a small portion of pure rotation spectrum for any given Exptl. setup.

Level Diagram



Spectrum



$B_v = B_e - \alpha_e(v + 1/2)$ $\alpha_e \approx 0.01\ B_e$

distinguish hot band from isotope by size of expected isotope fractional shift.

“hot bands” interspersed among cold band, even though $\omega \gg B$

Almost regular pattern of lines separated by 2B ($-4J^3D$ makes lines draw closer together at high J)

intensity $$\propto \frac{S^{\Omega\Omega}_{J'J''}}{2J''+1} N_v g J_< \underbrace{\left(N_{J''M} - N_{J'M}\right)}_{\text{specific M value}} \propto N_{v=0}\, \underset{200\text{ cm}^{-1}\text{ at RT} \qquad \text{vibration population}}{e^{-\frac{\hbar\omega_e v}{\boxed{kT}}}} (2J''+1) \underbrace{\frac{\hbar\nu_{ROT}}{kT}}_{\text{Derive below}}$$

NON-LECTURE

$$e^{-F(J'')/kT} \overset{J+1\leftarrow J}{-} e^{-F(J')/kT} = \overset{\Delta M = 0\text{ (Z-polarized)}}{\left[1 - \frac{F(J'')}{kT} - 1 + \frac{F(J')}{kT}\right]} = \overset{(2J''+1)\text{ from M-degeneracy}}{\frac{F(J') - F(J'')}{kT}} = \frac{\hbar\nu_{ROT}}{kT}$$

How to assign? Can’t see entire pattern. $\Delta\nu = \boxed{2BJ}$

Can usually guess R_e to ~10% so B_e to ~20%

given a line at 15GHz, probably J = 2 ← 1 next line would be at 3/2 15 = 22.5 GHz

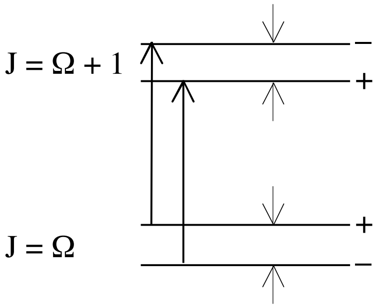
if it was 1 ← 0, next line would be at 2/1 15 = 30 GHz

if it was 3 ← 2, next line would be at 4/3 15 = 20 GHz

So assignment is based on a guess followed by at least one confirming measurement.

Non-$^1\Sigma^+$ states and polyatomic molecules: other kinds of transitions possible (always $M_{z,ii}$ $\Delta\Omega = 0$) for linear polyatomics and symmetric tops

For $\Omega \neq 0$, etc. (parity doubling)



can have $\Delta J = 0$ "Q branches"

Asymmetric tops → very complicated

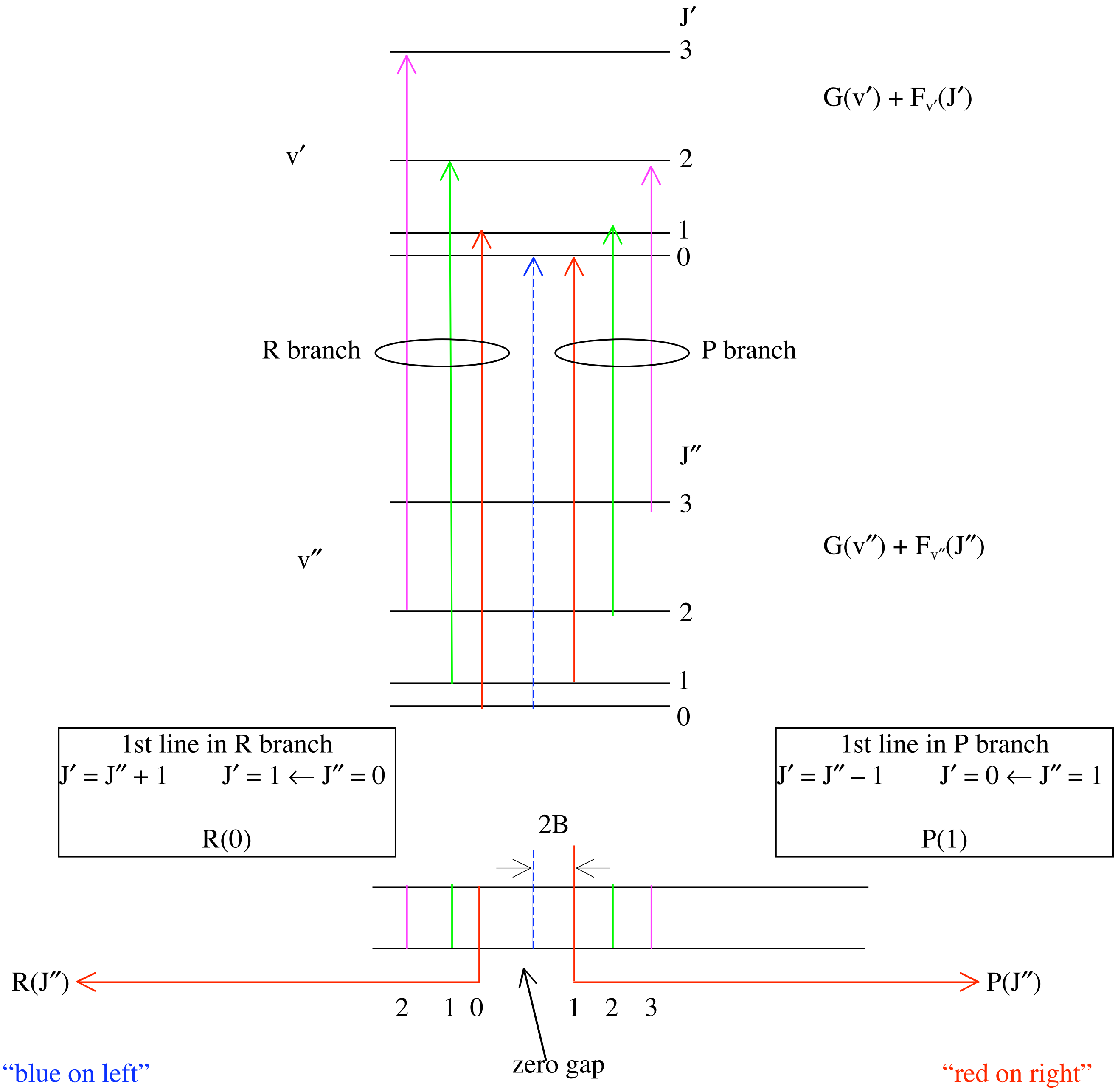
No electric dipole? e.g. O_2 $X^3\Sigma_g^-$ $\Delta\Sigma = \Delta\Omega \neq 0$ fine structure transitions due to <u>magnetic dipole</u>.

VIBRATION-ROTATION spectra — IR 100 - 5000 cm^{-1}
requires $dM_{z,ii}/dQ \neq 0$

for $^1\Sigma^+$ $\Delta J = \pm 1$ only $\Delta v = \pm 1$ strongest

$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \ldots$
$F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2$
$B_v = B_e - \alpha_e(v + 1/2)$
NOTE: Signs. Because almost always see $\omega_e x_e$, D_v, $\alpha_e > 0$ as defined above!

typical $\omega_e \approx 1000\ cm^{-1}$ Cs_2 42cm^{-1}, I_2 215 cm^{-1}, H_2 4400 cm^{-1}



Lines spaced by ≈2B with “zero-gap” of 4B where Q(0) would be.

R branch $\Delta J = +1$ $R(J'') = \Delta G + \Delta F = \Delta G + \overset{\text{always negative}}{\Delta B}J''^2 \boxed{+} (2B' + \Delta B)J'' + 2B'$

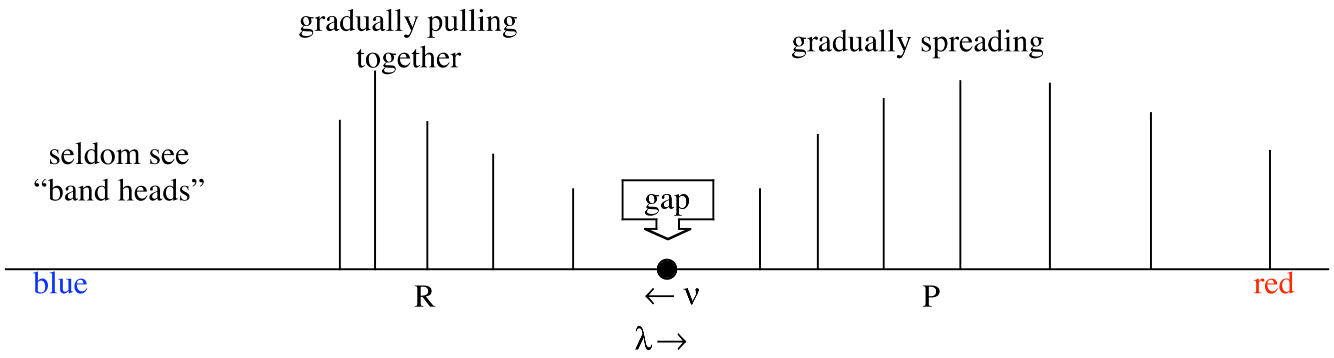
P branch $\Delta J = -1$ $P(J'') = \Delta G + \Delta F = \Delta G + \underbrace{\Delta BJ''^2}_{-\Delta v\alpha_e \text{ small negative quadratic term}} \boxed{-} \underbrace{(2B' - \Delta B)J''}_{\approx 2B' \text{ large linear term}}$

notation $\Delta G = G(v_>) - G(v_<) \equiv \Delta G\left(\frac{v_> + v_<}{2}\right)$

$\Delta G(1/2) = \omega_e - 2\omega_e x_e = \nu$

lines in R branch gradually pull closer together, branch goes to blue
lines in P branch gradually pull further apart, branch goes to red

Double Humped Appearance of Vibration-Rotation band



$I \sim (2J + 1)e^{-BJ(J+1)/kT}$

Finer details:

Hot Bands: $1 \leftarrow 0$ looks like $2 \leftarrow 1$ except

1. $2 \leftarrow 1$ is shifted $2\omega_e x_e$ to red
2. "constant" difference between rotational lines is smaller by $2\alpha_e$ (< ~1%)
3. identical quadratic term $\Delta B = \alpha_e$
4. intensity down by $e^{-\omega_e/kT}$

Isotopomer Bands $B_v \propto \mu^{-1}$ $\omega_e \propto \mu^{-1/2}$

intensity depends on isotopic abundance, NOT on T

Overtone Bands

1. $2 \leftarrow 0$ near $2\omega_e$
2. linear term ($2B' \pm \Delta B$) in rotational branches almost same as for $\Delta v = +1$ band.
3. quadratic term 2× as large → can sometimes see bandheads for high overtone bands
4. intensity weaker than $\Delta v = 1$ band, usually by 10 to 100×

ROTATIONAL ASSIGNMENT

trivial because of
* presence of zero gap
* no overlap of band with itself

pattern recognition trivial

Electronic Spectra

$^1\Sigma^+ - {}^1\Sigma^+$ for now — deal with non-$^1\Sigma^+$ soon.

No restriction on types of molecules. [Symmetry restrictions, $g \leftrightarrow u$, $\Sigma^+ \leftrightarrow \Sigma^+$, $\Delta S = 0$, $\Delta\Lambda = \Delta\Omega = 0, \pm 1$]

ν 10,000 cm^{-1} → 100,000 cm^{-1} VIS & UV & VUV

(not X-ray) because not sharp lines

Rotational Structure of one vibrational band of electronic transition: just like VIBRATION-ROTATION band but more can happen.

$\Delta J = \pm 1$ only

$\downarrow$ Band origin $\Delta T_e + G'(v') - G''(v'')$

$R(J) = \nu_0 + \Delta BJ^2 + (2B' + \Delta B)J + 2B'$ starts toward blue

$P(J) = \nu_0 + \Delta BJ^2 - (2B' - \Delta B)J$ starts toward red

Fortrat parabola — ambiguity about assignment

$Q(J) = \nu_0 + \Delta BJ^2 + \Delta BJ$ (not for ${}^1\Sigma^+ - {}^1\Sigma^+$) usually compact

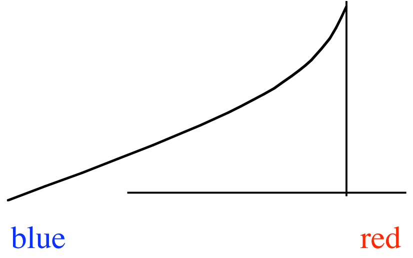
ΔB can be large and have either sign because $B' - B'' \neq -\alpha_e$

Heads form!

$\Delta B > 0$ $\quad R'_e < R''_e$

Head in P

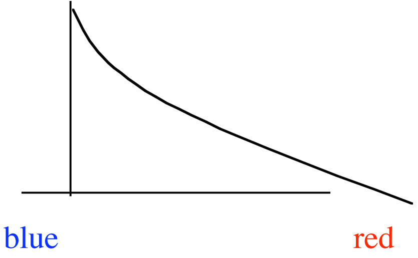
degrades to blue



$\Delta B < 0$ $\quad R'_e > R''_e$

Head in R

degrades to red



By inspection, can tell sign of $\Delta B \Rightarrow$ bonding nature of excited state.

At what J does head form?

How far is head from band origin?

$$\nu = \frac{dP(J)}{dJ} = 2\Delta BJ - (B' + B'')$$

Extremum

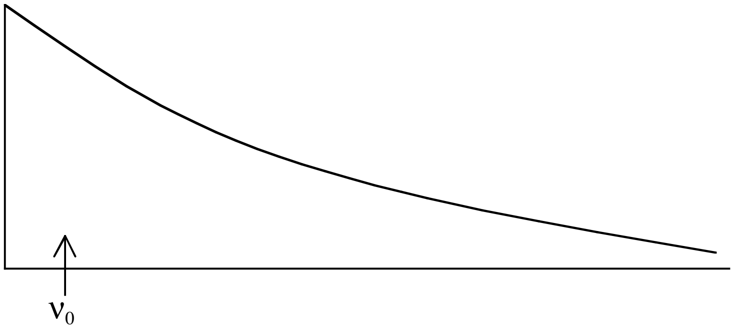
$$J^P_{\text{HEAD}} = \frac{B' + B''}{2\underbrace{\Delta B}_{>0}} \qquad \text{if } \Delta B > 0, \text{ then } J^P_{\text{HEAD}} \sim \frac{\bar{B}}{\Delta B}$$

$$J^R_{\text{HEAD}} = -\frac{(3B' + B'')}{2\underbrace{\Delta B}_{<0}} \qquad \text{if } \Delta B < 0, \text{ then } J^R_{\text{HEAD}} \sim -\frac{\bar{B}}{\Delta B}$$

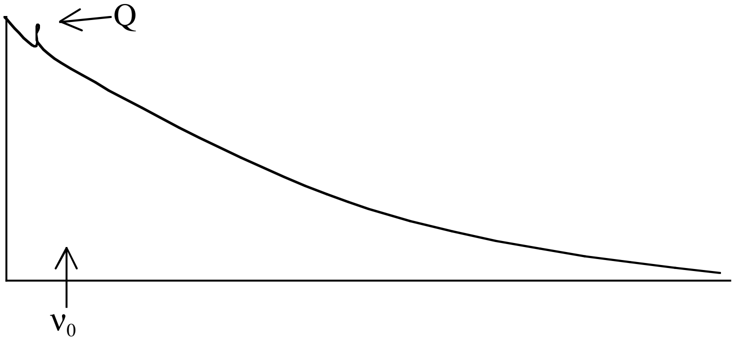
$$\left\{\begin{aligned} P\left(J^P_{\text{HEAD}}\right) - \nu_0 &= \Delta B\left[\frac{B' + B''}{2\Delta B}\right]^2 - (B' + B'')\left[\frac{B' + B''}{2\Delta B}\right] \\ &= -\frac{(B' + B'')^2}{4\Delta B} < 0 \qquad \text{seldom negligible} \qquad \sim -\left|\frac{\bar{B}^2}{\Delta B}\right| \\ R\left(J^R_{\text{HEAD}}\right) - \nu_0 &= -\frac{(3B' - B'')^2}{4\Delta B} + 2B' > 0 \qquad\qquad \sim +\left|\frac{\bar{B}^2}{\Delta B}\right| \end{aligned}\right.$$

Can't use easily picked-out head as approximation for band origin! Hard to find origin because no zero gap. Covered by returning branch.

|| type transition



⊥ type transition



Vibrational structure next time.