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5.80 Small-Molecule Spectroscopy and Dynamics  
Fall 2008

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**Lecture #13: Laser Schemes for Rotational Assignment**  
**First Lines for  $\Omega'$ ,  $\Omega''$  Assignments**

Last Time: Lagerqvist Strips – use of known  $\Delta_2 F(J)$  for either upper or lower state.

Simultaneous analysis of two vibrationally linked bands:  
 search for a C.D. that appears once in each band  
 correct numbering of R relative to P branch and correct absolute numbering

Computer automated term value method — valuable when there is no pattern. Based on term value redundancies from two linked bands and supplemented by intensity regularity.

Problem is that combination differences are “lost in crowd”

Today:

Patterns revealed by laser spectroscopy  
 Fluorescence Excitation Spectroscopy = Laser Induced Fluorescence (LIF)  
 Dispersed Fluorescence (DF)  
 Wavelength Selective Fluorescence Excitation  
 (Also lifetime-selected LIF)  
 OODR and SEP

Introduction to spectra for  $\Lambda \neq 0$  and/or  $S \neq 0$  states  
 Diagrams of allowed transitions  
 First lines as diagnostics  
 Unlinked sub-manifolds — need a model  
 Pattern-forming rotational quantum numbers

Next time: Read

- \* JTH, pp. 1-9 (at least)
- \* Symbols for Spectroscopy
- \* Report of sub-committee f
- \* nomenclature
- \* Rotation and Angular Momenta II
- \* Energy level Structure of  $^2\Pi$  and  $^2\Sigma^+$  states and JTH pages 9-13

What advantages might a laser bring to the assignment of an electronic band system?

1. Fluorescence Excitation Spectrum (known as LIF)

Scan laser, recording total fluorescence resulting as laser frequency is tuned.

Obtain spectrum essentially identical to an absorption spectrum.

\* A few exceptions when “quantum yield” of detected fluorescence is not identical for each line in spectrum.

Reasons? Predissociation (no fluorescence)  
 fluorescence branching ratios  
 perturbations  
 lifetime differences, collisional quenching, self-absorption, and transport out of field of view.

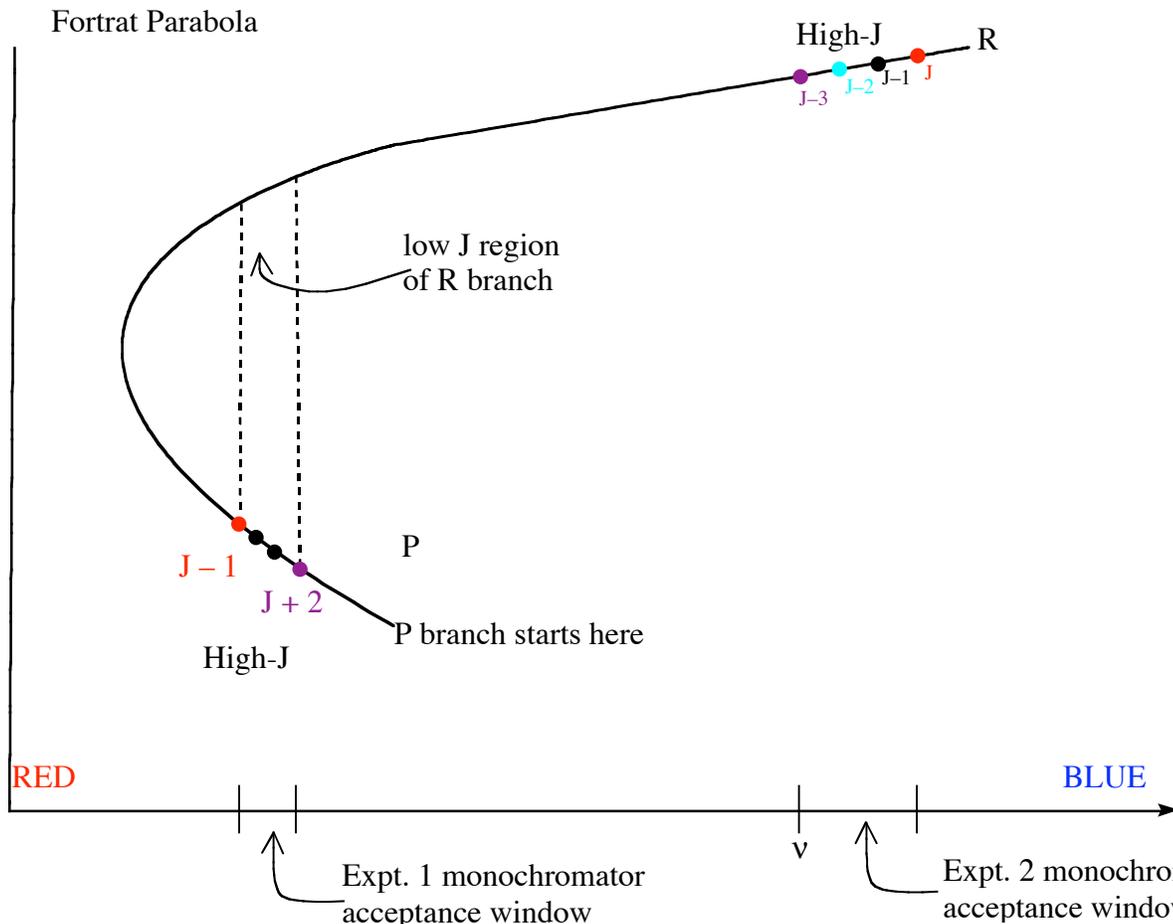


- \* There are not many isotopic species present.
- There are not many superimposed vibrational sequences.
- There are not more complicated band systems with  $S \neq 0$  present.

If there are many unrelated lines clustered together, the resultant dispersed fluorescence spectra will bear no systematic relationships to each other.

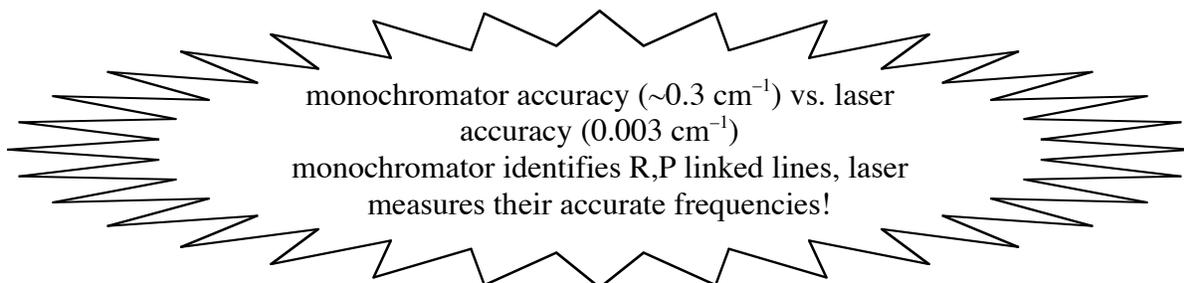
3. Wavelength selective fluorescence excitation spectra

requires tunable laser and monochromator.



What happens in Expt. 1? See two groups of lines — the high-J lines  $\{R(J - 3), \dots R(J)\}$  linked to  $\{P(J - 1), \dots P(J + 2)\}$  and some low-J lines linked to the other branch of the Fortrat parabola.

Expt. 2? See only the single group of high-J P-lines.



Now we are ready for more complexity. We have been ignoring the possibility that molecules might have electronic angular momenta in addition to nuclear rotation.

$\Lambda$ : projection of remnant of atomic L onto body fixed z-axis

S: total spin

$\Sigma$  projection of S on z-axis

$\Omega \equiv \Lambda + \Sigma$  OR projection of J on z-axis.

Convenient diagrams for summarizing levels and transitions.

$S = 0$   $^1\Lambda$  states

$\Omega = \Lambda$  (because  $S = \Sigma = 0$ )

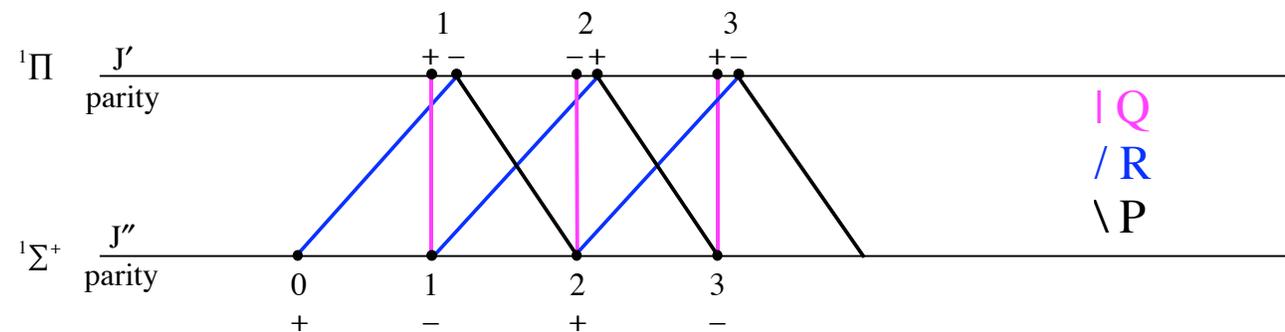
$J \geq \Omega$  (because J can never be smaller than its projection on any axis)

When  $\Omega \neq 0$ , have double parity ( $\Omega > 0$  and  $\Omega < 0$ ) called  $\Omega$ -doubling or  $\Lambda$ -doubling (parity is  $\sigma_v$  symmetry of  $2^{-1/2}[|\Omega\rangle \pm |-\Omega\rangle]$ ).

Can have  $\perp$  ( $\Delta\Omega = \Delta\Lambda = \pm 1$ ) and  $\parallel$  ( $\Delta\Omega = \Delta\Lambda = 0$ ) type transitions.

Always  $+ \leftrightarrow -$  parity selection rule. (e,f symmetry?)

$^1\Pi - ^1\Sigma^+$



Note that first lines in each branch are determined by  $\Omega'$  and/or  $\Omega''$ :

\* R(0) implies  $\Omega'' = 0$  and  $\Omega' \leq 1$

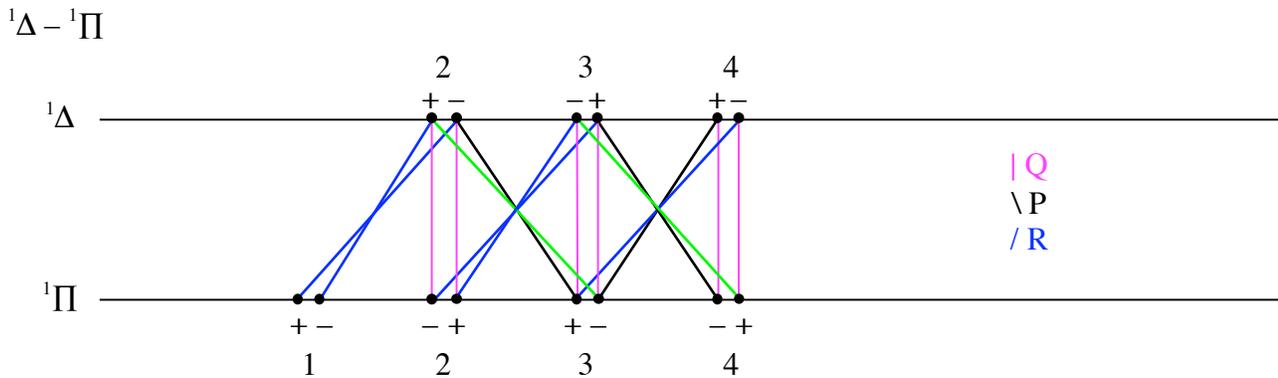
\* Q(1) implies  $\Omega''$  or  $\Omega'$  is double parity because there are no Q branches for  $\Sigma - \Sigma$  transitions

absence of Q(0) implies nothing because  $J' = 0 - J'' = 0$  is always forbidden

\* P(2) implies  $\Omega' = 1$ . Absence of P(1) implies  $\Omega' \neq 0$ .

Note that upper levels of Q branch lines are only sampled via Q lines!

No linkage between ( $^1\Pi_+$ , odd-J  $^1\Sigma^+$ ) and ( $^1\Pi_-$ , even-J  $^1\Sigma^+$ ). Must have a model for either  $^1\Sigma^+$  or  $^1\Pi$  that links the two groups of levels! Alternatively, could have microwave spectrum for  $^1\Sigma^+$  state which links the two groups.



First lines  $R_{+}(1), R_{-}(1) \Rightarrow \Omega'' = 1, \Omega' \leq 2$   
 $Q_{+}(2), Q_{-}(2) \Rightarrow \Omega' > 1$  (absence of Q(1) line)  
 $P_{+}(3), P_{-}(3) \Rightarrow \Omega' = 2$

Usually can't resolve +- and -+ line pairs at low J.

No linkage between  $(^1\Delta_{+}, ^1\Pi_{-})$  and  $(^1\Delta_{-}, ^1\Pi_{+})$ . Model required again!

Work out situation for  $^1\Pi - ^1\Pi$  yourselves.

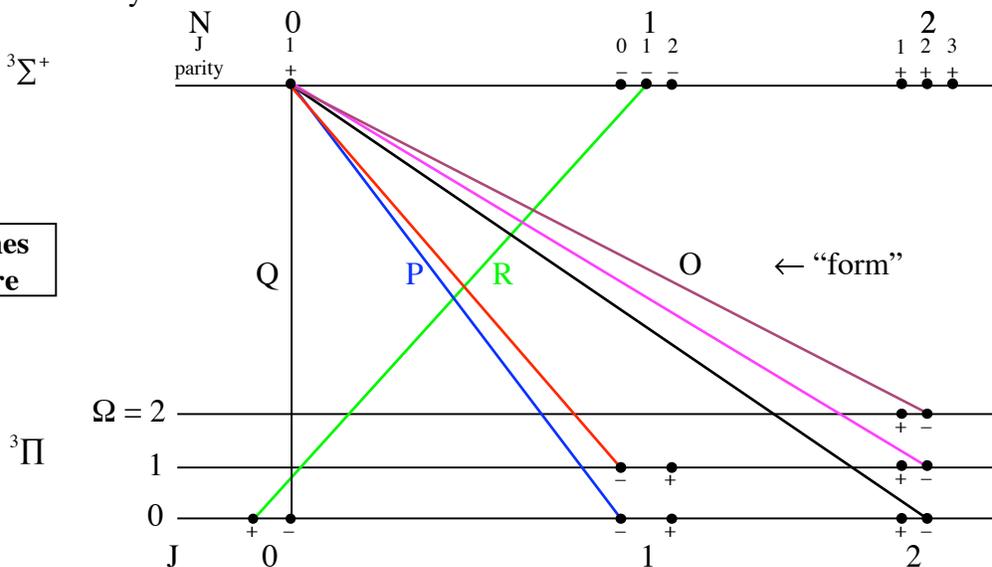
1st lines  $R(1)$   
 $Q(1)$   
 $P(2)$   
 again absence of linkage between  $(^1\Pi_{+}, ^1\Pi_{-})$  and  $(^1\Pi_{-}, ^1\Pi_{+})$ .

One example of an  $S = 1$  band system.

(case b)  
 $N$  is pattern forming  $BN(N + 1)$

All first lines shown here

(case a)  
 $J$  is pattern forming  $B_{\Omega}^{eff} J(J + 1)$



$N' - J''$  is difference between pattern-forming quantum numbers. Use this to name branches.

Always looking for pattern-forming rotational quantum number that gives  $^1\Sigma^+$ -like level pattern! For  $S \neq 0$  the pattern of branches, fine structure, and first lines is much more complicated than for  $S = 0$ . Need to compute level positions and relative intensities. Next time:  $\mathbf{H}^{\text{ROT}}$  and  $\mathbf{H}^{\text{SO}}$ .