5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #7: How to Assign an Atomic Spectrum

Finding lists “sensitive lines”
all lines in order of cm^{-1}
high accuracy helps!
No prior information?
predict what you expect

* never trivial
* always know when it’s right

Carrier
which atom?
which ionization state? experimental conditions
how violent?
absorption vs. emission

Getting Started
list all expected lowest-lying configurations, ~ two for each parity $\left(-1^{\Sigma \ell_i}\right)$

e.g.	Ti	$4s^2\,3d^2$	even parity
		$4s\,3d^3$	even parity
		$4s\,3d^2\,4p$	odd parity
		$3d^3\,4p$	odd parity

list the L–S–J or $(j_1, j_2)_J$ terms that arise from each configuration and estimate their energies based on estimates of $\zeta(n\ell)$, $F^k(n\ell,n'\ell')$, $G^k(n\ell,n'\ell')$ values from isoelectronic comparisons or shrewd guesses

set up Grotrian diagram organized according to rigorous (parity) and approximate symmetries
e.g (L,S) $-1^{\Sigma \ell_i}$ ↲

e.g.	odd parity	even parity	odd	etc.
	singlet	singlet	triplet	
	$^1S^\circ\ ^1P^\circ\ldots$	$^1S\ ^1P\ldots$	$^3S^\circ\ ^3P^\circ\ldots$	

SEE GROTRIAN DIAGRAM FOR Ca (next page)
only can see odd↔even transitions between configurations (entire configuration is odd or even)
mostly $\Delta S = 0$
$\Delta\ell = \pm 1$ (single orbital promotion)
$\Delta L = 0, \pm 1$
$\Delta J = 0, \pm 1$ $\Delta J = \Delta L$ strongest in a multiplet
(after correcting for $2J + 1$ degeneracy of initial state)
(intensity provides clues to both ΔJ and J assignments)

Key features
Rydberg series — nearly constant δ_ℓ (quantum defect)
cluster of lines — multiplets — repeated intervals and Landé Interval rule
extremely strong lines — “resonance lines”
“population funnels” in emission
excitation out of lowest state
(ground state or a metastable state)
see Grotrian diagram again

See Herzberg “Atoms” pages 177-181 The Interval Rule; Analysis of Multiplets

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Please see: Fig. 31 in Herzberg, G. *Atomic Sprectra and Atomic Structure*. New York, NY: Dover, 1944.

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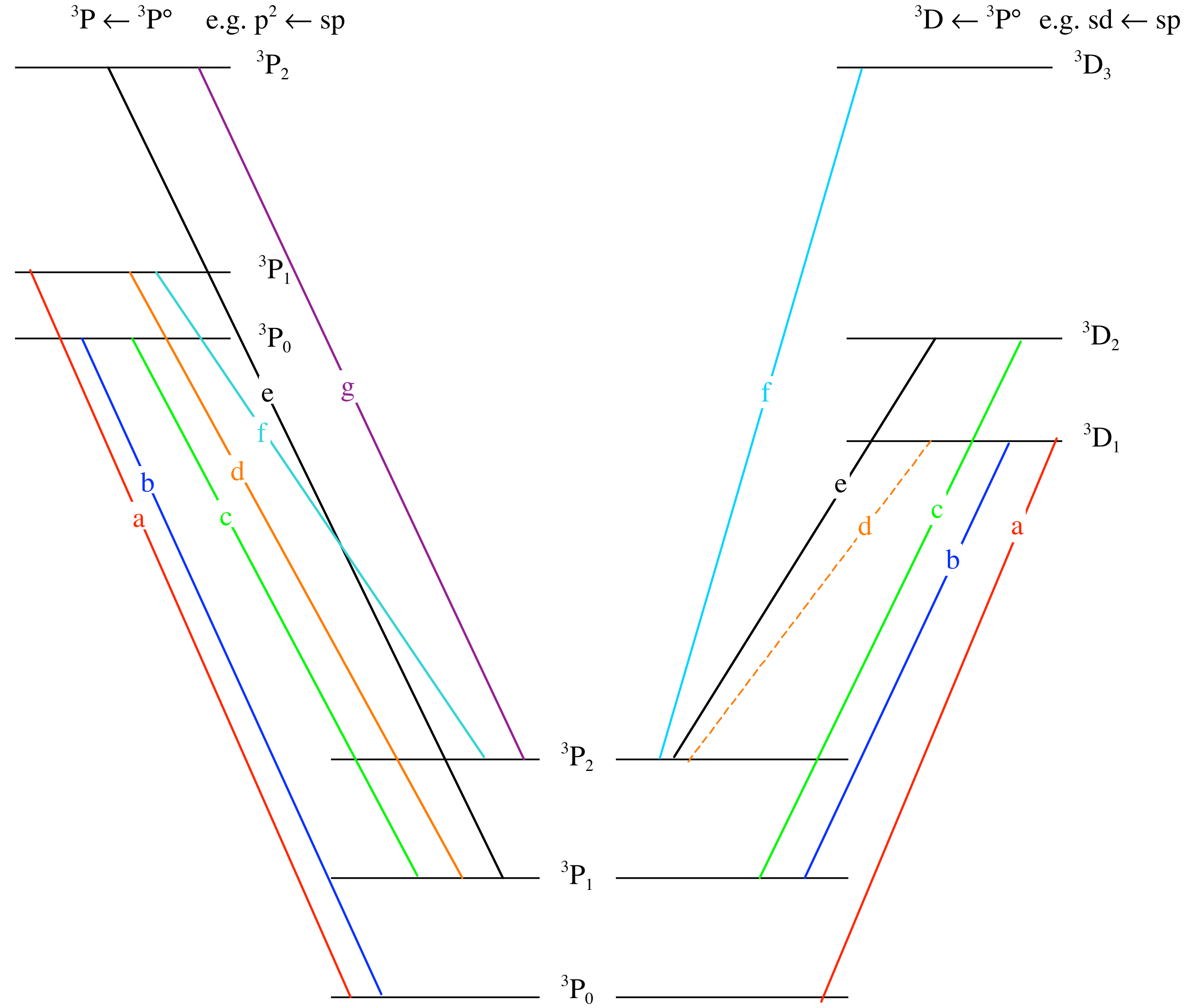
Figures 31 and 32 from Atomic Spectra and Atomic Structure by G. Herzberg, Dover, 1944.

TWO LINKED MULTIPLETS



3 (strong) + 4 (weak) lines

a – **b** = **d** – c	upper $^3P_{1,0}$
g – f = e – **d**	upper $^3P_{2,1}$
b – c = a – **b**	lower $^3P_{1,0}$
d – f = e – **g**	lower $^3P_{2,1}$

strongest bold

EXACTLY
REPEATED
INTERVALS

3 (strong) + 2 (weak) + 1 (very weak) lines

f – e	upper $^3D_{3,2}$
e – d = **c** – b	upper $^3D_{2,1}$
c – e = **b** – d	lower $^3P_{2,1}$
b – **a**	lower $^3P_{1,0}$

two intervals not redundantly sampled!

Multiplet Arrays

$^3P - {}^3P°$

		a	(a–b)	b
		(a–d)		(a–d)
e	(e–d)	d	(a–b)	c
(e–g)		(e–g)		
g	(e–d)	f		

$^3D - {}^3P°$

		c	(e–d)	b	(b–a)	a
		(c–e)		(c–e)		
f	(f–e)	e	(e–d)	d		

two possibilities for energy order within two linked multiplets to be decided by

* interval rule
* relative intensities
* # of lines
* monotonic behavior of intervals
(also along rows and columns)

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Please see: Fig. 34 in Herzberg, G. *Atomic Sprectra and Atomic Structure*. New York, NY: Dover, 1944.

Table 16

Fe I MULTIPLET [LAPORTE (82)]

(Wave-number differences are given in *italic* type. Numbers in parentheses above the wave numbers of the lines are estimated intensities. Superior letters *a*, *b*, *c*, etc., refer to Fig. 6, p. 7 of Atomic Spectra and Atomic Structure by G. Herzberg, Dover, 1944.)

J	*i*		*i* + 1		*i* + 2		*i* + 3		*i* + 4
	(40)[k]								
k	25,966.89								
	104.51								
	(40)[g]		(60)[l]						
k + 1	25,862.38	*168.92*	26,031.30						
	215.52		*215.53*						
	(10)[e]		(60)[f]		(80)[k]				
k + 2	25,646.86	*168.91*	25,815.77	*257.73*	26,073.50				
			294.45		*294.45*				
			(8)[b]		(60)[e]		(125)[l]		
k + 3			25,521.32	*257.73*	25,779.05	*351.30*	26,130.35		
					411.21		*411.19*		
					(5)[a]		(15)[d]		(200)[m]
k + 4					25,367.84	*351.32*	25,719.16	*448.50*	26,167.66

How to construct energy level diagram from transition array?

$$\mathbf{H}^{SO} \rightarrow \zeta\, L \cdot S$$

$$J = L + S \qquad J^2 = L^2 + S^2 + 2L\cdot S$$

$$L\cdot S = \frac{J^2 - L^2 - S^2}{2}$$

$$\langle L\cdot S \rangle = (\hbar^2/2)[J(J+1) - L(L+1) - S(S+1)]$$

Landé interval rule

$$E_{L-S-J} - E_{L-S-(J-1)} = \zeta\left(\hbar^2/2\right)[J(J+1) - (J-1)(J)] \propto J_>$$

Largest number of repeated intervals occurs when $\Delta L = 0$.

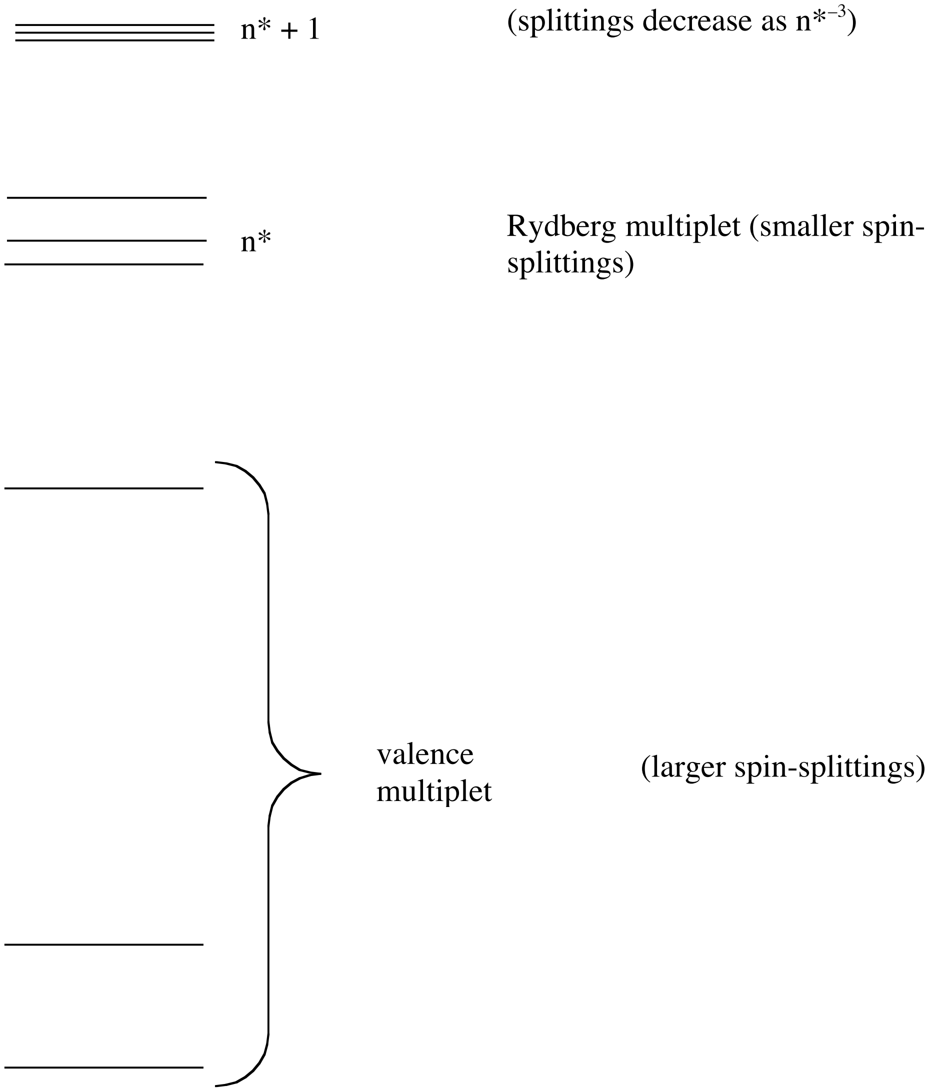
Look for near integer (or 1/2 integer) relationships between repeated intervals. If any grouping is suggested by the interval rule, one sets up a trial level diagram for both states and predicts frequencies of all unlinked transitions.

YOU STILL CAN'T TELL UP FROM DOWN!

* sometimes predict sign (and magnitude) of ζ from configuration and $\mathbf{H}^{\text{eff}}$ model

* other linkages — especially to a Rydberg series or to the ground state.

The convergence of a Rydberg series is always in the sense that levels get closer together as E increases and the spin-splitting always decreases as n^{*-3} (unless the spin-orbit splitting is in the ion-core).



The nature of the Rydberg series to which a given multiplet is connected by transitions (or to which it belongs) tells us the nominal configuration of that state.

Other tricks for assignment of atomic spectra.

Temperature

In absorption, signal is $\propto N_{nLSJ}$

vary N_{nLSJ} by changing T

$$N_{nLSJ} \propto \frac{(2J+1)e^{-E_{nLSJ}/\overset{\downarrow\ 0.695\ \text{cm}^{-1}\text{K}^{-1}}{kT}}}{\underset{\uparrow}{Q_{elect}}}$$

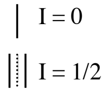
estimate by knowledge
of all states below
~ 5000 cm^{-1}
↓
7200K

Absorption lines from excited states are extremely sensitive to T (rapid increase in intensity as T increases).

Absorption lines from ground state decrease in intensity weakly as T increases (at constant total number density).

Isotope

Isotope shifts, especially for heavy atoms, are very small, except when one isotope has very different hfs from another.



$I = 0$ if even Z, even M

$F = \vec{I} + \vec{J}$

hfs can give information about configuration (see Tinkham, pages 193-206)

usually require super-high resolution

* Fermi-Contact - 1e$^-$ in ns orbital

$|\psi(r=0)|^2$ $\quad n^{*-3}$ scaling

* magnetic dipole $\quad I\cdot L,\ I\cdot S \propto 1/r^3 \rightarrow n^{*-3}$ scaling but only for orbitals from open-shells

* electric quadrupole — field gradient at nucleus

Zeeman Effect — apply magnetic field

Split each J into 2J + 1 M_J components

$$\mathbf{H}^{\text{Zeeman}} = -\underset{\text{magnetic moment}}{\mu}\cdot\underset{\text{ext. magnetic field}}{B}$$

Bernath:

$$E_{M_J} = \underbrace{\left[1 + \frac{J(J+1)+S(S+1)+L(L+1)}{2J(J+1)}\right]}_{g_J}\underset{\uparrow}{\mu_B} M_J B$$

1.4MHz/Gauss (Bohr magneton)
30000 MHz = 1cm^{-1}

Selection Rules: $\Delta M_J =$ 0 linearly polarized along field direction
±1 linearly polarized ⊥ to field direction
+1 or −1 circularly polarized (light propagating along field direction)

Note that the Zeeman splitting pattern is not trivial, but since all M's in upper state are split equally (ditto for lower state), it is easy to determine g'_J and g''_J, and from the # of M'_J and M''_J components, J′L′S′ and J″L″S″.

unless: * mixed L–S character (due to $\mathbf{H}^{SO}$)
* Paschen Back — L,S uncoupling (destruction of J)
* hfs

How high a magnetic field is needed to resolve all Zeeman components so that we can count M′'s and M″'s (upper and lower state M_J values)?

$$\Delta E(B) = \Delta E^\circ + \mu B[g'M' - g''M'']$$

for $M' = M'' + 1$ transitions (⊥ polarization)

$$\Delta E(B) = \Delta E^\circ + \underbrace{\mu B[M''(g' - g'')}_{\text{spacing of components}} + g']$$

$$\mu = 1.4\,\text{MHz}/\text{Gauss} = \frac{1.4}{30000}\,\text{cm}^{-1}/\text{Gauss}$$

$$0.03\ \text{cm}^{-1}\ \text{resolution} = \mu B_{\min}\,\Delta g$$

$$B_{\min} = \frac{0.03}{\frac{1.4}{30000}\Delta g} = \frac{643}{\Delta g}\text{Gauss}$$

$^3D_3$ — $^3P_2$

$$\Delta g = \frac{11}{6} - \frac{11}{6} = 0! \qquad \Delta J = \Delta L \rightarrow \Delta g = 0!$$

$^3D_2 - {}^3P_1$

$$\Delta g = \frac{13}{6} - \frac{5}{2} = -\frac{1}{3} \qquad \sim 2\text{kG required}$$

Stark Effect

Apply an electric field $\mathbf{H}^{\text{STARK}} = \mu(\text{odd parity})\cdot\varepsilon$

$$E^{(1)}_{nLSJM} = \langle nLSJM|\mathbf{H}^{\text{STARK}}|nLSJM\rangle = 0$$

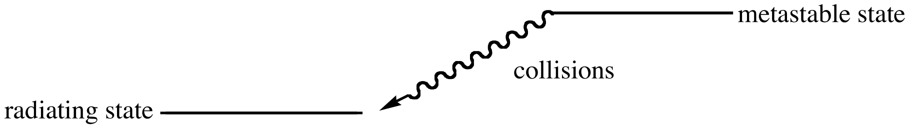
must consider only $E^{(2)} \propto \varepsilon^2 \sum \frac{|\langle nLSJM|\mu|n'L'S'J'M\rangle|^2}{E^o_{nLSJM} - E^o_{n'L'SJ'M}}$

0.5 MHz/(V/cm)·Debye

too small to be useful, except for Rydberg states where $\Delta E°$ can be very small
quenching of metastable states — turning on a forbidden transition

<u>Collisions</u>
- big effect on emission spectrum
- negligible effect on absorption spectrum

selective $\begin{Bmatrix}\text{quenching}\\ \text{excitation}\end{Bmatrix}$ across small ΔE gap



Long-Lived levels are easily quenched.