5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1976

Examination #1 ANSWERS
March 12, 1976

Closed Book
Slide Rules and Calculators Permitted

Answer any THREE of the four questions. You may work a fourth problem for extra credit.
All work will be graded but no total grade will exceed 80 points.

1. A. (10 points) Give a concise statement of Hund's three rules.

First rule: The lowest energy state belonging to a configuration has maximum S.
Second Rule: Of the states of maximum spin, the lowest term has maximum L.
Third Rule: The lowest J–state of the lowest term is the one with maximum J for a more than half-filled shell and minimum J for less than half-filled shell.
None of the Hund's rules apply to any but the lowest energy term belonging to a configuration.

B. (10 points) State the definition of a vector operator.

B is a vector with respect to **A** if
$[\mathbf{A}_i, \mathbf{B}_j] = \epsilon_{ijk} i\hbar \mathbf{B}_k$

C. (10 points) If **B** and **C** are vector operators with respect to **A**, then what do you know about matrix elements of **B**·**C** in the $|AM_A\rangle$ basis?

B·**C** is scalar with respect to **A**, therefore
$\left\langle A' M'_A | \mathbf{B} \cdot \mathbf{C} | A M_A \right\rangle = \delta_{A'A} \delta_{M'_A M_A} \langle A || \mathbf{B} \cdot \mathbf{C} || A \rangle$
independent of M_A.

D. (5 points) The atomic spin-orbit Hamiltonian has the form

$$\mathbf{H}^{\mathrm{SO}} = \sum_i \xi(r_i) \boldsymbol{\ell}_i \cdot \mathbf{s}_i$$

Classify $\mathbf{H}^{\mathrm{SO}}$ as vector or scalar with respect to **J**, **L**, and **S**. State whether $\mathbf{H}^{\mathrm{SO}}$ is diagonal in the $|JM_J LS\rangle$ or $|LM_L S M_S\rangle$ basis.

$\mathbf{H}^{\mathrm{SO}}$ is scalar, vector, vector with respect to J, L, S. $\mathbf{H}^{\mathrm{SO}}$ is diagonal with respect to J and M_J but not L and S in the $|JM_J LS\rangle$ basis but diagonal in nothing in the $|LM_L S M_S\rangle$ basis.

2. Consider the following multiplet transition array:

Lower State (L″, L″)

	J	?		?		?
		(180)		(16)		(0)
	?	16934.63	48.15	16982.78	64.20	17046.98
				50.51		50.48
				(240)		(16)
Upper	?			17033.29	64.17	17097.46
State						63.10
(L′,S′)						(310)
	?					17160.56

Intensities are in parentheses above transition frequencies in cm^{-1}; line separations in cm^{-1} are given between relevant transition frequencies.

A. (10 points) Use the Landé interval rule

$$E(L, S, J) - E(L, S, J-1) = \zeta(nLS)J$$

to determine J′ and J″ values. Rather than list the J′ and J″ assignments of each line, only <u>list J′ and J″ for the line observed to be most intense **and** for the line observed to be least intense</u>.

Consider upper state term separations first

$$\frac{E(J_{\text{MAX}}) - E(J_{\text{MAX}}-1)}{E(J_{\text{MAX}}-1) - E(J_{\text{MAX}}-2)} = \frac{J_{\text{MAX}}}{J_{MAX}-1} = \frac{63.10}{50.50} = \frac{5}{4}$$

Upper state J ranges 5↔3
Lower state:

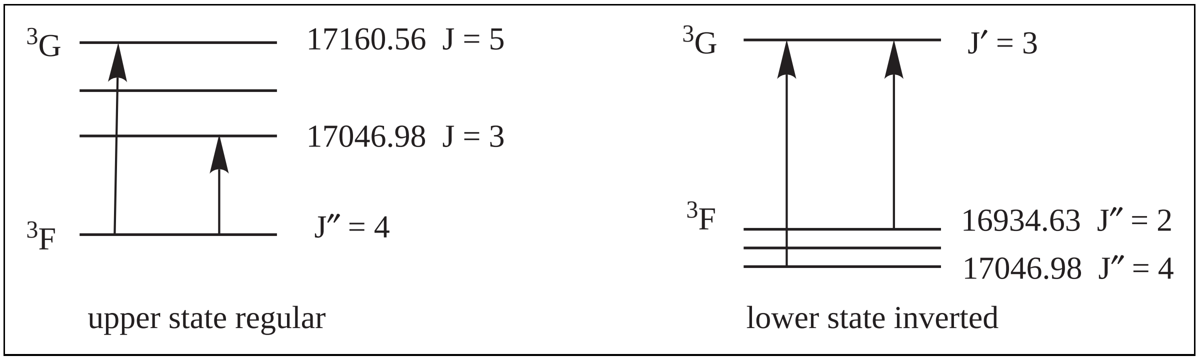
$$\frac{J_{\text{MAX}}}{J_{MAX}-1} = \frac{64.18}{48.15} = \frac{4}{3}$$

lower state J ranges 4↔2
Most intense line 17160.56 cm^{-1} in $J'' = 4 \leftrightarrow J' = 5$
Least intense line 17046.98 cm^{-1} in $J'' = 4 \leftrightarrow J' = 3$

B. (10 points) Use the range of J′ and J″ and the intensity distribution (i.e., that the most intense transition is not $\Delta J = 0$) to determine the term symbols (^{2S+1}L) for the upper and lower states. Assume $\Delta S = 0$.

Range of J implies either $S = 1$, $L' = 4$, $L'' = 3$ or $L = 1$, $S' = 4$, $S'' = 3$
The second possibility is $\Delta S \neq 0$ forbidden.
Upper state is ^3G, Lower state is ^3F.

C. (5 points) Is the upper state regular (highest J at highest term energy) or inverted (highest J at lowest term energy)? Is the lower state regular or inverted? [Partial energy level diagrams might be helpful here.]



3. A. (5 points) List the L-S terms that arise from the $(ns)(np)^2$ and $(ns)^2(np)$ configurations. [HINT: $(np)^2$ gives ^{1}S, ^{3}P, ^{1}D; to get sp^2 couple an s electron to these three states.]

$(ns)(np)^2 \to {}^2\text{S}, {}^2\text{P}, {}^4\text{P}, {}^2\text{D}$
$(ns)^2(np) \to {}^2\text{P}^\circ$

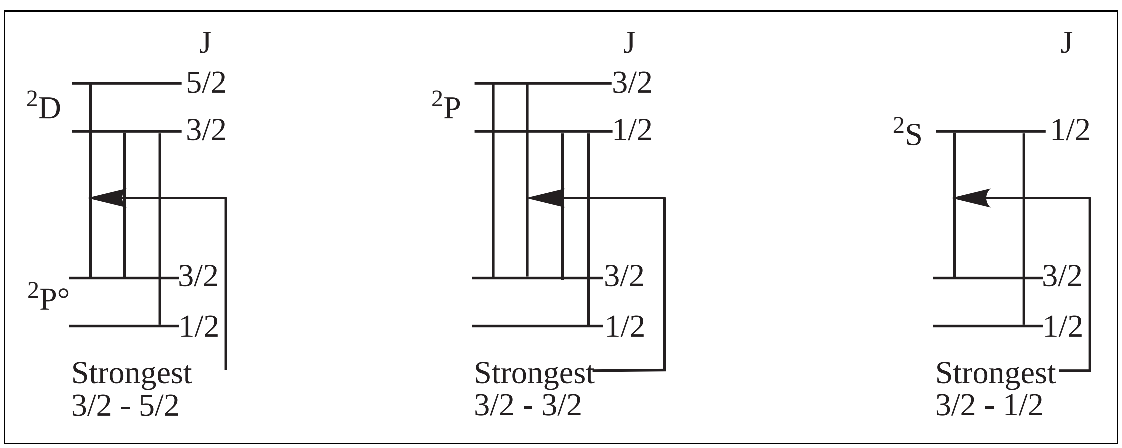
B. (5 points) Which configuration gives rise to odd terms and which to even?

$(ns)(np)^2$ is even because $\Sigma\ell_i = 2$
$(ns)^2(np)$ is odd because $\Sigma\ell_i = 1$

C. (5 points) List the electric dipole allowed transitions between terms of the sp^2 and s^2p configurations. (Ignore fine-structure splitting of L-S terms into J-states.)

^{2}S — ^{2}P°
^{2}P — ^{2}P°
^{2}D — ^{2}P° are the allowed transitions.

D. (10 points) Construct qualitative energy level diagrams on which you display all allowed J″–J′ components of $^2P^\circ - {}^2S$, $^2P^\circ - {}^2P$, and $^2P^\circ - {}^2D$ transitions. Indicate which J″–J′ line you would expect to be strongest for each of these three transitions.



4. (25 points) Calculate transition probabilities for the two transitions

$$\boxed{\begin{array}{l} nsnp\ ^1P^\circ_{10} \to (np)^2\ ^1S_{00} \\ nsnp\ ^1P^\circ_{10} \to (np)^2\ ^1D_{20} \end{array}}$$

given the following information:

$$\begin{aligned}
{}^1P^\circ_{10} &= |J=1, M_J=0, L=1, S=0\rangle \\
&= \frac{1}{\sqrt{2}}|s0^- p0^+| - \frac{1}{\sqrt{2}}|s0^+ p0^-| \\
{}^1S_{00} &\equiv |J=0, M_J=0, L=0, S=0\rangle \\
&= \frac{1}{\sqrt{3}}|p1^- p-1^+| - \frac{1}{\sqrt{3}}|p1^+ p-1^-| + \frac{1}{\sqrt{3}}|p0^+ p0^-| \\
{}^1D_{20} &\equiv \frac{1}{\sqrt{6}}|p1^+ p-1^-| - \frac{1}{\sqrt{6}}|p1^- p-1^+| + \frac{2}{\sqrt{6}}|p0^+ p0^-|
\end{aligned}$$

The electric dipole transition moment operator, $\boldsymbol{\mu}$, does not operate on spin coordinates, is a one-electron operator, and is a vector with respect to $\boldsymbol{\ell}_i$. $nsnp \to (np)^2$ transitions are $\Delta\ell = +1$ processes. The relevant $\Delta\ell = +1$ matrix elements, as given by the Wigner-Eckart theorem for vector operators are

$$\begin{aligned}
\left\langle n, \ell=1, m_\ell=1 \left| \frac{1}{2}(\boldsymbol{\mu}_+ + \boldsymbol{\mu}_-) \right| n, \ell=0, m_\ell=0 \right\rangle &= -\frac{1}{\sqrt{2}}\mu_+(ns) \\
\left\langle n, \ell=1, m_\ell=0 \left| \boldsymbol{\mu}_z \right| n, \ell=0, m_\ell=0 \right\rangle &= \mu_+(ns) \\
\left\langle n, \ell=1, m_\ell=-1 \left| \frac{1}{2}(\boldsymbol{\mu}_+ + \boldsymbol{\mu}_-) \right| n, \ell=0, m_\ell=0 \right\rangle &= +\frac{1}{\sqrt{2}}\mu_+(ns)
\end{aligned}$$

where $\mu_+(ns)$ is the reduced matrix element $\langle np||\boldsymbol{\mu}||ns\rangle$.

Since $\boldsymbol{\mu}$ is a one electron operator, the two-electron Slaters must match for one spin-orbital and must have identical spin in the other. This means we need only consider part of $^1S_{00}$ and $^1D_{20}$.

$^1S_{00} \rightarrow \frac{1}{\sqrt{3}}|p0^+ \ p0^-|$

$^1D_{20} \rightarrow \frac{2}{\sqrt{6}}|p0^+ \ p0^-|$

because the $|p1^+ \ p-1^-|$ and $|p1^- \ p-1^+|$ Slaters differ from the $|s0^- \ p0^+|$ and $|s0^+ \ p0^-|$ Slaters by two spin-orbitals. So we do not even need to evaluate matrix elements to get the ratio of transition probabilities

$$\frac{^1P^\circ_{10} - {}^1S_{00}}{^1P^\circ_{10} - {}^1D_{20}} = \frac{\left(\frac{1}{\sqrt{3}}\right)^2}{\left(\frac{2}{\sqrt{6}}\right)^2} = \frac{1}{2}$$

Actually evaluating matrix elements gives

$$\left[\left\langle {}^1P^\circ_{10} |\boldsymbol{\mu}| {}^1S_{00}\right\rangle\right] = \frac{1}{\sqrt{6}}\left[\left\langle \left|s0^- p0^+\right| \boldsymbol{\mu} \left|p0^+ p0^-\right|\right\rangle - \left\langle \left|s0^+ p0^-\right| \boldsymbol{\mu} \left|p0^+ p0^-\right|\right\rangle\right]$$

$$= \frac{1}{\sqrt{6}}\left[-\mu_+(ns) - \mu_+(ns)\right] = -\frac{2}{\sqrt{6}}\mu_+(ns)$$

$$\text{Probability is} |\langle 1|\mu|2\rangle|^2 = \frac{2}{3}|\mu_+(ns)|^2 \quad \text{for } P^\circ - S$$

$$= \frac{4}{3}|\mu_+(ns)|^2 \quad \text{for } P^\circ - D$$

Show all your work including false starts. If you are unable to express the transition probabilities in terms of $\mu_+(ns)$, lavish partial credit will be given for the ratio of transition probabilities

$$\frac{^1P^\circ_{10} - {}^1S_{00}}{^1P^\circ_{10} - {}^1D_{00}}.$$