5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1976

Examination #1
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.

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

   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?

   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 $|JM_JLS\rangle$ or $|LM_LSM_S\rangle$ basis.

2. Consider the following multiplet transition array:

Lower State (L″, S″)

	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 list J′ and J″ for the line observed to be most intense **and** for the line observed to be least intense.

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 $\Delta S = 0$.

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.]

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

   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.)

   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

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

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

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

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