5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Problem Set #3

1. (a) Write out the electron configurations for the molecules O_2^+, O_2, O_2^-, and O_2^{2-}.

   (b) Determine the ground-state term symbols $\left(^M\Lambda_{g,u}\pm\right)$ for O_2^+, O_2, O_2^-, and O_2^{2-}. If there are two or more low-lying states, select one as that of the ground state and justify your selection.

2. (a) Using symbols appropriate to the separated-atom approximation to a molecular orbital, write the electronic configuration of lowest energy for the diatomic species C_2, NO^+, and S_2.

   (b) Write the term symbols $\left(^M\Lambda_{g,u}\pm\right)$ for all the electronic states derivable from the configuration of lowest energy for all three species. Which of these states will have non-zero magnetic moments?

3. Gaseous HCl is normally a 3 : 1 mixture of $H^{35}Cl$ and $H^{37}Cl$. To a high approximation, the rotational energy levels of such diatomic rotators are

$$E(J)(\text{in cm}^{-1}) = J(J+1)\overline{B} - J^2(J+1)^2\overline{D}$$

   where $\overline{B}$, the rotational constant, is larger by a factor 1.0015 for $H^{35}Cl$ than for $H^{37}Cl$, and the centrifugal distortion constant $\overline{D}$ is the same for both molecules within the error of its measurement.

   (a) Derive an expression for the separation of the pure rotational absorption lines of $H^{35}Cl$ and $H^{37}Cl$ as a function of J', the J–value for the upper state ($\Delta J = J' - J'' = +1$).

   (b) What is the spacing in cm^{-1} of the two lines for which $J' = 10$?

4. The "transition moment," or the probability of transition, between two rotational levels in a linear molecule may be assumed to depend only on the permanent electric dipole moment of the molecule and thus to be the same for all allowed pure-rotational transitions. In the pure-rotational *emission spectrum* of $H^{35}Cl$ gas, lines at 106.0 cm^{-1} and 233.2 cm^{-1} are observed to have equal intensities. What is the temperature of the gas? The rotational constant B for $H^{35}Cl$ is known to be 10.6 cm^{-1}, and the ratio hc/k has the value 1.44 cm·deg.

5. What would happen to the Birge-Sponer extrapolation scheme for a molecular potential correlating with ionic states of the separated atoms?

6. The ground state and a low-lying excited electronic state of the BeO molecule have the following properties

Term symbol	$^1\Sigma^+$	$^1\Pi$
Electronic energy, T_e/cm^{-1}	0	9405.6
ω_e/cm^{-1}	1487.3	1144.2
$\omega_e x_e/cm^{-1}$	11.8	8.4
$r_e/10^{-8}cm$	1.33	1.46

(Note that the electronic energy T_e is the energy from the minimum of one curve to the minimum of the other; this is not equal to the vibrational origin of the $0 - 0$ band.)

(a) Construct a Deslandres table of the vibrational band origins of the $^1\Pi - {}^1\Sigma^+$ system, for $v'' = 0$ through 3 and $v' = 0$ through 5. Which of these vibrational bands would you expect to be the most intense, when the system is observed in absorption? Comment on the relative intensities that you would expect for the other bands in your table.

(b) In the rotational structure of the individual vibronic bands in this system, what branches would you expect to observe? In which branch would you expect to observe a band head? Calculate the transition in J that will give rise to a line at the band head, and the distance in cm^{-1} from the band head to the vibrational band origin.

(c) What would you guess about the MO configurations corresponding to these two states? (**HINT:** Note that BeO is isoelectronic with C_2, so that the MO's may be expected to be somewhat similar, except that the *g-u* property will be lost, and the orbitals will be distorted toward the higher nuclear charge of the O-atom.) Would you suspect the presence of any other excited electronic states *below* the $^1\Pi$ state? If so, what would its term symbol be?

7. The following bands are observed in the second positive system of nitrogen (units are reciprocal centimeters corrected to vacuum):

35,522 cm^{-1}	29,940 cm^{-1}	25,913 cm^{-1}
35,453	29,654	25,669
33,852	29,010	25,354
33,751	28,819	25,003
33,583	28,559	24,627
32,207	28,267	24,414
32,076	27,949	24,137
31,878	27,451	23,800
31,643	27,226	23,414
30,590	26,942	23,016
30,438	26,621	
30,212	26,274	

Arrange these in a Deslandres table, and find values for ω_e'', $\omega_e x_e''$, ω_e', and $\omega_e x_e'$. *Important Suggestion*: Look at the pattern of bands first, before doing anything else. Do any natural groupings seem to suggest

themselves? It may help to draw a "stick spectrum" of the band origins, to scale, in order to pick out these patterns. Remember that bands having the same Δv fall along diagonals on the Deslandres table.)

Is there any suggestion of a cubic term in either state? If so, derive an expression for the third difference, $\Delta^3 G_{v+1/2}$, including terms in $\omega_e y_e \left(v + \frac{1}{2}\right)^3$ in $G_{v+1/2}$, and estimate $\omega_e y_e$.

8. The first strong electronic band system of carbon monoxide (the ground-state vibrational frequency of which is observed at 2140 cm^{-1} in the infrared) appears in absorption at room temperature at about 1550 Å in the vacuum ultraviolet. The system shows a progression with a spacing of 1480 cm^{-1}. The vibronic bands show a single set of unperturbed P–, Q–, and R–branches degraded to the red. Analysis by combination differences of these branches gives $B'_e = 1.61$ cm^{-1}, $B''_e = 1.93$ cm^{-1}. In each band, the lines nearest the origin are $P(2)$, $Q(1)$, and $R(0)$.

   (a) Deduce all you can about the two electronic states involved in the transition from these data and your general knowledge of the properties of carbon monoxide.

   (b) Sketch the lower portions of the potential curves in cm^{-1} for CO, roughly, to scale, from these data [find the harmonic force constant, and use the potential $U(r) = \frac{1}{2}k(r - r_e)^2$]. Use the Franck-Condon principle to find the strongest vibronic bands in the spectrum.

   (c) Interpret the electronic terms of the two states in terms of the most likely MO configurations of each.

   (d) The dipole moment of the ground state of CO is about 0.1 Debye (1 Debye = 10^{-18} esu-cm). Show how an optical Stark effect experiment can be used to find the dipole moment of the excited states; estimate the magnitudes of the splittings for the $P(2)$, $Q(1)$, and $R(0)$ lines, for an applied field of 10,000 V/cm (1 statvolt = 300 ordinary volts), and an assumed excited-state moment of 1.0 Debye.

9. (a) What states arise from the $\sigma^2 \sigma*$, $\sigma^2 \pi$, and $\sigma \pi^2$ configurations? (There should be a total of 6 states.)

   (b) Write the linear combinations of Slater determinants which correspond to the e–parity components of each of these states. (There should be a total of 9 component states, hence 9 linear combinations.)

   (c) Which of these 9 substates can perturb each other? Make a table specifying the terms in the Hamiltonian $\left(\mathbf{H}_{\text{Elect}}, \mathbf{H}^{\text{SO}}, \mathbf{H}_{\text{Coriolis}}\right)$ which cause these perturbations.

   (d) Calculate all possible nonzero spin-orbit perturbation matrix elements between $|\Lambda S \Sigma\rangle |\Omega J M|\rangle_e$ states in terms of the one-electron parameters

$$a_1 \equiv \langle \sigma^* | \xi \ell_- | \pi \rangle$$
$$a_2 \equiv \langle \sigma | \xi \ell_- | \pi \rangle$$
$$a_3 \equiv \langle \pi | \xi \ell_z | \pi \rangle .$$

(There will be at least 7 nonzero matrix elements.)

(e) In the absence of substate mixing, between which of these 9 e–parity substates can there exist electric dipole allowed R or P branch transitions?

(f) Express the relative <u>intensities</u> of the following electric dipole transitions in terms of the one-electron matrix element $\mu_\perp \equiv \langle \sigma | \mu_- | \pi \rangle$:

$$\sigma^2 \pi \; ^2\Pi_{1/2} \rightarrow \sigma\pi^2 \; ^2\Sigma^+$$

$$\sigma^2 \pi \; ^2\Pi_{3/2} \rightarrow \sigma\pi^2 \; ^2\Sigma^+$$

$$\sigma^2 \pi \; ^2\Pi_{1/2} \rightarrow \sigma\pi^2 \; ^2\Sigma^-$$

$$\sigma^2 \pi \; ^2\Pi_{1/2} \rightarrow \sigma\pi^2 \; ^2\Delta_{3/2}$$

$$\sigma^2 \pi \; ^2\Pi_{3/2} \rightarrow \sigma\pi^2 \; ^2\Delta_{3/2}$$

So there are some semi-empirical relationships among isoconfigurational transition intensities!

10. (a) Construct the Hamiltonian matrix for a $^5\Delta$ state by evaluating the matrix elements of $\mathbf{H}^{\mathrm{ROT}} = B(\mathbf{J}-\mathbf{L}-\mathbf{S})^2$ and $\mathbf{H}^{\mathrm{SO}} = A\mathbf{L} \cdot \mathbf{S}$ in the Hund's case 'a' e/f (parity) basis.

(b) Construct the matrix of second-order Van Vleck Transformation corrections to $\mathbf{H}^{\mathrm{ROT}} + \mathbf{H}^{\mathrm{SO}}$ which results from the r–dependence of the "constants" B_v and A_v. Define centrifugal distortion parameters

$$D_v \equiv - \sum_{v' \neq v} \frac{\langle v|B(r)|v'\rangle \langle v'|B(r)|v\rangle}{E_v - E_{v'}}$$

$$A_{D_v} = 2 \sum_{v' \neq v} \frac{\langle v|A(r)|v'\rangle \langle v'|B(r)|v\rangle}{E_v - E_{v'}}$$

$$A_v^\circ = \sum_{v' \neq v} \frac{\langle v|A(r)|v'\rangle \langle v'|A(r)|v\rangle}{E_v - E_{v'}}$$

and express the matrix elements in terms of these three parameters.