5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
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Problem Set #3 ANSWERS

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

ANSWER:

$$\begin{aligned} O_2^+ &\rightarrow KK(2s\sigma_g)^2(2s\sigma_u^\star)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g^\star) \\ O_2 &\rightarrow KK(2s\sigma_g)^2(2s\sigma_u^\star)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g^\star)^2 \\ O_2^- &\rightarrow KK(2s\sigma_g)^2(2s\sigma_u^\star)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g^\star)^3 \\ O_2^{2-} &\rightarrow KK(2s\sigma_g)^2(2s\sigma_u^\star)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g^\star)^4 \end{aligned}$$

(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.

ANSWER:
$O_2^+ \rightarrow {}^2\Pi_g$ (only term arising)
$O_2 \rightarrow {}^1\Delta_g, {}^1\Sigma_g^+, {}^3\Sigma_g^-$
By Hund's rules ${}^3\Sigma_g^-$ ground state [largest S and largest Λ]
$O_2^- \rightarrow {}^2\Pi$ (only term arising)
$O_2^{-2} \rightarrow {}^1\Sigma_g^+$ (only term arising)

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.

ANSWER:

$$\begin{aligned} C_2 &: KK(2s\sigma_g)^2(2s\sigma_u^\star)^2(2p\pi_u)^4 \\ NO^+ &: KK(2s\sigma_g)^2(2s\sigma_u^\star)^2(2p\sigma_g)^2(2p\pi_u)^4 \\ S_2 &: KK(2s\sigma_g)^2(2s\sigma_u^\star)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g^\star)^4(2p\sigma_u^\star)^2(3s\sigma_g)^2(3s\sigma_u^\star)^2(3p\sigma_g)^2(3p\pi_u)^4(3p\pi_g^\star)^2 \end{aligned}$$

(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?

ANSWER: C_2 from configuration in (a) only term ${}^1\Sigma_g^+ \leftarrow$ ground state. There will be no magnetic moment from this configuration.
NO^+ only term arising is ${}^1\Sigma^+$ there will be no magnetic moment.
S_2: ${}^1\Delta_g$, ${}^3\Sigma_g^-$, ${}^1\Sigma_g^+$ The ground state is ${}^3\Sigma_g^-$ by Hund's Rules and it will have a magnetic moment.
The ${}^1\Delta_g$ state will also have a non-zero magnetic moment.

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.

For $H^{35}Cl$ and $H^{39}Cl$

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

where $\overline{D}_{H^{35}Cl} = \overline{D}_{H^{37}Cl}$ and $\overline{B}_{H^{35}Cl} = 1.0015\overline{B}_{H^{37}Cl}$

(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 ($\Delta J = J' - J'' = +1$).

ANSWER:

Find ΔE as a function of J'

$\Delta J = +1 \Rightarrow J' - J'' = 1 \Rightarrow J'' = J' - 1$

$\Delta E(J'', J') = J'(J'+1)\overline{B} - J'^2(J'+1)^2\overline{D} - J''(J''+1)\overline{B} + J''^2(J''+1)^2\overline{D}$

$\Delta E(J') = [J'(J'+1) - (J'-1)J']\overline{B} + [(J'-1)^2J'^2 - J'^2(J'+1)^2]\overline{D} = [J'(J'+1-J'+1)]\overline{B} + [J'^2((J'-1)^2 - (J'+1)^2)]\overline{D}$

$$\delta E = 0.003\overline{B}J' \left\{ \begin{array}{ll} \Delta E(J') = 2J'\overline{B} - 4J'^3\overline{D} & \text{for } H^{37}Cl \\ \Delta E(J') = 2.003J\overline{B} - 4J'^3\overline{D} & \text{for } H^{35}Cl \end{array} \right\} \overline{B} = \overline{B}_{H^{37}Cl}$$

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

ANSWER: Find the spacing for the two lines where $J' = 10$.

$$\text{for } J' = 10 \qquad \delta E = 0.03\,\overline{B}_{H^{37}Cl}$$

$$= 0.0301\,\overline{B}_{H^{35}Cl}$$

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.

ANSWER: Since the transition moment is the same

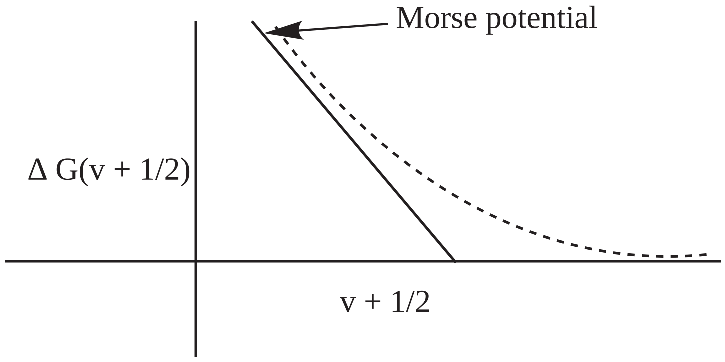
$$\begin{aligned} I_{106.0\text{cm}^{-1}} = (2J' + 1)e^{-BJ'(J'+1)/kT} &= I_{233.2\text{cm}^{-1}} \\ &= (2\widetilde{J'} + 1)e^{-B\widetilde{J'}(\widetilde{J'}+1)/kT} \end{aligned}$$

$$\begin{aligned} \text{since} \qquad \Delta E &= 2J'B \\ 106.0\text{cm}^{-1} &= 2BJ' \Rightarrow J' = 5 \\ 233.2\text{cm}^{-1} &= 2B\widetilde{J'} \Rightarrow \widetilde{J'} = 11 \end{aligned}$$

$$\begin{aligned} \text{Thus } 11e^{-318\text{cm}^{-1}/kT} &= 23e^{-1399.2/kT} \\ \Rightarrow 11e^{\frac{-457.5}{T}} &= 23e^{\frac{-2013.2}{T}} \\ 2.398 + \frac{457.5}{T} &= 3.135 + \frac{-2013.2}{T} \\ \frac{1557.7}{T} &= 0.737 \\ \Rightarrow T &= 2110\ {}^\circ K \end{aligned}$$

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

ANSWER:
For correlation to ions, the potential would be $\frac{1}{r}$ at long distances, hence would have an infinite number of vibrational levels. So a Birge-Sponer plot would approach zero asymptotically:



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
$\omega_e x_e/\text{cm}^{-1}$	11.8	8.4
$r_e/10^{-8}\text{cm}$	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.

ANSWER

$v''\backslash v'$	0	1	2	3	4	5
0	9234.9	10362.3	11472.8	12566.6	13643.7	14703.9
1	7771.3	8898.6	10009.2	11103.0	12180.1	13240.2
2	6331.1	7458.5	8569.1	9662.9	10739.9	11800.1
3	4914.6	6042.0	7152.6	8246.4	9323.4	10383.6

The most intense bands in absorption would be those from $v'' = 0$ because of the Boltzmann distribution.

(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.

ANSWER

P, Q, & R branches since this is a $^1\Pi - {}^1\Sigma^+$ transition.

$r_{e_\Pi} > r_{e_\Sigma} \Rightarrow B_{e_\Pi} < B_{e_\Sigma}$ thus you would expect a band head in the R branch.

$B_e = \frac{h}{8\pi^2 c\mu r_e^2}$

$B'_e = 1.37\ \text{cm}^{-1}$

$B''_e = 1.65\ \text{cm}^{-1}$

$J''_{\text{head}} = \frac{B''-3B'}{2(B'-B'')} \approx \frac{B''_e-3B'_e}{2(B'_e-B''_e)} \cong 4$

$J'_{\text{head}} = 5$

The head occurs $+8\ \text{cm}^{-1}$ from the 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?

ANSWER

$^1\Sigma^+$: $(1\sigma)^2(2\sigma)^2(3\sigma^2)(4\sigma)^2(1\pi)^4$

$^1\Pi, ^3\Pi$: $(1\sigma)^2(2\sigma)^2(3\sigma^2)(4\sigma)^2(1\pi)^3(5\sigma)$

The $^3\Pi$ may be lie below the $^1\Pi$ state.

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

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

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 $\omega_e y_e$.

ANSWER

$v'\backslash v''$	0	1	2	3	4	5	6	7	8
0	29654	27949	26274	24627	23016				
1	31643	29940	28267	26621	25003	23414			
2	33583	31878	30212	28559	26942	25354	23800		
3	35453	33751	32076	30438	28819	27226	25669		
4	—	35522	33852	32207	30590	29010	27451	25913	24414

for the lower state $\overline{\Delta^2 G_{v+1/2}} = -29.3 \Rightarrow \omega_e x_e'' = 14.6\ \text{cm}^{-1}$

$$\omega_e'' = \Delta G_{v+1/2} + 2(v+1)\omega_e x_e''$$

$$\overline{\omega_e''} = 1733\ \text{cm}^{-1}$$

for the upper state $\overline{\Delta^2 G_{v+1/2}} = -71.8\ \text{cm}^{-1} \Rightarrow \omega_e x_e' = 35.9\ \text{cm}^{-1}$

$$\overline{\omega_e'} = 2074\ \text{cm}^{-1}$$

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 $R(0)$.

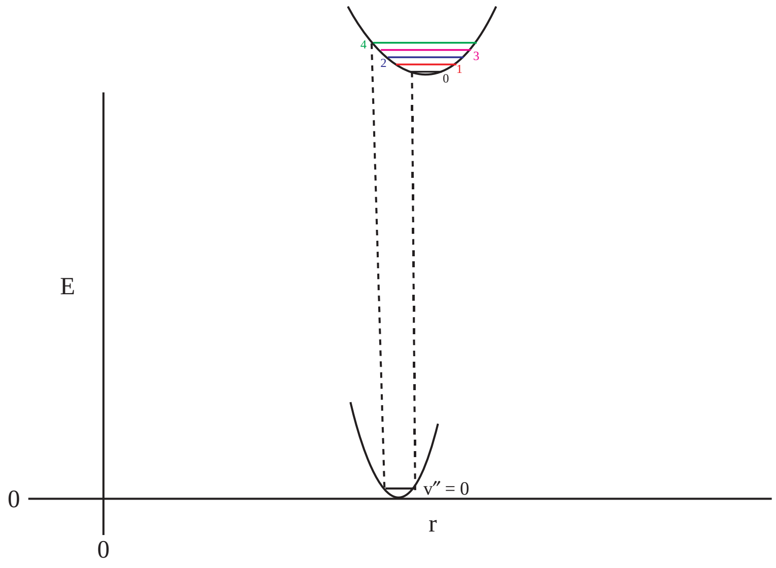
   (a) Deduce all you can about the two electronic states involved in the transition from these data and your general knowledge of the properties of carbon monoxide.

   ANSWER
   The ground state of CO is $^1\Sigma^+$ and since P, Q, and R branches are observed, the upper state has $\Lambda \neq 0$.

$$R'_e = \left(\frac{h}{8\pi^2 c\mu B'_e}\right)^{1/2} = 1.24\text{Å}$$
$$R''_e = 1.13\text{Å}$$

   (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.

   ANSWER



From the Franck-Condon principle it appears that the (1, 0), (2, 0), (3, 0), (4, 0), and (5, 0) bands will be the strongest. The strongest of them will probably be the (2, 0) band since it has the largest FC factor (from the graph).

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

ANSWER

Ground State: $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2 - {}^1\Sigma^+$

Excited State: $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(2\pi) - {}^1\Pi, {}^3\Pi$

One might think its a ${}^1\Pi - {}^1\Sigma^+$ transition (actually these are the "forbidden" Cameron bands due to the $a^3\Pi - X^1\Sigma^+$ transition of CO).

(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.

ANSWER

?????

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.)

ANSWER

$\sigma^2\sigma^* - {}^2\Sigma^+$

$\sigma^2\pi - {}^2\Pi$

$\sigma\pi^2 - {}^2\Sigma^+, {}^2\Delta, {}^4\Sigma^-, {}^2\Sigma^-$

(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.)

ANSWER

e–parity states transform as $\sigma_v\varphi_e = (-1)^{J-1/2}\varphi_e$

$\sigma^2\sigma^*$ ${}^2\Sigma^+$ $\varphi_e = 2^{-1/2}\left[\left|{}^2\Sigma^+_{1/2}\right\rangle + \left|{}^2\Sigma^+_{-1/2}\right\rangle\right] = 2^{-1/2}[|0^+0^-0^{+*}| + |0^+0^-0^{-*}|$

$\sigma\pi^2$ ${}^2\Sigma^+$ $\varphi_e = 2^{-1}[|0^+1^- - 1^+| - |0^+1^+ - 1^-| + |0^-1^- - 1^+| - |0^-1^+ - 1^-|]$

${}^2\Sigma^-$ $\varphi_e = 12^{-1/2}[2|0^-1^+ - 1^+| - |0^+1^- - 1^+| - |0^+1^+ - 1^-| - 2|0^+1^- - 1^-|$
$+|0^-1^+ - 1^-| + |0^-1^- - 1^+|]$

${}^4\Sigma^-_{1/2}$ $\varphi_e = 6^{-1/2}[|0^-1^+ - 1^+| + |0^+1^- - 1^+| + |0^+1^+ - 1^-| + |0^+1^- - 1^-|$
$+|0^-1^+ - 1^-| + |0^-1^- - 1^+|$

${}^2\Delta_{5/2}$ $\varphi_e = 2^{-1/2}[|0^+1^+1^-| + |0^- - 1^+ - 1^-|]$

${}^2\Delta_{3/2}$ $\varphi_e = 2^{-1/2}[|0^-1^+1^-| + |0^+ - 1^+ - 1^-|]$

${}^4\Sigma^-_{3/2}$ $\varphi_e = 2^{-1/}[|0^+1^+ - 1^-| + |0^-1^- - 1^-|]$

$\sigma^-\pi$ ${}^2\Pi_{1/2}$ $\varphi_e = 2^{-1/2}[|0^+0^-1^-| + |0^+0^- - 1^+|]$

${}^2\Pi_{3/2}$ $\varphi_e = 2^{-1/2}[|0^+0^-1^+| + |0^+0^- - 1^-|]$

(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.

ANSWER:

	$\boldsymbol{\sigma^2\sigma^*}$	$\boldsymbol{\sigma^2\pi}$		$\boldsymbol{\sigma\pi^2}$					
	$^2\Sigma^+$	$^2\Pi_{1/2}$	$^3\Pi_{3/2}$	$^2\Sigma^+$	$^2\Sigma^-$	$^4\Sigma^-_{1/2}$	$^4\Sigma^-_{3/2}$	$^2\Delta_{3/2}$	$^2\Delta_{5/2}$
$^2\Sigma^+$		$\mathbf{H}^{\text{SO}} + \mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{el}}$					
$^2\Pi_{1/2}$	$\mathbf{H}^{\text{SO}} + \mathbf{H}^{\text{cor}}$		$\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{SO}}+\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{SO}}+\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{SO}}$		$\mathbf{H}^{\text{cor}}$	
$^2\Pi_{3/2}$	$\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{cor}}$		$\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{cor}}$		$\mathbf{H}^{\text{SO}}$	$\mathbf{H}^{\text{SO}}+\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{cor}}$
$^2\Sigma^+$	$\mathbf{H}^{\text{el}}$	$\mathbf{H}^{\text{SO}}+\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{cor}}$		$\mathbf{H}^{\text{SO}}$	$\mathbf{H}^{\text{SO}}$			
$^2\Sigma^-$		$\mathbf{H}^{\text{SO}}+\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{SO}}$					
$^4\Sigma^-_{1/2}$		$\mathbf{H}^{\text{SO}}$		$\mathbf{H}^{\text{SO}}$			$\mathbf{H}^{\text{cor}}$		
$^4\Sigma^-_{3/2}$			$\mathbf{H}^{\text{SO}}$			$\mathbf{H}^{\text{cor}}$			
$^2\Delta_{3/2}$		$\mathbf{H}^{\text{cor}}$	$\mathbf{H}^{\text{SO}}+\mathbf{H}^{\text{cor}}$						$\mathbf{H}^{\text{cor}}$
$^2\Delta_{5/2}$			$\mathbf{H}^{\text{cor}}$					$\mathbf{H}^{\text{cor}}$	

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

$$a_1 \equiv \langle\sigma^*|\xi\boldsymbol{\ell}_-|\pi\rangle$$

$$a_2 \equiv \langle\sigma|\xi\boldsymbol{\ell}_-|\pi\rangle$$

$$a_3 \equiv \langle\pi|\xi\boldsymbol{\ell}_z|\pi\rangle\,.$$

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

ANSWER

$$\left\langle{}^2\Pi_{3/2}|\mathbf{H}^{\text{SO}}|{}^4\Sigma^-_{3/2}\right\rangle = \tfrac{1}{2}a_2$$

$$\left\langle{}^2\Pi_{1/2}|\mathbf{H}^{\text{SO}}|{}^4\Sigma^-_{1/2}\right\rangle = \frac{\sqrt{3}}{6}a_2$$

$$\left\langle{}^2\Pi_{1/2}|\mathbf{H}^{\text{SO}}|{}^2\Sigma^-\right\rangle = \frac{-\sqrt{6}}{12}a_2$$

$$\left\langle{}^2\Pi_{1/2}|\mathbf{H}^{\text{SO}}|{}^2\Sigma^+, \sigma\pi^2\right\rangle = \frac{\sqrt{2}}{4}a_2$$

$$\left\langle{}^2\Pi_{3/2}|\mathbf{H}^{\text{SO}}|{}^2\Delta_{3/2}\right\rangle = -\tfrac{1}{2}a_2$$

$$\left\langle{}^4\Sigma^-_{1/2}|\mathbf{H}^{\text{SO}}|\overbrace{\;{}^2\Sigma^+_{\frac{1}{2}}\;}^{\sigma\pi^2}\right\rangle = \frac{-\sqrt{6}}{3}a_2$$

$$\left\langle{}^2\Pi_{1/2}|\mathbf{H}^{\text{SO}}|{}^2\Sigma^+_{\frac{1}{2}}, \sigma^2\sigma^\star\right\rangle = a_1$$

$$\left\langle{}^2\Sigma^+, \sigma\pi^2|\mathbf{H}^{\text{SO}}|{}^2\Sigma^-\right\rangle = \frac{\sqrt{3}}{3}a_2$$

(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?

ANSWER

Allowed R or P branch transitions:

$^2\Sigma^+, \sigma^2\sigma^\star \rightarrow {}^2\Pi_{1/2,3/2}$

$^2\Sigma^{+,-}, \sigma\pi^2 \rightarrow {}^2\Pi_{1/2,3/2}$

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

$^2\Pi_{3/2} \rightarrow {}^2\Delta_{5/2}$

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

$$\begin{aligned}
&\sigma^2\pi\ {}^2\Pi_{1/2} \rightarrow \sigma\pi^2\ {}^2\Sigma^+\\
&\sigma^2\pi\ {}^2\Pi_{3/2} \rightarrow \sigma\pi^2\ {}^2\Sigma^+\\
&\sigma^2\pi\ {}^2\Pi_{1/2} \rightarrow \sigma\pi^2\ {}^2\Sigma^-\\
&\sigma^2\pi\ {}^2\Pi_{1/2} \rightarrow \sigma\pi^2\ {}^2\Delta_{3/2}\\
&\sigma^2\pi\ {}^2\Pi_{3/2} \rightarrow \sigma\pi^2\ {}^2\Delta_{3/2}
\end{aligned}$$

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

ANSWER

$I \propto |\langle 1|\boldsymbol{\mu}|2\rangle|^2$ where $\boldsymbol{\mu} = \sum_i \boldsymbol{\mu}_i = \sum_i \boldsymbol{\mu}_{xi} + \boldsymbol{\mu}_{yi} + \boldsymbol{\mu}_{zi}$

In this case, all transitions have $\Delta\Lambda = \pm 1 \Rightarrow \langle\boldsymbol{\mu}_{zi}\rangle = 0$

so $\boldsymbol{\mu} = \sum_i \frac{1}{2}(\boldsymbol{\mu}_{+i} + \boldsymbol{\mu}_{-i}) + \frac{i}{2}(\boldsymbol{\mu}_{+i} - \boldsymbol{\mu}_{-i})$ (the $\boldsymbol{\mu}_{\pm i}$'s are one electron operators).

The relative intensities are derived using the linear combination of Slaters from part (b) of this problem.

$\sigma^2\pi\ {}^2\Pi_{1/2} \rightarrow \sigma\pi^2\ {}^2\Sigma^+$: $I \propto \frac{\mu_\perp^2}{8}$

$\sigma^2\pi\ {}^2\Pi_{3/2} \rightarrow \sigma\pi^2\ {}^2\Sigma^+$: $I \propto \frac{\mu_\perp^2}{8}$

$\sigma^2\pi\ {}^2\Pi_{1/2} \rightarrow \sigma\pi^2\ {}^2\Sigma^-$: $I \propto \frac{3}{2}\mu_\perp^2$

$\sigma^2\pi\ {}^2\Pi_{1/2} \rightarrow \sigma\pi^2\ {}^2\Delta_{3/2}$: $I \propto \mu_\perp^2$

$\sigma^2\pi\ {}^2\Pi_{3/2} \rightarrow \sigma\pi^2\ {}^2\Delta_{3/2}$: $I \propto 0$

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

ANSWER

$^5\Delta$ State:

$$\left|{}^5\Delta_4\right\rangle_{\substack{e\\f}} = \frac{1}{\sqrt{2}}\left[\left|{}^5\Delta_4\right\rangle \pm \left|{}^5\Delta_{-4}\right\rangle\right]$$

$$\left|{}^5\Delta_3\right\rangle_{\substack{e\\f}} = \frac{1}{\sqrt{2}}\left[\left|{}^5\Delta_3\right\rangle \pm \left|{}^5\Delta_{-3}\right\rangle\right]$$

$$\left|{}^5\Delta_2\right\rangle_{\substack{e\\f}} = \frac{1}{\sqrt{2}}\left[\left|{}^5\Delta_2\right\rangle \pm \left|{}^5\Delta_{-2}\right\rangle\right]$$

$$\left|{}^5\Delta_1\right\rangle_{\substack{e\\f}} = \frac{1}{\sqrt{2}}\left[\left|{}^5\Delta_1\right\rangle \pm \left|{}^5\Delta_{-1}\right\rangle\right]$$

$$\left|{}^5\Delta_0\right\rangle_{\substack{e\\f}} = \frac{1}{\sqrt{2}}\left[\left|{}^5\Delta_0, \Lambda = 2\right\rangle \pm \left|{}^5\Delta_0, \Lambda = -2\right\rangle\right]$$

	$^5\Delta_4$	$^5\Delta_3$	$^5\Delta_2$	$^5\Delta_1$	$^5\Delta_0$
$^5\Delta_4$	$T_e + G(v) + B_v(J(J+1) - 14) + 4A_v$	$-2B_v[(J+4)(J-3)]^{1/2}$	0	0	0
$^5\Delta_3$	$-2B_v[(J+4)(J-3)]^{1/2}$	$T_e + G(v) + B_v(J(J+1) - 4) + 2A_v$	$-B_v[6(J-2)(J+3)]^{1/2}$	0	0
$^5\Delta_2$	0	$-B_v[6(J-2)(J+3)]^{1/2}$	$T_e+G(v)+B_v(J(J+1)+2)$	$-B_v[6(J+2)(J-1)]^{1/2}$	0
$^5\Delta_1$	0	0	$-B_v[6(J+2)(J-1)]^{1/2}$	$T_e + G(v) + B_v(J(J+1) + 4) - 2A_v$	$-2B_v[J(J+1)]^{1/2}$
$^5\Delta_0$	0	0	0	$-2B_v[J(J+1)]^{1/2}$	$T_e + G(v) + B_v[J(J+1) + 2] - 4A_v$

(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.

ANSWER

Second Order Corrections

Diagonal Elements:

$^5\Delta_4 \rightarrow -[(J(J+1)-14)^2 + 4(J+4)(J-3)]D_v + 16A_v^{\circ} + 8A_{D_v}[J(J+1)-14]$
$^5\Delta_3 \rightarrow -[(J(J+1)-4)^2 + 4(J+4)(J-3) + 6(J-2)(J+3)]D_v + 4A_v^{\circ} + 4A_{D_v}[J(J+1)-4]$
$^5\Delta_2 \rightarrow -[(J(J+1)+2)^2 + 6(J-2)(J+3) + 6(J-1)(J+2)]D_v$
$^5\Delta_1 \rightarrow -[(J(J+1)+4)^2 + 6(J-1)(J+2) + 4J(J+1)]D_v + 4A_v^{\circ} - 4A_{D_v}[J(J+1)+4]$
$^5\Delta_0 \rightarrow -[(J(J+1)+2)^2 + 4J(J+1)]D_v + 16A_v^{\circ} - 8A_{D_v}[J(J+1)+2]$

Off Diagonal Elements $x = J(J+1)$:

$^5\Delta_4, {}^5\Delta_3 \rightarrow +2\left[\{(x-4)+(x-14)\}[(J+4)(J-3)]^{1/2}\right]D_v - 12A_{D_v}[(J+4)(J-3)]^{1/2}$
$^5\Delta_3, {}^5\Delta_2 \rightarrow +\left[\{(x-4)+(x+2)\}[6(J-2)(J+3)]^{1/2}\right]D_v - 2A_{D_v}[6(J-2)(J+3)]^{1/2}$
$^5\Delta_1, {}^5\Delta_0 \rightarrow +2\left[\{(x+4)+(x+2)\}[J(J+1)]^{1/2}\right]D_v + 12A_{D_v}[J(J+1)]^{1/2}$
$^5\Delta_2, {}^5\Delta_1 \rightarrow +\left[\{(x+2)+(x+4)\}[6(J-1)(J+2)]^{1/2}\right]D_v + 2A_{D_v}[6(J-1)(J+2)]^{1/2}$