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5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1987

Problem Set #3

1. Hund's Coupling Cases.

- (a) Write the case (a) e and f -symmetry 3×3 effective Hamiltonian matrices for the ${}^2\Pi$, ${}^2\Sigma^+$ problem we have considered in Lecture. Include only the zeroth and first order matrix elements of \mathbf{H}^{ROT} and \mathbf{H}^{SO} . Show that the effective rotational constants for ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ are $B \pm B^2/A$ near the case (a) limit.
- (b) Consider the case (b) limit where $A \ll BJ$. Form the approximate case (b) eigenfunctions for ${}^2\Pi$ as

$$\psi_{\pm} = 2^{-1/2} \left[|{}^2\Pi_{1/2}\rangle \pm |{}^2\Pi_{3/2}\rangle \right]$$

and re-express the full 3×3 matrix in this basis.

- (i) You will find that both of the ${}^2\Pi$ eigenstates follow a $BN(N+1)$ rotational energy level expression. Which group of states (E_+ , ψ_+) or (E_- , ψ_-) corresponds to $N = J + 1/2$ and which to $N = J - 1/2$?
- (ii) What is the ΔN selection rule for spin-orbit ${}^2\Pi \sim {}^2\Sigma^+$ perturbations?
- (iii) What is the ΔN selection rule for $\mathbf{BJ} \cdot \mathbf{L}$ ${}^2\Pi \sim {}^2\Sigma^+$ "L-uncoupling" perturbations?
- (c) Consider the case (c) limit for a "p-complex". This means that the ${}^2\Pi$ and ${}^2\Sigma^+$ states correspond to the $\lambda = 1$ and $\lambda = 0$ projections of an isolated $\ell = 1$ atomic orbital. In this case $\langle {}^2\Pi | \mathbf{BL}_+ | {}^2\Sigma^+ \rangle = B[1 \cdot 2 - 0 \cdot 1]^{1/2} = 2^{1/2}B$. $B_{\Pi} = B_{\Sigma} = B$, $\langle {}^2\Pi | \mathbf{AL}_+ | {}^2\Sigma^+ \rangle = 2^{1/2}A$, $A_{\Pi} = A$. Write the case (c) matrix and find the eigenvalues for $E_{\Pi} = E_{\Sigma} = E$. What is the pattern forming rotational quantum number when $A \gg BJ$? For each J-value you should find two near degenerate pairs of e, f levels above one e, f pair. What is the splitting of these two groups of molecular levels? How does this compare to the level pattern (degeneracies and splitting) for a 2P atomic state?
- (d) Consider the case (d) limit for a "p-complex". Use the same definitions of E_{Π} , E_{Σ} , B_{Π} , B_{Σ} , A_{Π} , α , β as for case (c) but set $A = 0$. Your transformed case (b) matrix will be helpful here. Show that R is the pattern forming quantum number by finding the relation between R and J for each of the six same- J , e/f eigenvalues.

2. J. I. Steinfeld, p. 193, #2.

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.	9,405.6
ω_e/cm^{-1}	1,487.3	1,144.2
$\omega_e x_e/\text{cm}^{-1}$	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.

- Construct a Deslandres table of the vibrational band origins of the $^1\Pi - ^1\Sigma^+$ system, for $v'' = 0 - 3$ and $v' = 0 - 5$. 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.
- In the rotational structure of the individual vibrational bands in this system, what branches would you expect to observe? In which branch would you expect to observe a band head? Identify the $J' - J''$ transition 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.
- 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 MOs 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?

3. J. I. Steinfeld, pp. 193-4, #3.

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

35,522	29,940	25,913
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 $(v + 1/2)$ in the vibrational energy level spacings of either electronic state? If so, derive an expression for the third difference, $\Delta^3 G_{v+1/2}$, including terms in $\omega_e y_e (v + \frac{1}{2})^3$ in $G_{v+1/2}$ and estimate $\omega_e y_e$.

4. J. I. Steinfeld, p. 195, #6.

Draw two Morse curves defined by the following constants:

$$\begin{array}{ll} T_e'' = 0 \text{ cm}^{-1} & T_e' = 10,000 \text{ cm}^{-1} \\ D_e'' = 10,000 \text{ cm}^{-1} & D_e' = 5,000 \text{ cm}^{-1} \\ R_e'' = 1.44 \times 10^{-8} \text{ cm}^{-1} & R_e' = 1.54 \times 10^{-8} \text{ cm}^{-1} \\ \omega_e'' = 582 \text{ cm}^{-1} & \omega_e' = 308 \text{ cm}^{-1} \end{array}$$

and determine the two strongest transitions originating from $v' = 19$. Use a reduced mass of $\mu = 6.857$ amu.

Plot $V'(R) - V''(R)$ vs. R . Use this curve to determine:

- The long and short wavelength limits of all bound-bound transitions in this system which possess significant intensity;
- The long and short wavelength limits of strong bands from $v' = 19$;
- Plot the R-value(s) sampled vs. transition energy for the progression of bands ($v' = 19, v''$) for $v'' = 0$ through the maximum v'' level that can be reached via non-negligible Franck-Condon factor from $v' = 19$.
- The wavelength region(s) in which erratic intensity variations occur. Which v' levels participate in such transitions? Why?

5. Effective Hamiltonian Matrices.

(a) Set up the Hamiltonian,

$$\mathbf{H} = \mathbf{H}^{\text{ROT}} + \mathbf{H}^{\text{SPIN-ORBIT}}$$

for the 9 basis functions:

	Λ	S	Σ	Ω	
${}^3\Pi$	1	1	1	2	$ {}^3\Pi_2\rangle v_\Pi\rangle$
	-1	1	-1	-2	$ {}^3\Pi_{-2}\rangle v_\Pi\rangle$
	1	1	0	1	$ {}^3\Pi_1\rangle v_\Pi\rangle$
	-1	1	0	-1	$ {}^3\Pi_{-1}\rangle v_\Pi\rangle$
	1	1	-1	+0	$ {}^3\Pi_0\rangle v_\Pi\rangle$
${}^3\Sigma^+$	-1	1	1	-0	$ {}^3\Pi_{-0}\rangle v_\Pi\rangle$
	0	1	1	1	$ {}^3\Sigma_1^+\rangle v_\Sigma\rangle$
	0	1	0	0	$ {}^3\Sigma_0^+\rangle v_\Sigma\rangle$
	0	1	-1	-1	$ {}^3\Sigma_{-1}^+\rangle v_\Sigma\rangle$
					.

Let

$$\alpha \equiv \langle \Lambda = 1 | \mathbf{A} \mathbf{L}_+ | \Lambda = 0 \rangle$$

$$\beta \equiv \langle \Lambda = 1 | \mathbf{L}_+ | \Lambda = 0 \rangle$$

and use

$$\langle 1 | \mathbf{H} | 2 \rangle = (-1)^{2J+S_1+S_2+\sigma_1+\sigma_2} \langle -1 | \mathbf{H} | -2 \rangle$$

where $\sigma = 1$ for Σ^- states and 0 for all other states, to ensure phase consistency for

$$\langle \Lambda = 1 | \mathbf{H} | \Lambda = 0 \rangle \text{ and } \langle \Lambda = -1 | \mathbf{H} | \Lambda = 0 \rangle$$

matrix elements.

(b) Construct the e/f parity basis using the following phase definitions

$$\sigma_v |v, n \Lambda^\sigma S \Sigma, \Omega J M\rangle = (-1)^{J-2\Sigma+S+\sigma} |v, n - \Lambda^\sigma S - \Sigma, -\Omega J M\rangle$$

$$\text{e-levels} \quad \sigma_v \psi = +(-1)^J \psi$$

$$\text{f-levels} \quad \sigma_v \psi = -(-1)^J \psi.$$

(c) Factor the 9×9 Hamiltonian into a 5×5 matrix and a 4×4 matrix using the e/f basis functions.(d) Obtain the centrifugal distortion correction terms for the $\langle {}^3\Pi_0 | \mathbf{H} | {}^3\Pi_0 \rangle_e$, $\langle {}^3\Pi_1 | \mathbf{H} | {}^3\Pi_1 \rangle_e$, and $\langle {}^3\Pi_1 | \mathbf{H} | {}^3\Pi_0 \rangle_e$ matrix elements.

$$D_\Pi \equiv - \sum_{v_\Pi'} \frac{\langle v_\Pi | B | v_\Pi' \rangle^2}{E_{\Pi_v}^0 - E_{\Pi_{v'}}^0}.$$

- (e) Obtain the correction terms for the effect of remote ${}^3\Sigma^+$ levels on ${}^3\Pi$ for the $\langle {}^3\Pi_0 | \mathbf{H} | {}^3\Pi_0 \rangle_{e \text{ and } f}$ and $\langle {}^3\Pi_1 | \mathbf{H} | {}^3\Pi_1 \rangle_{e \text{ and } f}$ matrix elements.

$$o \equiv \sum_{v'_\Sigma} \frac{\left[\frac{1}{2} \alpha \langle v_\Pi | v'_\Sigma \rangle \right]^2}{E_{\Pi v}^0 - E_{\Sigma v'}^0}$$

$$p \equiv 4 \sum_{v'_\Sigma} \frac{\left[\frac{1}{2} \alpha \beta \langle v_\Pi | v'_\Sigma \rangle \langle v_\Pi | B | v'_\Sigma \rangle \right]}{E_{\Pi v}^0 - E_{\Sigma v'}^0}$$

$$q \equiv 2 \sum_{v'_\Sigma} \frac{\left[\beta \langle v_\Pi | B | v'_\Sigma \rangle \right]^2}{E_{\Pi v}^0 - E_{\Sigma v'}^0}$$

Express the diagonal contributions to the Λ -doubling of the $\Omega = 0$ and 1 ${}^3\Pi$ substates in terms of the o , p , and q -parameters.