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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 #2
Due March 9, 1987

Readings:

J. I. Steinfeld, pp. 39-73, 77-79, 92-110, 113-142

Handouts:

Anharmonic Oscillator, Vibration-Rotation Interaction	(Lecture #3 supplement)
Energy Levels of a Vibrating Rotor	(Lecture #23 supplement)
Construction of Potential Curves by the RKR Method	(Lecture #4 supplement)
Van Vleck Transformation	(after Lecture #2)

1. An atom is in a $(3d)^2\ ^3P_0$ state.
 - (a) List all L-S-J terms to which an electric dipole allowed transition might occur.
 - (b) List all two-electron configurations into which electric dipole allowed transitions can occur from $(3d)^2\ ^3P_0$.
2. J. I. Steinfeld, p. 111, #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 ($^M\Lambda_{g,u}^\pm$) 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.
3. J. I. Steinfeld, p. 111, #3.

Use the "Gilmore diagrams" provided for O_2 , N_2 , NO , and H_2 :

 - (a) Sketch the expected low-resolution absorption spectrum to be expected for each of these four molecules between 1,000 and 10,000 Å.
 - (b) A photoionization experiment is carried out by shining light on a gas sample placed between two electrodes. A positive ion current is measured between the cathode and ground. For the four molecules, what is the longest wavelength of light that would be effective in producing a measurable ion current (this is called the "photoionization threshold")?
 - (c) The first positive bands ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) of nitrogen are observed in an "active nitrogen" discharge, in which the active species are predominantly ground state N atoms. Suggest a mechanism for the population of the excited state.
 - (d) When solutions of hydrogen peroxide and "Clorox" are mixed, a red chemiluminescence near 7,600 Å is observed. What might this be caused by?

4. J. I. Steinfeld, p. 143, #5.

The squared “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 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 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. J. I. Steinfeld, p. 143, #6.

The harmonic oscillator wave functions for the levels $v = 0$ and $v = 1$ are

$$\psi_0 = \left(\frac{a}{\pi}\right)^{1/4} \exp\left(\frac{-a(r - r_e)^2}{2}\right),$$

$$\psi_1 = \left(\frac{4a^3}{\pi}\right)^{1/4} \Delta r \exp\left(\frac{-a(r - r_e)^2}{2}\right),$$

in which a is a constant. These functions are orthogonal and normalized to unity.

(a) Show that ψ_0 and ψ_1 are orthogonal.

(b) Calculate the average value of $(r - r_e)^{-2}$ for the state $v = 1$.

Also calculate B_v (in cm^{-1}) for $v = 0$ and 1 . Why is $B_1 > B_0$ for a harmonic oscillator? Why is $B_1 < B_0$ for almost all real molecules?

6. J. I. Steinfeld, p. 143, #7.

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

7. You are going to use the Van Vleck Transformation (a fancy name for second-order quasi-degenerate perturbation theory) to solve a coupled harmonic oscillator problem. Consider

$$\mathbf{H} = \mathbf{H}_x^0 + \mathbf{H}_y^0 + \zeta x^2 y^2$$

and let

$$\omega_x = \omega_y.$$

(a) Given that

$$\langle n_x | x^2 | n_x \rangle = \frac{\hbar}{m\omega} (n_x + 1/2)$$

$$\langle n_x | x^2 | n_x \pm 2 \rangle = \frac{\hbar}{2m\omega} [n_x^2 + n_x + 1 \pm (2n_x + 1)]^{1/2}$$

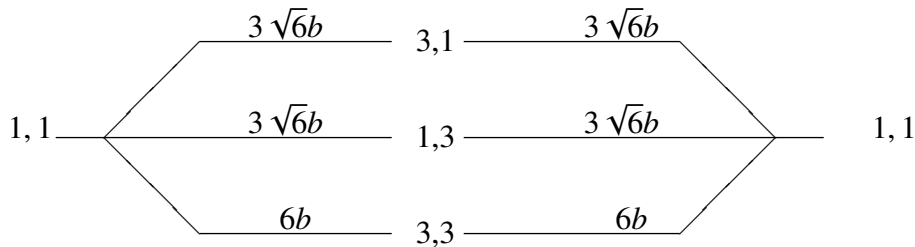
$$\frac{\zeta \hbar}{4m^2 \omega^3} \equiv b.$$

Construct the \mathbf{H} matrix through

$$n = n_x + n_y = 4.$$

Notice that the matrix factors nicely into an odd n and an even n block.

- (b) Apply the Van Vleck transformation to the $n = 0, 1,$ and 2 blocks. Assume that $\hbar\omega \gg b$. Be sure to include corrections due to off-diagonal elements with $n > 4$ basis functions. Your bookkeeping will be simplified if you make use of “railroad” diagrams. For example,



The diagram places the initial and final basis functions at left and right and in the middle **all** basis functions that can simultaneously have non-zero matrix elements with both. Above each line is the actual value of the matrix element. All that remains is to look up the relevant energy denominators. The correction to the $1, 1; 1, 1$ matrix element is (neglecting b terms in denominators)

$$-\frac{54b^2}{2\hbar\omega} - \frac{54b^2}{2\hbar\omega} - \frac{36b^2}{4\hbar\omega}.$$

- (c) Now that you have effectively uncoupled the $n = 0, 1, 2$ blocks from all other blocks, you can focus your attention individually on these $1 \times 1, 2 \times 2,$ and 3×3 isolated effective Hamiltonians. Construct the $(2, 0) \pm (0, 2)$ and $(1, 0) \pm (0, 1)$ basis functions. This is called a “Wang Transformation”. Can you suggest any physical basis for this additional factorization? You should find that the $n = 0 - 2$ part of this Hamiltonian is now fully diagonal. Draw an energy level diagram for $n = 0$ through 2 which compares your eigenvalues against unperturbed ($b = 0$) levels.