5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Problem Set #3

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. A new superheavy element, Dk or Dreckium[1], has recently been discovered at Berkeley. Its atomic number is 120 and it is in Group IIA of the periodic table. The following Dk I spectral lines have been observed (relative intensities in parentheses):

in absorption at	T = 1000K	T = 2000K	Emission
39511 cm^{-1}	—	(0)	✓
37474	(0)	(1)	✓
34796	(2)	(4)	✓
31176	(10)	(20)	✓
27506	(0)	(0)	✓
27228	(1)	(1)	✓
26116	(55)	(110)	✓
20179	(80)	(60)	(100)
19901	(1100)	(1000)	(2200)
19484	(1900)	(2400)	(7000)
19427	(900)	(700)	(1300)
19149	(1400)	(1300)	(2800)
19051	(1200)	(900)	(1600)

(✓ observed but no intensity available)

Additional lines observed in emission include (many others are omitted from this table)

20722 cm^{-1}

18685

16007

12387

7327

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[1] Dk was independently discovered in the Soviet Union, but they call it Merdium, and, because of the peculiarities of the Cyrillic alphabet, symbolize it by Sh.

and a group of 6 lines (listed in the main table above) with relative intensities quite different from those observed in absorption. The emission intensities for these 6 lines are included in the table of absorption lines.

(a) Assign the observed spectra and construct an energy level diagram. You should make use of all the tricks used by spectroscopists:

   (i) search for repeated frequency intervals;

   (ii) search for progressions described by $A - B/n^2$ where A and B are constants and n is the principal quantum number;

   (iii) take advantage of relative intensity information, especially temperature dependent intensities;

   (iv) analogies with other group IIA atomic spectra (HINT: note that the energy of $(n - 2)f$ and $(n - 1)d$ orbitals decreases relative to ns and np as n increases);

   (v) Hund's rules;

   (vi) The Landé interval rule.

You should also assume that I have not included any misleading information such as lines belonging to another atom or to Dk II, transitions in which the lower level does not belong to one of the four predicted low–lying configurations involving 8s, 8p, 7d and 6f orbitals, or transitions involving significantly perturbed levels. Atomic spectroscopists should be so fortunate! Because Dk is a heavy atom, there is at least one (weak) intercombination transition.

(b) Can you explain why the lines 20179, 19901, and 19484 cm^{-1} exhibit intensity enhancements in emission at high pressure and in regions of a discharge in which large electric potential gradients exist?

(c) Is the energy level diagram for Dk sufficiently complete that the electronic partition function,

$$Q_e = \sum_{\text{all states } i} g_i \exp[-E_i/kT],$$

may be calculated at 3000K? If one or more electronic terms are missing, what would be the fractional error in Q_e, assuming plausible term energies? How would you devise an experiment which samples $Q_e(T)$ with accuracy sufficient to locate a missing low–lying electronic term? Is it likely that all of the necessary quantities could be measured with sufficient accuracy to prove that a low–lying electronic term had escaped detection?

3. Bernath, Chapter 6, Problem #3, page 197.

A triatomic molecule has the formula A_2B. Its microwave spectrum shows strong lines at 15, 30, 45,... MHz, and no other lines. Which of the following structures is (are) compatible with this spectrum?

(a) linear AAB

(b) linear *ABA*

(c) bent *AAB*

(d) bent *ABA*

4. Bernath, Chapter 6, Problem #5, page 197.

   The F_2O molecule of C_{2v} symmetry has an O—F bond length of 1.405 Å and an FOF bond angle of 103.0°.

   (a) Calculate A, B, and C for F_2O.

   (b) Will the microwave spectrum of F_2O show a–, b–, or c–type transitions?

   (c) Predict the frequency of the $J = 1 - 0$ microwave transition?

5. Bernath, Chapter 6, Problem #8, pages 197–198.

   The following is a complete list of observed transitions involving levels $J = 0$, 1, and 2 for two isotopes of formaldehyde in their vibrational ground states:

$H_2^{12}C^{16}O$ (MHz)	$H_2^{13}C^{16}O$ (MHz)
71.14	—
4,829.66	4,593.09
14,488.65	13,778.86
72,837.97	71,024.80
140,839.54	137,449.97
145,602.98	141,983.75
150,498.36	146,635.69

   (a) Assign these microwave transitions for both isotopomers. Assume that H_2CO belongs to the C_{2v} point group and estimate a molecular geometry using bond-length tables. Assign the spectrum by prediction of the expected rotational spectrum.

   (b) What are A, B, and C for the two isotopic species? Since we have neglected centrifugal distortion, it will not be possible to fit all transitions exactly with only three rotational constants. Devise a procedure that gives a "best fit" to all lines.

   (c) Explain why the inertial defect

$$\Delta = I_C - I_A - I_B$$

   is a good test for planarity. Why does H_2CO appear not to be planar from the microwave spectrum?

   (d) Obtain a best possible geometry for H_2CO using your A, B, C values for the two isotopes.

6. Bernath, Chapter 6, Problem #20, page 199.

The application of an electric field to a molecular system partially lifts the M_J degeneracy. This Stark effect may be treated as a perturbation of the rotational energies. The perturbation Hamiltonian $\mathbf{H}' = -\mu_z E_z$, where z is a lab frame coordinate and E_z is the electric field along the laboratory z–axis.

(a) Show that there will be no first-order Stark effect for a linear molecule.

(b) Develop a formula for the second-order Stark effect of a linear molecule.