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5.80 Small-Molecule Spectroscopy and Dynamics  
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MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
Chemistry 5.76  
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**Problem Set #2**

- In the spectrum of rubidium, an alkali metal, the short-wavelength limit of the diffuse series is 4775 Å. The lines of the first doublet in the principal series ( $5^2P_{3/2} \rightarrow 5^2S_{1/2}$  and  $5^2P_{1/2} \rightarrow 5^2S_{1/2}$ ) have wavelengths of 7800 Å and 7947 Å, respectively.
  - By means of term symbols, write a general expression for the doublets of the sharp series, giving explicitly the possible values for  $n$ , the principal quantum number.
  - What is the spacing in  $\text{cm}^{-1}$  of the first doublet in the sharp series?
  - Compute the first ionization potential of rubidium in  $\text{cm}^{-1}$  and electron-volts (eV).
- In the first transition row of the Periodic Table there is a regular trend in ground-state multiplicities from calcium (singlet) to manganese (sextet) to zinc (singlet), with one exception.
  - Why does the multiplicity rise to a maximum and then fall?
  - Explain the discontinuity shown by chromium (atomic number 24).
  - Niobium, the element under vanadium in the second transition row, also shows a discontinuity in multiplicity, though vanadium does not. Explain.
- Atomic eigenfunctions contain a factor  $\exp(iM\phi)$ . When the atom is in a magnetic field  $B$ , the quantum number  $M$  represents the projection of the  $J$ -vector on  $B$  ( $-J \leq M \leq +J$ ). The usual selection rules for  $L$ ,  $S$ , and  $J$  still hold for moderate  $B$ , and in addition a selection rule governing the values of  $\Delta M$  becomes important. The dipole-moment operators for transitions involving  $M$  are  $ce\epsilon_{\parallel}$  and  $c'e\epsilon_{\perp} \cos\phi$ . The coefficients  $c$  and  $c'$  are non-zero constants (for the purposes of this problem);  $e$  is the charge on the electron; and  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  are the components of the electric field of the radiation parallel and perpendicular to  $B$ . Derive the selection rules for  $\Delta M$  for radiation polarized parallel and perpendicular to  $B$ .
- Calculate the Zeeman pattern to be expected for the sodium  $D$ -lines at 10,000 gauss ( $G$ ). You may neglect nuclear hyperfine interactions. Indicate the polarization of each Zeeman line, that is, whether the electric vector of the emitted radiation is parallel to the applied magnetic field ( $\pi$ -component) or perpendicular to it ( $\sigma$ -component).

- (a) Show qualitatively the Stark effect to be expected for the sodium *D*-lines. The splittings are proportional to what power of the electric field strength?
- (b) What do you think might happen to a beam of ground-state sodium atoms passing through a strong inhomogeneous magnetic field? a strong inhomogeneous electric field?
5. An atom is in a  $(2p)^2\ ^3P_o$  state.
- A. List all of the L–S terms to which an electric dipole allowed transition might occur. Specify *J* values and whether the state must have a <sup>o</sup> right superscript.
- B. List all two electron configurations to which allowed transitions occur.
6. A new superheavy element, Dk or Dreckium, has recently been discovered. 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 <sup>-1</sup>	—	(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)

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

20722 cm<sup>-1</sup>

18685

16007

12387

7327

and a group of 6 lines 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;
  - (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 three predicted low-lying configurations involving  $8s$ ,  $8p$ , and  $7d$  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  $19484 \text{ cm}^{-1}$  exhibit intensity enhancements in emission at high pressure and in regions of a discharge in which large electric potential gradients exist?