Advanced class - Atomic and molecular spectroscopy

Q1. Advanced physical chemistry 1999, Q4

Answer TWO of the following three parts.

A. Predict the ordering of the lowest four excited terms of the helium atom which arise from excitation of one electron into the n=2 shell. Include in your answer a discussion of the following: Russell-Saunders coupling, Hund's rules, electron spin correlation, effective nuclear charge.

Explain why some of these excited states are metastable with respect to decay to the ground state and comment on the relevance of this metastability to the mechanism for population inversion in the helium-neon laser.

Transitions of the type $1s^2 \rightarrow 2s^1 2p^1$ have been observed for the helium atom. Comment on this observation in the context of configuration interaction.

B. The vibrational Raman spectrum of D_2 shows Stokes lines at the following displacements from the exciting line (in cm^{-1}).

3390.0 cm^{-1}
3278.0 cm^{-1}
3164.8 cm^{-1}
2812.5 cm^{-1}
2690.7 cm^{-1}
2566.8 cm^{-1}

A broad central peak is also observed at approximately 2990 cm^{-1}.

Draw an energy level diagram to illustrate the observed transitions.

Using the method of combination differences, or otherwise, determine values of the rotational constants B_0, B_1 and B_e, and the equilibrium bond length for D_2 (you may ignore centrifugal distortion). Explain whether you would expect the equilibrium bond length for H_2 to differ from this value.

The vibrational Raman spectrum of the D_2 molecule shows an 'intensity alternation'. Write down the complete set of nuclear spin wavefunctions for this molecule (for the deuterium nucleus, I=1) and use these to explain the intensity alternation. Predict the relative intensities at 300 K of the first three lines in the S branch of the Raman spectrum listed above (you may ignore the rotational dependence of the transition moment.)

$$hc/k_BT = 4.795 \times 10^{-3} \text{ cm at 300 K}$$

The relative atomic mass of deuterium is 2.

C. The rotational energy of a three-dimensional body is given in classical mechanics by the expression:

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

where J_a, J_b and J_c are components of the total angular momentum about three perpendicular axes through the centre of mass of the body, and I_a, I_b, I_c are moments of inertia about those axes.

Starting from the classical energy expression, show that the following energy level formulae may be deduced.

i) For a spherical top molecule ($I_a=I_b=I_c$): $E/hc = BJ(J+1)$
ii) For a prolate symmetric top molecule ($I_a<I_b=I_c$) $E/hc = BJ(J+1) + (A-B)K^2$

where $B=h/(8\pi^2cI_b)$ and $A = h/(8\pi^2cI_a)$.

What does the quantum number K represent, and what range of values can it take for a given J?

Sketch an energy level diagram for a prolate symmetric top molecule ($I_a<I_b=I_c$) for values of J up to 2, and indicate the quantum numbers and degeneracies of each level.

Predict the appearance of the rotational spectrum of a prolate symmetric top molecule on the basis of the energy level formula given above.

The through space H-H distance in the symmetric top molecule CH_3F is 192 pm. Calculate a value for the A rotational constant in this molecule.
[The relative atomic mass of hydrogen is 1.]

Q2. Advanced physical chemistry 2000, Q3

a) Determine the possible numbers of vibrational degrees of freedom in a tetra-atomic molecule. Why does this number depend on the structure of the molecule?

b) Five fundamental vibration bands are found in the infrared (IR) and Raman (R) spectra of an X_2H_2 molecule, as follows:

3374 cm^{-1}	(R)
3287 cm^{-1}	(IR)
1974 cm^{-1}	(R)
729 cm^{-1}	(IR)
612 cm^{-1}	(R)

i) What can be deduced about the molecular structure from the fact that no line is both R and IR active?

ii) Given that the molecule is C_2H_2, identify the type of each vibration as C-H or C-C bond stretch, or bend.

iii) By consideration of the R and IR activity, and the frequencies, assign a symmetry to each mode (a full normal mode analysis is not required).

iv) Sketch the form of the atomic displacements in each mode.

c) Sketch the appearance of the rotational structure that you would expect to see in

i) The IR band at 729 cm^{-1}

ii) The Raman band at 3374 cm^{-1}

given that the most populated level at room temperature is $J_{max}=9$.

d) The equilibrium rotational constants, B_e, of the molecules C_2H_2 and C_2D_2 are 1.188 cm^{-1} and 0.8556 cm^{-1}, respectively. Determine the C-C and C-H(D) bond lengths, assuming that they are not affected by isotopic substitution.
[You may use the conversion $B(cm^{-1})=16.857/I(u\ Å^2)$ and take the hydrogen isotopic masses to be 1.0 u and 2.0 u exactly.]

Q3. Advanced physical chemistry 2000, Q5

a) The lowest energy atomic absorption line of He^+ ions is at a photon energy of 40.814 eV, while that of atomic H atoms is at 10.197 eV.

i) Give the configurations and term symbols for ht estates involved in the transitions.

ii) Explain why the ratio of photon energies is very close to four.

iii) Explain why the ratio is not exactly four.

b) At very high resolution the He^+ line at 40.814 eV is found to be a doublet, with a splitting of 0.0007 eV.

i) Explain why the line is split.

ii) Estimate the splitting of the line at 10.197 eV in the spectrum of atomic H.

c) The first absorption line in the spectrum of neutral He is at a photon energy of 21.217 eV.

i) Give the configurations and term symbols for the states involved.

ii) Suggest reasons why the measured width of this line as seen in emission depends on the pressure and temperature of He gas in a lamp from which it is emitted.

iii) Explain why this He emission line splits into three components when a strong magnetic field is applied to its source, whereas the He^+ doublet line at 40.814 eV splits into a larger number of components.

d) The 21.217 eV line of He is the first member of a Rydberg series, with the following photon energies:

Quantum number n	2	3	4	5
Energy E_n/eV	21.217	23.086	23.742	24.045

Using the Rydberg formula, $E_n = I - R/(n-\delta)^2$, where I is the ionisation energy and δ is the quantum defect;

i) Show that for $\delta \ll 1$

$$\frac{E_{n+1} - E_n}{R} \approx \frac{1}{n^2} - \frac{1}{(n+1)^2} + 2\delta\left(\frac{1}{n^3} - \frac{1}{(n+1)^3}\right)$$

[Recall that for $x \ll 1$, $1/(1-x)^m \approx 1 + mx$.]

ii) Use the first two energies and the result above to estimate the quantum defect.

iii) Hence estimate the ionisation potential of He as accurately as possible from the data given.
[Hint: the Rydberg constant, R, can be obtained from the data given in part a). No graph or recursive (iterative) calculation is required.]

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