MAASAI MARA UNIVERSITY

REGULAR UNIVERSITY EXAMINATIONS

2017/2018 ACADEMIC YEAR

FIRST YEAR SECOND SEMESTER EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE (CHEMISTRY)

SCHOOL OF SCIENCE

COURSE CODE: CHE 8213

COURSE TITLE: ATOMIC AND MOLECULAR SPECTROSCOPY

Date: 14/12/2018 TIME: 8.00 – 11.00 AM

INSTRUCTIONS

1. The paper consists of four questions
2. QUESTION ONE is compulsory and carries 30 marks
3. Attempt any other two (2) questions, each carries 20 marks

QUESTION ONE – THIRTY MARKS

a) The emission spectrum of atomic hydrogen shows lines at 82 259, 97 492, 102 824, 105 292, 106 632, and 107 440 cm^{-1}, which correspond to transitions to the same lower state. Determine

(i) The ionization energy of the lower state. **[6 Marks]**

(ii) The value of the Rydberg constant for hydrogen **[2 Marks]**

b) Not all possible electron transitions are permissible thus a spectrum doesn't arise from the transition of an electron from any initial orbital to any other orbital. Explain. **[4 Marks]**

c) Distinguish between singlet and triplet states **[2 Marks]**

d) To identify the orbitals to which a 4d electron may make electric-dipole allowed radiative transitions **[3 Marks]**

e) Identify the levels that may arise from spin–orbit coupling in the configurations

(i) d^1, (ii) s^1.

f) The origin of the D lines in the spectrum of atomic sodium is shown in Figure 1. Calculate the spin–orbit coupling constant for the upper configuration of the Na atom. **[3 Marks]**

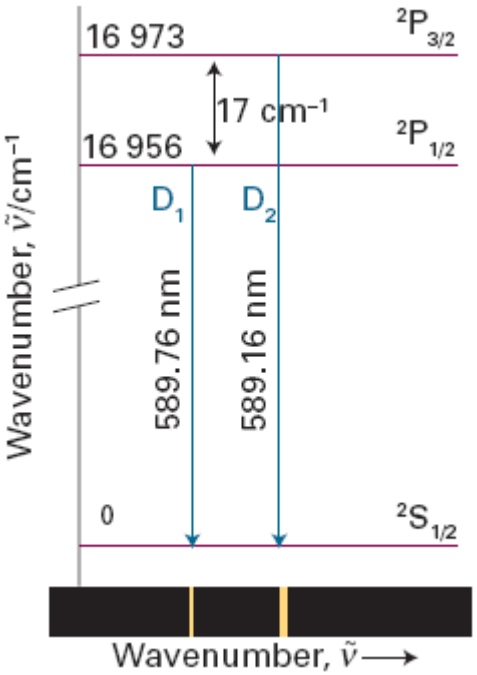

Figure 1: The energy-level diagram for the formation of the sodium D lines.

g) Write the term symbols arising from the ground-state configurations of

(i) Na, (ii) F, and (iii) the excited configuration of C: $1s^2 2s^2 2p^1 3p^1$. **[6 Marks]**

h) Predict the form of the rotational Raman spectrum of $^{14}N_2$, for which = 1.99 cm^{-1}, when it is exposed to 336.732 nm laser radiation. **[4 Marks]**

QUESTION TWO – TWENTY MARKS

(a) Describe the following radiative processes:
(i) Stimulated absorption **[2 Marks]**
(ii) Spontaneous emission **[2 Marks]**

(b) With the aid of a diagram, describe the empirical (observation based) distinction between fluorescence and phosphorescence **[5 Marks]**

(c) Describe the physical origins of linewidths in the absorption and emission spectra of gases, liquids, and solids. **[9 Marks]**

(d) Specify and account for the selection rules for transitions in hydrogenic atoms. **[2 Marks]**

QUESTION THREE – TWENTY MARKS

(a) Describe the mechanism of fluorescence. In what respects is a fluorescence spectrum not the exact mirror image of the corresponding absorption spectrum? **[10 Marks]**

(b) Discuss the mechanism of phosphorescence **[10 Marks]**

QUESTION FOUR – TWENTY MARKS

(a) Discuss the physical origins of the gross and specific selection rules for rotational and vibrational Raman spectroscopy. **[4 Marks]**

(b) State the exclusion rule for vibrational spectra of polyatomic molecules **[1 Marks]**

(c) Suppose that you wish to characterize the normal modes of benzene in the gas phase. Why is it important to obtain both infrared absorption and Raman spectra of your sample? **[2 Marks]**

(d) Consider the vibrational mode that corresponds to the boat-like bending of a benzene ring. Is it (i) Raman, (ii) infrared active? Explain **[3 Marks]**

(e) The following data were obtained for the absorption by a dye dissolved in methylbenzene using a 2.50 mm cell. Calculate the molar absorption coefficient of the dye at the wavelength employed:

[dye]/(mol dm^{-3})	0.0010	0.0050	0.0100	0.0500
T /(per cent)	73	21	4.2	1.33×10^{-5}

[7 Marks]

(f) Explain the origin of the term ground state symbol $^2P_{3/2}$. **[3 Marks]**