KENYATTA UNIVERSITY

UNIVERSITY EXAMINATIONS 2011/2012

SECOND SEMESTER EXAMINATION FOR THE DEGREE OF BACHELOR OF SCIENCE

SCH 203: THEORY OF SPECTROSCOPIC METHODS

DATE: TUESDAY 27TH MARCH 2012 **TIME: 11.00 A.M. – 1.00 PM.**

INSTRUCTIONS

Answer ALL questions.

Some useful Data

Avogadro constant, $N_A = 6.023 \times 10^{23}\ mol^{-1}$ Plank's constant, $h = 6.626 \times 10^{-34}$ J s

$\nu_s = \nu_i \pm B[4j + 6]$ $\varepsilon_v = (v + ½)\bar{\omega}_e - (v + ½)^2 \bar{\omega}_e \chi_e$

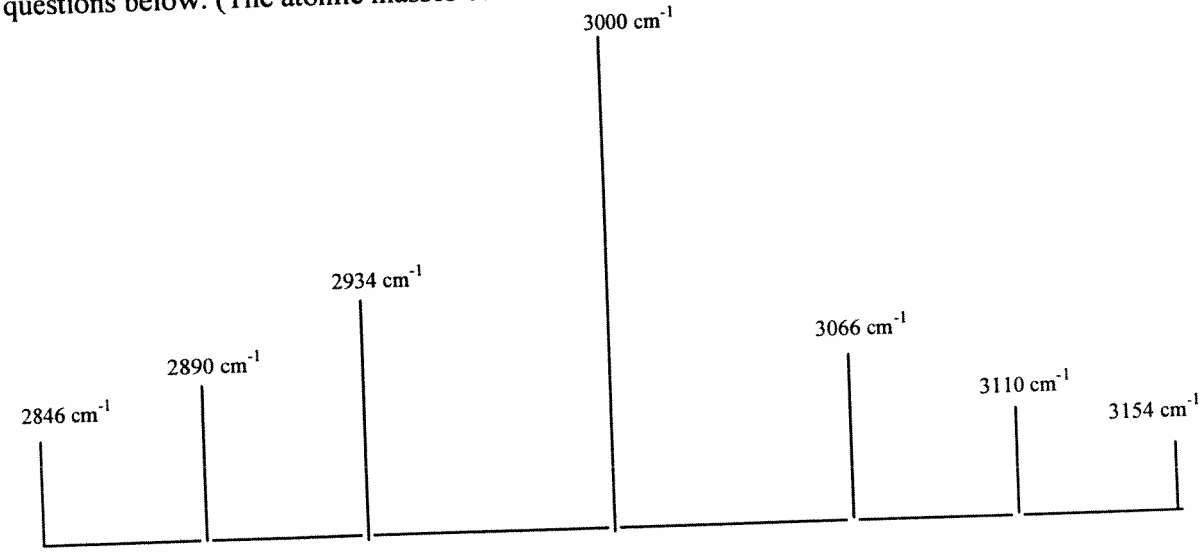
Question 1

a) What is the requirement for molecules to have microwave spectrum? (2 marks)

b) What can Raman spectroscopy is used for (4 marks)

c) Use a diagram and briefly describe the energy processes that give rise to Rayleigh, Stokes and anti-Stokes scattering involving a photon and a molecule. (6 marks)

d) Use the rotational Raman spectra of a diatomic D–F molecule provided to answer the questions below. (The atomic masses of D and F are 2.014 and 18.998 respectively)



Raman Sptectrum

(i) State the selection rules for rotational Raman. (2 marks)

(ii) Identify the Stoke and anti-Stoke lines. (2 marks)
(iii) Determine the value of rotational constant, B (2 marks)
(iv) Determine the moment of inertia and bond length of diatomic D–F molecule. (6 marks)

Total = 24 marks

Question 2

a) State the selection rules for harmonic and anharmonic oscillators. (2 marks)

b) An infrared spectra of an anharmonic oscillator shows an intense peak at 2885.9cm^{-1} and a weak peak at 5668.0cm^{-1} use values to determine.
   i. Harmonic constant $\bar{\omega}_e$ (2 marks)
   ii. Anharmonic constant χ_e (2 marks)
   iii. The first hot band ($v = 2 \rightarrow v = 3$) (3 marks)

c) In real cases, vibrators are also rotating. Use the fundamental band to explain the effect of rotations to the infrared spectra. (4 marks)

Total = 13 marks

Question 3

a) Calculate the energy per photon and energy mole of photons in joules for radiation of 300 nm (3 marks)

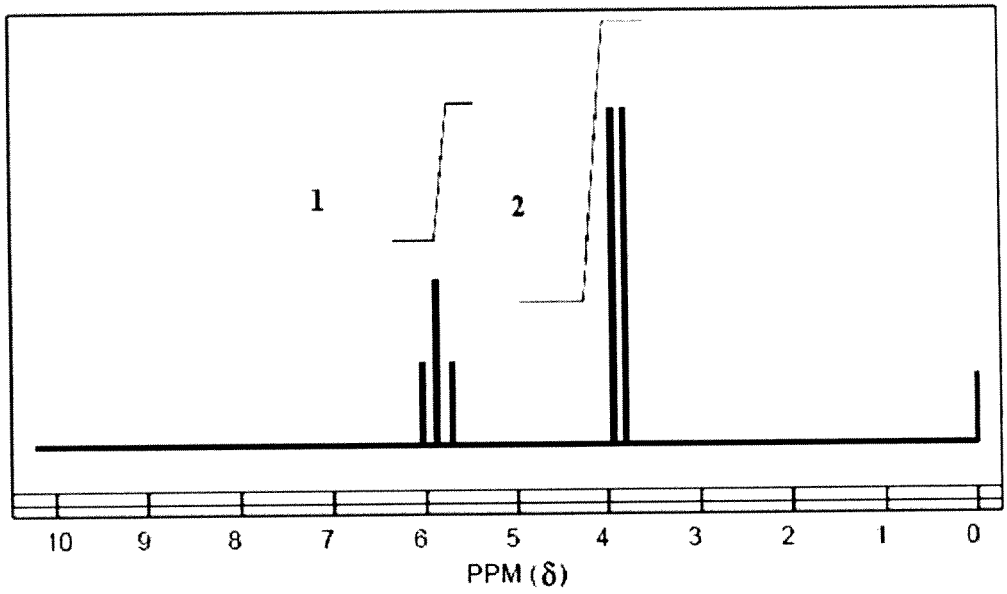
b) Briefly explain the following terms used in spectroscopy.
   i. Fundamental band
   ii. Chemical shift
   iii. Harmonic oscillator
   iv. Chromophore (8 marks)

c)
   i. Sketch the normal vibrational modes of CO_2 (4 marks)
   ii. State which modes are IR/Raman active (4 marks)

Total = 19

Question 4

a) Below is a NMR spectrum of compound (A) of molecular formula $C_2H_3Cl_3$, done at 100 MHz.
   i. Interpret the spectrum and deduce its structure. (4 marks)
   ii. What is the effect of running the spectrum at 300 MHz (2 marks)



b) State the compound used as the internal reference for proton NMR chemical shifts and give reasons why it is preferred. (4 marks)

c) The hydrogen fine structure involve 1s1 (ground state) to np1(excited states) transition. Determine the:

i. The ground state term(s) (1 mark)

ii. The excited state term(s) (1 mark)

d) Show that this transition is fully allowed (2 marks)