**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2014, for Internal Students of the Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the Associateship**

**CHEMISTRY FOUNDATION PAPER TWO**

**Thursday 16th January 2014, 14:00-16:15**

**USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.**

**Found/0114 Turn Over**

**1.IS1 – Introduction to Spectroscopy and Characterisation**

**This question is worth 25 marks.**

Answer part a) and **EITHER** part b) **OR** part c) of this question.

**Useful isotope data** (all masses are relative atomic masses)

1H = 1.0078 ; 12C = 12.0000 ; 35Cl = 34.9689 ; 16O = 15.9949

1. Answer **ALL** parts of this question.



The sketch above shows a simplified vibrational/rotational absorption spectrum for a simple diatomic.

1. State the Born-Oppenheimer approximation in this context.

(2 marks)

1. Using an energy level diagram, identify the transitions occurring for each peak. Identify the P and R branches. Why is the Q branch invisible?

(6 marks)

1. Why do the bands converge at higher energies?

(2 marks)

1. Using the sketch above as a basis for your answer, sketch a simplified vibrational/rotational spectrum for HCl for ∆J ±0,1,2,3,4,5.

[You may assume the following isotopic abundances 1H = 100%, 35Cl = 75%, 37Cl = 25%]

(5 marks)

QUESTION CONTINUED OVERLEAF

1. Answer **BOTH** parts of this question.
2. A molecule is observed to undergo a molecular transition using electromagnetic radiation at a frequency of 51.5 THz. Identify the type of molecular transition occurring.

Convert this energy to kJ mol-1, and comment on your answers.

(5 marks)

1. Carbon monoxide is observed to have an intense absorption at 2143 cm-1. Calculate the force constant and period of vibration for this molecule, stating any assumptions made.

(5 marks)

1. Answer **BOTH** parts of this question.
2. A solution of a metal complex is observed to have a transmission of 33 % at a wavelength of 442 nm. Given that the pathlength of the absorption cell is 5 mm, and that the molar absorption coefficient is 3,200 mol-1 dm3 cm-1, calculate the concentration of the solution.

(3 marks)

1. Identify how many molecular vibrations are expected from acetylene (C2H2), together with sketches of the molecule to indicate the vibrations.

Does this molecule have a pure rotational spectrum? Explain your answer.

(7 marks)

**1.IS2 – Introduction to Spectroscopy and Characterisation**

**This question is worth 25 marks.**

Answer part a) and **EITHER** part b) **OR** part c) of this question.

1. Ethanoic acid is reacted with compound **A**, under acidic conditions, to yield compound **B** and water (see Scheme below). Compound **B** has the molecular formula C4H8O2 and shows IR absorptions at 1750 and 1240 cm-1.

Identify **A** and **B**. Assign the IR absorptions observed for **B**. Sketch the 1H and 13C{1H} NMR spectra observed for **A** and **B**. You should explain the chemical shifts, relative integrals and multiplicities observed.



[You may assume coupling occurs only through 3 bonds or fewer and that 1H, I=½ is 100% abundant; all other nuclei are NMR inactive.]

(15 marks)

1. Answer **BOTH** parts of this question.
2. Explain why the molecular ion observed in the mass spectrum of ClBr3 consists of five peaks, each separated by 2 atomic mass units. Calculate the masses and relative intensities of the peaks.

[You may assume that the relative abundance of the isotopes are: 35Cl = 75%, 37Cl = 25%, 79Br = 51%, 81Br = 49%]

(6 marks)

1. Explain the order of the IR stretching frequencies observed for: CN- > CO > NO (4 marks)

1. Compound **C** shows the following spectroscopic characteristics.

The IR spectrum shows strong absorptions at 1694 and 807 cm-1.

The 1H NMR spectrum shows a singlet at 9.89 ppm, of relative intensity 1, and two doublets, each showing a relative intensity of 2, at 7.67 and 7.60 ppm, respectively.

The mass spectrum shows a molecular ion at *m/z*: 186 (49%) and 184 (51%). There are also major fragmentation peaks at *m/z:* 185, 183, 157 and 155 amu.

Identify **C** and explain the data. Your answer should include a full assignment of all the data and a sketch of its structure.

(10 marks)

**1F1 – Chemical Reactivity and Characterisation**

**NB. ‘Half a question’ (out of 12.5 marks)**

Give the reaction type for **THREE** of the following reactions. For the reactions of metal containing compounds give the oxidation state for **ALL** metal atoms. For other reactions draw appropriate arrows to indicate the direction of electron flow.



(4 marks each plus 0.5 bonus mark)

**1.O5 – Introduction to Physical Organic Chemistry**

**NB. ‘Half a question’ (out of 12.5 marks)**

Answer part a) and **EITHER** part b) **OR** part c) of this question.

1. Answer **ALL** parts of this question.
2. Using a reaction energy profile to illustrate transition states, explain why bromination of propane yields a higher ratio of secondary to primary haloalkane than chlorination.

(3.5 marks)

1. Write balanced equations for the reactions of carboxylic acid **2** with the sodium salts of both carboxylic acids **1** and **3** indicating which side of the reaction the equilibrium is favoured, and calculate the equilibrium constant for each reaction.



(3 marks)

1. Acid catalysed hydrolysis of the two esters shown below, occurs by two different mechanisms. State the most likely mechanism for hydrolysis, and draw the mechanism for the acid catalysed hydrolysis reactions of **ONE** of the two esters.

(4 marks)



Ester 1 Ester 2.

QUESTION CONTINUED OVERLEAF

1. How could radiolabelling be used to determine whether the ester below undergoes acyl-oxy or alkyl-oxy acid catalysed hydrolysis?

(2 marks)



1. The hydrolysis of chloromethane (CH3Cl) has a substantial negative entropy of activation (ΔS‡). What information does this provide about the mechanism for the reaction and the degree of order in the transition state?

(2 marks)