Autumn Examinations

Exam Code(s)          CHEMISTRY CH401
Exam(s)               Final examination for the Degree of B.Sc. Honours
Module Code(s)        CH448
Module(s)             Spectroscopic & Physical Methods and Applications
Paper No.             1

External Examiner(s)  Prof. Tia Keyes
Internal Examiner(s)  Prof. P.V. Murphy, Dr. N. Geraghty, Dr. L. Ronconi, Dr. A.G. Ryder, Prof. R. Woods

Instructions:          Answer 3 questions in total
                        Use a separate answer book for each question
                        Each question carries 100 marks distributed as shown where appropriate. Leave the first page of the answer book blank and list on it clearly the number of the question attempted.

Duration              Two (2) Hours
No. of Pages          7
Department(s)         Chemistry
Course Co-ordinator(s) Dr. A.G. Ryder

Requirements:
Statistical/ Log Tables x
Graph Paper           x
1. Microscopy: Answer all parts (a-d)

(a) Explain how an ICCD detector operates. Give a list of the major pros and cons of this type of detector. Illustrate your answer with appropriate diagrams. [30 marks]

(b) Describe using a detailed and labelled diagram, the construction and operation of a modern epi-fluorescence microscope. Explain the four key components of such a system. [30 marks]

(c) Define what is meant by the terms refraction, refractive index, and dispersion. Illustrate your answer with appropriate diagrams and equations. [30 marks]

(d) Define Numerical Aperture for a simple lens. What are the advantages and disadvantages of using a High NA objective in microscopy? [10 marks]

2. NMR: Answer all parts (a-b)

Correlation Tables are provided at the end of the examination paper.

(a)

(i) Sketch the $^1$H-NMR spectrum you would expect for the molecule A. The sketch should indicate the approximate chemical shift and the splitting pattern of each signal in the spectrum: [13 marks]

(ii) Sketch the $^{13}$C-NMR spectrum that would be obtained for A. The sketch should indicate the approximate chemical shift of each signal in the spectrum [7 marks]

(iii) Sketch the DEPT spectrum that would be obtained for A. The chemical shift of each signal in the spectrum should be clearly indicated. [5 marks]
(b) A substance B has the molecular formula C_{10}H_{12}O_{2} and its IR spectrum contains strong absorption bands at 1701, 1202 and 835 cm\(^{-1}\). Its \(^1\)H-NMR spectrum (CDCl\(_3/\)TMS) is shown in Fig. 1; apart from those shown, there were no other signals in the \(^1\)H-NMR spectrum. The integration values for each signal appear below the baseline and the exact chemical shifts appear above each signal.

![Fig. 1](image)

The \(^{13}\)C-NMR for A is shown in Fig 2; note there is a small but clearly labelled signal at 130.18 ppm. The signal at 0.0 ppm is due to TMS, the reference substance, and those at 76-78 ppm to CDCl\(_3\). An analysis of the DEPT spectrum of A produced the information given in Table 1.

<table>
<thead>
<tr>
<th>Signal (ppm)</th>
<th>196.58</th>
<th>162.88</th>
<th>130.53</th>
<th>130.18</th>
<th>114.10</th>
<th>63.73</th>
<th>26.25</th>
<th>14.65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of hydrogens attached to C-atom responsible for signal</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 1
(i) Use this information to determine the structure of A. [45 marks]

(ii) Using a structural diagram of the molecule, assign all the signals in the $^1$H-NMR spectrum to the appropriate hydrogen atoms and account for the coupling patterns of the signals. (You are not required to distinguish between the signals at $\delta$ 6.91 and 7.92.) [10 marks]

(iii) Sketch the COSY spectrum that you would expect to obtain for A and explain what information can be deduced from this 2-D spectrum. [10 marks]

(iv) Sketch the HMQC spectrum that would be obtained for A in the $\delta$ 0.0 – 5.0, 0.0-70.0 ppm region. [5 marks]

(v) Again using a structural diagram, assign the IR bands to the appropriate bonds in the structure [5 marks]
(a) The electronic spectrum of the low-spin $d^5$ octahedral complex ion $[\text{Fe}^{III}(\text{CN})_6]^{3-}$ shows absorptions at 420 ($\lambda_1$), 302 ($\lambda_2$) and 215 ($\lambda_3$) nm.

i. With reference to the Tanabe-Sugano diagram for $d^5$ octahedral complexes above reported, identify the ground state and assign each band to the corresponding electronic transition (hint: consider spin-allowed transitions only). [14 marks]

ii. Given that for $[\text{Fe}^{III}(\text{CN})_6]^{3-}$ $\Delta_0/B \approx 37.5$, with the aid of the Tanabe-Sugano diagram above reported, calculate the Racah parameter $B$, the crystal-field splitting energy $\Delta_0$ (in both cm$^{-1}$ and kJ mol$^{-1}$) and the Crystal-Field Stabilization Energy (CFSE, the mean pairing energy being 24,000 cm$^{-1}$ per pair). Which transition corresponds to the $t_{2g}^4e_g^{-1} \leftrightarrow t_{2g}^5e_g^{0+}$? [26 marks]

iii. Consider the general case of a high-spin $d^5$ octahedral complex. What kind of electronic spectrum would you expect? Can you suggest a ligand “L” for an high-spin complex of the type $[\text{Fe}^{III}L_6]$? Justify all your statements. [18 marks]
(b) Describe and discuss the main features of the CO stretching vibrations in transition metal-carbonyl complexes. How many CO stretching bands can be recorded in [M(CO)₆]-type derivatives? Are they IR- and/or Raman-active? [23 marks]

(e) Predict the appearance of the ¹⁹F and ¹⁹⁵Pt{¹H} NMR spectra for the square-planar complex [PtF₂(NH₃)₂] (hint: both ¹⁹F and ¹⁹⁵Pt have I = ½, and are 100% and 33.8% naturally abundant, respectively). Would recording either of these NMR spectra allow you to discriminate between the cis and the trans isomers? [19 marks]

4. **Answer all parts (a-b)**

You perform an analysis of protein-drug binding using Bio-layer Interferometry (BLI) and obtain the following sensorgrams. The kinetic binding rates (k_on and k_off) were determined by fitting to the sensorgrams, and are shown in the figure.

(a) Explain why it is apparent from the sensorgrams that equilibrium binding has not been achieved this experiment, and discuss how you would alter the experiment to achieve equilibrium. [30 marks]

(b) If the natural ligand has a binding free energy of –15 kJ/mol for this protein, does this drug have a higher affinity than the natural ligand? Show your calculations. [70 marks]