0063

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

Semester 1 Examinations 2005-2006

Exam Code(s)	3BS9 and 3ER3
Exam(s)	Third Science Chemistry
Module Code(s)	CH308
Module(s)	Determination of Molecular Structure
Paper No.	
Repeat Paper	
External Examiner(s)	Professor J.A.S. Howell
Internal Examiner(s)	Professor P. McArdle, Professor R.N. Butler, Professor. M. J. Hynes, Professor. D. Cunningham Dr. W. Carroll and Dr. P. O'Leary

Instructions: **Answer 4 questions**

Duration	**2 Hours**
No. of Pages	5 including this page
Department(s)	Chemistry
Course Director(s)	Professor P. McArdle

Requirements:
MCQ
Handout
Statistical Tables
Graph Paper
Log Graph Paper
Other Material

1. Answer **each** of the following.

(a) List the five symmetry operation elements **[5 marks]**

(b) Explain why BF_3 possesses an S_3 axis but NH_3 does not. **[5 marks]**

(c) What symmetry elements are lost on going from NH_3 to NH_2Cl? **[5 marks]**

(d) How do the rotation axes and planes of cis- and trans-N_2F_2 differ? **[5 marks]**

(e) In BCl_3, what single symmetry describes S_3^3?

In BCl_3, what single symmetry operation describes S_3^6? **[5 marks].**

2. Answer **each** of the following:

(a) The vibrational modes of XeF_2 are at 555, 515 and 213 cm^{-1} but only two are infra-red active. On the other hand, the vibrational modes of SF_2 are at 838, 813 and 357 cm^{-1} and all three are infra-red active. Use these data to predict the structures of XeF_2 and SF_2. Are your structures consistent with those predicted by valence shell electron pair repulsion theory (VSEPRT)? Assign the vibrational modes for both molecules. **[12 marks]**

(b) With the aid of an appropriate diagram clearly explain why the second order reflection from the (1,0,0) set of planes can be regarded as the first order reflection from the (2,0,0) set of planes. **[7 marks]**

(c) With the aid of a diagram explain that while it is unnecessary to include a C-centred face centred cell in the tetragonal system it is necessary to do so in the orthorhombic system **[6 marks]**

3. Answer **all parts** of the following:

An ionic compound of U^{+4} which contains only uranium and fluorine in the anions and potassium cations crystallises in the cubic system and gives rise to a powder diffraction pattern exhibiting the following six largest d-spacings (Å) 5.32, 4.61, 3.26, 2.78, 2.66, 2.31.

(a) Index the data. **[6 marks]**

(b) Find the unit cell parameter. **[8 marks]**

(c) Given that the first reflection occurs at a 2-theta value of 16.643°, calculate the wavelength of the x-radiation used for the data collection. **[4 marks]**

(d) Given that the unit cell contains four uranium atoms and that the density of the compound is 4.141 g cm^{-3} derive a formula for the ionic compound. **[7 marks]**

(Assume the following atomic weights: K, 39.098; F, 18.998; U, 238.029 and Avogadro's number is 6.022×10^{23})

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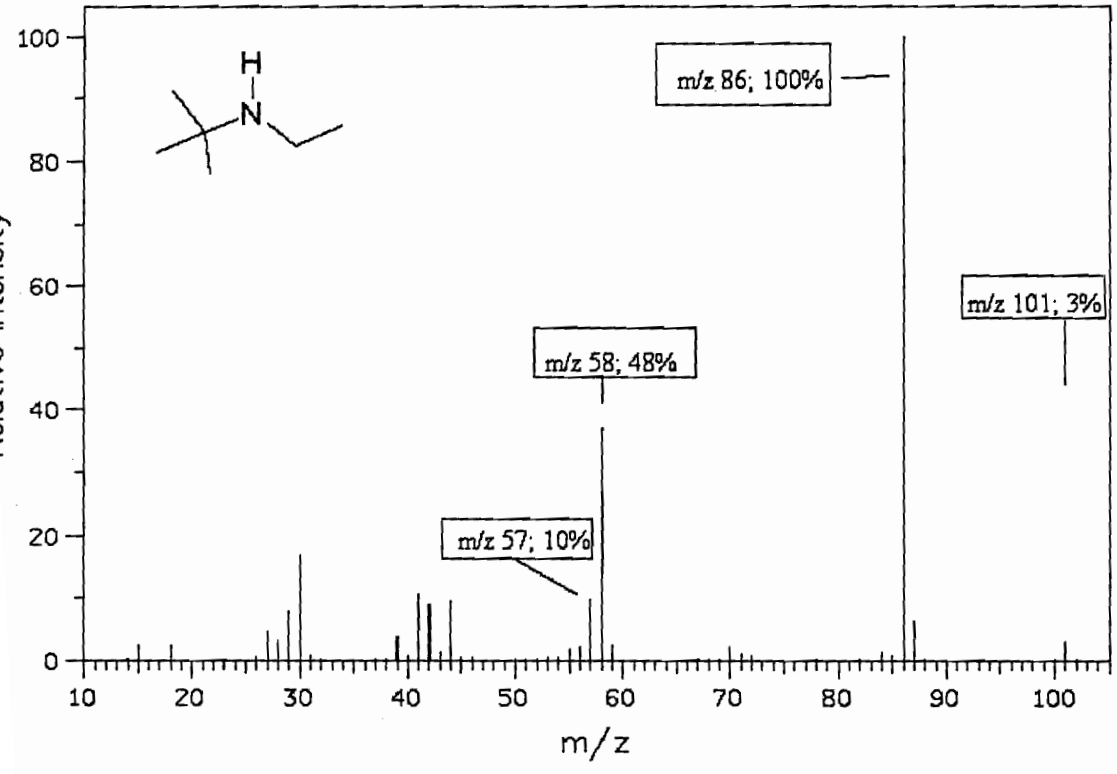
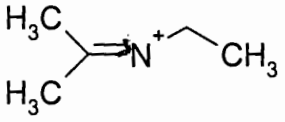
Answer **(a) and (b)**.

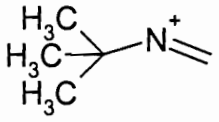
(a) Electron Impact ionisation (EI), Chemical Ionisation (CI) and Matrix Assisted Laser Desorption Ionisation (MALDI) are commonly used ionisation techniques in mass spectrometry. In the case of two of the listed ionisation methods outline the process involved in ionisation of the analyte. Also outline the type of ions produces and how likely they are to fragment. **[10 marks]**

(b) The mass spectrum of N-ethyl-*tert*-butylamine is shown below. What is the structure of the ion detected at m/z 101? The signal detected at m/z 86 is due to two ions which are shown below. How is each of these two ions formed from the molecular ion? The ions detected at m/z 58 and 57 are derived from fragmentation of the two ions shown (m/z 86). What is the fragmentation mechanism for the formation of the ions detected at m/z 58 and m/z 57 and what are their structures?





m/z 86



m/z 86

[15 marks]

A 316 stainless steel stent is passivated in a 20% nitric acid solution held at a temperature of 50 ^{0}C for 10 minutes. What surface analytical techniques would you use in order to explore any structural or chemical changes brought about by this treatment?

[25 marks]

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6. Answer **(a)** and **(b)**.

(a) A normal polymer sample contains molecules with a variety of lengths and it is only possible to quote an average value of the molar mass. Discuss. **[10 marks]**

(b) The following data were obtained for intrinsic viscosity of some polyisobutylene samples in CCl_4 solutions at 30 ^{0}C.

$[\eta]$ cm^3 g^{-1}	M_w, g mol^{-1}
430	12,60,000
206	4,63,000
78	1,10,000
43	48,000
15	10,000

Verify by a suitable plot that the data fit to the equation $[\eta] = KM_w^{\alpha}$ and determine the values of K and α.

7. **Answer <u>each</u> of the following:**

(a) Describe the phenomenon of "shielding" and briefly explain the proton chemical shifts you would expect from the different types of protons in the following molecules:

$CH_3–CH_2–CH_3$ **1** $CH_2=CH–CH_3$ **2** $CH_2=CH–OCH_3$ **3**

[6 marks]

(b) Explain the origin of spin-spin coupline (splitting) in proton NMR spectra and illustrate your explanation using the molecule ethanal ($CH_3CH=O$). **[6 marks]**

(c) The proton NMR signals for the CH_2 groups in the following molecule all overlap. Suggest and explain any methods by which the individual signals could be separated:

$Br–CH_2–CH_2–CH_2–Cl$ **[6 marks]**

(d) Show how the proton NMR spectrum of pure methanol changes as the temperature is gradually raised from -40 °C to 40 °C. Calculate the rate of proton exchange between methanol molecules at 4°C, the coalescence point of the multiplet, (MeOH, J, 5.2Hz)

[7 marks]

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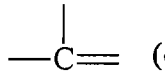
8. Answer <u>each</u> of the following

(a) Explain the main features of an NMR spectrometer which produce normal and off-resonance ^{1}H decoupled ^{13}C NMR spectra. **[6 marks]**

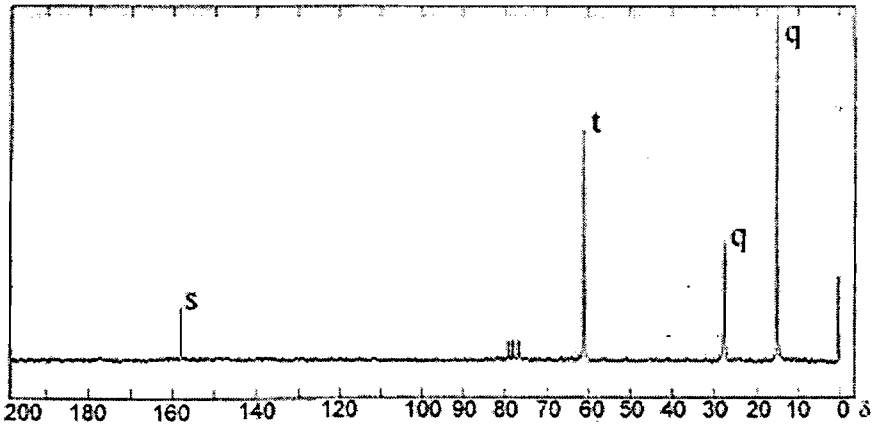
(b) Comment on the ***<u>relative intensities</u>*** of the carbon-13 signals to be expected from the carbon atoms in the following units:



(quaternary), —CH=, —CD=

[5 marks]

(c) A compound of formula $C_4H_9NO_2$ gave the carbon-13 NMR spectrum shown, in $CDCl_3$ as solvent. The multiplicities of the signals in the off-resonance decoupled spectrum are shown by the letter on the signals. Determine the structure of the molecule and explain the spectrum. **[14 marks]**



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