GX 368

Ollscoil *na* hÉireann, Gaillimh
National University *of* Ireland, Galway

AUTUMN 2002

THIRD UNIVERSITY B.Sc. EXAMINATION IN SCIENCE (INCLUDING DENOMINATED DEGREES)

Determination of Molecular Structure (CH308)

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Time Allowed: Two Hours

Answer 4 questions

All questions carry equal marks. Leave the first page of the Answer Book blank and list on it clearly the numbers of the questions attempted.

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

(a) Clearly outline the problems that would arise in attempting to solve a crystal structure totally from powder diffraction data. **[9 marks]**

(b) The powder diffraction pattern of germanium yields the following five largest d-spacings (Å): 3.266, 2.000, 1.706, 1.414 and 1.298. In fact, the second and fifth expected reflections were not observed. The experimentally determined density of germanium is 5.235 g. cm.$^{-3}$. The atomic weight of germanium is 72.61 and Avogadro's number is 6.022 x 10^{23}/mol..

(i) Index the data.
(ii) Calculate the number of germanium atoms per unit cell.
(iii) If the fifth expected reflection had been observed, calculate the d-spacing that would be associated with it.
(iv) Provide a diagram showing the positions of germanium atoms in the unit cell.
[16 marks]

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

(a) (i) Clearly outline the origin of Bravais lattices. Provide diagrams of the cubic and orthorhombic Bravais lattices. With the aid of a diagram, explain why it is unnecessary to have an end face centred Bravais lattice in the tetragonal crystal system. **[5 marks]**

(ii) What is the origin of the 230 space groups? **[3 marks]**

(iii) Describe how Miller indices are assigned to sets of planes and provide a diagram showing the (3, 2, 0) set of planes for an orthorhombic crystal. **[4 marks]**

(b) Complete the following multiplication table for the C_{2v} point group. Comment on your results with specific reference to the C_{2v} point group **[13 marks]**.

E	C_2	σ	σ'
C_2			
σ			
σ'			

3. List the symmetry elements and symmetry operations of the following species, assign them to the correct point group and group the operations into classes **[25 marks]**

NCl_3, ICl_2^-, SF_4^{2-}, NH_2^-, $POCl_3$, CH_2FCl

[You **must** use the correct structures for the species above]

4. The molar masses of a series of homodisperse polystyrene samples were measured by osmosis. The limiting viscosity number (intrinsic viscosity) [η] was found for each sample in toluene at 30^0C using an Ubbelohde viscometer and the results are given below:

M/g mol^{-1}	[η] / m^3 kg^{-1}
76,000	0.0382
135,000	0.0592
163,000	0.0696
336,000	0.1054
440,000	0.1292

Find K and α (Mark Houwink Equation) for polystyrene in toluene at 30^0C **[12 marks]**

Various amounts of each of the samples were mixed together and the flow times in the viscometer for different concentrations of this mixture in toluene were determined as shown below:

C / kg m^{-3}	**Time / s**
0.0	100
1.0	114
1.3	118
2.0	128
4.0	160

Calculate the average molar mass of the mixture. (Assume the density is constant.) What type of average is it ? **[13 marks]**

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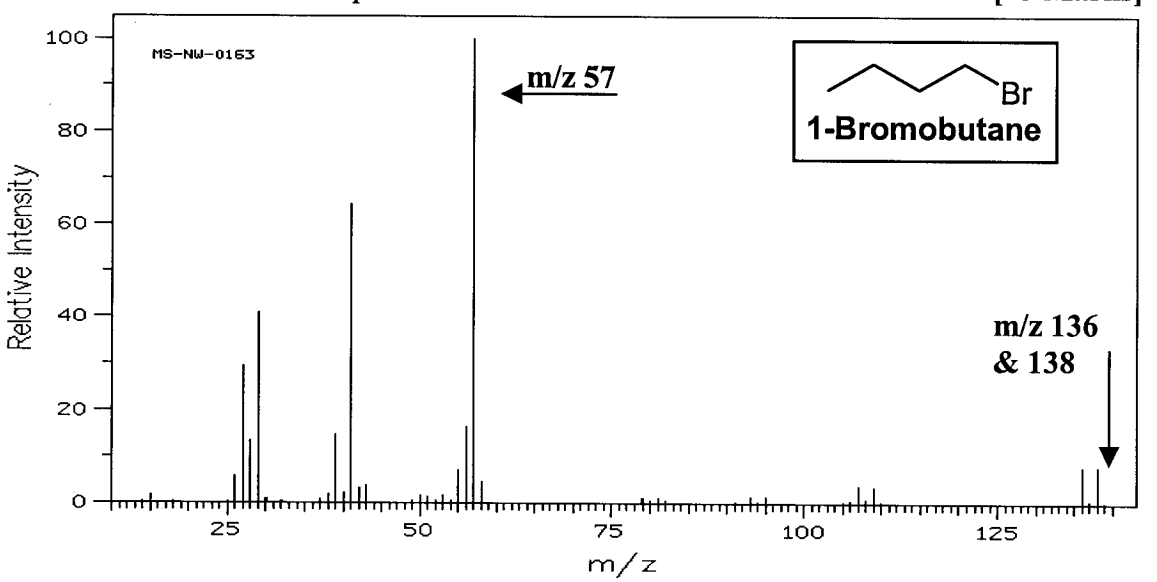
5. Describe some of the more important chemical and structural information which can be obtained from the surface analysis of materials using secondary ion mass spectrometry (SIMS) **[25 marks]**

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

(a) Briefly describe, with the aid of a diagram, how Matrix Assisted Laser Desorption Ionisation (MALDI) causes formation of ions in the vapour phase **[10 Marks]**

(b) The electron impact ionisation spectrum of 1-bromobutane is given below. Account for the major peaks (as indicated) in the spectrum. Include in your answer a detailed rationalisation of the peaks at m/z 136 and 138 **[15 Marks]**



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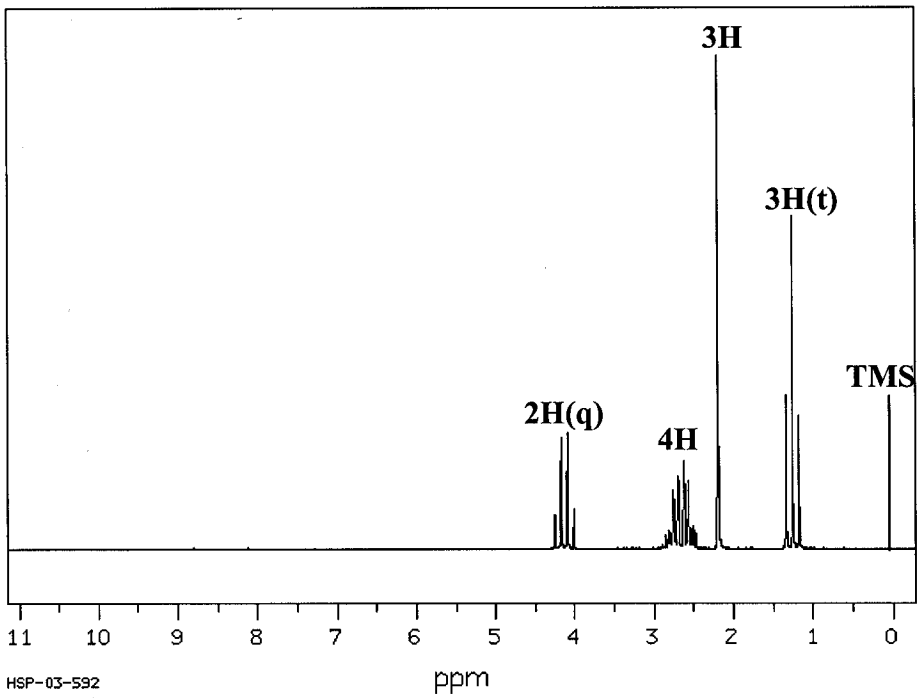
7. Answer **(a)** and **(b)**.

(a) Briefly explain the cause of spin-spin splitting in proton NMR spectra and draw the spectrum you would expect from $CH_3CH_2CH_2Cl$.
How would the spectrum change if it were measured on 100MHz and 400MHz machines? **[12 marks]**

(b) A product of formula $C_7H_{12}O_3$ was isolated from a chemical reaction. Its IR spectrum showed a strong absorption at $1730cm^{-1}$. The Figure shows its proton NMR spectrum along with the number of H-atoms in each signal.
Assign a structure to the compound and briefly explain your argument. **[13 marks]**



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

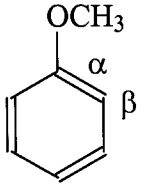
(a) Explain the factors which control chemical shifts in proton and carbon-13 NMR spectra and comment on the chemical shifts (ppm) of the following compounds.

$CH_3–CH_3$	$CH_2=CH_2$	C_6H_6
δ_H, 0.96, δ_C 5.7	δ_H, 5.84, δ_C 123.3	δ_H 7.26, δ_C 128.5

[12 marks]

(ii) Predict how the methoxy group would change the shifts at the α- and β- carbons in the following compounds, methylvinylether and methoxybenzene (anisole).

$CH_2=CH–O–CH_3$
β α



[13 marks]

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