

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

Semester 1 Examinations 2001/2002

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

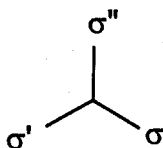
All questions carry 25 marks distributed as shown. Leave the first page of the Answer Book blank and list on it clearly the numbers of the questions attempted.

- 1. Answer (a) and (b)**
- (a)** By means of a flow chart, outline the step by step procedure for solving a crystal structure and briefly outline the potential problems that would be encountered at each step if x-ray powder diffraction data alone were available. [12 marks]
- (b)** A double salt has the formula $\text{CsV}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ and has a density of 2.042 g cm^{-3} . Its x-ray powder diffraction pattern yields the following six largest d-spacings (Å): 7.18, 6.23, 5.56, 5.08, 4.40 and 4.15. The first two reflections that would be anticipated for the Bravais lattice adopted by the salt are missing as a result of special absences. Given that there are four vanadium atoms per unit cell, determine the value of n in the molecular formula of the salt. (Atomic weights are: Cs, 132.905; V, 50.942; S, 32.06; O, 16.0; H, 1.008. Avogadro's number is $6.022 \times 10^{23}/\text{mol}$.) [13 marks]

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2. Answer (a) and (b)
- (a) Show that you understand the difference between a symmetry element and a symmetry operation by defining the five basic symmetry elements and giving examples of the symmetry operations generated by them. [5 marks]
- (b) List the symmetry elements and operations for the following species and assign each of them to its own point group: NH_3 , NHF_2 , PCl_5 , POCl_3 , ethane, BF_3 . [20 marks]
- [You must use the correct structures for the species in (b)]

3. Answer (a), (b) and (c)
- (a) Assuming a D_{3h} point group, use the diagram below to deduce the results of the following operations:
- | | | | | |
|-------|-----------------------|---------------------|--------------------|-----------|
| (i) | $EC_3 = ?$ | $C_3E = ?$ | Comment on result. | [2 marks] |
| (ii) | $C_3C_3^2 = ?$ | $C_3^2C_3 = ?$ | Comment on result. | [2 marks] |
| (iii) | $\sigma C_3 = ?$ | $C_3\sigma = ?$ | Comment on result. | [2 marks] |
| (iv) | $\sigma\sigma' = ?$ | $\sigma'\sigma = ?$ | Comment on result. | [2 marks] |
| (v) | $C_3\sigma C_3^2 = ?$ | | Comment on result | [2 marks] |



- (b) Clearly outline the origin of Bravais lattices and crystal systems and comment on the distribution of Bravais lattices among the orthogonal crystal systems. What is the origin of the 230 space groups? [9 marks]
- (c) Describe how Miller indices are assigned to single planes and to sets of planes. Provide a diagram showing the (1,2,3) plane in an orthorhombic unit cell and a further diagram illustrating the (2,3,0) set of planes. [6 marks]

4. Answer (a) and (b).

- (a) Describe some of the more important chemical information which can be obtained from the surface of materials using X-ray photoelectron spectroscopy. [12 marks]
- (b) The following number of X-rays were counted over the same period from a specimen containing iron and nickel and two elemental standards using a SEM-EDAX spectrometer. The background has already been subtracted.

X-ray line	Unknown	Element
Fe K_α	31906	106602
Ni K_α	72062	103853

The beam voltage was 20kV and the X-ray take-off angle was 45° . Show how this information can be used to give quantitative data concerning the alloy composition. [13 marks]

5. Answer (a) and (b).

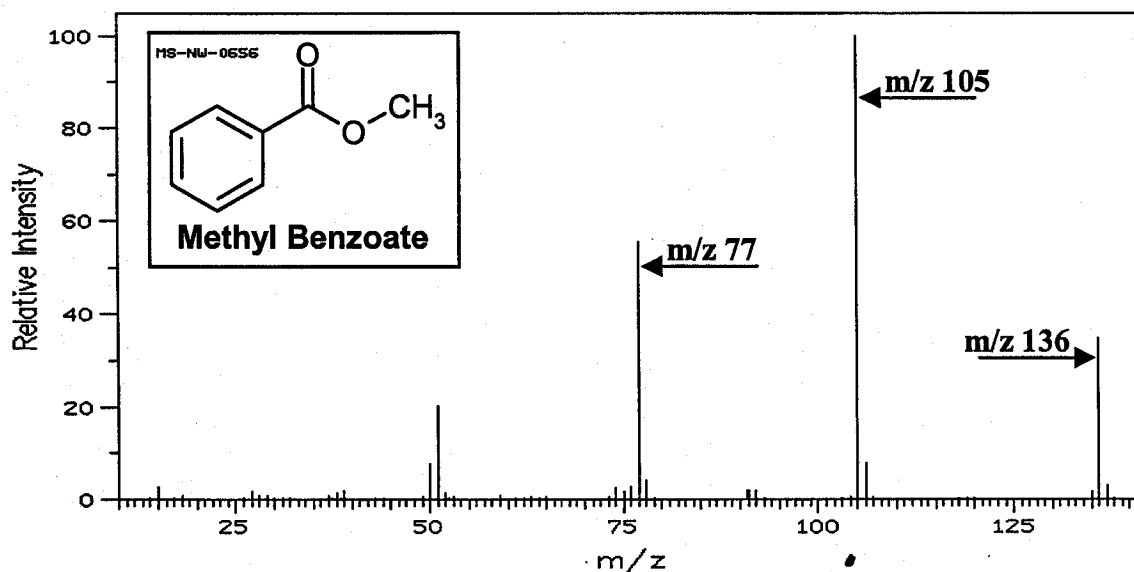
- (a) A normal polymer sample contains molecules with a variety of lengths and it is only possible to quote an average value of the molar mass. Discuss. [10 marks]
- (b) Given the following osmotic pressure data for solutions of poly(vinylacetate) in toluene at 310K:

C/kg m ⁻³	2.0	4.0	6.0	8.0	10.0
π/Nm^{-2}	33.56	69.44	107.64	148.16	190.10

Calculate the number average molar mass and the second virial coefficient. What structural information may be obtained from this coefficient? [15 marks]

6. Answer each of the following:

- (a) Briefly describe, with the aid of a diagram, how a time of flight (TOF) mass analyser works [7 Marks]
- (b) What effect does the introduction of a reflectron (ion mirror) onto the TOF mass analyser have? [3 Marks]
- (c) The electron impact ionisation spectrum of methyl benzoate is given below. Account for the major peaks (as indicated) in the spectrum. [5 Marks each]



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7. Answer each of the following:

(i) Describe the main features of a modern carbon-13 NMR spectrometer and explain why it is more difficult to measure a carbon-13 NMR signal than a proton NMR signal from an unlabelled organic molecule. [9 marks]

(ii) Explain the shielding effects that cause the following proton and carbon-13 chemical shifts for the molecules (A) and (B).

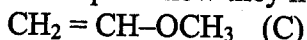


δ_{H} 0.96; δ_{C} 5.7

δ_{H} 5.84; δ_{C} 123.3

[8 marks]

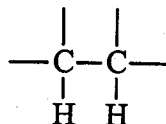
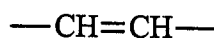
(iii) Predict the proton and carbon-13 chemical shifts of all the H and C atoms in molecule (C) and explain how they have changed relative to the corresponding shifts in (A) and (B).



[8 marks]

8. Answer each of the following:

(i) Explain the origin of spin-spin splitting in proton NMR spectra and summarize the structural information available from the magnitude of the 3-bond coupling constant, $^3J_{\text{H--H}}$, in the structures (A) and (B)



(A)

(B)

[13 marks]

(ii) A compound of formula $\text{C}_8\text{H}_9\text{Br}$ displays the proton NMR spectrum in the Figure, including an electronic integration. The signal at 2.0δ contains 3H atoms. Determine the structure of the molecule and briefly explain your assignments. [12 marks]

Figure. Proton NMR Spectrum

