UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Pertama
Sidang Akademik 2002/2003

September 2002

KAA 503 – Molecular Spectroscopy

Time : 3 hours

Please make sure this paper consists of SEVEN printed pages before anwering the questions.

Answer FIVE questions. Only the first five questions answered by the candidate will be marked.

1. (a) Explain the advantages of biochemical enzymatic analysis in the determination of blood glucose.

(6 marks)

(b) Discuss, by giving an example of a spectroscopic determination, the advantages and disadvantages of derivative spectroscopy.

(6 marks)

(c) A 10.0 cm^3 aliquot of an aqueous solution of quinine was diluted to 25 cm^3 and found to have an absorbance of 0.217 at 348 nm when measured in a 1.00 cm pathlength cell. A second 10.0 cm^3 aliquot was mixed with 5.00 cm^3 of a solution containing 27.3 ppm of quinine. After dilution to 25 cm^3 this solution had an absorbance of 0.474 when measured in the same 1.00 cm pathlength cell. Calculate the amount of quinine, in ppm, in the original aqueous solution.

(8 marks)

.../2-

2. (a) How many normal modes of vibration are possible for SO_2 and which of these modes are infrared active?

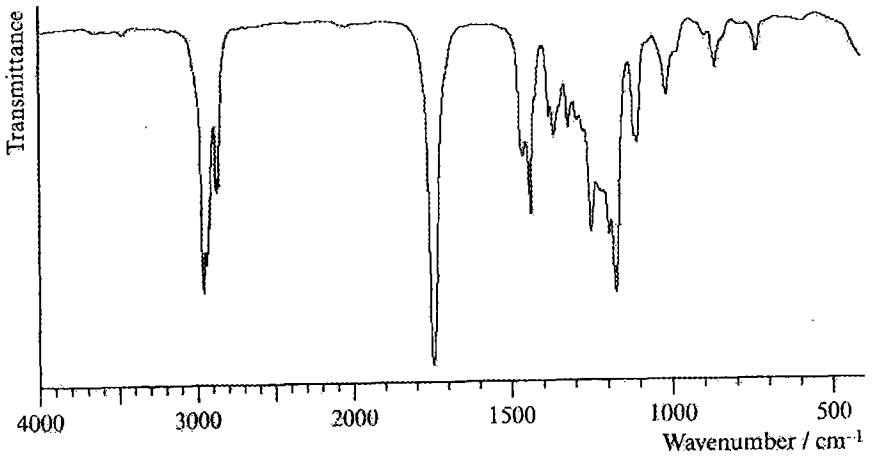
(6 marks)

(b) Assuming identical force constants (k) for ^{12}C-H and ^{12}C-D (D = deuterium), calculate the ratio $\bar{\nu}_{C-H}/\bar{\nu}_{C-D}$. Explain the significance of this ratio.

(6 marks)

(c) Analyse the following infrared spectrum of a compound having composition C, 64.6%; H, 10.8%; O, 24.6%. Assign a probable structure for the compound in agreement with the spectroscopic data.

(8 marks)



3. (a) What is Larmor frequency?

(3 marks)

(b) What is the Larmor frequency of ^{1}H, ^{13}C, ^{19}F and ^{31}P at 18.78 T?
(γ_{1H} = 267.512 MHz T^{-1}, γ_{13C}/γ_{1H} = 0.2514, γ_{19F}/γ_{1H} = 0.9408 and γ_{31P}/γ_{1H} = 0.4048)

(3 marks)

(c) What are satellite peaks? How satellite peaks can be differentiated from spinning sidebands?

(4 marks)

(d) Why the resonance of the carbon of $CDCl_3$ appears as a triplet in a ^{13}C NMR spectrum?

(4 marks)

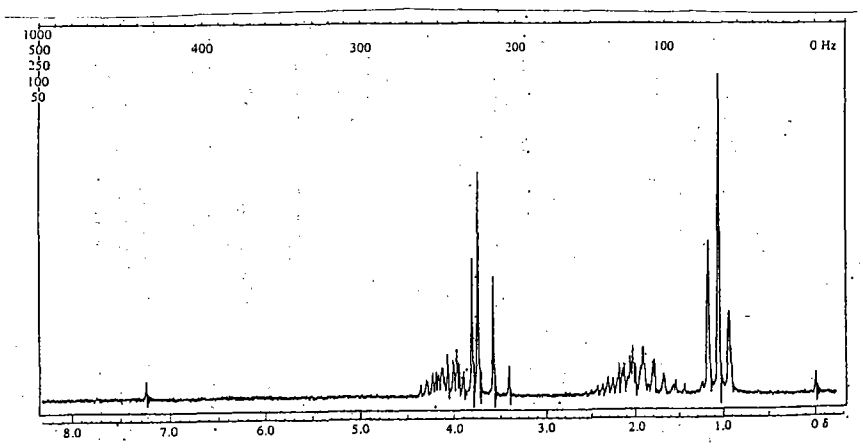
(e) Why NMR spectroscopy is said to be a less sensitive technique than IR or UV spectroscopy?

(6 marks)

4. (a) One of the isomers of dichloropropane, $C_3H_6Cl_2$, has a proton NMR spectrum consisting of a triplet (δ 3.7 ppm) and a quintet (δ 2.2 ppm). Determine its identity and explain your answer.

(5 marks)

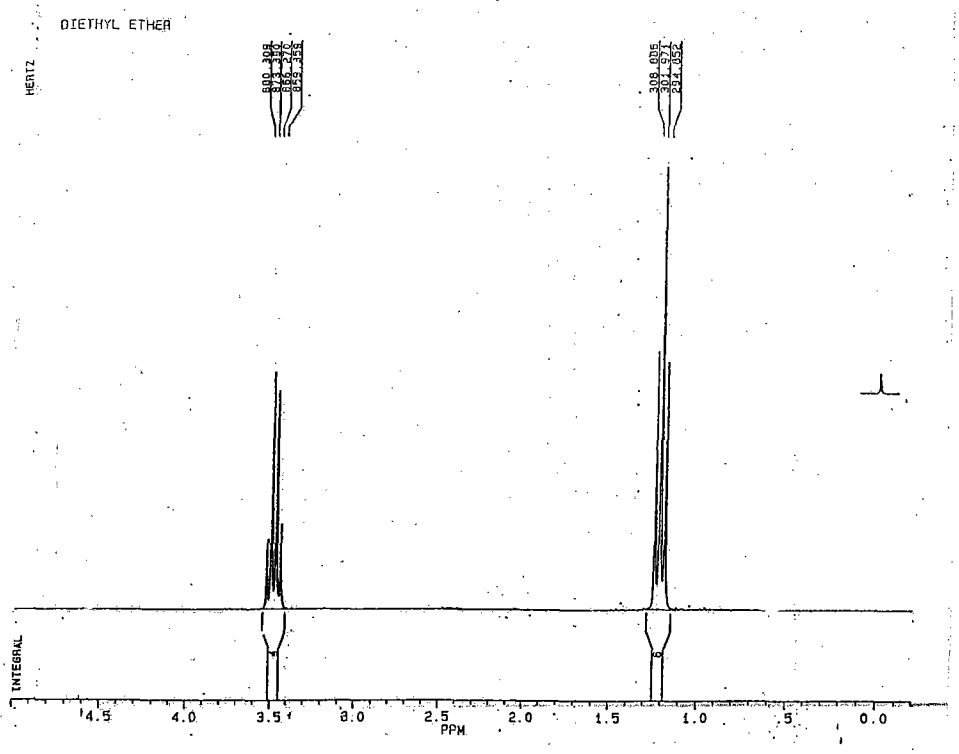
(b) The proton NMR spectrum of 1,2-dibromobutane was recorded at 30 °C and it is shown in figure 4.1. Explain its complexity.



Rajah 4.1 : Proton NMR spectrum of 1,2-dibromobutane at 30°C (60 MHz, in $CDCl_3$)

(5 marks)

(c) Describe in condensed format the data from the spectrum in figure 4.2



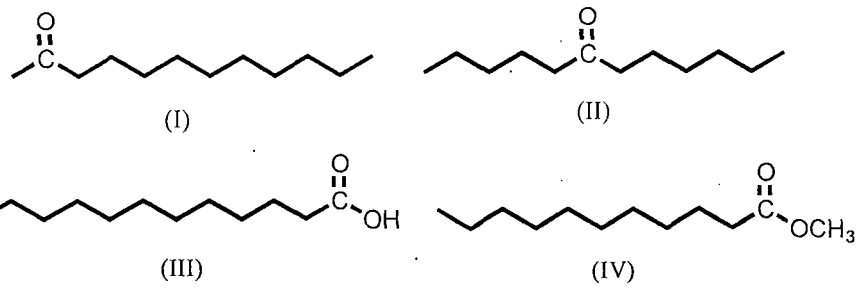
Rajah 4.2 : The 250-MHz ^{1}H spectrum of diethyl ether

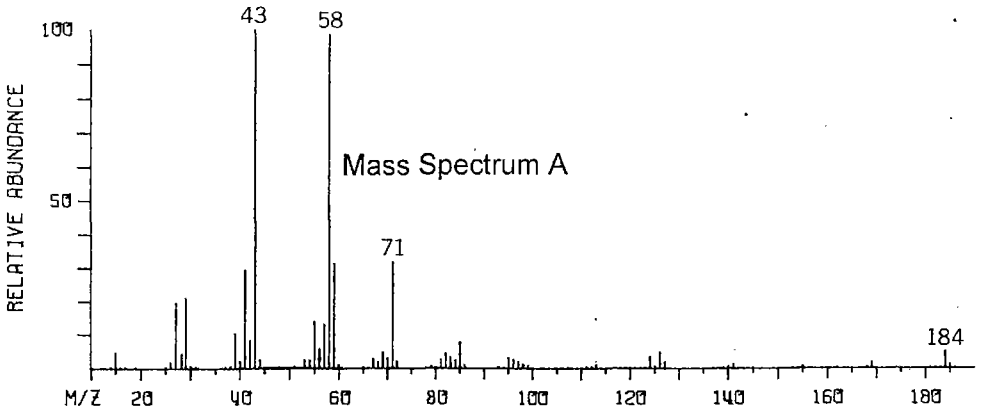
(5 marks)

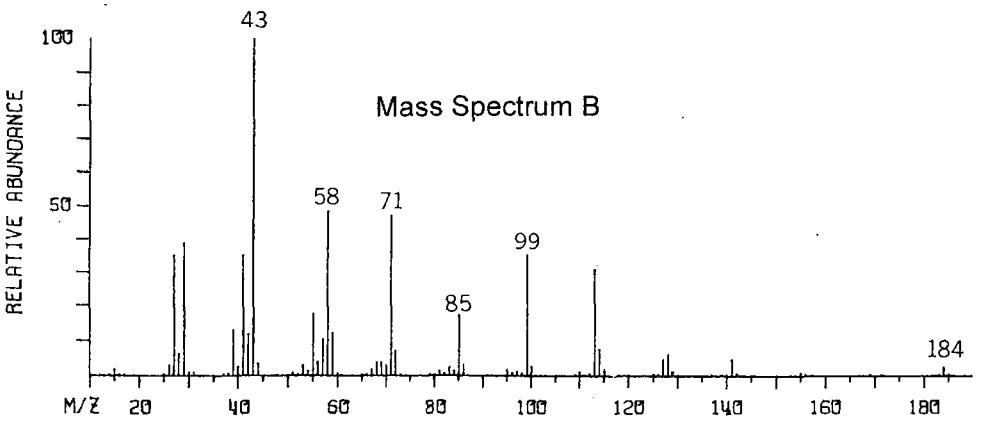
(d) Provide and explain two fundamental reasons why a 600 MHz NMR spectrometer is better than a 300 MHz NMR spectrometer?

(5 marks)

5. The mass spectra below (A – D) are for the following compounds;







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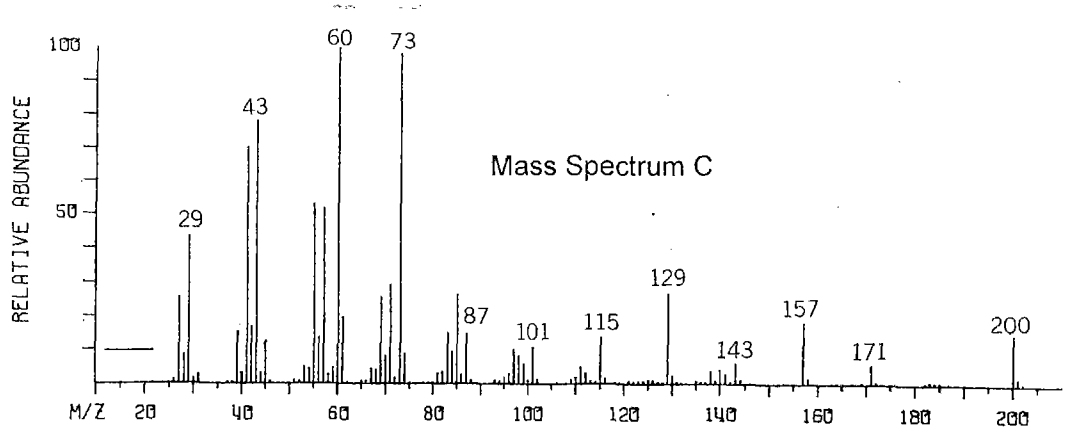
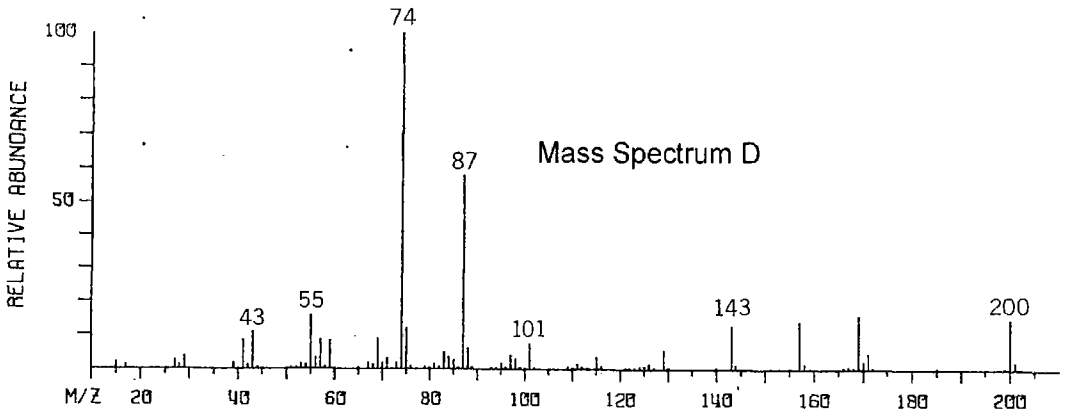




(a) Match these structures with their respective mass spectrum.

(8 marks)

(b) Draw the structure of the ion for the base peak in each spectrum.

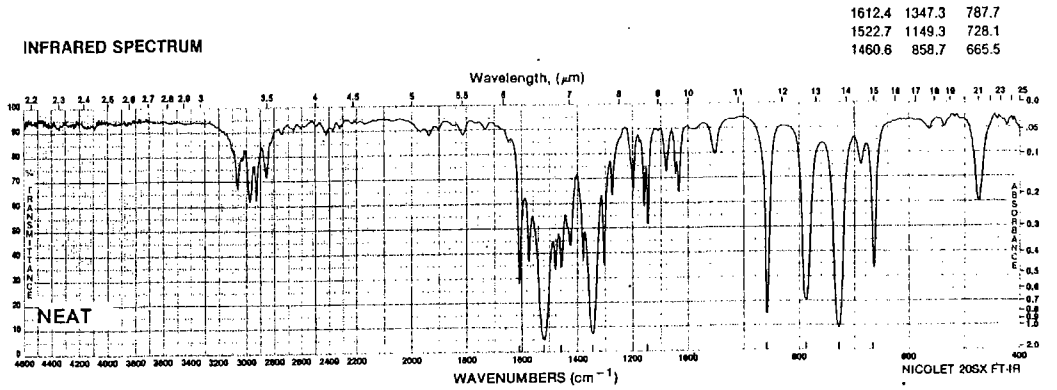
(4 marks)

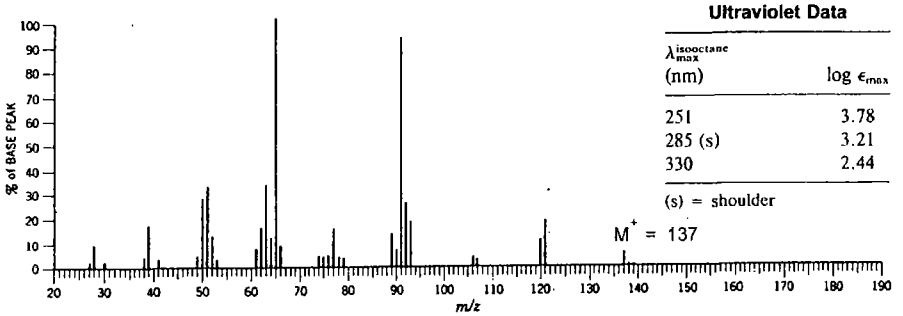
(c) Prove your choice by describing the fragmentation for **any one of the characteristic peaks, m/z**, in each spectrum.

(8 marks)

6. The following set of spectra is for an organic compound. Determine the structure of this compound. Briefly explain your structural elucidation.

(20 markah)

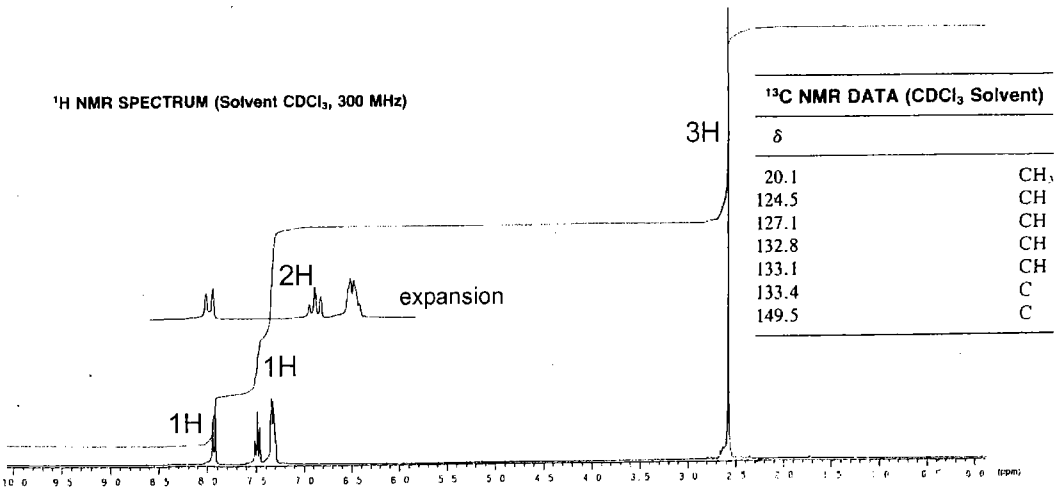




Ultraviolet Data

$\lambda_{max}^{isooctane}$ (nm)	log ϵ_{max}
251	3.78
285 (s)	3.21
330	2.44

(s) = shoulder



^{13}C NMR DATA ($CDCl_3$ Solvent)

δ	
20.1	CH_3
124.5	CH
127.1	CH
132.8	CH
133.1	CH
133.4	C
149.5	C

oooOooo