

---

UNIVERSITI SAINS MALAYSIA

First Semester Examination  
Academic Session 2004/2005

October 2003

**KAA 503 – Molecular Spectroscopy**

Time : 3 hours

---

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

Answer FIVE questions.

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

1. (a) With the aid of a labeled schematic diagram, explain the principles of a double beam UV-visible spectrophotometer. (5 marks)
- (b) Explain why the peaks observed in the UV-visible spectrum are broad rather than sharp. (5 marks)
- (c) Apply the Woodward rules (Table 1) to predict the  $\lambda_{\text{max}}$  for the three different steroids (A – C) shown below. Explain the method used in your calculation and correlate the calculated values with the structure of the compounds.

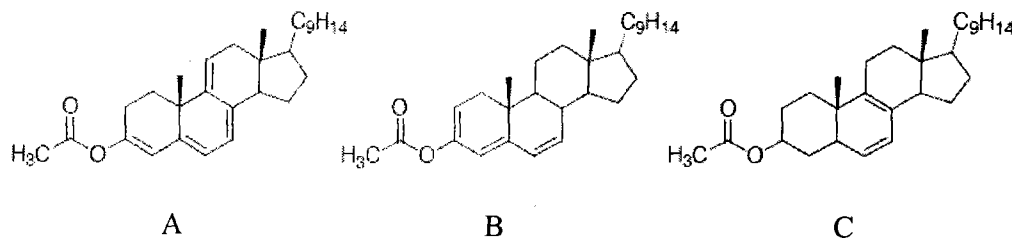


Table 1: Values of  $\lambda$  for the various components when applying the Woodward Rules for diene absorption

Component	$\lambda$ (nm)
Acyclic diene	217
Heteroannular diene	214
Homoannular diene	253
Double bond extending conjugation	30
Alkyl group or ring residue	5
Exocyclic double bond	5
O (acyl)	0
O (alkyl)	6
S (alkyl)	30
Cl, Br	5
N (alkyl) <sub>2</sub>	60

(10 marks)

2. (a) Whereas in IR dispersive instruments a narrow range of frequency, ideal monochromatic radiation, reaches the detector at any given time, in FTIR spectrometers, a broadband of IR frequencies reaches the detector all at once. By providing the schematic diagram of both types of instruments discuss the principles of operation of the monochromator in the dispersive instrument and the Michelson interferometer in the FTIR instrument.

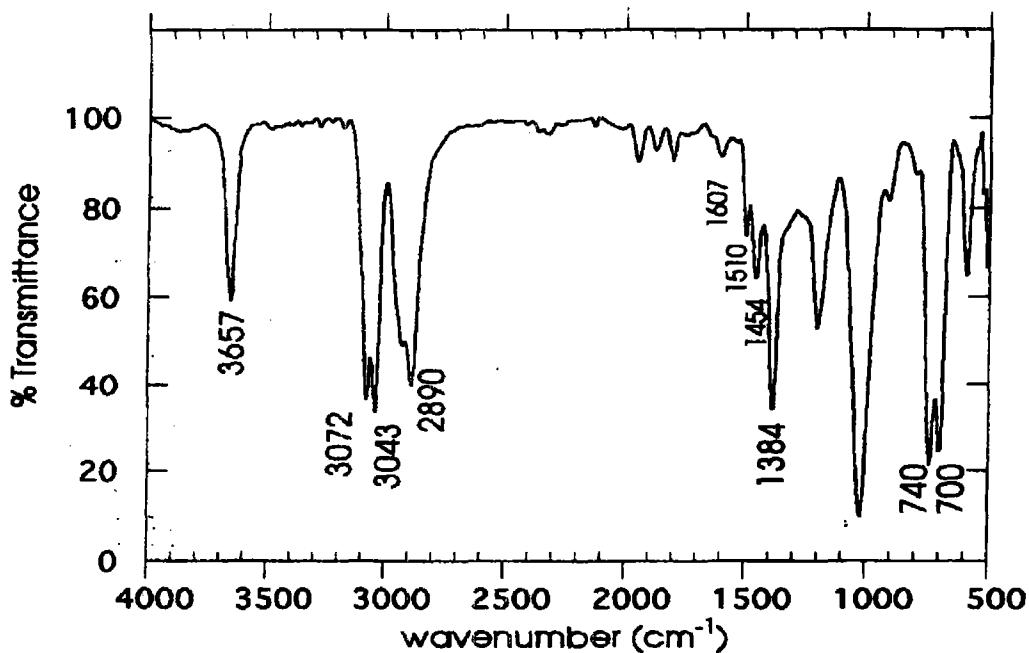
(10 marks)

- (b) The FTIR spectrum shown below belongs to one of the following compounds:

- A.  $\text{PhCH}_2\text{OH}$   
 B.  $\text{PhCH}_2\text{NH}_2$   
 C.  $\text{PhCH}_2\text{CHO}$

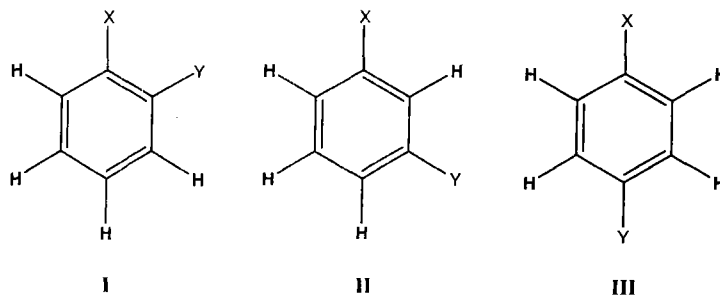
Identify the compound from the FTIR spectrum below and carry out the IR band assignment for the compound.

(10 marks)



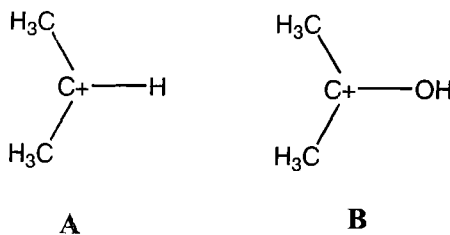
3. (a) Given the following magnetogyric ratios ( $\gamma$ ,  $10^6 \text{ rad T}^{-1} \text{ s}^{-1}$ )  $^1\text{H}$ , 267.52;  $^{13}\text{C}$ , 67.28;  $^{15}\text{N}$ , -27.13;  $^{19}\text{F}$ , 251.82;  $^{31}\text{P}$ , 108.39.
- (i) Determine the Larmor Frequency,  $\nu_L$ , for a  $^1\text{H}$ ,  $^{15}\text{N}$  and  $^{31}\text{P}$  when the magnetic flux density,  $B_0$ , is 14.09 T.
- (ii) Calculate the maximum possible NOE,  $\eta$ , in  $^1\text{H}\{-^{19}\text{F}\}$ ,  $^{13}\text{C}\{-^{19}\text{F}\}$  and  $^{15}\text{N}\{-^1\text{H}\}$  spectra. (6 marks)
- (b) What magnetic field strength is necessary in an instrument designed for studying  $^1\text{H}$  NMR at (i) 300 MHz, and (ii) 600 MHz? (Note:  $\gamma$  of  $^1\text{H}$  is  $267.52 \times 10^6 \text{ rad T}^{-1} \text{ s}^{-1}$ ). (3 marks)
- (c) The chemical shift position for the proton resonance in benzene ( $\text{C}_6\text{H}_6$ ) is  $\delta$  7.27. How many hertz is this from the TMS resonance when the instrument is working at (i) 60 MHz, and (ii) 400 MHz? (3 marks)
- (d) Besides gain in spectral resolution, state and explain one other advantage that can be obtained by acquiring a  $^1\text{H}$  NMR spectrum using an instrument working at 600 MHz as compared to that working at 60 MHz? (4 marks)
- (e) Explain why the sensitivity of NMR spectroscopy is relatively low compared to other absorption techniques such IR and UV spectroscopy. (4 marks)
4. (a) One of the isomers of chloronitropropane ( $\text{C}_3\text{H}_6\text{ClNO}_2$ ) has a  $^1\text{H}$  NMR spectrum consisting of a triplet at  $\delta$  5.8, an approximate quintet at  $\delta$  2.3 and another triplet at  $\delta$  1.1. What isomer is this? (5 marks)

- (b) How many carbon signals will each of the structure depicted below (**I**, **II** and **III**) exhibit if  $X \neq Y$ ? Repeat your analysis for the situation where  $X = Y$ .



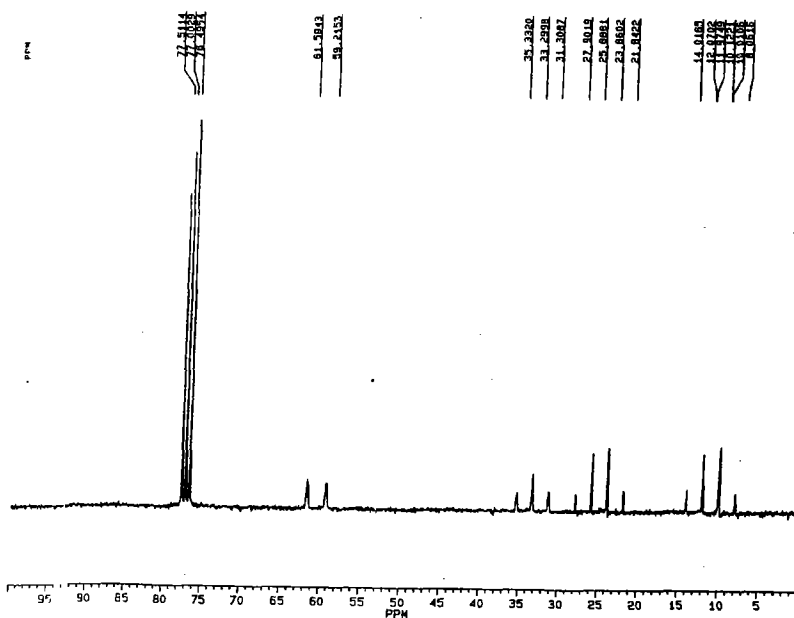
(5 marks)

- (e) One of the carbenium ions (**A** and **B**) shown below exhibits a  $^{13}\text{C}$  signal at  $\delta$  320.6 for the charged carbon, while the other's occurs at  $\delta$  250.3. Which chemical shift belong to **A** and which belong to **B**? Clarify your answer.

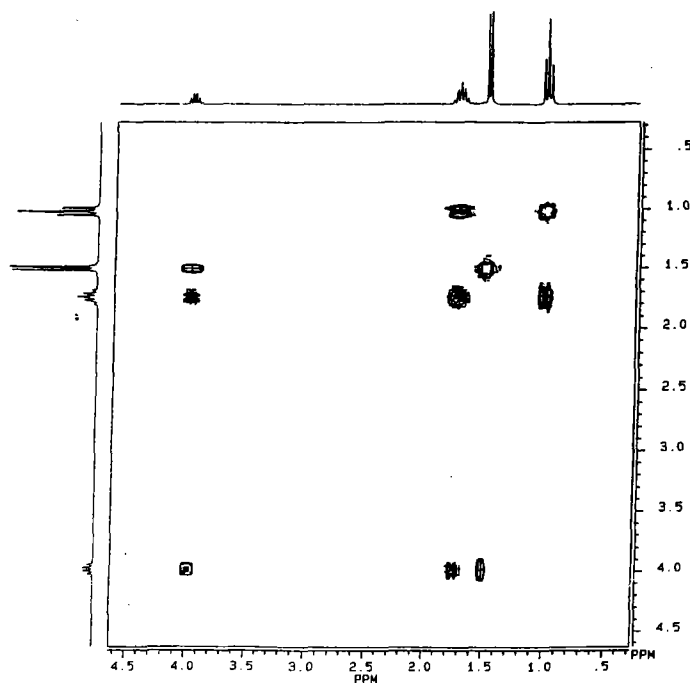


(5 marks)

- (d) Deduce the structure of the compound,  $C_4H_9Cl$ , whose  $^{13}C$  NMR (without proton decoupling) and 2D hydrogen COSY spectra are shown below.



The 62.5 MHz  $^{13}C$  spectrum of  $C_4H_9Cl$ , acquired without proton decoupling



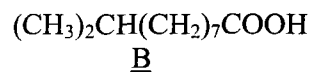
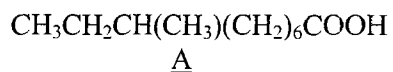
The 2D hydrogen COSY spectrum of  $C_4H_9Cl$

(5 mark)

...7/-

5. (a) Explain the principle of tandem mass spectrometry. (5 marks)

(b) Sketch the negative ion tandem mass spectra of the following two isomeric carboxylic acids. Explain how they can be differentiated.



(15 marks)

6. (a) Sketch the mass spectrum of  $\text{CH}_2\text{Br}_2$ . (5 marks)

(b) What resolution is required to distinguish between the molecular ions of  $\text{C}_{10}\text{H}_{21}\text{CHO}$  and  $\text{C}_{12}\text{H}_{26}$ ? (5 marks)

(c) Explain the principle of Fast Atom Bombardment as an ionization technique. (5 marks)

(d) Interpret the following peaks in the mass spectrum of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$   
 $m/z$  72, 57, 44, 43, 41, 39, 29, 15.

(5 marks)

Isotope	Relative abundance (%)	Mass (Da)
$^1\text{H}$	99.985	1.007825
$^2\text{H}$	0.015	2.0140
$^{12}\text{C}$	98.90	12.00000
$^{13}\text{C}$	1.10	13.003355
$^{16}\text{O}$	99.76	15.994915
$^{17}\text{O}$	0.04	16.000131
$^{18}\text{O}$	0.20	17.999160
$^{79}\text{Br}$	50.69	78.918336
$^{81}\text{Br}$	49.31	80.916289