UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2005/2006

November 2005

KAA 503 – Molecular Spectroscopy

Time: 3 hours

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

Answer any FIVE questions.

If you answer more than five questions, only the first five questions will be marked.

1. (a) Account for the differences in the observed λ_{max} values within each group of compounds below in terms of electronic transitions:

(i) $CH_2=CH_2$, 165 nm
$CH_2=CH-CH=CH_2$, 217 nm
$CH_2=CH-CH=CH-CH=CH_2$, 268 nm

(ii) C_6H_6 , 254 nm
$C_6H_5NH_2$, 280 nm
$C_6H_5NH_3^+$, 254 nm

(6 marks)

(b) UV-Visible Luminescence Spectroscopy refers to three spectroscopic techniques, namely:

(i) fluorescence

(ii) phosphorescence

(iii) chemiluminiscence

Briefly discuss the underlying principles of each technique in terms of the electronic transitions and energy transfer between electronic states.

(6 marks)

(c) The reaction between I^- and $[S_2O_8]^{2-}$ occurs as follows:

$$[S_2O_8]^{2-} + 2I^- \longrightarrow 2[SO_4]^{2-} + I_2$$

$$I_2 + I^- \longrightarrow [I_3]^-$$

Describe an experiment to determine the rate of reaction given that the species $[I_3]^-$ absorb at 353 nm with $\log\varepsilon = 4.41$.

(8 marks)

2. (a) For dimethlyarsine, $(CH_3)_2AsH$, an IR band thought to be due to As-H stretch, is observed at 2080 cm^{-1}. For the deuterated compound, $(CH_3)_2AsD$, the band is shifted to 1475 cm^{-1}. Do the data support the assignment of the band as an As-H stretch?

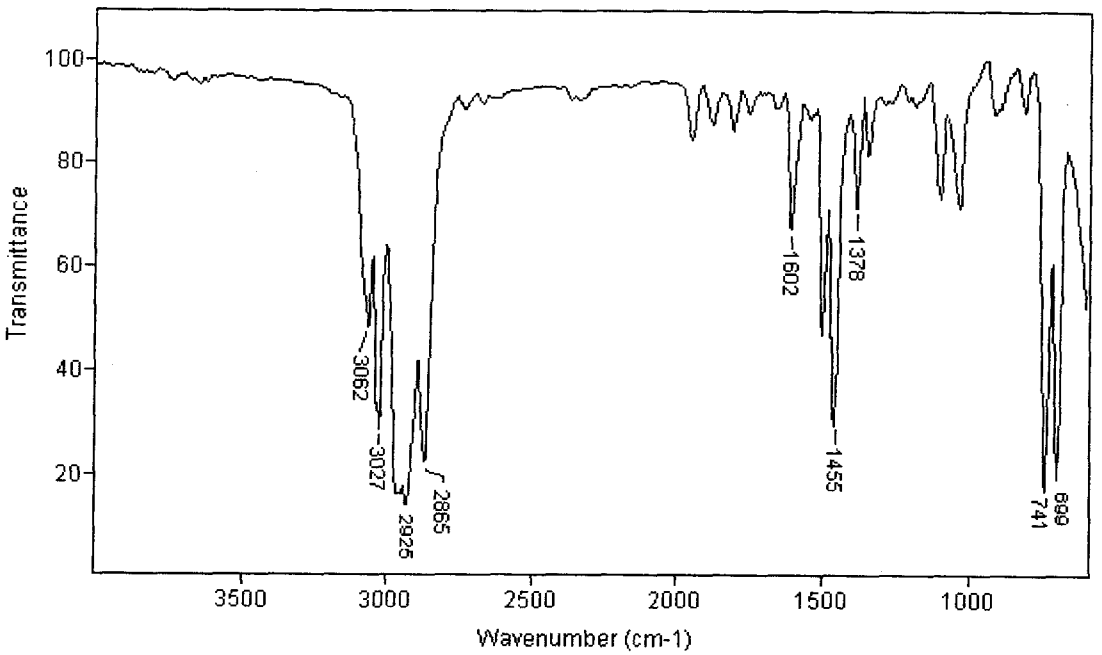
(6 marks)

(b) ATR, or Attenuated Total Reflectance is a technique that can be used for acquiring the IR spectrum of polymer membranes. Draw the schematic diagram of this FTIR accessory and explain the principles of the acquisition technique.

(6 marks)

(c) The IR spectrum of a compound having molecular formula C_8H_{10} is shown below. Identify the compound and assign the major peaks in the spectrum.

(8 marks)



3. (a) At what magnetic field strength do ^{13}C nuclei precess at a frequency of 200 MHz? (The magnetogyric ratio, γ, of ^{13}C is 67.264 x 10^6 rad T^{-1} s^{-1}).

(3 marks)

(b) At 18.79 T, what is the precession frequency of a ^1H nucleus? (The magnetogyric ratio, γ, of ^1H is 267.512 x 10^6 rad T^{-1} s^{-1}).

(3 marks)

(c) The chemical shift position for the proton resonance in $CHCl_3$ is δ 7.26. How many hertz is this from the TMS resonance when the instrument is working at 600 MHz?

(3 marks)

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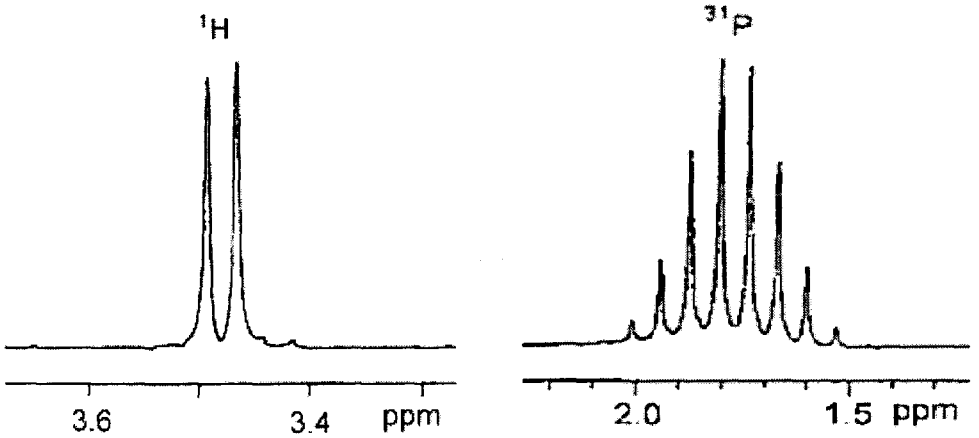
(d) Explain why the sensitivity of NMR spectroscopy is relatively low compared to that of IR spectroscopy.

(5 marks)

(e) The ^{1}H and ^{31}P NMR spectra of trimethyl phosphate, $(CH_3O)_3PO$, are given below. Rationalise the appearance of both spectra.



(6 marks)

4. (a) Draw proton multiplets for each of the following molecular fragments using the following typical values of coupling constants: $^{3}J_{HH}$ = 7 Hz; $^{2}J_{HF}$ = 60 Hz; $^{3}J_{HF}$ = 20 Hz. Indicate the sizes of the coupling constants in the multiplets and also give the relative intensities of individual spectral lines.

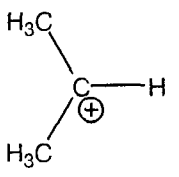
(i) $-OCH_2CH_3$

(ii) $-OCH(CH_3)_2$

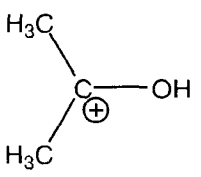
(iii) $-OCH_2CHFCl$

(6 marks)

(b) One of the carbocations (**A** and **B**) shown below exhibits a ^{13}C signal at δ 320.6 for the charged carbon, while the other's occurs at δ 250.3. Which chemical shift belong to **A** and which belong to **B**? Clarify your answer.



A



B

(5 marks)

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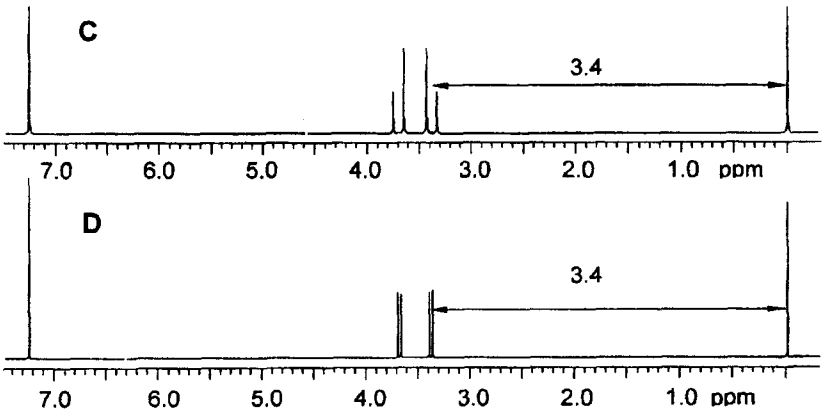
(c) Two ^{1}H NMR spectra, acquired using spectrometers with different magnetic field strengths, are shown below. The doublets (J_{HH} = 10 Hz) belong to two mutually coupled protons.

(i) Which of the two spectra, **C** or **D**, was acquired using the spectrometer with a stronger magnetic field? Explain your reasoning.

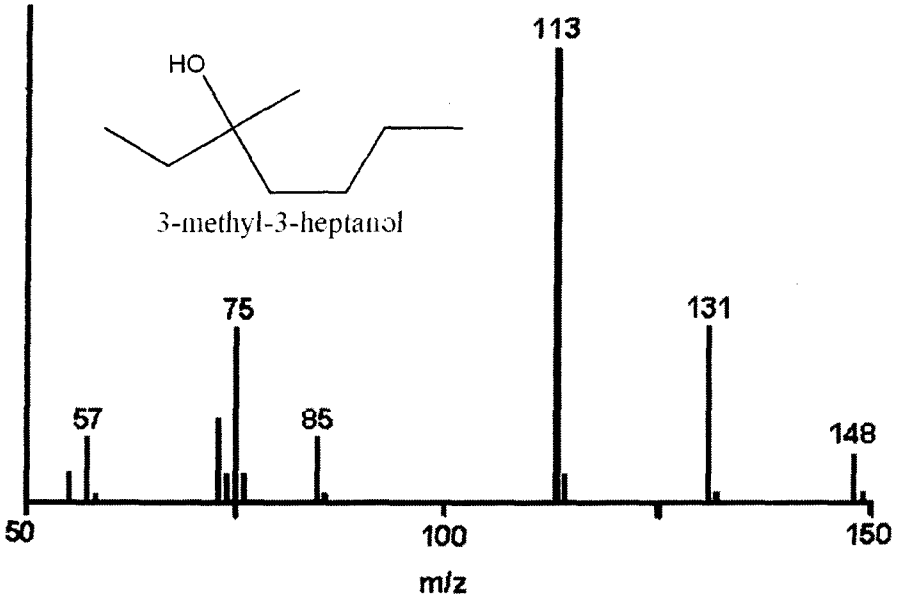
(ii) Why the intensities of the lines of the two doublets are distorted in spectrum **C** but not **D**?

(iii) Calculate the field strength in Tesla of the magnet that was used to acquire spectrum **C**. The magnetogyric ratio of ^{1}H is 267.512 x 10^{6} rad T^{-1} s^{-1}. [Use the coupling constant and spectrum **C** to work out your answer.]



(9 marks)

5. (a) The mass spectrum below is for 3-methyl-3-heptanol taken under chemical ionization condition using ammonia (NH_3) as reagent gas. Suggest the structures of all the ions whose m/z peaks are shown in the spectrum.



(5 marks)

(b) List down five types of ionization techniques in mass-spectrometry and explain in detail one of the techniques.

(5 marks)

(c) Describe how a Time of Flight mass spectrometer analyse the mass of ions produced after ionization and fragmentation of a compound in the ionization chamber. The equation for mass analysis should be included in your description.

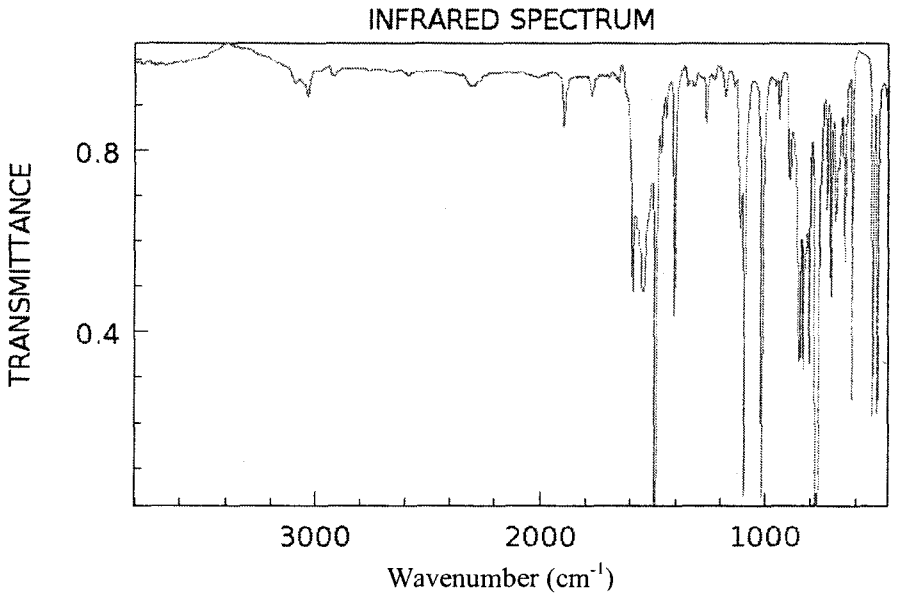
(5 marks)

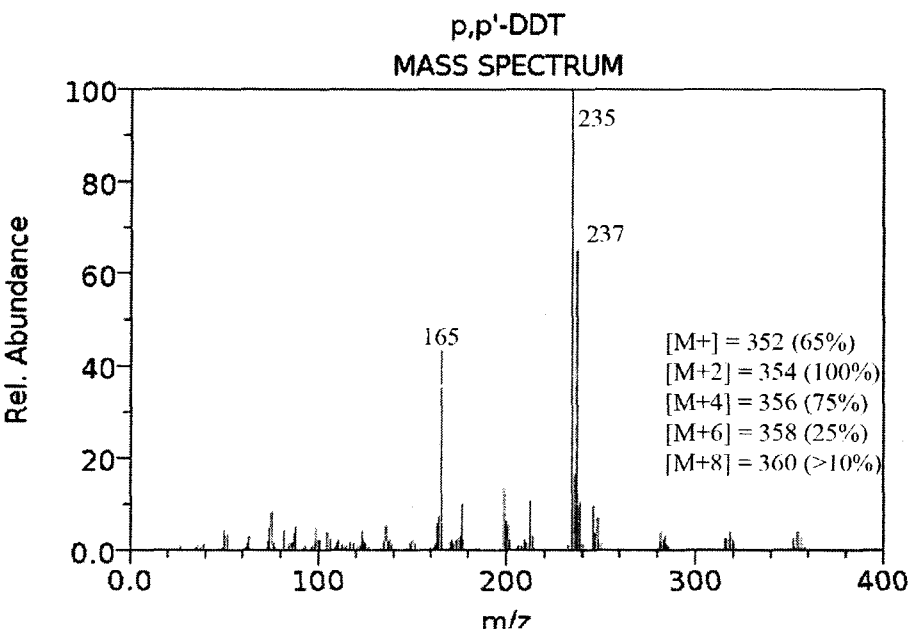
(d) Discuss the factors that influence the ion abundance for a particular compound in the mass spectrum.

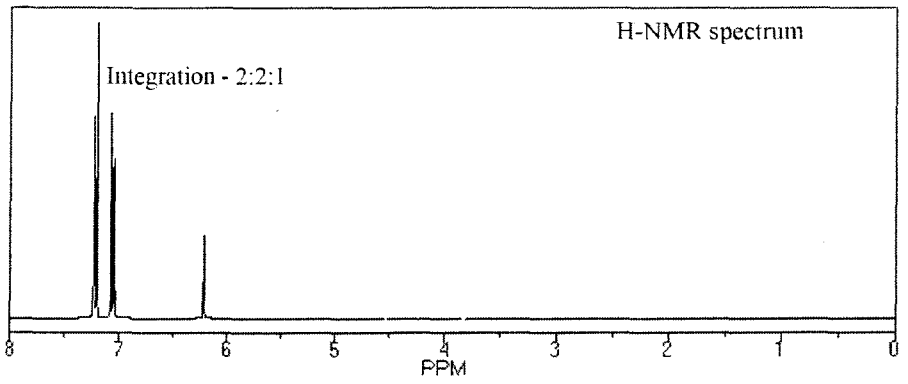
(5 marks)

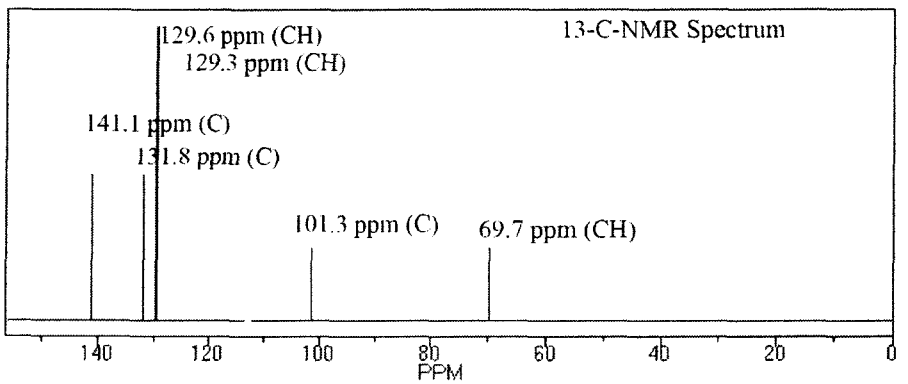
6. p,p'-DDT is a molecule with five chlorine atoms which had been used as an anti-malarial pesticide. The spectral data for this compound are shown below. Determine the structure of p,p'-DDT and provide detailed explanation on your structural determination.

(20 marks)






H-NMR spectrum
Integration - 2:2:1
8
7
6
5
4
3
2
1
0
PPM


13-C-NMR Spectrum
129.6 ppm (CH)
129.3 ppm (CH)
141.1 ppm (C)
131.8 ppm (C)
101.3 ppm (C)
69.7 ppm (CH)
140
120
100
80
60
40
20
0
PPM

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