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UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2003/2004

October 2003

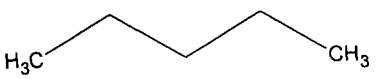
KAA 503 – Molecular Spectroscopy

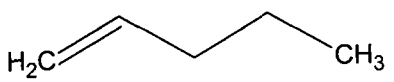
Time : 3 hours

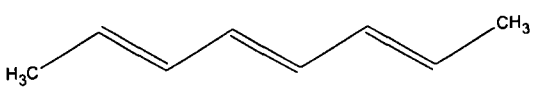
Please make sure this paper consists of SEVEN printed pages before answering the questions.

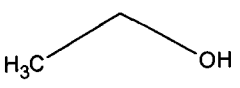
Answer FIVE questions. Only the first five questions answered by the candidate will be marked.

1. (a) Suggest which types of transitions ($\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$) give rise to significant features in the electronic spectra of

(i) pentane, 

(ii) pent-1-ene, 

(iii) octa-2,4,6-triene, 

(iv) ethanol, 

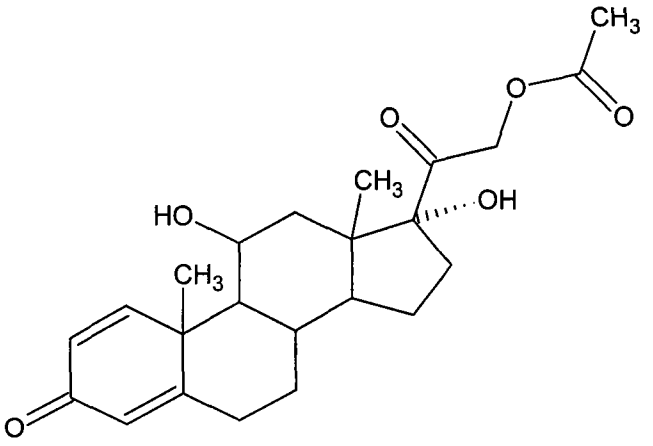
Give reasons for your answers.

(8 marks)

(b) Discuss the deviations from linearity of the Beer Lambert Law in terms of fundamental, instrumental and chemical aspects.

(12 marks)

2. (a) Prednisolone Acetate has the following structure:



(i) Estimate the infrared functional group frequencies of all the functional groups present.

(ii) Calculate λ_{max} for the UV spectrum of the compound.

(10 marks)

(b) Explain what is meant by the occurrence of Fermi resonance between the fundamental bands and overtones in the infrared spectrum of a compound.

(4 marks)

(c) The table below shows the frequency, $\bar{\nu}$ and the force constant, k of several diatomic molecules. Explain the correlation between the frequency ($\bar{\nu}$), force constant (k) dan reduced mass (μ) based on the following data:

Molecule	$\bar{\nu}$ /cm^{-1}	k / (N m^{-1})
HCl	2885	4.8×10^2
Cl_2	557	3.2×10^2
Br_2	321	2.4×10^2
CO	2143	1.9×10^4
NO	1876	1.6×10^4

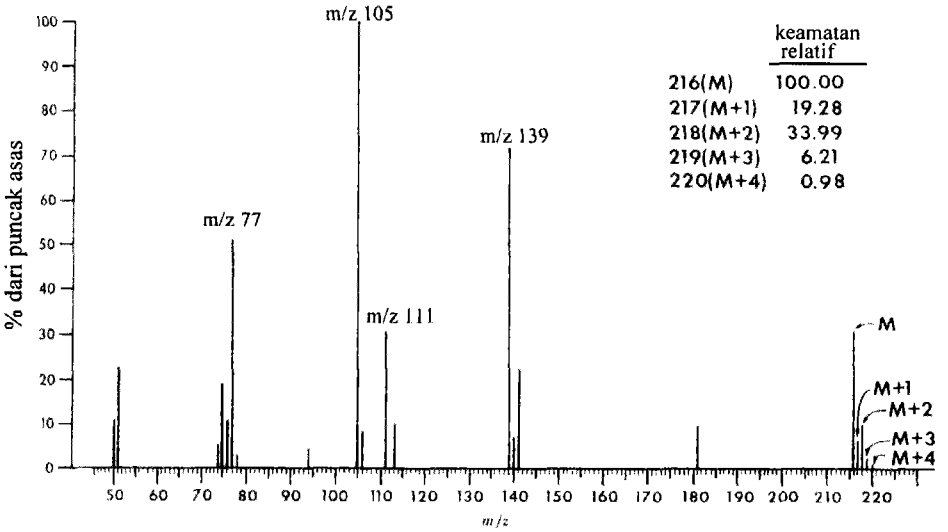
(6 marks)

3. (a) The mass spectrum below is for *p*-klorobenzofenone (*p*-Cl-C_6H_4-COC_6H_5).

(i) Draw all the structures of the fragments ions whose m/z values are shown.

(ii) Write down the formula with exact isotop number for each of the ion in the molecular ion group (M^+ hingga $[M+4]^+$).

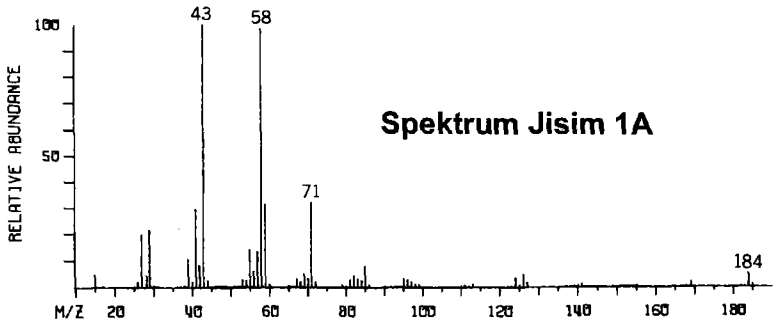
(8 marks)

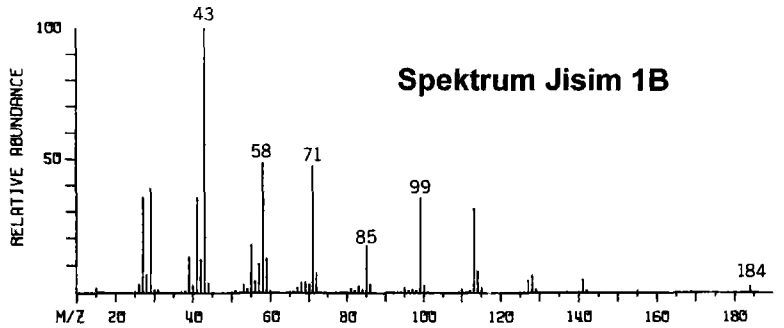


(b) Determine the structure of the following pairs of isomers from their respective mass spectra.

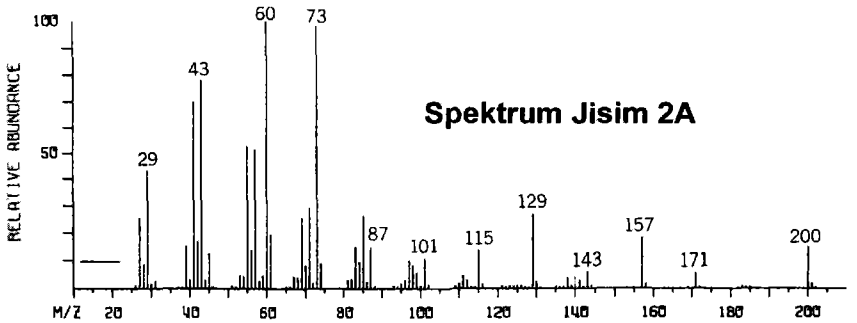
(12 marks)

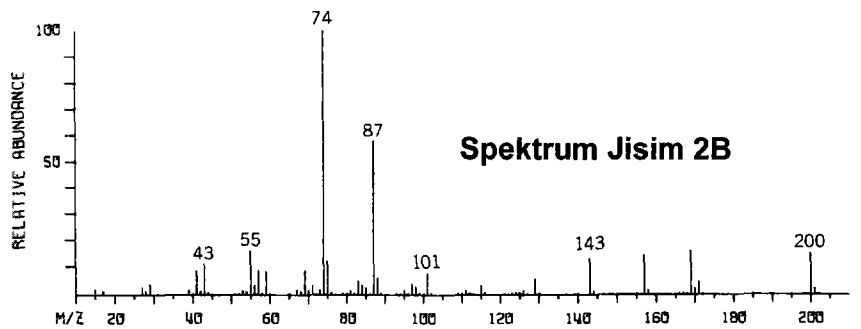
(i) Mass spectra 1A dan 1B for isomer with molecular formula $C_{12}H_{24}O$.





(ii) Mass spectra 2A dan 2B for isomer with molecular formula $C_{12}H_{24}O_2$.

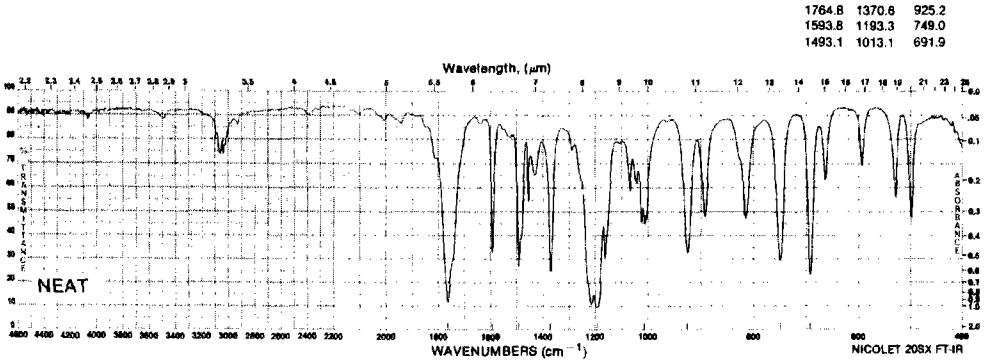




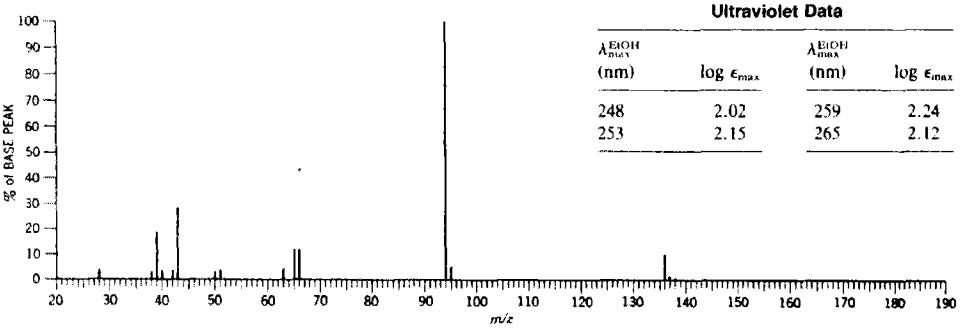
4. Describe how the structure of compound X may be determined from the following set of spectra.

(20 marks)

INFRARED SPECTRUM



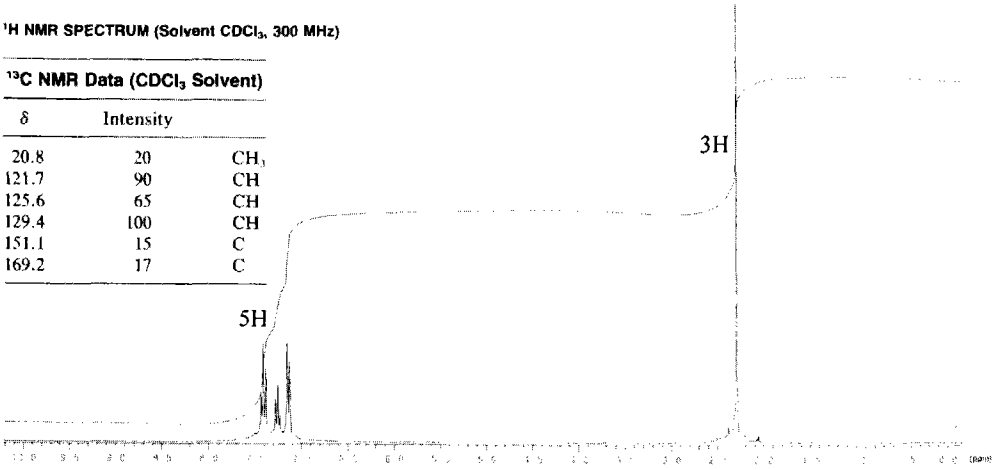
MASS SPECTRAL DATA (Relative Intensities)



Ultraviolet Data

λ_{max}^{EtOH} (nm)	log ϵ_{max}	λ_{max}^{EtOH} (nm)	log ϵ_{max}
248	2.02	259	2.24
253	2.15	265	2.12

^{1}H NMR SPECTRUM (Solvent $CDCl_3$, 300 MHz)



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

δ	Intensity	
20.8	20	CH_3
121.7	90	CH
125.6	65	CH
129.4	100	CH
151.1	15	C
169.2	17	C

5. (a) There are two FT-NMR spectrometers at the School Of Chemical Sciences, Universiti Sains Malaysia: Bruker Avance-300 and Bruker Avance-400. What is the Larmor frequency (**v**) of ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{31}P nuclei for each of the spectrometer? (γ for ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{31}P is 267.512×10^{6}, 67.264×10^{6}, 251.667×10^{6}, -53.142×10^{6}, and 108.29×10^{6} rad T^{-1} s^{-1}, respectively).

(8 marks)

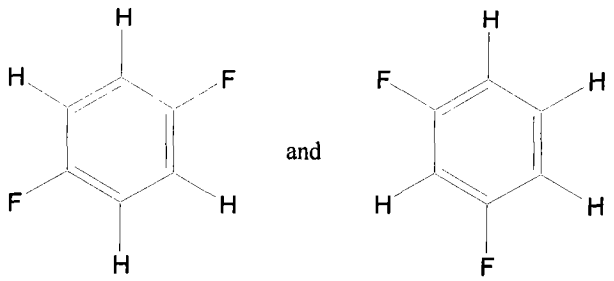
(b) What is a rotating frame of reference?

(2 marks)

(c) Write the pulse sequence and briefly described the behavior of the net nuclear magnetic moment (**M**) in a spin echo experiment.

(6 marks)

(d) Identify and explain briefly the type of hydrogen/fluorine spin system (according to Pople notation) for the structures below:

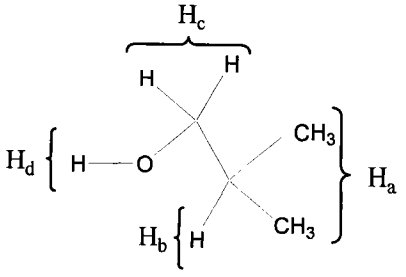


(4 marks)

6. (a) Why ^{1}H resonance of tetramethylsilane (TMS) has satellite peaks? Provide two ways of differentiating satellite peaks from spinning side bands.

(4 marks)

(b) Predict in detail and draw the 300-MHz spectrum (with the x axis approximated to 0.01 ppm divisions) of isobutyl alcohol based on the following spectroscopic parameters: δ for H_a, H_b, H_c and H_d is 0.915, 1.76, 3.40 and 1.98 ppm, respectively; $^{3}J_{ab} = 6.7$ Hz, $^{3}J_{bc} = 6.6$ Hz, $^{3}J_{cd} = 5.6$ Hz.



(8 marks)

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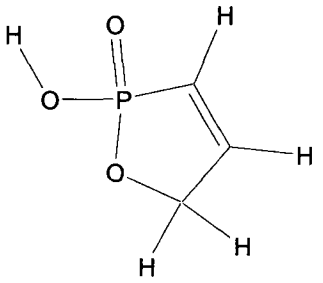
(c) Describe the ^{1}H NMR spectrum of isobutyl alcohol in condensed format.

(3 marks)

(d) Predict the multiplicity of each signal in the ^{1}H and ^{31}P NMR spectra of the molecule represented by the structure below.



(5 marks)

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