UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2011/2012

January 2012

KAA 503 – Molecular Spectroscopy
[Spektroskopi Molekul]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of TWENTY FOUR pages of printed material before you begin the examination.

Instructions:

Answer **FIVE** (5) questions. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

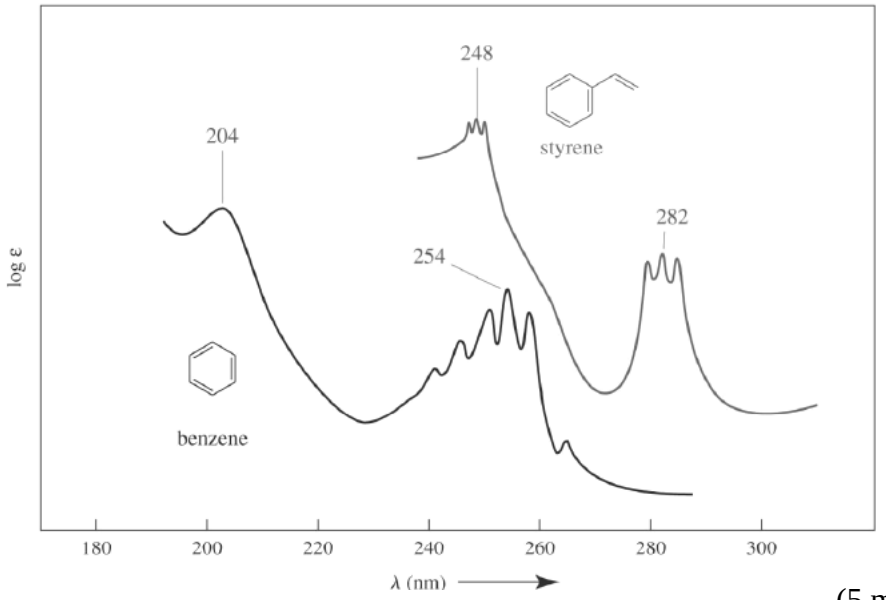
Answer each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

In the event of any discrepancies, the English version shall be used.

…2/-

1. (a) The UV-Vis spectra of benzene and styrene are shown below. Explain the differences in the peak positions in both spectra.



(5 marks)

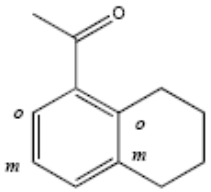
(b) In fluorescence spectroscopy, the electronic transition occurs between two singlet states, whereas in phosphorescence spectroscopy the electronic transition occurs between a triplet and singlet state. Explain how the transitions occur and result in a difference of emission lifetimes.

(5 marks)

(c) Molar absorbtivities from $n \rightarrow \pi^*$ transitions are relatively low, and range from 10 to 100 L mol^{-1} cm^{-1} . Transitions from $\pi \rightarrow \pi^*$ normally give molar absorbtivities between 1000 and 10,000 L mol^{-1} cm^{-1}. Illustrate each transition with one example and give reasons for these observations.

(5 marks)

(d) Use the benzoyl correlations given below to predict the λ_{max} of the following compound.



BENZOYL CORRELATIONS

X-C6H4-CO-Z

Base:

where Z = H, 250;	X-C6H4-COH (benzaldehydes)
where Z = aliphatic, 246;	X-C6H4-COR (acetophenones, etc.)
where Z = O-H / O-R, 230	X-C6H4-COOH / X-C6H4-COOR (acids / esters)

Auxochromes:

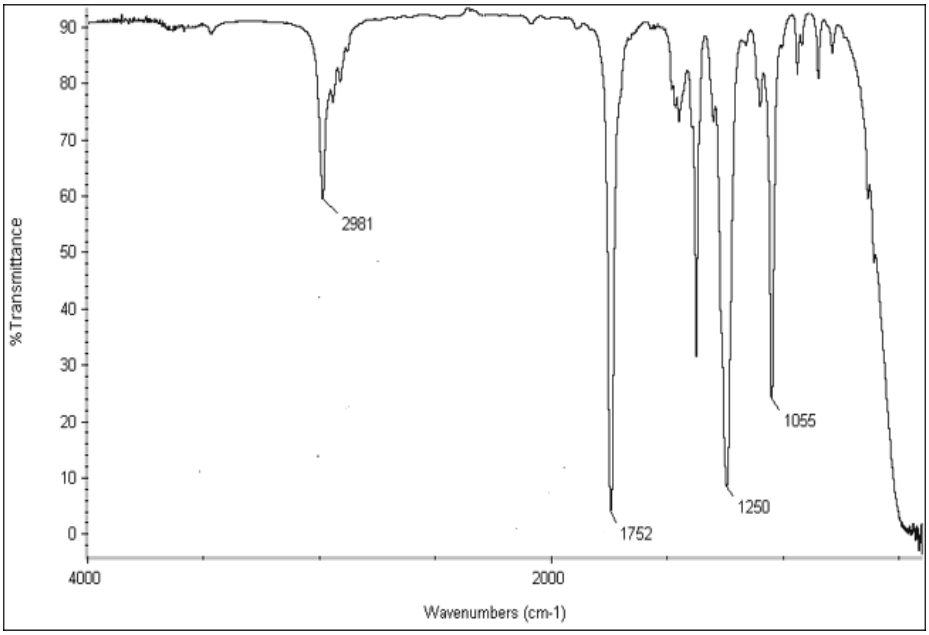
X	***o-,m-***	***p-***
NR_2	20	85
O-H, O-R	7	25
aliphatic	3	10
Br	2	15
Cl	0	10

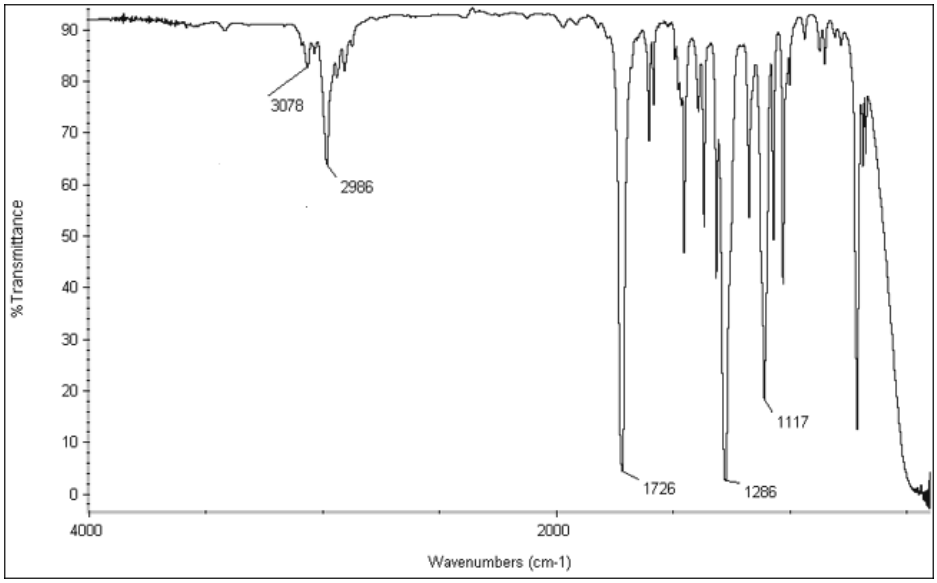
(5 marks)

2. (a) Describe and explain two advantages of FT-IR spectroscopy over dispersive IR spectroscopy.

(4 marks)

(b) The two FTIR spectra below are those of ethyl benzoate and ethyl acetate. Identify which spectrum belongs to which compound and assign the labelled bands to the corresponding vibrations of the molecules.





(6 marks)

(c) Solid mixtures with different % concentrations of caffeine in starch were prepared, and the ratio of the absorbance at 743 and 995 cm^{-1} for caffeine and starch were computed. The caffeine concentration and corresponding measured absorbance ratio, A_{743}/A_{995}, for each mixture is given below. The A_{743}/A_{995} ratios for several unknown samples containing caffeine were also measured. The results are shown below. What were the concentrations of caffeine in the mixtures *A* – *D*?

% Concentration of caffeine	A_{743}/A_{995}
2	0.16
4	0.36
6	0.56
8	0.76
10	0.96

Mixture of caffeine and starch	A_{743}/A_{995}
A	0.30
B	0.53
C	0.61
D	0.88

(5 marks)

(d) Infrared spectroscopy is uniquely suited to the analysis of thin films on surfaces, especially shiny metallic surfaces. Very small quantities of mold release agents, lubricating oils, greases, cutting fluids, and polishing compounds can all be detected and identified by FTIR. Discuss the FTIR technique used in the plating industries to detect plating failures due to contamination on metal surfaces.

(5 marks)

3. (a) Predict the multiplicity and indicate the relative intensity of each ^{1}H NMR signal for the following molecule (note that coupling by P can be observed via three bonds):

(6 marks)

(b) Using the coupling constants values of $^{3}J_{HH}$ = 7 Hz and $^{2}J_{HF}$ = 60 Hz, draw the ^{1}H multiplets for the following molecule:

(6 marks)

(c) What magnetic field strength is necessary in an instrument designed for studying ^{1}H NMR at (i) 300 MHz, and (ii) 600 MHz? (Note: γ of ^{1}H is 267.52×10^{6} rad T^{-1} s^{-1}).

(4 marks)

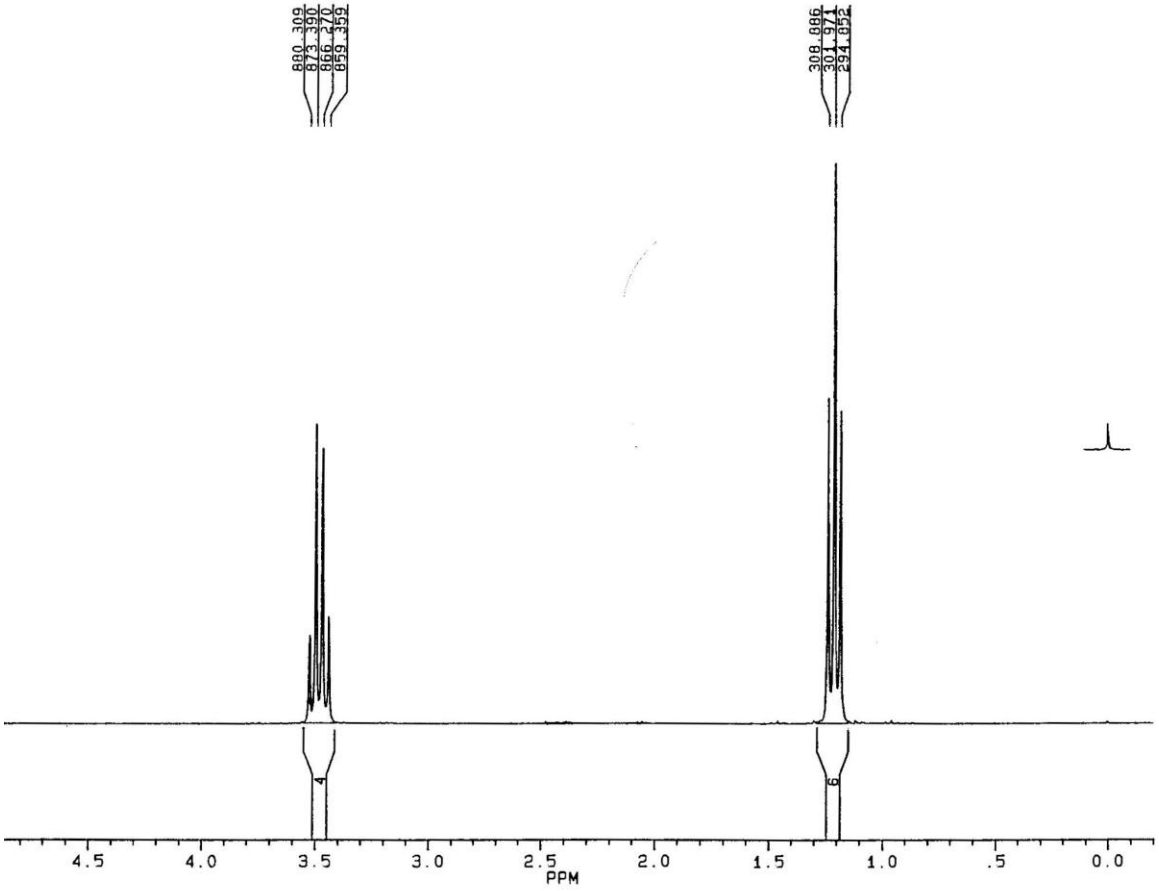
(d) Calculate the maximum NOE, η, for proton-decoupled ^{13}C and ^{31}P NMR spectra using the following information: the magnetogyric ratio,γ, for ^{1}H, ^{13}C and ^{31}P is 267.512×10^{6} rad T^{-1} s^{-1}, 67.264×10^{6} rad T^{-1} s^{-1} and 108.29×10^{6} rad T^{-1} s^{-1}, respectively.

(4 marks)

4. (a) One of the isomers of bromonitropropane, $C_3H_6BrNO_2$, has a proton NMR spectrum consisting of a triplet at δ 5.9, an approximate quintet at δ 2.4 and a triplet at δ 1.3. What is the structure of this isomer?

(6 marks)

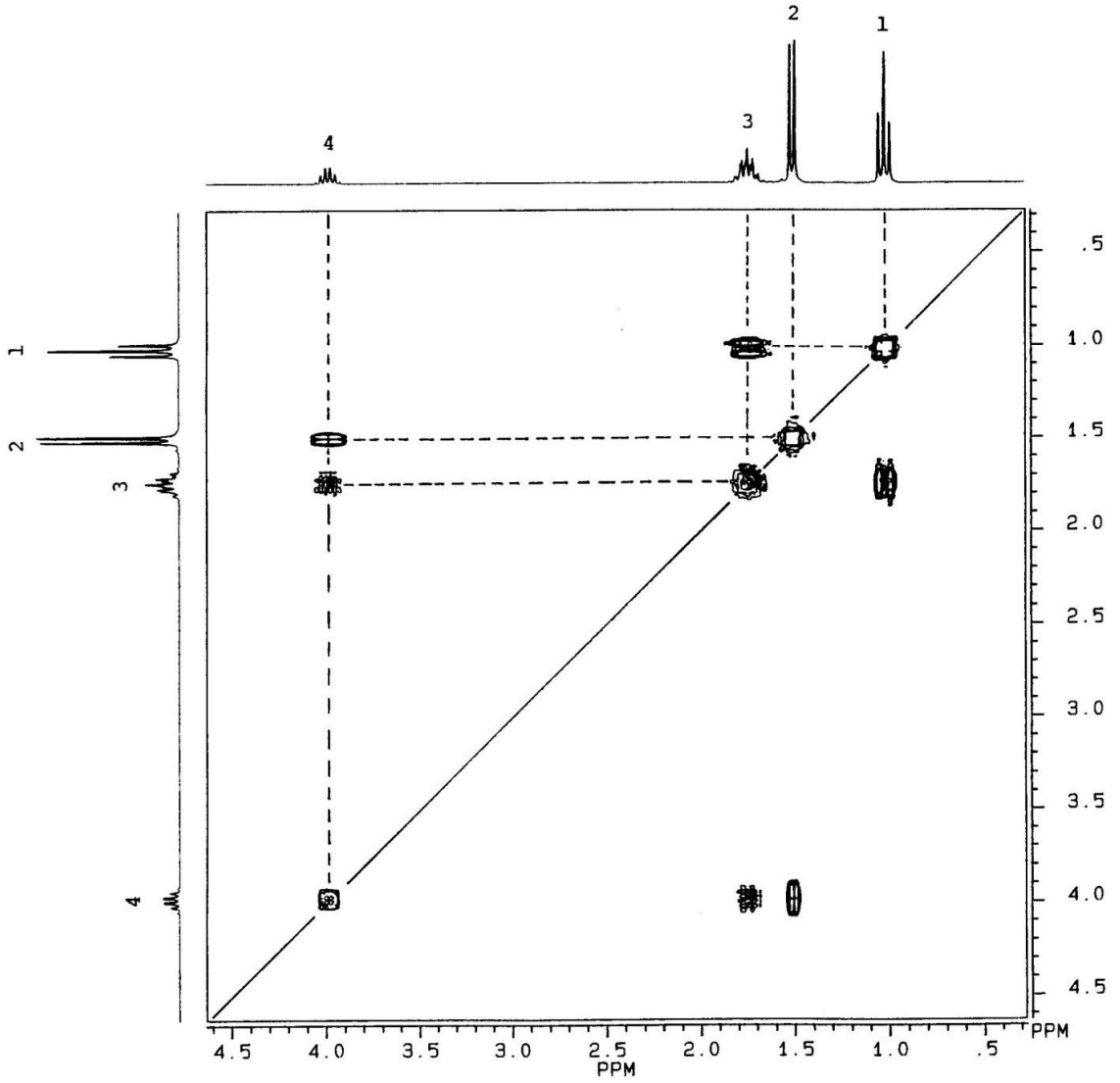
(b) Describe the NMR spectrum of diethyl ether depicted below in the form of condensed format.



The 250-MHz ^{1}H spectrum of diethyl ether.

(6 marks)

(c) Deduce the structure of C_4H_9Cl using its ^1H-^1H COSY spectrum shown below.



^1H-^1H COSY spectrum of C_4H_9Cl

(8 marks)

5. (a) For molecular mass spectrometry, explain the difference between Electron Impact ionization (EI) and Chemical Ionization (CI), and state when each of them could be used.

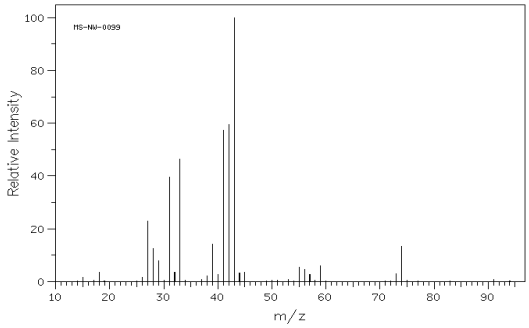
(6 marks)

(b) Examine the mass spectra of the three isomers of butanol shown below. Match each isomer to its spectra, and briefly explain how you choose which spectrum represents which isomer.

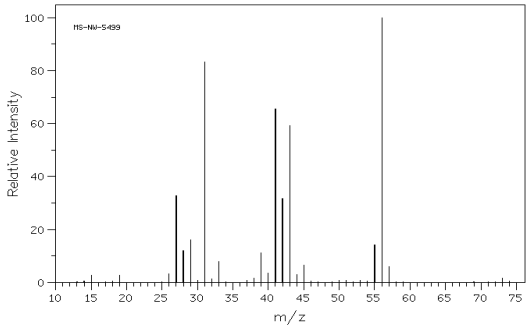
(i) Butan-1-ol

(ii) Butan-2-ol

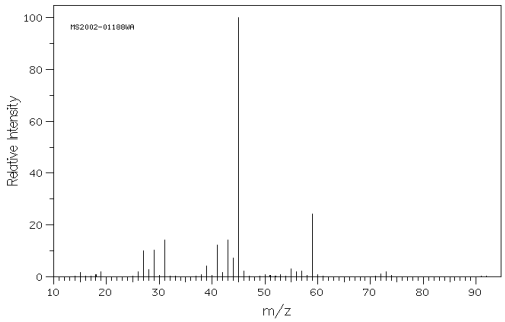
(iii) 3-Methylpropan-1-ol



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
15	1.5	31	39.7	41	57.3	56	4.6
18	3.4	32	3.6	42	59.4	57	2.8
26	1.6	33	46.3	43	100.0	59	5.9
27	23.0	38	2.1	44	3.2	73	3.1
28	12.4	39	14.1	45	3.6	74	13.3
29	8.0	40	2.8	55	5.5		



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
15	2.8	31	83.4	41	65.6	56	100.0
19	2.8	32	1.4	42	31.6	57	5.9
26	3.2	33	7.9	43	59.3	73	1.7
27	32.7	38	1.7	44	3.0		
28	12.1	39	11.2	45	6.6		
29	16.1	40	3.6	55	14.1		



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
15	1.7	31	14.1	45	100.0	72	1.0
19	1.8	39	4.1	46	2.2	73	1.9
26	1.8	41	12.2	55	3.0		
27	10.1	42	1.5	56	2.0		
28	2.6	43	14.1	57	2.2		
29	10.2	44	7.2	59	24.3		

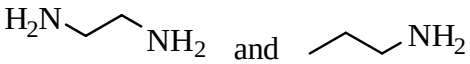
(6 marks)

(c) What are the major differences expected between the mass spectra of the following isomeric compounds?

(i) $CH_3CH_2CH_2OH$ and $CH_3OCH_2CH_3$.

(ii) $CH_2(Cl)CH_2CH_2Cl$ and $CH(Cl)_2CH_2CH_2Cl$.

(iii) 3-pentanone and 3-methyl-2-butanone.

(iii)  and

(4 marks)

(d) Show equations for the major fragmentations you would expect from the molecular ions of the following compounds. List the *m/z* of the product ions.

(i) $C(CH_3)_3OCH_2CH_3$

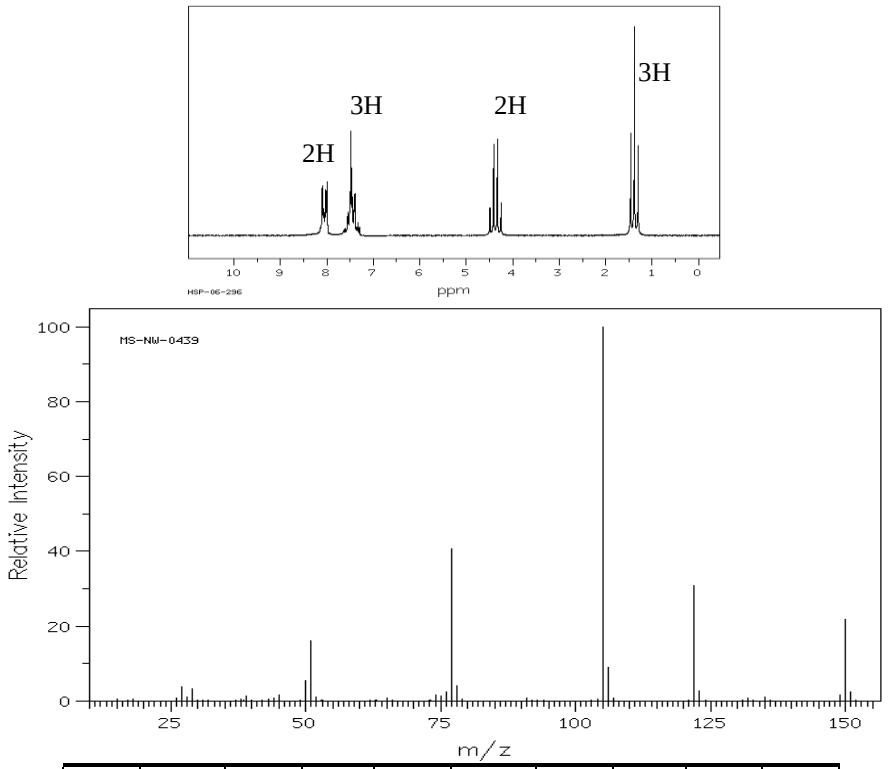
(ii) $CH_3(CH_2)_3CH_3$

(4 marks)

6. (a) Explain the principles of time-of-flight and ion trap mass analyzers.

(6 marks)

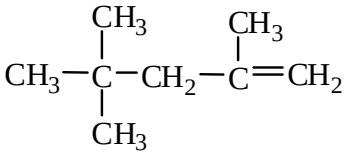
(b) ^{1}HNMR and mass spectrometry spectra and data (*m/z*) for an unknown compound are given below. Use both of the provided spectra to elucidate the structure of the compound. What fragment is responsible for the peaks at *m/z* 105 and 77?



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
50	5.4	51	16	77	40.6	78	4.0	105	100
122	30.7	123	2.6	150	21.8	151	2.3		

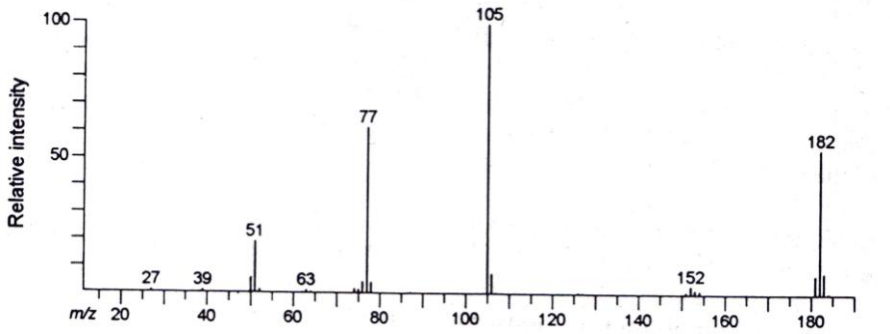
(5 marks)

(c) Show the equation to account for the major fragment ions that occur at *m/z* 97 and *m/z* 57 in the mass spectrum of the following compound.



(3 marks)

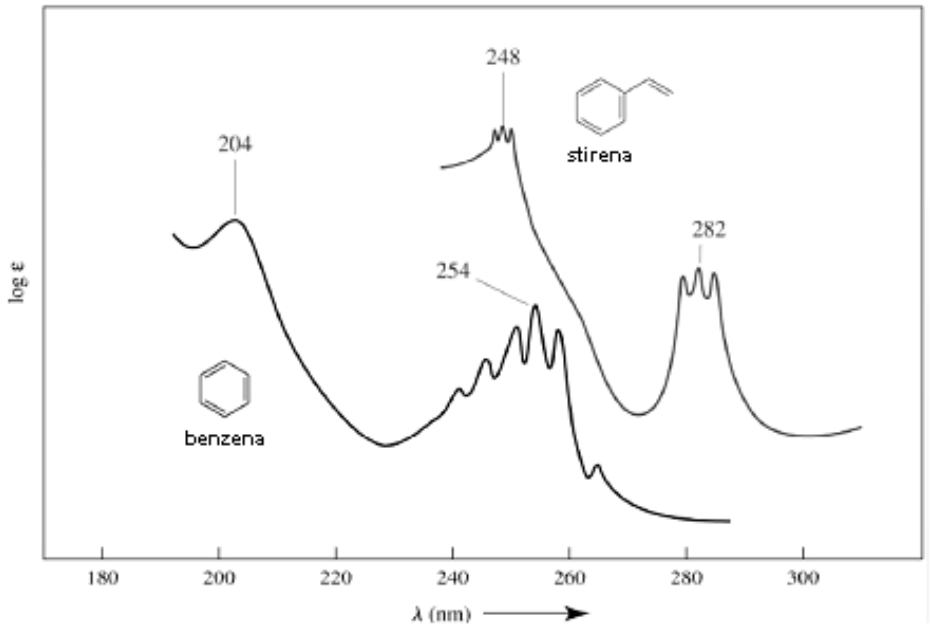
(d) The exact mass of a compound determined by high-resolution mass spectrometry is 182.07316. With the help of the spectrum below, suggest a structure for the compound.



m/z	% Intensity	*m/z*	% Intensity	*m/z*	% Intensity	*m/z*	% Intensity
38	0.4	64	0.6	105	100	153	1.8
39	1.1	74	2.0	106	7.8	154	1.4
50	6.2	75	1.7	107	0.5	181	7.4
51	19	76	4.3	126	0.6	182	55
52	1.4	77	62	127	0.4	183	8.3
53	0.3	78	4.2	151	1.1	184	0.6
63	1.3	104	0.4	152	3.4		

(6 marks)

1. (a) Spektrum UV-Vis bagi benzena dan stirena ditunjukkan di bawah. Jelaskan perbezaan dalam posisi puncak yang diperhatikan dalam kedua-dua spektrum.



(5 markah)

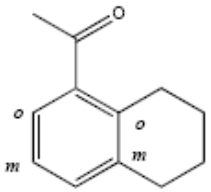
(b) Dalam spektroskopi pendafluor, peralihan elektron berlaku antara dua keadaan singlet, manakala dalam spektroskopi pendarfosfor peralihan elektron berlaku antara suatu keadaan triplet dan singlet. Jelaskan bagaimana peralihan tersebut berlaku dan mengakibatkan perbezaan dalam masa hayat pemancaran.

(5 markah)

(c) Kedayaserapan molar dari peralihan $n \rightarrow \pi^*$ adalah rendah secara relatif, dan didapati dalam julat 10 hingga 100 L mol^{-1} cm^{-1}. Peralihan dari $\pi \rightarrow \pi^*$ biasanya memberi kedayaserapan molar antara 1000 dan 10,000 L mol^{-1} cm^{-1}. Gambarkan setiap peralihan dengan suatu contoh dan jelaskan pemerhatian tersebut.

(5 markah)

(d) Guna korelasi benzoil yang diberi di bawah untuk meramalkan λ_{max} bagi sebatian berikut.



KORELASI BENZOIL

X-C_6H_4-CO-Z

Bes:

di mana Z = H, 250;	X-C_6H_4-COH (benzaldehid)
di mana Z = alifatik, 246;	X-C_6H_4-COR (asetofenon, dsb.)
di mana Z = O-H / O-R, 230	X-C_6H_4-COOH / X-C_6H_4-COOR (asid / ester)

Auksokrom:

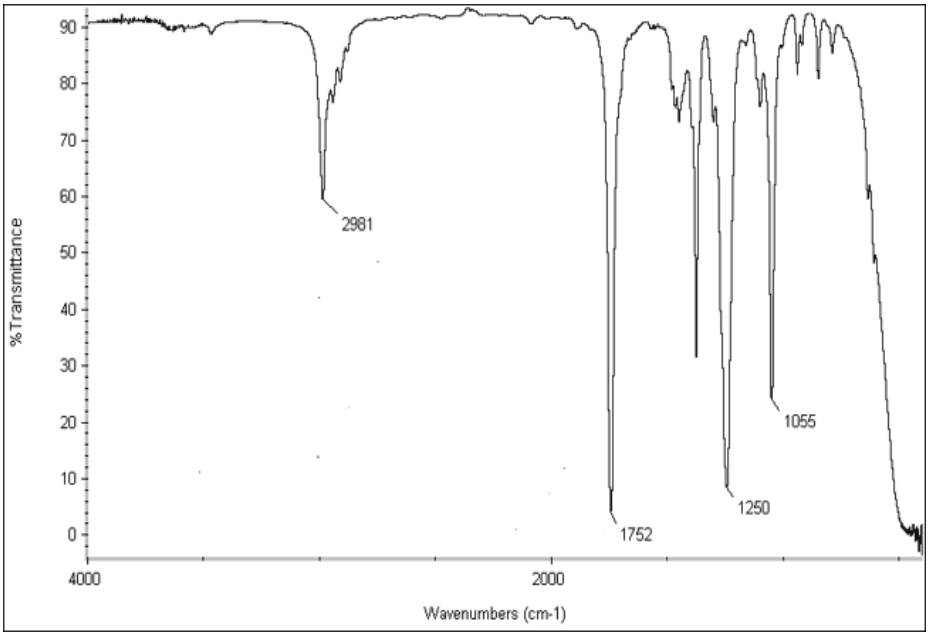
X	***o-,m-***	***p-***
NR_2	20	85
O-H, O-R	7	25
Alifatik	3	10
Br	2	15
Cl	0	10

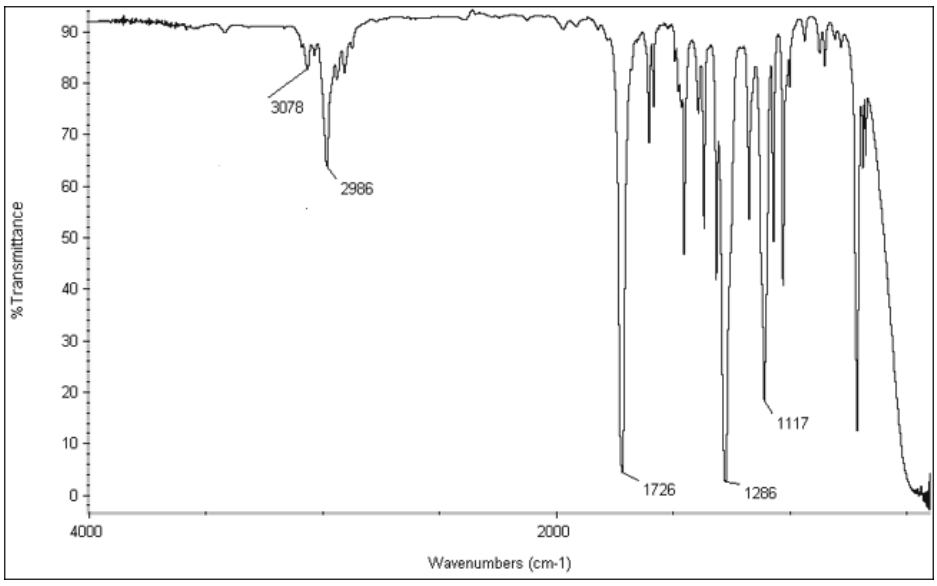
(5 markah)

2. (a) Huraikan dan jelaskan dua kelebihan bagi spektroskopi FT-IR dibandingkan dengan spektroskopi IR dispersif.

(4 markah)

(b) Dua spektrum FTIR di bawah adalah untuk etil benzoat dan etil asetat. Kenalpasti spektrum yang mana dipunyai oleh sebatian yang mana dan peruntukkan jalur berlabel terhadap getaran bersepadan bagi molekul tersebut.





(6 markah)

(c) Campuran pepejal dengan % kepekatan kafein berbeza dalam kanji disediakan, dan nisbah dayaserapan pada 743 dan 995 cm^{-1} untuk kafein dan kanji dikira. Kepekatan kafein dan nisbah dayaserapan terukur, A_{743}/A_{995}, bagi setiap campuran diberi di bawah. Nisbah A_{743}/A_{995} bagi beberapa sampel mengandungi kafein yang tidak diketahui kepekatan juga diukur. Keputusannya ditunjukkan di bawah. Apakah kepekatan kafein dalam campuran *A* – *D*?

% Kepekatan kafein	A_{743}/A_{995}
2	0.16
4	0.36
6	0.56
8	0.76
10	0.96

Campuran kafein dan kanji	A_{743}/A_{995}
A	0.30
B	0.53
C	0.61
D	0.88

(5 markah)

(d) Spektroskopi inframerah adalah sesuai secara unggul untuk analisis filem nipis pada permukaan, terutamanya pada permukaan logam berkilau. Kuantiti terlalu kecil bagi agen pelepas acuan, minyak pelincir, gris, bendalir memotong dan bahan menggilap boleh dikesan dan dikenalpasti oleh FTIR. Bincangkan teknik FTIR yang digunakan dalam industri saduran untuk mengesan kegagalan saduran disebabkan oleh kecemaran pada permukaan logam.

(5 markah)

3. (a) Ramalkan kemultipelan dan tunjukkan intensiti relatif bagi setiap isyarat ^{1}H NMR pada molekul berikut:

(6 markah)

(b) Dengan menggunakan nilai pemalar pengkupelan bagi $^{3}J_{HH}$ = 7 Hz dan $^{2}J_{HF}$ = 60 Hz, lukiskan multiplet ^{1}H bagi molekul berikut:

(6 markah)

(c) Magnet dengan kekuatan medan apakah yang diperlukan dalam sesuatu instrumen untuk mengaji ^{1}H NMR pada (i) 300 MHz, dan (ii) 600 MHz? (Perhatian: γ bagi ^{1}H adalah 267.52 x 10^{6} rad T^{-1} s^{-1}).

(4 markah)

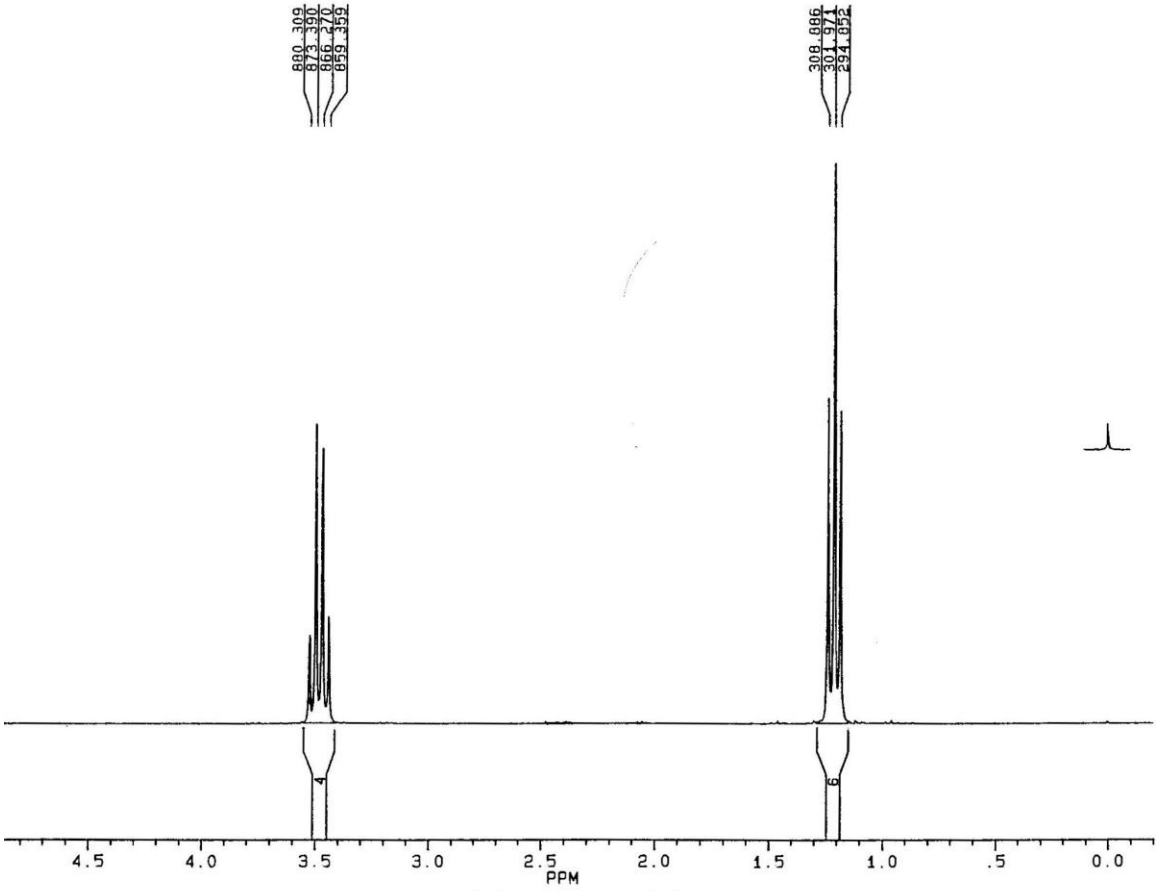
(d) Kirakan nilai NOE, η, yang maksima bagi spektrum ternyahganding proton ^{13}Cdan ^{31}P dengan menggunakan maklumat berikut: γ bagi ^{1}H, ^{13}C dan ^{31}P adalah masing-masing, 267.512 x 10^{6} rad T^{-1} s^{-1}, 67.264 x 10^{6} rad T^{-1} s^{-1} dan 108.29 x 10^{6} rad T^{-1} s^{-1}.

(4 markah)

4. (a) Satu daripada isomer bromonitropropana, $C_3H_6BrNO_2$, mempunyai spektrum ^{1}H NMR yang mengandungi satu triplet pada δ 5.9, satu quintet pada lingkungan δ 2.4 dan satu lagi triplet pada δ 1.3. Apakah struktur isomer ini?

(6 markah)

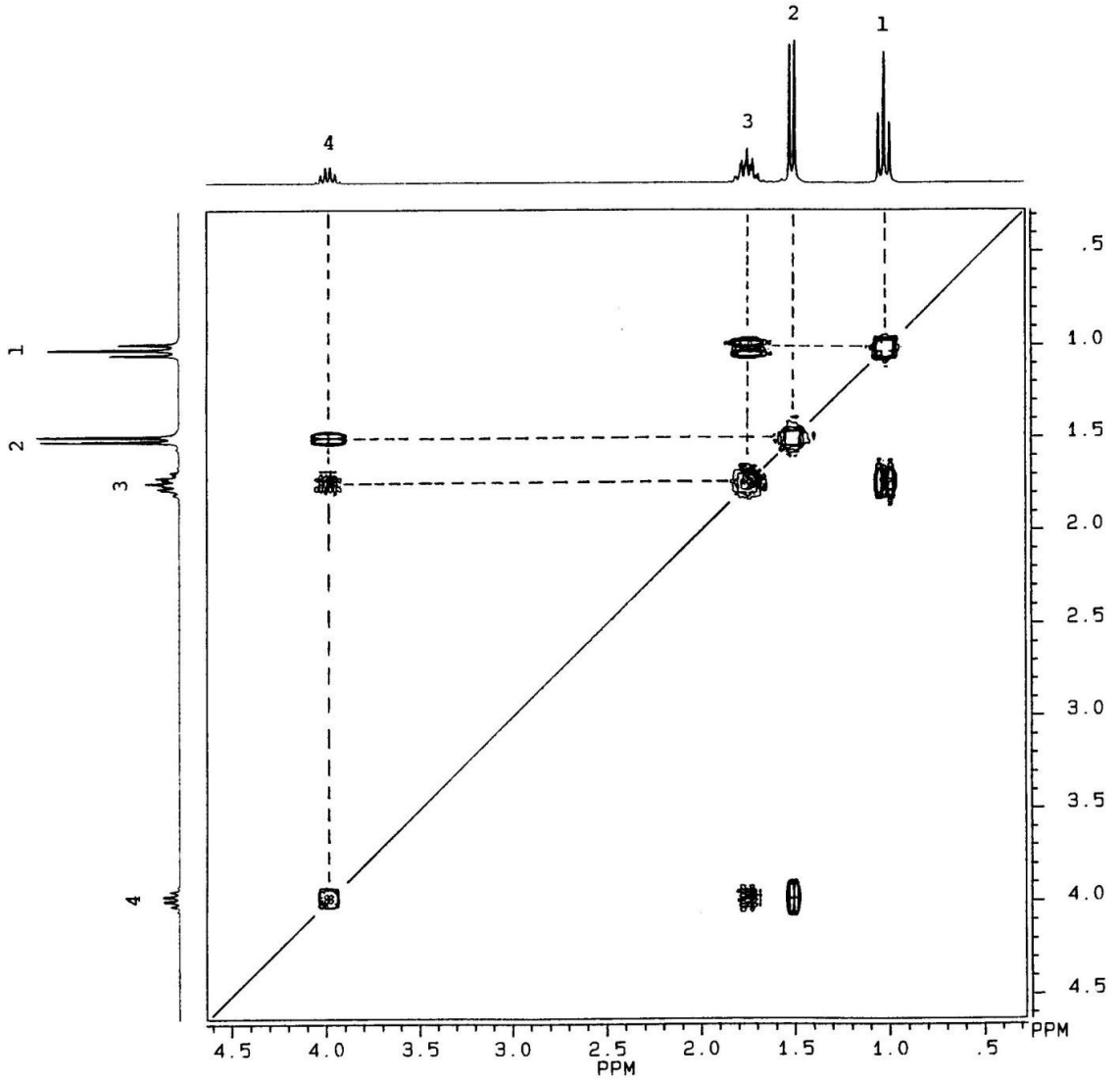
(b) Perikan spektrum NMR dietil eter yang dikemukakan di bawah dalam bentuk format jitu.



Spektrum 250 MHz 1H dietil eter

(6 markah)

(c) Jelaskan struktur C_4H_9Cl dengan menggunakan spektrum ^1H-^1H COSYnya seperti yang diberikan di bawah.



Spektrum ^1H-^1H COSY C_4H_9Cl

(8 markah)

5. (a) Untuk spektrometri jisim molekul, jelaskan perbezaan antara pengionan impak elektron (EI) dan pengionan kimia (CI), dan nyatakan bila setiap dari kaedah tersebut boleh digunakan.

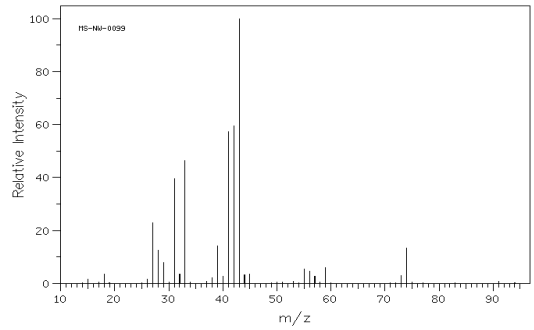
(6 markah)

(b) Lihat dengan teliti spektrum jisim bagi tiga isomer butanol yang ditunjukkan di bawah. Padankan setiap isomer dengan spektrumnya, dan beri penjelasan ringkas bagaimana anda pilih spektrum yang mana dipunyai oleh isomer yang mana.

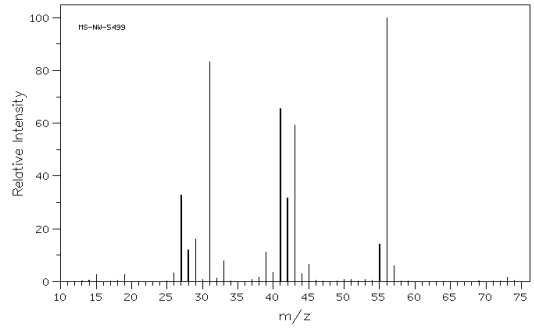
(i) Butan-1-ol

(ii) Butan-2-ol

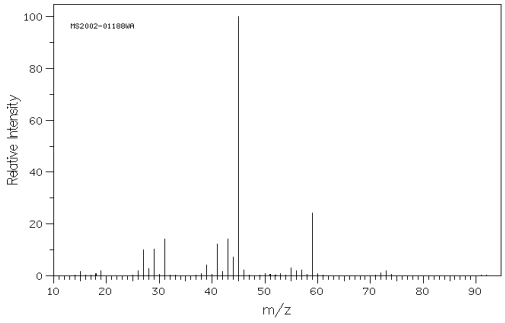
(iii) 3-Metilpropan-1-ol



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
15	1.5	31	39.7	41	57.3	56	4.6
18	3.4	32	3.6	42	59.4	57	2.8
26	1.6	33	46.3	43	100.0	59	5.9
27	23.0	38	2.1	44	3.2	73	3.1
28	12.4	39	14.1	45	3.6	74	13.3
29	8.0	40	2.8	55	5.5		



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
15	2.8	31	83.4	41	65.6	56	100.0
19	2.8	32	1.4	42	31.6	57	5.9
26	3.2	33	7.9	43	59.3	73	1.7
27	32.7	38	1.7	44	3.0		
28	12.1	39	11.2	45	6.6		
29	16.1	40	3.6	55	14.1		



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
15	1.7	31	14.1	45	100.0	72	1.0
19	1.8	39	4.1	46	2.2	73	1.9
26	1.8	41	12.2	55	3.0		
27	10.1	42	1.5	56	2.0		
28	2.6	43	14.1	57	2.2		
29	10.2	44	7.2	59	24.3		

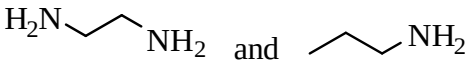
(6 markah)

(c) Apakah perbezaan ketara antara spectrum jisim bagi sebatian isomer yang berikut?

(i) $CH_3CH_2CH_2OH$ dan $CH_3OCH_2CH_3$.

(ii) $CH_2(Cl)CH_2CH_2Cl$ dan $CH(Cl)_2CH_2CH_2Cl$.

(iii) 3-pentanon and 3-metil-2-butanon.

(iv)  and

(4 markah)

(d) Tunjukkan persamaan untuk kecaian ketara yang anda akan dijangka dari ion molekul bagi sebatian berikut. Senaraikan nilai *m/z* bagi ion hasil itu.

(i) $C(CH_3)_3OCH_2CH_3$

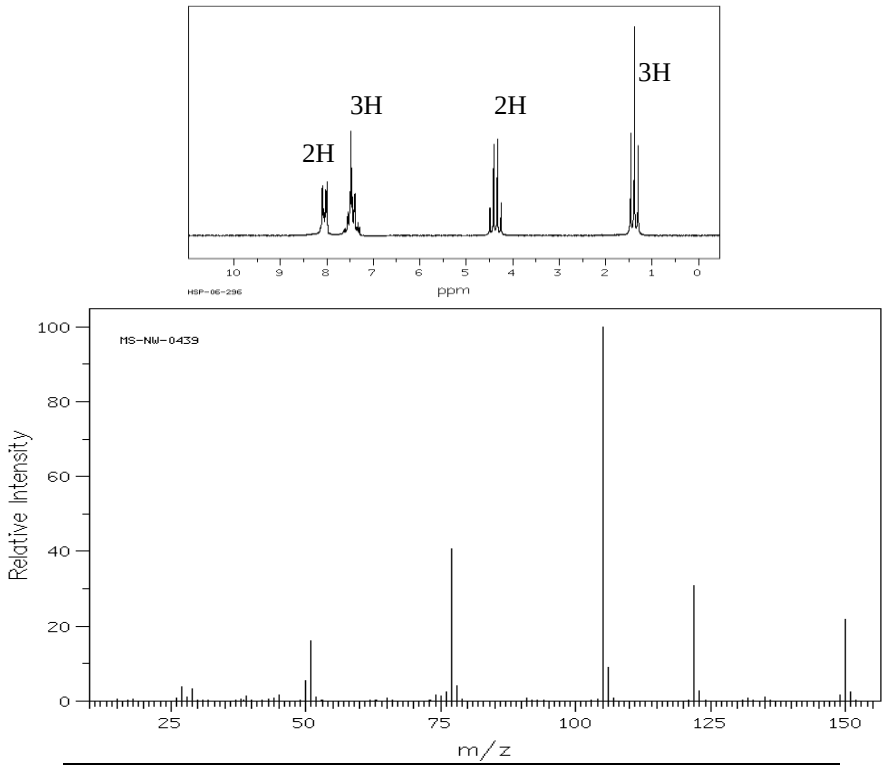
(ii) $CH_3(CH_2)_3CH_3$

(4 markah)

6. (a) Jelaskan prinsip penganalisis jisim masa-untuk-perjalanan dan perangkap ion.

(6 markah)

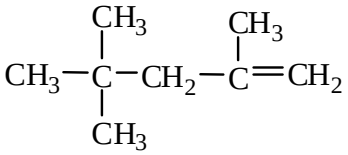
(b) Spektrum dan data (*m/z*) bagi ^{1}HNMR dan spektrometri jisim untuk suatu sebatian yang tidak diketahui diberi di bawah. Guna spektrum ynag diberikan untuk menentukan struktur sebatian itu. Apakah serpihan yang menyebabkan puncak pada *m/z* 105 dan 77?



m/z	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.	*m/z*	Int.
50	5.4	51	16	77	40.6	78	4.0	105	100
122	30.7	123	2.6	150	21.8	151	2.3		

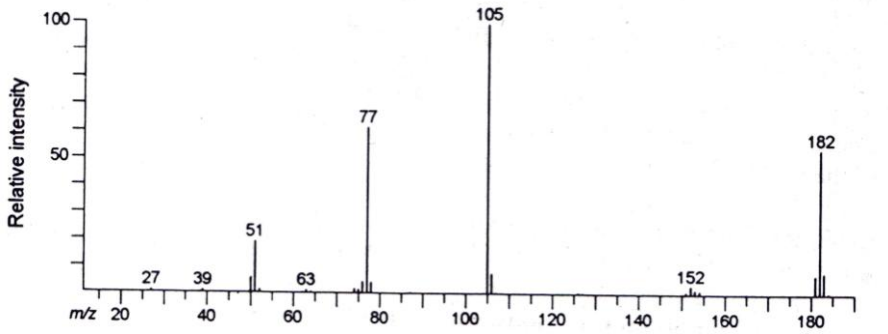
(5 markah)

(c) Tunjukkan persamaan untuk menjelaskan ion serpihan ketara yang berlaku pada *m/z* 97 dan *m/z* 57 dalam spectrum jisim sebatian berikut.



(3 markah)

(d) Jisim tepat bagi suatu sebatian ditentukan dengan spektrometri jisim resolusi tinggi ialah 182.07316. Dengan bantuan spektrum di bawah, cadangkan suatu struktur bagi sebatian tersebut.



m/z	% Intensiti	*m/z*	% Intensiti	*m/z*	% Intensiti	*m/z*	% Intensiti
38	0.4	64	0.6	105	100	153	1.8
39	1.1	74	2.0	106	7.8	154	1.4
50	6.2	75	1.7	107	0.5	181	7.4
51	19	76	4.3	126	0.6	182	55
52	1.4	77	62	127	0.4	183	8.3
53	0.3	78	4.2	151	1.1	184	0.6
63	1.3	104	0.4	152	3.4		

(6 markah)

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