THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Assignment III (Test) — 2008/2009

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

$\left(1\frac{1}{2}\text{ hours}\right)$

8th April 2009 (Wednesday) 4.00 p.m. — 5.30 p.m.

- Answer all 40 questions (40 x 2.5 = 100 marks)
- Choose the most correct answer to each of the questions and mark this answer with an "X" on the answer script in the appropriate box.
- Use a **PEN** (not a PENCIL) in answering.
- Any answer with more than **one** "X" marked will be considered as an *incorrect* answer.
- Marks will be deducted for incorrect answers (0.4 per answer).
- The use of a non-programmable electronic calculator is permitted.
- Logarithm tables will be provided.

Gas constant (R)	=	$8.314\ \text{JK}^{-1}\text{mol}^{-1}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ \text{mol}^{-1}$
Faraday constant (F)	=	$96,500\ \text{Cmol}^{-1}$
Planck constant (h)	=	$6.63\times10^{-34}\ \text{Js}$
Velocity of light (c)	=	$3.0\times10^{8}\ \text{ms}^{-1}$
Standard atmospheric pressure	=	$10^{5}\ \text{Pa}\left(\text{Nm}^{-2}\right)$
$\text{Log}_e(X)$	=	$2.303\ \text{Log}_{10}(X)$

1. Consider the following statements.
In FT NMR spectroscopy the free induction decay signal

(i) due to chemically equivalent protons in a sample is a damped oscillation.

(ii) originates during the de-excitation process of magnetic nuclei.

(iii) is Fourier transformed to obtain the NMR spectrum.

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

2. A (bare) ^{13}C nucleus is placed in the magnetic field of a 600 MHz NMR spectrometer. The magnetogyric ratios of ^{1}H and ^{13}C, respectively, are $2.6752\times10^{8}\ \text{rad s}^{-1}\ \text{T}^{-1}$ and $6.7283\times10^{7}\ \text{rad s}^{-1}\ \text{T}^{-1}$. What is the nuclear magnetic resonance frequency of ^{13}C?

(a) 2385.6 MHz (b) 160.2 MHz (c) 150.9 MHz
(d) 948.1 MHz (e) 170.9 MHz

3. A sample is placed in an FT NMR spectrometer. Consider the following statements about the (equilibrium) macroscopic magnetisation, $\overline{M}_0$, due to chemically equivalent protons in this sample. Immediately after the application of a

(i) 90^0_X pulse the component of macroscopic magnetisation in the direction of the applied magnetic field is zero.

(ii) 90^0_Y pulse or a 90^0_X pulse the macroscopic magnetisation will be in a plane perpendicular to the applied magnetic field.

(iii) 90^0_Y pulse the macroscopic magnetisation begins to change its direction due to relaxation processes.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

4. Consider the nuclei, , ^{13}C, ^{14}N and ^{12}C. Which set of numbers best represents the spin quantum numbers of the above nuclei, respectively. Here N_1 and N_2 are odd and even integers respectively.

(a) $0, \frac{1}{2}N_2, \frac{1}{2}N_1$. (b) $0, \frac{1}{2}N_2, N_1$. (c) $0, \frac{1}{2}N_1, \frac{1}{2}N_2$.
(d) $\frac{1}{2}N_1, \frac{1}{2}N_2, 0$ (e) $\frac{1}{2}N_2, \frac{1}{2}N_1, 0$.

5. In a continuous wave NMR spectrometer

(i) the radio waves absorbed by the sample is measured.

(ii) the sample is rotated in order to minimise the effects of inhomogeneity of the applied magnetic field..

(iii) the axis of the detector coil is perpendicular to the direction of the applied magnetic field.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

6. Which of the following statements about the low resolution proton NMR spectrum (i.e disregarding the scalar coupling of protons) of a sample of $CH_3CH_2CH_2CH_2CH_3$, at room temperature, is correct?

(a) There is only one line since it is a saturated hydrocarbon.

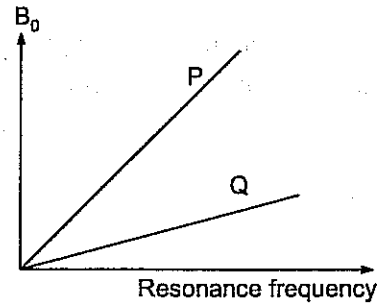
(b) There are only two lines corresponding to the protons in CH_2 and CH_3 groups.

(c) There are only three lines at an intensity ratio 3:2:1.

(d) There are only four lines at an intensity ratio 6:2:2:2.

(e) There are only five lines at an intensity ratio 3:2:2:2:3.

7. The relationship of the resonance frequencies of two nuclei, P and Q, with spin quantum number, $I = \frac{1}{2}$, to the applied magnetic field strength, B_0, is shown below.



Consider the following statements.

(i) The magnetogyric ratio of P is greater than that of Q.

(ii) The separation between the NMR spectral lines produced by P and Q, in the absence of scalar coupling, increases with increasing magnetic field strength.

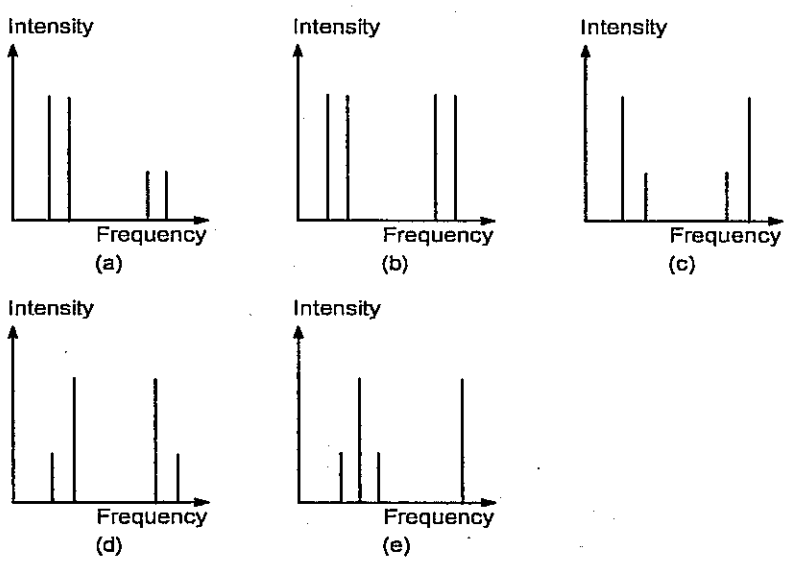
(iii) The Larmor frequency of P is greater than that of Q at a given magnetic field strength..

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

Use the following information and the diagrams given below in answering questions 8 and 9.

The scalar coupling constant of two protons in a molecule, X, which has no other magnetic nuclei, is 6.0 Hz. The separation between the resonance frequencies of the two protons in a 100 MHz NMR spectrometer is 30 Hz.



8. Which diagram best represents the high resolution NMR spectrum of X recorded with a 80 MHz NMR spectrometer.

9. Which diagram best represents the high resolution NMR spectrum of X recorded with a 500 MHz NMR spectrometer.

10. The chemical shift of the protons in CH_3 in a CH_3CH_2OH molecule is 1.00. when TMS is used as the reference. Consider the following statements.

(i) The chemical shift of the proton on OH has to be greater than 1.00.

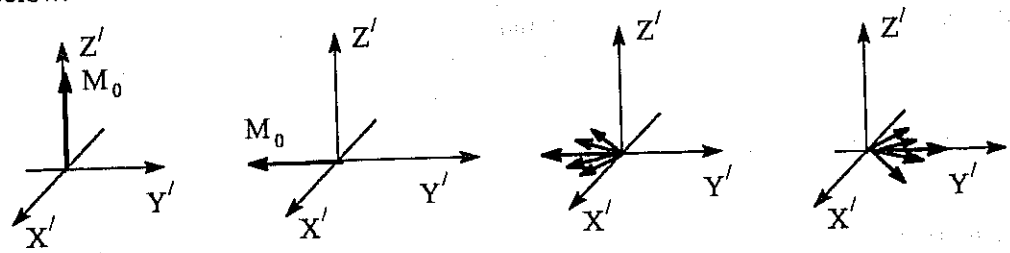
(ii) In the NMR spectrum the line due to TMS appears at a higher frequency than that due to the protons in CH_3.

(iii) Out of the three types of protons, the proton on OH has the highest chemical shift.

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

11. The orientations of equilibrium macroscopic magnetisation and the orientation of magnetisation in the XY–plane (in the rotating frame) due to chemically equivalent protons in an FT NMR sample during the application of a pulse/delay sequence is shown below.



Which of the following best describes the pulse sequence used in the above experiment.

(a) 270°_{X} pulse – delay τ – 180°_{X} pulse.

(b) 270°_{Y} pulse – delay τ – 180°_{Y} pulse.

(c) delay τ – 90°_{X} pulse – 180^{0}_{Y} pulse.

(d) 180°_{X} pulse – delay τ – 180°_{X} pulse.

(e) 90°_{Y} pulse – 180°_{X} pulse – delay τ.

12. A student recorded the low resolution proton NMR spectrum of a solution of pure CH_3CH_2OH and CH_3CONH_2. The concentrations of these compounds in the solution satisfies $[CH_3CH_2OH] = 2[CH_3CONH_2]$. If we denote the intensities of the lines due to the protons in OH and NH_2 in this spectrum by I_{OH^-} and I_{NH_2}, respectively, then $I_{OH^-} : I_{NH_2}$ is equal to

(a) 2:1 (b) 1:2 (c) 4:1 (d) 1:4 (e) 1:1

13. Tetramethyl silane (TMS) is commonly used as a reference compound in the NMR spectroscopy of ^1H, because of the following essential properties.

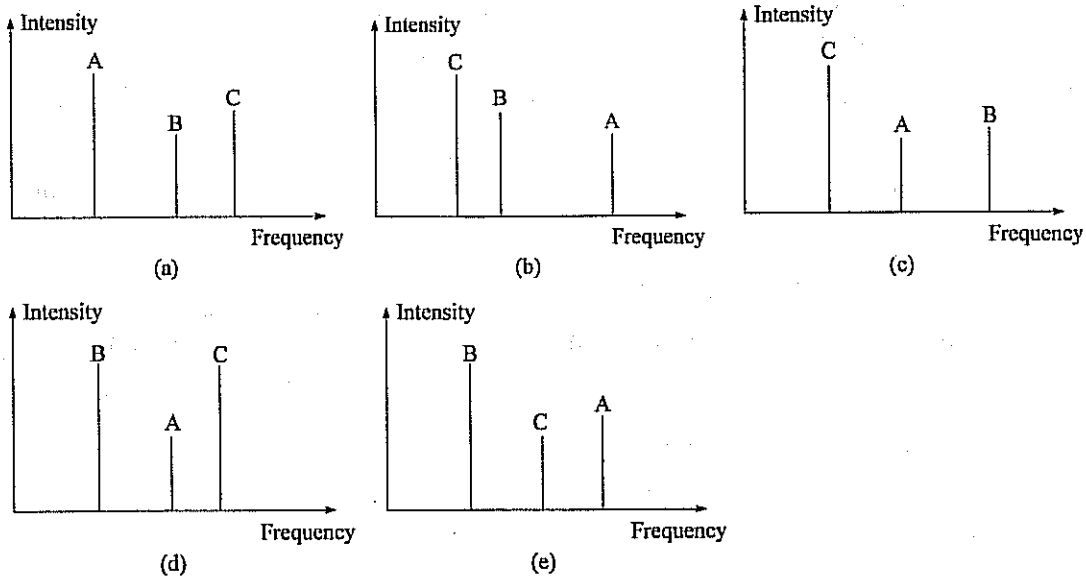
(i) All the protons in it are in the same chemical environment (at temperatures where most of the experiments are performed) and gives one line in the NMR spectrum.

(ii) It is chemically inert (in environments commonly encountered in experiments).

(iii) The protons in it resonate in the same region of frequency where the protons in most of the commonly used organic compounds resonate.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

14. A certain molecule has three groups, A, B and C having ^1H nuclei. In each group the ^1H nuclei are chemically equivalent. Between groups they are chemically non–equivalent. Also they are not (scalar) coupled to any nucleus. The shielding is highest for the nuclei in B. Electron density around nuclei in C is much higher than that around the nuclei in A. Which of the following figures may describe the NMR spectrum of these ^1H ?



15. Consider the following statements.

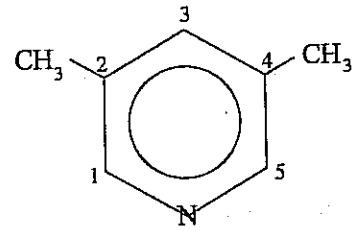
(i) Magnetically equivalent nuclei in a molecule have the same coupling constant with a given neighbouring nucleus.

(ii) Magnetically equivalent nuclei in a molecule have the same chemical shift.

(iii) In NMR spectroscopy, two nuclei in a molecule, belong to the same element in the periodic table, may <u>not</u> be chemically equivalent.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

16. Consider the following statements made on the protons in the molecule shown below.



(i) Protons in positions 1 and 5 are chemically equivalent.

(ii) Protons in the two CH_3 groups are chemically equivalent (at sufficiently high temperature).

(iii) Protons in positions 1 and 5 are magnetically equivalent.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

17. Consider the following statements.

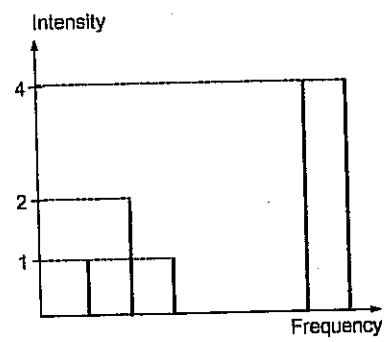
(i) Dephasing of the spins in the XY plane in a spin–echo experiment is due to the inhomogeneity in the applied magnetic field.

(ii) A spin–echo experiment is customarily used in measuring the spin–lattice relation time.

(iii) In a spin–echo experiment, a 180° pulse is used to refocus the spins fanned out in the XY plane.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

18. The NMR spectrum of three nuclei, of the same chemical species, of spin quantum number, $I = \frac{1}{2}$, in a molecule (having no other magnetic nuclei) is shown in the figure to the right. Two of these nuclei are chemically and magnetically equivalent. Which of the following statements describes best the nature of scalar coupling among these nuclei?



(a) It is an AB spin system.
(b) It is an AMX spin system
(c) Cannot predict the spin system without knowing chemical formula of the molecule.
(d) It is an AC spin system
(e) It is an AX spin system.

19. Consider the following statements (as applied in NMR spectroscopy).

(i) Transverse relaxation is due to spin-spin interactions.

(ii) Spin–lattice relaxation is also called longitudinal relaxation.

(iii) Spin–lattice relaxation may lead to a change in energy of the spin system.

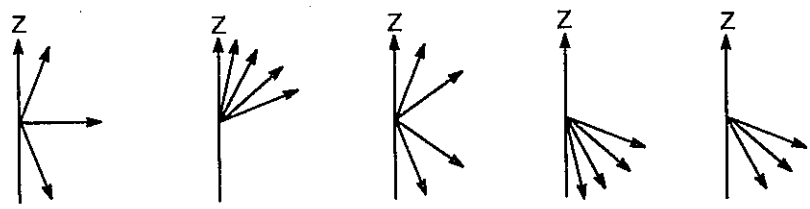
The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

20. What best describes two groups of ^{13}C in a molecule with chemical shifts 7.0 and 0.0. and the scalar coupling constant 0.31?

(a) It is an AB spin system.
(b) It is an AMX spin system
(c) Cannot predict the spin system without knowing chemical formula of the molecule.
(d) It is an AC spin system
(e) It is an AX spin system.

21. The possible orientations of the spin of a nucleus with spin quantum number, $I = 3/2$, are best illustrated by



(a) (b) (c) (d) (e)

Use the following data in answering questions 22 and 23.

$I = 1$ *for* ^{2}H *and* $I = 5/2$ *for* ^{15}N.

22. What is the multiplicity of ^{2}H resonance in $^{15}N^{2}H_{2}{}^{12}COONa$?

(a) 2 (b) 3 (c) 4 (d) 5 (e) 6

23. What is the multiplicity of ^{15}N resonance in $^{15}N^{2}H_{2}{}^{12}COONa$?

(a) 2 (b) 3 (c) 4 (d) 5 (e) 6

24. The energy of a first order spin system having two nuclei, 1 and 2, of the same chemical species placed in a magnetic field of intensity B_0 is given (in standard notation) by

(a) $E = -\gamma\hbar B_0(1-\sigma_1)m_{I_1} + \gamma\hbar B_0(1-\sigma_2)m_{I_2} - hJm_{I_1}m_{I_2}$

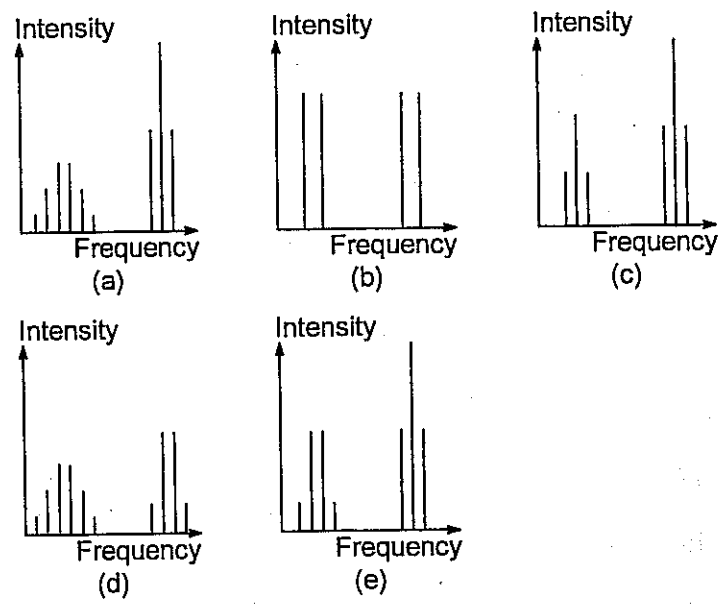
(b) $E = +\gamma\hbar B_0(1-\sigma_1)m_{I_1} - \gamma\hbar B_0(1-\sigma_2)m_{I_2} + hJm_{I_1}m_{I_2}$

(c) $E = -\gamma\hbar B_0(1-\sigma_1)m_{I_1} + \gamma\hbar B_0(1-\sigma_2)m_{I_2} - hJm_{I_1}m_{I_2}$

(d) $E = -\gamma\hbar B_0(1-\sigma_1)m_{I_1} - \gamma\hbar B_0(1-\sigma_2)m_{I_2} - hJm_{I_1}m_{I_2}$

(e) $E = -\gamma\hbar B_0(1-\sigma_1)m_{I_1} - \gamma\hbar B_0(1-\sigma_2)m_{I_2} + hJm_{I_1}m_{I_2}$

25. A molecule has three groups of protons, X, Y and Z, where the protons in any one group are chemically and magnetically equivalent. These three groups form an AMX spin system. X, Y and Z groups have 3, 4 and 2 protons respectively. In an NMR experiment, the spectrum of the protons in X and Z groups was recorded while simultaneously irradiating the sample with radio waves of frequency equal to the NMR resonance frequency of the protons in Y. Which of the following diagrams best describes the recorded NMR spectrum of the protons in X and Z?



26. In the classical view of NMR phenomenon, the magnetic moment of a magnetic nucleus placed in a magnetic field

(a) gets aligned along the magnetic field.

(b) precesses about the direction of the applied magnetic field.

(c) remains stationary in time in the laboratory frame.

(d) precesses about an axis which is perpendicular to the applied magnetic field.

(e) None of the answers (a), (b), (c) or (d) is correct.

27. (i) Decoupling of spins in $^{13}CH_3COONa$, at room temperature, is an example of homonuclear decoupling.

(ii) An AB spin system may become an AX spin system with the increase in the applied magnetic field.

(iii) In the double resonance method the NMR spectra get simplified due to decoupling of nuclear spins.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

28. Consider the following statements (as applied in NMR spectroscopy).

(i) Spin–lattice relaxation is a first order rate process.

(ii) Spin–lattice relaxation time is the time taken by a spin system to make its macroscopic magnetisation zero after a 180° pulse.

(iii) Spin–lattice relaxation time is equal to the reciprocal of the spin–lattice relaxation rate constant.

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

29. The energy difference between the α and β states of a nucleus with spin, $I=\frac{1}{2}$, in an NMR sample kept in an NMR spectrometer is 9.75×10^{-23} J. What is the ratio of populations of α and β states at 100 K in this spectrometer?

(a) 1.0000:0.932 (b) 1.0000:0.893 (c) 1.0000:989
(d) 1.0000:0.993 (e) 1.0000:0.943

30. A sample is placed in an FT NMR spectrometer. Consider the following statements about the (equilibrium) macroscopic magnetisations, $\overline{M}_1$ and $\overline{M}_2$, of two groups of chemically non–equivalent protons in this sample.

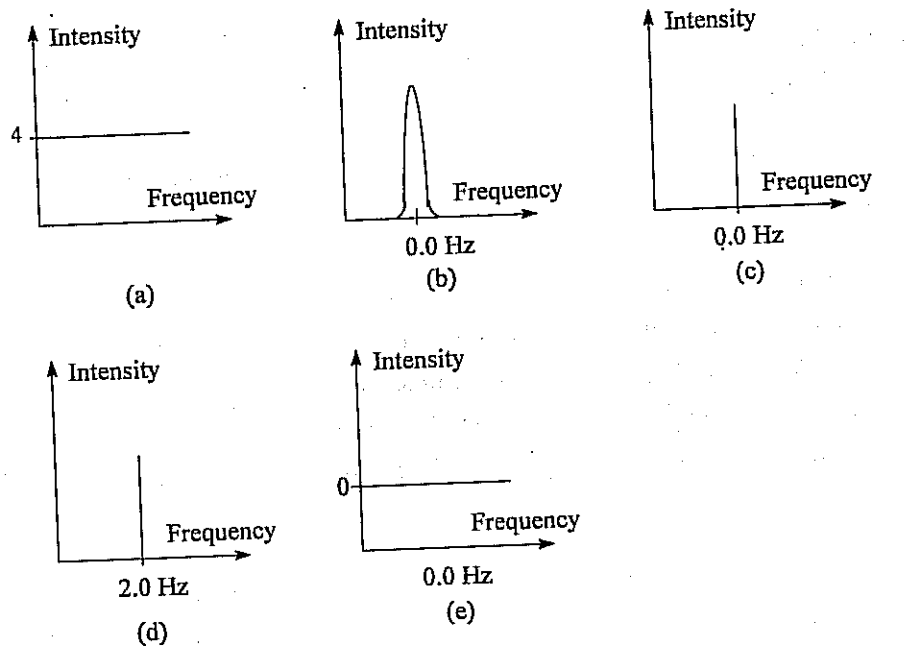
(i) The frequency of the pulse that is used to rotate $\overline{M}_1$ is the same as that is used to rotate $\overline{M}_2$.

(ii) A 90°_X pulse given to rotate $\overline{M}_1$ will also rotate $\overline{M}_2$ by 90° about the X–axis.

(iii) A 90°_Y pulse given to rotate $\overline{M}_1$ may not rotate $\overline{M}_2$ by 90° about the Y–axis

The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

Use the following five diagrams, (a), (b), (c), (d) and (e) in answering questions 31, 32 and 33.



31. Which figure best describes the Fourier transform of the function $f = 2 \times \exp(-2t)$ (where t is the time).

32. Which figure best describes the Fourier transform of the function $f = \text{constant} = 4$

33. Which figure best describes the Fourier transform of the function $f = 4 \times \sin(4\pi t)$ (where t is the time).

34. Advantage/s of FT NMR over CW NMR spectroscopy is/are that

(i) a reference standard (e.g. TMS) is <u>not</u> needed in FT NMR.

(ii) one does <u>not</u> have to perform signal averaging in FT NMR.

(iii) one does <u>not</u> have to scan the sample a number of times in FT NMR.

(a) Only (i) (b) Only (ii) (c) Only (iii).
(d) Only (i) and (ii) (e) None of the <u>answers</u> (a), (b), (c) or (d) is correct.

35. Consider the following statements about magnetic nuclei of a particular chemical species, with spin, $I = 1$, in a molecule, in a sample placed in an NMR spectrometer. Label the spin states with $m_I = -1$ and $m_I = +1$ as χ and ψ respectively:

(i) The population difference between χ and ψ states increases with increasing strength of the applied (static) magnetic field in the spectrometer (at constant temperature).

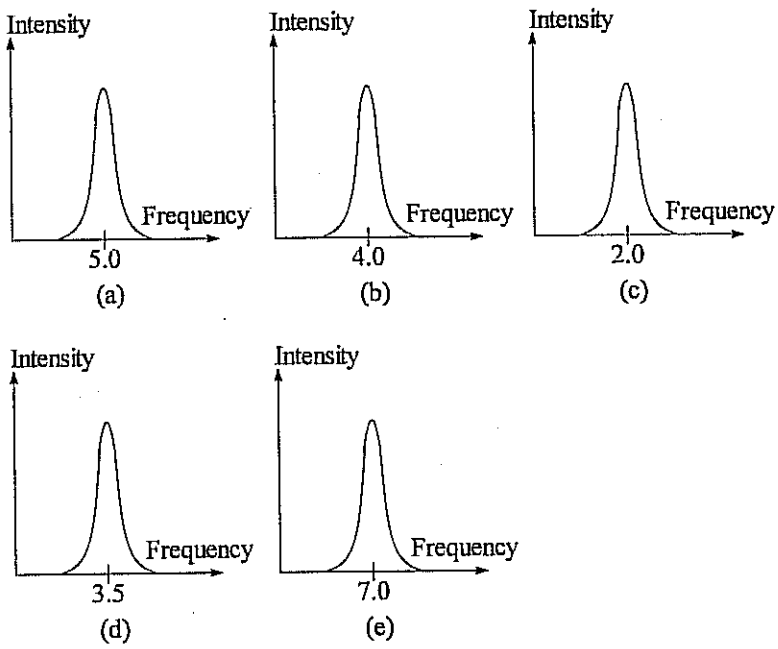
(ii) χ state has a higher energy than the ψ state in the static magnetic field of the spectrometer.

(iii) The population difference between χ and ψ states decreases with increasing temperature of the sample.

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

36. Which of the following figures best describes the Fourier transform of the function $f = 5.0 \times \exp(-4.0\,t) \times \sin(14\pi\,t)$ (where t is the time).

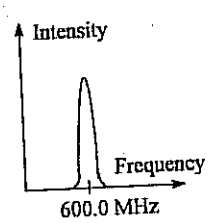


37. A particular (bare) nucleus has a resonance frequency of 175.0 MHz in a magnetic field of strength 7.5 T. What is the magnetogyric ratio of the nucleus?

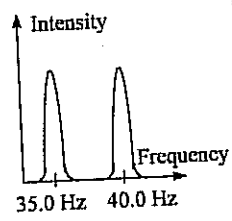
(a) 1.47×10^8 rad s^{-1} T^{-1} (b) 7.33×10^7 rad s^{-1} T^{-1}
(c) 2.33×10^7 rad s^{-1} T^{-1} (d) 1.37×10^8 rad s^{-1} T^{-1}
(e) 3.47×10^8 rad s^{-1} T^{-1}

Use the following data and the following five diagrams in answering questions 38 and 39.

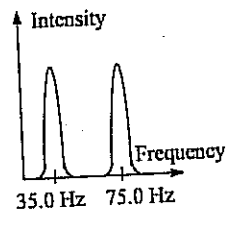
A molecule has ^1H in two different chemical environments denoted by A and B. The resonance frequencies of A and B in a 600 MHz FT NMR spectrometer are 600.000035 MHz and 600.000040 MHz.



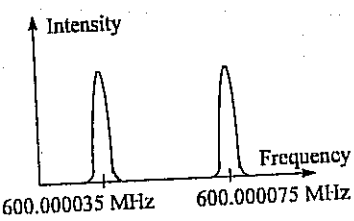
(a)



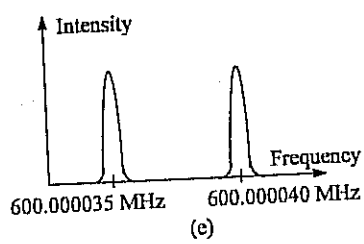
(b)



(c)



(d)



(e)

38. Which figure best represents the NMR spectrum corresponding to the FID signal due to A and B when the detector is placed in the laboratory frame.

39. Which figure best represents the NMR spectrum corresponding to the FID signal due to A and B when the detector is placed in the rotating frame.

40. Consider the following statements.

(i) The nuclear magnetic resonance frequency of a magnetic nucleus increases with increasing static magnetic field of the NMR spectrometer.

(ii) In general the resolution of an NMR spectrometer increases with increasing static magnetic file in it.

(iii) A 600 MHz NMR spectrometer has a higher static magnetic field than that in a 500 NMR spectrometer.

The correct statements out of (i), (ii) and (iii) above are

(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme/Stand alone course — Level 5
Assignment III (Test) — 2008/2009

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

MCQ Answer Sheet: Mark a cross (×) over the box that corresponds to the most suitable answer.

Reg. No.

FOR EXAMINER'S USE ONLY		
Answers	No.	Marks
Correct		
Wrong		–
Unmarked		0.0
Total		

1	a	b	c	d	e	2	a	b	c	d	e	3	a	b	c	d	e	4	a	b	c	d	e
5	a	b	c	d	e	6	a	b	c	d	e	7	a	b	c	d	e	8	a	b	c	d	e
9	a	b	c	d	e	10	a	b	c	d	e	11	a	b	c	d	e	12	a	b	c	d	e
13	a	b	c	d	e	14	a	b	c	d	e	15	a	b	c	d	e	16	a	b	c	d	e
17	a	b	c	d	e	18	a	b	c	d	e	19	a	b	c	d	e	20	a	b	c	d	e
21	a	b	c	d	e	22	a	b	c	d	e	23	a	b	c	d	e	24	a	b	c	d	e
25	a	b	c	d	e	26	a	b	c	d	e	27	a	b	c	d	e	28	a	b	c	d	e
29	a	b	c	d	e	30	a	b	c	d	e	31	a	b	c	d	e	32	a	b	c	d	e
33	a	b	c	d	e	34	a	b	c	d	e	35	a	b	c	d	e	36	a	b	c	d	e
37	a	b	c	d	e	38	a	b	c	d	e	39	a	b	c	d	e	40	a	b	c	d	e