

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme — Level 5

Assignment II (Test) — 2015/2016



CMU 3131/CME 5131 — Concepts 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																		

Reg. No.:

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CMU 3131/CME 5131 — Concepts in Spectroscopy



1 hour

4th May 2016 (Wednesday)

4.15 p.m. — 5.15 p.m.

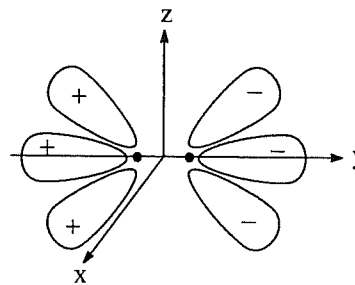
- ⊗ Answer all 25 questions (25 x 4 = 100 marks)
- ⊗ Choose the most correct answer to each of the questions and mark this answer with an “X” on the answer script in the appropriate box.
- ⊗ Use a **PEN** (not a PENCIL) in answering.
- ⊗ Any answer with more than **one** “X” marked will be considered as an *incorrect* answer.
- ⊗ Marks will be deducted for incorrect answers (0.6 per incorrect answer).
- ⊗ The use of a non-programmable electronic calculator is permitted.
- ⊗ Mobile phones are **not** allowed.

- ⊗ Please write your mailing address on the back of the MCQ answer sheet.

Gas constant (R)	=	8.314 JK ⁻¹ mol ⁻¹
Avogadro constant (N _A)	=	6.023 × 10 ²³ mol ⁻¹
Faraday constant (F)	=	96,500 C mol ⁻¹
Planck constant (h)	=	6.63 × 10 ⁻³⁴ Js
Velocity of light (c)	=	3.0 × 10 ⁸ ms ⁻¹
Standard atmospheric pressure	=	10 ⁵ Pa (Nm ⁻²)
Log _e (X)	=	2.303 Log ₁₀ (X)

1. Consider the following statements about the following electronic configuration of Cr, 1s²2s²2p⁶3s²3p⁶3d⁵4s¹.
- (i) 3d and 1s shells are partially filled.
 - (ii) The highest spin multiplicity an electronic state of Cr in the above configuration can have is 7.
 - (iii) The number of different orbital occupations possible in the above mentioned configuration is one.
- The correct statement/s 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) Only (iii).
2. What are the inversion symmetries of the wave functions corresponding to the two electronic configurations $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^2$ and $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^1$ of diatomic molecule and its ion, respectively?
- (a) u and g
 - (b) g and u
 - (c) u and u
 - (d) g and g
 - (e) None of the answers (a), (b), (c) or (d) is correct.

3. Consider the following statements about a (hypothetical) molecular orbital of a homonuclear diatomic molecule which is shown in the figure. (y-axis is a C_2 axis of this orbital.)



- (i) It has *ungerade* symmetry.
 (ii) It has “-” symmetry with respect to a reflection through the yz-plane.
 (iii) It has “-” symmetry with respect to a reflection through the xz-plane.

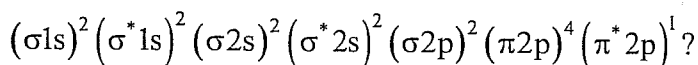
The correct statements out of (i), (ii) and (iii) above are

- (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.
4. A molecular orbital of a homonuclear diatomic molecule was formed using two d-orbitals on each of the nuclei. $m_l = -2$ for each these atomic orbitals. Consider the following statements about this molecular orbital.
- (i) It is a δ molecular orbital.
 (ii) $\lambda = -2$ for this orbital.
 (iii) It has to be a bonding molecular orbital since the value of m_l is the same for the two atomic orbitals used in forming it.

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.
5. Consider the following electronic configurations, γ^1 , $\delta\delta'$, σ^2 and π^4 , of a diatomic molecule indicated in standard notation. Which of the following best indicates the possible spin multiplicities of these configurations, respectively?
- (a) 3, 2, 1,1 (b) 2, 2, 1,1 (c) 1, 1, 1,2
 (d) 1, 1, 3,1 (e) 2, 1, 1,1

6. What are the possible values of the quantum number, M_z , for the total orbital angular momentum of a diatomic molecule in the electronic configuration



- (a) -2 and +1 (b) -1 and +1 (c) -1, +1 and +2
 (d) +1 and +2 (e) -1 and +2
7. A diatomic molecule has an electronic configuration so that the configuration of the partially filled shells can be represented by $\pi\pi'$. The possible electronic states of the molecule are $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$, $^3\Sigma^-$, $^1\Delta$ and $^3\Delta$. What is the lowest energy state of the molecule according to Hund's rules?

- (a) $^1\Sigma^-$ (b) $^1\Sigma^+$ (c) $^3\Delta$ (d) $^1\Delta$ (e) $^3\Sigma^+$

8. A homonuclear diatomic molecule has the electronic configuration $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g^* 2p)^2$. Which of the following best represents all possible electric states of this molecule?

- (a) $^1\Sigma_g^-$, $^3\Sigma_g^-$ and $^1\Delta_g$ (b) $^1\Sigma_g^+$, $^2\Sigma_g^-$ and $^1\Delta_g$ (c) $^1\Sigma_g^+$, $^3\Sigma_g^-$ and $^3\Delta_g$
 (d) $^1\Sigma_g^+$, $^3\Sigma_u^-$ and $^1\Delta_g$ (e) $^1\Sigma_g^+$, $^3\Sigma_g^-$ and $^1\Delta_g$

9. Consider the following three electronic transitions.

- (i) $^3\Phi_g \leftarrow ^3\Delta_u$
 (ii) $^3\Sigma_u^+ \leftarrow ^3\Sigma_g^+$
 (iii) $^3\Delta_g \leftarrow ^3\Sigma_g^-$

Out of (i), (ii) and (iii), which transition/s can take place due to the absorption of electromagnetic radiation?

- (a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
 (d) All (i), (ii) and (iii) (e) Only (ii).

In answering questions 10 and 11, use the data in a part of a Deslandres table given here for an electronic transition $A^1\Pi \leftarrow X^1\Sigma^+$ of a diatomic molecule. The wave numbers of the vibronic transitions are reported in units of cm^{-1} .

$\nu' \backslash \nu''$	0		1
0	64758	b	62613
	a		1485
1	66234	c	64098
	1448		1441
2	67682	d	65539

10. Consider the following values calculated by a student.

- (i) $a = 1476 \text{ cm}^{-1}$
 (ii) $b = 2145 \text{ cm}^{-1}$
 (iii) $c = 2136 \text{ cm}^{-1}$

The correct value/s 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) Only (iii).

11. The anharmonicity constant, x_e' , in higher energy electronic state is best represented by

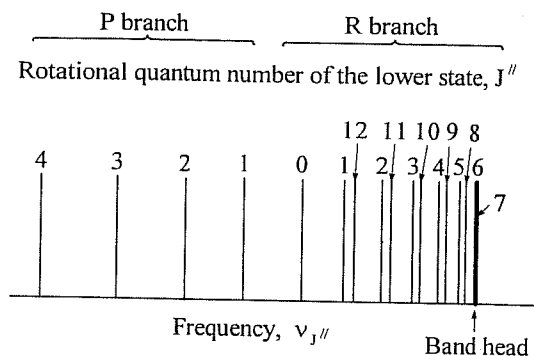
- (a) 0.009 (b) 0.120 (c) 0.090
 (d) 0.180 (e) 0.150

12. Using the observed lines in the vibronic spectrum of a diatomic molecule, a student determined, by least squares fitting, the relationship $(\Delta E/\text{cm}^{-1}) = -3.00x + 600.0$

where $\Delta E = \Delta E_n$ when $x = n = 0, 1, 2, 3, \dots$. Here $\Delta E_n = \epsilon_{n+1} - \epsilon_n$ where ϵ_n is the n^{th} vibrational energy level in the 2^{nd} electronic excited state of the molecule. What is the dissociation energy, D_0 , in the 2^{nd} electronic excited state of the molecule?

- (a) $100,000 \text{ cm}^{-1}$ (b) $60,000 \text{ cm}^{-1}$ (c) $25,000 \text{ cm}^{-1}$
 (d) $40,000 \text{ cm}^{-1}$ (e) $80,000 \text{ cm}^{-1}$

13. The rotational fine structure in the electronic spectrum of a diatomic molecule is schematically represented in the figure to the right. Consider the following statements about this diatomic molecule.

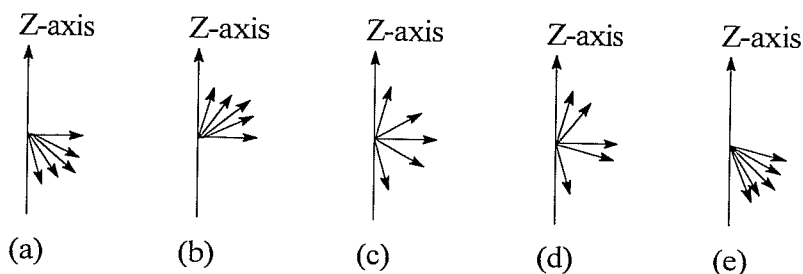


- (i) $B' < B''$
 (ii) The equilibrium bond length of the molecule in the higher energy electronic state is smaller than that in the lower energy state
 (iii) The lines due to the rotational transitions $J'' = 6 \rightarrow J' = 7$ and $J'' = 7 \rightarrow J' = 8$ appear at approximately the same frequency.

The correct statement/s 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) Only (iii).

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



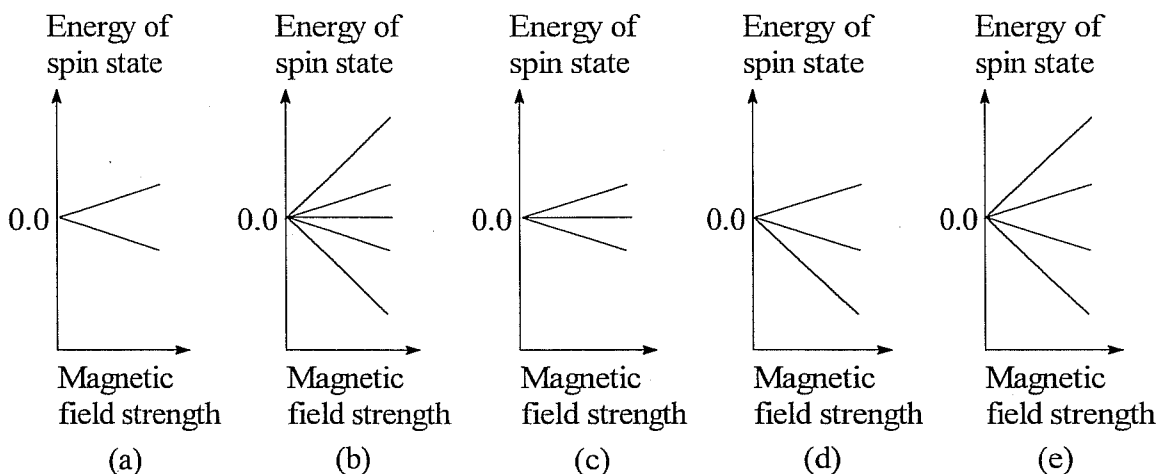
15. In a nuclear reactor scientists prepared three exotic nuclei ${}_{47}^{108}\text{P}$, ${}_{47}^{109}\text{Q}$ and ${}_{48}^{110}\text{R}$ where the superscripts and subscripts indicate the mass and atomic numbers of the nuclei, respectively. Consider the following statements about the spin quantum numbers of these three nuclei.

- (i) Spin quantum number of ${}_{47}^{108}\text{P}$ is an integer.
 (ii) Spin quantum number of ${}_{47}^{109}\text{Q}$ is a half integer.
 (iii) Spin quantum number of ${}_{48}^{110}\text{R}$ is zero.

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. In standard notation the energy, U , of a spin state of a nucleus having a positive magnetogyric ratio, placed in a magnetic field is given by $U = -\gamma \left(\frac{h}{2\pi} \right) m_I B_0$. Which of the following diagrams best represents the variation of the energies of **all** possible spin states of a nucleus with the spin quantum number, $I = 3/2$, with the magnetic field strength?



17. A student found out that three groups of protons, A, B and C, in a molecule shows chemical shifts 9, 4 and 1 (in δ -scale in ppm), respectively, when TMS is used as the reference. Consider the following statements on what can be deduced from these observations.
- Electron density around protons in A is smaller than that around protons in B.
 - Protons in C are more shielded than those in B.
 - The chemical shift of TMS is greater than 9 ppm.

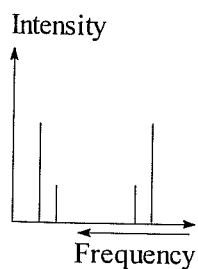
The correct statements out of (i), (ii) and (iii) above are

- Only (i) and (ii).
 - Only (i) and (iii).
 - Only (ii) and (iii).
 - All (i), (ii) and (iii)
 - None of the answers (a), (b), (c) or (d) is correct.
18. An NMR spectrometer with a 20.0 Tesla superconducting magnet was used to obtain a ^{13}C NMR spectrum of a molecule with two chemically different ^{13}C nuclei. The separation between the two ^{13}C resonances was found to be 1000 Hz. What is the chemical shift difference between the two ^{13}C nuclei?

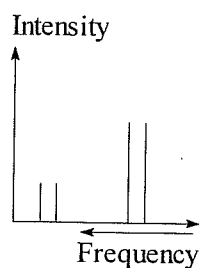
$$\left[\gamma(^{13}\text{C}) = 6.7283 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1} \right]$$

- 1.5 ppm
- 3.7 ppm
- 4.7 ppm
- 4.0 ppm
- 8.0 ppm

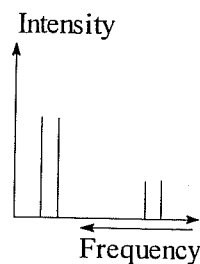
19. Two nuclei, with spin quantum number $I = \frac{1}{2}$, in a molecule, which has no other magnetic nuclei, form an AB spin system. Which of the following best describes the NMR spectrum of the molecule?



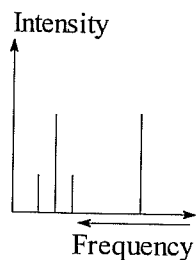
(a)



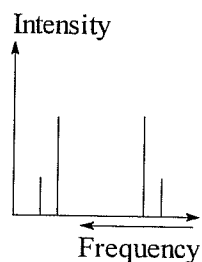
(b)



(c)

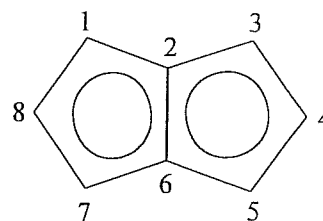


(d)



(e)

20. Consider the following statements made on the protons in the aromatic molecule, C_8H_6 which has the structure shown in the figure to the right.



- (i) Protons in positions 4 and 8 are chemically equivalent.
 (ii) Protons in positions 1 and 5 are magnetically equivalent.
 (iii) Protons in positions 3 and 7 are chemically equivalent.

The correct statement/s 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) Only (i)

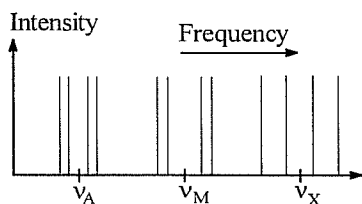
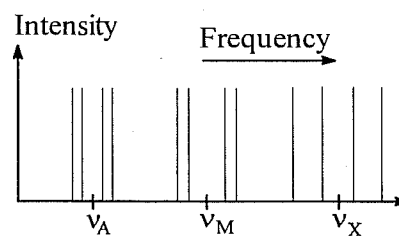
21. Two protons appear in a molecule in two different chemical environments. In a particular spectrometer, their chemical shifts are 14.0 and 1.0. Their scalar coupling constant is 1.10. What best describes the spin system formed by them?

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

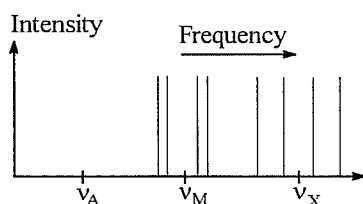
22. Which of the following statements about the low resolution proton NMR spectrum (i.e. disregarding the scalar coupling of protons) of a sample of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, at room temperature, is correct?

- (a) There is only one line since it is a saturated hydrocarbon.
- (b) There are only four lines.
- (c) There are only five lines at an intensity ratio, 3:2:2:2:3.
- (d) There are only two lines at an intensity ratio, 5:1.
- (e) There are only three lines at an intensity ratio, 3:2:1

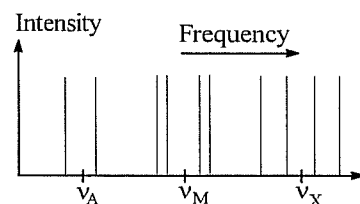
23. The NMR spectrum of three protons in a molecule, which form an AMX spin system, recorded by a student, is shown in the figure. Here, ν_A , ν_M and ν_X are the Larmor frequencies of the three protons. Using the same spectrometer he then recorded the NMR spectrum of the same sample but simultaneously irradiating it with radiation of frequency ν_A . Which of the following figures best represents the NMR spectrum he recorded this time?



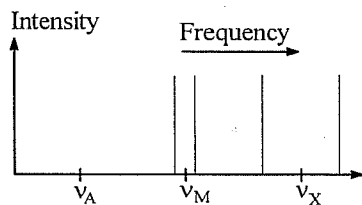
(a)



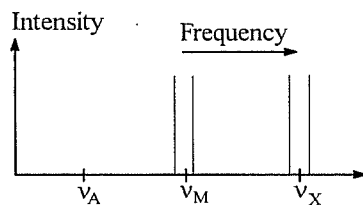
(b)



(c)



(d)



(e)

24. Suppose that we want to calculate the NMR energy levels for a system of three protons where the protons 2 and 3 are in an identical chemical environment. In this case, neglecting indirect spin-spin interactions the NMR interaction energy for the quantum mechanical spin state $\alpha(1)\alpha(2)\beta(3)$, in standard notation, is given by

(a) $-\frac{1}{2}(\hbar/2\pi)(1-\sigma_1)\gamma B_0$

(b) $-\frac{1}{2}(\hbar/2\pi)(1-\sigma_1)\gamma B_0 - \frac{1}{2}(\hbar/2\pi)(1-\sigma_2)\gamma B_0$

(c) $-\frac{1}{2}(\hbar/2\pi)(1-\sigma_2)\gamma B_0$

(d) $-\frac{1}{2}(\hbar/2\pi)(1-\sigma_1)\gamma B_0 + \frac{1}{2}(\hbar/2\pi)(1-\sigma_2)\gamma B_0$

(e) $-\frac{1}{2}(\hbar/2\pi)(1-\sigma_1)\gamma B_0 + \frac{1}{2}(\hbar/2\pi)(1-\sigma_2)\gamma B_0 + \frac{1}{2}(\hbar/2\pi)(1-\sigma_3)\gamma B_0$

25. Consider the following statements about the reasons as to why TMS is accepted as the chemical shift standard reference compound in ^1H NMR spectroscopy.

- (i) Because of the very fast internal rotation about the C-Si bonds and because of high molecular symmetry, all twelve protons of TMS are equivalent and thus gives rise to a single sharp NMR resonance peak.
- (ii) It is polar and reacts easily with almost all the chemical compounds containing protons.
- (iii) The protons in TMS are highly shielded and thus the proton resonance signal of TMS occurs at lower frequency than most of the other proton resonances.

The correct statement/s 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) Only (ii)