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28 JUL 2018

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme — Level 5

Assignment II (Test) — 2017/2018

EXAMINATION



CYU5301 — Concepts in Spectroscopy

MCQ Answer Sheet: Using a **PEN** (not a pencil) mark a cross (x) over the box that corresponds to the most suitable answer.

Reg. No.

*Sample*

FOR EXAMINER'S USE ONLY		
Answers	No.	Marks
Single marked		
Unacceptably marked		
Total marked		
Unmarked		0.0
Correct		
Incorrect		—
Total		
Correct + Incorrect		

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																		

# THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Assignment II (Test) — 2017/2018

CYU5301 — Concepts in Spectroscopy



1 hour

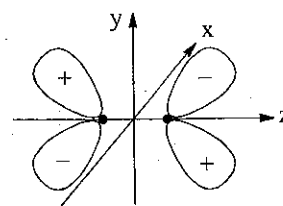
28<sup>th</sup> July 2018 (Saturday)

9.00 a.m. — 10.00 a.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 <sup>-1</sup> mol <sup>-1</sup>
Avogadro constant (N <sub>A</sub> )	=	6.023 × 10 <sup>23</sup> mol <sup>-1</sup>
Faraday constant (F)	=	96,500 Cmol <sup>-1</sup>
Planck constant (h)	=	6.63 × 10 <sup>-34</sup> Js
Velocity of light (c)	=	3.0 × 10 <sup>8</sup> ms <sup>-1</sup>
Standard atmospheric pressure	=	10 <sup>5</sup> Pa (N m <sup>-2</sup> )
Log <sub>e</sub> (X)	=	2.303 Log <sub>10</sub> (X)

1. Consider the following relationships which represent the effect of reflection and inversion operations on the  $\pi_g^*$  orbital of a homonuclear diatomic molecule, shown in the figure. Here,  $\hat{\sigma}_\alpha$  and  $\hat{i}$  represent a reflection operation through plane  $\alpha$  and an inversion operation through the centre of inversion of the molecule, respectively. [Origin of the coordinate system is located at the bond midpoint.]



(i)  $\hat{\sigma}_{xy}(\pi_g^*) = +(\pi_g^*)$

(ii)  $\hat{\sigma}_{yz}(\pi_g^*) = +(\pi_g^*)$

(iii)  $\hat{i}(\pi_g^*) = +(\pi_g^*)$

The correct relationships 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.

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2. The ground state electronic configuration of the last two shells of an exotic atom is  $(n-1)s^2 (n-1)p^6 (n-1)d^{10} (n-1)f^5 ns^2 np^6 nd^{10}$ . Which of the following best represents two of the possible occupations of electrons in the  $(n-1)f$ -level in the above configuration in standard notation?

[ $f_\alpha$  represents the  $(n-1)f$ -orbital with the quantum number,  $m_l = \alpha$ ]

- (a)  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_{+2})^1 (f_{+4})^1$  and  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_0)^1 (f_{+1})^1$ .
- (b)  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_{+2})^2$  and  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_{+2})^1 (f_{+3})^1$
- (c)  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_{+2})^1 (f_{+3})^1$  and  $(f_{-4})^1 (f_{-2})^1 (f_{-1})^1 (f_{+2})^1 (f_{+3})^1$
- (d)  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_{+2})^1 (f_{+3})^1$  and  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_{+3})^2$
- (e)  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_{+2})^1 (f_{+3})^1$  and  $(f_{-3})^1 (f_{-2})^1 (f_{-1})^1 (f_0)^1 (f_{+3})^1$

3. The reflection operation,  $\hat{\sigma}_{xy}$ , of a function,  $f$ , of the position coordinates  $(x, y, z)$  through the  $xy$ -plane is defined by  $\hat{\sigma}_{xy}f(x, y, z) = f(x, y, -z)$ . Consider the following statements about the symmetry of the three functions,  $f_1(x, y, z)$ ,  $f_2(x, y, z)$  and  $f_3(x, y, z)$ , with respect to reflection through the  $xy$ -plane.

- (i)  $f_1(x, y, z) = x + y + z$  has no symmetry.
- (ii)  $f_2(x, y, z) = x + y + z^2$  has + symmetry.
- (iii)  $f_3(x, y, z) = (x + y)z + z^3$  has - symmetry.

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. Two identical atoms, a and b, formed a chemical bond between them forming a homonuclear diatomic molecule. In the process a molecular orbital was formed by the overlap of two atomic orbitals with  $m_l = +3$ . Consider the following statements about this molecular orbital.

- (i) The molecular orbital has the quantum number  $\lambda = 3$ .
- (ii) It has to be a bonding molecular orbital since  $m_l$  values of the two atomic orbitals are positive.
- (iii) It is a  $\phi$  molecular orbital.

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).

5. Which of the following indicates possible spin multiplicities of the molecular electronic configurations,  $\pi^3(\pi')^1$ ,  $\sigma\sigma'$ , and  $\pi^4$ , respectively.

- (a) 3, 0 and 0 (b) 0, 1 and 1. (c) 1, 1 and 1.  
 (d) 1, 3 and 2 (e) 2, 3 and 3.

6. In general an electronic state of a diatomic molecule is represented by the term symbol  $^{2S+1}Q_{\alpha}^{\beta}$ . Consider the following statements about this term symbol.

- (i)  $\beta$  indicates the inversion symmetry of the electronic state.
- (ii) The term symbol of an electronic state in a molecule may not have any symbol in place of  $\beta$ , i.e. a term symbol of the form  $^{2S+1}Q_{\alpha}$ .
- (iii) The term symbol of an electronic state in a molecule may not have any symbol in place of  $\alpha$ , i.e. a term symbol of the form  $^{2S+1}Q^{\beta}$ .

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.

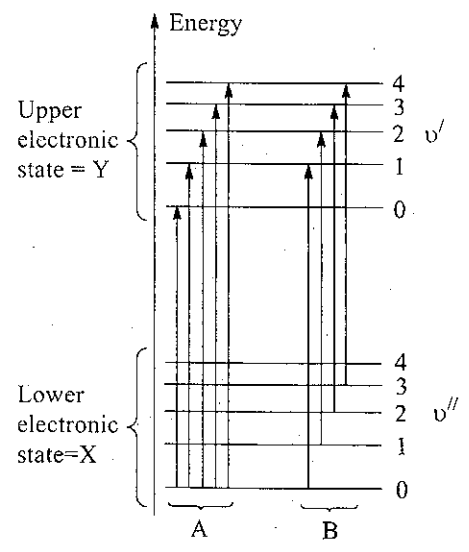
7. Consider the following statements about the properties of the electronic state of a diatomic molecule whose state symbol is  $^1\Sigma_g^+$ .

- (i) Its spin multiplicity is one.
- (ii) It is symmetric with respect to inversion through the inversion center of the molecule.
- (iii) The electronic configuration corresponding this electronic state has no partially filled (molecular electronic) shells.

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.

**Questions 8 and 9 are based on the data shown in the following figure.**

The vibrational energy levels associated with two electronic states, X and Y, of a diatomic molecule, which behaves as an anharmonic oscillator, are shown in the figure to the right. Two sets, A and B, of possible vibrational transitions are also shown. Vibrational quantum numbers of X and Y ( $\nu''$  and  $\nu'$ , respectively) are also indicated.



8. Consider the following statements.
- (i) The transitions in set A leads to a progression in the electronic spectrum of the molecule.
  - (ii) The lowest energy transition in A is not allowed by the selection rules since  $\Delta\nu = 0$  for it.
  - (iii) The line in the electronic spectrum due to transition  $\nu'' = 1 \rightarrow \nu' = 2$  in B appears at a lower frequency than the one due to the transition  $\nu'' = 0 \rightarrow \nu' = 1$  in A.

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.

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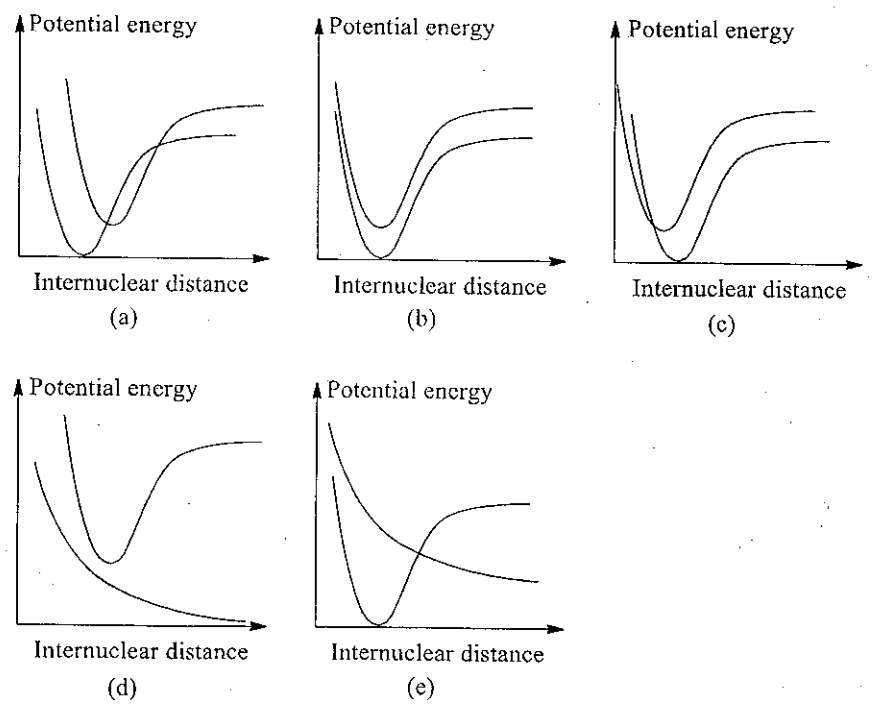
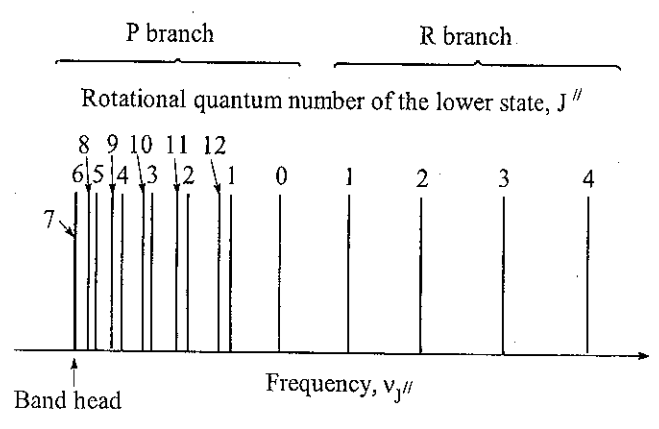
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9. Consider the following statements.
- (i) The difference in frequencies of the adjacent lines in the electronic spectrum due to the vibronic transitions in set A can be used to evaluate the equilibrium vibration frequency of the molecule in the electronic state X.
  - (ii) The difference in frequencies of the adjacent lines in the electronic spectrum due to the vibronic transitions in set B can be used to evaluate the equilibrium vibration frequency of the molecule in the electronic state Y.
  - (iii) The transitions in set B leads to a sequence in the electronic spectrum of the molecule.

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.

10. The positions of the spectral lines in the rotational fine structure in the electronic spectrum of a diatomic molecule is shown in the figure to the right. Which of the following diagrams best represents the potential energy versus internuclear distance of the two electronic states involved in producing this spectrum?



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11. Rotational constants of a diatomic molecule in the excited electronic state and in the ground electronic state are  $10.590 \text{ cm}^{-1}$  and  $9.531 \text{ cm}^{-1}$ , respectively. The electronic and vibrational energy difference for a particular vibronic transition, in wave number units, is  $5000.000 \text{ cm}^{-1}$ . What is the position of the first line in P branch in units of  $\text{cm}^{-1}$ ?

$$\left[ \bar{\nu}_{J''}(\text{P}) = (\bar{B}' - \bar{B}'')(J'')^2 - (\bar{B}' + \bar{B}'')J'' + (\Delta\bar{E}_{\text{Elec}} + \Delta\bar{E}_{\text{Vib}}) \right]$$

- (a) 5021.180                      (b) 5044.478                      (c) 4960.768  
 (d) 4978.453                      (e) 4980.938

12. Consider the following statements about the rotational fine structure associated with a particular vibronic transition in a diatomic molecule. The rotational constants of the molecule in the upper and lower electronic states are the same.

- (i) A band head may appear in the P-branch.  
 (ii) A band head may appear in the R-branch.  
 (iii) There will not be a band head.  
 (iv) Cannot predict in which branch the band head will appear.

The correct statement/s out of (i), (ii), (iii) and (iv) above are

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

13. Consider the following statements.

- (i) Internal conversion is a radiationless (no radiation) transition of a molecule from one electronic state to another electronic state with the same spin multiplicity.  
 (ii) The total energy of the molecule remains the same during an internal conversion.  
 (iii) The two electronic states involved in fluorescence have the same spin multiplicity.

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. In a nuclear reactor scientists prepared three exotic nuclei  ${}_{48}^{110}\text{P}$ ,  ${}_{47}^{108}\text{Q}$  and  ${}_{47}^{109}\text{R}$  where the superscripts and subscripts indicate the mass and atomic numbers of the nuclei, respectively. The nuclear spin quantum number of  ${}_{47}^{109}\text{R}$  is  $3/2$ . Consider the following statements about these three nuclei.

- (i)  ${}_{48}^{110}\text{P}$  is not a magnetic nucleus.  
 (ii) The spin quantum number of  ${}_{47}^{108}\text{Q}$  is not an integer.  
 (iii)  ${}_{47}^{109}\text{R}$  is a quadrupolar nucleus.

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.

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15. The magnetogyric ratios of two magnetic nuclei, A and B are denoted by  $\gamma_A$  and  $\gamma_B$ . They satisfy the relationship,  $\gamma_A > \gamma_B$ . A molecule of compound X has only one A nucleus and only one B nucleus. In the (low resolution) NMR spectrum of X, recorded using a 500 MHz spectrometer, the lines due to A and B appear at frequencies  $\nu_A$  and  $\nu_B$  where  $\nu_A > \nu_B$ . Consider the following statements.

- (i) If both bare nuclei A and B are placed in a 700 MHz NMR spectrometer then the Larmor frequency of A is higher than that of B.
- (ii) One can definitely say that in a molecule of X, the shielding of B is larger than that of A.
- (iii) In a molecule of X, the electron density around A may be larger than that around B.

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) Only (ii).

16. The Larmor frequency of a bare nucleus Q when recorded using a 600 MHz NMR spectrometer is found to be 500 MHz. A molecule of compound Y contains only one Q nucleus. Q produces a line in the (low resolution) NMR spectrum of Y at 450 MHz when recorded using a 600 MHz NMR spectrometer. Which of the following best represents the value of the shielding constant of Q in Y.

- (a) 0.9    (b) 0.7    (c) 0.5
- (d) 0.3    (e) 0.1

17. Consider the following statements.

- (i) The gross selection rule in NMR spectroscopy of a nucleus is that the nuclear spin quantum number of it should be greater than zero.
- (ii) The specific selection rule in (absorption) NMR spectroscopy of a nucleus is  $\Delta m_I = +1$  (where  $m_I$  is the quantum number for the z-component of nuclear spin).
- (iii) Continuous wave NMR spectroscopy is based on absorption of photons by nuclei.

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 (low resolution) proton NMR spectrum of  $\text{CH}_3\text{CH}_2\text{CHCl}_2$  (at room temperature) has only three lines (peaks) with an intensity ratio 1:2:3. We can say that the

- (i) resonance frequency of the strongest line is larger than that of the weakest line.
- (ii) three protons in  $\text{CH}_3$  are in the same (or nearly the same) chemical environment.
- (iii) line with lowest intensity is due to the proton in  $\text{CHCl}_2$ .

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.

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19. In a particular NMR spectrometer, the resonance frequencies of a magnetic nucleus, X, in two different chemical environments, P and Q, in a molecule are  $\nu_P$  and  $\nu_Q$ . It is known that  $\nu_P - \nu_Q = 100$  Hz. The resonance frequency,  $\nu_0$ , of the bare nucleus X in the same spectrometer is 500 MHz. Consider the following statements.

(i) On  $\delta$ -scale, the chemical shift of a nucleus, with respect to a reference, is given by

$$\delta = \frac{\nu_{\text{Sample}} - \nu_{\text{Reference}}}{\nu_0} \times 10^6 \text{ where the symbols have their usual meaning.}$$

(ii) On  $\delta$ -scale, the difference in chemical shift of X in the two chemical environments, P and Q, is given by  $\delta_P - \delta_Q = 0.2$  ppm.

(iii) Shielding of X in environment P is higher than that in Q.

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. Consider three protons in three different chemical environments in a molecule. Neglecting indirect spin-spin interactions, the NMR interaction energy for the quantum mechanical spin state  $\alpha(1)\alpha(2)\alpha(3)$  of these three protons (in standard notation) is given by

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

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

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

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

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

21. Consider an AMX spin system of protons in a molecule (which has no other magnetic nuclei) with spin-spin couplings,  $J_{AM} = 14$  Hz,  $J_{AX} = 6$  Hz and  $J_{MX} = 3$  Hz. The expected pattern for the NMR signal due to M nucleus has 4 lines with intensity ratio

(a) 1:1:1:1 and line separation 3,12,3 Hz.

(b) 1:3:3:1 and line separation 6,12,6 Hz.

(c) 1:1:1:1 and line separation 6,8,6 Hz.

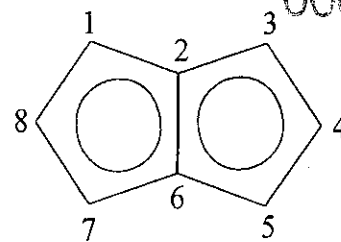
(d) 1:3:3:1 and line separation 6,7,6 Hz.

(e) 1:1:1:1 and line separation 3,11,3 Hz.



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X, m

22. Consider the following statements made on the protons in the aromatic molecule,  $C_8H_6$  which has the structure shown in the figure.



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

23. Two protons appear in a molecule in two different chemical environments. In a particular spectrometer, their chemical shifts are 12.0 and 1.0. Their scalar coupling constant is 0.67. What best describes the spin system formed by them?

- (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.

24. Which of the following statements is true for magnetically equivalent (magnetic) nuclei?

- (a) Magnetically equivalent nuclei do not give rise to peaks in the NMR spectrum.
- (b) Spin-spin interactions between magnetically equivalent nuclei do not lead to any splitting in NMR absorption peaks.
- (c) Magnetically equivalent nuclei do not have spin-spin interactions with the spins of neighbouring magnetic nuclei.
- (d) Magnetically equivalent nuclei do not have identical spin-spin interactions with the spins of neighbouring groups.
- (e) Only protons can be magnetically equivalent to each other.

25. Consider the following statements about a continuous wave NMR spectrometer.

- (i) The sample used in recording the NMR spectrum is rotated in order to minimise the effects of inhomogeneity of the applied magnetic field,  $B_0$ .
- (ii) The radio waves emitted by the sample is measured.
- (iii) The axis of the detector (receiver) 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.