

## THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme — Level 4

Assignment II (Test) — 2019/2020

## CYU5301 — 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. of Q	Marks
Single marked		
Unacceptably marked		
Total marked		
Unmarked		0.0
Correct		
Incorrect		0.0
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																		

**Reg. No.:** .....

**Name:** .....

**Address:** .....

.....

.....

.....

# THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Assignment II (Test) — 2019/2020

CYU5301 — Concepts in Spectroscopy



1 hour

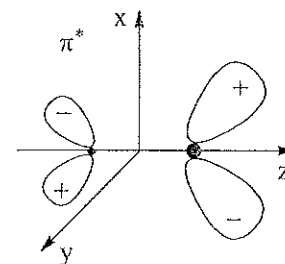
11<sup>th</sup> September 2019 (Wednesday)

4.15 p.m. — 5.15 p.m.

- ⊗ Answer all 25 questions (25 x 4 = 100 marks)
  - ⊗ Choose the most correct answer to each question and mark this answer with an “X” on the MCQ answer sheet 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.
  - ⊗ **Only** the answers given in the MCQ answer sheet will be marked. (Any other attached sheets will **NOT** be marked)
  - ⊗ 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 C mol <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 (Nm <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  $\pi^*$  orbital of a heteronuclear diatomic molecule, shown in the figure. This  $\pi^*$  orbital was obtained through the overlap of  $p_x$  orbitals in the two atoms. Here,  $\hat{\sigma}_\alpha$  and  $\hat{i}$  represent a reflection operation through plane  $\alpha$  and an inversion operation through the bond midpoint, respectively. [Origin of the coordinate system is located at the bond midpoint.]



(i)  $\hat{\sigma}_{xy}(\pi^*) = -(\pi^*)$

(ii)  $\hat{\sigma}_{xz}(\pi^*) = +(\pi^*)$

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

The correct relationship/s out of (i), (ii) and (iii) above is/are

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

2. Consider the following statements.

In general, a molecular electronic configuration

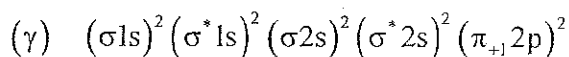
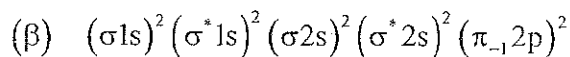
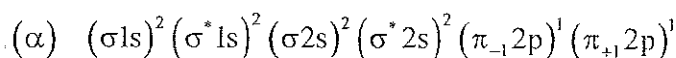
- (i) indicates the number of electrons in molecular electronic shells.
- (ii) indicates the number of electrons in individual molecular orbitals.
- (iii) may have open shells.

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.

**Use the following information in answering questions 3 – 5.**

Three orbital occupations, ( $\alpha$ ), ( $\beta$ ) and ( $\gamma$ ), of a heteronuclear diatomic ion are shown below.



3. Consider the following statements.

- (i) All three orbital occupations belong to the same electronic configuration.
- (ii) Orbital occupation ( $\alpha$ ) can give a triplet state.
- (iii) Orbital occupation ( $\alpha$ ) **cannot** give a singlet state.

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 following statements.

- (i) Spin multiplicity of ( $\beta$ ) can be three.
- (ii) Spin multiplicity of ( $\gamma$ ) is one.
- (iii) Spin multiplicity of ( $\alpha$ ) can be one.

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 statements about Q in the term symbol,  $^{2S+1}Q_{\alpha}^{\beta}$ , for the electronic states arising out of the orbital occupations.
- ( $\alpha$ ) can have only  $\Sigma$  states.
  - ( $\beta$ ) can have only  $\Sigma$  states.
  - ( $\gamma$ ) can have only  $\Sigma$  states.

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

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

6. Consider the following statements.

- (i) The electronic wave function/s corresponding to the electronic configuration

$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^2$  has/have gerade inversion symmetry.

- (ii) The electronic wave function/s corresponding to the electronic configuration

$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^3$  has/have ungerade inversion symmetry.

- (iii) The electronic wavefunctions of heteronuclear diatomic molecules do **not** have either gerade or ungerade inversion 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.

7. Consider the following statements.

- (i) The electronic wave function/s corresponding to the electronic configuration

$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4$  has/have **only** + reflection symmetry.

- (ii) The total number of  $\Sigma$  states with + reflection symmetry generated by the electronic

configuration  $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^1 (\pi_u 3p)^1$  is equal to the total number of  $\Sigma$  states with – reflection symmetry generated by it.

- (iii) The total number of  $\Sigma$  states with + reflection symmetry generated by the electronic

configuration  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\delta 3d)^1 (\delta 4d)^1$  is **not** equal to the total number of  $\Sigma$  states with – reflection symmetry generated by it.

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).

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

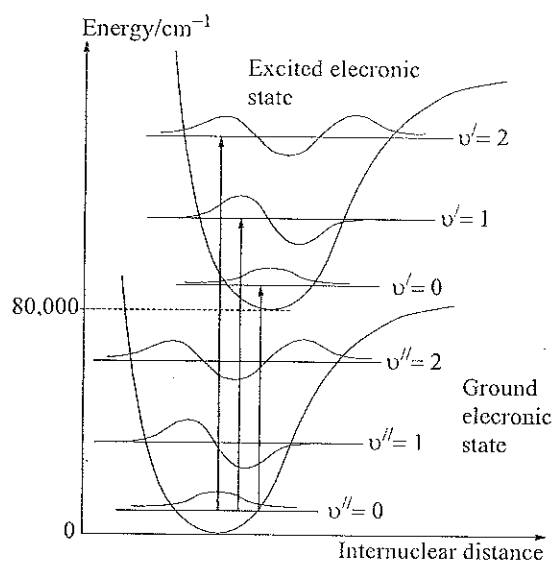
- (i) It belongs to a homonuclear diatomic molecule.
- (ii) The total spin,  $S$ , of this state is zero.
- (iii) The electronic configuration corresponding this electronic state may have partially filled (molecular electronic) shells.

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.

Use the following information in answering questions 9 and 10.

The potential energy curves and the first three vibrational energy levels of the electronic ground and excited states of a diatomic molecule are shown in the figure. The vibrational wavefunctions associated with the energy levels are also shown. The equilibrium vibration frequency and the anharmonicity constants in the ground state are  $\bar{\omega}_e'' = 3500 \text{ cm}^{-1}$  and  $x_e'' = 0.100$ . For the excited state they are  $\bar{\omega}_e' = 2500 \text{ cm}^{-1}$  and  $x_e' = 0.040$ .



9. Consider the following statements.

- (i) Out of the three transitions indicated by vertical arrows, the most probable transition is  $v'' = 0 \rightarrow v' = 0$ .
- (ii) The excited state is a bound state of the molecule.
- (iii) The rotational constant of the molecule in the excited state,  $B_{\text{EX}}$ , is smaller than that in the ground state,  $B_{\text{Gr}}$ , i.e.  $B_{\text{EX}} < B_{\text{Gr}}$ .

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 wave number, in  $\text{cm}^{-1}$ , of the photon required to bring about the transition  $v'' = 0 \rightarrow v' = 0$  is best represented by

- (a) 82,887.5
- (b) 80,437.5
- (c) 78,887.5
- (d) 87,562.5
- (e) 79,562.5

11. Consider the following statements.

- (i) The specific selection rule for a vibrational transition in electronic spectroscopy of a diatomic molecule is  $\Delta v = 0, \pm 1, \pm 2, \dots$
- (ii) The specific selection rule for a rotational transition in electronic spectroscopy of a diatomic molecule is  $\Delta J = 0, \pm 1$ .
- (iii) In general, one may be able to observe P, Q and R branches in the rotational fine structure in the vibronic spectrum corresponding to the vibrational transition  $v' = 1 \leftarrow v'' = 0$  of a diatomic 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.

12. Consider the following statements about the rotational fine structure in an electronic spectrum of a diatomic molecule. As usual, the rotational constants in the upper and lower energy electronic states are represented by  $B'$  and  $B''$  respectively.

- (i) There will **not** be a band head if  $B' = B''$ .
- (ii) Q branch has more than one line if  $B' = B''$ .
- (iii) Band head appears in the R branch if  $B' < B''$ .

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

13. Consider the following statements.

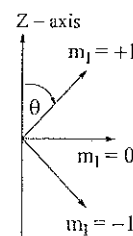
- (i) In *static quenching*, a quenching agent forms a non-fluorescent complex with the fluorescent molecule and thereby reduce the fluorescence.
- (ii) In *dynamic quenching* the quenching agent accepts energy from an electronically excited state of a molecule leading to an electronic de-excitation.
- (iii) In general, in *fluorescence*, the frequency of the emitted photons is higher than the frequency of the absorbed photons that produce the excited molecules.

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. Possible orientation of the spin angular momentum vector of a nucleus with the spin quantum number,  $I = 1$ , corresponding to different  $m_I$  values, are shown in the figure. What best represents the value of the angle,  $\theta$ , in degrees?

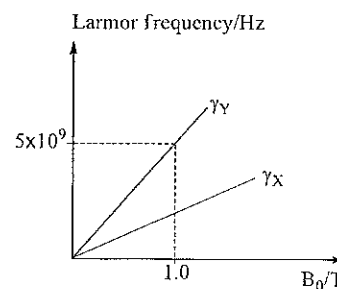
- (a) 25
- (b) 35
- (c) 45
- (d) 60
- (e) 70



15. The Larmor frequency of a proton X in a molecule, in a 500 MHz spectrometer is 499.998693 MHz. In the same spectrometer, protons in TMS resonate at 499.997473 MHz. The chemical shift of X, in  $\delta$  scale, in ppm, is best represented by

- (a) 1.25
- (b) 4.42
- (c) 1.00
- (d) 2.44
- (e) 9.00

16. The variation of the Larmor frequency of two bare nuclei, X and Y, with an applied magnetic field strength,  $B_0$ , is shown in the figure. Here,  $\gamma_X$  and  $\gamma_Y$  are the magnetogyric ratios of X and Y, respectively. For both X and Y,  $I = 1/2$ . Consider the following statements.



- (i)  $\gamma_Y < \gamma_X$ .
- (ii)  $\gamma_Y = 3.14 \times 10^{10} \text{ rad s}^{-1} \text{ T}^{-1}$ .
- (iii)  $|\nu_X - \nu_Y|$ , where  $\nu_X$  and  $\nu_Y$  are the NMR resonance frequencies of X and Y, increases with increasing magnetic field strength.

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

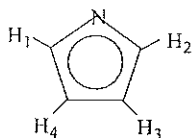
- (a) Only (i) and (ii).      (b) Only (i) and (iii).      (c) Only (ii) and (iii).  
 (d) Only (i)      (e) Only (ii).
17. Consider the following statements.
- (i) Keeping the magnetic field strength constant and changing the frequency of radiation in NMR spectroscopy is called *sweeping*.
- (ii) Gross selection rule in NMR spectroscopy is  $I \geq 1$  where I is the magnetic quantum number of the nucleus.
- (iii) The static magnetic field strength in a 800 MHz NMR spectrometer is higher than that in a 600 MHz NMR spectrometer.

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

- (a) Only (i) and (ii).      (b) Only (i) and (iii).      (c) Only (ii) and (iii).  
 (d) Only (i)      (e) Only (iii).
18. Two protons resonate at 500.234567 MHz and 500.234575 MHz in an NMR spectrometer. Their scalar coupling constant is 1.4 Hz. 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.

19. Consider the following statements.

- (i) The three protons in the  $-\text{CH}_3$  group in a  $\text{CH}_3\text{CH}_2\text{OH}$  molecule (at room temperature) are *magnetically* equivalent.
- (ii) The three protons in the  $-\text{CH}_3$  group in a  $\text{CH}_3\text{CH}_2\text{OH}$  molecule (at room temperature) are *chemically* equivalent.
- (iii) Protons 1 and 2 in the molecule



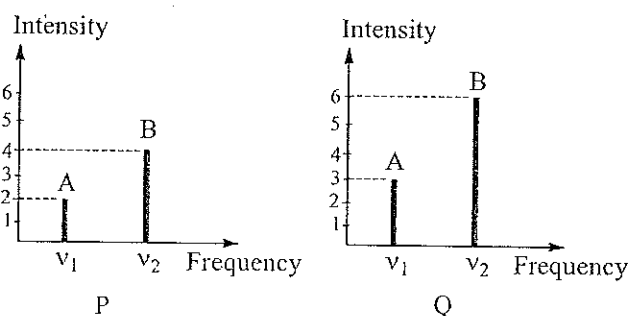
are *magnetically* equivalent.

The correct statement/s out of (i), (ii) and (iii) above is/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).



20. A student was given two solutions, P and Q, of the same compound X. The figure shows the low resolution NMR spectra of two groups of protons, A and B, in X, recorded by the student using these two solutions. [The spectrometer was operated under the same conditions when recording the two spectra. The units of the axes in the two spectra are the same.]



Consider the following statements.]

- In one molecule of X, group B can only have either 4 or 6 protons.
- $N_A : N_B = 1 : 2$  where  $N_A$  and  $N_B$  are the number of protons in groups A and B in one molecule, respectively.
- Concentration of X in Q is higher than the concentration of X in P.

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

- Only (i) and (ii).
- Only (i) and (iii).
- Only (ii) and (iii).
- Only (ii)
- Only (iii).

21. A molecule has four protons, labelled as 1, 2, 3 and 4, in two different chemical environments. Protons 1 and 2 are in the same chemical environment with shielding constant  $\sigma$ . Protons 3 and 4 are in the same chemical environment with the shielding constant  $\sigma'$ . The molecule is placed in an NMR spectrometer with a static magnetic field strength,  $B_0$ . The magnetogyric ratio of a protons is  $\gamma$ .

Consider the following statements.

- The interaction energy of the  $\alpha\alpha\beta\alpha$  spin state of the four protons is given by

$$E(\alpha\alpha\beta\alpha) = -\left[ h\gamma(1-\sigma)B_0/2\pi \right].$$

- The transition  $\alpha\alpha\beta\alpha \rightarrow \alpha\beta\alpha\alpha$  **cannot** produce a line in the NMR spectrum.
- The frequency of the line, in the NMR spectrum, produced by the transition

$$\alpha\alpha\beta\alpha \rightarrow \alpha\alpha\beta\beta \text{ is } \left[ \gamma(1-\sigma')B_0 \right] / 2\pi.$$

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

- Only (i) and (ii).
- Only (i) and (iii).
- Only (ii) and (iii).
- All (i), (ii) and (iii).
- Only (iii).

22. Consider the following statements about a continuous wave NMR spectroscopy.

- The sample used in recording the NMR spectrum is rotated in order to minimise the effects of inhomogeneity of the applied magnetic field,  $B_0$ .
- The axis of the detector coil is perpendicular to the direction of the applied magnetic field.
- The radio waves emitted by the sample is measured.

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.