00082

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme — Level 4

Assignment I (Test) — 2019/2020

CYU5301 — Concepts in Spectroscopy

MCQ Answer Sheet: Mark a cross $(\times)$ 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																		

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2. Consider the following statements.

(i) The gross selection rule in IR spectroscopy states that a diatomic molecule must change its dipole moment during vibration in order for it to show an IR spectrum.

(ii) The specific selection rule in IR spectroscopy of a diatomic molecule which behaves as a harmonic oscillator is $\Delta\upsilon = \pm 1$, where υ is the vibrational quantum number.

(iii) The specific selection rule in microwave spectroscopy of a diatomic molecule which behaves as a rigid rotor is $\Delta J = \pm 1$, where J is the rotational quantum number.

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.

3. A hypothetical molecule has rotational, vibrational and electronic energy levels only. Most probably, in absorption spectroscopy of this molecule

(i) mixed transitions involving only the vibrational and rotational energy levels occur in the *IR region* of the electromagnetic spectrum.

(ii) mixed transitions involving only the vibrational and electronic energy levels occur in the *IR* of the electromagnetic spectrum.

(iii) pure rotational transitions occur in the *microwave region* of the electromagnetic 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.

4. Pick the set which has the largest number of molecules which **show** microwave spectra.

(a) CH_3CH_3, $CH_2=CH_2$, $CHCl_3$

(b) NH_3, CH_3COCH_3, BF_3

(c) CH_3COOH, $CH_2=O$, CH_2Cl_2

(d) CH_4, SF_6, CCl_4

(e) C_2H_2, CH_3OH, CH_3CH_2OH

5. Consider the following statements regarding the overtones in the IR spectrum of a heteronuclear diatomic molecule, AB.

(i) In general the intensity of an overtone *decreases* with *increasing* vibrational quantum number of the excited level involved.

(ii) The 3rd overtone is due to the transition $\upsilon = 0 \rightarrow \upsilon = 3$, where υ is the vibrational quantum number.

(iii) The intensity of an overtone may decrease when the temperature of the sample is increased.

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 (ii).

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THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5
Assignment I (Test) — 2019/2020
CYU5301 — Concepts in Spectroscopy

1 hour

18th August 2019 (Sunday) 9.00 a.m. — 10.00 a.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)	=	$8.314\ JK^{-1}mol^{-1}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ mol^{-1}$
Faraday constant (F)	=	$96,500\ Cmol^{-1}$
Planck constant (h)	=	$6.63\times10^{-34}\ Js$
Velocity of light (c)	=	$3.0\times10^{8}\ ms^{-1}$
Standard atmospheric pressure	=	$10^{5}\ Pa\left(Nm^{-2}\right)$
$Log_e(X)$	=	$2.303\ Log_{10}(X)$

1. Consider the following statements.....
   (i) Spectroscopy always involves the measurement of *absorbed* intensity of electromagnetic radiation by a sample of molecules.
   (ii) In obtaining the vibrational and/or rotational spectrum, the molecules in the sample *exchange* energy with the incident beam of electromagnetic radiation in the spectrometer.
   (iii) Raman spectroscopy is based on *scattering* of photons by the molecules in a 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.

6. In an experiment, a student prepared an exotic heteronuclear diatomic molecule XY at low temperature. It dissociated when the temperature was increased.
Consider the following statements about the molecule XY.

(i) In standard notation, the vibrational energy levels of XY are given by $\varepsilon_\upsilon = h\left(\upsilon+\frac{1}{2}\right)\omega_e - h\left(\upsilon+\frac{1}{2}\right)^2 \omega_e x_e$.

(ii) The difference in energy between two adjacent vibrational levels of XY becomes smaller with increasing vibrational quantum number.

(iii) At low temperature, the vibrational absorption spectrum of XY **cannot** have more than one line.

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).

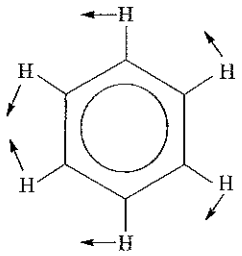
7. The *fundamental* in the IR spectrum of a diatomic molecule AB appears at 1860.00 cm^{-1}. The *anharmonicity constant* of AB is 0.07332. The equilibrium vibration frequency and the frequency of the 2nd overtone in the IR spectrum of AB, respectively, are

(a) 2179.62 cm^{-1} and 3943.50 cm^{-1} (b) 1903.98 cm^{-1} and 5544.42 cm^{-1}
(c) 1903.98 cm^{-1} and 5555.42 cm^{-1} (d) 2243.98 cm^{-1} and 4621.14 cm^{-1}
(e) 2179.62 cm^{-1} and 4621.14 cm^{-1}

8. Consider the linear molecule C_6H_2. Which set of numbers best represents, respectively, the number of translational, rotational and vibrational degrees of freedom the molecule has?

(a) (2, 2, 20) (b) (2, 2, 19) (c) (2, 3, 19) (d) (3, 2, 20) (e) (3, 2, 19)

9. A normal mode of benzene is shown in the figure. The carbon nuclei do not move in this normal mode and the hydrogen nuclei move in the plane of the molecule.
Consider the following statements about this normal mode.



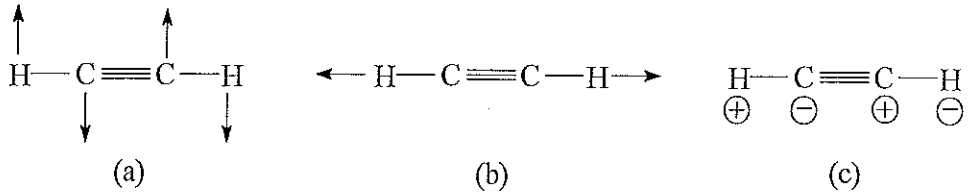
(i) It is IR active.

(ii) It is a perpendicular mode.

(iii) The dipole moment of the molecule does **not** change during vibration in this normal mode.

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).

10. Consider the following statements about the three normal modes of C_2H_2 shown below.



(a) (b) (c)

(i) The normal modes (a) and (c) are *accidentally* degenerate.

(ii) The normal mode (b) is IR inactive.

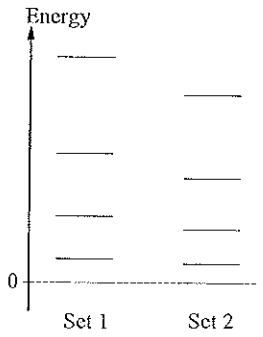
(iii) The normal modes (a) and (c) have the same equilibrium vibration frequency.

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).

11. The experimental spectrum of a linear polyatomic molecule is fitted well to the expression $\bar{\nu}/\left(\mathrm{cm}^{-1}\right) = 20.84\,(J+1) - 0.0088\,(J+1)^3$. The symbols have their usual meaning. The rotational constant and the centrifugal distortion constant of the molecule, respectively, in units of cm^{-1}, are

(a) 20.84 and 0.0088 (b) 10.42 and 0.0044 (c) 20.84 and 0.0088
(d) 5.21 and 0.0088 (e) 10.42 and 0.0022

12. The figure shows two sets of the first 5 rotational energy levels of a diatomic molecule, AB. One set is calculated *assuming* AB to be a non-rigid rotor. The other set is calculated *assuming* AB to be a rigid rotor (at the same bond length). Consider the following statements about them.



(i) Set 1 represents the rotational energies of AB if it is a non-rigid rotor.

(ii) The frequency corresponding to the rotational transition $J = 3 \rightarrow J = 4$ calculated with Set 1 is larger than that calculated with Set 2.

(iii) Under both assumptions (rigid and non-rigid rotor), the specific selection rule in microwave absorption spectroscopy of AB is $\Delta J = +1$.

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 (ii).

13. The vibrational energy levels of a polyatomic molecule (with non-degenerate normal modes) designated by (0,0,0), (0,1,0), (0,0,4,) and (2,3,1) are called, respectively,

(a) fundamental level, ground level, overtone level and combination level

(b) ground level, fundamental level, combination level and overtone level

(c) ground level, fundamental level, overtone level and combination level

(d) ground level, fundamental level, overtone level and hot level

(e) fundamental level, ground level, combination level and combination level

14. Consider the following statements.

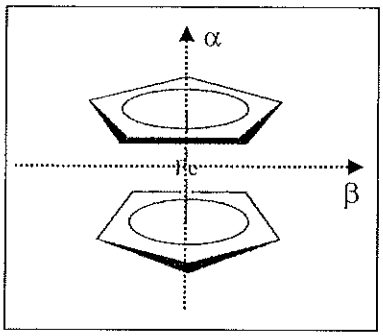
(i) The ellipsoid of inertia of trans $-SF_4I_2$ is an ellipsoid of revolution.

(ii) A molecule which does not have at least one rotational axis of symmetry of order greater than two does **not** have an ellipsoid of inertia.

(iii) The ellipsoid of inertia of SF_6 is spherical.

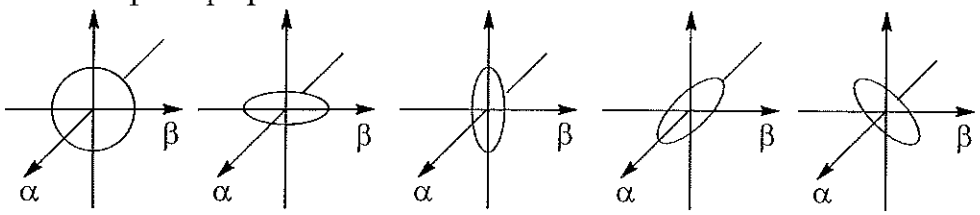
The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

Use the following information in answering questions 15 – 17.

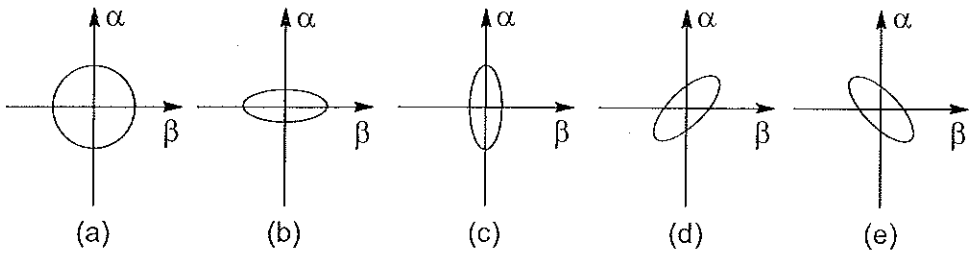


Ferrocine molecule, in its staggered configuration, is shown in the figure. Axis α is the principal axis of the molecule. Axis β is perpendicular to α and passes through the Fe nucleus. Moment of inertia of the molecule about α and β are I_α and I_β, respectively. They have the relationship $I_\beta > I_\alpha$.

15. Which of the following best represents the cross section of the ellipsoid of inertia of ferrocine on a plane perpendicular to α?



16. Which of the following best represents the cross section of the ellipsoid of inertia of ferrocine on the $\alpha\beta$ plane?



17. Consider the following statements about the ferrocine molecule.

(i) The inertia ellipsoid of the molecule is a prolate ellipsoid.

(ii) It is a symmetric top molecule.

(iii) Two principal moments of inertia of the molecule are equal to each other.

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 18 and 19.

Imagine the situation where a student generating the Raman spectrum of a sample of molecules having only two energy levels, ε_1 and ε_2 where $\varepsilon_1 = 0.5\times10^{-23}$ J and $\varepsilon_2 = 1.5\times10^{-23}$ J. The frequency, ν, of the radiation beam used in generating the Raman spectrum was 1.0×10^{10} Hz.

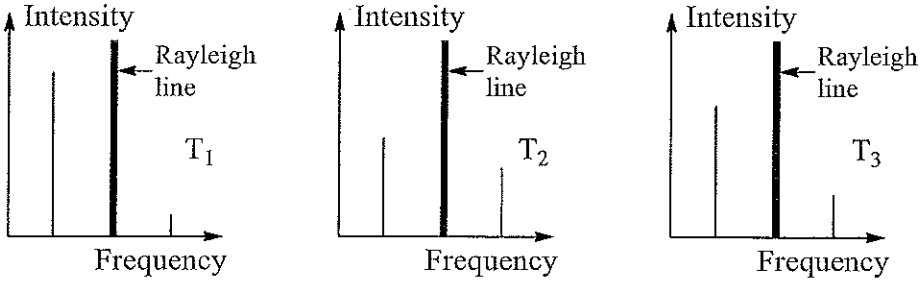
18. Which of the following best represents the absolute value of the observed Raman shift, i.e. $|\Delta\nu|$, in units of Hz?

(a) 0.5×10^{10} (b) 1.0×10^{10} (c) 1.5×10^{10} (d) 2.0×10^{10} (e) 2.5×10^{10}

19. What is the maximum number of lines/peaks the student may have observed in the Raman spectrum he/she generated in the above mentioned experiment?

(a) 1 (b) 2 (c) 3 (d) 4 (e) 5

20. A hypothetical molecule has only two energy levels. Assume that the following figure schematically represents the Raman spectrum of a gaseous sample of those molecules obtained by a student at three different temperatures, T_1, T_2 and T_3.



Which of the following best represents the relationship among the temperatures?

(a) $T_1 > T_2 > T_3$ (b) $T_1 < T_2 < T_3$ (c) $T_1 > T_3 > T_2$
(d) $T_1 < T_3 < T_2$ (e) None of the answers (a), (b), (c) or (d) is correct.

21. Consider the following statements about the polarisability of a chemical bond.

(i) The polarisability of a chemical bond is *least* along the bond axis and *largest* in a direction perpendicular to it.

(ii) The polarisability (in any direction) of a *given chemical bond* increases when the bond is stretched and decreases when the bond is compressed.

(iii) The change in polarisability of a bond is larger when it is shortened by a distance δr than it is elongated by the same distance, δr.

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.

22. Consider the following statements about the polarisability ellipsoid of an H_2 molecule.

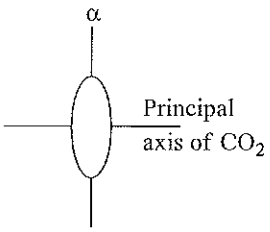
(i) It is an oblate ellipsoid.

(ii) It is a prolate ellipsoid.

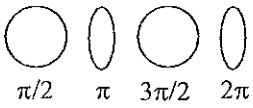
(iii) It becomes smaller when the bond is stretched.

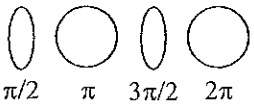
The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

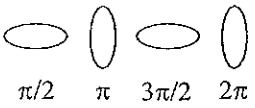
23. The cross section of the polarisability ellipsoid of a CO_2 molecule on the plane of the paper is shown in the figure.

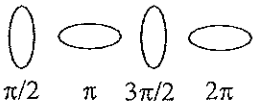


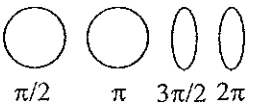
The series of cross sections of the polarisability ellipsoid of this CO_2 molecule on the plane of the paper when rotated by $\pi/2$, π, $3\pi/2$ and 2π about the axis α, (which is perpendicular to the principal axis of CO_2, passes through the centre of mass and lies on the plane of the paper) is best represented by,

(a) 

(b) 

(c) 

(d) 

(e) 

24. Out of C_2H_6, CH_4, SF_6, HCN, CH_3Cl, the molecules which can show a pure rotational Raman spectrum are

(a) C_2H_6, HCN, CH_3Cl

(b) CH_4, HCN, CH_3Cl

(c) CH_4, SF_6, CH_3Cl

(d) CH_4, C_2H_6, CH_3Cl

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

25. The Raman active vibrational normal mode/s of CO_2 is/are

(a) Only symmetric stretching mode.

(d) Only the bending mode.

(b) Only the anti-symmetric stretching and bending modes.

(c) Only the symmetric stretching and bending modes.

(e) All symmetric stretching, anti-symmetric stretching and bending modes.