

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Assignment I (Test) — 2017/2018

CYU5301 — Concepts in Spectroscopy



1 hour

24th June 2018 (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 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.

Gas constant (R)	=	8.314 JK ⁻¹ mol ⁻¹
Avogadro constant (N _A)	=	6.023 × 10 ²³ mol ⁻¹
Faraday constant (F)	=	96,500 Cmol ⁻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)

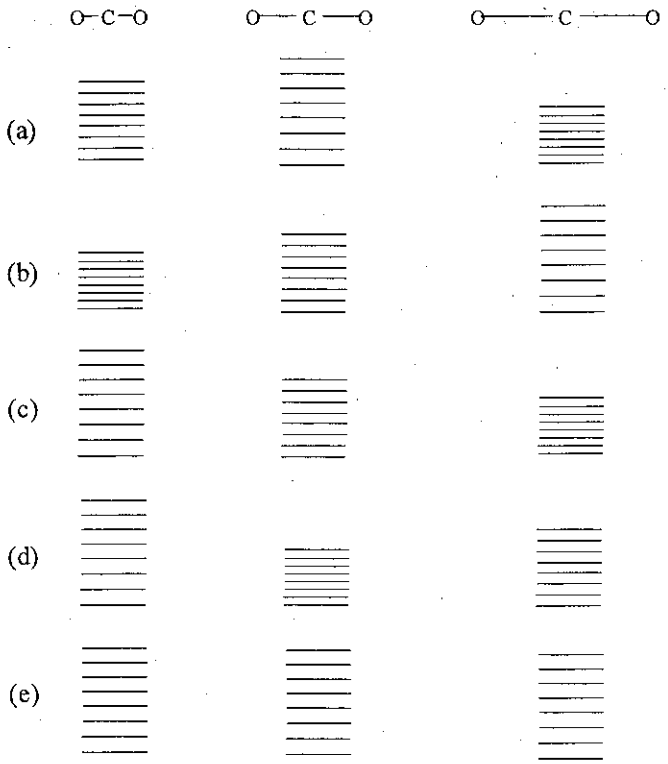
1. Consider the following statements.

- (i) In absorption of radiation by a molecule, the Bohr condition may be given by $h\nu = E_i - E_f$. Here, h and ν are the Planck constant and frequency of the absorbed photon, respectively. E_i and E_f are the energy of the molecule before and after the absorption, respectively.
- (ii) In an emission process, the Bohr condition gives the *relationship* between the frequency of the photon emitted by a molecule and the energy levels of that molecule which are involved in the accompanying transition.
- (iii) A relationship similar to the Bohr condition may be used to calculate the frequency shifts encountered in Raman spectroscopy.

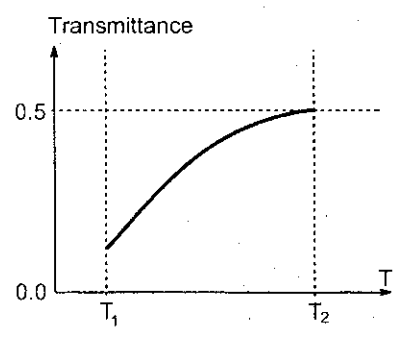
The correct statements out of (i), (ii) and (iii) above are

- (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. What is the equilibrium vibration frequency of the diatomic molecule, AB, if the force constant of the A–B bond is 864.0 Nm⁻¹? [Relative atomic masses: A = 1.00, B = 19.0].
- (a) 3.72 × 10¹⁴ Hz
 - (b) 1.18 × 10¹⁴ Hz
 - (c) 2.24 × 10¹⁴ Hz
 - (d) 5.14 × 10¹⁴ Hz
 - (e) 1.68 × 10¹⁴ Hz

3. The following diagram indicates the first eight rotational energy levels of CO₂ at three different C–O bond lengths. At each bond length, the molecule is assumed to behave as a rigid rotor. Which set, out of (a), (b), (c), (d) and (e), best describes the variation of the spacing in rotational energy levels of CO₂ as the C–O bond length increases.



4. Using a spectrometer, a student measured the transmittance of a sample of a dilute aqueous solution of a pure compound A, in the temperature range T_1 to T_2 . The sample was in a sealed sample tube of length l . Her results are shown in the figure. It is known that A does not undergo any reaction in the above temperature range in aqueous medium. Consider the following statements.



- (i) In the spectrometer, the sample absorbed more radiation energy at T_1 than at T_2 .
- (ii) The concentration of A is lowest at T_1 .
- (iii) The molar extinction coefficient of A at T_1 is higher than that at T_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) Only (i).

5. Consider the following statements.

- (i) Anharmonic oscillator model could explain the existence of *more than one line/band* in the (pure vibrational) IR spectrum of a diatomic molecule.
- (ii) There can be only one line/band in the (pure vibrational) IR spectrum of H^{37}Cl since it has a very *strong bond*.
- (iii) A diatomic molecule which behaves as a harmonic oscillator cannot dissociate.

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.

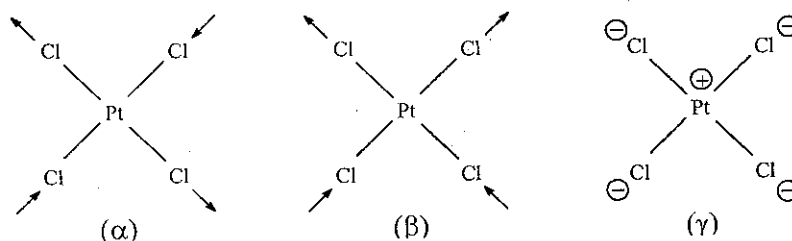
6. Consider the following statements.

- (i) A *linear molecule* has a larger number of vibrational degrees of freedom than a *non-linear molecule* having the same number of nuclei.
- (ii) A *linear molecule* has a smaller number of rotational degrees of freedom than a *non-linear molecule*.
- (iii) A *linear molecule* has the same number of translational degrees of freedom as in a *non-linear 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.

7. Three normal modes, α , β and γ , of planar $[\text{PtCl}_4]^{2-}$ ion are shown in the following figure in standard notation.



Consider the following statements.

- (i) (α) is a perpendicular normal mode and can show an IR spectrum.
- (ii) (β) can show an IR spectrum.
- (iii) (γ) is a parallel normal mode and can show an IR spectrum.

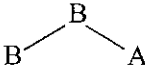
The correct statements out of (i), (ii) and (iii) above are

- (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.

8. A polyatomic molecule has four non-degenerate normal modes. In the IR spectrum, it produces four lines, corresponding to the 1st, 2nd, 3rd and 4th normal modes, at frequencies ν_1 , ν_2 , ν_3 and ν_4 respectively. The molecule behaves as a harmonic oscillator in each of these normal modes. What is the correct relationship between ν_2 and ν_3 if the vibrational energy levels (1,3,4,0) and (1,4,2,0) are accidentally degenerate?

- (a) $\nu_3 = \nu_2$ (b) $3\nu_3 = 4\nu_2$ (c) $4\nu_3 = 3\nu_2$
 (d) $\nu_3 = 2\nu_2$ (e) $2\nu_3 = \nu_2$

9. Three fundamental bands are observed in the infrared spectrum of a triatomic molecule AB_2 . We can say that

- (i) if AB_2 is a *bent molecule* then its structure has to be 
 (ii) if AB_2 is a *linear molecule* then its structure has to be B-B-A.
 (iii) AB_2 has a *permanent* dipole moment.

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

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

10. Consider the following statements.

- (i) A CO_2 molecule has a doubly degenerate normal mode.
 (ii) Degenerate vibrational normal modes of a polyatomic molecule have the same equilibrium vibration frequency.
 (iii) The number of *distinct* equilibrium vibration frequencies of a planar molecule, AB_4 , cannot exceed 9.

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. In a diatomic molecule the centrifugal distortion

- (i) makes the energy of a rotational level higher than the corresponding level in the rigid rotor approximation.
 (ii) *reduces the separation* between adjacent lines in the microwave spectrum with increasing rotational quantum number.
 (iii) allows the molecule to *stretch* at higher rotational energy.

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. The specific selection rule in the rotational spectroscopy of a diatomic molecule, which is elastic, is

- (a) $\Delta J = \pm 1, \pm 2, \dots$ (b) $\Delta J = 0, \pm 1$ (c) $\Delta J = \mp 1$
 (d) $\Delta J = \pm 1, \mp 3, \mp 5, \dots$ (e) None of the answers (a), (b), (c) or (d) is correct.

13. Consider the following statements.

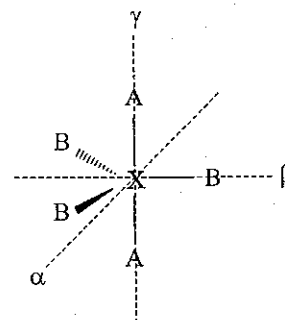
- (i) Spectroscopy always involves the measurement of *absorbance* of electromagnetic radiation by a sample of molecules.
 (ii) In obtaining the vibrational and/or rotational spectrum, the molecules in the sample *exchange* energy with the incident beam of electromagnetic radiation in the spectrometer.
 (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.

Use the following information in answering questions 14, 15, 16 and 17.

The molecule, XB_3A_2 has a trigonal bipyramidal geometry as shown in the figure. Bond lengths X-A and X-B are equal. All three B-X-B angles are equal. Mass of an A nucleus is twice as much as that of B. (i.e. $m_A = 2m_B$). X-A and X-B bond lengths are denoted by a and b . Axis β passes through one X-B bond. Axis γ is the same as the A-X-A axis. Axis α is perpendicular to β and γ .



$$\left[\sin(60^\circ) = \sqrt{3}/2, \quad \cos(60^\circ) = 1/2 \right]$$

14. Which of the following expressions best represents the moment of inertia of XB_3A_2 molecule about γ ?

- (a) $I_\gamma = 3m_B b^2$ (b) $I_\gamma = 2m_A a^2$
 (c) $I_\gamma = m_A a^2 + 3m_B b^2$ (d) $I_\gamma = 2m_A a^2 + 3m_B b^2$
 (e) $I_\gamma = 2m_A a^2 + 6m_B b^2$

15. Which of the following expressions best represents the moment of inertia of XB_3A_2 molecule about β ?

- (a) $I_\beta = 2m_A a^2 + 3m_B b^2$ (b) $I_\beta = 2m_A a^2 + 3m_B b^2/4$
 (c) $I_\beta = m_A a^2 + 3m_B b^2$ (d) $I_\beta = m_A a^2 + 3m_B b^2/2$
 (e) $I_\beta = 2m_A a^2 + 3m_B b^2/2$

16. Which of the following expressions best represents the moment of inertia of XB_3A_2 molecule about α ?

- (a) $I_\alpha = 2m_A a^2 + 3m_B b^2$ (b) $I_\alpha = 2m_A a^2 + 3m_B b^2/4$
 (c) $I_\alpha = m_A a^2 + 3m_B b^2$ (d) $I_\alpha = m_A a^2 + 3m_B b^2/2$
 (e) $I_\alpha = 2m_A a^2 + 3m_B b^2/2$

17. Which of the following classifications of best represents the rotational characteristics of XB_3A_2 if X-A and X-B bond lengths are equal; i.e. $a = b$?

- (a) Spherical top. (b) Prolate symmetric top (c) Oblate symmetric top
 (d) Asymmetric top (e) None of the answers (a), (b), (c) or (d) is correct.

18. Consider the following statements.

- (i) The *frequency* of the radiation corresponding to a particular line in the Raman spectrum of a molecule cannot be used in evaluating molecular parameters without knowing the frequency of the incident radiation.
 (ii) The Raman shift of a photon takes a *positive* value when the molecule which scattered it undergoes a *de-excitation*.
 (iii) The *change in wavelength* of a Raman scattered photon is proportional to the energy change of the molecule involved in the scattering process.

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.

19. A molecule has only three energy levels which are equally spaced. The separation between any two adjacent energy levels is 7.0000×10^{-21} J. It is known that the Raman selection rules allow transitions from any energy level to any other energy level. Imagine that a student obtaining the Raman spectrum of the molecule with a beam of electromagnetic radiation of frequency 4.0000×10^{13} Hz, at a temperature where all three energy levels are appreciably populated. Consider the following statements regarding the student's observations in this experiment.

- (i) The maximum number of anti-Stokes lines the student can observe is two.
 (ii) An anti-Stokes line may appear with a frequency shift approximately equal to 1.2066×10^{13} Hz
 (iii) A Stokes line may appear at a frequency approximately equal to 1.8884×10^{13} Hz.

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).

20. Consider the following statements about the Raman spectrum produced by a pure sample of gaseous molecules having only two energy levels.

- (i) The intensity of the Stokes line will *decrease* with increasing temperature of the sample.
- (ii) The intensity of the anti-Stokes line will *increase* with increasing temperature of the sample.
- (iii) The intensity of both the Stokes line and the anti-Stokes line will increase with increasing pressure at constant temperature.

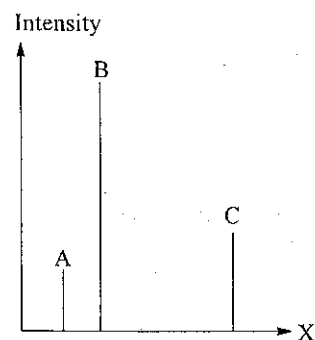
The correct statements out of (i), (ii) and (iii) above are

- (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.

21. The specific selection rule in vibrational Raman spectroscopy of a molecule which behaves as an anharmonic oscillator is

- (a) $\Delta v_k = \pm 1$ (b) $\Delta v_k = \pm 2$ (c) $\Delta v_k = \pm 1, \pm 2, \pm 3, \dots$
- (d) $\Delta v_k = \pm 0$ (e) None of the answers (a), (b), (c) or (d) is correct.

22. A student recorded the vibrational Raman spectrum of a tri-atomic molecule under low resolution. The Raman spectrometer used by the student plots the X-axis of the spectrum either in wave number or wavelength. The recorded spectrum with the fundamental Stokes and anti-Stokes bands (lines) is schematically represented in the figure. B is the Rayleigh line.



Consider the following statements.

- (i) The X-axis may not be in units of cm^{-1} .
- (ii) C is an anti-Stokes line.
- (iii) The student has made a mistake since the shifts of lines A and C from B are not equal.

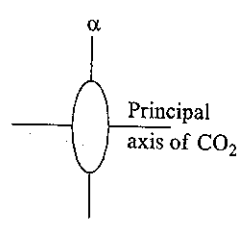
The correct statements out of (i), (ii) and (iii) above are

- (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 molecules/ions that can show a *pure rotational* Raman spectrum out of HCN, SF_6 , PtCl_4^{2-} and C_5H_5^- are

- (a) HCN, SF_6 and C_5H_5^- (b) SF_6 , PtCl_4^{2-} and C_5H_5^-
- (c) HCN, SF_6 and PtCl_4^{2-} (d) HCN, PtCl_4^{2-} and C_5H_5^-
- (e) None of the answers (a), (b), (c) or (d) is correct.

24. 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 and passing through the centre of mass and lies on the plane of the paper, (in the same order as they appear in the rotational operation) are given by

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

25. Variation of intensity of the anti-Stokes lines in the pure rotational Raman spectrum of a linear molecule, at room temperature, is fully described by

