

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme — Level 5

Assignment I (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.:** .....

**Name:** .....

**Address:** .....

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B. Sc. Degree Programme — Level 5

Assignment I (Test) — 2015/2016

CMU 3131/CME 5131 — Concepts in Spectroscopy



1 hour

9<sup>th</sup> April 2016 (Saturday)

9.00 a.m. — 10.00 a.m.

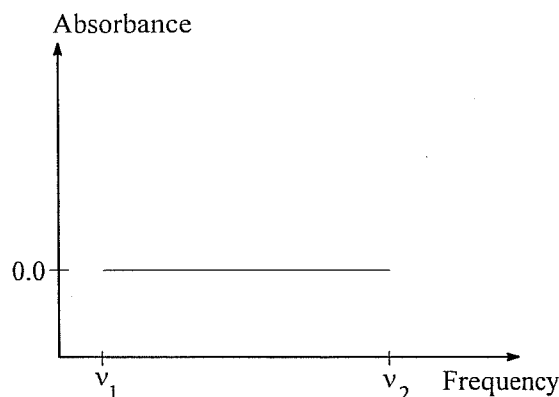
- ⊗ Answer all 25 questions (25 x 4 = 100 marks)
- ⊗ Choose the most correct answer to each of the questions and mark this answer with an “X” on the answer script in the appropriate box.
- ⊗ Use a **PEN** (not a PENCIL) in answering.
- ⊗ Any answer with more than **one** “X” marked will be considered 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.

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. The spectrum of a pure compound A, in aqueous medium, recorded by a student in the frequency range  $\nu_1$  to  $\nu_2$  using a double beam absorption spectrometer, is shown here.

Assuming that there is no experimental error, one can definitely say that

- (i) Substantial, net exchange of energy between A molecules in the sample and the radiation beam has not taken place.
- (ii) There are no energy levels in a molecule of A (in solution) so that the difference in energy between two of them is equal to the energy of a photon in the beam of radiation of frequency in the range  $\nu_1$  to  $\nu_2$ .
- (iii) Most of the photons in the beam of radiation passed through the sample of 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.

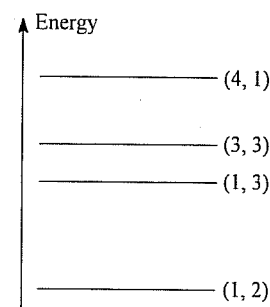
2. Consider the following statements.

- (i) The anharmonicity constant of a *diatomic molecule* will not be zero if the molecule behaves as a *Harmonic oscillator*.
- (ii) The anharmonicity of vibrations leads to the appearance of more than one line in the IR spectrum of a *diatomic molecule*.
- (iii) A molecule whose anharmonicity constant is zero 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.

3. A hypothetical molecule has only four energy levels which are labelled by two quantum numbers  $(\lambda, \gamma)$ . The values of the quantum numbers of these energy levels are indicated in the diagram. The specific selection rules in absorption spectroscopy of a sample of these molecules are  $\Delta\lambda = 0, 1, 2$  and  $\Delta\gamma = \pm 1, \pm 2$ . The maximum number of lines that may be observed in the absorption spectrum of the sample is



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

4. The anharmonicity in vibrations of a polyatomic molecule

- (i) may *lift (remove) the degeneracy* of a vibrational energy level derived in harmonic oscillator approximation.
- (ii) does not alter the *number of normal modes* in a polyatomic molecule.
- (iii) may change the *energy of vibrational levels* from those values calculated using harmonic oscillator approximation.

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.

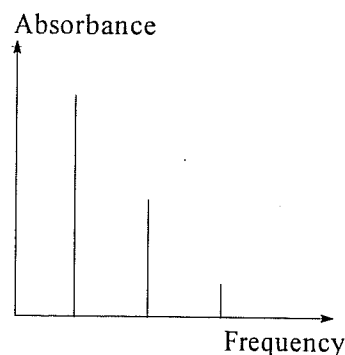
5. Consider the molecules HBr, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, NO and IBr.

- (i) H<sub>2</sub> and N<sub>2</sub> cannot show absorption spectra in microwave or infrared regions of the electromagnetic spectrum since their dipole moment is zero at any bond length.
- (ii) HBr, NO and IBr may show IR spectra since they are molecules that have dipole moments which change during vibration.
- (iii) Even though O<sub>2</sub> is a *paramagnetic* molecule, it cannot show a microwave 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.

6. The full IR spectrum of a sample of a diatomic molecule is shown in the figure.



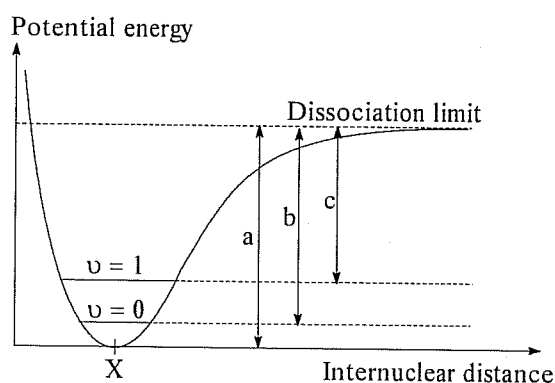
Consider the following statements about the nature of the molecule.

- (i) The molecule vibrates like an anharmonic oscillator.
- (ii) The energy gap between two adjacent vibrational energy levels of the molecule becomes smaller with increasing vibrational quantum number.
- (iii) The molecule is a homonuclear 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.

7. The potential energy curve together with the first two vibrational energy levels of a diatomic molecule, Q, are shown in the figure.



Consider the following statements.

- (i) X is equal to the equilibrium bond length of the molecule.
- (ii) For the molecule, the dissociation energy  $D_0 = b$ .

- (iii) The minimum energy that has to be supplied to dissociate a Q molecule in its first vibrational excited level is equal to 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.

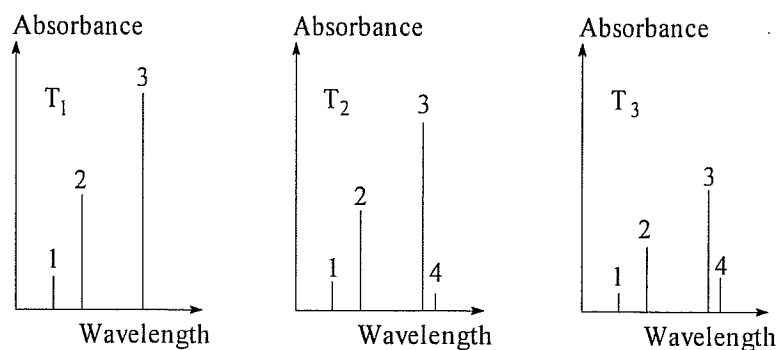
8. The *fundamental* in the IR spectrum of  $^{14}\text{N}^{16}\text{O}$  appear at  $1876.06\text{ cm}^{-1}$ . The *anharmonicity constant* of  $^{14}\text{N}^{16}\text{O}$  is 0.007332. The equilibrium vibration frequency and the frequency at the 2<sup>nd</sup> overtone in the IR spectrum of  $^{14}\text{N}^{16}\text{O}$ , respectively are

- (a)  $1910.98\text{ cm}^{-1}$  and  $5544.42\text{ cm}^{-1}$
- (b)  $1903.98\text{ cm}^{-1}$  and  $5544.42\text{ cm}^{-1}$
- (c)  $1903.98\text{ cm}^{-1}$  and  $5555.42\text{ cm}^{-1}$
- (d)  $1910.98\text{ cm}^{-1}$  and  $5555.42\text{ cm}^{-1}$
- (e)  $1915.98\text{ cm}^{-1}$  and  $5544.42\text{ cm}^{-1}$

9. The number of vibrational normal modes in the molecules,  $\text{H}_2\text{O}_2$ ,  $\text{C}_2\text{H}_2$  and  $\text{C}_5\text{H}_5\text{N}$ , respectively, are

- (a) 6, 6, 27
- (b) 4, 4, 28
- (c) 5, 5, 28
- (d) 6, 7, 28
- (e) 6, 7, 27

10. The full IR spectrum of a diatomic molecule, Y, recorded at 3 different *temperatures*,  $T_1$ ,  $T_2$  and  $T_3$ , is shown in the following diagram.



Consider the following statements.

- (i) The absorption line 4 may be a hot band.
- (ii) The order of temperatures must be  $T_1 < T_2 < T_3$ .
- (iii) The lines 1 and 2 may be overtones.

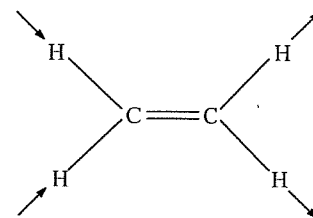
The correct statements out of (i), (ii) and (iii) above are

- (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. A normal mode of ethylene molecule is shown in the figure.

Consider the following statements.

- (i) It is a perpendicular mode.
- (ii) This mode may give rise to an IR spectrum.
- (iii) It is not a bending mode.



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.

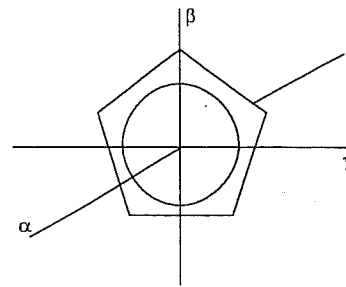
- (i) A diatomic molecule does not have a bending mode.
- (ii) In a vibrational normal mode of a polyatomic molecule, always the nuclei move in such away so that the bond angles remain constant.
- (iii) A  $\text{CCl}_4$  molecule has a symmetric stretching normal mode.

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 data given below in answering questions 13 and 14.

Three principal axes,  $\alpha$ ,  $\beta$  and  $\gamma$ , of the ellipsoid of inertia of the  $C_5H_5^-$  ion is shown in the diagram to the right. Axes  $\beta$  and  $\gamma$  are on the plane of the ion and  $\alpha$  is perpendicular to the plane of the ion. It is known that  $I_\alpha > I_\beta$  where  $I_\alpha$  and  $I_\beta$  are the moments of inertia of the ion about the  $\alpha$  and  $\beta$  axes.



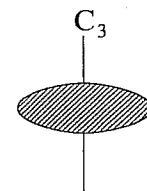
13. In standard notation a correct identification (as a, b and c) of the principal axes of inertia is

- (a)  $\alpha \equiv a$ ,  $\beta \equiv b$ ,  $\gamma \equiv c$
- (b)  $\alpha \equiv b$ ,  $\beta \equiv c$ ,  $\gamma \equiv a$
- (c)  $\alpha \equiv a$ ,  $\beta \equiv c$ ,  $\gamma \equiv b$
- (d)  $\alpha \equiv c$ ,  $\beta \equiv b$ ,  $\gamma \equiv a$
- (e) None of the answers (a), (b), (c) or (d) is correct.

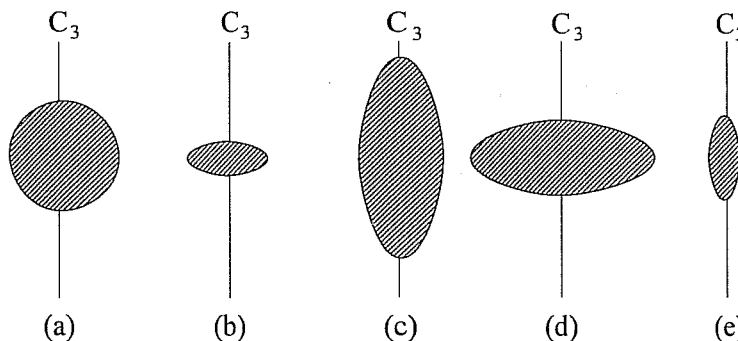
14.  $C_5H_5^-$  ion is

- (a) a spherical top.
- (b) a prolate symmetric top.
- (c) an oblate symmetric top.
- (d) an asymmetric top.
- (e) either a spherical top or an asymmetric top.

15. The inertia ellipsoid of  $BF_3$  (at its equilibrium configuration) with respect to the principal axis,  $C_3$ , is shown in the figure to the right.



The inertia ellipsoid of the same molecule where all three BF bonds are elongated up to  $2x$ , where  $x$  is the equilibrium BF bond length, drawn on the same scale as the diagram to the right, is best represented by



16. The ellipsoid of inertia of a molecule whose principal axis is

- (i) a  $C_4$  axis
- (ii) a  $C_3$  axis
- (iii) a  $C_2$  axis

is an *ellipsoid of revolution*.

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.

17. Consider the following statements.

- (i) In accidental degeneracy, an energy level in a vibrational normal mode may become equal or nearly equal to the energy level of another normal mode which is non-degenerate with it.
- (ii) In a linear asymmetric molecule (e.g. HCN), the vibrational energy levels in one bending mode are not accidentally degenerate with the vibrational energy levels in the other bending mode.
- (iii) In a linear symmetric molecule (e.g.  $CO_2$ ), the vibrational energy levels in one bending mode are accidentally degenerate with the vibrational energy levels in the other bending mode.

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. Consider the following statements.

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

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

- (a)  $CH_4$ , HCN,  $CH_3Cl$
- (b)  $CH_4$ ,  $SF_6$ ,  $CH_3Cl$
- (c)  $CH_4$ ,  $C_2H_6$ ,  $CH_3Cl$
- (d)  $C_2H_6$ , HCN,  $CH_3Cl$
- (e) None of the answers (a), (b), (c) or (d) is correct



20. Two energy levels of a molecule are denoted by  $E_1$  and  $E_2$ , and the Planck constant is denoted by  $h$ . Consider the following statements about the Raman spectrum of this molecule.

- (i) One may observe a line at a Raman shift,  $\Delta\nu = (E_1 - E_2)/h$ .
- (ii) One can observe a maximum of only two different Raman shifts.
- (iii) One may observe a line at a Raman shift,  $\Delta\nu = (E_2 - E_1)/h$ .

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 other answers is correct.

21. In Raman spectroscopy of a sample of molecules

- (i) the *Rayleigh line* is due to electromagnetic radiation with the same frequency as the incident radiation.
- (ii) *Stokes lines* correspond to electromagnetic radiation of frequency less than that of the incident radiation.
- (iii) *Anti-Stokes lines* are associated with the loss of *energy* by 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 other answers is correct.

22. Consider the following statements.

- (i) Transitions among vibrational energy levels of a molecule may give rise to a Raman spectrum.
- (ii) Transitions among electronic energy levels of a molecule cannot give rise to a Raman spectrum.
- (iii) Transitions among rotational energy levels of a molecule may give rise to a Raman 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 other answers is correct.

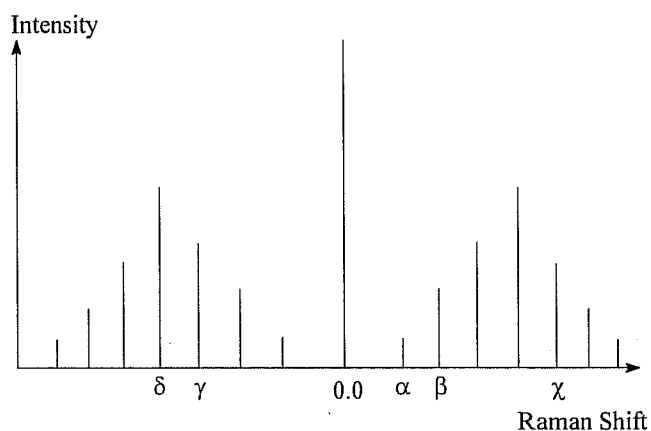
23. Consider the following statements.

- (i) The *bending mode* of  $\text{CO}_2$  is Raman *active*.
- (ii) The *bending mode* of  $\text{HCN}$  is Raman *inactive*.
- (iii) The *symmetric stretching mode* of  $\text{CO}_2$  is Raman *active*.

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 other answers is correct.

24. To a good approximation, a particular diatomic molecule, AB, may be assumed to behave as a rigid rotor. The pure rotational Raman spectrum of AB recorded at 298 K is given below.



$\alpha, \beta, \gamma, \delta$  and  $\chi$  are the Raman shifts of the lines depicted in the above figure. It has been observed that  $\alpha = 120.00 \text{ cm}^{-1}$ .

The value of  $\chi$  in  $\text{cm}^{-1}$  is

- (a)  $-400.00$     (b)  $400.00$     (c)  $-360.00$     (d)  $440.00$     (e)  $480.00$
25. The cross section of the polarisability ellipsoid of  $\text{CH}_3\text{Cl}$  on a plane perpendicular to the C—Cl bond is best represented by

