THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Assignment I (Test) — 2008/2009

CHU 3128/CHE 5128 — Special Topics in Spectroscopy



 $\left(1\frac{1}{2} \text{ hours}\right)$

17th February 2009 (Tuesday)

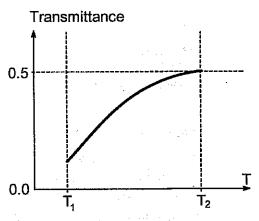
4.00 p.m. – 5.30 p.m.

- \triangle Answer all 40 questions (40 x 2.5 = 100 marks)
- Example 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 (0.4 per answer).
- The use of a non-programmable electronic calculator is permitted.
- Logarithm tables will be provided.

Gas constant (R)	. <u>-</u>	8.314 JK ⁻¹ mol ⁻¹
Avogadro constant (NA)	=	$6.023 \times 10^{23} \text{ mol}^{-1}$
Faraday constant (F)	=	96,500 Cmol ⁻¹
Planck constant (h)	=	6.63×10^{-34} Js
Velocity of light (c)	==	$3.0 \times 10^8 \text{ m s}^{-1}$
Standard atmospheric pressure	=	$10^5 \text{ Pa} \left(\text{N m}^{-2} \right)$
$\log_{e}(X)$	=	2.303 Log ₁₀ (X)



- The results obtained by a student who measured the transmittance of a sample of a dilute aqueous solution of a pure compound A 0.5 in the temperature range T₁ to T₂ in a sealed sample tube of length l, is depicted in the figure. It is known that A does not undergo any reaction in the above temperature range in aqueous medium. One can definitely say that
 - (i) at temperature T₁ the sample used absorbed almost all the radiation incident on it.



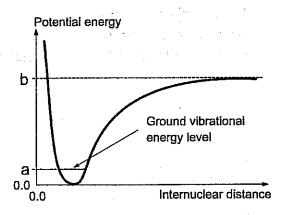
- (ii) the molar extinction coefficient of A has its lowest value at T_2 .
- (iii) the concentration of A is lowest at T_1 .

- (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 figure to the right in answering Questions 2 and 3

A heteronuclear diatomic molecule, AB, behaves as an anharmonic oscillator and its potential energy can be approximated by the Morse potential, a sketch of which is depicted in the figure to the right



2. Consider the following statements.

- (i) AB dissociates when its vibrational energy becomes greater than b.
- (ii) AB does not have a zero point energy since it behaves as an anharmonic oscillator.
- (iii) The difference in energy between two adjacent vibrational energy levels of AB becomes smaller as the vibrational energy increases.

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 <u>answers</u> (a), (b), (c) or (d) is correct.

3. Consider the following statements.

- (i) The vibrational energy of AB at its dissociation limit is b.
- (ii) $D_0 = b a$
- (iii) $D_e = b$

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.

4. 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 assymmetric molecule (e.g.HCN), the vibrational energy levels in one bending mode are <u>not</u> accidentally degenerate with the vibrational energy levels in the other bending mode.
- (iii) In a linear symmetric molecule (e.g. CO₂), the vibrational energy levels in one bending mode are accidentally degenerate with the vibrational energy levels in the other bending mode.

- (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.
 - (i) A molecule which does <u>not</u> have at least one rotational axis of symmetry of order greater than two does not have an ellipsoid of inertia.
 - (ii) The ellipsoid of inertia of SF₆ is spherical.
 - (iii) . The ellipsoid of inertia of trans $-\mathrm{SF_4I_2}$ is an ellipsoid of revolution.

- (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. What is the equilibrium vibration frequency of a heteronuclear diatomic molecule AB if the force constant of the A-B bond is 515.0 Nm⁻¹? [Relative atomic mass of A = 35 and B = 2].
 - (a) 4.05×10^{13} Hz
- (b) 2.03×10^{13} Hz
- (c) 1.48×10^{13} Hz

- (d) 6.44×10^{13} Hz
- (e) 3.22×10^{13} Hz
- 7. Consider the following statements regarding the overtones in the IR spectrum of a diatomic molecule.
 - (i) The intensity of an overtone <u>may</u> decrease when the temperature of the sample is increased.
 - (ii) The 1st overtone is due to the transition $v = 0 \rightarrow v = 2$ where v is the vibrational quantum number.
 - (iii) In general the intensity of an overtone decreases with increasing vibrational quantum number of the excited level involved.

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)

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- (e) None of the answers (a), (b), (c) or (d) is correct.
- 8. A planar molecule has a C_6 axis perpendicular to its plane of symmetry which coincides with a principal axis of inertia denoted by α . The other two principal axes of inertia lie in the plane of the molecule and are denoted by β and γ . It is known that the principal moments of inertia satisfies the relationship $I_{\alpha} > I_{\gamma}$. In standard notation a correct identification of the principal axes of inertia is
 - (a) $\alpha \equiv b$, $\beta \equiv c$, $\gamma \equiv b$
 - (b) $\alpha \equiv a$, $\beta \equiv c$, $\gamma \equiv b$
 - (c) $\alpha \equiv c$, $\beta \equiv b$, $\gamma \equiv a$
 - (d) $\alpha \equiv a$, $\beta \equiv b$, $\gamma \equiv c$
 - (e) None of the answers (a), (b), (c) or (d) is correct.

- A student was asked to record the microwave and IR spectra of a pure gaseous sample of a diatomic molecule. He could obtain a clear strong microwave spectrum. However, the IR spectrum did not have clear strong peaks. Based only on these results one may correctly say that
 - (i) The two atoms in the molecule are not of the same element...
 - (ii) The student may not have recorded the IR spectrum over a sufficiently large frequency range to obtain peaks in it.
 - (iii) The gross selection rule prohibits vibrational transitions that may give rise to an IR spectrum.

(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. In an absorption or an emission process, the Bohr condition may be expressed as $\Delta E = \frac{v}{B}$ where ν is the frequency of a photon involved, ΔE is the energy change undergone by the molecule and β is a positive constant. In this equation
 - (i) $\Delta E = |E_1 E_2|$ where E_1 may be the final energy level and E_2 may be the initial energy level of the molecule respectively.
 - (ii) $\Delta E = E_i E_f$ for an emission process where E_f and E_i are the final and initial energy levels of the molecule respectively.
 - (iii) $\beta = \frac{1}{\text{Planck constant}}$.

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. (i) The specific selection rule in microwave spectroscopy of a rigid diatomic molecule is $\Delta J = \pm 1$.
 - (ii) The gross selection rule in IR spectroscopy states that a diatomic molecule must have a permanent dipole moment in order for it to show an IR spectrum.
 - (iii) The specific selection rule in the IR spectroscopy of a real diatomic molecule is $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

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 equilibrium vibration frequency and the anharmonicity constant of a diatomic molecule are denoted by ω_e and x_e respectively. The vibrational energy levels, E_{ν} , where ν is the vibrational quantum number, are given by
 - (a) $E_{\nu} = h \omega_{e} \left[1/2(\nu+1) x_{e}(\nu+1/2)^{2} \right]$
 - (b) $E_{\nu} = h \omega_{e} \left[(\nu + 1/2) + 1/2 x_{e} (\nu + 1)^{2} \right]$
 - (c) $E_{\nu} = h \omega_{e} \left[(\nu + 1/2) 1/2 x_{e} (\nu + 1)^{2} \right]$
 - (d) $E_{v} = h \omega_{e} \left[(v+1/2) + x_{e} (v+1/2)^{2} \right]$
 - (e) $E_{\nu} = h \omega_{e} \left[(\nu + 1/2) x_{e} (\nu + 1/2)^{2} \right]$
- 13. The maximum number of degrees of freedom possessed by a system of six particles is
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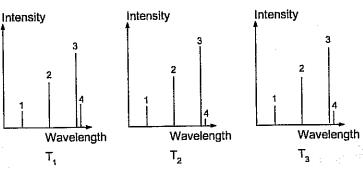
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- (b) 6
- (c) 12
- (d) 18
- (e) 24

Use the following diagram in answering questions 14 and 15.

The <u>full</u> (low resolution) IR spectrum of a hetero-nuclear diatomic molecule, AB, recorded at 3 different *temperatures*, T_1 , T_2 and T_3 , is schematically represented in the following diagram. Line 4 is known to be due to a hot band.



14 The relationship satisfied by the temperatures is

$$T_1 = T_3 > T_2$$

$$\text{product}(b) - T_1 > T_2 = T_3$$

(c)
$$T_2 > T_3 > T_1$$

(d)
$$T_3 > T_1 > T_2$$

$$T_1 > T_3 > T_2$$

- 15. Consider the flowing statements.
 - (i) Line 1 may represent the fundamental band.
 - (ii) Line 2 may represent the 1st overtone.
 - (iii) Line 3 may represent the 2nd overtone.

- (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.
- 16. Consider the following statements.
 - (i) The appearance of overtones in the IR spectrum of a diatomic molecule indicates that the molecule behaves as an anharmonic oscillator.
 - (ii) Overtones may not be observed in the IR spectrum of H₂ because it has no permanent dipole moment.
 - (iii) Two frequencies where the overtones appear in the IR spectrum are sufficient to calculate the equilibrium vibration frequency and the anharmonicity constant 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.
- 17 Consider a vibrational transition in a diatomic molecule denoted by m ← n where m and n are (positive) integers. One can <u>definitely</u> say that this transition.
 - (i) gives rise to an overtone in the IR spectrum if n = 0.
 - (ii) leads to vibrational de-excitation if m = 0.
 - (iii) gives a hot band in the (absorption) IR spectrum if m > n > 0.

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. A hypothetical molecule having an even number of nuclei has rotational, vibrational and electronic energy levels <u>only</u>. Most probably, in absorption spectroscopy of this molecule
 - (i) the pure rotational transitions occur in the *microwave region* of the electromagnetic spectrum.
 - (ii) the electronic transitions occur in the *UV-visible region* of the electromagnetic spectrum.
 - (iii) mixed transitions involving <u>only</u> the electronic and vibrational energy levels occur in the *IR region* of the electromagnetic spectrum.

- (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.

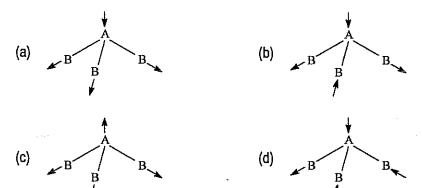
- 19 The frequency, ν_h , of the hot band due to the transition $2\leftarrow 1$ in a diatomic molecule may be given (in standard notation) by
- (b) $v_h = (1 2x_c)\omega_e$
- (c) $v_h = (1-3x_e)\omega_e$

- (a) $v_h = (1 x_e) \omega_e$ (d) $v_h = (1 4x_e) \omega_e$
 - (e) None of the answers (a), (b), (c) or (d) is correct.
- 20 (i) A linear molecule has a lesser number of vibrational degrees of freedom than a non-linear molecule having the same number of nuclei.
 - (ii) A linear molecule has a lesser number of rotational degrees of freedom than a non-linear molecule.
 - (iii) A linear molecule has a lesser number of translational degrees of freedom than a non-linear molecule. 💎 📑

- (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 number of normal modes in the molecules HCN , SF_6 and C_6H_6 , respectively, are
 - (a) 4, 15, 30
- (b) 3, 16, 31
- (c) 4, 15, 31

- (d) 4, 16, 30
- (e) None of the answers (a), (b), (c) or (d) is correct.
- 22. The symmetric stretching mode of a pyramidal AB₃ molecule may be represented by



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

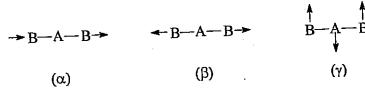
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23. Some normal modes of a linear molecule, AB2, may be represented by

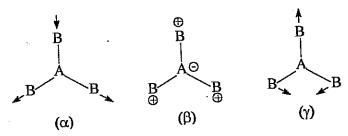


- The three modes are termed as asymmetric stretching, symmetric stretching and bending modes.
- (ii) The mode depicted by (γ) is an asymmetric mode.
- (iii) The bond lengths, A-B, remain the same during vibration in mode depicted by (y).

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.
- 24. Consider the following 3 normal modes of a planar AB₃ molecule.



- (i) (α) is a parallel mode.
- (ii) (β) is a parallel mode.
- (iii) (γ) is a perpendicular 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.
- 25. The anharmonicity of vibrations of a polyatomic molecule
 - (i) may split the degeneracy of a vibrational energy level, in a particular mode, observed in harmonic oscillator approximation.
 - (ii) may increase or decrease the number of normal modes in a polyatomic molecule.
 - (iii) does not change the energy of vibrational levels from those values calculated using. harmonic oscillator approximation.

- (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.

- 26. In a diatomic molecule the centrifugal distortion
 - (i) pushes rotational levels towards higher energy.
 - (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.

- (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.
- 27. The specific selection rule in the rotational spectroscopy of a diatomic molecule, which is elastic, is
 - (a) $\Delta J = \mp 1, \mp 2,...$
 - (b) $\Delta J = 0, \mp 1$
 - (c) $\Delta J = \mp 1$

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- (d) $\Delta J = \mp 1, \mp 3, \mp 5,...$
- (e) None of the answers (a), (b), (c) or (d) is correct.
- 28 If the BF bond length and the mass of an F nucleus are denoted by x and m_F respectively, then the principal moments of inertia of a BF₃ molecule are given by

$$\sin(60^{\circ}) = \frac{\sqrt{3}}{2}$$
 and $\cos(60^{\circ}) = \frac{1}{2}$

- (a) $I_a = \frac{3}{2} m_F x^2$, $I_b = \frac{3}{2} m_F x^2$, $I_c = 3 m_F x^2$
- (b) $I_a = 3 m_F x^2$, $I_b = \frac{3}{2} m_F x^2$, $I_c = \frac{3}{2} m_F x^2$
- (c) $I_a = 3m_F x^2$, $I_b = \frac{3}{2}m_F x^2$, $I_c = 3m_F x^2$
- (d) $I_a = \frac{3}{2}m_F x^2$, $I_b = 3m_F x^2$, $I_c = \frac{3}{2}m_F x^2$
- (e) None of the answers (a), (b), (c) or (d) is correct.
- 29 The relationship among the principal moments of inertia of a spherical top and asymmetric top molecules, respectively, are
 - (a) $0 \neq I_a = I_b \neq I_c$ and $0 \neq I_a \neq I_b = I_c$
 - (b) $0 \neq I_a = I_b = I_c$ and $0 \neq I_a \neq I_b \neq I_c$
 - (c) $0 \neq I_a \neq I_b = I_c$ and $0 \neq I_a \neq I_b \neq I_c$
 - (d) $0 \neq I_a = I_b = I_c$ and $0 \neq I_a = I_b \neq I_c$
 - (e) None of the answers (a), (b), (c) or (d) is correct.

30 A molecule having

- (i) no axes of symmetry is an asymmetric top.
- (ii) only one axis of rotation, C_n , with $n \ge 3$ is a symmetric top.
- (iii) only one improper axis of symmetry, S4, is a symmetric top.

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.
- 31 The shape of the ellipsoid of inertia of a BF₃ molecule, with respect to its principal axis of rotation, C3, is best described by









- (e) None of the above answers (a), (b), (c) or (d) is correct.
- 32 Consider the following statements.
 - (i) A spherical top molecule has a permanent dipole moment
 - (ii) In standard notation the rotational energy levels of a rigid spherical top molecule are given by the expression $\varepsilon_J = B J (J+1)$
 - (iii) Though a rigid spherical top molecule has rotational energy levels it does not 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.
- 33 In standard notation the rotational energy levels of a non-rigid oblate symmetric top molecule is given by the following expression

$$\varepsilon_{JK} = BJ(J+1) - D_J J^2 (J+1)^2 + (C-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2$$

The specific selection rules in microwave spectroscopy of such a molecule are $\Delta J = 0, \pm 1$ and $\Delta K = 0$. Which of the following set of constants can be calculated using the microwave spectrum of the molecule?

- (a) B,C and D₁.
- (b) B,C and D_{IK}
- (c) $B,C,D_{\mbox{\tiny J}}$ and $D_{\mbox{\tiny JK}}$

- (d) B, D_J and D_{JK}
- (e) None of the answers (a), (b), (c) or (d) is correct.

- 34 In rotational spectroscopy using Stark effect, the sample is placed in an electric field of strength E, which is perpendicular to the microwave beam. The electric field lifts the degeneracy of some rotational energy levels of molecules. Consider the following statements.
 - (i) Stark effect is used to find the dipole moment of a molecule.
 - (ii) In a symmetric top molecule splitting of energy levels due to Stark effect is proportional to E^2 .
 - (iii) For a linear molecule splitting of energy levels due to Stark effect is proportional to E²

- (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.
- 35 In microwave spectroscopy the space where the sample is placed (in the microwave spectrometer) is always evacuated to minimise the
 - (i) absorption of microwaves by N₂ which is the most abundant gas in atmosphere.
 - (ii) absorption of microwaves by gases in atmosphere...
 - (iii) effect of molecules in the atmosphere on the microwave spectrum of the sample.

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

(a) Only (i) and (ii).

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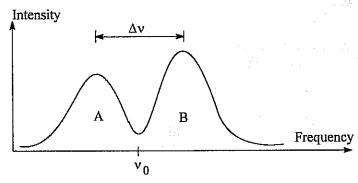
 $0,\pm 1$

- (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 diagram in answering questions 36 and 37.

The fundamental band in the IR spectrum of a certain diatomic molecule is shown below.



- 36. (i) A and B are the P and Q branches respectively.
 - (ii) $v_0 = \omega_e (1-2 x_e)$ where ω_e and x_e are the equilibrium vibration frequency and the anharmonicity constant of the molecule.
 - (iii) Branches A and B are due to simultaneous rotational transitions.

- (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.

37.	The rotational c	onstant of the	diatomic mole	cule is 1.9125 cm ⁻¹	. Δv , in units of c	m ⁻¹ , at		
	(a) 51 (b) 52	(c) 57	(d) 61	(e) 69			
38	In the vibration rotation spectrum of a diatomic molecule							
	(i) P and Q branches cannot appear in the first overtone band.							
	(ii) The separation between the P and Q branch maxima in the fundamental band con be used to estimate the temperature of the sample.(iii) The separation between the P and Q branches in the fundamental band is the sam approximately the same as that the second overtone band.							
	The correct sta (a) Only (i) and (d) All (i), (ii) and	l (ii). (b) C	Inly (i) and (iii)	above are . (c) Only swers (a), (b), (c) on		e.T		
	•	•		· •				
39.	The specific sel	lection rules in	the vibrationa	l rotational spectros	scopy of a real diate	omic		
	(a) $\Delta v = \pm 1$ ar	$d \Delta J = 0$			•			
٠	(b) $\Delta v = \pm 1$ ar	$\Delta J = 0, \pm 1$						
	(c) $\Delta v = \pm 1, \pm 2$	2,±3, a	and $\Delta J = 0$					
	(d) $\Delta v = \pm 1, \pm 2$	2,±3,a	and $\Delta J = \pm 1$		#W- 1	f		
	(e) $\Delta v = \pm 1, \pm 2$	2,±3,a	and $\Delta J = 0, \pm 1$					
					\$255 			
40. (i) The centre of the ellipsoid of inertia of a molecule coincides with the centr of the molecule.								
	(ii) The distan inertia is p	ce from the ce proportional to	ntre, O, to a po the inertia of t	int, A, on the surfa- he molecule about t	ce of the ellipsoid of the axis OA.	of		
	(iii) An ellipsoid of inertia has three principal axes.							
	The correct sta (a) Only (i) an (d) All (i), (ii) a	d (ii). (b) (Only (i) and (iii	i) above are). (c) Only <u>swers</u> (a), (b), (c) c	(ii) and (iii). or (d) is correct.			