THE OPEN UNIVERSITY OF SRI LANKA
B. Sc. Degree Programme — Level 5
Assignment II (Test) — 2006/2007
CHU 3128/CHE 5128 — Special Topics in Spectroscopy

($1\frac{1}{2}$ hours)

21st August 2006 (Monday) 3.30 p.m. — 5.00 p.m.

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

Gas constant (R) = $8.314\ \mathrm{J K^{-1} mol^{-1}}$
Avogadro constant (N_A) = $6.023\times10^{23}\ \mathrm{mol^{-1}}$
Faraday constant (F) = $96{,}500\ \mathrm{C\,mol^{-1}}$
Planck constant (h) = $6.63\times10^{-34}\ \mathrm{J\,s}$
Velocity of light (c) = $3.0\times10^{8}\ \mathrm{m\,s^{-1}}$
Standard atmospheric pressure = $10^{5}\ \mathrm{Pa\,(N\,m^{-2})}$
$\mathrm{Log}_e(X)$ = $2.303\ \mathrm{Log}_{10}(X)$

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1. A hypothetical molecule has only two energy levels whose separation is 7.0000×10^{-21} J. In the Raman spectrum of the molecule, obtained with a beam of electromagnetic radiation of frequency 1.0000×10^{13} Hz, the

(a) anti Stokes line appears at a Raman shift of 5.58×10^{12} Hz

(b) anti Stokes line appears at a Raman shift of -5.58×10^{13} Hz

(c) Rayleigh line appears at a Raman shift of 1.0000×10^{13} Hz.

(d) Stokes line appears at a Raman shift of 5.58×10^{11} Hz

(e) anti–Stokes line appears at a Raman shift of 5.58×10^{11} Hz

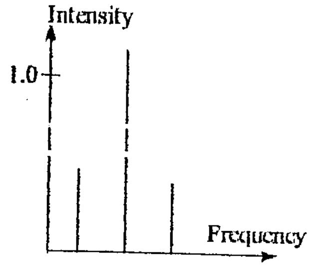
2. The molecules/ions that can show a *pure rotational* Raman spectrum out of, $C_5H_5^-$, SF_6, $CHCl_3$ and C_2ClBr are

(a) $C_5H_5^-$, SF_6 and $CHCl_3$. (b) $C_5H_5^-$, SF_6 and C_2ClBr.

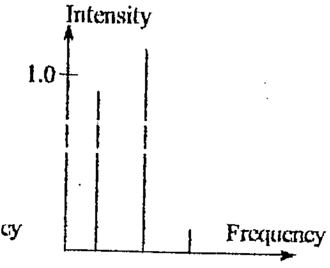
(c) $C_5H_5^-$, $CHCl_3$ and C_2ClBr. (d) SF_6, $CHCl_3$ and C_2ClBr.

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

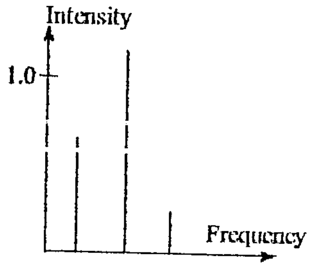
3. The Raman spectrum of a pure sample of a gaseous molecule having only two energy levels recorded at three different temperatures, T_1, T_2 and T_3 are schematically represented below.



T_1



T_2



T_3

The most probable relationship among the temperatures is

(a) $T_1 < T_2 < T_3$. (b) $T_3 < T_2 < T_1$ (c) $T_2 < T_1 < T_3$
(d) $T_2 < T_3 < T_1$ (e) $T_1 < T_3 < T_2$

4. (i) Raman spectroscopy can be done without using plane polarised radiation in the incident beam.

(ii) The *electric field* (at a point in space) changes along a straight line in plane polarised electromagnetic radiation.

(iii) The *magnetic field* (at a point in space) changes along a straight line in plane polarised electromagnetic radiation.

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. A Raman scattering experiment was performed with a beam of plane polarised electromagnetic radiation of wavenumber 1255 cm^{-1} using a sample of a pure compound. As usual, the scattered radiation was observed at right angles to the incident beam. The depolarisation ratio, ρ_P, of a certain Stokes line is 25/81. The most probable values of the amplitudes of the *perpendicular* and *parallel* electric fields (in arbitrary units), respectively, are

(a) 9 and 5 (b) 15 and 81 (c) 10 and 18
(d) 4 and 3 (e) 3 and 4

6. In *pure rotational* Raman spectrum of C_2H_2 you may be able to observe Stokes lines due to transitions with

(a) $\Delta J = +1$ only (b) $\Delta J = -2$ only. (c) $\Delta J = +2$ only.
(d) $\Delta J = -1$ only (e) $\Delta J = \pm 2$

7. (i) Depolarisation ratio of different lines in a Raman spectrum of a pure *substance may be different.*

   (ii) Radiation with a depolarisation ratio of zero, i.e. $\rho_P = 0$, may not be plane polarised.

   (iii) In standard notation depolarisation ratio is defined by $\rho_P = \dfrac{I_{\text{Perpendicular}}}{I_{\text{Parallel}}}$

   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.

8. (i) The electromagnetic radiation generated by a very hot metal rod is not plane polarised..

   (ii) The *magnitude* of the *electric* field vector varies in time in monochromatic plane polarised electromagnetic radiation.

   (iii) The *magnitude* of the *magnetic* field vector remains constant in time in monochromatic plane polarised electromagnetic radiation.

   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.

9. A Raman spectrum of a pure sample of gaseous diatomic compound was obtained using an incident beam of electromagnetic radiation of frequency 5.22×10^{11} Hz. Among others, spectral lines were observed at frequencies 1.24×10^{11} Hz, 5.22×10^{11} Hz and 1.34×10^{11} Hz. Consider the following statements.

   (i) The line at frequency 5.22×10^{11} Hz is the Rayleigh line.

   (ii) The line at frequency 1.24×10^{11} Hz is a Stokes line.

   (iii) The line at frequency 1.34×10^{11} Hz is an anti–Stokes line.

   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.

10. The Raman active vibrational normal modes of a bent molecule A_2B are

    (a) Only symmetric stretching mode.

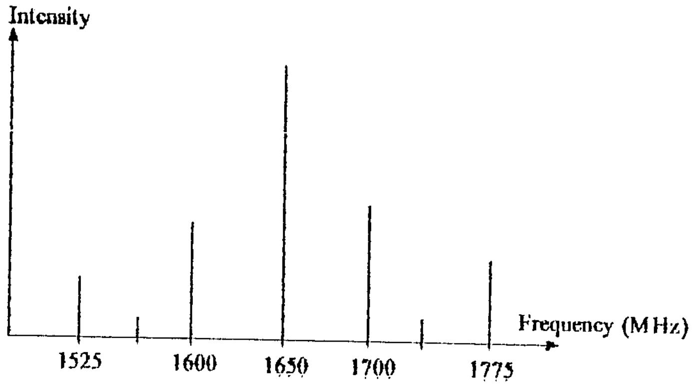
    (d) Only the bending mode.

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

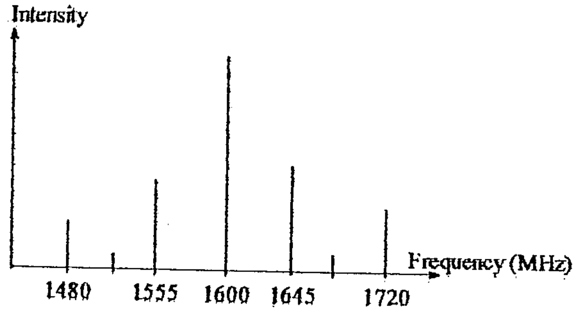
    (c) Only the symmetric stretching and bending modes.

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

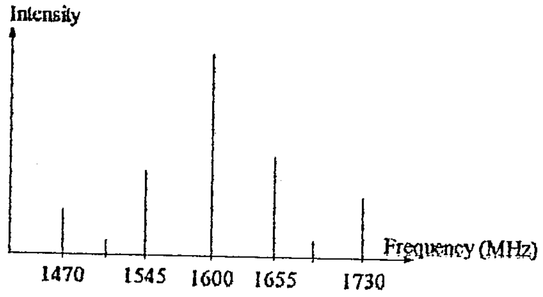
11. A schematic diagram of the Raman spectrum of a pure sample of a compound recorded with excitation radiation of wavenumber 1650 MHz is shown below.



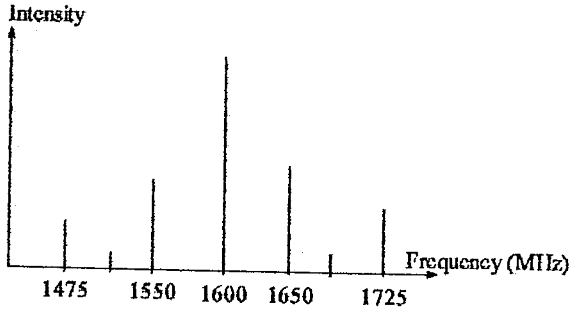
The Raman spectrum of a pure sample of the same compound recorded with excitation radiation of wavenumber 1600 MHz will be



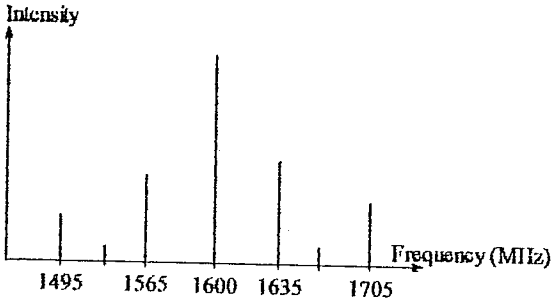
(a)



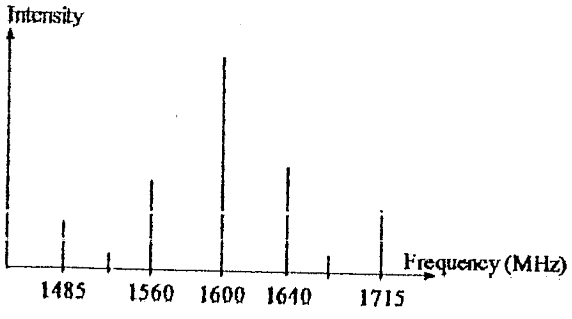
(b)



(c)



(d)



(e)

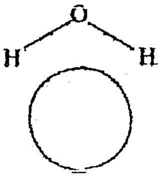
12. (i) The polarisability of O_2 along the bond axis remains constant during its vibrational motion.

(ii) The dipole moment induced in NO and ClO, in a direction perpendicular to the bond axis, by the same applied electric field, may be different.

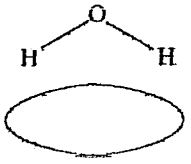
(iii) The polarisability of NO perpendicular to the bond axis is smaller than that along the bond axis.

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.

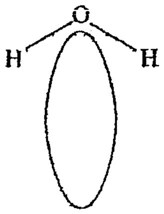
13. The cross section of the polarisability ellipsoid of a water molecule on the plane of the molecule is best represented by



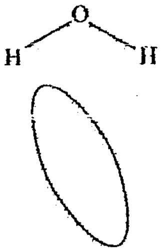
(a)



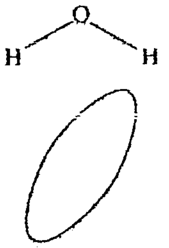
(b)



(c)



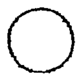
(d)



(e)

14. The cross section of the polarisability ellipsoid of BF_2Cl on the plane of the nolecule is best represented by

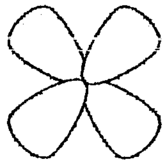
(a)



(b)

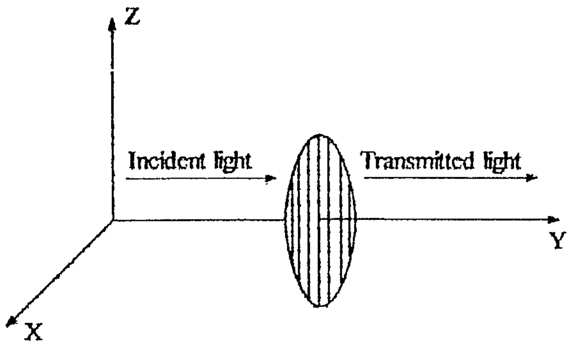
(c)

(d)



(e)

15. Consider the plane polarised radiation formed using a Polaroid whose direction of polarisation is parallel to the Z axis and placed in a plane parallel to the XZ plane as depicted in the following figure.



(i) The *magnetic field* in the transmitted light is parallel to the Z axis.

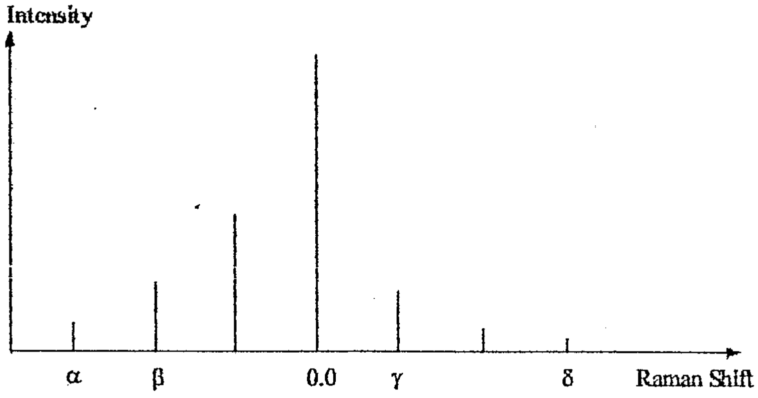
(ii) The *electric field* of the transmitted light will be perpendicular to the Z axis.

(iii) There will not be any *transmitted radiation* if the incident light is plane polarised having its plane of polarisation on YZ plane.

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.

Questions 16 – 19.

Use the following figure, which schematically represents the low resolution pure vibrational Raman spectrum of a diatomic molecule AB, in answering the questions 16 – 19.



α, β, γ and δ are the Raman shifts of the lines depicted in the above figure. It has been observed that $\beta = -5668\ \text{cm}^{-1}$ and $\gamma = 2886\ \text{cm}^{-1}$

16. The equilibrium vibrational frequency of AB, in cm^{-1} is

(a) 2890 (b) 2930 (c) 2950 (d) 2990 (e) 2999

17. The anharmonicity constant of AB is

(a) 0.0164 (b) 0.0174 (c) 0.0184 (d) 0.0194 (e) 0.0199

18. The value of α in cm^{-1} is

(a) − 8970 (b) − 8350 (c) − 8870 (d) − 8557 (e) − 8346

19. The value of δ in cm^{-1} is

(a) 8346 (b) 8970 (c) 8350 (d) 8870 (e) 8557

20. Consider the Raman spectrum of a hypothetical molecule having only three (non-degenerate) energy levels at energies $\varepsilon, 2\varepsilon, 3\varepsilon$ and 5ε.

(i) The difference in frequency between any two adjacent Stokes lines is equal to ε/h where h is the Planck constant.

(ii) The intensity of the anti–Stokes line/s is/are larger than the corresponding Stokes line/s.

(iii) There *can be <u>only</u> a maximum of four* Stokes lines and *a maximum four* anti–Stokes line in the Raman spectrum of this 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 <u>answers</u> (a), (b), (c) or (d) is correct.

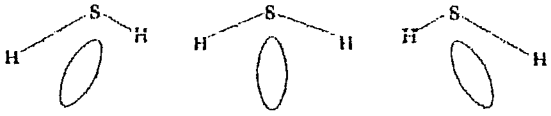
21. (i) A molecule that has a *spherical* polarisability ellipsoid does not show a pure rotational Raman spectrum.

(ii) NO molecule *does not* show a pure rotational Raman spectrum since it has a permanent dipole moment.

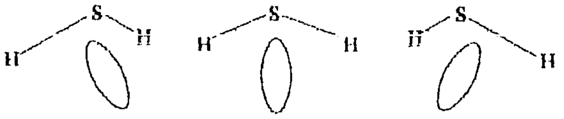
(iii) C_2H_2 <u>does not</u> show a pure rotational Raman spectrum since it has a centre of symmetry.

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

22. Which of the following diagram best represents the variation of the cross section of the polarisability ellipsoid, on the plane of the molecule of H_2S, during vibration in its anti–symmetric stretching mode. In each of the diagrams the picture in the middle corresponds to the equilibrium bond length.



(a)



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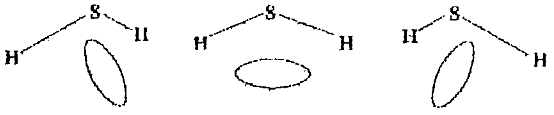

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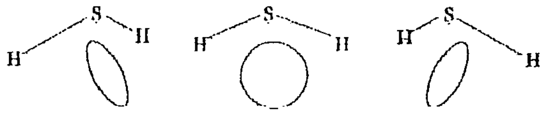
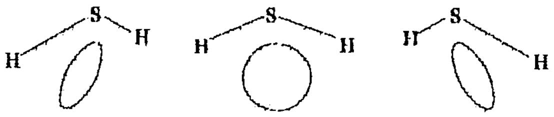


(d)



(e)

23 The rule of mutual exclusion

(i) can be applied to a molecule with a centre of symmetry,

(ii) involves vibrational Raman spectra of molecules.

(iii) can be applied to a molecule without a centre of symmetry if it has highly electronegative atoms..

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 In standard notation, rotational energy levels of a rigid *oblate symmetric top* (e.g. $PtCl_4^{2-}$) are given by $E_{J,K} = B(cm^{-1})J(J+1)+\left[C(cm^{-1})-B(cm^{-1})\right]K^2$. The specific selection rule in pure rotational Raman spectroscopy of such a molecule is

(a) $\Delta K = 0,\ \Delta J = 0,\pm1,\pm2$ for $K = 0$ and $\Delta K = 0,\ \Delta J = 0,\pm1,\pm2$ for $K \neq 0$

(b) $\Delta K = 0,\ \Delta J = 0,\pm2$ for $K = 0$ and $\Delta K = 0,\ \Delta J = 0,\pm2$ for $K \neq 0$

(c) $\Delta K = 0,\ \Delta J = 0,\pm2$ for $K = 0$ and $\Delta K = 0,\ \Delta J = 0,\pm1,\pm2$ for $K \neq 0$

(d) $\Delta K = 0,\ \Delta J = 0,\pm1$ for $K = 0$ and $\Delta K = 0,\ \Delta J = 0,\pm1,\pm2$ for $K \neq 0$

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

25. In standard notation the wavenumbers (in cm^{-1}) of the photons corresponding to the S–branch of *Stokes lines* in the pure rotational Raman spectrum of PtCl_4^{2-}, recorded with an incident beam of radiation of wavenumber $\bar{\nu}_0$, are given by

(a) $\bar{\nu}_S = \bar{\nu}_0 + 2B(\text{cm}^{-1})(2J+3)$ (b) $\bar{\nu}_S = \bar{\nu}_0 - 2B(\text{cm}^{-1})(2J+3)$

(c) $\bar{\nu}_S = \bar{\nu}_0 - B(\text{cm}^{-1})(2J+3)$ (d) $\bar{\nu}_S = \bar{\nu}_0 + B(\text{cm}^{-1})(2J+3)$

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

26. Consider the following statements.

(i) Though O_2 is a homonuclear diatomic molecule, it shows a pure rotational Raman spectrum since it is paramagnetic.

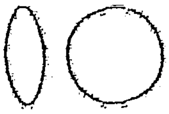
(ii) Pyridine, C_6H_5N, can show a pure rotational Raman spectrum since its polarisability ellipsoid is not spherical.

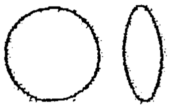
(iii) A pyramidal molecule, AB_3, will show a pure rotational Raman spectrum.

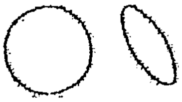
The correct statements out of (i), (ii) and (iii) above are
(a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
(d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

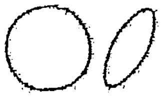
27. Consider a molecule of acetylene whose internuclear axis coincides with the plane of this paper. The cross section of the polarisability ellipsoid of this molecule on the plane of this paper is . The cross section of the polarisability ellipsoid of this molecule on the plane of this paper when it is rotated by $\pi/2$ and π, respectively, bout an axis perpendicular to the internuclear axis and passing through the centre of inversion of the molecule are best represented by


(a)


(b)


(c)


(d)


(e)

28. The specific selection rule in the vibrational rotational Raman spectroscopy of a diatomic molecule is

(a) $\Delta\upsilon = \pm1, \pm2, \pm3, \ldots$ and $\Delta J = 0, \pm1$

(b) $\Delta\upsilon = \pm2$ and $\Delta J = 0, \pm2$

(c) $\Delta\upsilon = \pm1, \pm2, \pm3, \ldots$ and $\Delta J = \pm2$

(d) $\Delta\upsilon = \pm1, \pm2, \pm3, \ldots$ and $\Delta J = 0, \pm2$

(e) $\Delta\upsilon = \pm1$ and $\Delta J = 0, \pm1$

29. Following table summarises the observations of the vibrational Raman and IR spectra of a molecule with the molecular formula A_2B.

Normal mode	Raman	IR
1	Observed	Observed
2	Observed	Observed
3	Observed	Observed

One can definitely say that

(a) the structure of the molecule is not ABA if it is linear.

(b) the structure of the molecule has to be AAB.

(c) there is an experimental error in the above observations since all the normal modes of a triatomic molecule cannot be simultaneously active in both IR and Raman spectra.

(d) the structure of the molecule has to be ABA

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

30. Consider the following statements about the vibrational Raman spectrum of CO_2.

(i) Symmetric stretching gives a polarised line/band.

(ii) Anti–symmetric stretching gives a depolarised line/band.

(iii) Bending gives a polarised line/band.

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.

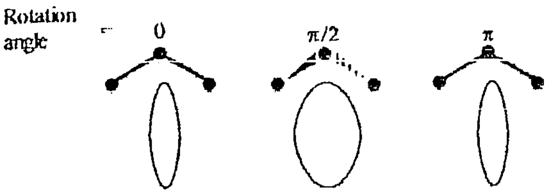
31. The relative intensities of Stokes and anti–Stokes limes may be used to estimate the temperature of a sample of molecules using the following equation given in standard notation.

$$\frac{\text{Intensity of anti-Stokes line}}{\text{Intensity of Stokes line}} = \left[\frac{\nu_0 + |\Delta\nu|}{\nu_0 - |\Delta\nu|}\right]^4 \exp\left(-\frac{h|\Delta\nu|}{kT}\right)$$

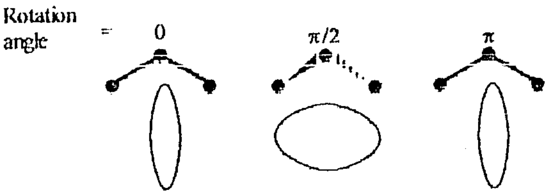
In some arbitrary units, the intensity of the anti–Stokes line at a Raman shift of 460 cm^{-1} in the vibrational Raman spectrum of CCl_4 is 9.2. In the same units, the intensity of the corresponding Stokes line is 76.0. If the wave length of the incident radiation is 5145 Å then the best estimate of the temperature of the sample of CCl_4 used in generating the spectrum is

(a) 255 K. (b) 266 K (c) 277 K (d) 288 K (e) 299 K

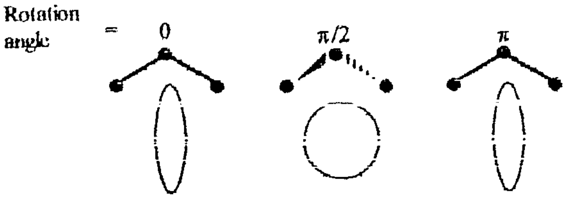
32. Consider a bent triatomic molecule with the structure ABA. The plane of the molecule is the same as the plane of this paper. Which best describes the cross section of the polarisability ellipsoid on this paper when the molecule is rotated by $\pi/2$ and π about its principal axis.



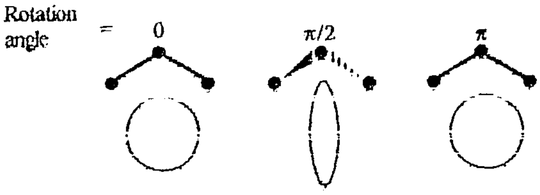
(a)



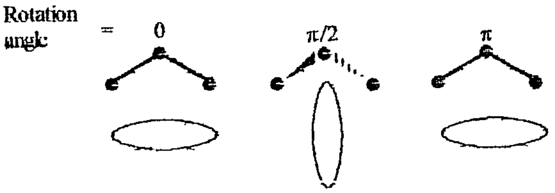
(b)



(c)



(d)



(e)

33. For a hydrogen sulphide molecule, the Raman scattered radiation due to the

(i) symmetric stretching mode

(ii) asymmetric stretching mode

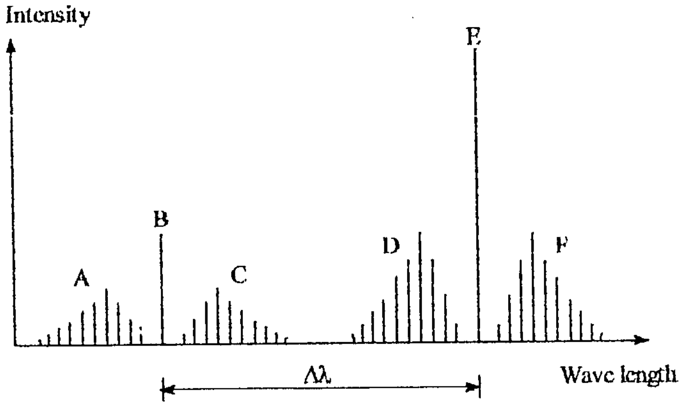
(iii) bending mode

is polarised.

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.

Questions 34 – 37.

Use the following diagram in answering the questions 34 37.



The above diagram shows a part of the vibrational rotational Raman spectrum of a diatomic molecule. E is the Rayleigh line.

34. Lines in bands D and F represent

(a) Stokes and anti–Stokes lines of vibrational overtones respectively.

(b) Stokes and anti–Stokes lines, respectively, which correspond to pure rotational transitions.

(c) anti–Stokes and Stokes lines, respectively, which correspond to pure rotational transitions.

(d) O and S branches respectively.

(e) P and R branches respectively.

35. Lines in bands A and C in the fundamental vibrational band correspond to

(a) Q and R branches respectively.

(b) P and Q branches respectively.

(c) P and R branches respectively.

(d) O and S branches respectively.

(e) S and O branches respectively.

36. Line/s in band B in the fundamental vibrational band correspond to

(a) S branch.

(b) O branch.

(c) Q branch.

(d) P branch.

(e) R branch.

37. The wave number difference, $\overline{\nu}$, corresponding to $\Delta\lambda$ is

(a) $\overline{\nu} = \left(1 - 3x_{e,k}\right)\overline{\omega}_{e,k}$

(b) $\overline{\nu} = \left(1 - 2x_{e,k}\right)\overline{\omega}_{e,k}$

(c) $\overline{\nu} = 2\left(1 - 3x_{e,k}\right)\overline{\omega}_{e,k}$

(d) $\overline{\nu} = \left(1 - 4x_{e,k}\right)\overline{\omega}_{e,k}$

(e) $\overline{\nu} = 5\left(1 - 6x_{e,k}\right)\overline{\omega}_{e,k}$

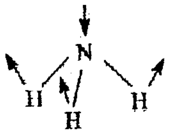
38. (i) In general. *Raman spectroscopy* can be done with a *smaller* sample than that is required in (absorption) IR spectroscopy using a standard IR spectrometer.

(ii) In general a state of the art *Raman spectrometer* is more expensive than a state of the art *IR spectrometer.*

(iii) Raman spectra of *hygroscopic and/or air sensitive* compounds can be obtained by placing it in a sealed glass tubing, which cannot be done in IR spectroscopy since glass absorbs IR radiation.

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.

39. Consider the following symmetric bending vibrational mode of NH_3



(a) It is Raman inactive.

(b) It is Raman active and gives a depolarised line in the Raman spectrum.

(c) It is Raman active and gives a polarised line in the Raman spectrum.

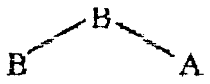
(d) The Raman activity of it cannot be predicted.

(e) It can be Raman active only at very low temperatures.

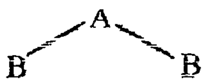
40. The IR and Raman spectral data of a molecule with the chemical formula B_2A is summarised below.

$\tilde{\nu}/\mathrm{cm}^{-1}$	IR spectrum	Raman spectrum
589	Strong: *PQR branches appear*	---
1285	Very strong: *Only PR branches*	Very strong: *Polarised*
2224	Very strong: *Only PR branches*	Strong: *Depolarised*

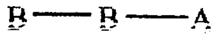
The structure of molecule has to be



(a)



(b)



(c)

(d)

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