

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Assignment II (Test) — 2008/2009

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

(1½ hours)

11th March 2009 (Wednesday)

4.00 p.m. — 5.30 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 JK ⁻¹ mol ⁻¹
Avogadro constant (N _A)	=	6.023 × 10 ²³ mol ⁻¹
Faraday constant (F)	=	96,500 C mol ⁻¹
Planck constant (h)	=	6.63 × 10 ⁻³⁴ Js
Velocity of light (c)	=	3.0 × 10 ⁸ m s ⁻¹
Standard atmospheric pressure	=	10 ⁵ Pa (Nm ⁻²)
Log _e (X)	=	2.303 Log ₁₀ (X)

1. A molecule has only three energy levels which are equally spaced. The separation between any two adjacent energy levels is 8.0000×10^{-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 1.5000×10^{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 student will observe two Stokes lines.
- (ii) An anti-Stokes line may appear with a frequency shift approximately equal to 1.2066×10^{13} Hz
- (iii) An anti-Stokes line may appear at a frequency approximately equal to 3.9133×10^{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) None of the answers (a), (b), (c) or (d) is correct.

2. (i) Always vibrational Raman spectroscopy has to be done 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.

3. Consider the following statements.

- (i) Radiation with a depolarisation ratio of zero, i.e. $\rho_p = 0$, is plane polarised.
- (ii) Depolarisation ratio of different lines in the Raman spectrum of a pure *compound* has to be the same.

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

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 answers (a), (b), (c) or (d) is correct.

4. A Raman spectrum of a pure sample of gaseous diatomic compound was obtained using an incident beam of electromagnetic radiation of frequency 7.54×10^{12} Hz. Among others, spectral lines were observed at frequencies 3.56×10^{12} Hz, 7.54×10^{12} Hz and 9.78×10^{12} Hz. Consider the following statements.

- (i) The line at frequency 7.54×10^{12} Hz is the Rayleigh line.
- (ii) The line at frequency 3.56×10^{12} Hz is a Stokes line.
- (iii) The line at frequency 9.78×10^{12} Hz is an anti-Stokes line.

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

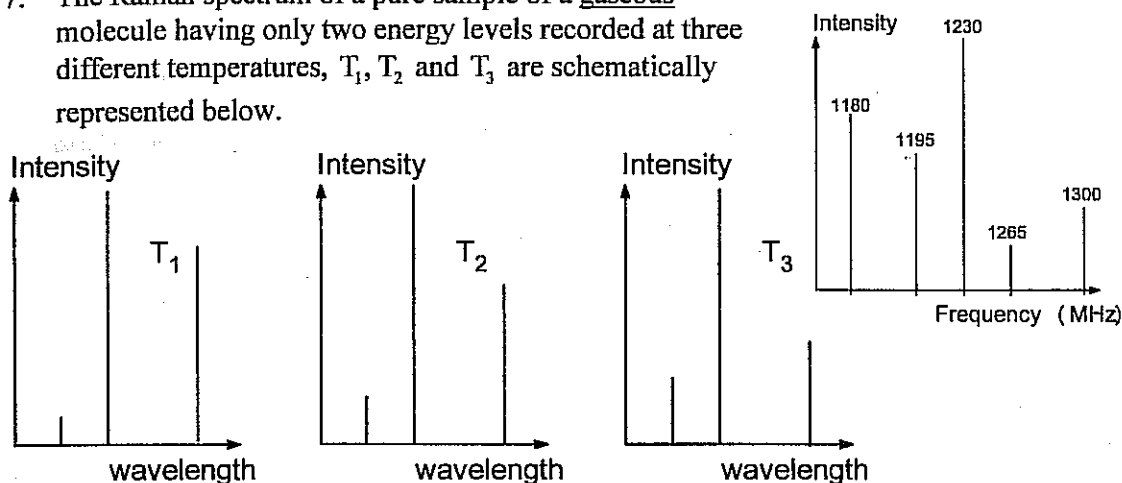
- (a) Only (i) and (ii). (b) Only (i) and (iii). (c) Only (ii) and (iii).
 (d) All (i), (ii) and (iii) (e) None of the answers (a), (b), (c) or (d) is correct.

5. The molecules that can show a *pure rotational* Raman spectrum out of, C_6H_6 , CH_4 , $trans-SF_4Cl_2$ and $cis-SF_4Cl_2$ are

- (a) C_6H_6 , CH_4 and $trans-SF_4Cl_2$. (b) C_6H_6 , CH_4 and $cis-SF_4Cl_2$.
 (c) CH_4 , $trans-SF_4Cl_2$ and $cis-SF_4Cl_2$ (d) C_6H_6 , $trans-SF_4Cl_2$ and $cis-SF_4Cl_2$.
 (e) None of the answers (a), (b), (c) or (d) is correct.

6. The Raman active vibrational normal modes of a linear symmetric molecule A_2B are
- Only symmetric stretching mode.
 - Only the bending mode.
 - Only the anti-symmetric stretching and bending modes.
 - Only the symmetric stretching and bending modes.
 - All symmetric stretching, anti-symmetric stretching and bending modes.

7. 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.



The most probable relationship among the temperatures is

- $T_1 < T_2 < T_3$.
- $T_3 < T_2 < T_1$.
- $T_2 < T_1 < T_3$.
- $T_2 < T_3 < T_1$.
- $T_1 < T_3 < T_2$.

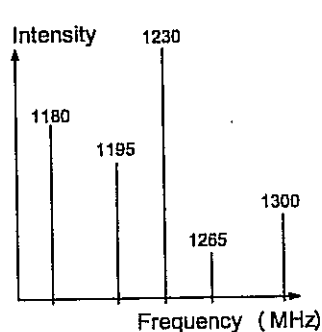
8. Consider the Raman spectrum of a hypothetical molecule having only three (non-degenerate) energy levels at energies ϵ , 2ϵ , 3ϵ and 4ϵ .

- The intensity of the Stokes line/s is/are larger than the corresponding anti-Stokes line/s.
- The difference in frequency between any two adjacent Stokes lines is equal to ϵ/h where h is the Planck constant.
- There can be only a maximum of three Stokes lines and a maximum three anti-Stokes line in the Raman spectrum of this molecule.

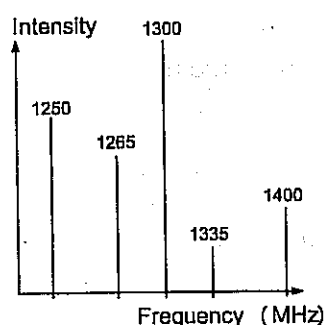
The correct statements out of (i), (ii) and (iii) above are

- Only (i) and (ii).
- Only (i) and (iii).
- Only (ii) and (iii).
- All (i), (ii) and (iii)
- None of the answers (a), (b), (c) or (d) is correct.

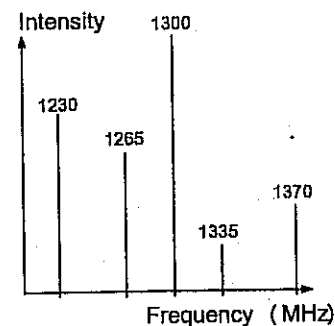
9. A schematic diagram of a part of the Raman spectrum of a pure sample of a compound recorded with excitation radiation of frequency 1230 MHz is shown in the diagram to the right. The numbers written above each spectral line indicates the frequency of radiation corresponding to that line in MHz. Which of the following best represents the same part of the Raman spectrum recorded with excitation radiation of frequency 1300 MHz.



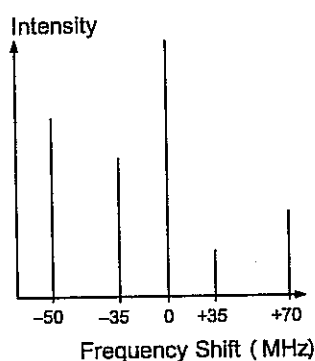
(a)



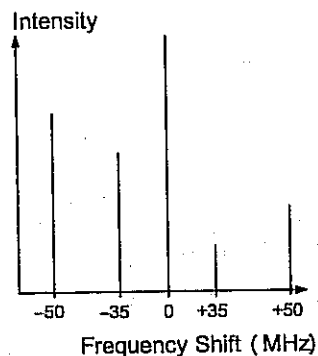
(b)



(c)



(d)



(e)

10. (i) The polarisability of N_2 along the bond axis changes during its vibrational motion.
 (ii) The dipole moment induced in CO and HCl, in a direction perpendicular to the bond axis, by the same applied electric field, has to be the same.
 (iii) The polarisability of CO perpendicular to the bond axis is smaller than that along the bond axis.

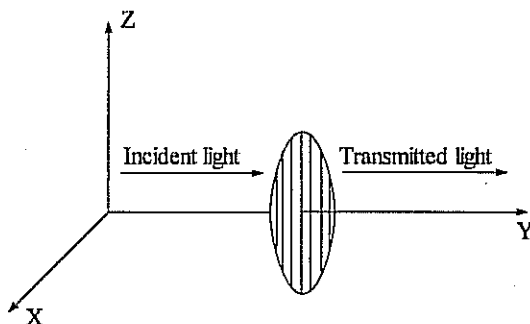
The correct statements out of (i), (ii) and (iii) above are

- (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.

11. In *pure rotational* Raman spectrum of $H-C \equiv C-C \equiv C-H$ you may be able to observe anti-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) $\Delta J = \pm 2$

12. 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.



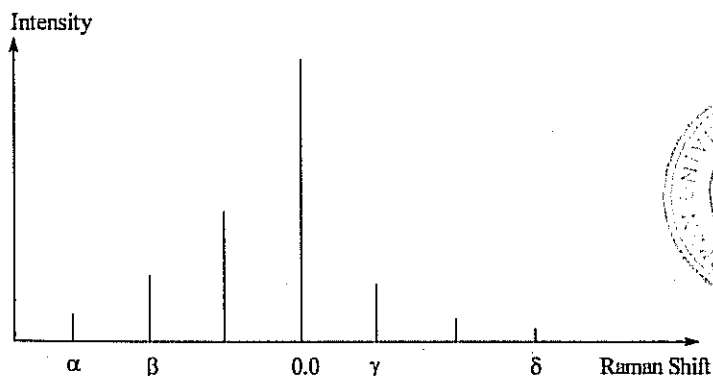
- (i) The *magnetic field* in the transmitted light is parallel to the X axis.
 (ii) The *electric field* of the transmitted light will be parallel to the Z axis.
 (iii) There will not be any *transmitted radiation* if the incident light is plane polarised having its plane of polarisation on YZ plane.

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 13 – 16.

Use the following figure, which schematically represents the low resolution pure vibrational Raman spectrum of a diatomic molecule AB, in answering the questions 13 – 16.



α , β , γ and δ are the Raman shifts of the lines depicted in the above figure. It has been observed that $\alpha = -8280 \text{ cm}^{-1}$ and $\gamma = 2880 \text{ cm}^{-1}$

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

- (a) 2940 (b) 2950 (c) 2990 (d) 2995 (e) 3000

14. The anharmonicity constant of AB is
 (a) 0.0164 (b) 0.0174 (c) 0.0184 (d) 0.0200 (e) 0.0250

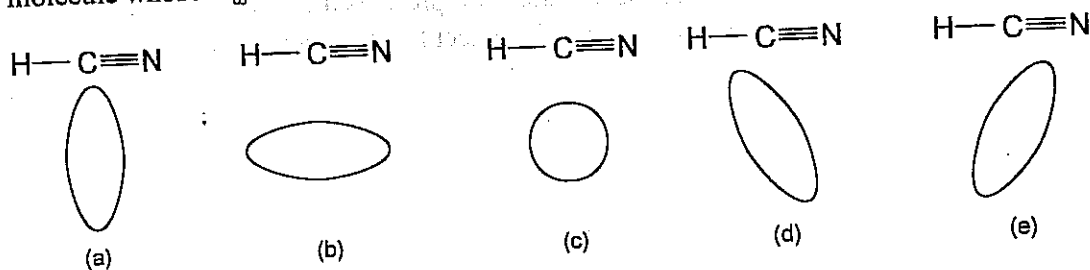
15. The value of β in cm^{-1} is
 (a) -5510 (b) -5520 (c) -5640 (d) -5760 (e) -5800

16. The value of δ in cm^{-1} is
 (a) 8280 (b) 8290 (c) 8330 (d) 8340 (e) 8350

17. A Raman scattering experiment was performed with a beam of plane polarised electromagnetic radiation of wavenumber 3450 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 $9/16$. The most probable values of the amplitudes of the *parallel* and *perpendicular* electric fields (in arbitrary units), respectively, are

(a) 9 and 16 (b) 15 and 81 (c) 3 and 4
 (d) 5 and 3 (e) 8 and 6

18. The expected cross section of the polarisability ellipsoid on this paper, of a HCN molecule whose C_∞ coincides with the paper, is best represented by

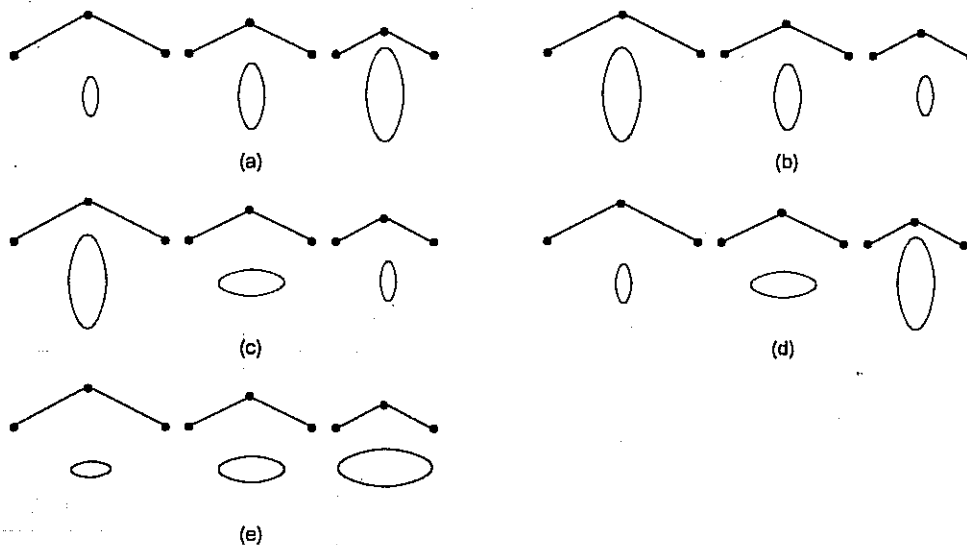


19. (i) A molecule that has a *spherical* polarisability ellipsoid cannot show a pure rotational Raman spectrum.
 (ii) C_2H_2 does not show a pure rotational Raman spectrum since it has a centre of symmetry.
 (iii) Sodium can form a diatomic molecule in vapour phase under exotic conditions. This diatomic molecule, Na_2 , can 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.

20. Which of the following diagram best represents the variation of the cross section of the polarisability ellipsoid, on the plane of the molecule of a bent molecule A_2B , during vibration in its symmetric stretching mode. In each of the diagrams the picture in the middle corresponds to the equilibrium bond length.



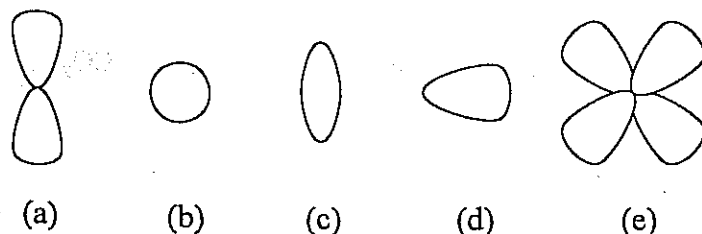
21. The rule of mutual exclusion

- (i) is not applicable to C_2H_2 since there is no nucleus on the centre of inversion of the molecule.
 (ii) is applicable to the vibrational Raman spectroscopy of $PtCl_4^{2-}$.
 (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.

22. The cross section of the polarisability ellipsoid of $trans-SF_4I_2$ molecule on the plane of SF_4 is best represented by

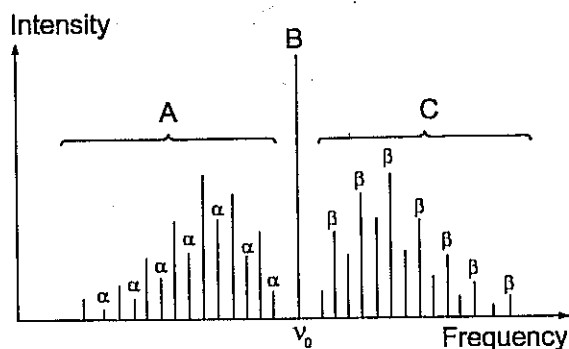


23. In standard notation the wavenumbers (in cm^{-1}) of the photons corresponding to the S-branch of Stokes lines in the pure rotational Raman spectrum of PtCl_4^{2-} , recorded with an incident beam of radiation of wavenumber $\bar{\nu}_0$, are given by

- (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

24. Consider the following statements.

- (i) Pyridine, $\text{C}_6\text{H}_5\text{N}$, can show a pure rotational Raman spectrum since its polarisability ellipsoid is not spherical.
 (ii) Though N_2 is a homonuclear diatomic molecule, and thus have no permanent dipole moment, it shows a pure rotational Raman spectrum.



(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.

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

- (a) $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ and $\Delta J = 0, \pm 1$
 (b) $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ and $\Delta J = 0, \pm 2$
 (c) $\Delta v = \pm 2$ and $\Delta J = 0, \pm 2$
 (d) $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ and $\Delta J = \pm 2$
 (e) $\Delta v = \pm 1$ and $\Delta J = 0, \pm 1$


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

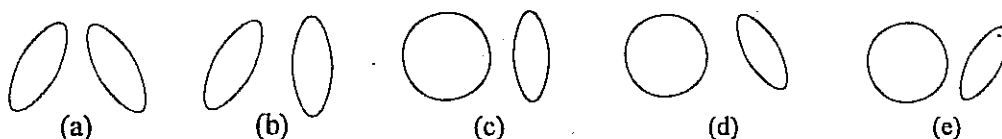
- (i) Anti-symmetric stretching gives a polarised line/band.
 (ii) Symmetric stretching gives a polarised line/band.
 (iii) Bending does not give a polarised or depolarised line/band.

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.

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, about an axis perpendicular to the internuclear axis and perpendicular to the axis of the molecule and passing through the centre of inversion of the molecule are best represented by



28. 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	Not observed	Observed
2	Observed	Not observed
3	Not observed	Observed

One can definitely say that the molecule, A_2B ,

- (i) has a centre of symmetry.
- (ii) has to be linear.
- (iii) obeys the rule of mutual exclusion.

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

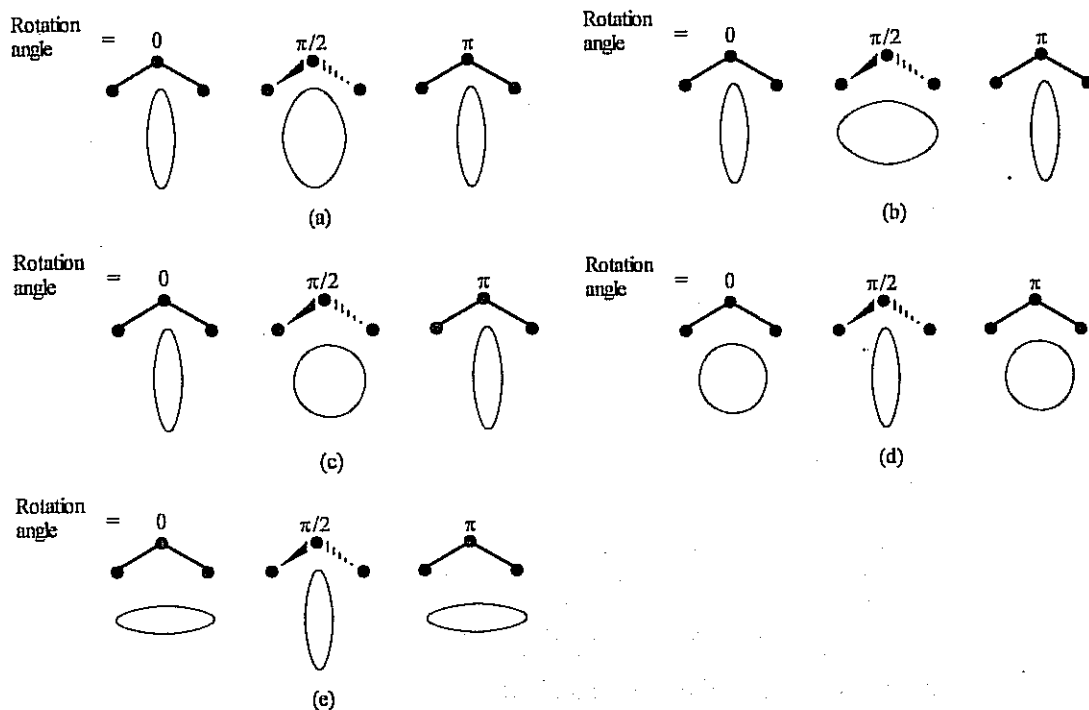
- (a) Only (i) and (ii).
- (b) Only (i) and (iii).
- (c) Only (ii) and (iii).
- (d) All (i), (ii) and (iii)
- (e) None of the answers (a), (b), (c) or (d) is correct.

29. (i) The *magnitude* of the *electric* field vector does not vary in time in monochromatic plane polarised electromagnetic radiation.
- (ii) The electromagnetic radiation generated by a very hot metal sheet is not plane polarised.
- (iii) One can obtain non-monochromatic plane polarised electromagnetic radiation by merging two beams of plane polarised radiation of different frequency so that their planes of polarisation coincide.

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.

30. 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.



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

- (i) asymmetric stretching mode
- (ii) symmetric stretching mode
- (iii) bending mode

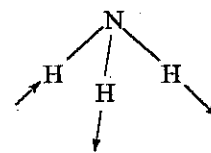
is polarised.

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.

32. Consider the following anti-symmetric stretching 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.



33. The pure rotational Raman spectrum of ammonia, obtained with incident radiation of frequency, ν_0 , is schematically represented in the diagram to the right. Consider the following statements.

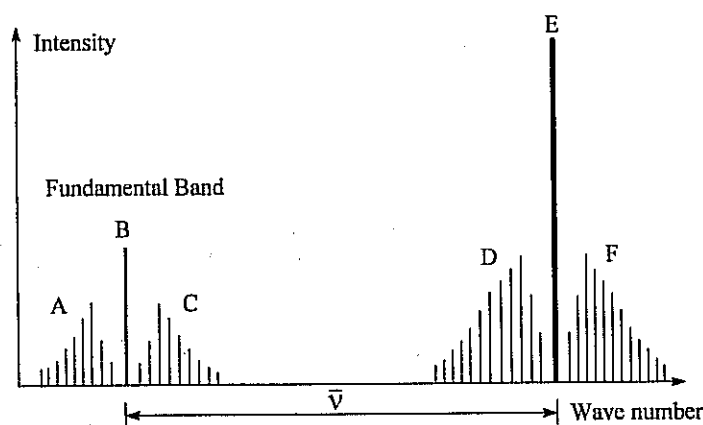
- (i) The spectral lines β in band C are only due to anti-Stokes lines in the S-branch.
- (ii) The spectral lines α in band A are only due to Stokes lines in the R-branch.
- (iii) B is due to Rayleigh scattering.

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 which correspond to pure rotational transitions.
 - (b) Stokes and anti-Stokes lines of vibrational overtones respectively.
 - (c) P and Q branches respectively.
 - (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) S and O branches respectively.
 - (d) P and R branches respectively.
 - (e) O and S branches respectively.

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

- (a) S branch.
- (b) Q branch.
- (c) P branch.
- (d) O branch.
- (e) R branch.

37. In standard notation

- (a) $\bar{\nu} = (1 - 2x_{e,k})\bar{\omega}_{e,k}$
- (b) $\bar{\nu} = 2(1 - 3x_{e,k})\bar{\omega}_{e,k}$
- (c) $\bar{\nu} = 3(1 - 4x_{e,k})\bar{\omega}_{e,k}$
- (d) $\bar{\nu} = 4(1 - 5x_{e,k})\bar{\omega}_{e,k}$
- (e) $\bar{\nu} = 5(1 - 6x_{e,k})\bar{\omega}_{e,k}$

38. Four fundamental vibrational bands are observed in the IR and Raman spectra of a molecule AB_3 . The observations are summarised in the following table.

ν/cm^{-1}	Raman spectrum	IR spectrum
450	Observed Depolarised	Observed Perpendicular
610	Observed Polarised	Observed Parallel
940	Observed Depolarised	Observed Perpendicular
982	Observed Polarised	Observed Parallel

Consider the following statements about AB_3 molecule.

- (i) The structure of the molecule may be planar.
- (ii) The structure of the molecule may be pyramidal.
- (iii) The normal modes which lead to the spectral lines at 610 cm^{-1} and 982 cm^{-1} are symmetric modes.

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. (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.

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

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

The vibrational Raman spectrum of CCl_4 was recorded at 300 K. In some arbitrary units, the intensity of the Stokes line at a Raman shift of -500 cm^{-1} was found to be 75.0. If the wave number of the incident radiation is 19000 cm^{-1} , then the best estimate of the intensity (in the same units) of the anti-Stokes line at a Raman shift of 500 cm^{-1} is

- (a) 8.34 (b) 9.01 (c) 5.76 (d) 7.89 (e) 6.79