



Model Questions For Semester-V B.Sc Chemistry Honours

(Physical Chemistry)

- 1) What are the essential conditions for obtaining microwave and infrared spectra? Show pictorially that HCl is microwave active but HI is not.
- 2) Describe the important applications of microwave and infrared spectra.
- 3) Describe a method to determine the dissociation energy of a diatomic molecule.
- 4) The spectrum of HCl shows a very intense absorption at 2886 cm^{-1} , a weaker one at 5668 cm^{-1} and a very weak one at 8347 cm^{-1} . Calculate the equilibrium vibration frequency and the anharmonicity constant.
- 5) The number of molecules in the higher excited states are known to decrease with increasing rotational quantum numbers but the intensity of the rotational transition increases and passes through a maximum. Discuss.
- 6) Write down the expression for the rotational energy of a polyatomic molecules. The difference in the successive energy levels is very close for polyatomic molecules. Why?
- 7) What are the reasons to believe molecular vibrations to be anharmonic?
- 8) The rotational spectra of H^{127}I shows equidistant lines separated by 12.8 cm^{-1} . Calculate the internuclear distance.
- 9) What is a rigid rotator? Give the energy expression for a rigid rotator and show that the difference between the lines of the microwave spectra of CO is equispaced.
- 10) The rotational spectrum of $^{79}\text{Br}^{19}\text{F}$ shows a series of equidistant lines spaced 0.71433 cm^{-1} . Calculate the moment of inertia of the molecule and determine the wave number for the $J=5 \rightarrow J=6$ transition.
- 11) What are the reasons to believe that the diatomic molecule is a non-rigid rotator? Write down the energy expression of a non-rigid rotator and; show that the lines are not equispaced
12. (a) In the analysis of rotational spectra the population of the excited state level is important though it is immaterial in case of its vibrational spectra at the ordinary temperature. Show mathematically, (differences in energy levels between $J=0 \rightarrow J=1$ and $v=0 \rightarrow v=1$, have been assumed to be 2 cm^{-1} and 1000 cm^{-1} respectively).
 - (b) Write the correct answer:-
 - (i) The rotational spectra of MO has a series of lines equally spaced by 3.842 cm^{-1} .
 - (ii) The frequency corresponding to the transition $J=1 \rightarrow J=2$ is 1.931 cm^{-1} or 3.812 cm^{-1} . The fundamental frequency of H_2 , is approximately: half that of D_2 or 1.414 times of D_3 or twice that of D_2 .



- 13) Write down the expressions for the energies of a harmonic oscillator and an anharmonic oscillator explaining all the terms, Discuss how the vibrational spectrum of a diatomic molecule is modified due to anharmonicity.
- 14) The force constant for H^{35}Cl is $4.81 \times 10^5 \text{ Nm}^{-1}$ (or dynes cm^{-1}). Find the fundamental vibrational frequency.
15. (a) What do you mean by rigid and nonrigid rotors?
(b) Rotational energy levels of diatomic molecule are not equispaced but spectral lines are equispaced. Explain.
(c) The bond length of HF is 0.918 \AA . Calculate frequencies in cm^{-1} for the line in the rotational spectrum for the transitions $J=0 \rightarrow J=1$ and $J=3 \rightarrow J=2$
16. (a) The vibrational rotational spectra of a molecule consist of branches of lines around the central line. Explain.
(b) Write appropriate expressions for energies of a classical vibrator and a quantum mechanical oscillator. Graphically represent the energy levels of the latter for vibrational quantum number $v = 0, 1$ and 2 . What is the significance of the energy in the state $v=0$.
- 17) The fundamental vibrational frequency of HCl molecule is 2886 cm^{-1} . Calculate the force constant for stretching of HCl in dynes cm^{-1} .
- 18) State whether the following statements are correct or false:
- 19) In a certain state, rotational energy of a nonrigid rotor is higher than that of rigid rotor.
- 20) Spherical top molecules do not give pure rotational spectra. Explain with two examples.
- 21) The pure rotational spectrum of a diatomic molecule will consist of a series of lines with constant frequency separation. Explain.
- 22) Distinguish between 'Curie temperature' and 'Neel temperature*.
- 23) For a linear molecule OCS, if the values of moment of inertia $\text{O}^{16}=\text{C}^{12}=\text{S}^{32}$ and $\text{O}^{16}=\text{C}^{12}=\text{S}^{34}$ are given then explain how the bond lengths r_{co} are measured.
- 24) For an anharmonic oscillator the lines in IR spectrum are not equally spaced — Explain using appropriate equation.
- 25) Two adjacent lines in the microwave spectrum of HCN have frequencies of 17.73×10^6 and 26.59×10^6 cycles/sec. Calculate the moment of inertia of HCN.
26. (a) Although CO_2 is microwave inactive, it may be infrared active. Explain.
(b) Write down the expression for zero-point energy for the anharmonic oscillator, explaining the terms involved. Arrange the following bonds in increasing order of intensity of IR absorption band: *N-H*, *C-H*, and *O-H*.
- 27) Give a schematic representation of three fundamental vibrations of water molecule.



28) The first line ($J=0$ to $J=1$) in the pure rotational spectrum of CO occurs at the frequency of 1.153×10^{11} cycles/sec. Calculate the bond length of CO . [J = rotational quantum number, $A = 6.624 \times 10^{-27}$ erg.s.].

(e) Explain the following statements :

(i) Bond angles are much more easily deformed than the bonds.

29) Assuming that rotational and vibrational energy changes occur independently write down the expression for the vibrational-rotational energies of a diatomic, explaining the terms involved. Use it to find for the frequency of the IR spectral line for the transition from $v=0$ to $v=1$ and $\Delta J=+1$. [v = vibrational quantum number, J = rotational quantum]

30) The frequency of the $O-H$ stretching vibration in CH_3OH is 3300 cm^{-1} . Estimate the frequency of $O-D$ stretching vibration in CH_3OD . 4

31) The fundamental band for CO in its IR spectrum is centered at 2143 cm^{-1} and the first overtone at 4259.7 cm^{-1} . Calculate the equilibrium oscillator frequency, ν_e and the anharmonicity constant, x_e . Also calculate the zero-point energy of CO .

32) State whether correct or false :

(i) The absorption band due to common functional group is independent on the structure of the molecule.

(ii) Stretching frequency of $C=O$ less than that of $C=S$.

(iii) Presence of hydrogen bonding increases the vibrational frequency of a $O-H$ bond.

(iv) Fingerprint bands establish conclusively the identity of two samples.

(v) The rotational energy of any molecule is given by $BhJ(J+1)$, provided the centrifugal distortion is neglected (Rotational constant = B).

(vi) In homonuclear diatomic molecules, all 'u' MOs are antibonding. ('u' ungerade).

33) State the factor(s) on which the relative intensities of the pure rotational spectral lines depend. Arrive at suitable expression to explain the dependence of the relative intensities of such lines on rotational levels.

(b) Calculate the maximum populated level (J_{\max}) of $H^{35}Cl$ at 300 K. Given rotational constant (B) = 10.4398 cm^{-1} . 4

(c) (i) From the following, list the molecules which are microwave active and which are IR active:



34) Derive an expression classically for the vibrational energy of a rigid diatomic molecule. Write down the corresponding expression obtained quantum mechanically and hence compare the results obtained, by these two approaches.

35) In the infrared spectrum of $H^{79}Br$, there is an intense line at 2559 cm^{-1} . Calculate the force constant of $H^{79}Br$, and the period of vibration of $H^{79}Br$.

36) Write down the expressions for the potential energy and vibrational energy of a diatomic molecule considering anharmonic oscillation. Explain the terms involved. Show schematically the

variation of potential energy of a diatomic molecule as a function of internuclear distance for harmonic as well as anharmonic oscillations in the same plot

37) The first rotational absorption of $^{12}\text{C}^{16}\text{O}$ has been observed at $\nu = 3.84235 \text{ cm}^{-1}$ and that of $^{13}\text{C}^{16}\text{O}$ at $\nu = 3.7337 \text{ cm}^{-1}$. Taking the mass of ^{16}O to be 15.9949 and that of ^{12}C to be 12.00, calculate the atomic weight of ^{13}C . Assume that the bond length is unchanged by isotopic substitution.

38. (a) Mention the basic differences between

(iii) Symmetric tops and asymmetric tops.

(b) Explain briefly the 'overtone transitions' and 'hot bands' in R spectrum.

39) Calculate zero point vibrational energy of CO_2 . Given the 'observed frequencies' of normal are 1330 cm^{-1} , 667 cm^{-1} and 2349 cm^{-1} .

d) Explain why CO_2 is microwave inactive but it may be IR active?

40) What are the basic assumptions of the rigid rotator model? Assuming that the rotation of HCl molecule obeys the rigid rotator model, calculate its bond length if the difference between 2 successive spectral lines is 20.3 cm^{-1} .

41. (a) State and explain Stark-Einstein's law of Photochemical equivalence.

(b) Explain the kinetics of Photodimerisation of Anthracene.

(c) Calculate the amount of energy when reacting system absorbs radiation of wavelength 4000 \AA .

(d) In Photo decomposition of HI vapour at $\lambda = 2070 \text{ \AA}$ absorption of each calorie gave 1.44×10^{-5} gms of hydrogen. Calculate quantum yield.

42. Write short note on

i) Fluorescence ii) Frank-Condon Principle iii) Photostationary Equilibrium v) Stern-Volmer Equation.

43.(a) Illustrate with diagrams, the different types of primary photochemical processes.

(b) Elaborate the reasons for obtaining low and high quantum efficiencies.

(c) An uranyl oxalate actinometer was irradiated for 15 minutes with light of wavelength 4350 \AA and oxalic acid equivalent to 12.0 ml of .011 molar KMnO_4 was found to have been decomposed. The quantum efficiency of the actinometer at this wavelength being 0.58, calculate the average energy of the light used in quanta per second.

44. (a) Discuss briefly the role of photochemical reactions occurring in the atmosphere in causing depletion of ozone layer.

(b) Write notes on any two of the following:

(i) Frank-Condon Principle and pre-dissociation. (ii) Photosensitizers.

(iii) Fluorescence and phosphorescence.

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45. (a) Write the correct answer or fill up the blank where necessary :

- (b) The process of returning of a molecule from excited singlet state to ground state with emission of radiation is known as : (i) chemiluminescence , (ii) fluorescence (iii) phosphorescence
- (c) The quantum yield of a photochemical reaction is—
 (i) always less than unity (ii) always equal to unity (iii) always greater than unity (iv) can have any value >0 depending on reaction.
- (d) The unit of extinction coefficient is—
- (e) The reverse of photochemical reaction is called—
 (i) Phosphorescence (ii) fluorescence (iii) photosensitization (iv) Chemiluminescence
- (f) State and explain Einstein's law of photo-chemical equivalence. Describe, with a suitable example, the principle involved in the determination of quantum yield of a photochemical reaction by chemical actinometry.
- (g) In an experiment on the photolysis of gaseous HI ($2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$) with light of 2537 \AA , it was found that absorption of 3.07×10^{10} ergs of energy decomposed 1.30×10^8 molecules of HI. Calculate the 'quantum yield' of the reaction.
- (d) What is your inference if the quantum efficiency is much higher or lower than unity.
46. Write notes on any *three* of the following:
 (a) Lambert-Beer's law, (b) Photodimerisation of anthracene, (c) Chemiluminescence and bioluminescence, (d) Photochemistry of air pollution. (e) Flash photolysis techniques.
- 47.(a) A source of light emits radiation from 290nm to 700nm. Calculate the energy in Einstein at the two extreme wavelengths.
 (b) State Lambert – Beer's law. What is meant by optical density of a solution? Does it depends on wave length of light used?
 (c) Give an account of photosensitized reaction with examples.
48. Write notes on
 (a) Fluorescence, (b) Determination of quantum yield of photochemical reaction,
 (c) Thermal and photochemical reaction, (d) Potential energy diagram,
 (e) Photochemical smog.
- 49.(a) State whether correct or false:
 (i) Fluorescence is a non-radiative process.
 (iv) Molar extinction coefficient is unit less.
 (vi) According to Einstein's law of photochemical equivalency each molecule which takes part in a photochemical reaction absorbs one quantum of radiation.
 (viii) 'einstein' has the same value for radiations of all wavelengths.

50. (a) What do you mean by Quantum yield? Should quantum yield vary with time? Explain. Show that for the photochemical decomposition of HI, the quantum efficiency is two. Is it a chain reaction?

(b) In the photochemical reaction



Calculate the Quantum yield. Given the wavelength of irradiation is 253.7nm and irradiation time is 837 minutes, Energy absorbed = 3.436×10^8 ergs and HCl formed = 2.296×10^{-5} mol.

51. (a) explain the terms:

(i) Optical density, (ii) Photosensitization, (iii) Predissotiation.

(b) State whether the following statements are correct or false:

(ii) The 'Quantum Yield' depends on light intensity.

(v) Phosphorescence emission occurs at wavelength which is lower than that of fluorescence emission.

(c) Explain the following statements :

(ii) The photochemically activated molecules may return to the ground state by non-radiative paths.

52 (a) Define 'molar extinction coefficient' and state the factors on which it depends.

(b) Show that the 'quantum yield' for the photochemical dimerisation of anthracene in benzene is independent of intensity of light. [Given that the reaction proceeds through excitation in the first step followed by simultaneous dimerisation and fluorescence in the second step].

(c) In an absorption cell, the transmission of a 0.1 M solution of a substance X is 80% and that of a 0.1 M solution of another substance Y is 60% at a given wave length. What is the transmittance of a solution that is simultaneously 0.1 M in X and 0.1 M in Y?

(d) State the difference between ' photostationary' equilibrium and 'thermal equilibrium*.

f) Deduce an expression for the quantum yield for the photochemical decomposition of CH_3CHO .

53. (a) State whether the following statements are true or false.

(v) Photosynthesis is an example of a photosensitized reaction.

(vi) Phosphorescence occurs at a lower wavelength compared to fluorescence.

(viii) Radiationless transition from an excited singlet to the triplet state is known as internal conversion

b) What is the main utility of the Flash Photolysis technique?

54. (a) State the Franck Condon principle. How can this be used to explain Pre-dissociation?

(b) Explain what is meant by the optical density of a solution. Does it depend on wavelength?

(c) At 600nm, one filter transmits 65% of the incident light and another transmits 45% of it.

What is the transmittance of the combination of the 2 filters at the same wavelength? 55. (a)

Write short notes on (any three) (i) Photochemical smog. (ii) Photostationary equilibrium.

(iv) Quenching of fluorescence.