Total number of printed pages–8

1 (Sem–5/FYUGP) CHE04MJ

2025

CHEMISTRY

(Major)

Paper : CHE0500404

(Light–Matter Interaction)

Full Marks : 45

Time : 2 hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions : 1×5=5

   (i) Define quantum efficiency.

   (ii) What is absorption cross section ?

   (iii) Mention the selection rules in electronic spectroscopy.

   (iv) What do you mean by fingerprint region in IR spectroscopy ?

   (v) What is Raman effect ?

2. Answer ***any five*** of the following questions : 2×5=10

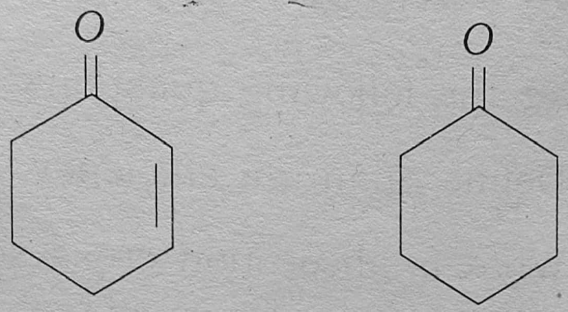
(i) State the Grotthus-Drapper Law and Stark-Einstein Law.

(ii) What is meant by inverted multiplets ?

(iii) Mention the energies and time required for electronic, vibrational and rotational transitions.

(iv) Define chromophores and bathochromes with examples.

(v) Which one of the following ketones will have higher IR carbonyl stretching frequency and why ?



(vi) Which of the following diatomic molecules do not absorb in the Infra-red region ?

HCl, $ClBr$, N_2, H_2, O_2

(vii) What do you mean by spin-orbit coupling ? Explain with an example.

(viii) Why is methanol a good solvent for UV but not for IR spectroscopy ?

(ix) What do you mean by Fundamental vibrations and overtones ?

(x) The first line in the rotational spectrum of carbon monoxide has a frequency of $3.8424\,cm^{-1}$, calculate the rotational constant and hence the bond length of carbon monoxide molecule.

(Given : mass of $12C = 12.0000u$ and mass of $16O = 15.9949u$)

3. Answer ***any four*** questions from the following : 5×4=20

(i) (a) When a dilute solution of anthracene in benzene is exposed to UV light, the system exhibits fluorescence with small ϕ of dimerization reaction. As the concentration of anthracene is increased, the fluorescence falls off and ϕ of dimerization increases towards a limiting value where fluorescence is practically eliminated. What is this phenomenon called ? Explain the phenomenon. 3

(b) What are radiative and non-radiative processes ? Explain with example. 2

(ii) State and explain Franck-Condon principle. Explain how this principle is helpful in predicting the shapes of absorption bands. 3+2=5

(iii) (a) On irradiating CCl_4 with the 435.8nm mercury line, the Raman lines are observed at 439.9, 441.8, 444.6, and 450.7nm. Calculate the Raman frequencies (in cm^{-1}) of CCl_4. 3

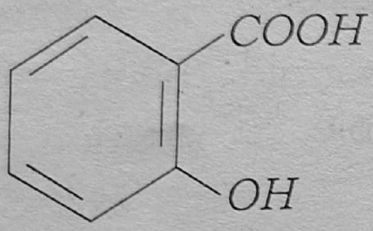
(b) The intensities of the Stokes lines are greater than the anti-Stokes lines. Explain. 2

(iv) The analytical data and the molecular mass determination gave C_8H_8O as the molecular formula of the compound. The compound burns with a sooty flame and gave an oxime with hydroxylamine hydrochloride. Following absorption bands appear in its Infra-red spectrum :

(i) 2825cm^{-1}, (ii) 2717cm^{-1}, (iii) 3060cm^{-1} and (iv) 1700cm^{-1} (s) and 830cm^{-1}. Suggest the functional groups and bonds present and give a probable structure of the compound.

(v) (a) State Hooke's law. The $C-H$ str vibration in chloroform occurs at $3000\,cm^{-1}$. Calculate the $C-D$ str frequency in deutero chloroform. 3

(b) How will you distinguish between the following pair of molecules on the basis of Infra-red spectroscopy ? 2



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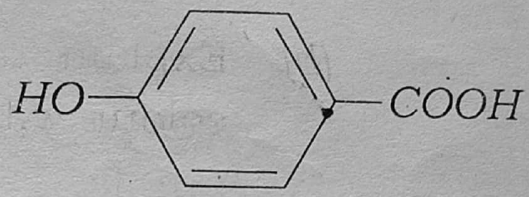


(vi) (a) What is meant by a selection rule ? Give the selection rule for a rotating diatomic molecule modelled as a rigid rotor. 1+2=3

(b) Explain the variation in the intensity of signals in rotation spectrum as a function of rotational quantum number. 2

(vii) (a) What do you mean by 'photosensitized reactions'? Give example of *one* such reaction that is useful to living system. 3

(b) Differentiate between fluorescence and phosphorescence, providing examples of each. 2

(viii) (a) What are the effects of polarity of the solvent on (i) $\sigma \rightarrow \sigma^*$, (ii) $\pi \rightarrow \pi^*$, (iii) $n \rightarrow \pi^*$ and (iv) $n \rightarrow \sigma^*$ transitions ? Show with a diagram the relative frequencies of these electronic transitions.

(b) Explain the quinonoid theory of colour with suitable illustration. 3+2=5

4. Answer ***any one*** question : 10×1=10

(i) (a) Considering a two level system, discuss Einstein's mechanism of absorption and emission of light. 5

(b) What do you mean by Rayleigh, Stokes and anti-Stokes lines in a Raman spectrum ? How do the characteristics of a Raman spectrum depend on (i) the nature of substance and (ii) the wave length of the radiation ? 5

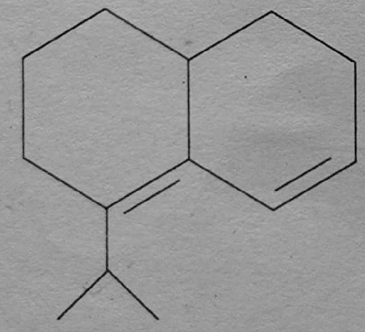
(ii) (a) The most intense line of a rotational transition of HCl is the 10 to 11 transition at 25°C. Will the position of this line change on (i) replacing H by D (ii) increasing the temperature? 5

(b) Discuss the concept of anharmonicity in molecular vibrations and its significance in vibrational spectroscopy. 5

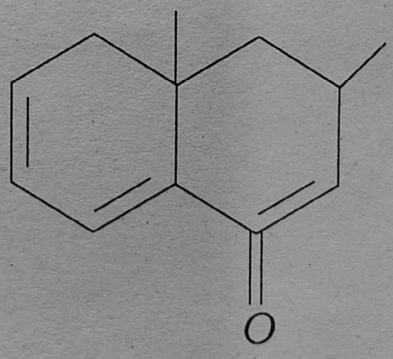
(iii) (a) Describe Jablonski diagram showing the primary and secondary processes and its significance in photochemical processes. 5

(b) Calculate λ_{max} for the following compounds using Woodward-Fieser rules. 5

(1)



(2)



(iv) (a) Guanosine is known to have a maximum absorbance value of 275*nm*. Its molar absorptivity is $8400 M^{-1} cm^{-1}$. The width of the cuvette is 1*cm* and the spectrophotometer finds an absorbance of 0.70. What is the concentration of the sample? 3

What are Einstein's *A* and *B* Co-efficients? 2

(b) Show that for rotational spectrum of a diatomic molecule, the rotational quantum number for the maximum populated level is given by

$$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$ 5