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1 (Sem-5/FYUGP) CHE04MJ

2025

CHEMISTRY

(Major)

Paper : CHE0500404

(Light-Matter Interaction)

Full Marks : 45

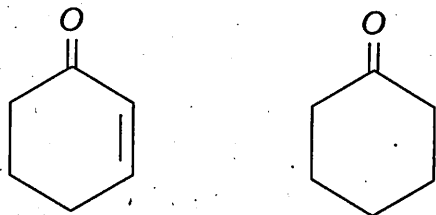
Time : 2 hours

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

1. Answer the following questions : $1 \times 5 = 5$
- (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 Grothaus-Draper 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, N₂, H₂, O₂

- (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 $^{12}\text{C} = 12.0000u$ and mass of $^{16}\text{O} = 15.9949u$)

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

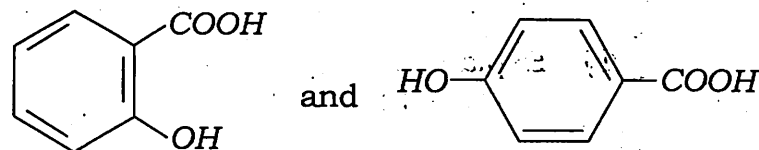
(iii) (a) On irradiating CCl_4 with the 435.8nm mercury line, the Raman lines are observed at 439.9 , 441.8 , 444.6 , and 450.7nm . Calculate the Raman frequencies (in cm^{-1}) of CCl_4 . 3

(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 $\text{C}_8\text{H}_8\text{O}$ 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 3000cm^{-1} . Calculate the C-D str frequency in deuterio chloroform. 3

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



(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

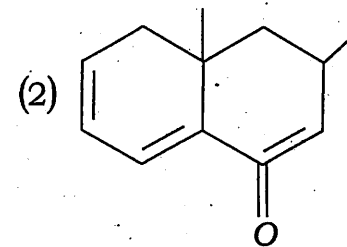
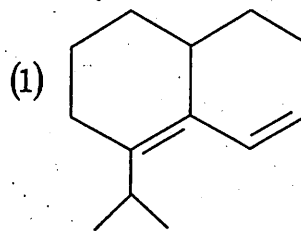
(b) What do you mean by Rayleigh, Stokes and anti-Stokes lines in a Raman spectrum? How do the characteristics of a Raman spectrum depend on (i) the nature of substance and (ii) the wave length of the radiation? 5

(ii) (a) The most intense line of a rotational transition of HCl is the 10 to 11 transition at $25^\circ C$. 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



(iv) (a) Guanosine is known to have a maximum absorbance value of 275nm . Its molar absorptivity is $8400\text{M}^{-1}\text{cm}^{-1}$. The width of the cuvette is 1cm 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

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