

Total number of printed pages-7

14 (CHM-1) 105

2022

CHEMISTRY

Paper : CH-105

(Spectroscopy-I)

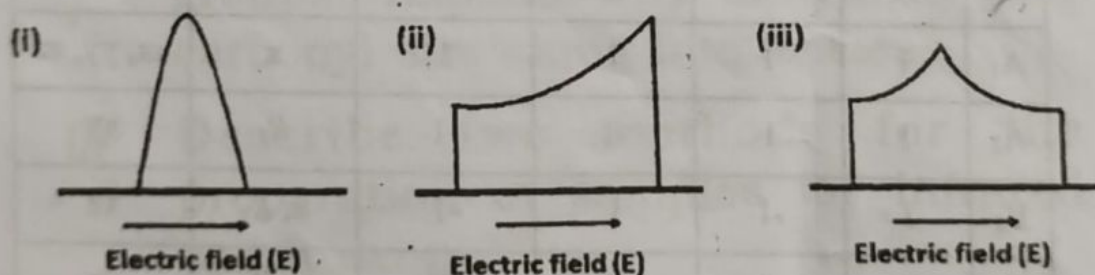
Full Marks : 60

Time : Three hours

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

1. Answer **any two** questions : $5 \times 2 = 10$

(a) How is stimulated emission different from induced ^{spontaneous} emission? Sketch the first order derivative spectrum of the following absorption spectra :



(b) Show that benzene molecule is an oblate symmetric rotor.. [Given

$$r_{(C-C)} = 1.39 \text{ \AA} \text{ and } r_{(C-H)} = 1.09 \text{ \AA}]$$

Contd.

- (c) For a two-level system (ground level 1 and upper level 2), prove that Einstein co-efficients B_{12} and B_{21} are all equal. Can the co-efficient A_{12} exist?
2. Derive the selection rule for a diatomic molecule which can be approximated as a rigid rotor in rotational spectroscopy. 7
3. Answer **any five** of the following questions: $3 \times 5 = 15$
- (a) With an example, show that IR spectroscopy can be used to distinguish between the keto and enol tautomers of a β -diketone.
- (b) How does the stretching frequency of dioxygen change upon binding with hemoglobin and hemerythin in Raman spectrum?
- (c) H_2O belongs to the C_{2v} point group, for which the character table is shown below:

C_{2v}	E	C_2	$\sigma_v(x,z)$	$\sigma_v'(y,z)$		
A_1	1	1	1	1	z	xx, yy, zz
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The Mulliken symbol for the asymmetric stretching vibration is

(i) A_1	(ii) A_2	(iii) B_1	(iv) B_2
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- (d) Which of the following pairs of molecules provide highest and lowest internal double bond absorption frequencies in IR spectra, respectively?

A)	 and 
B)	 and 
C)	 and 
D)	 and 

- (e) Arrange various compounds, viz., anhydride, acid chloride, ester, aldehyde, ketone, carboxylic acid and amide in increasing order of the $C=O$ stretching vibrations for carbonyl groups. Explain why anhydride has carbonyl stretching frequencies.
- (f) Describe two methods for the preparation of samples for infrared spectroscopy.
- (g) How many IR-active $M-Cl$ stretches should be observed for (i) $cis-MCl_2(PR_3)_2$, and (ii) $trans-MCl_4(PR_3)_2$ complexes?

(h) Explain why the C=O stretching vibration of an aldehyde gives rise to very strong absorption in the infrared, yet the absorption due to C=C vibration in an alkene is normally very weak.

(i) Describe schematically how the H-bonded OH stretching frequency of alcohols changes with the addition of the solvent CHCl_3 .

(j) The spectral line shape is never perfectly Gaussian or Lorentzian but is a convolution of Gaussian and Lorentzian line shape function. Briefly explain this statement.

4. Benzene, C_6H_6 belongs to the D_{6h} point group. Given below is the character table for this. The reducible representation for the vibration modes is

$$\Gamma_{\text{reducible}} = 2A_{1g} + A_{2g} + A_{2u} + 2B_{1u} + 2B_{2g} + 2B_{2u} + E_{1g} + 3E_{1u} + 4E_{2g} + 2E_{2u}$$

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	σ_h	$2S_6$	$2S_3$	σ_v	$3\sigma_v'$	$3\sigma_v''$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	R_z
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	$x^2 + y^2, z^2$
B_{1g}	1	-1	1	1	1	1	1	-1	1	1	1	1	(R_x, R_y)
B_{2g}	1	-1	1	1	-1	-1	1	-1	1	1	-1	-1	(xz, yz)
E_{1g}	2	1	-1	2	0	0	2	1	-1	2	0	0	$(x^2 - y^2, xy)$
E_{2g}	2	-1	-1	2	0	0	-2	-1	1	-2	0	0	z
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	(x, y)
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	
B_{1u}	1	-1	1	1	1	1	-1	-1	-1	-1	1	1	
B_{2u}	1	-1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	
E_{1u}	2	1	-1	2	0	0	-2	-1	1	2	0	0	
E_{2u}	2	-1	-1	2	0	0	2	1	-1	-2	0	0	

(a) How many vibrational does benzene have?

(b) How many of these modes are infrared active and to which representation do they belong?

(c) Which of the infrared active modes are degenerate in energy and what is the degeneracy for each?

(d) How many of these modes are Raman active and to which representation do they belong?

(e) Which of the Raman active modes are degenerate in energy and what is the degeneracy for each?

(f) Which of the infrared modes are also Raman active? 3

5. Answer the following questions: 5×5=25

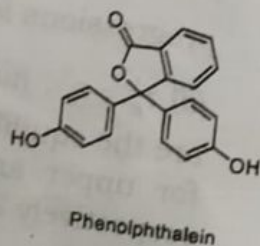
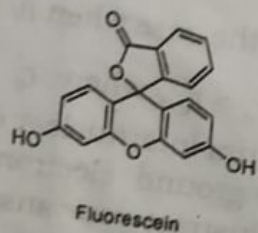
(a) What is Franck-Condon principle in electronic spectroscopy? How does it predict the intensities of vibrational progressions for the case when (i) $r_e' < r_e''$, (ii) $r_e' \approx r_e''$, (iii) $r_e' > r_e''$, where r_e' and r_e'' are the equilibrium internuclear distance for upper and ground electronic state respectively? Illustrate your answer with diagrams.

- (b) What are selection rules in electronic spectroscopy? Explain them with examples. Write down the significance of transition moment integral in electronic transition.

Or

Explain the solvent effect in electronic transitions found in $\alpha\beta$ -unsaturated carbonyl compounds. Why does 2-methylbiphenyl absorb at a lower wavelength in comparison to biphenyl?

- (c) Indicate, with the help of Jablonski diagram, the processes by which the excited electronic state gets deactivated. List the primary differences between the processes. Fluorescein exhibits fluorescence but phenolphthalein is non-fluorescent, why?



Or

What is fluorescence quenching? Mention its types. Indicate the differences in the types of quenching with respect to the fluorescence lifetime. Explain using Stern-Volmer plot.

- (d) Define fluorescence quantum yield. Describe the method of calculating the quantum yield of a sample. When irradiated with a light of 5000 Å, 1×10^{-4} mole of a substance is decomposed. How many photons are absorbed during the reaction if its quantum yield is 10.00.

$$(N_A = 6.022 \times 10^{23} \text{ mol}^{-1})$$

- (e) How is CD different from ORD? Write the minimum amount of samples required for each technique. Draw the CD curves for a pair of enantiomers. How do you determine the absolute configuration of chiral compound using CD?