THE AMERICAN COLLEGE, MADURAI

(An Autonomous Institution Affiliated to Madurai Kamaraj University)
Re-accredited (2nd Cycle) by NAAC with Grade "A", CGPA – 3.46 on a 4-point scale

Backlog Arrear Examination, March, 2021

CHE/CHS 3616/3522 **PHYSICAL CHEMISTRY-V** **Max: 75 mks**
Time: 2 hrs

SECTION A **Answer ANY FIVE questions** **(5 X 15 = 75)**

1. Derive the expression for moment of inertia for rigid diatomic molecules. Determine ε_J for transition from J = 0 → J = 1 and $\ddot{\upsilon}_{J \rightarrow J+1}$.

2. (a) In detail explain occurrence of stokes and anti-stokes lines in Raman spectra for linear molecules. (10)
   (b) Explain the dissociation of molecules based on electronic spectra. (5)

3. (a) Explain the principle of EPR and arrive at the Bohr frequency condition. (2+4)
   (b) Give the principle of NMR and discuss about NMR active and inactive nuclei with examples. (2+3)
   (c) What is the standard used for NMR? Why it is preferred? (1+3)

4. (a) Arrive at the IR and Raman active modes for water molecule. (10)
   (b) Define order of a group. State rearrangement theorem. List the properties of a group. (1+1+3)

5. (a) Write a note on chemiluminescence and photosensitization. (6)
   (b) Distinguish between thermal and photochemical reactions. (6)
   (c) State and explain Stark-Einstein law of photochemical equivalence? (3)

6. (a) State and explain Franck-Condon principle. (5)
   (b) Calculate the ESR frequency of an unpaired electron in a magnetic field of 0.33T, given that for the free electron, $g_e = 2$ and $\mu_B = 9.273X10^{-24}$ JT^{-1} (3)
   (c) Prove that $\sigma_{(xz)}x\sigma_{(xy)} = \sigma_{(xy)}x\sigma_{(xz)} = C_{2(x)}$ (3)
   (d) Explain laser action with reference to a three level and a four level laser. (4)

7. (a) In a 1 T NMR, frequency of ^{19}F is 40.06 MHz. Calculate the magnetic ratio of ^{19}F. (2)
   (b) Explain the breakdown of Born-Oppenheimer approximation, interaction of rotations and vibrations in detail. (4)
   (c) In detail explain the various photophysical processes involved in a photochemical reaction using Jablonski diagram. (6)
   (d) The molar extinction coefficient of phenanthroline complex of iron(II) is 12,00 dm^{3+} mol^{-1} cm^{-1} and the minimum detectable absorbance is 0.01. Calculate the minimum concentration of the complex that can be detected in a Lamber-beer law cell of path length 1.00 cm. (3)

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CHARACTER TABLES

C_2	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	−1	x, y, R_x, R_y	yz, xz

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
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

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5		$\varepsilon = \exp(2\pi i/3)$
A'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
E'	1	ε	ε^*	1	ε	ε^*	(x, y)	$(x^2 - y^2, xy)$
	1	ε^*	ε	1	ε^*	ε		
A''	1	1	1	−1	−1	−1	z	
E''	1	ε	ε^*	−1	$-\varepsilon$	$-\varepsilon^*$	(R_x, R_y)	(xz, yz)
	1	ε^*	ε	−1	$-\varepsilon^*$	$-\varepsilon$		

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)