



Name :

CHEMISTRY

CHE 2C.05 : Theoretical Chemistry – II

Max. Marks : 60

SECTION – A

Answer **all** questions, **each** in **one** word or sentence. **Each** question carries **1** mark.

1. Define principal axis. What is the principal axis of benzene ?
 2. What is the tetrahedral group with inversion ? Name a molecule that belongs to this group.
 3. State little orthogonality theorem.
 4. What is an irreducible representation ?
 5. What is meant by Doppler broadening ?
 6. Which of the following molecules show a rotational microwave spectrum :
 - a) O_2
 - b) HCl
 - c) IF
 - d) F_2 ?
 7. Define coupling constant.
 8. State Franck-Condon principle.
- (8×1=8)**

SECTION – B

Answer **eight** questions. Answer may be in **two** or **three** sentences. **Each** question carries **2** marks.

9. Construct a group multiplication table for C_{2h} .

P.T.O.



10. Show that the symmetry operations C_3^1 and C_3^2 are conjugates in the group C_{3v} .
11. A molecule contains following symmetry operations : $E, 2C_6, 2C_3, C_2, 3\sigma_d, 3\sigma_v$. Write down the symmetry point group, number of classes and order.
12. What is meant by direct product representation ?
13. What is the point group of a cube ? Write down its symmetry elements.
14. Prove by matrix method, $C_{2(z)} \cdot i = i \cdot C_{2(z)} = \sigma_{(xy)}$.
15. Is it possible to employ microwave studies for direct estimate of the abundance of isotopes ? Explain.
16. What are the differences between the harmonic oscillator potential and the Morse potential ? What is the value of potential energy for the Morse function for $r=0$ and $r=\infty$?
17. What effect would be the raise in temperature would have on the intensity of various Raman lines and why ?
18. What is g-factor ?
19. Write down the effect of solvents on electronic transitions.
20. What is anisotropy effect ?

(8×2=16)

SECTION – C

Answer **four** questions, **each** in **one** paragraph. **Each** question carries **3** marks.

21. Show that when n is even, the reciprocal of S_n^m is S_n^{n-m} .
22. Consider the rotation of one cyclopentadienyl ring about the perpendicular axis in ferrocene molecule. Explain the point groups corresponding to various rotamers with figures.
23. Reduce the following representations of C_{3v} :

C_{3v}	E	$2C_3$	$3\sigma_v$
$\begin{bmatrix} a \\ b \end{bmatrix}$	6	3	0
	7	1	-3



24. Derive the representation of the P_x orbital of oxygen in water molecule.
25. For HCl, the rotational constant is 10.593 cm^{-1} and the centrifugal distortion constant, D is 0.00053 cm^{-1} . Calculate the first four rotational levels. Also, calculate the force constant for HCl from the value of D .
26. Write down the advantages and applications of Raman scattering over IR spectrum.
27. Explain predissociation.
28. Explain AMX spin system with example. (4×3=12)

SECTION – D

Answer either **A** or **B** of **each** question. **Each** question carries **6** marks.

29. A) Write down in detail the rules of assigning Mulliken symbols to representations.

OR

- B) Construct the character table for C_{2h} .

30. A) Explain how group theory enables one to construct the hybrid orbitals of molecules taking BF_3 as an example.

OR

- B) Derive a representation for the three σ -bonds of BF_3 using the character table given below and thus determine the IR active modes of vibrations.

31. A) Discuss vibrational coarse structure or progressions.

OR

- B) Give an account of how Raman spectra of diatomic molecules give valuable information about their molecular structure and other properties. Also, explain quantum theory of Raman spectra.



32. A) Write notes on :

- Chemical shift.
- Shielding and deshielding effects.

OR

B) Explain ESR spectroscopy. Describe how ESR spectrum helps to study free radicals and unstable paramagnetic substances. (4×6=24)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
$A1'$	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A2'$	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
$A1''$	1	1	1	-1	-1	-1		
$A2''$	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)