



Reg. No. :

Name :

**II Semester M.Sc. Degree (Reg./Suppl./Imp.) Examination, April 2019
(2014 Admission Onwards)**

**CHEMISTRY
CHE 2C05 : Theoretical Chemistry – II**

Time : 3 Hours

Max. Marks : 60

SECTION – A

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

1. What is identity element ?
2. What is order of a group ?
3. What is a character ?
4. In a given representation, the character of all matrices belonging to operations in the same class are _____
5. In hydrogen molecule, when hydrogen is replaced by Deuterium, what will happen to the rotational constant, B ?
6. What is transition moment integral ?
7. Which transition has the smallest molar absorptivity ?
a) $\pi - \pi^*$ b) $\sigma - \sigma^*$ c) $n - \pi^*$ d) $\sigma - \pi^*$
8. Write down the value of nuclear spin in ^{19}F and ^{31}P . (8×1=8)

SECTION – B

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

9. Prove that the order of any subgroup 'g' of a group of order 'h' must be a divisor of 'h'.
10. Define similarity transformation.

P.T.O.

11. What is an abelian group ?
12. Differentiate between reducible and irreducible representation.
13. Differentiate between operator E and Mulliken symbol, E.
14. Name the various regions of electromagnetic spectrum.
15. What are the selection rules in IR spectroscopy ?
16. What is Doppler broadening ?
17. What are anti-stokes lines ?
18. Write the effect of solvents in electronic transition.
19. What is TMS ? What is its use in NMR spectroscopy ?
20. Define nuclear magneton. (8×2=16)

SECTION – C

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

21. What are the conditions that must be satisfied by any set of elements to form a mathematical group ?
 22. Construct a representation for Pz orbital on the oxygen atom of H₂O.
 23. Determine the hybridization in BF₃ using the D_{3h} character table given below.
- | D _{3h} | E | 2C ₃ | 3C ₂ | σ _h | 2S ₃ | 3σ _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) |
24. What are the rules in assigning Mulliken symbols to various representations ?
 25. The first line in the rotational spectrum of CO has a frequency of 3.8424 cm⁻¹. Calculate the rotational constant and hence the C-O bond length.

26. Give an account of how Raman spectrum gives valuable information about molecular structure.
27. Explain the factors affecting chemical shift.
28. Explain spin-lattice relaxation. (4×3=12)

SECTION – D

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

29. A) Construct the reducible representation for H₂O molecule from the Cartesian co-ordinates of atoms.

OR

- B) i) Assign the point groups to following molecules and justify : eclipsed ethane, staggered ethane, benzene.
ii) Explain with examples improper axis and improper rotation. What are the different kinds of operations generated by S_n (n = odd and even) operation ?

30. A) State and explain Great Orthogonality Theorem. Also, discuss the important rules about irreducible representations and their characters.

OR

- B) Derive the character table for C_{3v}.

31. A) Explain the rule of mutual exclusion. Sketch and explain the polarisability ellipsoids of various modes of vibration of CO₂ molecule. Which of these are Raman active ?

OR

- B) Discuss vibrational coarse structure or progressions.

32. A) With the help of Franck-Codon principle, illustrate the shapes of the absorption bands.

OR

- B) What is coupling constant ? Explain the effect of coupling between two neighboring nuclei on the splitting pattern of their NMR signals. (4×6=24)