K22P 0156

Reg. No. : .....

Name : .....

II Semester M.Sc. Degree (C.B.S.S. – Reg./Supple./Imp.) Examination, April 2022
(2018 Admission Onwards)
CHEMISTRY
CHE 2C.05 : 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 dihedral plane of symmetry ?
2. What are conjugate elements ?
3. What is the point group of a cube ? Write down its symmetry elements.
4. A character table has the following operations : E, $2C_3$, C_2, $3\sigma_v$, $3\sigma_d$ and one other class containing two equivalent operations. What is the missing operation ?
5. Calculate the bond length of CO molecule whose rotational constant is 1.92118 cm^{-1}.
6. What is the region of electromagnetic spectrum to which a frequency of 6×10^{13} Hz belongs ?
7. Which kind of spectroscopy could be used to measure the binding energy of an electron in the $1\pi_u$ molecular orbital of O_2 ?
8. ^{13}C NMR is much simpler to interpret than proton NMR. Why ? **(8×1=8)**

SECTION – B

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

9. What are the criteria that need to be satisfied by a set of elements to form a group ?
10. Show that σ_v and σ_v' are members of the same class in C_{3v}.
11. Arrange various operations generated by C_6 axis into different classes.

P.T.O.

12. What are orthogonal matrices ? Write down the orthogonal matrices of σ_{xz} and $C_2(z)$.
13. Write a note on improper rotations.
14. What is meant by direct product representation ?
15. Why is the Q branch not seen in the vibrational rotational spectrum ?
16. Calculate the zero point energy of hydrogen molecule. Given, the fundamental vibrational frequency = 4400 cm^{-1}.
17. Write down the advantages of Raman scattering over IR spectrum.
18. Explain the rule of mutual exclusion.
19. What is spin-spin relaxation ?
20. Which is the free radical used in the calibration of ESR spectra and why ? **(8×2=16)**

SECTION – C

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

21. Construct a group multiplication table for C_{3v}.
22. State and explain Great Orthogonality theorem. What are the important rules that can be deduced from the theorem ?
23. Reduce the following representation of C_{3v}.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_a	5	2	–1
Γ_b	7	1	–3

24. Show that when n is even, the reciprocal of S_n^m is S_n^{n-m}.
25. What are the factors on which the intensity of spectral lines depends ?
26. For the molecule HBr, B = 253.771 GHz and υ_0 = 79.414 THz. Under the rigid rotator-Harmonic oscillator approximation, calculate the frequencies of the first two lines of the R and P branches for the vibrational-rotational spectrum of HBr.
27. Discuss the various types of electronic transitions giving examples.
28. Explain shielding and deshielding effects in NMR spectra. **(4×3=12)**

SECTION – D

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

29. A) Draw a standard flowchart that shows the steps in assigning point group to a molecule.

OR

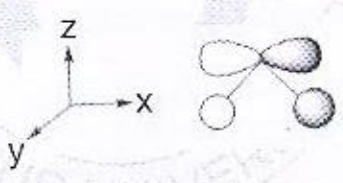
B) Construct the character table for C_{2h}.

30. A) Determine the IR and Raman active modes of vibrations in trifluoroborane using character table given below.

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)

OR

B) Derive a representation for the molecular orbital of water molecule shown below.



31. A) What is Fortrat parabola ? Obtain the expression for the band head in terms of B′ and B″.

OR

B) Explain the classical and quantum theory of Raman spectroscopy.

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

OR

B) Explain (a) Factors affecting chemical shift and (b) Applications of ESR. **(4×6=24)**