

Reg. No

Name

19P2033

MSc DEGREE END SEMESTER EXAMINATION - MARCH/APRIL 2019

SEMESTER 2 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY

COURSE : 16P2CHET07 / 16P2CPHT07 : PHYSICAL CHEMISTRY - II

(For Regular - 2018 Admission and Supplementary - 2017/2016 Admissions)

Time : Three Hours

Max. Marks: 75

Section A

Answer any 10 (2 marks each)

1. Explain the mutual exclusion regarding the IR and Raman activity of vibrations.
2. What is Lamb-dip spectroscopy? Explain
3. Does the initial excitation in Raman spectroscopy take place to a stationary state of the system? Explain.
4. State the guiding principle for investigating the vibrational structure of electronic spectra
5. The absorption spectrum of O₂ molecule shows vibrational structure which becomes a continuum at 56.876cm⁻¹. The upper electronic state dissociate into one ground state atom and one excited atom. The excitation energy for this process 15875cm⁻¹. Estimate the dissociation energy of the ground state of O₂ in kJmol⁻¹.
6. What is meant by laser action? Mention three types of energies that can be used to bring out population inversion.
7. Draw the EPR spectrum of methyl free radical.
8. Explain chemical exchange phenomena in NMR with ethanol as example?
9. Does ¹⁹F exhibit nuclear magnetic resonance? Why?
10. What are the factors influencing 'g' values?
11. Discuss Zeeman splitting with an example.
12. What is non first order spectra?
13. Describe the appearance of the NMR spectrum of methanol when it is (i) very dry and (ii) has a trace of water added to it. Account for the difference.

(2 x 10 = 20)

Section B

Answer any 3 (5 marks each)

14. Analyse the vibrations of CO₂ molecule to assess which are Raman active and which are IR active?
15. Derive an expression for the moment of inertia of a diatomic rigid rotor.
16. Describe Born-Oppenheimer approximation

17. Explain ^1H - ^1H COSY NMR spectroscopy.
18. How many ^{13}C peaks should be seen in the broad band decoupled spectrum of each of the following compounds? a) Methane b) Chloromethane c) Benzene d) Toluene e) Naphthalene

(5 x 3 = 15)

Section C

Answer any 2 (5 marks each)

19. The rotational spectrum of gaseous HBr has a series of equally spaced lines separated by 16.94 cm^{-1} . Calculate the moment of inertia and bond length for HBr ($H = 1.008$, $Br = 79.909$).
20. With which type of spectroscopy would one observe the pure rotation spectrum of H_2 ? If the bond length of H_2 is 0.07417 nm , what would be the spacing of the lines in the spectrum?
21. (a) How many hertz does 1 ppm correspond to, for a ^1H NMR instrument operating at a radiofrequency of 60 MHz?
(b) Calculate the magnetic field (in Tesla) required for flipping a ^1H nucleus in an NMR spectrometer operating at 400 MHz. [Given: $\gamma = 2.67 \times 10^8\text{ T}^{-1}\text{ s}^{-1}$, $\pi = 3.14$]
22. (a) Calculate the NMR frequency (in MHz) of the proton (^1H) in a magnetic field of intensity 1.4092 Tesla .
(b) A compound shows a Proton-NMR peak at 240 Hz down field from the TMS peak in a spectrometer operating at 60 MHz . What are the values of chemical shifts δ and C in ppm relative TMS.

(5 x 2 = 10)

Section D

Answer any 2 (15 marks each)

23. Using the energy level expression and the selection rules draw an energy level diagram and the spectral transitions for the microwave spectrum of a rigid diatomic rotor. Also show the appearance of the spectrum.
24. (a) State and illustrate with suitable potential energy curves, the Frank-Condon principle in the vibronic spectrum of a diatomic molecule. Briefly discuss
(b) Predict the kind of electronic transitions in (i) Cl_2 and (ii) $\text{C}=\text{O}$ group. Also give their intensity.
(c) What is meant by population inversion? Mention any one method of achieving it.
25. Explain the application of Mossbauer spectroscopic techniques in the study of Fe (II) and Fe (III) cyanides
26. Write a note on
 - a. Factors influencing Vicinal coupling
 - b. 2D NMR spectroscopy

(15 x 2 = 30)

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