

THIRD SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2017

(CUCSS)

Chemistry

CH 3C 09—MOLECULAR SPECTROSCOPY

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Part A*Answer all questions.**Each question carries 1 weightage.*

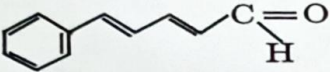

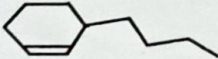
1. Calculate the band width of radiation with a lifetime of 100 microseconds.
2. Find the frequency in cm^{-1} for a rotational transition from $J = 9$ to $J = 10$. Rotational constants is 10 cm^{-1}
3. Define normal mode of vibration.
4. Nitric oxide (NO) shows a Q branch in the vibration rotation spectrum. Why ?
5. A proton absorbs 900 Hz down field with respect to TMS in a 300 MHz NMR instrument. Calculate the chemical shift δ (delta).
6. How many lines do you expect in the EPR spectrum of NH_3 radical ? Justify your answer.
7. What is Cotton effect ?
8. Metal-ligand vibrations are observed at low frequencies. Why ?
9. What do you mean by first order NMR spectrum ?
10. Explain with example 'double resonance' in NMR experiment.
11. Distinguish between base peak and molecular ion peak in mass spectrum.
12. What is nitrogen rule ?

(12 × 1 = 12 weightage)

Part B*Answer any eight questions.**Each question carries 2 weightage.*

13. How would you determine dipole moment of a molecule from microwave spectroscopy ? Explain.
14. Microwave spectrum of HCl shows a series of lines with a spacing 21.4 cm^{-1} . Calculate the bond length.
15. Write Morse equation. Represent graphically. Show that real molecules obey simple harmonic oscillator approximation for low amplitude vibrations.

Turn over

16. How would you rationalise electronic spectra of conjugated molecules from particle in one-dimensional box model ?
17. Suggest an experiment to determine spin-spin relaxation time. Discuss.
18. What is NOE ? Discuss.
19. What is Kramer's theorem ? Discuss its applications.
20. With the help of suitable example, explain isomer shift.
21. Predict λ_{\max} for .
Justify your answer.
22. IR spectra of few compounds are given below. Select compounds from the list that matches each of IR spectra data :
- | | |
|------------------------|--|
| (i) Benzamide | (a) 3080(s), 3000-2800, 2230(s), 1450(s), 760(s), 688(s). |
| (ii) Benzoic acid | (b) 3380(m), 3300(m), 3200-3000, 2980(s), 2870(m), 1610(m), 900-700 (b). |
| (iii) Benzonitrile | (c) 3080(w), 3000-2800, 1315(s), 1300(s), 1155(s). |
| (iv) Biphenyl | (d) 2955(s), 2850, 1120(s). |
| (v) Diphenyl sulfone | (e) 2946(s), 2930(m), 1550(s), 1386(m). |
| (vi) Formic acid | (f) 2900(b, s), 1720 (b, s). |
| (vii) Isobutylamine | (g) 3030(m), 730(s), 690(s). |
| (viii) 1-nitro propane | (h) 3200-3400, 1685(b, s), 705(s). |
| (ix) Dioxane | (i) 3350(s), 3060(m), 1635(s). |
23. You are given the compound  Br. List all types of spin systems, chemically equivalent protons, magnetically equivalent protons, enantiotopic protons and diastereotopic protons.
24. You are given the compound. 
Predict one major fragmentation pathway. Justify your answer.

(8 × 2 = 16 weightage)

Part C

*Answer any two questions.
Each question carries 4 weightage.*

25. State Franck Condon principle. Discuss its importance in understanding vibrational character of electronic spectra of diatomic molecules.
26. Briefly discuss theory of FT NMR.
27. Write a brief account of the ionization techniques in mass spectrometry.
28. Write a brief account of the theory of optical rotatory dispersion.

(2 × 4 = 8 weightage)