Birla Institute of Technology & Science, Pilani (Raj)
II Semester, 2017-2018
CHEM G554 Physical Methods in Chemistry
Comprehensive Examination (Open Book)

Max. Marks: 60 (30%) **4 May 2018** **Duration: 3hrs.**

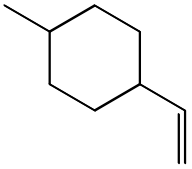
Instructions to the student:

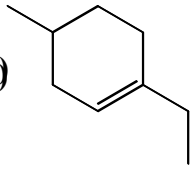
1) There are six questions in total; answer all the questions.
2) Start answering each question on a fresh page and answer all parts of a question together.
3) Data wherever required can be taken from the text and reference books.
4) Write brief answers to the point with proper justification.

1. **a)** Consider ^{14}N NQR spectrum of ammonia and ammonium ion. How many lines would you expect in the spectrum with and without magnetic field in each case? **[3]**

b) Roughly sketch the ^{182}W Mössbauer spectrum of a compound where ^{182}W is found in a non-cubic environment. Justify your answer with energy transition diagrams. **[3]**

c) Predict the ^{13}C NMR δ values for the following two compounds. **[4]**

i) 

ii) 

2. **a)** A compound of Molecular formula C_8H_{16} shows ^{13}C-NMR signals at δ values of 135, 130, 41, 32, 28, 20, 13 and 11. Identify the compound. **[3]**

b) Consider a compound of molecular formula C_6H_4BrCl. Predict the ratio of relative abundances of M, M+1, M+2, M+3, M+4 and M+5 ions. **[3]**

c) Consider the compound $Me_2P\text{-}CF_3$; roughly sketch the ^{19}F and ^{1}H NMR spectra (separately) for this compound with stick-branching diagram. **[4]**

3. **a)** What is the minimum resolution required for a mass spectrometer to identify the following ions separately? $C_7H_7^+$ (m/z = 43.0544) and CH_3CO^+ (m/z = 43. 0183)? **[2]**

b) The tropylium ion $C_7H_7^+$ looses acetylene at the second field free region of the mass spectrometer. What will be the m/z value of the corresponding metastable ion? **[2]**

c) A mass spectrum shows the highest m/z value peak at m/z = 57; There are peaks at m/z values 54 and 43; there are no peaks at m/z values 56 and 55. Can the peak at m/z = 57 be identified as the molecular ion? Explain your answer. **[2]**

d) Try to sketch the EPR (ESR) spectrum of (**a)** Benzene anion and **(b)** phenoxide anion (phenol in basic solutions) by using a stick-branch diagram. Explain all the steps involved in construction of the spectrum. Assume only the most abundant isotopes are present. **[4]**

4. **a)** Stilbene ($C_6H_5\text{-}CH{=}CH\text{-}C_6H_5$) is known to exhibit geometrical isomerism. One of the isomer has a UV absorption maximum at 295 nm, while the other isomer has its absorption maximum at 280 nm. Draw the structures corresponding to the above wavelengths and justify your answer. **[2]**

b) Two isomeric lactones, $C_5H_8O_2$, show a characteristic infrared absorption at 1810cm^{-1}. The ^{1}H NMR spectrum of isomer A has singlets at 1.1 and 2.2 ppm with peak area ratios of 3:1. Isomer B has singlets at 1.2 and 4.0 ppm with area ratios of 3:1. Propose structures for A and B. **[4]**

c) Make rough sketches of 2D-COSY and HETCOR spectrum of m-dinitrobenzene. **[4]**

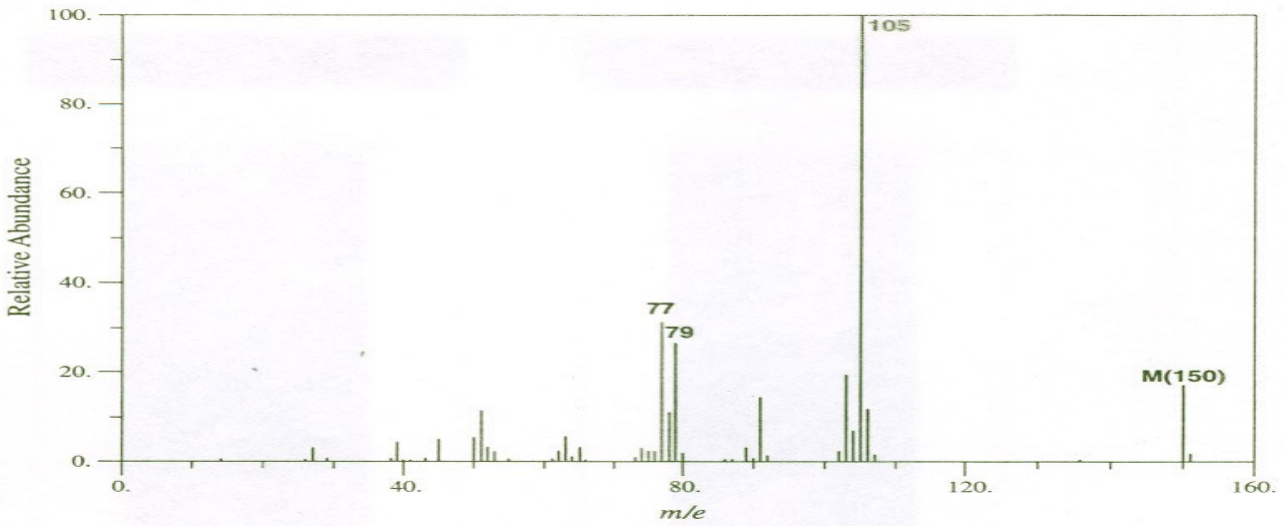
5. **a)** In the ESCA spectrum of phenylacetate the number of how many 1s peaks are expected for carbon and oxygen? **[2]**

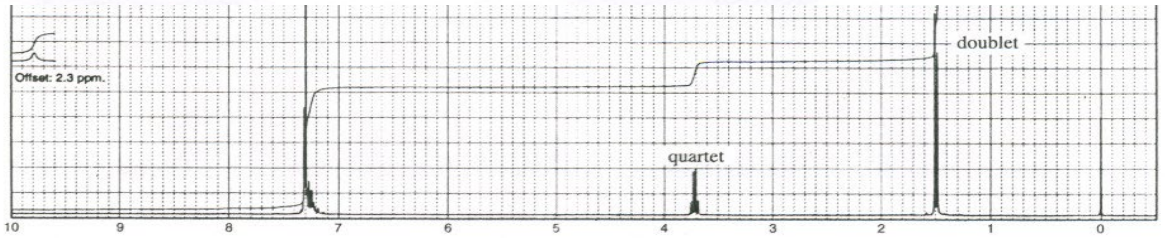
b) The proton NMR spectrum of a compound of empirical formula $C_3H_5ClF_2$ is as follows: (δ 3.6 (triplet, J=12.0Hz, 12 squares) and 1.7(triplet, J = 18.0Hz, 18 squares)). Assign the structure of the compound and interpret the spectrum. **[4]**

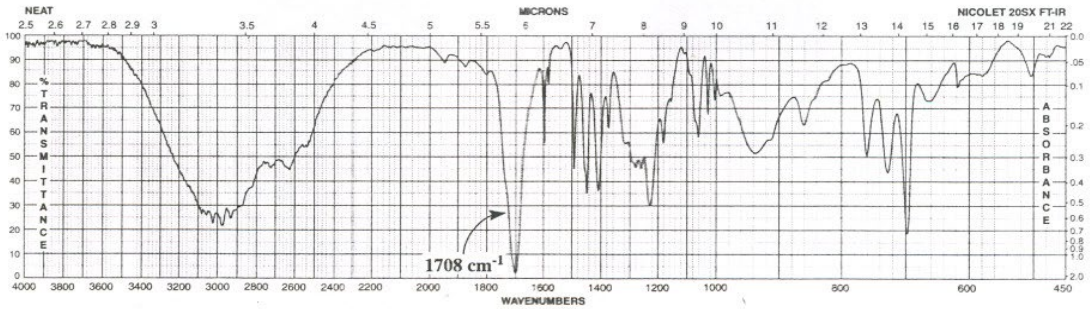
P.T.O.

5. c) (i) Consider the mass spectrum of $(BrCH_2CH_2)_2O$. Predict any two major fragments. Write their structure, m/z values and the mechanism by which these are produced. **(ii)** On the basis of mass spectral data how will you differentiate methyl butyrate ($CH_3OCOCH_2CH_2CH_3$) from methyl isobutyrate ($CH_3OCOCH(CH_3)_2$) **(iii)** pentanoic acid from 2-methyl-butanoic acid ? **[2+1+1 = 4]**

6. a) Given below are the mass, IR and ^1H NMR spectra of an organic compound which contains 72 % C and 6.67 % H. Identify the compound. Justify your answer. **[4]**







b) Derive structural formula that is consistent with the data given below. The relative molar mass was determined from the mass spectrum of the substance. The ultraviolet spectrum is given for aqueous solution; the infrared data shows only those prominent absorptions in the region (4000-1429 cm^{-1}); the ^1H NMR spectrum is given for deuteriochloroform solution. **[4]**

Relative Molar Mass: 110

UV: λ_{max} 239 nm. ε 21,400.

IR: λ_{max} 3077-2857 (m), 1661(w), 1608(w), and 1449cm^{-1} (m).

NMR: 6.00(singlet, 6.4 squares), 1.90(singlet, 17.9 squares), and 1.83δ (singlet, 18.6 squares)

c) How will you differentiate 2,5-heptanedione and 3,5-heptanedione by IR spectrometry? **[2]**

----------end----------