BENGAL ENGINEERING AND SCIENCE UNIVERSITY, SHIBPUR
M. Sc. (APPLIED CHEMISTRY) 3rd SEMESTER EXAMINATIONS, 2011

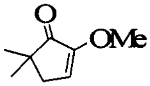
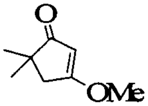
Applications of Spectroscopy and Solid State Chemistry (PGC- 304)

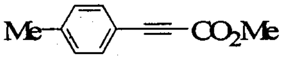
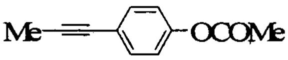
Full Marks: 100 **Time: 4 hrs**

Use separate answer script for each group.
*Answer any **FIVE** questions from each group.*

Group A

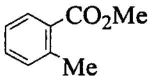
1. (a) Explain how could you use IR spectroscopy to distinguish the following pair of compounds?

(i)  and 

(ii)  and 

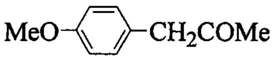
(b) Calculate the three *J* values that contribute to the following <u>ddd</u> splitting (doublet of doublet of doublet) which shows 8 lines. The position of each of the lines in Hz is given below:
1611.27, 1606.90, 1603.06, 1600.78, 1598.64, 1596.60, 1593.25, 1589.11
(c) Determine a unique structure consistent with the following proton NMR data.
^{1}H NMR (δ): 5.39 (s, 1H), 5.29 (s, 1H), 2.87 (s, 1H), 1.90 (s, 3H).
In addition to the PMR, here is some other useful information: Molecular weight is 66;
IR (cm^{-1}): 3275 (m), 3030 (m), 2900 (s), 2150 (m), 1655 (w)
^{1}C NMR (δ): 126.0, 123.3, 84.9, 76.1, 23.2 3+3+4

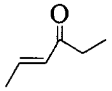
2. (a) Discuss with an example how spin decoupling technique (double resonance) can be used for simplification of complex proton NMR.
(b) With the following spectral data suggest a suitable structure of the compound. Give reasons in favour of your answer.
MS (m/z): 134 (M^{+}, 15), 105 (100), 77 (40).
IR (cm^{-1}): 1680 (significant peak);
^{1}H NMR (δ): 9.58 (d, 1H, $J = 8$ Hz), 7.46 (d, 2H, $J = 7.5$ Hz), 7.38 (d, 1H, $J = 16$ Hz), 6.68 (d, 2H, $J = 7.5$ Hz), 6.54 (d, 1H, $J = 16$ Hz), 3.00 (s, 6H);
^{13}C NMR: δ 207, 159, 130, 126, 114, 55, 50, 29.
(c) Write the mass fragmentation patterns of the following compounds:

(i) $CH_3CH_2CH_2CO_2CH_2CH_3$ and (ii) 

3+4+3

3. (a) Predict the approximate chemical shifts, multiplicities and J values for the absorptions in the proton NMR spectrum of the following compounds:

(i) 

and (ii) 

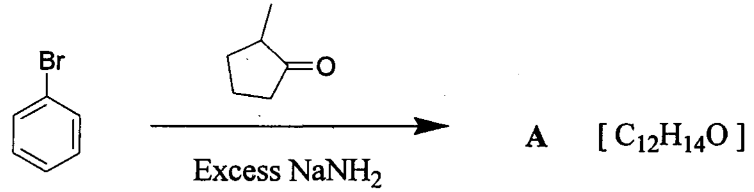
(b) Distinguish the following pairs of compounds using ^{13}C-NMR spectroscopy (proton decoupled):
(i) *m*-Xylene and *o*-Xylene; (ii) Ethyl 2-chlorobenzoate and Ethyl 2,6-dichlorobenzoate

(c) Deduce the structure of the following compound having molecular weight 113, with the help of following spectral data:

IR (cm^{-1}): 2960 (m), 2260 (m), 1747 (s), 1200 (s);
^{1}H NMR (δ): 4.3 (q, 2H), 3.5 (s, 2H), 1.3 (t, 3H);
^{13}C NMR (δ): 163, 113, 63, 25, 14.

4+2+4

4. (a) Determine the structure of **A** with the help of following spectral data and write a suitable mechanism for transformation to **A**.



IR (cm^{-1}): 3060, 2920, 1675, 1600;
^{1}H NMR (δ): 7.50 (d, 1H, $J = 7.5$ Hz), 7.43 (ddd, 1H, $J = 7.5, 7.5, 1.5$ Hz), 7.22-7.55 (m, 2H), 3.07 (m, 1H), 2.5-2.7 (m, 2H), 1.8-2.0 (m, 2H), 1.4-1.6 (m, 2H), 1.39 (d, 3H, $J = 6.9$ Hz);
^{13}C NMR (δ): 208.1, 143.0, 139.3, 131.8, 127.7, 126.3, 125.1, 41.2, 34.4, 34.2, 20.4, 19.3.

(b) The C–N stretching frequency in metal complexes is generally higher than the value of free CN^{-} ion while the opposite holds true for the carbonyl complexes – explain.

(c) Plot a graph for the variation of polarizability α with displacement coordinate x during the normal mode in CO_2 molecule and discuss how your conclusion supports the mutual exclusion principle.

5+2+3

5. (a) Account for the following trend in IR frequencies

$[Cr(CN)_5(NO)]^{4-}$ $\gamma_{(NO)} = 1515$ cm^{-1}
$[Mn(CN)_5(NO)]^{3-}$ $\gamma_{(NO)} = 1725$ cm^{-1}
$[Fe(CN)_5(NO)]^{2-}$ $\gamma_{(NO)} = 1939$ cm^{-1}

(b) A molecule of formula $Cr(CO)_2(CN)_2Br_2$ has been synthesized. In the IR spectrum, it has two bands attributable to C–O stretching, but only one band attributable to C–N stretching. What is the most likely structure of this molecule?

(c) Account for the observation that $[Co(CO)_3(PPh_3)_2]^{+}$ has only a single carbonyl stretching frequency.

4+3+3

6. (a) How many peaks would you expect for pyrazine radical anion with Na^+ as counter-ion in EPR spectrum? Also write down the appropriate spin Hamiltonian. (^1H, $I = 1/2$; ^{14}N, $I = 1$; ^{23}Na, $I = 3/2$)
(b) In the complex $[Fe(H_2O)_4(NO)_2]^{2+}$, there are two equivalent ^{14}N atoms. Predict the number of EPR lines the solution EPR spectrum will exhibit under situation (a) ^{57}Fe and ^{14}N (a) ^{56}Fe and ^{15}N and (a) ^{56}Fe and ^{14}N. (^{56}Fe, $I = 0$; ^{57}Fe, $I = 1/2$; ^{14}N, $I = 1$; ^{15}N, $I = 1/2$)

4+(2+2+2)

Group B

7. Write short notes on following structures:
(i) Spinel (ii)Wurzite (iii) Sphalerite 4+3+3

8. (a) Show the radius-ratios for tetrahedral and octahedral are 0.225 and 0.414, respectively.
(b) Draw the Bravais lattices of the following structures and mention their essential symmetry with unit cell specification:
(i) body-centred and (ii) simple tetragonal (3+3)+(2+2)

9. (a) What are 'Stacking faults'?
(b) Elaborate how 'Screw Dislocations' are generated.

(3 + 7)

10. (a) Which is faster, dehydration of copper sulfate or dehydration of chrome alum and why?
(b) Discuss Enantiotropy and Monotropy.
(c) Write a note on Polytypism. (1½ + 4 + 4½)

11. (a) What is Moseley's law? With a schematic design of a filament X-ray tube describe how X-rays are generated from a Cu target.
(b) Illustrate the term 'Systematic Absences'.

(1 + 5) + 4

12. Write notes on:

(i) Type I Superconductors (ii) Persistent current & Flux Quantization (iii) Josephson Effect.
(3½ + 3 + 3½)