End-Sem Exam: CH4204 (Spring 2019)

Total marks: 50 **Time: 150 min**

Please answer Part A and B in separate answer sheets. No marking for answering Part A in Part B answer sheets and vice versa.

Part A (10×2=20 marks)

Answer all questions for Part A.

1. Draw the Plane Group representation of P3 with along with lattice points and symmetry.

2. There are distinct 2D lattices called as Bravais lattice. What are those? Draw them with respect to *a,b* and θ

3. How many symmetry operations are possible in 2D lattices? What are those?

4. Construct the Ewald Sphere for X-ray wave length λ and prove that

$$\sin\theta = \left(\frac{1}{d_{hkl}}\right) \Big/ \left(\frac{2}{\lambda}\right)$$

5. Find out all limiting conditions and the space group for these reflections

hkl				
	111	011	110	020
	112	021	120	040
	212	012	310	060
	312	101	200	002
	322	203	400	004
	332	303	600	006

6. Fill in the blanks.

Real Space	Reciprocal Space
• **Bond Lengths (Å)** • **Bond Angles (º)** • **Crystal Faces** • **Unit Cell (*a, b, c*, α, β, γ)** • **Electron Density, $\rho(x\,y\,z)$** • **Atomic Coordinates – $x\,y\,z$** • **Thermal Parameters – B_{ij}**	

7. Draw the Miller İndices (210) for Cubic lattice. Show the intercept points.

8. Draw $P2_1$ Space group with all lattice points with symmetry and mention if it is centro-symmetric or not and the Z value and Enantiomorphous or not.

9. Draw P2/m Space group with all lattice points with symmetry and mention if it is centro-symmetric or not and the Z value and Enantiomorphous or not.

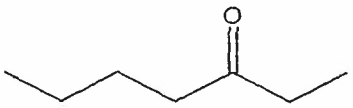
10. Draw $P2_{1/C}$ Space group with all lattice points with symmetry and mention if it is centro-symmetric or not and the Z value and Enantiomorphous or not.

Part B (30 marks)

11. n-propyl bromide shows 3 peaks in the ^1H NMR spectra at 1, 1.9 and 3.4 ppm. Assign the peaks to the appropriate protons in the molecule. Also mention the multiplicity pattern of each of the peaks. Draw ^1H NOE difference spectra when the peak at 1.9 ppm is irradiated. (4 marks)

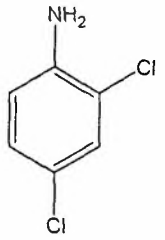
12. The molecule shown below exhibits the following strong peaks in its EI-MS spectrum. Explain the origin of the peaks clearly mentioning the fragmentation pattern. If there are multiple species contributing to the same peak, please indicate each one of them.

(3 marks)



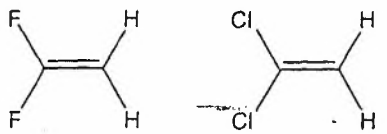
m/z: 71, 72, 58

13. Calculate the relative ratio of the peaks M, M+2 and M+4 in the MS spectrum for the following molecule. The ratio of the relative abundance of ^{35}Cl and ^{37}Cl is 3:1. (3 marks)



14. Which of the following statements (a, b or c) is correct? Explain. (2 marks)

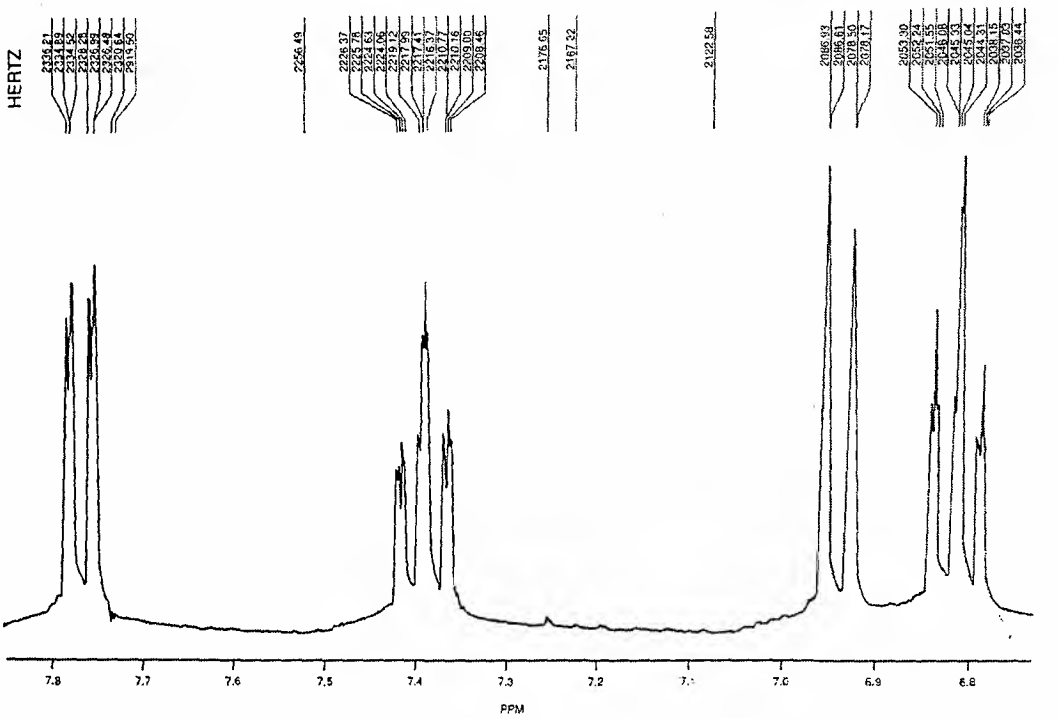
a) The two F nuclei in **A** are magnetically equivalent but the two Cl nuclei in **B** are magnetically non-equivalent.
b) The two F nuclei in **A** are magnetically non-equivalent and the two Cl nuclei in **B** are magnetically non-equivalent.
c) The two F nuclei in **A** are magnetically non-equivalent but the two Cl nuclei in **B** are magnetically equivalent.



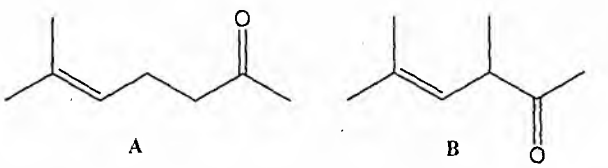
15. Spectral data for isomeric compounds **A** and **B** is summarized below. Determine the molecular formula and then the structures for compounds **A** and **B**. Assign the proton NMR peaks. (5 marks)

Compound A: MS: m/z = 148 (M, 7%), 106 (8%), 105 (100%), 77 (29%), 51 (8%)
IR (neat): 1675 cm^{-1}; **^{1}H NMR** ($CDCl_3$): 1.20 (d, J = 7 Hz, 6H), 3.53 (septet, J = 7 Hz, 1H), 7.94 (m, 2H), 7.68 (m, 1H), 7.3 (m, 2H).
Compound B: IR (neat): 1705 cm^{-1}; **^{1}H NMR** ($CDCl_3$): 0.95 (t, J = 7 Hz, 3H), 2.35 (q, J = 7 Hz, 2H), 3.6 (s, 2H), 7.20 (m, 5H).

16. A compound with the molecular formula $C_8H_8O_3$ shows the following set of peaks in the ^{1}H NMR: 3.9 (s, 3H), 6.8 (t, 1H), 6.95 (d, 1H), 7.4 (t, 1H), 7.75 (d, 1H) and 10.7 (br s, 1H). The expansion of the peaks between 6.8 and 7.8 is shown below (hyperfine splitting is also observed). A broad peak around 3200-3500 cm^{-1} and a strong peak at 1680 cm^{-1} are visible in its IR spectra. Determine the structure of the compound and assign all the peaks to the appropriate protons in the molecule. (5 marks)



17. A compound with the molecular formula $C_8H_{14}O$ shows the following ^1H NMR spectra: 1.62 (s, 3H), 1.7 (s, 3H), 2.1 (s, 3H), 2.25 (m, 2H), 2.35 (t, 2H), 5.1 (t, 1H). The normal carbon NMR and DEPT spectral data are also provided. First, assign the DEPT spectral data to the types of carbon atoms present in the molecule. Then based on the ^1H NMR and DEPT, decide which of the structures **A** or **B** actually represent the dataset provided here? Assign all the peaks in the ^1H NMR spectra to the appropriate protons in the correct molecule. (4 marks)



Normal Carbon	DEPT-135	DEPT-90
18 ppm	Positive	No peak
23	Negative	No peak
26	Positive	No peak
30	Positive	No peak
44	Negative	No peak
123	Positive	Positive
133	No peak	No peak
208	No peak	No peak

18. The *(E)*- and (Z)-isomers of 2-bromo-2-butene (C_4H_7Br) are difficult to distinguish by ^1H NMR spectroscopy. Both isomers have 3 resonances. In principle, the isomers could be distinguished using a NOESY spectrum. On two separate NOESY spectra, draw the strong peaks (diagonal and off-diagonal) that you would expect to see in the spectra of *(E)*-2-bromo-2-butene and *(Z)*-2-bromo-2-butene. (4 marks)