

This question paper contains 6 printed pages]

BR—18—2016

FACULTY OF SCIENCE

M.Sc. (Second Year) (Third Semester) EXAMINATION

OCTOBER/NOVEMBER, 2016

(Revised Course)

CHEMISTRY

Paper CH-531

(Advanced Spectroscopic Methods)

(Wednesday, 16-11-2016)

Time : 2.00 p.m. to 5.00 p.m.

Time—Three Hours

Maximum Marks—50

N.B. :— (i) All questions are compulsory.

(ii) Figures to the right indicate full marks.

(iii) Multiple Choice Questions (MCQs) should be attempted only once on page number three of answer-book with complete answer.

1. Attempt any *five* of the following : 10

(a) Explain the choice of solvent in UV Spectroscopy.

(b) Explain mass spectroscopic fragmentation of acetophenone.

(c) Pentanoic acid gives m/z 60 in mass spectrum. Explain.

(d) Calculate the number of fundamental modes of vibration in BCl_4^- .

(e) Enumerate in brief basic principles of ^{13}C —NMR spectroscopy.

(f) O_2 and O_2^+ show ESR spectra. Explain.

(g) In PMR spectrum, aldehydic proton appears in the far downfield region ($\delta = 9 - 10$ ppm)

(h) The UV spectrum of ethylene shows absorption at 171 nm but butadiene shows absorption at 217 nm.

2. Attempt any *four* of the following : 10

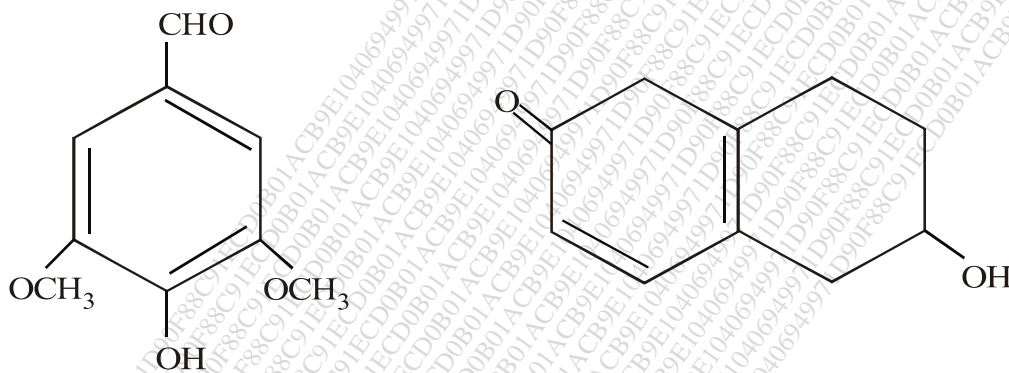
(a) Assign the structure of compound using given PMR data :

Molecular formula : $\text{C}_{10}\text{H}_{13}\text{Cl}$

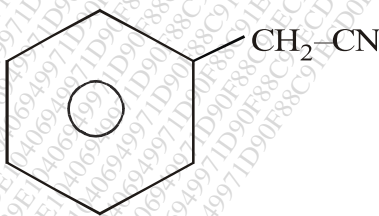
δ 1.57 (S, 6H), δ 3.07 (S, 2H), δ 7.27 (S, 5H).

P.T.O.

- (b) Give the structure of compound $C_{10}H_{20}O$ whose mass shows m/z value of 15, 43, 57, 91, 105 and 148.
- (c) What will be force constant for the bond in N_2 , if fundamental vibrational frequency is $7 \times 10^{-13} s^{-1}$. (Given : $N = 14.007$)
- (d) Calculate λ_{max} for the following compounds :



- (e) Explain the formation ion from the following molecule :



$m/e = 177, 91, 90, 77, 65.$

- (f) Calculate the ESR frequency in MHz of an unpaired electron in magnetic field 0.33 T.

Given :

For free electron, $\delta = 2$

$\beta = 9.273 \times 10^{-24} \text{ JT}^{-1}$

$h = 6.626 \times 10^{-34} \text{ JS}^{-1}$

3. Attempt any two of the following :

10

(a) An organic compound with $\text{MFC}_{11}\text{H}_{14}\text{O}_2$ shows the following spectral data. Assign the structure and justify the spectral data :

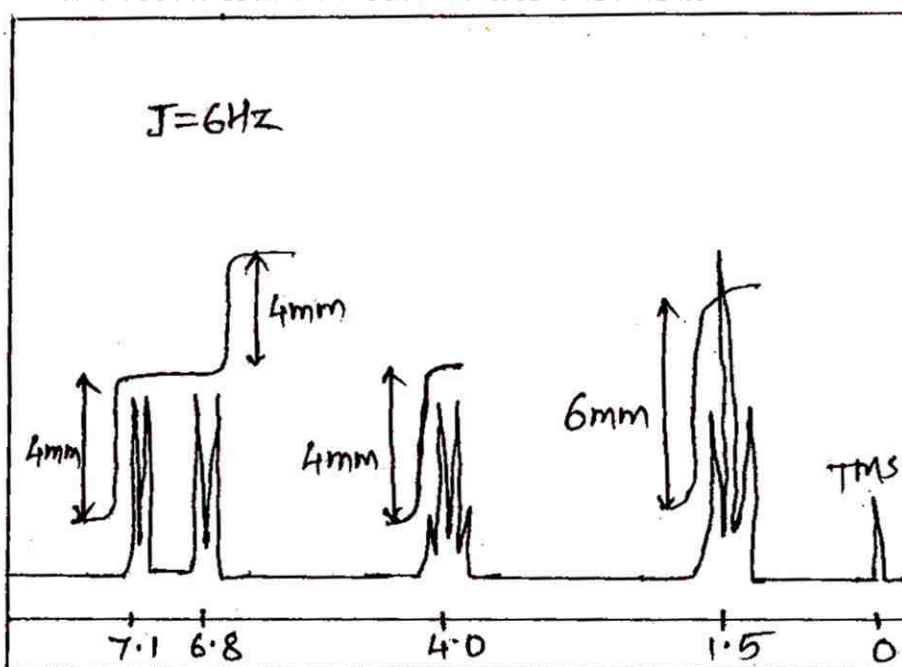
PMR (δ PPM) : 7.18 – 7.38 (5H, m)

5.71 (2H, q)

4.50 (2H, s), 4.06 (4H, t), 2.63 (1H, s)

^{13}C NMR δ (PPM) : 58.5 (t), 65 (t), 72.5 (t), 127.8 (d), 127.9 (d),
128.0 (d), 128.5 (d), 132.4 (d), 137.8 (s).

(b) A compound having molecular formula $\text{C}_8\text{H}_9\text{OBr}$ shows the following NMR spectrum. Deduce its structure.



P.T.O.

- (c) An organic compound which elemental analysis is C = 55.8% and H = 7.0% and exhibits the following spectral data :

IR = 1765, 1635, 1380, 1220, 985, 950 cm^{-1}

MS(m/z) = 86, 43, 27

PMR (δ) = 2.1 (3H, s), 4.4 (1H, dd, J = 9 and 3 Hz)

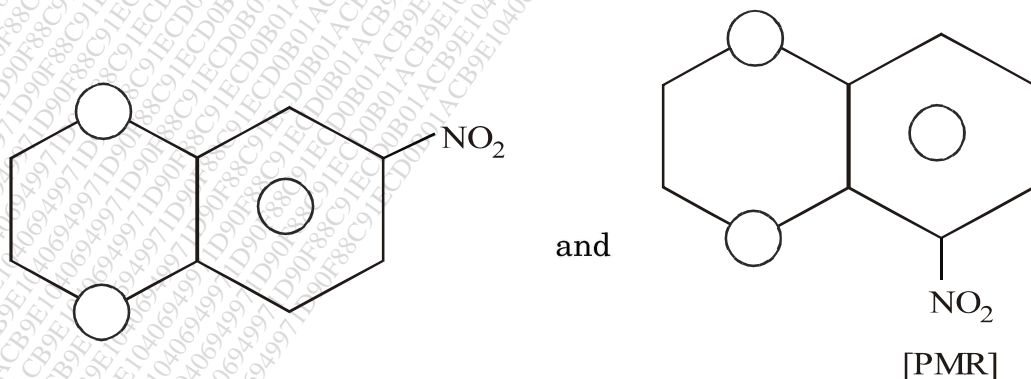
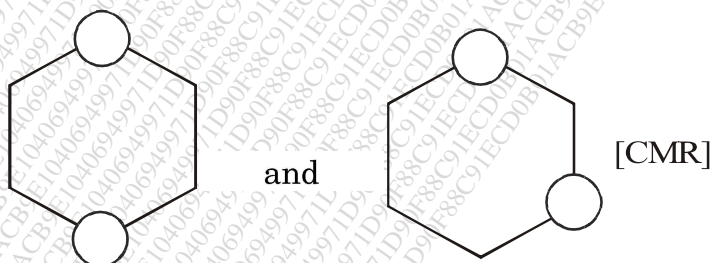
4.8 (1H, dd, J = 16 and 3 Hz)

7.2 (1H, dd, J = 16 and 9 Hz)

Assign the structure of compound.

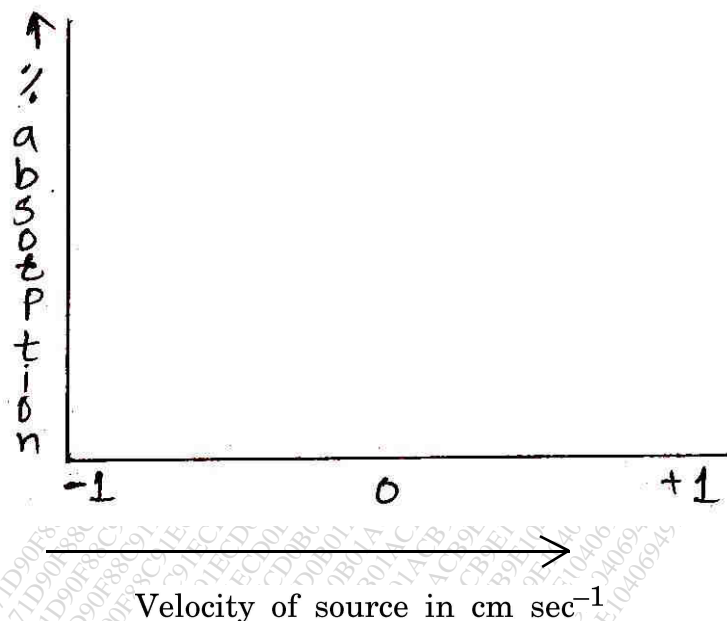
4. Attempt any *two* of the following : 10

- (a) Distinguish between the following pairs by using the indicated spectral method.



- (b) Explain in detail 1 : 4 : 6 : 4 : 1 relative intensities in pyrazine radical.

- (c) Explain the mossbauer spectra represented by :



5. (A) Select the *correct* answer from the following multiple choice questions and rewrite complete answer : 5

(i) In proton-coupled CMR spectra spin-spin coupling is known as

- (a) Homonuclear coupling
 (b) Off resonance coupling
 (c) Non-decoupled coupling
 (d) Heteronuclear coupling

(ii) The presence of chlorine and bromine can be easily detected by

- (a) UV spectrum
 (b) IR spectrum
 (c) CMR spectrum
 (d) Mass spectrum

P.T.O.

- (iii) Mossbauer spectroscopy is the study of emission and reabsorption of
- (a) α rays
 - (b) β rays
 - (c) γ rays
 - (d) None of the above
- (iv) In IR spectrum, due to the presence of strong hydrogen bonding, the absorption band shifts to
- (a) Higher wave number
 - (b) Lower wave number
 - (c) Both
 - (d) No effect
- (v) Electromagnetic radiation used in 'H NMR spectroscopy' is
- (a) IR
 - (b) Microwave
 - (c) Radio
 - (d) None of the above
- (B) Write short notes on (any two) :
- (a) Spin-spin coupling in PMR
 - (b) Stretching and bending vibrations in IR-spectroscopy
 - (c) Chemical shift in mossbauer spectroscopy.

5