This question paper contains **9** printed pages]

AY—12—2018

FACULTY OF SCIENCE

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

MARCH/APRIL, 2018

(CBCS Pattern)

CHEMISTRY

Paper CH-531

(Advanced Spectroscopic Methods)

(Monday, 9-4-2018) **Time : 2.00 p.m. to 5.00 p.m.**

Time—3 *Hours* *Maximum Marks*—75

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 *three* of the following : 15

(*a*) Explain trans-stilbene absorbs at longer wavelength as compared to cis-stilbene in U.V. spectra.

(*b*) Explain the effect of H-bonding in I.R. absorption spectra.

(*c*) Explain the calculation of IR absorption frequency by using Hooke's law.

(*d*) Mass spectrum of toluene displays the following peaks :

m/e 92, 91, 65.

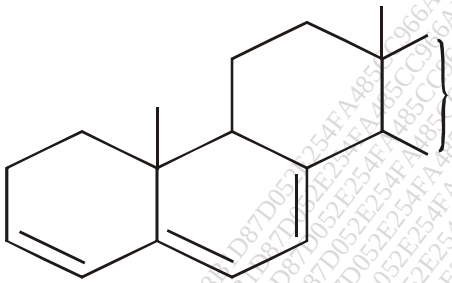
(*e*) TMS solvent used as standard reference in NMR spectroscopy.

P.T.O.

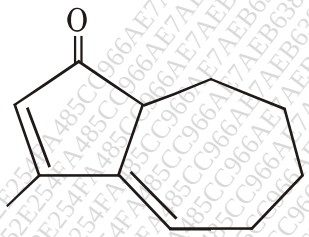
2. Attempt any *three* of the following : 15

(*a*) Calculate the λ_{max} (absorption maxima) for the following :

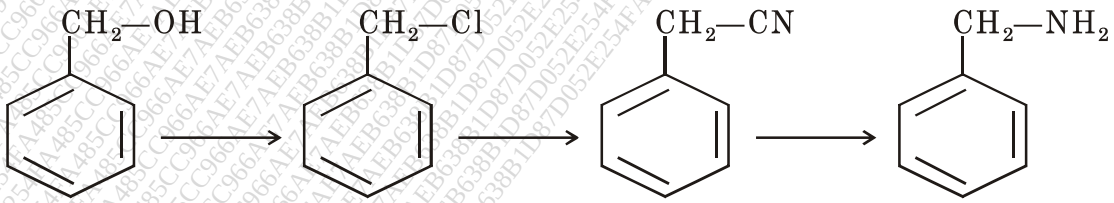
(*i*)



(*ii*)



(*b*) How will you monitor the following sequence of reaction by using IR spectroscopy :



(*c*) Deduce the structure of a compound using ^{13}C NMR data : Mol. formula :

$C_4H_8O_2$

δ : 20(*q*), 30(*q*), 70(*t*), 170(*s*).

(*d*) What will be the force constant for the bond in CO, if fundamental vibrational freuqency is 6.4296×10^{13} s^{-1}.

Given :

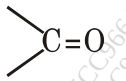
C = 12.011

O = 15.999.

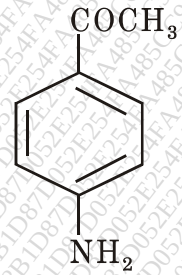
(*e*) Ethyl benzoate can display the characteristic peaks in mass spectrum : m/z = 150, 122, 105, 77. Explain the fragmentation pattern.

3. Solve the following : 7

(*a*) Offer explanation :

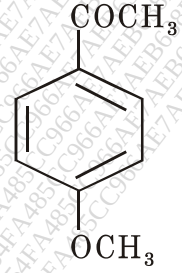
(*i*)  absorption frequency of the following compound in IR spectra :

(I)



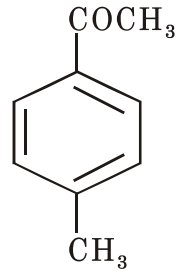
1677 cm^{-1}

(II)

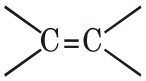


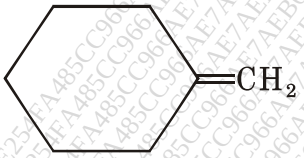
1684 cm^{-1}

P.T.O.

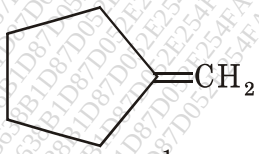
(III) 

1693 cm^{-1}

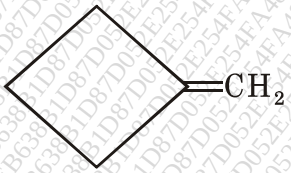
(*ii*)  stretching absorption frequency of the following compounds in IR spectra :



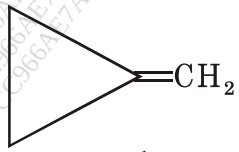
1651 cm^{-1}



1657 cm^{-1}



1690 cm^{-1}



1750 cm^{-1}

Or

(*i*) A compound with mol. formula $C_6H_{12}O_2$ shows four signals in ^1H NMR :

δ = 1.1 (S, 6H).

2.1 (S, 3H)

2.6 (S, 2H)

3.9 (S, 1H)

Propose a structure.

(*ii*) A compound with molecular formula :

C_5H_5N

shows three signals in ^{13}C—NMR :

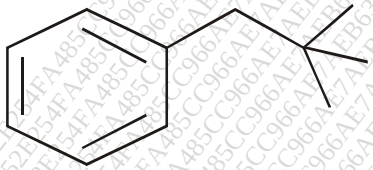
δ = 150.2 (d)

135.9 (d)

123.9 (d)

If off-resonance decoupled spectra deduce the structure of the compound.

(*b*) Explain the genesis of the ions : 8

(*i*) 

m/e = 148, 91, 65

(*ii*) 

m/e = 108, 107, 79, 77

Or

An organic compound with molecular formula $C_8H_{14}O_4$ shows the ahead spectral data. Assign the structure and justify the spectral data : 8

P.T.O.

UV : 213 nm ($\in_{max}$ 60)

IR : 2941-2857 cm^{-1} (m)

1745 cm^{-1} (s)

1458 cm^{-1} (m).

NMR : δ = 4.1 (*q*, 4H) (J = 7.2 CPS)

2.6 (*t*, 4H) (J = 7.3 CPS)

1.3 (*t*, 6H) (J = 7.2 CPS).

4. Solve the following :

(*a*) A compound with M.F. $C_{10}H_{12}O_2$ displays the following spectral data : 8

IR : 1690, 1600, 1580, 1490, 770, 690 cm^{-1}

PMR(δ) : 1.3 (*d*, 6H)

5.3 (septet, 1H)

7.3-7.7 (m, 5H)

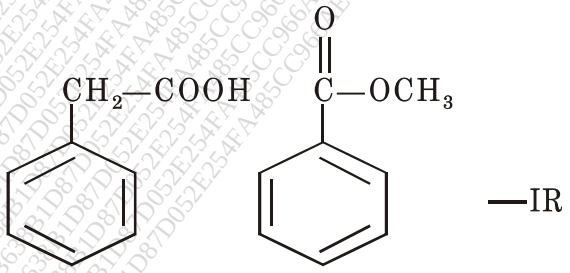
C-NNR (δ) : 22(*q*), 68(*d*), 128(*d*)

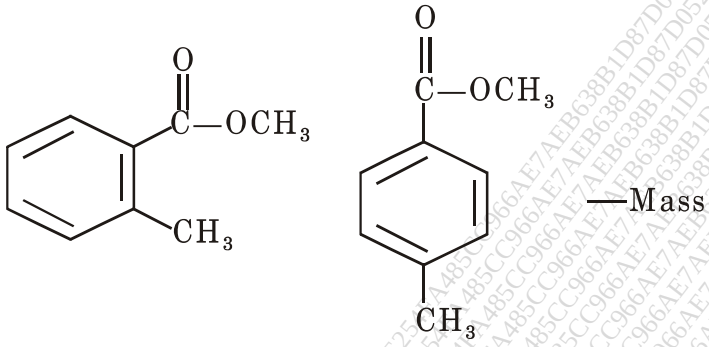
129(*d*), 131(*s*), 135(*d*)

175(*s*).

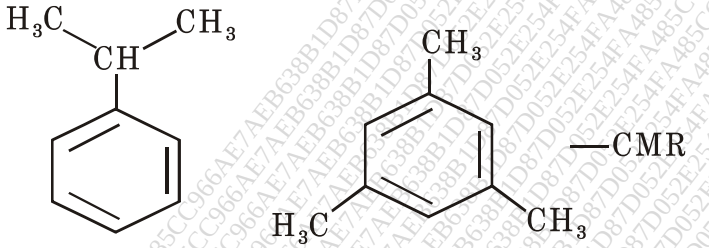
Or

Distinguish between the following pairs by using the indicated spectral method : 8

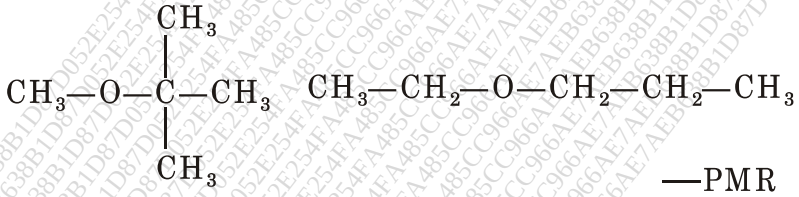




—Mass



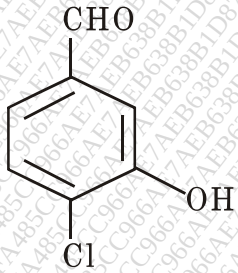
—CMR



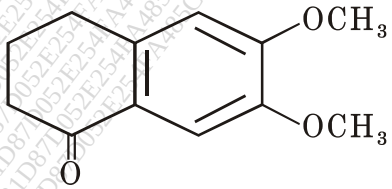
—PMR

(*b*) Calculate λ_{max} for the following compounds by A.I. Scott rules : 7

(*i*)



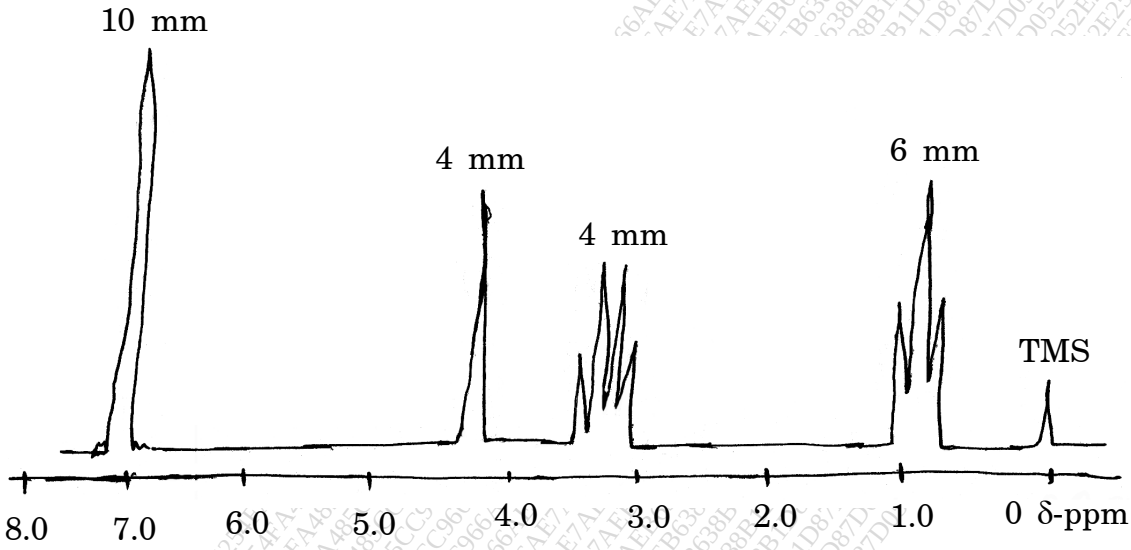
(*ii*)



P.T.O.

Or

A compound $C_9H_{12}O$ shows the following PMR spectra. Deduce the structure : 7



5. (A) Select the correct answer from the following Multiple Choice Questions and rewrite complete answer : 5

(*i*) K-band originate due to ..... transition.

(*a*) $n - \sigma^*$

(*b*) $n - \pi^*$

(*c*) $\pi - \pi^*$

(*d*) $\sigma - \sigma^*$

(*ii*) Total number of vibrational modes in HCN molecule is .....

(*a*) 2

(*b*) 3

(*c*) 4

(*d*) 5

(*iii*) P-xylene shows the total number of signal in PMR spectrum is .....

(*a*) one

(*b*) two

(*c*) three

(*d*) four

(*iv*) In ^{13}C NMR spectra chemical shifts normally in range between δ .....

(*a*) 0—10 ppm

(*b*) 0—15 ppm

(*c*) 0—100 ppm

(*d*) 0—220 ppm

(*v*) *n*-alkyl benzene gives base peak in mass spectra at m/e ratio .....

(*a*) 77

(*b*) 91

(*c*) 59

(*d*) 65

(B) Write short notes on (any *two*) : 10

(*i*) McLafferty rearrangement.

(*ii*) Combination band and Fermi resonance in IR.

(*iii*) Effect of polar solvent on $n - \pi^*$ and $\pi - \pi^*$ in UV spectra.