**DM-003-1104001**      Seat No. _____

# M. Sc. (Sem. IV) (CBCS) Examination

## March – 2022

### C - 401 : Advanced Spectroscopy

*(All Branches)*

**Faculty Code : 003**

**Subject Code : 1104001**

Time : $2\frac{1}{2}$ Hours]             [Total Marks : **70**

**Instruction :** All questions are compulsory and carry equal marks.

1   Answer the following : (Any **Seven**)        14

    (a)   Draw the schematic diagram of Mass spectrometer and write its functioning.

    (b)   Write the full form of following techniques:
        (1)   DQF-COSY
        (2)   TOCSY
        (3)   NOESY
        (4)   DEPT

    (c)   Discuss types of UV absorption shift.

    (d)   Draw the $^1$HNMR spectrum of Ethylbenzene and show the splitting pattern of signals.

    (e)   Define the terms, Base peak, Parent peak and Molecular ion peak in mass spectrometry.

    (f)   Draw the $^{13}$CNMR of following compound at 135° rotation.
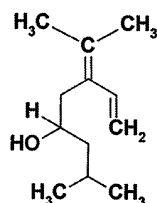


    (g)   Write the principle of Raman Spectroscopy.

    (h)   How many peaks are expected in methyl radical?

    (i)   Enlist the detector used in NIR-spectrophotometer.

    (j)   How many packs are expected in methyl radical?

**2** Answer the following : (Any **Two**)  14
  (a) Draw the schematic diagram of a laser Raman spectrometer and discuss source of light in details.
  (b) Discuss the advantage and disadvantage of NIR-spectroscopy.
  (c) Discuss the application of UV-spectroscopy in details.

**3** Answer the following :  14
  (a) Sketch the NMR spectrum of $A_2X$ and XYZ system with suitable example.
  (b) Describe HOMO COSY 2D NMR technique with suitable example.

**OR**

**3** Answer the following :  14
  (a) Calculate the 13C Value for following Compounds.
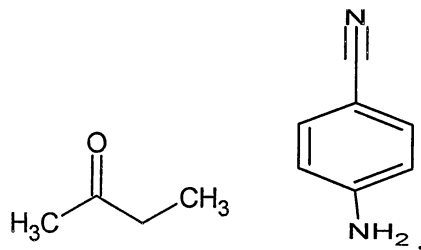


  (b) Discuss the factors affecting on chemical shift in NMR-spectroscopy.

**4** Answer the following :  14
  (a) Enlist the ionization techniques used in mass spectrometry and discuss any one in details.
  (b) How many $^{13}CNMR$ signals are possible for following compounds :
    (1) o-Dichlorobenzene
    (2) m-Dinitrobenzene
    (3) Cinnamic acid
    (4) m-Cyano bromobenzene

**5** Answer the following : (Any **Two**)  14
  (a) Discuss Woodward-Fieser rules for calculating absorption maxima in $\alpha, \beta -$ unsaturated carbonyl compounds in details.
  (b) Explain hyperfine splitting in ESR.
  (c) Discuss quantum mechanical theory of Raman effect.
  (d) Compare and differentiate NIR and IR spectrophotometer.

TABLE 5.0

| Substituent | C-1 (Attachment) | C-2 | C-3 | C-4 | C of Substituent (ppm from TMS) |
|---|---|---|---|---|---|
| H | 0.0 | 0.0 | 0.0 | 0.0 | |
| $CH_3$ | 9.3 | +0.7 | -0.1 | -2.9 | 21.3 |
| $CH_2CH_3$ | +15.6 | -0.5 | 0.0 | -2.6 | 29.2 ($CH_2$), 15.8 ($CH_3$) |
| $CH(CH_3)_2$ | +20.1 | -2.0 | 0.0 | -2.5 | 34.4 (CH), 24.1 ($CH_3$) |
| $C(CH_3)_3$ | +22.2 | -3.4 | -0.4 | -3.1 | 34.5 (C), 31.4 ($CH_3$) |
| $CH=CH_2$ | +9.1 | -2.4 | +0.2 | -0.5 | 137.1 (CH), 113.3 ($CH_2$) |
| $C\equiv CH$ | -5.8 | +6.9 | +0.1 | +0.4 | 84.0 (C), 77.8 (CH) |
| $C_6H_5$ | +12.1 | -1.8 | -0.1 | -1.6 | |
| $CH_2OH$ | +13.3 | -0.8 | -0.6 | -0.4 | 64.5 |
| $CH_2OCCH_3$ (=O) | +7.7 | -0.0 | -0.0 | -0.0 | 20.7 ($CH_3$), 65.1 ($CH_2$), 170.5 (C=O) |
| OH | +26.6 | -12.7 | +1.6 | -7.3 | |
| $OCH_3$ | +31.4 | -14.4 | +1.0 | -7.7 | 54.1 |
| $OC_6H_5$ | +29.0 | -9.4 | +1.6 | -5.3 | |
| $OCCH_3$ (=O) | +22.4 | -7.1 | -0.4 | -3.2 | 23.9 ($CH_3$), 169.7 (C=O) |
| CH (=O) | +8.2 | +1.2 | +0.6 | +5.8 | 192.0 |
| $CCH_3$ (=O) | +7.8 | -0.4 | -0.4 | +2.8 | 24.6 ($CH_3$), 195.7 (C=O) |
| $CC_6H_5$ (=O) | +9.1 | +1.5 | -0.2 | +3.8 | 196.4 (C=O) |
| $CCF_3$ (=O) | -3.6 | +1.8 | +0.7 | +6.7 | |
| COH (=O) | +2.9 | +1.3 | +0.4 | +4.3 | 168.0 |
| $COCH_3$ (=O) | +2.0 | +1.2 | -0.1 | +4.8 | 51.0 ($CH_3$), 166.8 (C=O) 168.5 |
| CCl (=O) | +4.6 | +2.9 | +0.6 | +7.0 | |
| $C\equiv N$ | -16.0 | +3.6 | +0.6 | +4.3 | 119.5 |
| $NH_2$ | +19.2 | -12.4 | +1.3 | -9.5 | |
| $N(CH_3)_2$ | +22.4 | -15.7 | +0.8 | -11.8 | 40.3 |
| $NHCCH_3$ (=O) | +11.1 | -9.9 | +0.2 | -5.6 | |
| $NO_2$ | +19.6 | -5.3 | +0.9 | +6.0 | |
| $N=C=O$ | +5.7 | -3.6 | +1.2 | -2.8 | 129.5 |
| F | +35.1 | -14.3 | +0.9 | -4.5 | |
| Cl | +6.4 | +0.2 | +1.0 | -2.0 | |
| Br | -5.4 | +3.4 | +2.2 | -1.0 | |
| I | -32.2 | +9.9 | +2.6 | -7.3 | |
| $CF_3$ | +2.6 | -3.1 | +0.4 | +3.4 | |
| SH | +2.3 | +0.6 | +0.2 | -3.3 | |
| $SCH_3$ | +10.2 | -1.8 | +0.4 | -3.6 | 15.9 |
| $SO_2NH_2$ | +15.3 | -2.9 | +0.4 | +3.3 | |
| $Si(CH_3)_3$ | +13.4 | +4.4 | -1.1 | -1.1 | |

[a] See D. E. Ewing, Org. Magn. Reson., 12, 499 (1979) for chemical shifts of 709 monosubstituted benzenes.

# TABLE 5.9

| Substituent | C-1 (Attachment) | C-2 | C-3 | C-4 | C of Substituent (ppm from TMS) |
|---|---|---|---|---|---|
| H | 0.0 | 0.0 | 0.0 | 0.0 | |
| CH₃ | 9.3 | +0.7 | −0.1 | −2.9 | 21.3 |
| CH₂CH₃ | +15.6 | −0.5 | 0.0 | −2.6 | 29.2 (CH₂), 15.8 (CH₃) |
| CH(CH₃)₂ | +20.1 | −2.0 | 0.0 | −2.5 | 34.4 (CH), 24.1 (CH₃) |
| C(CH₃)₃ | +22.2 | −3.4 | −0.4 | −3.1 | 34.5 (C), 31.4 (CH₃) |
| CH=CH₂ | +9.1 | −2.4 | +0.2 | −0.5 | 137.1 (CH), 113.3 (CH₂) |
| C≡CH | −5.8 | +6.9 | +0.1 | +0.4 | 84.0 (C), 77.8 (CH) |
| C₆H₅ | +12.1 | −1.8 | −0.1 | −1.6 | |
| CH₂OH | +13.3 | −0.8 | −0.6 | −0.4 | 64.5 |
| CH₂OCCH₃ ‖ O | +7.7 | ~0.0 | ~0.0 | ~0.0 | 20.7 (CH₃), 66.1 (CH₂), 170.5 (C=O) |
| OH | +26.6 | −12.7 | +1.6 | −7.3 | |
| OCH₃ | +31.4 | −14.4 | +1.0 | −7.7 | 54.1 |
| OC₆H₅ | +29.0 | −9.4 | +1.6 | −5.3 | |
| $\overset{O}{\overset{\|}{O}}$CCH₃ | +22.4 | −7.1 | −0.4 | −3.2 | 23.9 (CH₃), 169.7 (C=O) |
| $\overset{O}{\overset{\|}{C}}$H | +8.2 | +1.2 | +0.6 | +5.8 | 192.0 |
| $\overset{O}{\overset{\|}{C}}$CH₃ | +7.8 | −0.4 | −0.4 | +2.8 | 24.6 (CH₃), 195.7 (C=O) |
| $\overset{O}{\overset{\|}{C}}$C₆H₅ | +9.1 | +1.5 | −0.2 | +3.8 | 196.4 (C=O) |
| $\overset{O}{\overset{\|}{C}}$CF₃ | −5.6 | +1.8 | +0.7 | +6.7 | |
| $\overset{O}{\overset{\|}{C}}$OH | +2.9 | +1.3 | +0.4 | +4.3 | 168.0 |
| $\overset{O}{\overset{\|}{C}}$OCH₃ | +2.0 | +1.2 | −0.1 | +4.8 | 51.0 (CH₃), 166.8 (C=O) |
| $\overset{O}{\overset{\|}{C}}$Cl | +4.6 | +2.9 | +0.6 | +7.0 | 168.5 |
| C≡N | −16.0 | +3.6 | +0.6 | +4.3 | 119.5 |
| NH₂ | +19.2 | −12.4 | +1.3 | −9.5 | |
| N(CH₃)₂ | +22.4 | −15.7 | +0.8 | −11.8 | 40.3 |
| NH$\overset{O}{\overset{\|}{C}}$CH₃ | +11.1 | −9.9 | +0.2 | −5.6 | |
| NO₂ | +19.6 | −5.3 | +0.9 | +6.0 | |
| N=C=O | +5.7 | −3.6 | +1.2 | −2.8 | 129.5 |
| F | +35.1 | −14.3 | +0.9 | −4.5 | |
| Cl | +6.4 | +0.2 | +1.0 | −2.0 | |
| Br | −5.4 | +3.4 | +2.2 | −1.0 | |
| I | −32.2 | +9.9 | +2.6 | −7.3 | |
| CF₃ | +2.6 | −3.1 | +0.4 | +3.4 | |
| SH | +2.3 | +0.6 | +0.2 | −3.3 | |
| SCH₃ | +10.2 | −1.8 | +0.4 | −3.6 | 15.9 |
| SO₂NH₂ | +15.3 | −2.9 | +0.4 | +3.3 | |
| Si(CH₃)₃ | +13.4 | +4.4 | −1.1 | −1.1 | |

*See D. E. Ewing, *Org. Magn. Reson.*, 12, 499 (1979) for chemical shifts of 709 monosubstituted benzenes.

Table 3.13 δ values for the carbons in alkynes (sp)

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REPRESENTATIVE ALKYNES

acetylene (ethyne)  CH≡CH δ 72

R—C≡CH                    R—C≡C—R′           $C_6H_5$—C≡CH
  83  66                      82                  83  78

$C_6H_5$—C≡C—R                              $C_6H_5$—C≡C—$C_6H_5$
     86                                          90

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EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

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Chemical shift ($\delta$) = 72 + Σ(increments for carbon atoms)

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C—C—C—C—C≡C—C—C—C—C

$\delta$  $\gamma$  $\beta$  $\alpha$  |  $\alpha'$  $\beta'$  $\gamma'$  $\delta'$

increments  +0.5  0  +5  +7  |  −6  +2  −1  +0.5

base value 72

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TABLE 3.23

| Observed C | $A_n$ | ←———— $\alpha$ → | | $\gamma$ | $\delta$ |
|---|---|---|---|---|---|
| —$CH_3$ | 6.80 | $CH_3$ | 0 | −2.99 | 0.49 |
| | | $CH_2$ | 9.56 | | |
| | | CH | 17.83 | | |
| | | C | 25.48 | | |
| —$CH_2$— | 15.34 | $CH_3$ | 0.0 | −2.69 | 0.25 |
| | | $CH_2$ | 9.75 | | |
| | | CH | 16.70 | | |
| | | C | 21.43 | | |
| —CH | 23.46 | $CH_3$ | 0.0 | −2.07 | 0.0 |
| | | $CH_2$ | 6.60 | | |
| | | CH | 11.14 | | |
| | | C | 14.70 | | |
| —C— | 27.77 | $CH_3$ | 0.0 | 0.86 | 0.0 |
| | | $CH_2$ | 2.26 | | |
| | | CH | 3.96 | | |
| | | C | 7.35 | | |

*Note:* Methyl groups in $\alpha$ and all groups in $\beta$ have no effect. Groups in $\gamma$ position have negative or only slightly positive effect.
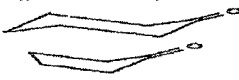
| | | |
|---|---|---|
| R—CHO, Ar—CHO, =CHO | aliphatic aldehydes | 200–205 |
| | aryl and conjugated aldehydes | 190–194 |
| R—CO—R', Ar—CO—R, Ar—CO—Ar, =CO | dialkyl ketones | 205–213 |
| | aryl and conjugated ketones | 196–199 |
| cyclohexanone derivatives | | 209–213 |
| cyclopentanone derivatives | | 214–220 |
| bicyclic ketones | | 215–219 |
| simple quinones | | 180–187 |
| R—COOH, R—COO⁻ | carboxylic acids and salts | 166–181 |
| R—COO—R', Ar—COOAr, =COO | aliphatic esters | 169–176 |
| | esters with conjugation in the acid or alcohol moiety | 164–169 |
| | lactones | 170–176 |
| —CO—O—CO— | anhydrides, all classes | 163–175 |
| —CON< | amides, all classes including lactams | 162–179 |

### Table 3.15 Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chains

$$X—C—C—C—C$$
$$\quad \alpha \quad \beta \quad \gamma$$

| $X$ | $\alpha$-shift | | | $\beta$-shift | $\gamma$-shift |
|---|---|---|---|---|---|
| | $X—CH_2—$ | $X—CH(R)—$ | $X—CR_2—$ | | |
| | 1° or | 2° or | 3° | | |
| —CH₃ | 9 | 6 | 3 | 9 | −3 |
| — R: see table 3.11 | | | | | |
| axial —CH₃ | 1 | — | — | 5 | −6 |
| equatorial —CH₃ (in cyclohexanes) | 6 | — | — | 9 | 0 |
| —CH=CH₂ | 22 | 16 | 12 | 7 | −1 |
| —C≡CH | 4 | — | — | 3 | −3 |
| —C₆H₅, —Ar | 23 | 17 | 11 | 10 | −3 |
| —F | 70 | — | — | 8 | −7 |
| —Cl | 31 | 35 | 42 | 10 | −5 |
| —Br | 19 | 28 | 37 | 11 | −4 |
| —I | −7 to 20 | — | — | 11 | −2 |
| —NH₂, —NHR, —NR₂ | 29 | 24 | 18 | 11 | −4 |
| —NO₂ | 62 | — | — | 3 | −5 |
| —NHCOR, —NRCOR | 10 | — | — | 0 | 0 |
| —NH₃⁺ | 25 | — | — | 7 | −3 |
| —CN | 3 | 4 | — | 1 | −3 |
| —SH | 2 | — | — | 2 | −2 |
| —OH | 50 | 45 | 40 | 9 | −3 |
| —OR | 50 | 24 | 17 | 10 | −6 |
| —OCOR | 52 | 50 | 45 | 7 | −6 |
| —COOH, —COOR, —CON< | 20 | 16 | 13 | 2 | −3 |
| —COR, —CHO | 30 | 24 | 17 | 2 | −3 |
| —SO₃H, —SO₂N< | 50 | — | — | 3 | 0 |

# Data Table for 13C NMR Spectroscopy

### TABLE 5.1

| 13C Atoms | Shift (ppm) (A) |
|---|---|
| α | +9.1 |
| β | +9.4 |
| γ | −2.5 |
| δ | +0.3 |
| ε | +0.1 |
| 1° (3°)ᵃ | −1.1 |
| 1° (4°)ᵃ | −3.4 |
| 2° (3°)ᵃ | −2.5 |
| 2° (4°) | −7.2 |
| 3° (2°) | −3.7 |
| 3° (2°) | −9.5 |
| 4° (1°) | −1.5 |
| 4° (2°) | −8.4 |

ᵃ The notations 1° (3°) and 1° (4°) denote a CH₃ group bound to a R₂CH group and to a R₃C group, respectively. The notation 2° (3°) denotes a RCH₂ group bound to a R₂CH group, and so on.

### TABLE 5.2

| Compound | C-1 | C-2 | C-3 | C-4 | C-5 |
|---|---|---|---|---|---|
| Methane | −2.3 | | | | |
| Ethane | 5.7 | | | | |
| Propane | 15.8 | 16.3 | 15.8 | | |
| Butane | 13.4 | 25.2 | 25.2 | | |
| Pentane | 13.9 | 22.8 | 34.7 | 22.8 | 13.9 |
| Hexane | 14.1 | 23.1 | 32.2 | 32.2 | 23.1 |
| Heptane | 14.1 | 23.2 | 32.6 | 29.7 | 32.6 |
| Octane | 14.2 | 23.1 | 32.2 | 29.9 | 29.9 |
| Nonane | 14.2 | 23.3 | 32.6 | 30.0 | 30.3 |
| Decane | 14.2 | 23.2 | 32.6 | 31.1 | 30.5 |
| Isobutane | 24.5 | 25.4 | | | |
| Isopentane | 22.2 | 31.1 | 32.0 | 11.7 | |
| Isohexane | 22.7 | 28.0 | 42.0 | 20.9 | 14.3 |
| Neopentane | 31.7 | 28.1 | | | |
| 2,2-Dimethylbutane | 29.1 | 30.6 | 36.9 | 8.9 | |
| 3-Methylpentane | 11.5 | 29.5 | 36.9 | (18.8, 3-CH₃) | |
| 2,3-Dimethylbutane | 19.5 | 34.3 | | | |
| 2,2,3-Trimethylbutane | 27.4 | 33.1 | 38.2 | 16.1 | |
| 2,3-Dimethylpentane | 7.0 | 25.3 | 36.3 | (14.6, 3-CH₃) | |

### TABLE 5.3

Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internalᵃ (+ downfield, − upfield)

| Y | α Terminal | α Internal | β Terminal | β Internal | γ |
|---|---|---|---|---|---|
| CH₃ | +9 | +6 | +10 | +8 | −2 |
| CH—CH₂ | +20 | | +6 | | −0.5 |
| C≡CH | +4.5 | | +5.5 | | −3.5 |
| COOH | +21 | +16 | +3 | +2 | −2 |
| COO⁻ | +25 | +20 | +5 | +3 | −2 |
| COOR | +20 | +17 | +3 | +2 | −2 |
| COCl | +33 | +28 | | | |
| CONH₂ | +22 | | +2.5 | | −0.5 |
| COR | +30 | +24 | +1 | +1 | −2 |
| CHO | +31 | | 0 | | −2 |
| Phenyl | +23 | +17 | +9 | +7 | −2 |
| OH | +48 | +41 | +10 | +8 | −5 |
| OR | +58 | +51 | +8 | +5 | −4 |
| OCOR | +51 | +45 | +6 | +5 | −3 |
| NH₂ | +29 | +24 | +11 | +10 | −5 |
| NH₃⁺ | +26 | +24 | +8 | +6 | −5 |
| NHR | +37 | +31 | +8 | +6 | −4 |
| NR₂ | +42 | | +6 | | −3 |
| NR₃⁺ | +31 | | +5 | | −7 |
| NO₂ | +63 | +57 | +4 | +4 | |
| CN | +4 | +1 | +3 | +3 | −3 |
| SH | +11 | +11 | +12 | +11 | −4 |
| SR | +20 | | +7 | | −3 |
| F | +68 | +63 | +9 | +6 | −4 |
| Cl | +31 | +32 | +11 | +10 | −4 |
| Br | +20 | +25 | +11 | +10 | −3 |
| I | −6 | +4 | +11 | +12 | −1 |

ᵃ Add these increments to the shift values of the appropriate carbon atom in Table 5.2 or to the shift value calculated from Table 5.1.
Source: F. W. Wehrli, A. P. Marchand, and S. Wehrli, Interpretation of Carbon-13 NMR Spectra, 2nd ed., London: Heyden, 1983.

### Table 5.14  δ values for the carbons in aromatic and heterocyclic molecules (sp² and sp¹ carbons listed)
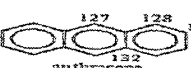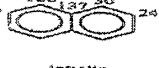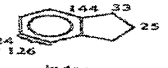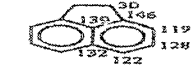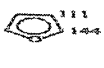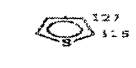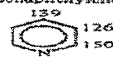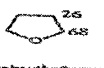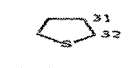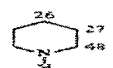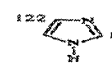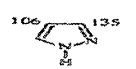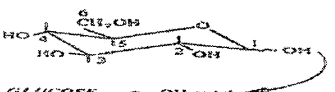
- benzene: 128
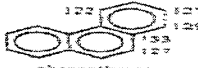- naphthalene: 136, 128, 126, 132
- anthracene: 127, 128, 125, 132
- phenanthrene: 122, 127, 129, 133
- tetralin: 129, 137, 30, 24, 126
- indane: 124 or 126, 144, 33, 25
- acenaphthene: 30, 136, 135, 119, 128, 132, 122
- acenaphthylene: 139, 128, 138, 124, 128, 127, 126
- furan: 111, 144
- thiophene: 127, 125
- pyrrole: 108, 118
- pyridine: 139, 126, 150
- tetrahydrofuran, THF: 26, 68
- tetrahydrothiophene: 31, 32
- pyrrolidine: 26, 47
- piperidine: 26, 27, 48
- imidazole: 122, 136
- pyrazole: 106, 135

GLUCOSE  (α − OH axial, β − OH equatorial)

| | C₁ | C₂ | C₃ | C₄ | C₅ | C₆ |
|---|---|---|---|---|---|---|
| α | 97 | 75 | 77 | 70 | 77 | 62 |
| β | 93 | 75 | 74 | 70 | 72 | 62 |