Max. Marks: 35   **12 May 2022**   **Duration: 3hrs.**

Instructions to the student:
1) There are eight questions in total; answer all the questions.
2) Write brief answers to the point with proper justification.
3) Start answering each question on a fresh page and answer all parts of a question together.
4) Open book test. Textbook, Ref. books, class notes, and printed slides are allowed. However, exchange of these materials is not allowed. Mobile phones, lap-tops etc. are to be switched off and kept away from you.
5) Any unfair means, if identified, will be sternly dealt with.
6) Data required are available in Text and/or Reference books. However, for quick reference the following often used constant values are given.

DATA: R = 8.3145 J mol^{-1} K^{-1}; **R**= 0.0820575 L atm K^{-1} mol^{-1}; **k** = 1.38065 x 10^{-23} J K^{-1};
    Avogadro's Number = N_A = 6.022142 x 10^{23} mol^{-1}; **h** = 6.626069 x 10^{-34} J s;
    e = 1.60216 x 10^{-19} C; m_e = 9.10938 x 10^{-31} kg; **F** = 96485.34 C mol^{-1};
    c = 2.99792458 x 10^8 m s^{-1}; ε_0 = 8.854188 x 10^{-12} C^2 N^{-1} m^{-2}; **g** = 9.807 m s^{-2}.

1.   a) Indicate the number of Nuclear Quadrupole Resonance lines expected for $K_3Co(CN)_6$ by an energy level diagram. ^{59}Co has I = 7/2 and a natural abundance of 100 %. No external magnetic field is applied. How will this spectrum differ from that of $K_3Co(CN)_5Br$? **[2]**
b) Roughly sketch the Mössbauer spectrum of $[Fe(H_2O)_6]Cl_2$ solid in presence and absence of a weak magnetic field. Consider only ^{57}Fe isotope of iron. Water is to be treated as a weak ligand.**[2]**

2. a) Write the most probable structure for the ions of m/z 96, 81, 68 and 67 found in the mass spectrum of 1-methylcyclohexene. **[2]**
b) Draw the structures of the compounds a) 4-ter.butyl phenol b) 2-ter.butyl phenol c) 2,6-di-ter.butyl phenol. These three compounds show different O-H stretching frequency patterns. (3605 and 3643 cm^{-1}), (3643 cm^{-1}), (3608 cm^{-1}). Identify which absorption belongs to which compound and explain your answer. **[2]**

3. a) Consider the isotopes of Boron: ^{10}B (I = 3, 20% Abundance); ^{11}B (I = 3/2, 80% Abundance). The coupling constants with proton are given as ^1J ($_{^1H - ^{10}B}$) = 27Hz and ^1J ($_{^1H - ^{11}B}$) = 80Hz. With the aid of stick and branch diagram, roughly sketch **i)** the ^{1}H NMR spectrum of $^{11}BH_4^-$ ion in solution. **ii)** the ^{1}H NMR spectrum of natural BH_4^- ion in solution. **[1.5 x 2 = 3]**
b) i) Consider "R" group substituted benzenes of molecular formula C_9H_{10}. Write two isomers which will have substantially different wavelengths of absorption in the electronic spectrum. **Ii)** For phenyl acetaldehyde write out the structure of an isomer that is likely to have a substantially different electronic spectrum. **[1 +1 = 2]**

4. Derive structural formula that is consistent with the data given below. The relative molar mass was determined from the mass spectrum of the substance. The ultraviolet spectrum is given for aqueous solution; the infrared data shows only those prominent absorptions in the region (4000-1429 cm^{-1}); the ^{1}H NMR spectrum is given for deuteriochloroform solution. **[5]**
Relative Molar Mass: 104
        UV: λ_{max} 203 nm. ε 40 (water)
        IR: λ_{max} 3125-2857 (m), 2695 (w), 2625 (w), 1718(s), and 1449cm^{-1} (m).
        NMR: 10.95(singlet, 5.4squares), 4.13(singlet, 11.0squares), 3.66(quartet, J = 7.1Hz, 10.6 squares), and 1.27δ (triplet, J = 7.1Hz, 16.2 squares)

5. a) Roughly sketch the ESR (EPR) spectrum of $^{13}CH_2D^•$ radical. Explain your spectrum by a stick branch diagram. **[2]**

b) Predict the ^{13}C Chemical shift positions for 5-ethylhept-3-yne. **[2]**

6. Make rough sketches of 2D-COSY and HETCOR spectrum of naphthalene. **[2 +2 = 4]**

7. Given below are the IR and ^1H NMR spectra of a compound of formula C_8H_{14}. Identify the compound. Justify your answer. The numbers above the NMR peaks indicate the intensity ratios. **[4]**
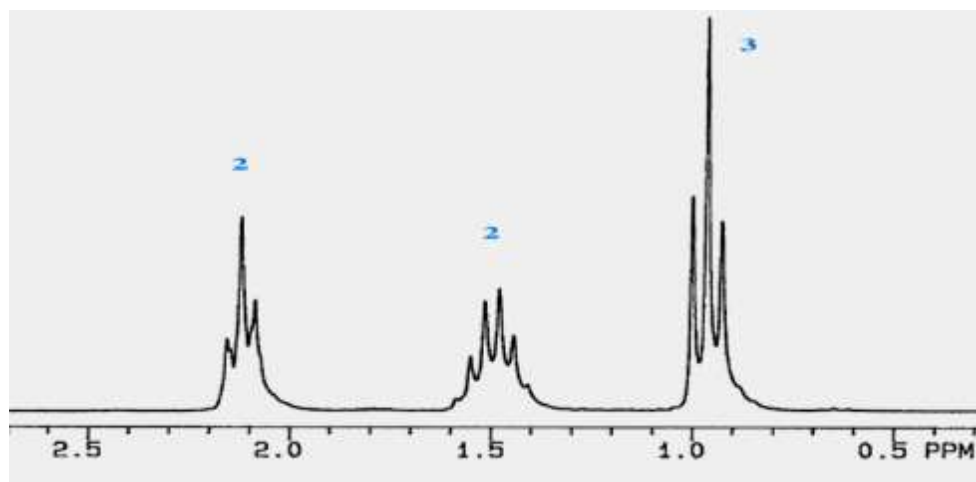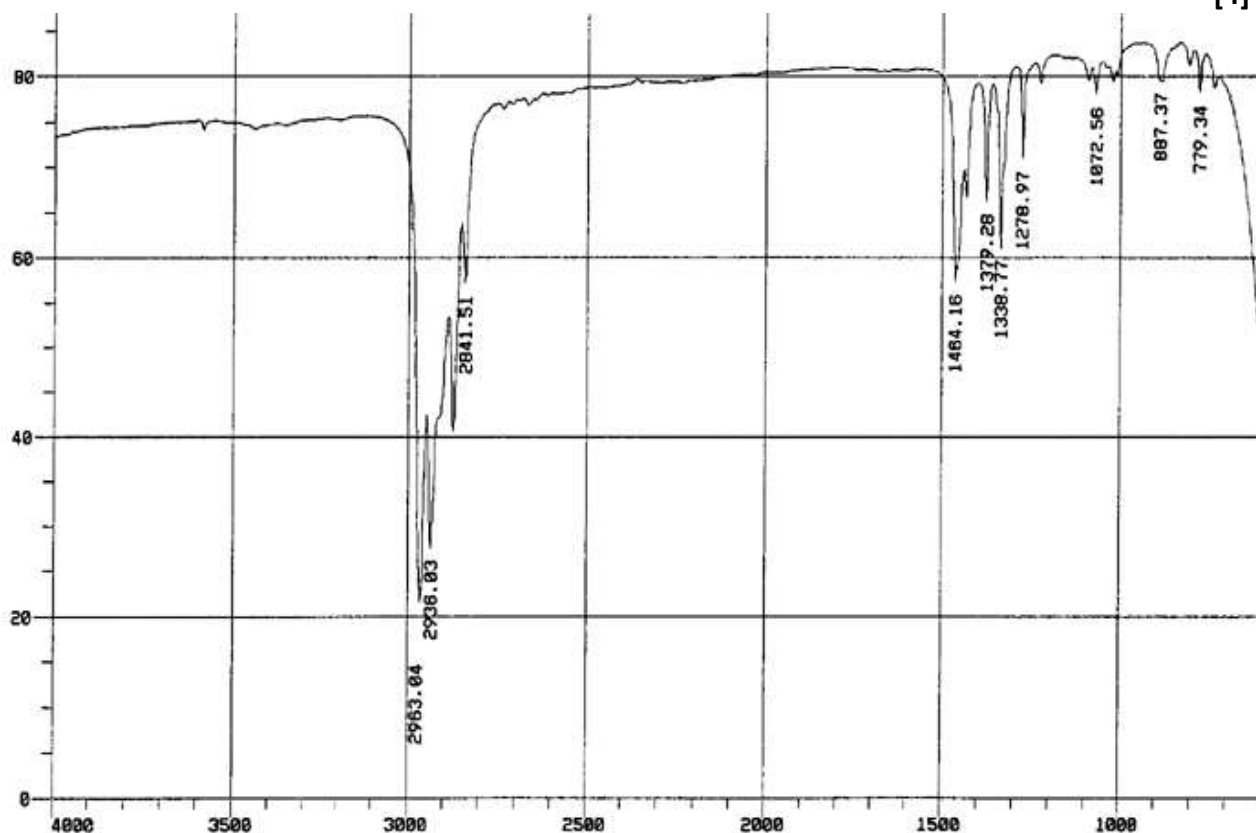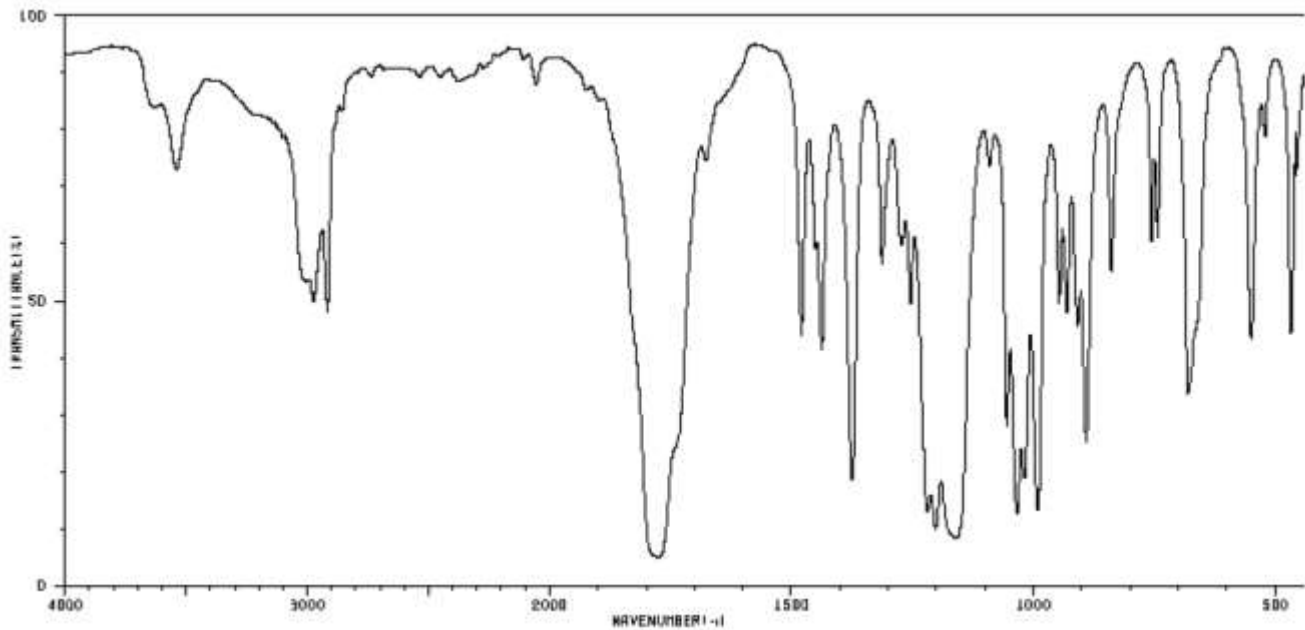
8. Deduce the structure that corresponds to the spectral data.   **[5]**

Mass spectrum: M: m/z 164 (100%); M + 1 m/z 165 (4.62%); M + 2 m/z 166 (98.1%).   IR

^{1}H-NMR: 4.3 ppm (triplet, integral = 1), 3.6 ppm (triplet, integral = 2), 1.5 ppm (quartet, integral = 2).

^{13}C-NMR (DEPT): 178.1 ppm (C), 65.0 ppm (CH), 46.7 ppm (CH$_2$), 33.3 ppm (CH$_2$).

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