

2018  
CHEMISTRY  
CHM-204  
SPECTROSCOPY-II  
Full Marks: 80  
Time: 3 Hours

*The figures in the margin indicate full marks for the questions :*

**1. Answer the following questions :**

- (a) How will you distinguish between 3-methyl and 4-methyl cyclohexenes on the basis of mass spectrometry? 3
- (b) Explain CI technique in mass spectrometry. 3

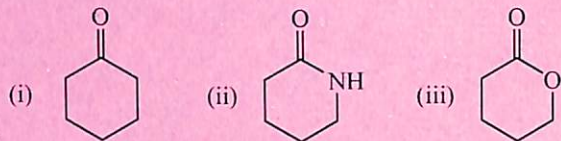
Or

Explain the even- and odd- electron rules in mass spectrometry with suitable examples.

- (c) Write the possible fragmentation patterns of the following compounds mentioning their base peaks in mass spectrum. (*Any two*) 2+2
- (i) Ethyl cyclopentane (ii) Cyclohexanone (iii) *n*-Butyl benzene

**2. Answer the following questions :**

- (a) Explain the significance of Hooke's law in IR spectroscopy with examples. 2
- (b) Show the different modes of vibrations present in carbon dioxide molecule and identify the IR active and inactive modes. 2
- (c) Write the conjugation and H-bonding effects on carbonyl stretching frequency with different examples. 3
- (d) Arrange the following structures in order of their increasing C=O stretching frequency and explain why.

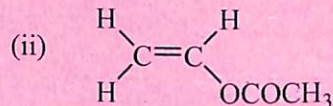


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**3. Answer the following questions (Any four) :**

**5x4=20**

- (a) Explain the importance of DEPT <sup>13</sup>C NMR technique. 5  
 (b) What do you mean by 2-D NMR spectrum? Explain COSY spectrum of ethyl vinyl ether. 1+4  
 (c) How coupling constant is different from the chemical shift? In the light of Karplus relationship, explain how the orientation of H-atoms affects the magnitude of coupling constant. 1+4  
 (d) What is shift reagent? Name at least two of it and write their structures. Discuss the use of shift reagents in simplification of <sup>1</sup>H NMR spectra. 1+2+2  
 (e) What do you mean by spin-spin splitting? Indicate the number of signals and the multiplicity of each signal in the NMR spectrum of each of the following compounds. 1+2+2



**4. Answer the following questions :**

- (a) Find all the vibrational modes of square planar complex PtCl<sub>4</sub><sup>2-</sup>. Identify the Pt-Cl stretching mode of vibrations. 3+1=4  
 (b) Photoelectrons ejected from N<sub>2</sub> with He (I) radiation (21.22 eV) had kinetic energy of 5.36 eV. What is the energy needed to remove an electron from the HOMO of the N<sub>2</sub> molecule (i.e., the 3σ<sub>g</sub> orbital)? 5  
 (c) Define circular dichroism and magnetic circular dichroism. Write their differences and explain how their measurements provide a useful physical method to determine molecular properties of inorganic compounds. 2+2+2

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**P.T.O.**

Or

Discuss the principle and application of CD and ORD techniques to transition metal complexes. 6

**5. Answer the following questions (Any five) :**

**5x5=25**

- (a) Explain with a suitable example how orientation of nuclear spins with respect to applied magnetic field leads to hyperfine splitting of EPR signals. Why EPR spectra are plotted in derivative mode? 3+2  
 (b) What are the various ways in which NMR spectroscopy proves itself as a useful physical method in the field of inorganic chemistry? Write briefly why it is not a straightforward option to use NMR spectroscopy for obtaining structural information on paramagnetic compounds. 2+3  
 (c) Explain how more than one unpaired electron results in more number of EPR lines than expected. The dinuclear Fe-Fe bonded species (η<sup>5</sup>-Cp)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub>, which contains both bridging as well as terminal CO ligands, shows two <sup>1</sup>H NMR signals at -70°C but only one at 28°C. Use this spectral information to identify the species present at the above temperatures. 2+3  
 (d) Explain how recoil of source and sample makes it impossible to record a Mössbauer spectrum in the gas phase. Mention the energy and lifetime ranges of the gamma-emitter for observing a good Mössbauer resonance. 5  
 (e) The centre of the ESR spectrum of methyl radical occurs at 329.4mT when the spectrometer is using 9.233X10<sup>9</sup> Hz microwave. What is its g-value? [1 tesla=10<sup>4</sup> gauss; β=9.27X10<sup>-21</sup> erg.gauss<sup>-1</sup>]. Sketch the NH<sub>2</sub> radical (I<sub>N</sub>=1, I<sub>H</sub>=1/2). Give reasons to your answer. 2+3  
 (f) What are the various factors that determine NMR signal strength in the context of multinuclear NMR spectroscopy? Explain how magnetic susceptibility of a paramagnetic complex can be measured by making use of NMR spectroscopy. 2+3

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