MANIPAL
ACADEMY of HIGHER EDUCATION
(Deemed to be University under Section 3 of the UGC Act, 1956)

Reg. No.										

DEPARTMENT OF SCIENCES, I SEMESTER M.Sc (CHEMISTRY)
END SEMESTER EXAMINATIONS, DECEMBER 2018

SUBJECT: SPECTROSCOPY-I [CHM – 4107]
(REVISED CREDIT SYSTEM-2017)

Time: 3 Hours Date: 28-12-2018 MAX. MARKS: 50

Note: (i) Answer **ALL** questions

(ii) Draw diagrams, and write equations wherever necessary

1A. Differentiate the following;
i) Blue shift and red shift in UV-spectroscopy
ii) Rigid and non-rigid rotational spectrum of a diatomic molecule

1B. Describe the technique and instrumentation involved in Raman Spectroscopy. Mention two advantages of laser source against other sources.

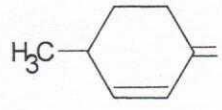
1C. State and deduce Lambert's law. The absorption spectrum for titanium peroxide complex ion in perchloric acid showed a maximum of 350 nm. The absorbance of a 32.0 μg/mL solution of titanium gave an absorbance of 0.56. An unknown solution treated in an identical fashion gave an absorbance of 0.651. Find out the concentration of the unknown by assuming identical cells.

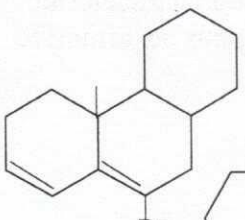
2+4+4

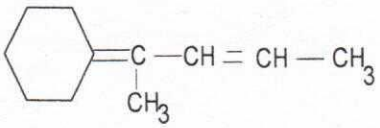
2A. Account for the following:
i) Stretching vibrations appear in the higher frequency than that of bending vibrations.
ii) Photocell is more sensitive than that of Photovoltaic cell as an UV detector

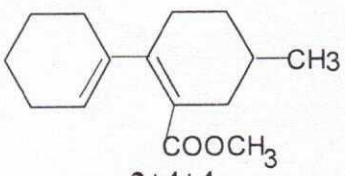
2B i) The rotational Raman spectrum of H_2 gas is found to consist of a series of Stokes and antistokes lines the first of which appears at 345.9 cm^{-1} relative to the source of excitation. Calculate the bond distance of H_2
ii) Derive mathematical expression for fundamental, first overtone and second overtone frequencies using an enharmonic oscillator model.

2C. Compute the λ_{max} for the following compounds based on the Woodward-Fieser rules for diene.

i) 

ii) 

iii) 

iv) 

2+4+4

3A. Based on the symmetry aspects explain why H_2O is a dipole while CH_4 is a non-dipole.

3B. i) Calculate the approximate wave number of the fundamental absorption peak due to the stretching vibrations of a carbonyl group. The force constant for a double bond has an approximate value of 1×10^6 dynes/cm. The masses of carbon and oxygen atoms are 1×10^{-26} and 2.6×10^{-26} kg per atom.

ii) Differentiate between the following;

a) IR and Raman spectroscopy

b) Coupled vibrations and fermi resonance

3C. What is Doppler effect? Explain the factors responsible for the intensity of spectral lines.

2+4+4

4A. What are the advantages in Atomic Absorption Spectroscopy of a heated graphite atomizer over a flame atomizer? Explain the background correction carried out in this spectroscopic technique.

4B. Find all the symmetry operations of orthoboric acid belonging to C_{3h} point group and identify the point group of chlorobenzene, CO_2 and naphthalene C_{2v}, $D_{\infty h}$, D_{2h}

4C. Identify the principal rotation axis and the reflection mirror planes of the following molecules based on the symmetry aspects of a molecule.

a) BF_3 C_3 b) $PtCl_4^{2-}$ C_4 c) Benzene C_6 d) Eclipsed ethane C_3

2+4+4

5A. Explain the following interferences observed in Atomic Absorption Spectroscopy with an example each.

i) Spectral Interference

ii) Ionization Interference

5B. Draw a schematic diagram of the instrumentation involved in Atomic Absorption Spectroscopy and explain the function of each of the parts.

5C. Determine the point groups of the given molecules by following the systematic procedure.

a) Planar cis H_2O_2 — C_{2V}

b) Ethylene — D_{2h}

c) Silicon tetrachloride — T_d

d) Sulphur hexafluoride — O_h

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