14 (CHM–2) 204

2022

CHEMISTRY

Paper : CH–204

(Spectroscopy 2)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

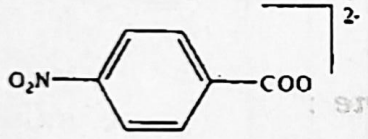
1. Answer ***any one*** : 5

   (a) Methyl radical in a CH_4 matrix at 4.2K displays four EPR signals with intensity ratio 1:3:3:1. Show the possible orientations of nuclear spins of the three protons with respect to the applied magnetic field B_0 to account for the observed spectrum.

(b) A paramagnetic species is analyzed by an EPR experiment using a microwave radiation of 9400*MHz*, which gives three signals in the intensity pattern 1:2:1 due to splitting of the EPR signal by two equivalent protons. Calculate the exact positions of the three signals in Gauss if the hyperfine coupling constant (A_H) of the protons is 100 Gauss. Given that $\mu_B = 9.3\times10^{-24} JT^{-1}$; $h = 6.6\times10^{-34} Js$ and $g = 2$. What is *X*-band EPR ?

2. Predict EPR spectra of the following with the help of Pascal-like triangle : ***(any two)*** 4×2=8

(a)



(*p*-nitrobenzoate dianion)

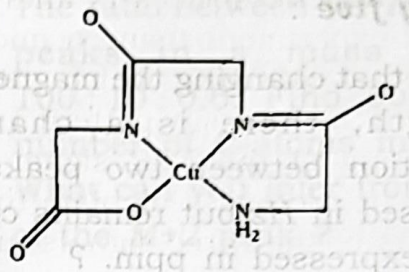
Given that :

$A_N = 9.0G$, $A_{H(1)} = 3.1G$ and $A_{H(2)} = 1.0G$

(b) Methoxymethyl radical $[H_2C(OCH_3)]$

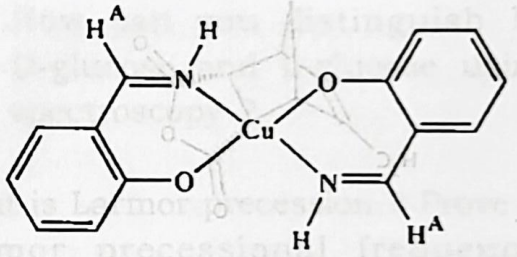
Given that : $A_{CH2} >> A_{CH3}$

(c)



Assume that : the unpaired electron delocalizes only over *Cu*(II) center and the three equivalent nitrogen atoms of the ligand; $A_{Cu} >> A_N$

(d)



Given that : hyperfine splitting is observed only due to *Cu*(II), two nitrogens and H_A set of hydrogens;

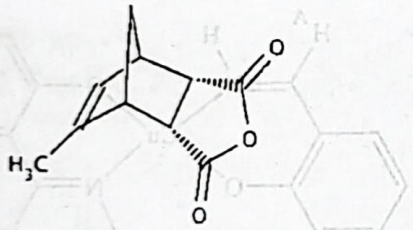
$A_{Cu} >> A_N, A_H$; $A_N = 11.1G$; $A_H = 5.5G$

3. What are zero field splitting and Kramer's degeneracy ? Use a *Mn*(IV) species in octahedral field to explain Kramer's degeneracy and predict the EPR spectrum of the species assuming that there is no contribution from the ligands in splitting the EPR signals. 2+4=6

4. Answer ***any five*** : 3×5=15

(a) Why is that changing the magnetic field strength, there is a change in separation between two peaks when expressed in *Hz* but remains constant when expressed in ppm. ?

(b) Find out the number of peaks in the broadband decoupled ^{13}C NMR spectrum of this molecule



(c) Highlight differences between the broadband decoupled and off-resonance decoupled ^{13}C *NMR* spectra of isopropyl alcohol.

(d) How many peaks are seen in the ^1H *NMR* spectrum of the BH_3 part of the molecule PPh_3BH_3, if the mass numbers of *B* and *P* are 11 and 31 respectively.

(e) The ratio between the *M*, *M*+1 and *M*+2 peaks in a mass spectrum is 100 : 10 : 0.6. Find out the possible number of C-atoms in the molecule. What can you infer from the intensity of the *M*+2 peak ?

(f) Find the ratio between the intensities of *M*, *M*+2 and *M*+4 peaks in a mass spectrum if 2 chlorine atoms are present in a sample.

(g) How can you distinguish between D-glucose and L-glucose using NMR spectroscopy ?

5. What is Larmor precession ? Prove that the Larmor precessional frequency of a magnetically active nucleus is equal to the applied frequency of the external magnetic field. 1+4=5

6. Consider a proton which has *two different* J-coupling values to *two other* hydrogens. Systematically predict the total number of peaks observed in *(a)* first order ^1H *NMR* spectrum and *(b)* second order ^1H *NMR* spectrum. 4

7. Write short notes on : ***(any two)*** 2×2=4

(a) Variable Temperature NMR spectroscopy

(b) Electrospray Ionization

(c) T_2 relaxation

8. The *MS* of an aldehyde with molecular formula $CH_3(CH_2)_3CHO$ shows a base peak at m/z = 43. Explain this observation. 3

9. In the mass spectrum of an organic compound, the *M* peak is at m/z = 135 (100%). *MS* also shows peaks at 136 (6.75%) and 137 (33.5%). The ^1H *NMR* of the compound shows three singlets in the ratio of 2:2:6 at 1.7, 4.2 and 3.1 *ppm* respectively. The IR spectrum also shows an intense peak at 1720/*cm* and a weak band at 3300/*cm*. The off-resonance ^{13}C *NMR* spectrum shows one intense quartet (63 *ppm*), two triplets (70, 43 *ppm*) and one singlet at 188 *ppm*. Answer the following questions :

(a) Using the *MS* data, evaluate the chemical formula of the compound. 3

(b) Find a possible structure of the compound. 2

(c) Mark the protons in the structure using Pople notation. 2

(d) Justify your structure by corroborating with the given spectroscopic evidences. 3