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14 (CHM-2) 204

2018

CHEMISTRY

Paper : CH-204

(Spectroscopy-2)

Full Marks : 60

Time : Three hours

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

Answer as instructed.

1. Find out true **or** false statements and write the corrected statement for the false ones :
(any five) 1×5=5

(a) Magnetization (M_z) along the direction of the magnetic field can be detected as its operator (I_z) commutes with the detection operator (I_y).

(b) Sensitivity of ^{13}C NMR is higher than ^1H .

Contd.

- (c) ^{11}B has an isotopic abundance and nuclear spin of $3/2$ and $\sim 80\%$, respectively.
- (d) ^{12}C has a nuclear spin quantum number $1/2$.
- (e) NMR signal can be detected in the absence of a magnetic field.
- (f) ^6Li is NMR active.
- (g) NOE intensity depends on $1/r^3$, where r is the distance between two atoms.

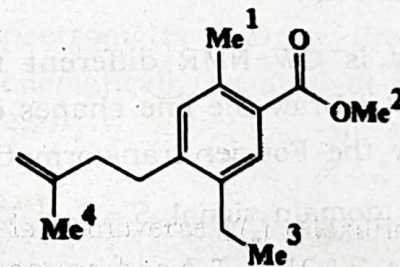
2. Illustrate briefly how the sensitivity of an NMR experiment depends on (use mathematical relation) $1 \times 3 = 3$

- (a) Magnetic field
- (b) Temperature
- (c) T_2 relaxation.

OR

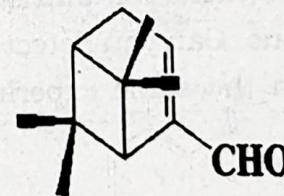
What is transverse (T_2) relaxation time? If a compound has a T_2 of 10^{-4} s, calculate the line width of the NMR signal. $1+2=3$

3. Arrange the labelled methyl protons (1-4) of the following compound in the increasing order of chemical shifts. Give brief explanation. 2



OR

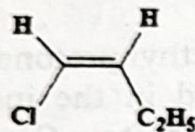
How many methyl proton signals are observed in the ^1H NMR spectrum of myrtenal? Explain briefly.



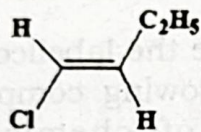
4. Answer **any three** :

3×3=9

- (a) How do you distinguish the following alkenes (A and B) on the basis of $^3J_{HH}$? Explain using Karplus equation.



A

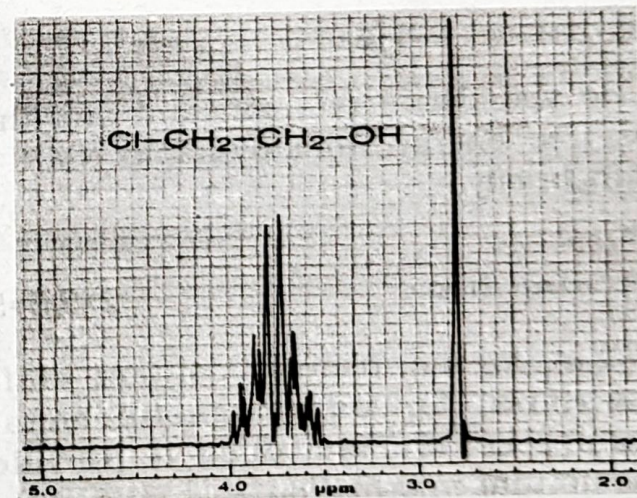


B

- (b) How is CW NMR different from FT NMR? Draw the line shapes obtained after the Fourier transformation of a time domain signal $S = S_0 e^{(-i\omega t)} e^{(-t/T_2)}$.
- (c) A radiofrequency pulse of $100\mu s$ is applied for a sample in a $100MHz$ (proton Larmour frequency) NMR spectrometer. Calculate the frequency width for excitation and convert it into ppm value. Can you detect the ^{13}C NMR signal in the same experiment?

- (d) Predict and draw the intensity pattern of the ^{13}C NMR spectrum of $DMSO-d_6$.

- (e) $60MHz$ 1H NMR spectrum of 2-chloroethanol shows strongly coupled spectrum. How do you simplify it? What will be the spin system of the methylene protons if spectrum is recorded in a $500MHz$ NMR spectrometer? Draw the spectrum schematically recorded at $500MHz$.



5. Predict and draw the ^{31}P NMR spectrum of $\text{H}_3\text{P} \cdot ^{11}\text{BCl}_3$ (^{11}B has a spin $3/2$) if

(a) $^1J_{\text{PH}} > ^1J_{\text{PB}}$ and

(b) $^1J_{\text{PH}} < ^1J_{\text{PB}}$

3

OR

Predict and draw the ^{11}B NMR spectrum of $\text{B}_{10}\text{H}_{10}^{2-}$ ion. Comment on the line width of the spectrum.

6. How many signals do you expect in low and high temperature measurements of the ^1H NMR spectra for the coordinated ethene in the complex $[\text{RhCp}(\text{C}_2\text{H}_4)_2]$? Explain briefly.

3

OR

How do you derive rate constant and the Gibbs free energy from dynamic NMR? Explain briefly.

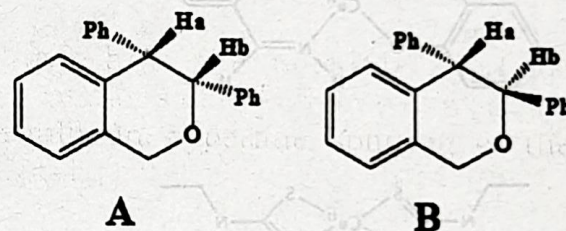
7. Answer **any two** :

$2 \times 2.5 = 5$

- (a) What is the pseudo contact shift observed for paramagnetic metal complexes? How does it provide structural information?

- (b) Why are the solid state NMR spectra broad? How do you simplify it?

- (c) How does the NOE depend on rotational correlation time (τ_c)? How do you use NOE to establish relative configurations of the following structures?



8. A paramagnetic compound is analyzed by an EPR experiment using a microwave radiation of 9400MHz . Predict the position of the EPR signal in Gauss. [Given that, $g_e = 2.0023$, $\beta_e = 9.274 \times 10^{-24}\text{J/T}$]. What are X- and P-band EPR?

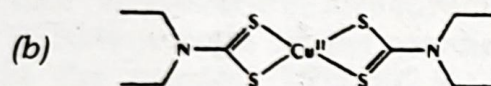
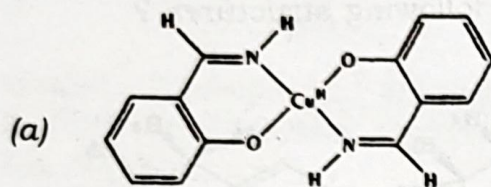
$4 + 1 = 5$

9. Show how the possible nuclear spin orientations of the protons in methyl radical results in hyperfine splitting of the EPR signal.

5

OR

Predict and justify the EPR spectrum observed for the following copper(II) complex (any one). 5

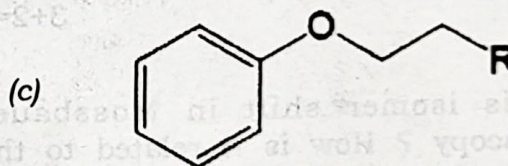
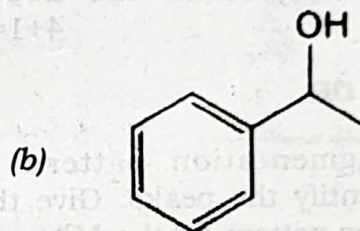
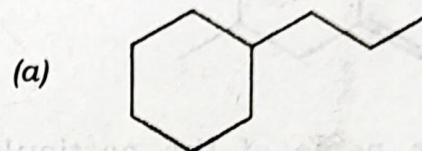


10. Write down the basic working principle of ESI-MS with representative diagram. 5

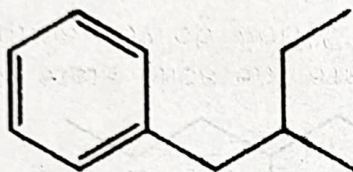
OR

What are the different analysis techniques used for detection of radicals/ions in the mass spectrometry? Explain with suitable examples. 5

11. Show the fragmentation pattern obtained for the following molecules in mass spectroscopy. Indicate m/z value for the major fragment (any two). 2×2.5=5



12. Explain the fragmentation pattern for the following molecule and identify the major peaks.



What is the name of the particular rearrangement involved in the above process?
4+1=5

OR

Explain the fragmentation pattern of ferrocene and identify the peaks. Give the isotopic distribution pattern for the M^{2+} peak in the mass spectra of $[Ru(bipy)_3]Cl_2$.
3+2=5

13. What is isomer shift in Mossbauer spectroscopy? How is it related to the s-electron densities and sizes of the ground and excited state nuclei? Give *two* examples of Mossbauer active nuclei other than ^{57}Fe . What are most suitable excited state lifetime and transition energy of nuclei for Mossbauer spectroscopy?
1+1+1+2=5

OR

$K_4Fe(CN)_6 \cdot 3H_2O$ displays one signal, whereas $K_3Fe(CN)_6$ gives two signals in Mossbauer spectra. Justify. Explain quadrupole splitting with suitable example.
2.5+2.5=5
