3 (Sem–6) CHM M 1

2021

CHEMISTRY

(Major)

Paper : 6·1

(*Spectroscopy*)

Full Marks : 60

Time : Three hours

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

GROUP– A

1.   Answer **all** questions :   1×5=5

 *(a)*   What is the ideal signal to noise ratio of a modern spectrophotometer ?   1

(b) Fill in the blank : 1

The Gaussian shape of a Doppler-broadened spectral line reflects the Boltzmann distribution of translational kinetic energies in the sample at the temperature of the experiment. The line _____ as the temperature is increased.

(c) Sketch the layout of a typical spectrometer. 1

(d) If the energy spacing between the consecutive translational, rotational and vibrational levels is considered, arrange them in decreasing order of energy spacing. 1

(e) Identify the regions of the electromagnetic spectrum to which the following transitions belong : 1

$$\sigma \to \sigma^*$$
$$n \to \pi^*$$
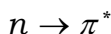
2. Answer **all** questions : 2×5=10

(a) Symmetric top molecules can be further subdivided. Explain this statement with examples. 2

(b) How would you expect widening of the slits in a spectrometer to affect its resolution and its sensitivity ?   2

*(c)* Convert the following spectroscopic quantities as indicated :   1+1

$2000\,cm^{-1}$ to μm

$9\,GHz$ to cm^{-1}

State in which region of the electromagnetic spectrum would you expect each to appear.

(d) Calculate the relative population of the first two rotational levels for HCl at $300\,K$, given that the value of rotational constant is $10{\cdot}59\ cm^{-1}$.   2

(e) The correct order of the ^1H NMR chemical shift values for the indicated hydrogen in the following compounds is

2̰
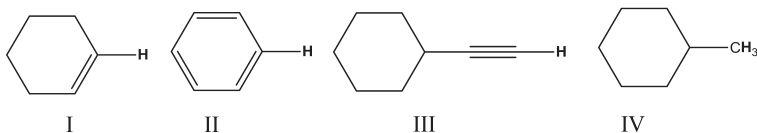
I   II   III   IV

(i)   I > II > III > IV

(ii)   II > I > III > IV

(iii)   III > II > I > IV

(iv)   II > III > IV > I

3. Answer **any three** among (a), (b), (c), (d) and (e) : 5×3=15

(a) Describe the factors (in brief) on which the line width of a spectral line depends.

When is line width called a natural line width ?

How is line width related to pressure ?

3+1+1=5

(b) (i) Taking the example of HCl molecule, discuss the physical origin of the gross selection rules for microwave spectroscopy. 2

(ii) The first line in the rotational spectrum of carbon monoxide is observed at 3·84235 cm^{-1}. Calculate the value of moment inertia (I_{co}) and interatomic distance (r_{co}) in carbon monoxide considering it as a rigid rotor. (Absolute mass of carbon and oxygen are 19·921×10^{-27} kg and 26·561×10^{-27} kg respectively). 3

(c) (i) What do you mean by chemical shift in NMR spectroscopy ? 2

(ii) Define the δ scale of chemical shift.

1

(iii) Why is TMS chosen as a reference in NMR spectroscopy ? 2

(d) (i) Show diagrammatically the vector summation of $l=\sqrt{2}$ and $s=\sqrt{3}/2.$ 2

(ii) Determine the term, symbols arising for the pair of non-equivalent electrons pd ? 3

(e) (i) For HCl, equilibrium oscillation frequency (ϖ_e) and anharmonicity constant (χ_e) values are given as 2990 cm^{-1} and 0·0174 respectively. Calculate the energy of absorption in cm^{-1} for the hot band in HCl. 2

(ii) The vibrational spectrum of compounds such as water is more complex than expected on the basis of fundamental frequencies. Explain. 3

GROUP–B

*Answer **any three** questions among 4, 5, 6, 7 and 8.*

4. (a) Explain with diagram, the appearance of $P-$, $Q-$, and R-branches in the rotation-vibration spectrum of a diatomic molecule. 5

(b) If the wave number of the $J = 3 \leftarrow 2$ rotational transition of $^1H\,^{35}Cl$ considered as a rigid rotor is 63·56 cm^{-1}. What is the (i) moment of inertia of the molecule (ii) the bond length of HCl? 5

5. (a) Distinguish between molecular ion peak and base peak in mass spectroscopy. 2

(b) In the mass spectrum of 2-methylpentane, prominent peaks are observed at m/z values of 71 and 43 respectively. Identify the species responsible for this peak showing fragmentation pattern. 3

(c) For a simple spectrometer, show that —

$$\frac{m}{z} = \frac{B^2 r^2}{2V}$$

where B, r, and V are magnetic field strength, radius of circular motion and electrostatic field of voltage. 5

6. (a) Discuss in brief, the principle of NMR spectroscopy. 3

(b) Between ethene and ethyne whose ^1H NMR appears more upfield. Why ?

2

(c) Sketch the ^1H NMR spectra of (i) pure sample of ethanol (ii) slightly impure sample of ethanol. Explain the difference in the spectra. 3+2

7. (a) In vibrational spectroscopy, what are the selection rules for harmonic and anharmonic oscillator ? 2

(b) Using Woodward rule show that λ_{max} of $\pi \rightarrow \pi^*$ transition in the following compound is 313 nm. 2
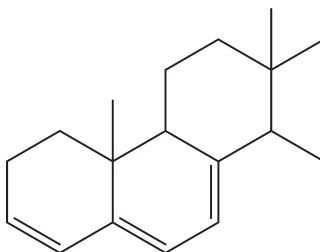
(c) What is the effect on $\pi \rightarrow \pi^*$ transition on increasing conjugation ? Explain using buta-1,3-diene and hexa-1, 3, 5-triene. 2

Contd.

(d) Electronic transitions are accompanied by vibrational transitions. Discuss with appropriate diagrams, how the electronic spectral lines would appear, if —

    (i) the internuclear distances in the excited and the ground state is equal

    (ii) the internuclear distances in the excited is smaller than in the ground state.   2+2

8. (a) Draw schematic diagram to show the effect of applied magnetic field (B_z) on the spin states of a proton.   2

    (b) The gyromagnetic ratio of a proton is $26 \cdot 75 \times 10^7 \ T^{-1} \ s^{-1}$. Calculate the value of Larmor frequency at an magnetic field of $14 \cdot 4 \ T$.   3

    (c) Discuss the effect of isotopic substitution in vibrational spectroscopy or rotational spectroscopy.   5

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