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6 SEM TDC CHM M 7 (N/O)

2018

(May)

CHEMISTRY

(Major)

Course : 607

(Spectroscopy)

The figures in the margin indicate full marks for the questions

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Choose the correct answer : 1×5=5

(a) Radio frequency radiations are useful in causing transition for

(i) mass spectrum

(ii) NMR spectrum

(iii) Raman spectrum

(iv) None of the above

(b) An auxochrome is one which is
  (i) colour enhancing
  (ii) a group or an atom with lone pairs of electrons
  (iii) extending conjugation
  (iv) All of the above

(c) The IR band spectra show the changes in vibrational and rotational energies of a molecule subject to selection rule
  (i) $\Delta v = 0,\ \Delta j = \pm 1$
  (ii) $\Delta v = \pm 1,\ \Delta j = \pm 1$
  (iii) $\Delta v = \pm 1,\ \Delta j = \pm 2$
  (iv) $\Delta v = 0,\ \Delta j = 0$

(d) Raman effect is
  (i) absorption of light
  (ii) emission of light
  (iii) inelastic scattering of light
  (iv) elastic scattering of light

(e) The multiplicity of signals in $CH_3CH_2OCH_2CH_3$ in NMR spectrum is
  (i) two triplets
  (ii) one triplet and one quartet
  (iii) two singlets
  (iv) two singlets and two triplets

(Continued)

2. Answer any *five* of the following : 2×5=10

(a) Compared to the number of bonds in a molecule, there are generally more number of peaks in the infrared spectrum. Explain.

(b) The nuclei ^{1}H and ^{13}C are suitable for NMR investigation. Explain why.

(c) Describe briefly 'fingerprint region' of infrared spectroscpy.

(d) Stokes lines are more intense than anti-Stokes lines. Explain.

(e) Microwave studies are done only in gaseous state. Why?

(f) Aniline absorbs at 280 nm, but in acidic medium this absorption band is seen at 203 nm. Explain giving proper reason.

UNIT—I

3. *(a)* Show that the lines in the rotational spectrum of a diatomic molecule are equispaced under rigid rotator approximation. 2½

(b) Find the value of rotational quantum number j in the most highly populated rotational level of CH_4 ($B = 5{\cdot}24\ cm^{-1}$) at room temperature. 2½

UNIT—II

4. *(a)* Explain the effect of anharmonicity on the vibrational spectra of diatomic molecules. 3

Or

Sketch the normal modes of vibration of a non-linear triatomic molecule AB_2 and predict the IR active bands. Give reason in support of your answer.

(b) Explain what will happen when a molecule is irradiated with infrared radiations. 2

(c) The C—H stretching vibration in chloroform occurs at 3000 cm^{-1}. Calculate the C—D stretching frequency in deuterochloroform. 3

UNIT—III

5. *(a)* Explain the application of Raman spectroscopy in determining the structure of a molecule with specific examples. 3

(b) A sample was excited by the 4358 Å line of mercury. A Raman line was observed at 4447 Å. Calculate the Raman shift in cm^{-1}. 3

Or

Discuss the quantum mechanical explanation of Raman effect.

(c) Write the condition for the molecule to be Raman active. 1

UNIT—IV

6. *(a)* State and explain Franck-Condon principle. 3

(b) Explain the effects of change of solvents on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. 2

(c) What do you mean by a good solvent in UV spectroscopy? 1

UNIT—V

7. *(a)* Write two applications of ESR spectroscopy. Predict the number of lines in the ESR spectra of the following systems : 1+1+1=3

(i) $CH_3\dot{C}H_2$

(ii) $\dot{C}H_3$

Or

Discuss briefly the principle of ESR spectroscopy. 3

(b) Discuss the relaxation processes in NMR spectroscopy. 3

Or

Describe Larmor precession and precessional frequency.

(c) Define coupling constant. 1

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Choose the correct answer : 1×5=5

(a) In order to be microwave active

(i) the molecule must have permanent dipole moment

(ii) the dipole moment of the molecule must change during vibration

(iii) the polarizability of the molecule must change during vibration

(iv) None of the above

(b) An auxochrome is one which is

(i) colour enhancing

(ii) a group or an atom with lone pairs of electrons

(iii) extending conjugation

(iv) All of the above

(c) For a linear molecule such as HCl, the number of modes of vibration is

(i) 0

(ii) 1

(iii) 2

(iv) 3

(d) Raman effect is
  (i) absorption of light
  (ii) emission of light
  (iii) inelastic scattering of light
  (iv) elastic scattering of light

(e) The NMR spectroscopy is useful for the detection of
  (i) hydrogen bonding
  (ii) aromaticity
  (iii) geometrical isomers
  (iv) All of the above

2. Answer any *five* of the following : 2×5=10

(a) What do you mean by a good solvent in UV spectroscopy and what is its effect on absorption maximum?

(b) Explain the fundamental vibrations and overtones.

(c) Microwave studies are done only in gaseous state. Explain why.

(d) Stokes lines are more intense than anti-Stokes lines. Explain.

(e) Write the selection rules for electronic transitions.

(f) Explain why TMS is used as a reference substance in NMR spectroscopy.

UNIT—I

3. *(a)* Show that the lines in the rotational spectrum of a diatomic molecule are equispaced under rigid rotator approximation. 2½

(b) The rotational spectrum of HCl molecules shows that the rotational lines are equally separated by $20{\cdot}70\ cm^{-1}$. Calculate the internuclear bond length. 2½

UNIT—II

4. *(a)* Show that the frequency of the absorbed radiation in pure vibrational spectra is equal to the fundamental frequency of vibration ν_0 of the molecule. 3

Or

Explain fundamental frequencies, overtones and combination bands with examples.

(b) Calculate the force constant for $H^{35}Cl$ from the fact that the fundamental vibrational frequency is $8{\cdot}667\times10^{13}\ s^{-1}$. 3

(c) Briefly describe Fermi resonance. 2

UNIT—III

5. *(a)* Explain the application of Raman spectroscopy in determining the structure of a molecule with specific examples. 3

(b) Discuss the quantum mechanical explanation of Raman effect. 3

(c) Write the condition for the molecule to be Raman active. 1

UNIT—IV

6. *(a)* State and explain Franck-Condon principle. 3

(b) The intensity of $\pi \rightarrow \pi^*$ transitions is 10 to 100 times stronger than $n \rightarrow \pi^*$ transitions. Explain. 2

Or

Distinguish redshift from blueshift with one example.

(c) What informations can be obtained from molar extinction coefficient? 1

UNIT—V

7. *(a)* Write two applications of ESR spectroscopy. Predict the number of lines in the ESR spectra of the following systems : 1+1+1=3

(i) $CH_3\dot{C}H_2$

(ii) $\dot{C}H_3$

Or

Explain spin-spin splitting. 3

(b) What is chemical shift in NMR spectroscopy? Mention the factors that affect chemical shift. 1+2=3

(c) Define coupling constant. 1

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