

Roll No.

E-308

M. Sc. (First Semester)

EXAMINATION, Dec.-Jan., 2020-21

CHEMISTRY

Paper Fourth

(Theory and Application of Spectroscopy—I)

Time : Three Hours]

[Maximum Marks : 80

[Minimum Pass Marks : 16

Note : Attempt all Parts as directed.

Part—A

1 each

(Objective/Multiple Choice Questions)

Note : Attempt all questions.

Choose the correct answer :

1. Microwave spectrum is observed due to the change of :

- (a) Orientation of molecules
- (b) Configuration of molecules
- (c) Electron distribution
- (d) Nuclear configuration

P. T. O.

2. According to Born-Oppenheimer approximation the best sequence of energy would be :

(a) $E_{\text{ele}} > E_{\text{vib}} > E_{\text{rot}} > E_{\text{tra}}$

(b) $E_{\text{vib}} > E_{\text{ele}} > E_{\text{rot}} > E_{\text{tra}}$

(c) $E_{\text{tra}} > E_{\text{rot}} > E_{\text{vib}} > E_{\text{ele}}$

(d) None of the above is correct

3. The force constants of four diatomic molecules are given below :

Molecule	$\frac{K}{\text{N M}^{-1}}$
F_2	450
HCl	510
CO	1860
N_2	2240

Which of the four molecules has the highest vibrational wave number ?

(a) N_2

(b) HCl

(c) CO

(d) F_2

4. Which of the following molecules will not display an infrared spectrum ?
- (a) CO_2
 - (b) N_2
 - (c) benzene
 - (d) HCCH
5. Electromagnetic waves consist of :
- (a) Compressions and rarefactions.
 - (b) Vibrating electric and magnetic fields.
 - (c) Particles of light energy.
 - (d) High-frequency gravitational waves.
6. The microwave active molecules are :
- (a) HCl, OCS
 - (b) CO, CO_2
 - (c) both (a) and (b)
 - (d) None of the above
7. Which molecules have three rotational constants of microwave spectrum ?
- (a) Prolate symmetric top
 - (b) Spherical top
 - (c) Asymmetric top
 - (d) Oblate symmetric top

8. Transition from one rotational state to other in rotational state is governed by :
- (a) Bohr quantum condition
 - (b) $\Delta J = \pm J$
 - (c) Molecule must have permanent dipole moment
 - (d) All of the above
9. Which spectroscopy is used in chemical examination of interstellar space ?
- (a) NMR spectroscopy
 - (b) Infrared spectroscopy
 - (c) Raman spectroscopy
 - (d) Microwave spectroscopy
10. Microwave spectroscopy is generally used to detect
- (a) Functional groups
 - (b) Double bonds
 - (c) Unpaired electrons
 - (d) Isotopes
11. Which statement is correct about the vibrational ground state of an H_2 molecule ?
- (a) The molecule is static in its ground state

- (b) The molecule is vibrating
 - (c) The molecule is in its lowest vibrational level but is not vibrating.
 - (d) In its vibrational ground state, the molecule has no vibrational energy
12. Match the molecular formula to the number of degrees of vibrational freedom. Which pair is correct ?
- (a) $\text{H}_2\text{S} : 4$
 - (b) $\text{CO}_2 : 3$
 - (c) $\text{SO}_2 : 3$
 - (d) $\text{CS}_2 : 3$
13. Which of the following statements is correct about the principal moments of inertia of an XY molecule that lies on the A axis ?
- (a) $I_A = 0$ and $I_B = I_C$
 - (b) $I_A = I_B$ and $I_C = 0$
 - (c) $I_A = I_B = I_C$
 - (d) $I_A > I_B$ and $I_B = I_C$
14. On which factors the vibrational stretching frequencies of diatomic molecule depend ?
- (a) Force constant

- (b) Atomic population
 - (c) Temperature
 - (d) Magnetic field
15. In IR spectroscopy which frequency range is known as the fingerprint region ?
- (a) $1400-900 \text{ cm}^{-1}$
 - (b) $667-1500 \text{ cm}^{-1}$
 - (c) $900-600 \text{ cm}^{-1}$
 - (d) $600-250 \text{ cm}^{-1}$
16. Raman effect is :
- (a) Absorption of light
 - (b) Emission of light
 - (c) Elastic scattering of light
 - (d) Inelastic scattering of light
17. The rotational Raman spectrum consists of a series of lines at frequencies of :
- (a) $6B, 8B, 16B \dots$
 - (b) $4B, 8B, 12B \dots$
 - (c) $6B, 12B, 18B \dots$
 - (d) $6B, 10B, 14B \dots$

18. When the scattered radiation has the same energy as the incident photon, the scattering is called :
- (a) Stokes
 - (b) Anti-stokes
 - (c) Rayleigh
 - (d) Raman
19. Selection rule for Raman spectroscopy :
- (a) $\Delta J = \pm 1$
 - (b) $\Delta J = 0, \pm 1, \pm 2, \dots$
 - (c) $\Delta J = \pm 2$
 - (d) $\Delta J = 0$
20. The transition zone for Raman spectra is :
- (a) Between vibrational and rotational level
 - (b) Between electronic levels
 - (c) Between magnetic levels of unpaired electrons
 - (d) Between magnetic levels of paired electrons

Part—B

(Very Short Answer Type Questions)

Note : Write answer in 2-3 sentences. Each question carries 2 marks.

1. Enlist different regions of electromagnetic spectrum.

2. Write any *one* advantage of a 'modulator' used in spectroscopic instrumentation.
3. What is the condition for a molecule to be microwave active ? Why ?
4. Write down *one* example of symmetric top and spherical top molecules.
5. What are basic differences between IR and FTIR spectroscopy ? Explain 'Pellet' making in IR spectroscopy
6. What is Fourier transformation ? Write the mathematical formula of FT process.
7. Write a brief note on factors affecting intensity of spectral lines.
8. Define degeneracy and explain it in detail for energy levels $J = 1$ and $J = 2$.

Part—C

(Short Answer Type Questions)

Note : Write answer in < 75 words. Each question carries 3 marks.

1. What is the effect of breakdown of Born-Oppenheimer approximation on P and R branches of the IR spectrum of a diatomic molecule ?

2. Write brief notes on any two of the following :
 - (a) Basic components of a spectrometer
 - (b) Natural line width and broadening
 - (c) Polarization and scattering
3. What should not be the physical state of the sample for microwave spectroscopy ? Give the simplified diagram of microwave spectrometer.
4. What is the effect of isotopic substitution on microwave spectra of linear diatomic molecule ?
5. What is the significance of zero point energy ? Obtain an expression for zero point energy of an anharmonic oscillator.
6. Write a short note on P, Q and R branches observed in IR spectrum of a diatomic molecule.
7. Why is the selection rule for pure rotational Raman spectrum $\Delta J = \pm 2$ and $\Delta J = \pm 1$ for pure rotational spectroscopy ?
8. What are the two methods of excitation of the samples in Raman spectroscopy ? Explain the instrumentation of Raman spectroscopy.

Part—D

(Long Answer Type Questions)

Note : Write answer in < 150 words. Each question carries 5 marks.

1. What is electromagnetic radiation ? Deduce relationships between various energy parameters of an electromagnetic radiation.

Or

Discuss the attainment of population inversion in case of a three-level laser system. Briefly explain the Doppler line broadening mechanism ?

2. What is microwave spectroscopy ? Classify of molecules in term of their internal rotation mechanism.

Or

The first line ($J = 0$) in the rotation spectrum of carbon monoxide is observed at 3.84235 cm^{-1} . Determine the r_{co}

value $[h = 6.626 \times 10^{-34} \text{ joules molecules}^{-1};$

$c = 3 \times 10^{10} \text{ cm s}^{-1}; \text{ abs. Mass of H-atom} = 1.673433 \times 10^{-27} \text{ kg}]$.

3. The equilibrium vibration frequency of the iodine molecule is 215 cm^{-1} and the anharmonicity constant (X_e) is 0.003. What is the intensity of the hot band for $V=1$ to V_2 , relative to the fundamental $V = 0$ to $V = 1$, if the temperature is 300 K.

Or

Discuss the Fourier Transformation. With necessary sketch explain principle, working method and applications of Fourier transform infrared (FTIR) spectroscopy.

4. Discuss the theory of pure rotational Raman spectra of linear molecule. Sketch the energy levels and the spectrum arising from transition between them.

Or

Write notes on the following :

- (a) Coherent anti-Stokes Raman spectroscopy
- (b) Application of Raman effect in molecular structures