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M.Sc. (First Semester)
EXAMINATION, Dec. - Jan., 2021-22
Paper Fourth
(Theory and Applications of spectroscopy - I)

Time : Three Hours   *[Maximum Marks : 80*

Section - A

(Objective/Multiple Choice Questions)

(1 mark each)

Note : Attempt all questions.

1. Select the correct statement from the following option.

   (A) Spectroscopic methods require less time and more amount of sample than classical methods.

   (B) Spectroscopic methods require more time and more amount of sample than classical methods.

   (C) Spectroscopic methods require less time and less amount of sample than classical methods.

   (D) Spectroscopic methods require more time and less amount of sample than classical methods.

2. How many degrees of freedom does a chemical compound of N atoms have?

   (A) 2N   (B) 2N + 1

   (C) 3N   (D) 3N + 1

3. For a particular vibrational mode to appear in the Raman spectrum, what must change?

   (A) Frequency of radiation

   (B) Intensity of radiation

   (C) Molecule's shape

   (D) Molecule's polarizability

4. What is the order of decreasing vibrational frequency for C - Cl, C - Br, C - C,   C - O and C - H?

   (A) C - H, C - C, C - O, C - Cl, C - Br

   (B) C - Cl, C - Br, C - C, C - H, C - O

   (C) C - O, C - H, C - Br, C - Cl, C - C

   (D) C - Br, C - Cl, C - C, C - O, C - H

5. Which of the following lines are most intense?

   (A) Stokes lines

   (B) Rayleigh-scattered lines

   (C) Anti-strokes lines

   (D) All have same intensity

6. For a particular vibrational mode to appear in the Raman specturm, What must change?

   (A) Frequency of radiation

   (B) Intensity of radiation

   (C) Molecule's shape

   (D) Molecule's polarizability

7. The elastic scattering of photons is called as_____

   (A) Atmospheric scattering

   (B) Rayleigh Scattering

   (C) Conserved Scattering

   (D) Raman Scattering

8. The number of vibrational modes for the acetaldehyde is:

   (A) 23

   (B) 24

   (C) 15

   (D) 9

9. The vibrational frequency of stretching vibration of the di-atomic molecule in the above question will be:

   (A) $v/2\pi = \sqrt{(\mu/k)}$

   (B) $v/2\pi = \sqrt{(k/\mu)}$

   (C) $v = 1/2\pi\sqrt{(\mu/k)}$

   (D) $v = 1/2\pi\sqrt{(k/\mu)}$

10. The solid samples are analysed in IR spectroscopic analysis by -

    (A) Preparing a solution of analyte

    (B) Using a mulling agent

    (C) Pyrrolysis

    (D) All of the above

11. Which of the following bending vibration takes place in different planes?

    (A) Asymmetric stretching

    (B) Rocking

    (C) Scissoring

    (D) Twisting

12. How many vibrational modes are possible for HCl?

    (A) 0

    (B) 1

    (C) 2

    (D) 3

13. Which of the following vibrational mode of CO_2 is IR active?

    (A) Symmetric stretching

    (B) Asymmetric stretching

    (C) Both A and B

    (D) None

14. Which of the following comparison is correct for solvent shift on the n $->\pi*$ transition of acetone?

(A) $H_2O=CH_3OH=C_2H_5OH=CHCl_3=C_6H_{14}$

(B) $H_2O>CH_3OH>C_2H_5OH>CHCl_3>C_6H_{14}$

(C) $H_2O<CH_3OH<C_2H_5OH<CHCl_3<C_6H_{14}$

(D) $H_2O>CH_3OH<C_2H_5OH<CHCl_3<C_6H_{14}$

15. What is the correct order of λ_{max} for $n->\pi*$ transition for the following three compounds?

(A) RCOOH > RCOOR' > RCONH$_2$

(B) RCOOH = RCOOR' = RCONH$_2$

(C) RCOOH = RCOOR' < RCONH$_2$

(D) RCOOH = RCOOR' > RCONH$_2$

16. The ultraviolet spectrum of benzonitrile shows a secondary absorption band at 271 nm. If a solution of benzonitrile in water, with a concentration of 1 x 10^{-4} molar solution is examined at 271 nm, what will be the absorbance reading $(\varepsilon = 1000)$ and what will be the intensity ratio, Io/I, respectively?

(A) 0.1, 1.26

(B) 0.2, 2.26

(C) 0.3, 3.26

(D) 0.4, 4.26

17. Why ketenes absorb in IR at a very high frequency (2150 cm^{-1})?

(A) The inner C is sp hybridized

(B) The more s character in a bond, the stronger it is

(C) Inner C is sp^2 hybridized

(D) Inner C is sp^3 hybridized

18. What is the number of vibrational degrees of freedom in $C_6H_5CH_3$?

(A) 39

(B) 15

(C) 18

(D) 40

19. Why Monomeric saturated aliphatic carboxylic acids show carbonyl stretching frequency near 1760 cm^{-1}, while saturated aliphatic ketones near 1720 cm^{-1}?

(A) Mesomeric (M) effect is dominant in acids over the inductive (1) effect

(B) 1 effect is dominant in carboxylic acids over the mesomeric effect

(C) 1 effect on ketones is dominant over the M effect

(D) M effect in ketones is dominant

20. The third and fourth line in the rotational Raman spectrum of CO are separate by 8cm⁻¹, The CO bond length is given by:

(A) $\sqrt{\dfrac{h}{16\pi^2 \mu c}}$

(B) $\sqrt{\dfrac{3h}{16\pi^2 \mu c}}$

(C) $\sqrt{\dfrac{5h}{32\pi^2 \mu c}}$

(D) $\sqrt{\dfrac{h}{32\pi^2 \mu c}}$

Section - B

(Very Short Answer Type Questions)

(2 marks each)

Note: Attempt any eight questions.

1. Write about the source of Raman spectroscopy.

2. Write about filters in Raman spectroscopy.

3. Write two applications of IR spectroscopy.

4. Define selection rules.

5. What is dispersion?

6. Write a note on Born - Oppenheimer approximation.

7. What is electromagnetic radiation?

8. Write a note on the thermistors used in IR spectroscopy.

9. Why is CH4 Raman active?

10. Write a note on Vibrational coarse structure.

Section - C

(Short Answer Type Questions)

(3 marks each)

Note: Attempt any eight questions:

1. Explain the different sampling techniques in IR spectroscopy

2. Explain factors determining the intensity of spectral lines.

3. Describe the brief rotational fine structure of electronic-vibration transitions.

4. Write a short note on P,Q and R branches observed in IR spectrum of a diatomic molecule.

5. Discuss the principle of IR spectroscopy in molecular structure elucidation.

6. What are symmetric and asymmertric vibrations? Explain with the example of H_2O molecule.

7. Explain the activity of the following molecules with respect to IR and microwave specturm. H_2, HCl, CO_2, H_4 & CH_3Cl

8. The first line in the rotational spectrum of ¹²C¹⁶O molecule is 3.84235cm⁻¹. Find out the bond length of the molecule.

Section - D

(Long Answer Type Questions)

(5 marks each)

Note : Attempt following questions.

1. (i) How does IR spectroscopy differ from Raman spectroscopy?

   (ii) Write about the sample in microwave spectroscopy.

   OR

   (i) Write about detectors in microwave spectroscopy.

   (ii) What is the condition for a molecule to be microwave active? Why?

2. (i) Why isoxygenmolecule does not microwave active?

   (ii) Explain various advantages of Fourier transform spectroscopy.

   OR

   (i) Unkonwn molecule with molecular formula $C_5H_{10}O$. Which of these five molecules is it most likely to be?
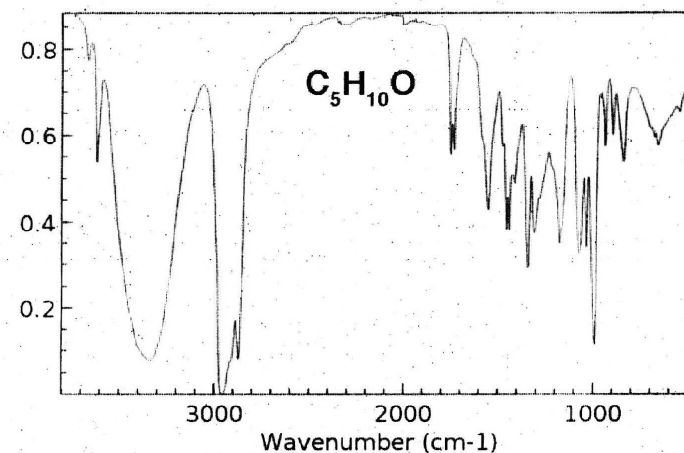
   Which of these molecules best corresponds to the IR spectrum below?

   a) b) c) d) e)

$C_5H_{10}O$
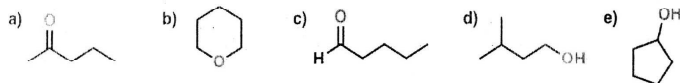
Wavenumber (cm-1)

(ii) Discuss the IR bands can be classified as strong (s), medium (m), or weak (w)

3. (i) Calculate the wavenumber shift for the vibrational mode of Cl_2, given that the force constant k for the bond is 3.23 N cm^{-1}.

   (ii) What advantages does Raman spectroscopy have for process monitoring?

   OR

   (i) The equilibrium vibration frequency of the iodine molecule is 215 cm^{-1} and the anharmonicity constant xe is 0.003. What is the intensity of the hot band for V = 1 to V = 2, realative to the fundamental V = 0 to V = 1, if the temperature is 300K?

   (ii) What is electromagnetic radiation?

4. (i)   Why are Raman signals weak?

    (ii)   Why do the anti - Stokes lines of carbon tetrachloride
           have the following order of intensity: 219 > 314 > 459
           cm^{-1}?

OR

    (i)   Which source is used in microwave spectrometer?

    (ii)   The average spacing between successive rotating
           lines of CO_2 is 3.826 cm^{-1}. Determine the transition
           which gives most intense spectral line at 3.

    (iii) Explain various advantages of Fourier transform
           spectroscopy.