



# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

## M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – NOVEMBER 2016

### CH 3810 - MOLECULAR SPECTROSCOPY

Date: 05-11-2016  
Time: 09:00-12:00

Dept. No.

Max. : 100 Marks

#### Part-A

Answer ALL questions.

(10 × 2 = 20)

1. Calculate the uncertainty in the excited state energy level when a molecule makes a transition between the ground and excited state with a lifetime of  $10^{-3}$  s.
2. Mention the difference between prolate and oblate symmetric top molecules.
3. The normal modes of vibration of CO<sub>2</sub> molecule are  $\nu_1=1330$ ,  $\nu_2=667$  and  $\nu_3=2349$  cm<sup>-1</sup>. Calculate its zero point energy.
4. What is the difference between mechanical and electrical anharmonicity?
5. Why are anti-Stokes lines less intense than Stokes lines?
6. Sketch the <sup>19</sup>F NMR of ClF<sub>3</sub> molecule.
7. What are Kramer's doublets?
8. Isomer shift is a function of 's' electron density-Justify.
9. The EPR spectrum of the radical AB<sub>3</sub>• shows 6 lines. Calculate the spin of the atom A.
10. Define coupling constant.

#### Part-B

Answer any EIGHT questions.

(8 × 5 = 40)

11. The fundamental and first overtone transition of <sup>14</sup>N<sup>16</sup>O are centered at 1876.06 cm<sup>-1</sup> and 3724.20 cm<sup>-1</sup> respectively. Evaluate the equilibrium vibration frequency and zero point energy. Mass of <sup>14</sup>N = 23.25 × 10<sup>-27</sup> kg and mass of <sup>16</sup>O = 26.56 10<sup>-27</sup> kg.
12. Calculate the average period of rotation of HCl molecule if it is in the J = 1 state. The internuclear distance of HCl is 0.1274 nm. The mass of hydrogen and chlorine atoms are 1.673 × 10<sup>-27</sup> kg and 58.06 × 10<sup>-27</sup> kg, respectively.
13. What are the causes of overtones and difference bands?
14. The first 3 stokes lines in the rotational Raman spectrum of <sup>16</sup>O<sub>2</sub> are separated by 14.4, 25.8 and 37.4 cm<sup>-1</sup> from the exciting radiation. Using the rigid rotor model, obtain the value of r<sub>0</sub>.
15. Explain the factors affecting the intensity of the spectral lines.
16. Discuss the Stark effect of J=0 → J=1 transition for a linear molecule.
17. Account for the following.
  - i) EPR spectra are recorded in first derivative mode.
  - ii) EPR is recorded in microwave region.
18. Discuss diamagnetic anisotropy with an example.
19. Explain the factors influencing geminal and vicinal coupling in NMR.
20. How are molecular ion and isotope peaks useful in the determination of molecular formula?
21. Explain the quadrupole transitions possible in spherically and axially symmetric fields.
- 22 a. Calculate the chemical shift of a <sup>1</sup>H-NMR signal which appears at 180 Hz in a 60 MHz instrument. Find out the frequency at which the same signal would appear in a 100 MHz instrument. (3)
- b. What is FID? (2)

### Part-C

Answer any **FOUR** questions.

(4 × 10 = 40)

- 23 a. Apply the selection rules for parallel and perpendicular vibrations of a symmetric top molecule and explain the formation of P, Q and R branches. (5)
- b. The equilibrium vibration frequency of iodine molecule is  $215 \text{ cm}^{-1}$  and the anharmonicity constant is 0.003. What is the intensity of the hot band  $\nu = 1 \rightarrow \nu = 2$  relative to that of the fundamental  $\nu = 0 \rightarrow \nu = 1$ , if the temperature is 300K? (5)
24. Explain the rotational Raman spectra of a linear molecule with an example.
- 25 a. Discuss the various types of transitions possible in electronic spectroscopy. (5)
- b. State the principle of i) PES and ii) Fluorescence. (5)
- 26 a. Explain the principle of heterocorrelation spectroscopy with an example. (6)
- b. Compare the  $^1\text{H-NMR}$  spectra of  $\text{PH}_3$  and  $\text{NH}_3$  molecules. (4)
- 27 a. What is quadrupole splitting? How will you account for the quadrupole splitting shown by  $\text{Fe}(\text{CO})_5$  molecule? (6)
- b. Predict the number of EPR transitions possible for low spin  $d^7$  octahedral complex. (4)
28. What is the principle of Mossbauer spectroscopy? Explain the spectral features of low and high spin iron complexes.

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