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End Semester Examination, December 2024
B.Sc. Chemistry (Honors) – Vth Semester
Molecular Spectroscopy & Photochemistry (BSCH303A)

Time: 2.5 hrs.

Max Marks: **50**

Note: *All Questions are compulsory. Marks are indicated against each question.*

PART-A

Q.1 *Attempt any five questions:*

- | | |
|--|-----------------------|
| (a) Explain the Born-Oppenheimer approximation. | [CO-1] [L-2] 2 |
| (b) List out which of the molecules can have a pure rotational spectrum?
Cl ₂ , OCS, CH ₄ , N ₂ O, HCl, O ₂ , CO ₂ | [CO-1] [L-1] 2 |
| (c) Explain the selection rules for vibrational spectroscopy of diatomic molecules. | [CO-1] [L-2] 2 |
| (d) Describe the term "quantum yield" in photochemistry. | [CO-1] [L-2] 2 |
| (e) Explain the rule of mutual exclusion. | [CO-1] [L-2] 2 |
| (f) Define the interaction of electromagnetic radiation with molecules and discuss the types of spectra generated. | [CO-1] [L-1] 2 |
| (g) Explain the primary and secondary process in photochemistry. | [CO-1] [L-2] 2 |

2x5

PART-B

- Q.2 (i) Explain the laws of photochemistry and their implications. [CO-4] [L-] **5**
(ii) The rotational spectrum of HCl shows a series of equidistant lines spaced 4.83 cm^{-1} apart. Calculate the moment of inertia and bond length of HCl molecule. [CO-2] [L-] **5**

OR

- (i) Describe isotopic substitution in rotational spectroscopy and its effect on the spectral lines.
(ii) Discuss the concept of anharmonicity in molecular vibrations and its significance in vibrational spectroscopy. [CO-2] [L-2] **5+5**

- Q.3 (i) What is the Raman effect? Describe the differences in intensity between Stokes and anti-Stokes lines in Raman spectra. [CO-3] [L-2] **5+5**

- (ii) Explain overtones and hot bands in vibrational spectroscopy.

[CO-3] [L-] **10**

OR

- (i) Describe the Franck-Condon principle and its relevance to electronic transitions.

(ii) Differentiate between fluorescence and phosphorescence, providing examples of each. [CO-2] [L-2] **5**
[CO-5] [L-4] **5**

Q.4 (i) Describe singlet and triplet states and discuss their roles in electronic spectroscopy. [CO-6] [L-2] **5**

(ii) Explain the terms dissociation and predissociation in electronic spectra. [CO-4] [L-2] **5**

OR

(i) What do you understand by P, Q, R branches in vibration- rotation spectra?

(ii) Explain the terms dissociation and predissociation in electronic spectra.

[CO- 4] [L-2] **5 + 5**

Q.5. (i) Describe Jablonski diagrams and their significance in photochemical processes? [CO-5] [L-4] **5 + 5**

(ii) The vibrational energy of a diatomic molecule is given by

$$G(v) = (v + \frac{1}{2})\bar{\nu}_e - (v + \frac{1}{2})^2\bar{\nu}_e x_e,$$

Where $\bar{\nu}_e$ is the fundamental frequency and x_e is the anharmonicity constant. In the case of HCl molecule in a particular excited state its infrared spectrum exhibits two transitions at 2885.96 cm^{-1} and 2864.79 cm^{-1} identified as transitions between the vibrational levels (4 $\rightarrow$ 5) and (5 $\rightarrow$ 6), respectively. Calculate the values of $\bar{\nu}_e$ and $\bar{\nu}_e x_e$ (in cm^{-1}) for the HCl molecule in this state?

OR

Write a short note on the following:

(i) Process of quenching in photochemical reactions

(ii) Lambert-Beer law

[CO- 6] [L-4] **5 + 5**