b) A molecule AB_2 has the following IR and Raman spectra. Discuss the molecular structure and assign the observed lines to molecular vibrations.

Frequency (cm^{-1})	IR	Raman
3750	Very strong	—
3650	Strong	Strong, polarized
1595	Very strong	—

c) Explain the nature of NQR spectrum of bromine in $AlBr_3$.

d) A doublet with intensity ratio 2 : 1 is observed for the photoelectron spectrum of argon, if excited by a less energetic source – explain. $4+3\frac{1}{2}+2+3$

M. Sc. Chemistry Examination, 2017

(4th Semester)

Physical Chemistry Special

Paper - XIV-P

Time : Two hours Full Marks : 50

Use a separate answerscript for each group.

UNIT – P- 4141

Answer ***any five*** questions

1. Define 'σ' in connection to the irreversible rate processes. What's its SI unit ? Write down whether it is intensive or extensive property with justification. What will be its values when the system is at non-equilibrium and equilibrium states ? 5

2. Derive the 'balance equation' for any property of an open system where inward flux, outward flux and change of the property within the system take place. 5

3. Consider the reaction : $A + B \rightleftharpoons P + Q$ (both reactions are elementary) and show that its overall rate is non-linearly related with its chemical affinity (A). Find the condition for which this rate will be linearly dependent of A. 5

4. Using a triangular chemical reaction system, derive :

$J_j = \sum_{k=1}^{n} L_{jk} X_k$ and $L_{jk} = L_{kj}$ (where $j \neq k$) (symbols have their usual meanings). 5

5. What are the differences between the *'equilibrium state'* and *'stationary state'* ? 'Glacier on Mountain top, maintaining constant mass and temperature' is an example of stationary state. – Justify. 5

6. Define *'electro-osmosis'* and *'streaming potential'* in connection to the electro-kinetic effect. Establish a relationship between them. 5

7. What is *bistability* property of a chemical reaction ? Why is this property essential for an 'Oscillatory Chemical Reaction' ? 5

UNIT – P- 4142

Answer question no. ***10*** and ***any one*** from question no. ***8*** and ***9***.

8. a) MASER was discovered before LASER although the basic principle for the two are similar – why ?

   b) Explain E-type and P-type delayed flurescences. How can one experimentally confirm whether a delayed fluorescence is E-type or P-type ?

   c) With an example illustrate why the chemical properties of a molecular system changes in the photoexcited state relative to its ground state. $3+(3+3)+3\frac{1}{2}$

9. a) Define oscillator strength. Calculate the oscillator strength of $^1A_{1g} \rightarrow {}^1B_{2u}$ transition in benzene at 256 nm for which ε_{max} = 150 L mol^{-1} cm^{-1} and the width at half height band is 4000 cm^{-1}.

   b) Explain with reasons :

      i) Fluorescein is highly fluorescent but tetraiodo fluorescein is nearly non-fluorescent.

      ii) At least three energy levels are required for laser action.

   c) The wavelength of the 0-0 transition of phenol and its anion in aqueous solution at 300K are 475 nm and 550 nm respectively. If the pK_a of pehnol in its ground state is 9·2, what is the pK_a of its lowest excited singlet state ?

$3\frac{1}{2}+(3+3)+3$

10. a) Calculate the recoil velocity and energy of the free Mössbauer nucleus ^{119}S when emitting a γ-ray of frequency $5{\cdot}76 \times 10^{18}$ Hz. What is the Doppler shift of the γ-ray frequency to an outside observer ?