Birla Institute of Technology and Science Pilani –333031, Rajasthan
2nd Semester 2016-2017, Mid-Semester Test
Course Title: Photochemistry & Laser Spectroscopy, Course No. CHEM F412
Max Marks: 60, Time: 1hr 30 mins, Date: 10.03.17

Answer all questions with proper units. Rough work can be done alongside your answer.

Q1. Explain briefly how three main factors become responsible for intensity of spectral lines.**5M**

Q2. Explain briefly how three factors become responsible for structureness of absorption spectra. **5M**

Q3. (a) Using PFEO model draw the π-electron orbital energy levels of naphthalein with proper nomenclature of orbital clearly showing electronic arrangements in each orbital at the ground state. **3.5M**

(b) (i) Write electronic configuration of the excited state for excitation of one electron from HOMO to LUMO of ground state of naphthalein, **(ii)** Determine total ring quantum number (Q) and terms corresponding to this electronic configuration, **(iii)** Write term symbols for all possible excited states corresponding to this electronic configuration, **(iv)** Determine the total number of nodal planes for each set of singlet states with same Q-value, **(v)** Draw nodal planes showing sign of wavefunctions and polarization of dipole oscillations for all singlet states. **1M+2M+2M+2M+6M**

Q4. What is the effect of polar protic solvents on the peak position of absorption spectra of a diene and an enone molecule. **4M**

Q5. It is known that theoretically forbidden $n_b \rightarrow \pi^*$ transition in formaldehyde shows weak absorption experimentally – Why? Explain with the help of group theory. Given that formaldehyde has normal modes of vibrations with a_1, b_1 and b_2 symmetries. **3M**

Q6. The following table represents the symmetry species of the PFEO electronic states of benzene:

Electronic states	^1A (ground state)	$^{1,3}L_b$	$^{1,3}L_a$	$^{1,3}B$
Symmetry species	$^1A_{1g}$	$^{1,3}B_{2u}$	$^{1,3}B_{1u}$	$^{1,3}E_{1u}$

(i) Which transition(s) is(are) spin as well as parity allowed? **1.5M**
(ii) Which transition(s) is(are) spin forbidden but parity allowed? **1M**
(iii) Which transition(s) is(are) spin, parity and symmetry allowed and why? Explain with the help of group theory. **3M**
(iv) Point out any one theoretically forbidden transition which shows absorption experimentally. Explain why with the help of group theory. **3M**

Q7. (i) What is Franck-Condon principle? Explain with an example. **(ii)** What is mirror symmetry relation in spectroscopy? **(iii)** The fluorescence quantum yield and excited singlet state lifetime of an aromatic molecule are 0.63 and 7.93 ns, respectively. Calculate the values of radiative and non-radiative rate constants. **3M+4M+3M**

P.T.O.

Q8. (i) What is the basic difference between excitation and emission spectra? **(ii)** What should be the characteristics of individual components in an ideal spectrofluorimeter. (iii) Write a short note on grating monochromator. **2M+4M+2M**

Character Table for the C_{2v} point group:

	E	C_2	$\sigma_{v(xz)}$	$\sigma_v'_{(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x

Character Table for the D_{6h} point group: