1989	Tanta University Faculty of Science Department of Chemistry			
	Final exam. for senior students of chemistry			
	Course title:	Physical Chemistry		Course Code: 14041
Date:	Jan. 5, 2013	Term: First	Total assessment Marks: 60	Time allowed: 3 H

Answer all questions of the following three sections

Section A: Molecular Photochemistry (20 marks)

1) State whether each of the following statements is true or false, if false, please, write down the true statements. (12 Marks)

1. The value of Φ_f can be enhanced relative to Φ_p by using solvents containing heavy atoms.
2. The lifetime τ_f is much shorter (faster) than τ_p and the mechanical rotating cylinder apparatus can be operated rapidly enough to enable fluorescence decay to be recorded.
3. The term excimer is used to denote an excited state dimeric species.
4. The rate constants for energy transfer increase as the energy of the donor triplet state falls below that of the acceptor triplet state.
5. The energy gap, $\Delta E(T_1 \sim So)$ is a factor which determines the relative magnitudes of Φ_f and $\Phi_{isc}(S_1 \sim T_1)$.
6. For reactions involving triplet states it is imperative to degas the system to remove dissolved oxygen.

2) Give short notes on *four* of the following: (8 Marks)

1. Some solvents such as benzene , acetone and isopropanol could be used as reactant molecules in the photochemical reactions.
2. Intramolecular energy transfer.
3. Wigner spin conservation rule.
4. The rate of decay of T_1 state describes the unimolecular and bimolecular processes.
5. Coupled transitions in donor and acceptor energy transfer.
6. Energy transfer between benzophenone and naphthalene.

Section B: Molecular Reaction Dynamics (20 marks)

3) A. Put true or false sign and correct the false answer. (5 Marks)

1. In case of activated complex the number of vibrational degree of freedom is $3(N_A + N_B)$ - 6 for non-linear molecule.

2. A chemical reaction that absorbs heat from the surroundings is said to be exothermic and has a -ve ΔH.

3. The energy of activation may also be calculated by another form of the Arrhenius equation as follows, $ln\frac{K_2}{K_1} = \frac{E}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$.

4. The rate constant in terms of collision theory is $K = Ae^{-E/RT}$, where in terms of entropy and activation energy is $K = v\, e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT}$.

5. Transition state theory states that molecules must collide with the proper orientation in order to react.

B. Derive the rate constant from transition state theory. (5 Marks)

4) A. Define the following: (4 Marks)

1. Stored energy
2. Saddle point
3. Steric factor
4. Activation energy

B. Calculate the value of frequency factor in $dm^3 mol^{-1} S^{-1}$ for the following reaction (atom + linear → linear) assuming that $q_{trans} = 10^8, q_{rot} = 10$, $q_{vib} = 1$ and $\frac{K_b T}{h} = 10^{13}\ s^{-1}$, Avogadro's constant is taken to be $10^{24}\ mol^{-1}$. (4 Marks)

C. Write only two reasons for the weakness of collision theory. (2 Marks)

EXAMINERS:	1- Prof. Dr. Shakir T. Abdel-Halim
	2- Dr. Eman Fahmy Aboelfetoh

Section C: Molecular spectroscopy. (20 marks)

1. Choose the correct answers: (write your choice only) (6 marks)

a- How many normal modes of vibration does methane have?
i- 15 ii- 12
iii- 9 iv- 6 (1 mark)

b- The width of a spectral band or line is affected by
i- Band position. ii- Collision broadening
iii- Population of states iv- Spacing between the energy levels. (1 mark)

c- Symmetric tops rotor as NH_3 has three moments of inertia I_a, I_b and I_c such that:
i- $I_a = 0, I_b = I_c$. ii- $I_a = I_b \neq I_c$.
iii- $I_a = 0, I_b \neq I_c$. iv- $I_a \neq I_b \neq I_c$. (1 mark)

d- For anharmonic oscillator potential energy diagram of diatomic molecule, the transition $v_1 \rightarrow v_2$ is called:
i- First overtone. ii- Fundamental absorption band
iii- Second overtone - iv- Hot band (1 mark)

e- For anharmonic oscillator potential energy diagram of diatomic molecule, the transition $v_0 \rightarrow v_2$ is called:
i- First overtone. ii- Fundamental absorption band.
iii- Second overtone. iv- Hot band. (1 mark)

f- The relative intensities of rotational spectral lines are function on
i- Boltzmann distribution function [exp $(-E_J / KT)$]. ii- Cell length.
iii- Number of fold degeneracy (2J+1). iv- (2J+1). exp $(-E_J / KT)$ (1 mark)

2. Put (√) at the correct sentence and (X) at the wrong one. (don't write the sentence). (5 marks)

a- Frank-Condon principle governs the relative intensities of transitions between vibrational energy levels of different electronic states. (1 mark)
b- A progression in absorption electronic spectrum is a series of bands with a common lower vibrational level. (1 mark)
c- Polarizability of H_2 molecule changes as the molecule vibrates. (1 mark)
d- The population in vibrational energy levels v_1 and v_0 are equals at 300 K.(mark)
e- Term symbol is an exact notation used in spectroscopy to define and characterize the energy states of atoms and molecule. (1 mark)

3. Draw an energy diagram to show Raman effect (Raleigh scattering, stokes and anti-stokes Raman). (3marks)

4. Compare between the energy levels and the position of rotational spectra in rigid and non-rigid di-atomic rotor. (3marks)

5. (3marks)
The fundamental and first overtone of $^1H^{35}Cl$ observed at 2886 cm^{-1} and 2668 cm^{-1} respectively. Calculate:
a- Equilibrium vibration frequency,
b- Anharmonity constant.

EXAMINERS:	Section A: Prof. Dr. Shaker Abd-Elhalem..	Section C: Prof. Dr. Samy Salem Assar.
	Section B: Dr. Eman Fahmy	

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