PHOTOCHEMISTRY I 2015

END-OF-TERM EXAMINATION

18 MAY 2015

Student : «NOM» «Prénom»

Seat No: «No»

Important information

- The overall duration of the test is **1 hour 30 min**.
- The collection of answer sheets must be **signed at the bottom of page 10**.
- Students can leave the examination room only after their answer sheets are returned **definitively** and their course evaluation questionnaire is completed.
- Besides normal writing tools and blank sheets, **no auxiliary material (formulary, handout, book, electronic device, ...) is allowed**.
- All **answers must be written in ink in the greyed boxes** (if necessary, use the back of the sheet indicating clearly "c.f. verso" in the appropriate box).
- **Draft sheets will not be collected** at the end of the examination and will therefore not be considered.
- **Provided explanations must be intelligible and allow the corrector to assess the level of understanding of their author.** However, the test is not an essay exercise. The text may then be written in point form.
- The maximum number of points assigned to each question is indicated. **The total number of points of the test is 80**. The note will be calculated based on a linear "federal" scale. The mark 4 threshold (after rounding) corresponds to a minimum of 44 points.

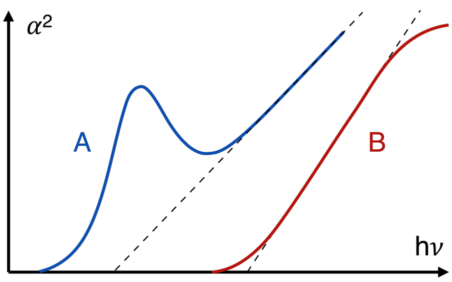
Question 1 [*3 points*]

Three molecules belonging to the same family are characterized by a fully allowed charge transfer π-π* electronic transition. These molecules differ from each other by the conceptual distance *R*, over which an elementary charge would be displaced during the transition.

Express the relationship between the distance *R* and the wavelength λ_{max} of the maximum of the absorption band of the molecules.

Question 2 [*5 points*]

The absorption spectra of two different semiconducting bulk materials A and B are sketched here below.



a) Which type of intrinsic electronic transition is characterizing both solids ? Justify the answer.

b) Provide a rationale for the dissimilar shapes of both absorption spectra and indicate which properties of the two semiconductors are responsible for these different aspects.

Question 3 [*6 points*]

The absorption spectrum of a solution of benzophenone displays two bands, whose respective maxima appear at wavelengths λ = 254 nm and λ = 338 nm.

a) Which types of electronic transition do the two absorption bands correspond to ?

b) Estimate the approximate values of the oscillating strength of the two respective bands and of the decadic molar extinction coefficient typically expected for both maxima. Justify the answers.

Question 4 [*5 points*]

With the help of an energy scheme, explain what is the *solvatochromism* of a chromophore characterized by an n-π^* type transition.

Question 5 [*6 points*]

Draw a Jablonski diagram for a typical organic chromophore, including explicitly all electronic excited states' deactivation pathways.

Question 6 [*5 points*]

An excitation energy of 4.4 eV can be deduced from the absorption threshold of the UV spectrum of naphthalene in solution in isopropanol. The excitation energy of the triplet state of the same molecule, as established from the phosphorescence spectrum, is 2.3 eV.

a) Identify and describe as much as possible the phenomenon that is responsible for this large energy difference.

b) Similar measurements carried out with a solution of benzophenone yield excitation energy values of 2.9 eV and 2.5 eV, respectively. Explain why the behavior of benzophenone is here in variance with that of naphtalene.

Question 7 [*3 points*]

What are the typical intermolecular distances on which energy transfer proceeding through respectively radiative, Förster, and Dexter mechanisms are likely to take place ?

Question 8 [*8 points*]

Using single photon counting technique, the excited state lifetime of a Ru^{II} complex in an air-saturated aqueous solution is determined as being τ_1 = 100 ns. Upon carefully degasing the solution, the excited state lifetime increases to a value τ_2 = 500 ns.

a) Provide a simple rationale for this observation. Which conclusions regarding the properties of the excited state of the complex can be drawn from it ?

b) Assuming that the kinetics of the excited state's quenching by oxygen is controlled by diffusion, estimate the concentration of dissolved O_2 in the air-saturated aqueous solution.

Question 9 [*10 points*]

The cyanine dye Cy3 ($\Delta E_{0,0}$ = 2.4 eV) is used as a redox photoinitiator in a photo-lithographic process along with N-phenylglycine (NPG) as an electron donor and the electron acceptor MCP^+. Standard oxidation potentials φ^0 (vs. standard calomel electrode, SCE) are provided for all three participants :

φ^0 ($Cy3^+$/Cy3) = + 1.63 V/SCE
φ^0 (NPG^+/NPG) = + 0.25 V/SCE
φ^0 (MCP^+/MCP) = – 0.65 V/SCE.

Write all thermodynamically feasible electron transfer reactions that can result from the photo-excitation of the dye and all electron back transfer processes. Calculate for each reaction the corresponding standard Gibbs free energy ΔG_r^0 [eV].

Question 10 [*6 points*]

Discuss the photochemistry of carbonyl chromophores. Specify in particular the type of electronic transition involved and compare the reactivity of ground- and excited states. Provide an example of a photochemical reaction taking place from the triplet excited state of the chromophore.

Question 11 [*6 points*]

Establish the energy diagram of O_2 molecular orbitals. Represent the electronic structures of the molecule in the ground state, as well as in the first two $^1\Delta_g$ and $^1\Sigma_g^+$ excited states. Why the interatomic distance O–O does not change upon excitation of dioxygen molecule to a singlet electronic state ?

Question 12 [*10 points*]

The lifetime of the $^1\Delta_g$ excited state of dioxygen molecule in the gas phase and in solution in CCl_4, heavy water (D_2O), and H_2O is $\tau = 3\cdot10^9$ μs, $3\cdot10^4$ μs, 100 μs, and 5 μs, respectively.

a) Explain the spread of lifetime values, with reference to the various possible excited state deactivation pathways.

b) Estimate the phosphorescence quantum yield Φ_p of $^1O_2$ dissolved in D_2O.

Question 13 [7 points]

List the various possible strategies that can be applied to minimize the photo-degradation of polymers. Provide for each of these strategies an example of a stabilizer commonly used as additive in commercial plastics (it is not necessary to give here any detailed chemical structure: indicate the family the molecule belongs to and/or the relevant functional groups it possesses).

Student's signature: ______________________________________