

PHOTOCHEMISTRY I

EXAMINATION JULY 6th, 2017

Development of the oral examination

Examination will develop within two different phases of 20 minutes each. At the beginning of the first phase, the candidate will pick up randomly a subject (see here below) that she/he will have to elaborate on. During the first 20' phase, the candidate will prepare her/his answers in the back of the room. The written form is recommended but is not compulsory.

The second 20' duration phase will constitute the proper oral examination. Answers prepared by the candidate on the chosen subject will serve as a conductor for the exam. Depending on explanations provided by the student, questions pertaining to the whole course matter could be asked. During the whole examination, no course support, note, book, nor any other auxiliary material will be authorized.

Elaborate on one of the following subjects:

A) Transition dipole moment

Intensity of a transition and oscillating strength – Relationship with the extinction coefficient (macroscopic aspect of light absorption) – Link between oscillating strength, transition energy and transition dipole moment – Examples

B) Electronic transitions

Frontier molecular orbitals – Types of electronic transitions – Case of organic compounds – Case of inorganic coordination compounds – Selection rules – Reactivity of molecular excited states

C) Photonics of solids

The Bloch-Brillouin model – Classification of solids – Intrinsic light absorption – Absorption spectra – Reactivity of solids under illumination – Direct and indirect transitions – Excitons – Quantum size effect

D) Molecular photophysics

Excited states deactivation pathways – The Jablonsky diagram – Kasha's rule – Kinetics of radiative and non-radiative deactivation processes – Solvation dynamics – Quantum yields – Stern-Volmer

E) Intermolecular energy transfer

Thermodynamic constraints – Mechanisms of intermolecular energy transfer – Critical distance for energy transfer – Spectral sensitization – Examples of practical cases

F) Photoredox reactions

Redox reactivity of electronic excited states – Charge separation and back-transfer – Thermodynamics of electron transfer – Kinetics of electron transfer: Marcus' theory – Case of semiconductors under illumination

G) Synthetic organic reactions

Photochemical reactivity of ethenes, polyenes and ethynes: type of transition involved, examples of reactions (isomerisation, electrocyclic reactions, Woodward-Hoffmann) – Photochemistry of the carbonyl chromophore : type of transition involved, reactivity of the excited state compared to that of the ground state, examples of reactions

H) Singlet oxygen

Electronic excited states of molecular oxygen – Production of 1O_2 (direct routes, sensitization) – Lifetime of singlet oxygen – Reactivity of 1O_2 – Examples of common reactions

I) Photochemistry of polymers

Photo-polymerization : interest, applications, mechanisms – Photo-crosslinking, application to photolithography – Photodegradation of polymers – Stabilizers, strategies, types and mode of action.