PhD Thesis proposal form

Discipline
(eg: Mathematics, Physics, Biology….)

Doctoral School
Chemitry at Paris-Sud university

Thesis subject title: Picosecond pulse radiolysis investigation of the direct effect of ionizing radiation

- Laboratory name and web site: Laboratoire de Chimie Physique, [http://www.lcp.u-psud.fr/](http://www.lcp.u-psud.fr/)
- PhD supervisor (contact person):
  - Name: Mehran Mostafavi
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- Thesis proposal (max 1500 words):
  See below

- Publications of the laboratory in the field (max 5):

  Time-Dependent Radiolytic Yield of OH Radical Studied by Picosecond Pulse Radiolysis";"El Omar, Abdel Karim; Schmidhammer, Uli; Jeunesse, Pierre; Larbre, Jean-Philippe; Lin, Mingzhang; Muroya, Yusa; Katsumura, Yosuke; Pernot, Pascal; Mostafavi, Mehran","","JOURNAL OF PHYSICAL CHEMISTRY A. , 2011,115, 9151.


  Picosecond Pulse Radiolysis of Direct and Indirect Radiolytic Effects in Highly Concentrated Halide Aqueous Solutions,Balcerzyk, Anna; Schmidhammer, Uli; El Omar, Abdel Karim; Jeunesse, Pierre; Larbre, Jean-Philippe; Mostafavi, Mehran. JOURNAL OF PHYSICAL CHEMISTRY A. 2011,115, 9151.
Specific requirements to apply, if any:

Master of Chemistry or Physical Chemistry

Thesis proposal:

**Picosecond pulse radiolysis investigation of the direct effect of ionizing radiation**

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Pr. Mehran Mostafavi

Radiation chemistry is extremely important for the world’s energy and environmental future. It touches our daily lives in very direct ways through nuclear power, radiation treatment of advanced materials, pollution abatement, sterilization of food and medicine, and its positive and negative consequences for human health. It also has a large impact indirectly as a technique for understanding chemical reactivity in general by approaching it from a different but complementary direction than photochemistry, electrochemistry and other techniques. Water radiolysis occurs in many situations (radiotherapy,[1] radiosterilization,[2] sewage treatment,[3] food irradiation, [4] etc.).

The framework in which water radiolysis occurs is now well understood experimentally as well as theoretically.[5, 6]

Among the themes running through this proposal is establishment of the fundamental science base for new, advanced nuclear fuel cycles, through understanding of the detailed mechanisms of the direct ionizing radiation effects in separation systems. Radiation chemistry plays a critical role in the design of effective, radiation-durable separations systems that minimize waste and environmental consequences. Key questions underlying this problem include how many radicals are created by ionizing radiation at early times (in solvents other than water and alcohols), what their reaction patterns are, and how those patterns may be altered in the presence of various solutes or in an ionic liquid solvent. This proposal looks at the fundamental aspects of these problems. The unique experimental capabilities offered by the ELYSE facility can provide a broad understanding of the elementary processes that lead to chemical change (radiation damage) following ionizing radiation in separations systems, waste forms, and other materials.

Since they are based on ionization, radiation chemistry techniques are naturally suited for studies of charge transport reactions that are key to several important areas in energy research, including solar photochemistry, catalysis, batteries, fuel cells, photochromic devices and electromechanical actuators. Pulse radiolysis studies remain essential to much of the proposed research in electron transfer.

This proposal applies radiation chemistry to investigate fundamental chemical problems relevant to the production and efficient use of energy and thus obtain unique insights not attainable...
with other techniques. These studies may play an important role in the development of safer, more effective, and environmentally beneficial processes for advanced nuclear fuel cycles and the chemical conversion of solar energy. One set of problems concerns processes occurring on very short time scales, including time-dependent yields, properties, geminate recombination, and reactivity of primary radiation products in non-aqueous polar solvents and ionic liquids. Another set of problems deals with reactivity of molecular and radical transients, where pulse radiolysis provides the most convenient or the only method to rapidly generate these species. Work in this area includes the reactivity of environmentally and biologically important nitrogen-oxygen species whose chemistry is poorly understood, proton and hydrogen atom transfer reactions that relate to solar fuel generation, and the photochemistry of radical ions.

The principal tool for this research is the ELYSE accelerator, which combines short pulses of electrons and laser light to produce, excite, and examine transient species with high time resolution. ELYSE's features are particularly well suited for studies of electron transfer, and mechanistic investigations of ultrafast reactivity. Ultra-short electron pulse of a few picoseconds has been already attained at ELYSE by employing laser driven photo-cathodes of Cs$_2$Te, which can be maintained inside the cavity, in radio frequency guns. Ancillary equipments such as a super-continuum white light generator of CaF$_2$, streak camera, and data acquisition system enables one to observe transient photo-absorption in a wide range of wavelength with a time resolution of several picoseconds. Worldwide, there are few research establishments that have such an apparatus, so ELYSE is potentially a very attractive facility to conduct radiation research which has not yet been done.

Most studies on the radiolysis of various solutes focused on dilute aqueous solution, on water decomposition radicals and intermediate transient products on time scales of nanoseconds or longer.[7] However, the radiolysis of highly concentrated aqueous solutions is still not well understood because many new factors, negligible in dilute systems, now come into play: the direct effects of ionizing radiation are no longer negligible, a fast electron transfer between ionized solute/solvent to surrounding solvents/solutes can occur, change of water properties such as viscosity can affect radical dynamics, the bimolecular rate constants can be affected by time or ionic strength. The direct effects of ionizing radiation on chemical system have not yet been elucidated, as it is extremely difficult to discern between the direct and indirect actions with time resolution of nanoseconds. The kinetics of reactions in highly concentrated aqueous solutions, especially on very short time scales (<ns) is, to date, not fully elucidated. The reaction mechanism is quite complicated with at least three effects that significantly influence reaction kinetics including: (i) ionic strength

![Figure 1: The ELYSE accelerator will allow achieving time resolutions that will allow accessing the direct effects of ionizing radiation in living systems](image)
effects, (ii) charge transfer complex formation between the cation and its counter anion and (iii) ion-pairing complex formation (between two reacting cations and a counter anion).

Recently, Balcerzyk et al. investigated the radiation chemistry of highly concentrated aqueous halide salt solutions using picosecond pulse radiolysis.[8] They succeeded in separating the direct and indirect effects from the viewpoint of the oxidation yield of halide anions. A new pathway leading to the oxidation of solutes via electron transfer from the solutes to ionized water molecule has been proposed; this is shown in the figure 2. However, in this study, only single atom anions – $\text{Br}^-$ and $\text{Cl}^-$, were used; the use of these anions is favored as they are some of the simplest known solutes and their chemistry and reaction pathways with water decomposition radicals, on nanosecond time scales, is well-known. A pending question remains what happens in highly concentrated aqueous solutions of more complicated solutes such as larger molecules or multi-valence ions.

![Mechanism in highly concentrated solutions](image)

**Figure 2: Steady state and pulsed radiolysis study of highly concentrated aqueous solutions**

A complete understanding of the electron transfer processes between ionized solute/solvent and surrounding molecules would benefit from extending this study to larger multi-atom solutes. If intra-molecular electron transfer process is fast, the inter-molecular electron transfer processes could be accelerated due to increasing number of surrounding solvent molecules. In addition, usage of multi-valence scavengers gives a more precise picture of the contact pair formation process on pico- to nanosecond time scale. The charge of the solute will also affect the time- and distance-dependent bimolecular reaction rate constants, and the difference would give information on the mesoscopic distribution of solutes and solvents in highly concentrated solutions. Further, non-ionic solute is suitable to extract information of direct effects contribution and fast electron transfer processes, of course, solubility can be a problem in this case. Pulse radiolysis has proven to be an extremely powerful technique for generating and monitoring the properties and reactivities of intermediates involved in such reactions, allowing complex mechanisms to be fully unraveled. Comparison studies on ionic liquids would help get answers to these questions, as the ionic liquids represent an extreme condition of aqueous salt solutions.

**References:**