Molecular simulations of ionizing irradiation of plutonium extractant solutions

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A PhD position in theoretical chemistry-physics is open from **October 2024** in France in the emerging field of ab initio simulation of molecules under ionizing radiation. The aim of these simulations will be to understand experimental data on picosecond pulsed radiolysis that are currently unpublished. The thesis will be carried out at the Marcoule CEA site (in Provence, near Avignon) and at the *Institut de Chimie Physique* of the Université Paris Saclay.

Scientific Context: The French CEA (*Atomic Energy Center*) develops separation processes for the multi-recycling of materials recoverable for energy, including plutonium. The preferred technology for separating plutonium is solvent extraction. In solvents, radiolysis phenomena generated by the presence of alpha radiation emitters such as plutonium are numerous. A better understanding of these phenomena is essential to develop and control these processes. The aim of this thesis will be to understand the mechanisms by which organic plutonium solutions are damaged by radiolysis, using numerical simulation. On a microscopic scale, the irradiation of matter by alpha particles begins with a significant deposition of energy in the electron cloud, leading to the excitation or ionization of the molecules in the medium. This process takes place on the attosecond time scale. The energy thus deposited is then dissipated in nuclear vibration modes, leading to the localization of charges on certain molecular fragments, the weakening of chemical bonds or even their rupture, and the production of reactive chemical species.

Methodologies: To simulate these ultrafast processes on the basis of first principles, Time-Dependent Density Functional Theory (TD-DFT) methods developed at ICP will be mobilized [1]. TD-DFT simulations consist in explicitly propagating in time the evolution of an electronic cloud subjected to a perturbation such as a collision by an alpha particle. These simulations give access to the amount of energy delivered to the system with atomic resolution, and to the dynamics of the electron cloud [2]. Coupling the TD-DFT simulation with the Newtonian molecular dynamics simulation of atomic nuclei, then gives access to the simulation of ultrafast chemistry taking place on femto- and picosecond timescales (Ehrenfest MD). Hybrid QM/MM (Quantum Mechanics/Molecular Mechanics) schemes, possibly polarizable, will be used to account for environmental effects (solvent, counterions) [1]. **The PhD student will thus be trained in a wide range of simulation techniques in the field of theoretical physical chemistry.**

Project planning. Firstly, the radiolysis of extractant molecules used in new uranium and plutonium separation processes currently under development at CEA will be studied with DFT. Secondly, the degradation of plutonium (IV) complexes will be studied. At each stage, the challenge will be to identify the degradation products and understand their ultra-rapid formation mechanisms. Comparison to experimental data obtained by picosecond pulsed radiolysis will be undertaken.

Expected skills from the candidate. The successful candidate will have a good background in physical and/or quantum chemistry, be motivated and hard-working. Previous experience in numerical

simulation, acquired for example during Master's research internships, will be an advantage. The thesis will be carried out under the joint supervision of D. Guillaumont (CEA) and A. de la Lande (CNRS, Université Paris Saclay), requiring the PhD candidate to be alternatively located for long periods on both CEA Marcoule and Université Paris Saclay sites.

Professional opportunities: The PhD student will be fully integrated into the scientific life of the two thesis laboratories, enabling him/her to acquire a broad knowledge of experimental and theoretical physical chemistry. They will be trained in a wide range of state-of-the-art computational chemistry approaches. Participation in national and international conferences and summer schools is planned. In addition, international exposure is planned through participation in the deMon developer consortium.

Working conditions The doctoral student's gross monthly compensation is € 2 406 (value July 2023, net wage is about € 1900). Doctoral students employed by the CEA benefit from the same advantages and duties as any CEA staff member (professional trainings, company canteen, vacations…).

How to apply: Interested candidates (we welcome applications from both men and women) should send a letter of application to Dominique Guillaumont and Aurélien de la Lande, together with a detailed CV and a transcript of their Master's grades. Two letters of recommendation should be sent separately by the authors of the letters.

Hosting laboratoiries:

The ICP is a major academic research laboratory of the Université Paris Saclay and the Centre National de la Recherche Scientifique. It conducts cutting-edge research in radiation chemistry, nanocatalysis, theoretical chemistry and biophysics. The ICP houses the ELYSE picosecond pulsed radiolysis platform, the only one of its kind in Europe, for the experimental study of short radiolysis times. It's located on the magnificent campus of Univerité Paris Saclay, in Orsay's Vallée de la Chevreuse. The campus is well connected to the city of Paris by public transport.

The LILA laboratory conducts studies related to actinide chemistry, radiolysis, and the interactions of radionuclides with organic molecules. Programs are carried out for industrial or academic clients and partners, often in collaboration with doctoral students from the laboratory, enabling a wide variety of topics to be addressed.

[1] Current status of deMon2k for the investigation of the early stages of matter irradiation by time-dependent DFT approaches. K A Omar, F A Korsaye, R Tandiana, D Tolu, J Deviers, X Wu et al. *Eur. J. Phys. S. T.* **232**, 2167–2193 (2023). [2] Irradiation of Plutonium Tributyl Phosphate Complexes by Ionizing Alpha Particles: A Computational Study. D Tolu, D Guillaumont, A de la Lande, *J. Phys. Chem. A.* **127**, 7045-7057 (2023).