Internship Proposal 2025

School - Location: CentraleSupélec, Gif-sur-Yvette (10 miles from Paris)	
Laboratory: SPMS	**Web site: https://spms.centralesupelec.fr/**
Name of the supervisor: Mehdi Adrien Ayouz and Brahim Dkhil	**Email: mehdi.ayouz@centralesupelec.fr**

Title: Possible degradation pathways in per- and polyfluoroalkyl substances (PFAS) using the piezo-photocatalysis process : a theoretical study supported by experimental inputs

Scientific field (one among the list- remove other choices):

Engineering & Technology: Chemical engineering

Free Key words: *ab initio* calculations, dissipative molecular dynamics, potential energy surface, polycarbonate, PFSA, classical molecular dynamics, ring polymer molecular dynamics, path integral molecular dynamics, piezo-photocatalysis c

Remarks: Possible joint PhD (cotutelle) with the University of Central Florida

Period: from now

Details for the subject:

General context:

Per- and polyfluoroalkyl substances (PFAS) are around 5,000 synthetic chemical molecules with carbon chains of varying lengths and fluorine atoms with the most known PFOA ($C_8F_{15}O_2H$), PFOS ($C_8F_{17}SO_3H$) or PFBS ($C_3F_9SO_3H$). These molecules are used in a wide range of industries, including automotive, textiles, food packaging, non-stick pans, cosmetics and electronics [1]. PFAS are today omnipresent in the environment, where they are released throughout their life cycle, from production to the destruction of products containing them [2]. Resistant to many forms of degradation, PFAS are highly persistent in the environment (from a few decades to several centuries), hence their nickname of "eternal pollutants" [3]. Recently, in SPMS laboratory at CentraleSupélec, University of Paris-Saclay, we developed a new and advanced oxidation process that is piezo-photocatalysis using laboratory-designed oxide nanoparticles [4,5] which are capable to efficiently degrade many antibiotics or endocrine disruptors including PFAS molecules. This piezo-photocatalysis technique exploits mechanical and light energy to activate the piezo-photocatalysts, yielding to the oxidation and hydrolysis of pollutant molecules like PFAS. For instance, light irradiation induces electrons in the valence band to move to the conduction band, generating photo-induced electron and hole pairs. These electron-hole pairs react then with available oxygen, water, and hydroxyl groups, leading to the formation of reactive oxygen species, namely ROS, such as hydroxyl radicals ($\dot{O}H$) and superoxide radical anions ($\dot{O}_2^-$). These reactive species attack and degrade, in their turn, pollutant molecules, tackling thus the challenge of persistent pollutants.

While our preliminary experimental results on piezo-photodegradation of PFAS using our nanoparticles are promising, still computational modeling are crucial in understanding the complex mechanisms that govern piezo-, photocatalysis, a prerequisite for the strategic design and engineering of effective semiconductor piezophotocatalyst systems.

Description of the work:

This internship project aims investigate the oxidation of PFAS by H, and its possible degradation pathways. For this purpose, quantum chemistry calculations will be performed to compute the full-dimensional potential energy surface of the complex PFAS+H. We will use the MP2 method throughout the Gaussian software [6]. We choose this calculation level due to its ability to provide a substantial amount of energy and gradient data across various structures within a reasonable computational timeframe. Since the system under study is complex and large, we will test the DFT calculation and finally choose the one that provides stability of the molecular properties. To obtain the equilibrium and transition state structures, we will compute the Global Reaction Route Mapping (GRRM).

This preliminary work will be followed by a PhD. devoted to understand the mechanisms and identify the intermediates to improve the piezo-photocatalysts, employed at SPMS. Theoretical studies will be conducted during this PhD. using different techniques that would provide a more realistic description of piezo-, photocatalysis process of PFAS. The obtained results will be compared to experiments carried out at SPMS.

References:

[1] Anses "PFAS : des substances chimiques dans le collimateur". 12 mai 2022. https://www.anses.fr/fr/content/pfas-des-substances-chimiques-dans-le-collimateur

[2] https://www.lemonde.fr/les-decodeurs/article/2023/02/23/polluants-eternels-explorez-la-carte-d-europe-de-la-contamination-par-les-pfas_6162942_4355770.html

[3] Sinclair, G.M., Long, S.M., Jones, O.A.H., 2020. What are the effects of PFAS exposure at environmentally relevant concentrations? Chemosphere 258, 127340

[4] W. Amdouni, M. Fricaudet, M. Otoničar, V. Garcia, S. Fusil, J. Kreisel, H. Maghraoui-Meherzi, B. Dkhil, $BiFeO_3$ Nanoparticles: The "Holy-Grail" of Piezo-Photocatalysts?. *Adv. Mater.* 2023, 35, 2301841

[5] W. Amdouni, M. Otoničar, D. Alamarguy, E. Erdem, P. Gemeiner, F. Mazaleyrat, H. Maghraoui-Meherzi, J. Kreisel, S. Glinsek, B. Dkhil , Enhancement of the Piezocatalytic Response of La-Doped $BiFeO_3$ Nanoparticles by Defects Synergy. *Small* 2024, 20, 2406425

[6] Gaussian 09, revision A.02, M. J. Frisch; et al.