PhD position | Theory of the complex luminescence properties of actinides

Contract	Fully funded 3-year PhD position starting October 2024
Institution	Institut des Sciences Chimiques de Rennes (ISCR)
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	Dr. Boris LE GUENNIC, Email: boris.leguennic@univ-rennes.fr

A full-time 3-year PhD position is available in the Theoretical Inorganic Chemistry (*Chimie Théorique Inorganique*, CTI) team at the Institut des Sciences Chimiques de Rennes (ISCR) under the supervision of Dr. Rémi Maurice and Dr. Boris Le Guennic. The position is for three years starting October 2024. The project is dedicated to the theoretical exploration of the complex luminescence properties of the actinides by means of advanced quantum chemistry methods.

The theoretical description of the luminescence properties of compounds containing actinides is particularly complex since it requires an adequate treatment of electronic correlation and relativistic effects, and this on an ensemble of quantum states of different nature. However, there is a major challenge in understanding these properties and more broadly all the physicochemical properties of the actinides since these are elements (i) naturally present in environment, (ii) present in the electronuclear cycle as fuel and thus also as waste, (iii) used as a target materials to produce superheavy elements and (iv) certain isotopes are of potential interest for nuclear medicine, be it for diagnosis, targeted therapy, or both ("theranostics").

Although theoretical studies are available concerning the luminescence of uranyl compounds [1], comprising uranium(VI), no systematic and detailed study has yet been achieved in cases for which the reference ground state of the actinide atom bears one f electron or more. The reason for this is quite simple, it means that this ground state already cannot be described by a so-called "single-determinant" approach, which means that routine methods of quantum chemistry such as DFT and TD-DFT are not methods of choice in this case.

An additional theoretical difficulty comes more generally from the lack of data available for the actinides and in particular for the rarest ones, both from the experimental and the theoretical points of view. Preliminary work carried out within the framework of ANR CHESS, led by Dr. Rémi Maurice, has enabled to show that most of the basis functions predefined and available in the major codes of quantum chemistry are unsuitable for describing the targeted transitions, for instance the $5f^0 6d^1 \rightarrow 5f^1 6d^0$ one associated with the luminescence of protactinium(IV) or also of uranium(V). It is in fact necessary to use basis functions have been generated to describe configurations differing in the respective occupations of levels 5f and 6d of the actinides [3], a situation which does not occur if the bases have only been optimized to describe the ground state and only certain types of excited states.

The thesis project will consist in three main steps:

1. A first methodological study based on absorption properties (vertical transitions) aiming at validating calculation protocols and basis functions for different actinides at different oxidation degrees of interest. This phase may include recontraction of known basis sets and/or generation of new basis sets for a finer description of absorption and thus also supposedly of luminescence.

2. A second methodological study targeting more specifically luminescence properties. The calculation protocols will be validated when applicable by comparison with experimental data. Otherwise, the dependence of the results on the computational degrees of freedom will be studied, and simplified protocols validated on the basis of the most precise calculations that we will be capable of handling.

3. A systematic study of the luminescence properties of a significant number of compounds, for which the luminescence properties are known (fine interpretations) or not (tentative predictions).

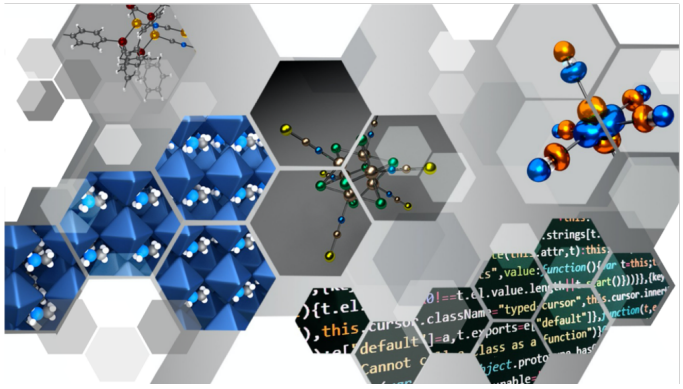
These studies will be notably grounded on relativistic and multiconfigurational wave function theory calculations, in line with the experience of the team [3]. In addition, the numerical determination of the excited-state geometries will potentially require the development of new in-house tools.

Related references

[1] H. Oher, F. Réal, T. Vercouter, V. Vallet, *Inorg. Chem.* **2020**, *59*, 5896–5906.
[2] B. O. Roos, R. Lindh, P.-Å Malmqvist, V. Veryazov, P.-O. Widmark, *Chem. Phys. Lett.* **2005**, *409*, 295.
[3] N. Zhutova, F. Réal, E. Renault, V. Vallet and R. Maurice *Phys. Chem. Chem. Phys.* **2023**, *25*, 24603.

Profile of the candidate | A degree in Chemistry or Physics is required. Solid background in at least one of the following topics is expected: molecular quantum chemistry (theory and/or practice), theoretical spectroscopy, crystal-field theory, and/or scientific programming. The successful candidate should be highly motivated and eager to learn and apply advanced modelling concepts. Communication skills and the ability to work in close collaboration with other theoreticians and experimentalists will be a plus.

The CTI team | The PhD student will work in the Theoretical Inorganic Chemistry (*Chimie Théorique Inorganique*, CTI) team at the Institut des Sciences Chimiques de Rennes (ISCR). The CTI team gathers computational chemists and physicists (15 permanent staff members plus students and post-docs) with complementary skills, working with a broad set of quantum chemical tools, ranging from high precision *ab initio* wave function-based calculations to fast semi-empirical methods. The CTI team is interested in diverse type of systems, including molecular species, bulk materials and surfaces, mainly of experimental and societal interest. The CTI team provides a stimulating scientific environment, offering team meetings, invited seminars as well as regularly receiving internationally-recognized visitors. The quantum chemistry codes necessary for the project are available together with considerable local, national and European computing resources.



Inquiries| Potential candidates should contact by email Dr. Rémi Maurice and Dr. Boris Le Guennic with an up-to-date CV and a motivation letter.