Sujet de thèse pour la rentrée 2018

Laboratoire : CEISAM, UMR 6230 CNRS – Université de Nantes

Titre du sujet de thèse :Etude théorique de Liaisons Halogène impliquant l'Astate

Theoretical investigation of At-mediated halogen bonds

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Financement : contrat doctoral de l'Université de Nantes (acquis)

Présentation du sujet :

The chemistry of astatine (At, Z = 85), a rare and radioactive chemical element, remains not well understood.[1] Expected applications in nuclear medicine (^{211}At isotope exhibits physical properties remarkably suited for some cancer treatments) require a better knowledge of its chemistry. The investigation of astatine chemistry gather several research teams, notably radio-, theoretical and synthetic chemists around the high energy ARRONAX cyclotron, operating in the Nantes area. **Access to the astatine production from this cyclotron gives us a decisive advantage to make breakthroughs at the international level**. Similarly to the other halogen elements, astatine was expected to form molecular interactions through halogen bonding. The halogen bond is an attractive interaction between a halogen electron deficient region, the so-called σ hole, and an electron rich site of a Lewis base. With our radiochemist colleagues from the SUBATECH laboratory, **we recently reported in the *Nature Chemistry* journal the very first characterization of At-mediated halogen bonds**.[2] Part of the challenge lies in the impossibility of using spectroscopic tools because of the minute amounts of astatine. Quantum mechanical calculations are essential to gain information at the molecular level and to rationalize the experiments.[3]

The work will be organized along two directions. The first one extends the current close collaboration with Dr. G. Montavon's team of radiochemists (SUBATECH laboratory, Nantes). The project consists to study the ability of various At-compounds to interact with a selection of Lewis bases (*B*) through halogen bonds. **Both a halogen-bond basicity scale** (through variation of the nature of *B*), **and a halogen-bond acidity scale** (through variation of the nature of the *R* substrate bearing At) **will be established**. For each *R*-At···*B* system, the nature of the halogen-bond complex and the corresponding thermodynamic constants will be predicted by relativistic DFT calculations. The second research project deals with the detailed analysis of the relativistic effects on At-mediated halogen bonds, and more particularly the analysis of the spin-orbit coupling (SOC) which can be very important for astatine compounds.[4] A first step will be to **characterize the SOC influence on the halogen-bond donor** (*R*-At) and thus on the σ hole properties. Relevant information can be obtained from the topological analysis of the electron localization function (ELF) and of the electronic density (QTAIM).[5] Depending on his/her skills, the candidate will participate to the development, conducted by Dr. J. Pilmé (LCT laboratory, Paris), of the SOC treatment in topological analyses of the electrostatic potential and of the local electrophilicity, useful descriptors of the σ hole. In a second step, the attention will be focused on **the study of the electron density rearrangement with SOC in halogen-bond complexes**.

DOI : [1] 10.1038/nchem.1580 ; [2] 10.1038/s41557-018-0011-1 ; [3] 10.1039/C8NJ00484F ; [4] 10.1002/anie.201608746 ; [5] 10.1007/978-3-319-29022-5_20.