Title Modeling of clusters of silver and hydrocarbon at the SCC-DFTB level: a challenge

ALAUZET Camille[A], **SIMON Aude**[A], **SPIEGELMAN Fernand**[A]

A) Laboratoire de Chimie et Physique Quantiques (LCPQ), Fédération FeRMI, UMR5626 Université de Toulouse [UT3 Paul Sabatier] & CNRS, 118 Route de Narbonne, 31062 Toulouse, France

calauzet@irsamc.ups-tlse.fr

The main aim of our research is to understand the formation and richness of stardust components and the role of metals in their growth. Particularly in carbon-rich dust, and especially in Polycyclic aromatic Hydrocarbons (PAHs), for which current formation models, which ignore the role of metals, are inadequate. More specifically, our work consists of carrying out theoretical studies on model systems made up of aggregates of silver and hydrocarbons, for which experimental results have already been obtained. Indeed, the formation of silver nanoparticles and a wide variety of molecules, in particular PAHs ($C_{14}H_{10}$ and $C_{16}H_{10}$) has been demonstrated experimentally during studies aimed at forming dust analogues by laser and plasma vaporization[1]. We would therefore like to study the structures, stability and formation of large aggregates. The use of the SCC-DFTB (Self-Consistent Charge Density Functional based Tight Binding) approach appeared to us as a method of choice for describing the electronic structure. The effectiveness of this method is based on the parameterization of atomic pairs. Parameters already exist ($DFTB^{hyb}$) but we were not satisfied with them because they were created and optimized for other systems than the ones we are interested in. We therefore propose a new set of parameters where the repulsion between pairs of atoms is obtained from MRCI data ($DFTB^{\gamma}$)[2]. In order to validate this new set of parameters we determine the geometrical structures and energy data for the model systems Ag_nC and Ag_nH, with $DFTB^{\gamma}$ and $DFTB^{hyb}$ and compare them to well-known DFT results[3,4]. Similar studies are carried out for more complex systems with different nature of chemical bonds, such as $Ag_nC_mH_p$ (m=1-3, n=2, p=0-2) and Ag_n-$C_{10}H_8$ aggregates, which have covalent bonds and weak metal-ligand bonds respectively. In most cases $DFTB^{\gamma}$ gives results closer to the DFT results than $DFTB^{hyb}$. Thanks to this study we are currently applying the $DFTB^{\gamma}$ Hamiltonian to the determination of the most stable structures of $Ag_nC_{2n}H_{0/n}$ complexes that would form in experimental reactors. These structures are determined by a global exploration method (Parallel Tempering Monte Carlo) performed with the deMonNano code[5]. We will present our initial results in this presentation.

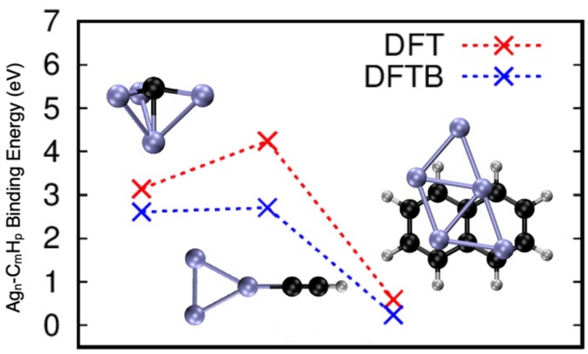

Figure 1: Binding energy of Ag_nC, $Ag_nC_mH_p$ and Ag_n-$C_{10}H_8$ clusters obtained from DFT with B3LYP-D3BJ functionals (red) DFTB with DFTBγ Hamiltonian (blue).

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