LABORATOIRE FRANCIS PERRIN
CEA/DSM/IRAMIS/SPAM - CNRS URA 2453

# SEMINAIRE SPAM / LFP


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**Le jeudi 6 Mai 2010 à 11h00**

**Bâtiment 522 - Salle 137**

## « Ligand and solvation effects on the redox properties of $Au_{55}$ action and applications to molecular logic »


The structural and electronic properties of the bare $Au_{55}$ cluster, and of the thiol passivated $Au_{55}(SCH_3)_{42}$, the redox active ligated $Au_{55}S(CH_2)_2CO_2(CH_2)_{10}bpy.2Cl$ and $Au_{55}(SCH_3)_{41}(S(CH_2)_2CO_2(CH_2)_{10}bpy).2Cl$ (bpy = N-methyl-4-4'-bipyridinium) complexes are studied at the DFT level in the gas phase and with an explicit water layer. For all complexes, neutral, positive and negative charge states are investigated. The thiol ligation distorts the outer layer of the approximate icosahedral geometry of the bare cluster, and induces a charge transfer from the gold core to the ligand shell. The anchoring of a single redox active ligand on the bare $Au_{55}$ leads to the formation of a cavity around the S-Au bond and we show that this cavity formation is prevented by the thiol ligands in $Au_{55}(SCH_3)_{41}(S(CH_2)_2CO_2(CH_2)_{10}bpy).2Cl$. The vertical addition of one electron to the $[Au_{55}\ S(CH_2)_2CO_2(CH_2)_{10}bpy.2Cl]^0$ cluster is followed by a charge transfer from the $Au_{55}$ core to the $bpy^{2+}$ ligand, which is accompanied by a mechanical motion of the redox active bpy arm driven by electrostatic interactions. The presence of a solvent shell does not alter the structure, but significantly decreases the computed charging energies of the clusters, making them comparable with experimental values. The computed redox potential differences are in good agreement with the experimental values. We then show with simulations that the redox states of the ligated $Au_{55}$ cluster can be selectively addressed and used to build logic machines.


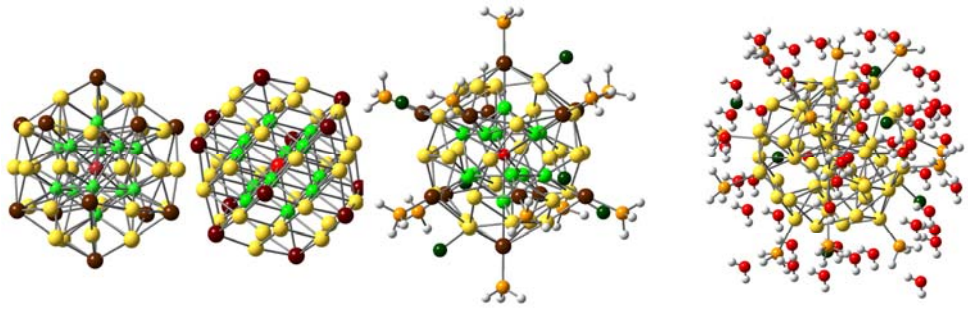

Figure : Distorted icosohedral and cubohedral bare $Au_{55}$, $Au_{55}(PH_3)_{12}Cl_6$ and $Au_{55}(PH_3)_{12}Cl_6$ . 54 $H_2O$.


1. G. Periyasamy, E. Durgun, J.-Y. Raty, and F. Remacle, DFT studies of solvation effects on the nanosize bare, thiolated and redox active ligated Au55 cluster, J. Phys. Chem. C, under revision, 2010.
2. G. Periyasamy and F. Remacle, Ligand and solvation effects on the Electronic Properties of Au55 clusters: a DFT study, NanoLett. 9: 3007-3011, 2009.


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